Direct Halogenation of TpRu(diene)Cl Preceding Ligand Exchange Reactions and Assessment of the Halogenated Complexes via Oxidation Potentials and Catalysis

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A Dissertation Presented to

the Faculty of the Department of Chemistry

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Hiroyuki Hattori

May 2019

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ABSTRACT

The focus of this dissertation centers on the direct on-metal halogenation of trispyrazoyl borate ligand (Tp) in TpRu(diene)Cl. The first chapter begins with the preparation of TpRu(diene)Cl complexes and assessment of their stability under different conditions. TpRu(diene)Cl complexes were halogenated in one step using sulfuryl chloride, NBS, and iodine in the presence of mCPBA and H_2O and then also functionalized through Sonogashira coupling reactions. Through this methodology, Tp^{Cl}Ru(diene)Cl, Tp^{Br}Ru(diene)Cl, Tp^{I}Ru(nbd)Cl, and, $Tp^{C\equiv CH}$Ru(nbd)Cl were synthesized via an unusual strategy.

The next chapter encompasses the syntheses of simple di-phosphine complexes (dppm to dppb) and mono-phosphine complexes from the Tp^{X}Ru(diene)Cl obtained in the previous chapter. By synthesizing the di-phosphine complexes of different P-P linker lengths, changes to the chemical properties of the complexes were investigated. Mono-phosphine complexes $Tp^{X}PPh_3Cl_2$ were synthesized via a reported reaction reported for $TpRuPPh_3Cl_2$, and other mono-phosphine complexes $Tp^{X}RuPPh_3(MeCN)Cl$ were derived from the counterpart $Tp^{X}RuPPh_3Cl_2$ with newly devised reaction conditions. These phosphine complexes, in addition to the new diene complexes, were analyzed with cyclic voltammetry.

Lastly, the synthesized complexes were subject to evaluation of their catalysis. Two investigatory reactions used were (1) propargylic substitution and furan synthesis from epoxy alkynes. Propargylic substitution reactions gave a mixture of copious compounds from which the product was not isolated. Furan synthesis gave the expected furan, but in an unexpectedly low yield. Increasing the catalyst loading barely enabled a comparison between differently halogenated complexes. In $Tp^{X}RuPPh_3Cl_2$ catalysis, $Tp^{Cl}RuPPh_3Cl_2$

gave a slightly higher yield (17%) than the analogues (14%). On the other hand, $TpRuPPh_3(MeCN)Cl$ (26%) and $Tp^lRuPPh_3(MeCN)Cl$ (28%) gave slightly higher yield than the chlorinated (23%) and brominated (22%) complex.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

BuLi	Butyllithium
BHT	Butylated hydroxytoluene
Bpin	Pinacolatoboron
CAN	Cerium Ammonium Nitrate
CHD	1,4-Cyclohexadiene
COD	1,5-Cyclooctadiene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CV	Cyclic Voltammetry
*m*CPBA	*meta*-chlorobenzoicperoxyacid
DMF	*N*, *N'*-dimethylformamide
dppm	Bis(diphenylphosphino)methane
dppe	Ethylenebis(diphenylphosphine)
dppp	1,3-Bis(diphenylphosphino)propane
dppb	1,4-Bis(diphenylphosphino)butane
HOMO	Highest occupied molecular orbital
KTp	Potassium tris-pyrazoyl borate
LUMO	Lowest unoccupied molecular orbital

NBD	Norbonadiene
NBS	*N*-Bromosuccinimide
NIS	*N*-iodosuccinimide
TEMPO	Tetramethylpiperidine 1-oxyl
TMEDA	Tetramethyethylenediamine
Tp	Trispyrazoyl borate
Tp^{Bpin}	Tris-(4-pinacolatoboropyrozoyl) borate
Tp^{Br}	Tris-(4-bromopyrazoyl) borate
$Tp^{C\equiv CH}$	Tris-(4-ethynylpyrazoyl) borate
Tp^{Cl}	Tris-(4-chloropyrazoyl) borate
Tp^{CN}	Tris-(4-cyanoprazoyl) borate
Tp^{F}	Tris-(4-fluoropyrazoyl) borate
Tp^{I}	Tris-(4-iodopyrazoyl) borate
Tp^{OH}	Tris-(4-hydroxypyrazoyl) borate
UV-Vis	Ultraviolet-Visible

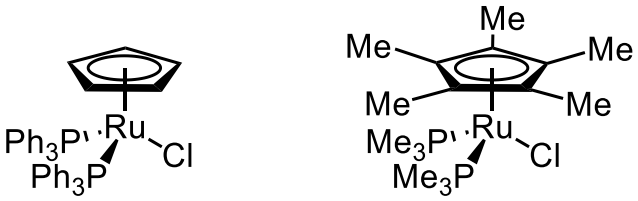
CHAPTER 1: Syntheses of $Tp^{X}Ru(diene)Cl$ Complexes and Documentation of Their Thermodynamic Stability

(Hattori, H.; Koo, H. D.; May, A. J. Direct Chlorination of Trispyrazolyl Borate Ligands in Tp-Ruthenium Complexes *Organometallics* **2017**, *36*, 4707−4712.)

1.1 Background

Cp (cyclopentadienyl) and Cp* (pentamethylcyclopentadienyl) ligands are common X type tridentate ligands found in many organometallic complexes.[1] They are 6 e^- donors that possess an aromatic five-membered ring (Scheme 1.1). Cp ligands coordinate to metals through π bonding interactions,[2] and the resulting complexes are predominantly of tetrahedral geometry. In the Cp* ligand, extra methyl groups around the ring make the ligand bulkier[3] (cone angle =146°) than Cp ligand (cone angle =100°), and the steric crush could hypothetically prevent some side reactions in catalysis.

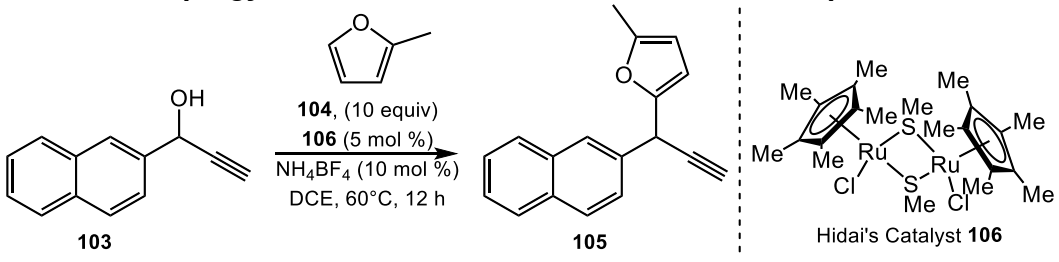
Scheme 1.1: Cp and Cp* ligands



101, Cp ligated complex **102**, Cp* ligated complex

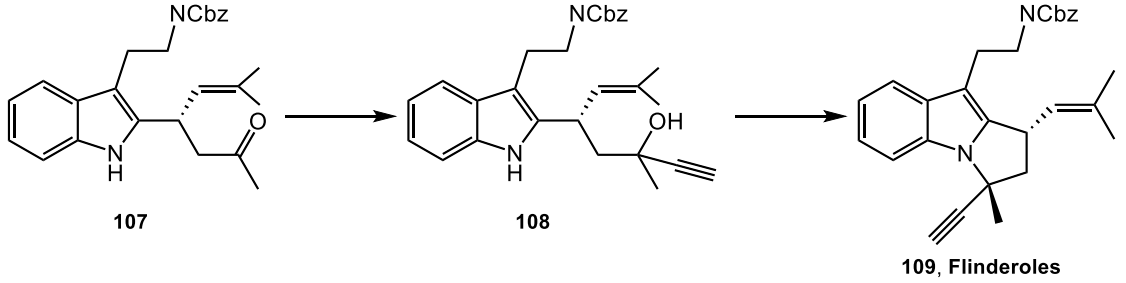
One captivating catalysis system for the propargylic substitution reaction was invented by the Hidai group.[4,5] The complex **106** is dimeric, and each ruthenium has one Cp* ligand displayed in a *cis*-fashion.

Scheme 1.2: Propargylic substitution reaction and Hidai's complex



Propargylic alcohols can be easily prepared from aldehydes or ketones in one step through Grignard reaction (Scheme 1.3). Subsequent intramolecular propargylic substitution reaction could rapidly construct a core structure of natural products. In this regard, the propargylic substitution reaction strategy is beneficial. However, most of the propargylic substitution reactions have following limitations. (1) Substrates need aryl substituent to achieve high yield. (2) Construction of quaternary center is still challenging. New catalysts that are capable of circumventing these problems are desired.

Scheme 1.3: An example of application of propargylic substitution reaction in total synthesis



107 **108** **109**, **Flinderoles**

Propargylic substitution reaction involves allenylidene formation (such as **110)** (Figure 1.1).[6] Carbons in the serial double bonds are counted as C_α, C_β, and C_γ from the metal center. Both C_α and C_γ are electrophilic because the LUMO (lowest unoccupied molecular orbital) of the allenylidene is localized on them while C_β is nucleophilic because the HOMO (highest occupied molecular orbital) centers on it.[7] Although both C_α and C_γ are the reactive sites for nucleophiles, the regioselectivity has to be discussed. Hard nucleophiles such as methoxide ion have the low-lying HOMO that interacts with the HOMO of the allenylidene. Superimposition of the frontier orbitals of allenylidene leaves a node on C_α and a lobe affected by the HOMO on $C\gamma$. Because the lone pair in the hard nucleophile is repelled by the lone pair in the HOMO of allenylidene, the it prefers $C\alpha$. Soft nucleophiles such as $P(C_2H_5)_3$ have the HOMO that is close in energy to the LUMO of

allenylidene. Therefore, the selectivity is dominated the sizes of the lobes in the LUMO. As a result, the nucleophilic attack takes oplace on Cγ.

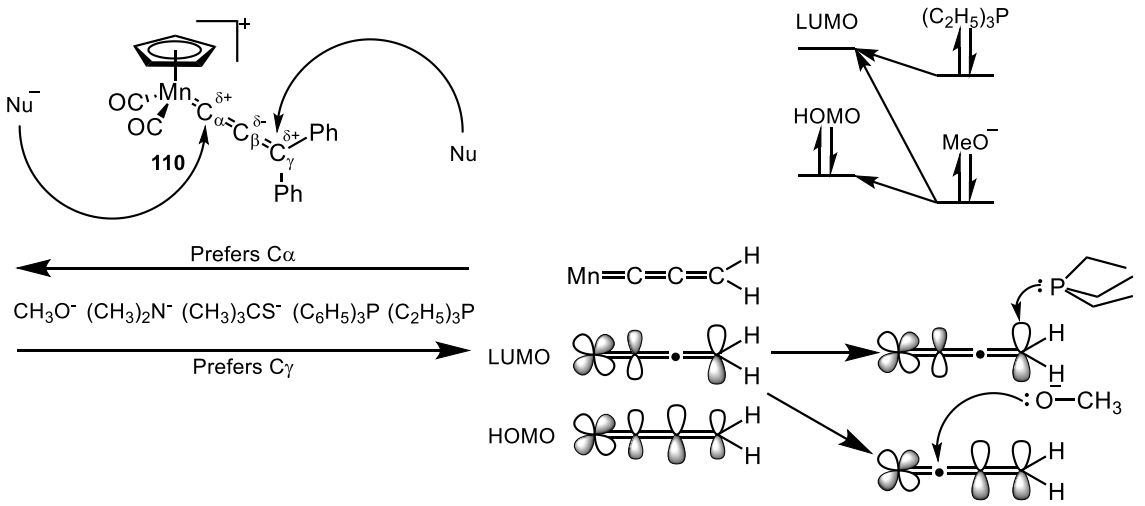
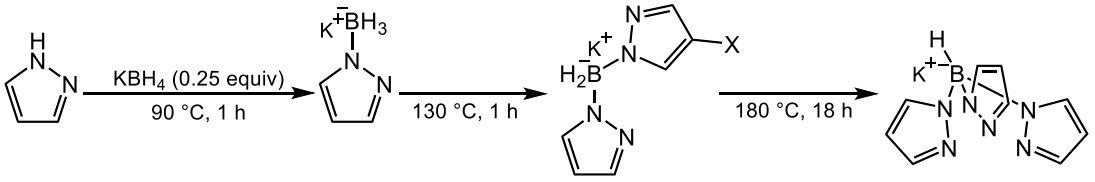


Figure 1.1: Selectivity by nucleophiles on Cα and Cγ.

The selectivity could be controlled by ancillary ligand too. Cp* ligand in Hidai's complex, for example, blocks the nucleophilic attack on Cα by the bulkiness of the ligand.

The trispyrazoyl borate ligand (Tp) is another well-known X type 6 e⁻ tridentate ligand found by Trofimenko in 1967. It was synthesized by heating a mixture of potassium tetrahydroborate (1 equiv) and pyrazole (4 equiv) (Scheme 1.4).[8]

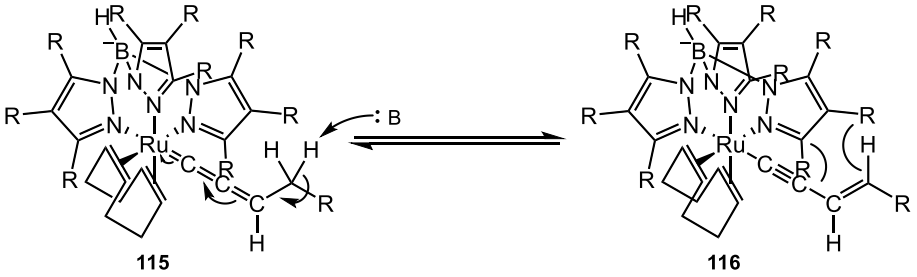
Scheme 1.4: Synthesis of potassium trispyrazoyl borate



The Tp ligand, prepared as a potassium salt (**114**), undergoes a ligand exchange reaction to coordinate to metals. In contrast to Cp ligands, Tp ligands coordinate to metals by σ bond interaction through the lone pairs on the three nitrogen atoms.[2] It is bulkier than a Cp ligand, and non-substituted Tp has a cone angle of 186°.[3] This property makes Tp

complexes good catalyst candidates for regioselective reactions because it blocks the C_α (Scheme 1.5). Another attractive feature of the Tp ligand is that there are more carbons to be functionalized: Cp has 5 carbon atoms in the ring that can be modified while Tp ligand has 9 sites. The addition of functional groups to the ligand was planned in hope that the functionalized Tp ligand would have different electronic and/or steric properties.

Scheme 1.5: Sterics and electrics of Tp ligand to suppress hypothetical side reactions



Adjustment of Proton Acidity by Electrics Suppression of Product Formation by Sterics

Many functionalized Tp complexes have been reported.[9] Relatively simple ones are Tp^{Me}, $Tp^{3,5\text{-}Me2}$, $Tp^{3\text{-}iPr2}$, $Tp^{3\text{-}Ph}$, Tp^{CF3}, Tp^{Cl}, Tp^{Br}, and Tp^{I} (Figure 1.2). Those ligands were synthesized by preparing the corresponding functionalized pyrazole first, which were treated with KBH_4 in similar conditions as Trofimenko's original procedures. Identical conditions for unfunctionalized pyrazole **111a** was sometimes not applicable to pyrazole derivatives **111b-111e** because the chemical and physical properties were different. For example, the melting point and boiling point of **111a** are 67 and 186 °C respectively. If the 4 poition is substituted with an F, both the melting point and boiling point drop dramatically to 34 and 86 °C respectively (Table 1.1). Heating up the mixture of 4-fluoropyrazole **111b** and KBH_4 would simply evaporate the pyrazole. The synthesis of **111b** was also too costly (above $100/250 mg). Equally importantly, some functional groups, such as OH or NH_2, would not tolerate the Tp synthesis.

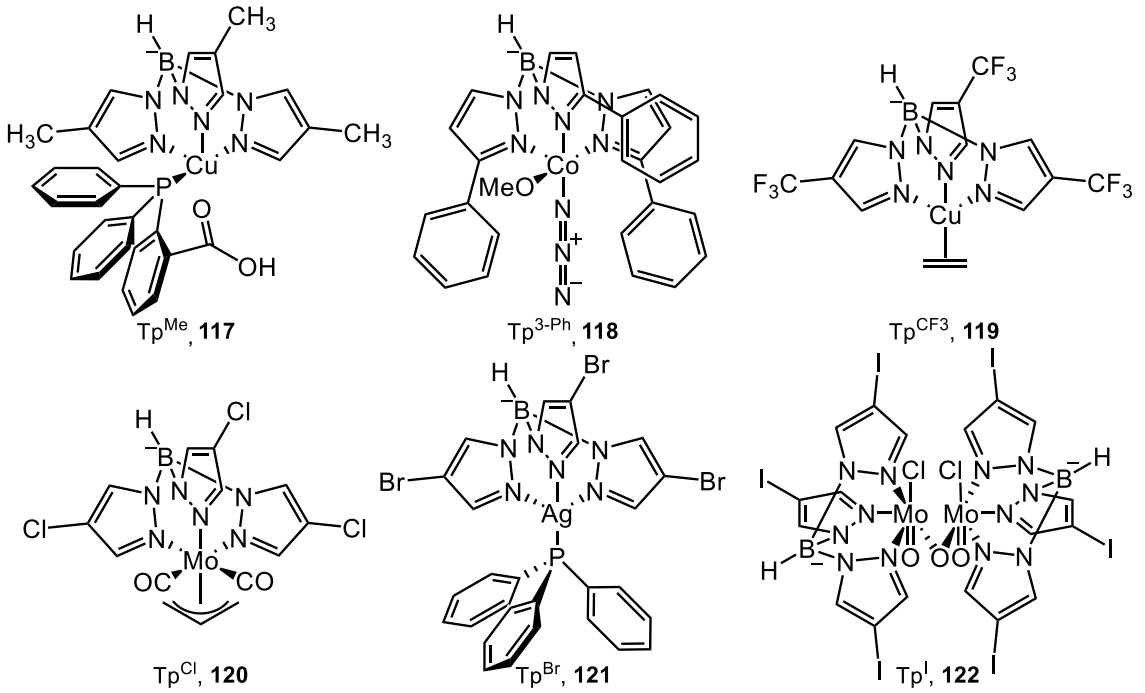
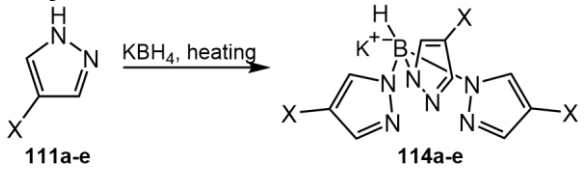


Figure 1.2: Complexes that have functionalized Tp ligands

Table 1.1: Boiling points and melting points of 111a-e along with the yields of the corresponding 114a-e by Kuo.

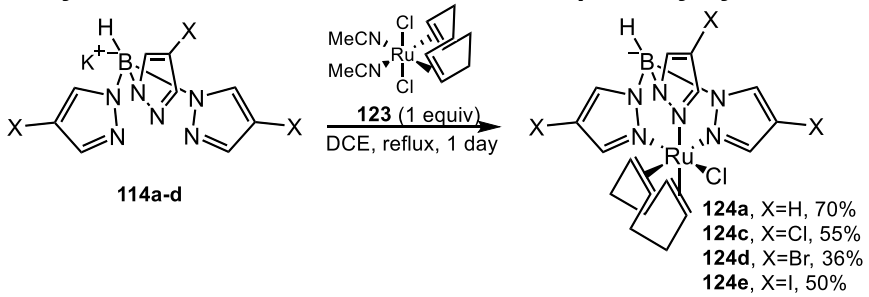


111a-e 114a-e

entry	X	MP (°C)	BP (°C)	yield (%)
1	H	67	186	70
2	F	34	86	N/A
3	Cl	75		50
4	Br	93	250	66
5	I	108	N/A	72

One could encounter another problem in the Tp ligand coordination step. Scheme 1.6 shows the product yields of **124a-d** by Kuo. The result shows that the yields of **124b-d** are generally lower than **124a**. In particular, the yield of **124d** is about a half of that of **124a**. Therefore, development of alternative way to synthesize Tp ligated metal complexes is desirable.

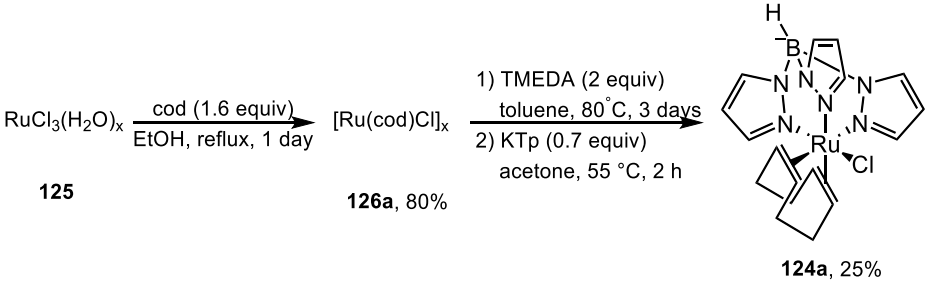
Scheme 1.6: Synthesis of 124a-d via the traditional pathway by Kuo



1.2 Syntheses of TpRu(diene)Cl as Hub complexes and their direct chlorination

The well-documented complex **124a** has been synthesized in three different ways.[10] The ruthenium trichloride is allowed to react with cyclobutadiene (cod) in the first step (Scheme 1.7). This bidentate ligand prevents a second Tp ligand from coordinating to the ruthenium to form a Tp sandwich complex.[10] The polymeric product **126a** was heated in toluene with TMEDA, which breaks up ruthenium congregation. After drying, the air sensitive brown residue was allowed to react with KTp in acetone to afford **124a** in 20 % overall yield. The orange complex **124a** was stable to air in both solution and solid phases.

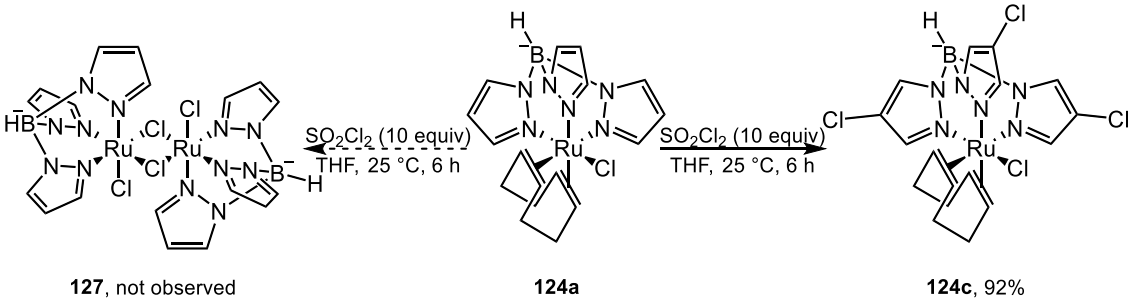
Scheme 1.7: Synthesis of TpRu(cod)Cl, 124a



One goal of this project was to synthesize a dimeric complex [TpRuCl-μ-(SMe)]$_2$, which resembles Hidai's catalyst, **106** (Scheme 1.8). Because this complex is Ru(III) while **124a** is Ru(II), the conversion should involve oxidation. A previous group member, Dong Hyun Koo, used sulfuryl chloride and obtained a single product. Characterization with X-ray crystallography revealed the unexpected and unprecedented complex **124c**, not the

desired dimeric product **121**. This accidental discovery in 2013 became the first stride to the development of direct halogenation of ruthenium Tp complexes.

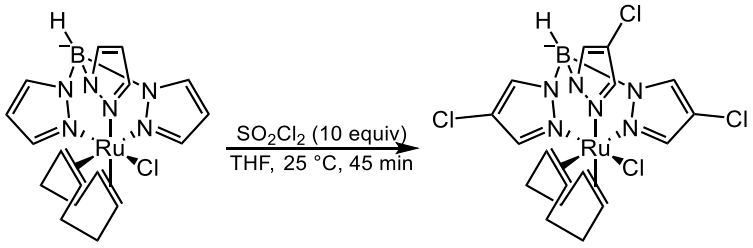
Scheme 1.8: The first direct chlorination of Tp in TpRu(cod)Cl 124c



127, not observed **124a** **124c**, 92%

Koo's first report of the direct chlorination used 10 molar equivalents of sulfuryl chloride, and the reaction time was as long as 6 hours. However, the quantity of SO_2Cl_2 could be reduced to 5 molar equivalents, and then the reaction was complete in 45 minutes (Scheme 1.9).

Scheme 1.9: Optimized direct chlorination of 124c



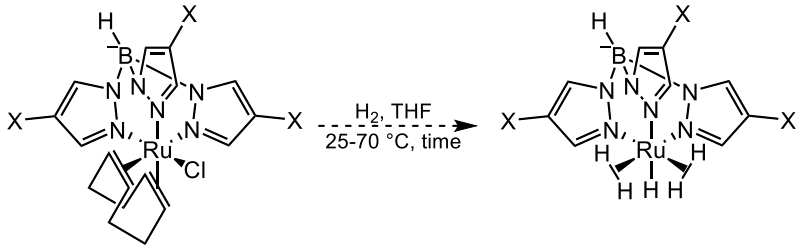
124a **124c**, 92%

Since SO_2Cl_2 did not successfully remove the cod ligand, other reagents were examined at different temperature ranges.

Hydrogenation of the cod ligand is expected to give hydride complex **128** (Table 1.2). Complex **124c** was dissolved in THF, and hydrogen in balloon was inserted in a flask. The TLC analysis only showed the reactant (entry 1). Ionic salt KPF_6 was added to the solution, and **124c** was attempted to be hydrogenated, but the result was the same (entry 2). A suspension of **124a** in THF was heated in H_2 atmosphere (entry 3). The mixture

turned blue, but the polarity of the compound changed. The isolated compound from the mixture however was the reactant.

Table 1.2: Hydrogenative removal of cod.

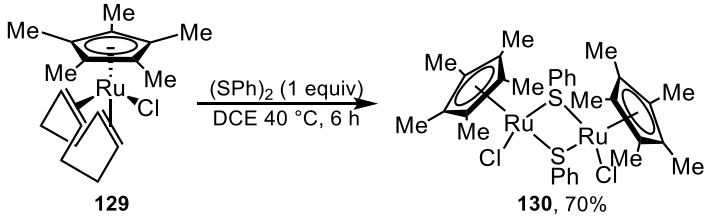


124c **128**

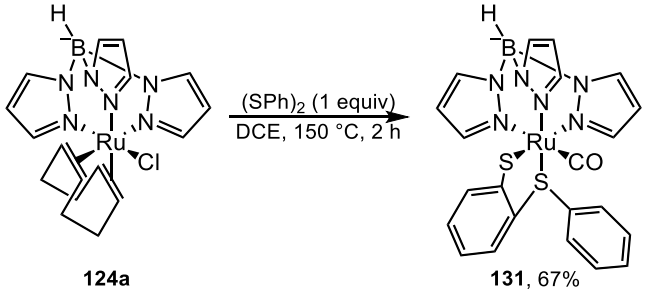
Entry	X	Reagents	Solvent	Temp (°C)	Time (h)	Result
1	Cl	H_2	THF	25	24	No reaction
2	Cl	H_2, KPF_6	THF	25	24	No reaction
3	H	H_2	THF	70	6	No desired product

Diphenyl disulfide is known to react with Cp*Ru(cod)Cl **129** at 40 °C to give a thiolate dimer **130** (Scheme 1.10).[2] On the other hand, the cod ligand in **124a** is tightly bound to the ruthenium. The reaction of **124a** with diphenyl disulfide at 150 °C successfully removed cod, but ended up with one S inserted on the *ortho*-position of the benzene ring.[11]

Scheme 1.10: Oxidative addition of dimethyl disulfide to ruthenium.



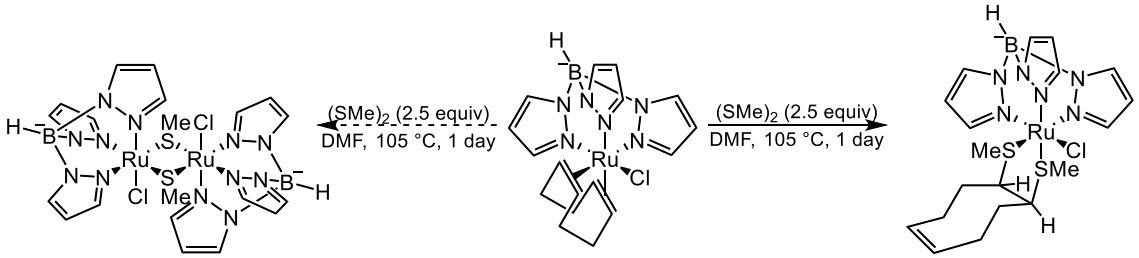
129 **130**, 70%



124a **131**, 67%

Switching the substituent on sulfur to Me, the same reaction was tested, but at varying temperatures. Complex **124a** did not react with dimethyl disulfide in the middle temperature range (Table 1.3, Entries 1-3, 50-80 °C). The reaction of **124a** was reasonably controlled with dimethyl disulfide at 100 °C (entry 4) One double bond of the cod reacted to give an S bridged complex while the other one remained intact when DMF was used as solvent. Standfest-Hauser surmised that the Tp ligand, a strong σ-donor, reinforces coordination of double bonds to the ruthenium center.[11]

Table 1.3: Dimethyl insertion between ruthenium and C=C bond.



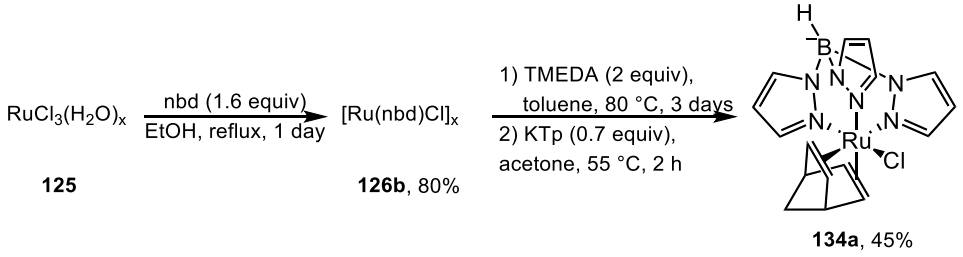
132 124c 133

Entry	Reagents	Solvent	Temp (°C)	Time (h)	Result
1	BH_3THF, $(SMe)_2$	THF	50	9	No reaction
2	$(SMe)_2$, KPF_6	Toluene	80	24	2 spots
3	$(SMe)_2$, KPF_6	Dioxane	80	24	No reaction
4	$(SMe)_2$	Dioxane	100	24	Complex Mixture
5	$(SMe)_2$	DMF	120	24	Complex mixture

Another famous diene that is used in coordination chemistry is norbonadiene (nbd), which has a bridge-head carbon between the double bonds. A known complex, **134a**, was synthesized in parallel with **124a** (Scheme 1.11).

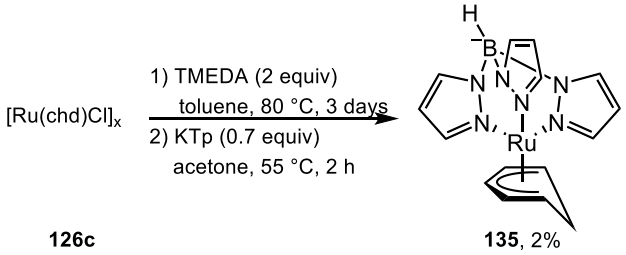
The first step gave reddish powder **126b** in 80% yield. It was treated with TMEDA, and then KTp to give **134a** in 45% yield, which is twice as much as **124a**. The yield was higher probably because double bond migration in nbd is blocked by the bridging carbons.

Scheme 1.11: Synthesis of 134a.



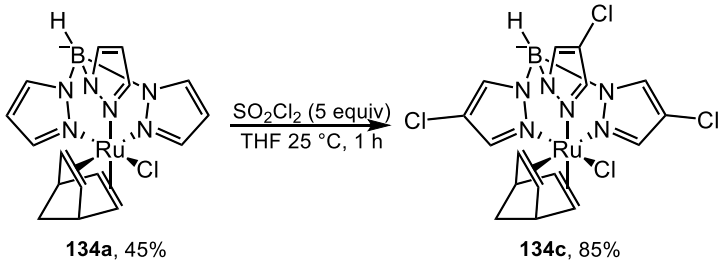
In an attempt to support this idea, ruthenium trichloride was treated with chd (1,4-cyclohexadiene), which gave a brown powder, probably $[Ru(chd)Cl]_x$ **126c** (Scheme 1.10). Interestingly, the attempted synthesis of TpRu(chd)Cl **134c** gave light yellow crystals (Scheme 1.12), which were characterized through X-ray crystallography as TpRuη^5-(C_6H_7), **135**. Formation of this complex should be accompanied by proton abstraction from the cyclohexadiene. A similar process was considered possible with cod ligand.

Scheme 1.12: Formation of 135 through isomerization of a double bond in chd.

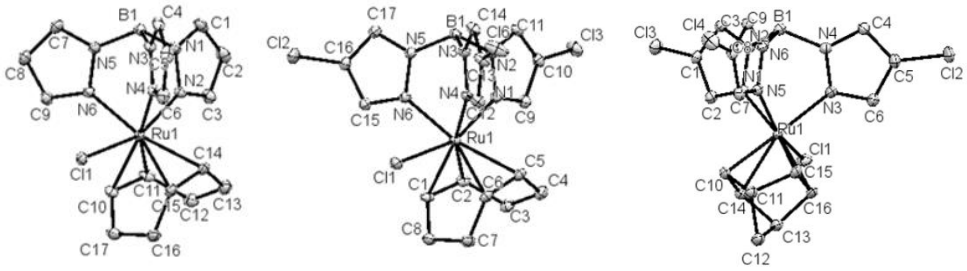


The Tp ligand of **134a** was chlorinated under the same optimum conditions as **124a**. The reaction cleanly gave **134c** in 85% yield (Scheme 1.13).

Scheme 1.13: Direct chlorination of 134a.



Complexes **124a**, **124c**, and **134c** were characterized by X-ray crystallography, and their structures are compared in Figure 1.3.



124a **124c** **134c**

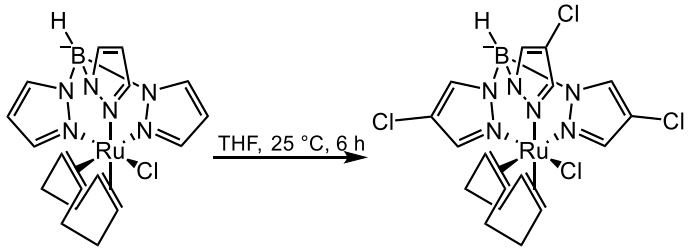
Figure 1.3: ORTEP diagram of complexes 124a (left), 124c (middle), and 134c (right).[16] Thermal ellipsoids are shown at the 50% probability level.

The diagram clearly shows that the Tp ligand was chlorinated at only the 4-positions of the pyrazole rings. Chlorination of the Tp ring did not change any of the bond lengths around the ruthenium (left and middle diagram). If one focuses on the distances between ruthenium and different dienes, the bond lengths between the ruthenium and double bond carbon atoms were slightly shorter in **134c** (2.2002(11) Å) than in **124c** (2.233(6) Å), which consistent with the discussion in a previous study.[12]

Although direct chlorination was found to be viable, the mechanism of the chlorination was unclear. Based on a structural analysis, the 4-position of the pyrazole ring is nucleophilic: the lone pair on the nitrogen atom bonded to the boron could flow into the double bond and the π electron subsequently move to the 4C. Because SO_2Cl_2 has two S-O double bonds, the chloride is electrophilic due to the high electronegativity of the SO_2 group. The "Cl^+" could be attacked by the C4 of the pyrazole rings. An hypothesis was made based on the well-known property of sulfuryl chloride to form chlorine gas.[13] To test these hypotheses, **124a** was treated with trifluoromethane sulfonate or chlorine gas (Scheme 1.14). A main difference between sulfuryl chloride and trifluoromethane sulfonate is the replacement of Cl with CF_3. Both groups are similarly electron withdrawing, but SO_2ClCF_3 cannot fragment into SO_2 and Cl_2 like SO_2Cl_2. The results of the control

reactions were distinctive: Cl_2 could react with Tp ligand, but SO_2CF_3Cl did not chlorinate the Tp at all.

Scheme 1.14: Mechanistic analysis of direct chlorination.



124a **124c**

SO_2CF_3Cl: 0%

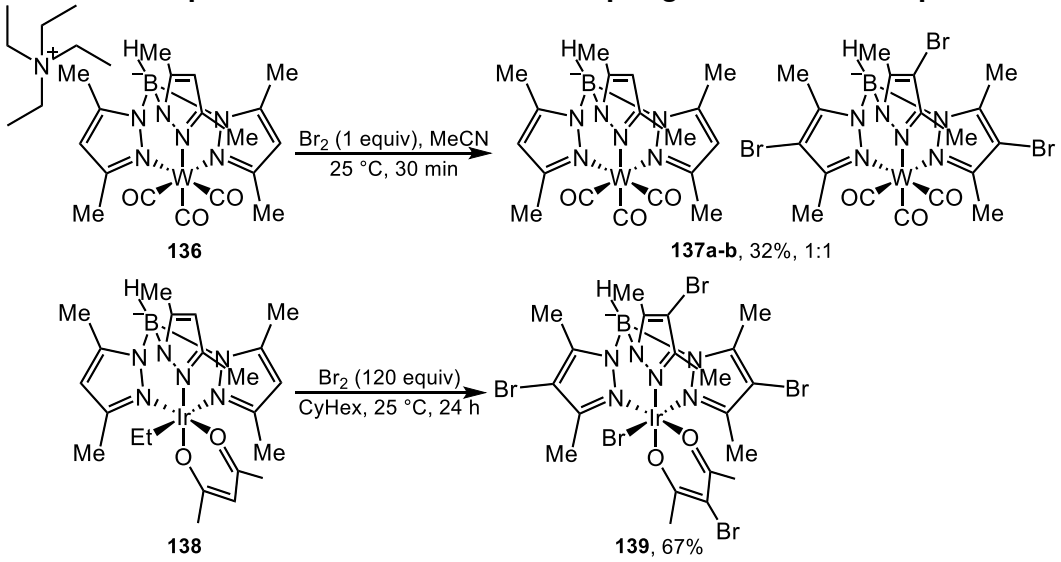
Cl_2: 52%

There are two common ways that chlorine reacts A) radical addition to alkane and B) polarization of electron distribution followed by nucleophilic attack from the double bond. If these principles are applied to the chlorination reaction of pyrazole, following processes might happen. Up to this point, neither mechanism was disproved.

1.3 Generalizing Direct Halogenation Based on Mechanistic Studies

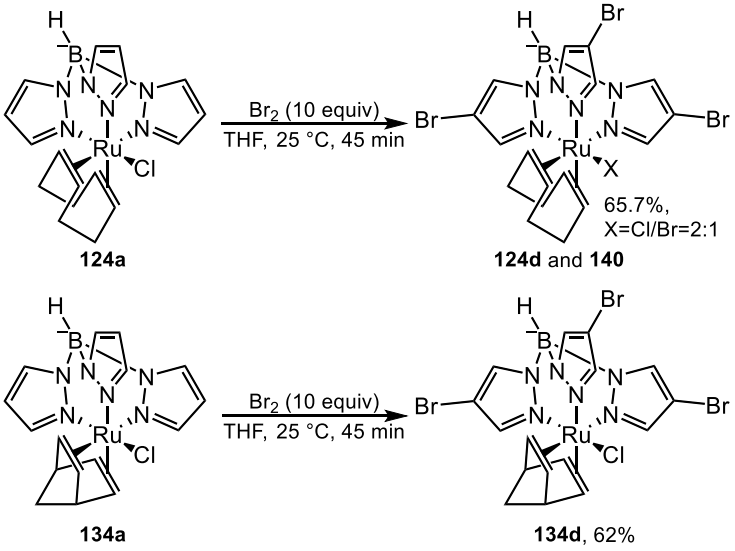
The next step was to expand the scope of the reaction to other halogens. Because the reaction with chlorine gas worked, it was proposed that the Tp could react with other halogen molecules as well. A literature search revealed a couple of precedents (Scheme 1.16). Bromination of a Tp* ligand took place when the Gable group tried to oxidize tungsten.[14] They isolated the oxidized product **137a-b** with and without bromination on the Tp* ligand. The yield was low because they did not use bromine in excess. Another example of direct bromination took place on an iridium complex.[15] This time, although bromine was used in excess, the reaction took place at the iridium center and the α position on the acetoacetonate (acac) ligand as well as on the Tp* ligand. These examples were not completely selective and have methyl groups on the 3 and 5 positions on the pyrazole rings, so that only one site was reactive.

Scheme 1.16: Reported direct bromination of Tp* ligand in metal complexes.



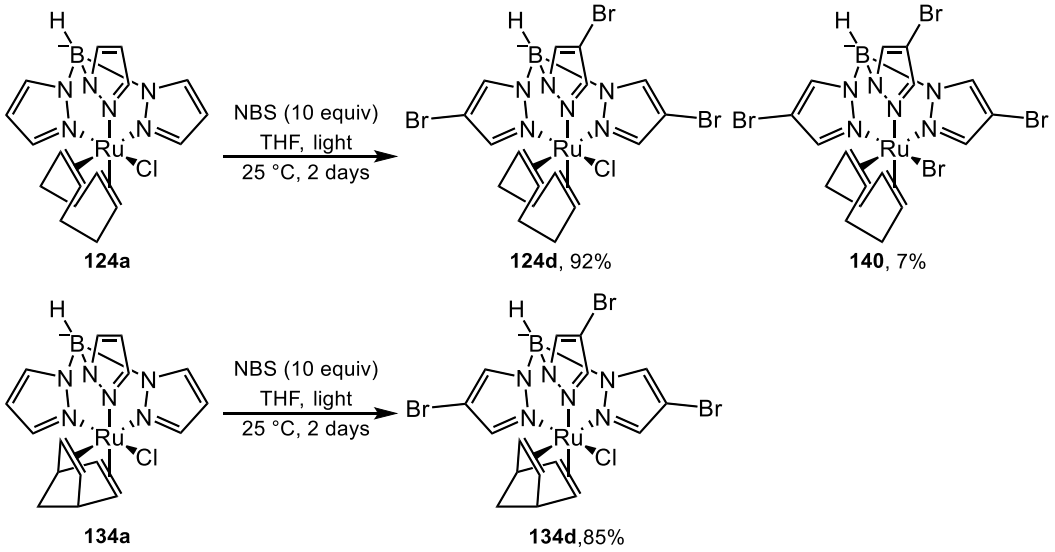
Putting plan into practice, **124a** was treated with 10 molar equivalents of Br_2. The reaction was complete in 45 minutes to give the expected product, **124d**, and Tp^{Br}Ru(cod)Br, **140** in a 2:1 ratio in 67% yield (Scheme 1.17). The latter was considered to be produced via the replacement of the Cl ligand-by Br^-. Bromination was also carried out on **134a**. Interestingly, the Ru-Cl bond was intact this time, and the reaction gave solely **134d** in 62% yield, which made the purification much easier.

Scheme 1.17: Direct bromination of 124a and 134a with bromine.



Although bromination with Br_2 was successful, the health hazards and difficulty in handling prompted a search for another reagent. Ten molar equivalents of a mild brominating agent, *N*-bromosuccinmide (NBS), was therefore assessed for the reaction (Scheme 1.18). Gratifyingly, a large scale NBS bromination (10 equiv) of **124a** gave **124d** in a 92% yield and Tp^{Br}Ru(cod)Br in a 7% yield despite a much longer reaction time (2 days). The Ru-Cl ligand displacement problem was mitigated with this milder reagent. Despite improved selectivity, complete separation of **124d** and **140** required three repetitive column chromatography purification. The NBS bromination with **134a** gave the brominated product **134d** in 85% yield as the only product, which made the purification easier. An intriguing feature of this reaction was that the reaction slows down in the absence of light, which is a typical feature of some radical reactions.

Scheme 1.18: Direct bromination of 124a and 134a with NBS



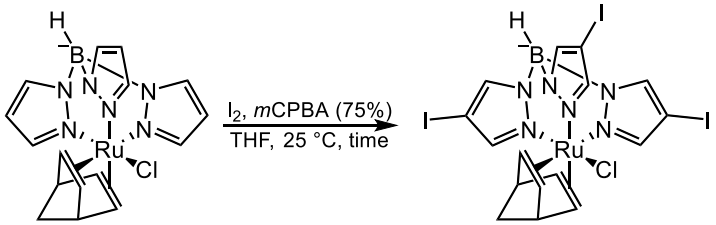
By incorporating the knowledge gained from the chlorination and bromination, design of the iodination can be more than simple I_2 conditions. Still, the first attempt to iodinate Tp ligand was to treat **134a** with I_2 (Table 1.4, entry 1). The Tp ligand was not iodinated at all. Iodination of at the C4 position of pyrazole was reported by the Antequera group that used a half equivalent of iodine and cerium ammonium nitrate (CAN).[16]

Therefore, the iodination of the Tp also was expected to be facilitated by an oxidizer. In lieu of using CAN, *m*CPBA was chosen as the oxidizer because it is a metal free reagent and slightly cheaper commercially. It was used as the commercially available impure form except for entries 5-7 (<77%). When iodine and/or mCPBA was present less than 10 equivalents, the reaction did not complete (entry 2). When 10 equivalents of iodine and *m*CPBA were added, the iodination was complete in 8 hours to afford the product in 48% yield (entry 3). Addition of two more equivalents of *m*CPBA shortened the reaction time by half, giving a comparable yield of 49% (entry 4). Interestingly, when purified *m*CPBA was used, the reaction mixture became light brown with a white suspension in two hours (entry 5). The analysis of the reaction mixture after the quench shows that the reactant remained mostly unreacted.

The purity of commercially available purified *m*CPBA was determined by iodometry analysis. It showed that the peroxide component of the commercially available formulation was 75.4% by weight, which is close to the description on the bottle. On the other hand, the purified *m*CPBA had 99.5% peracid contents by weight. This fact means that the impurity in the commercial batch must promote the reaction. The specification sheet says the reagent contains 6% 3-chlorobenzoic acid and 17% water. The purified *m*CPBA was doped with these additives in the reaction to identify which impurity played a key role. When similar amounts of *m*CBA to that in the commercial *m*CPBA was added, the result was the same as with pure *m*CPBA alone (entry 6). In sharp contrast, the addition of water gave a comparable yield of 52% as the iodination with the impure commercially available chemical (entry 7). The role of the water in the reaction is unclear, but it is possible I assert that water extends the lifetime of *m*CPBA. Washing *m*CPBA in benzene with basic solution (NaOH aq) destroys *m*CPBA. The addition of water might help the dissociation of proton form the *m*CBA to maintain the acidity of the mixture.

The importance of *m*CPBA lifetime is also demonstrated by premixing *m*CPBA (75.4%) and iodine in THF and stirring the mixture for 4 hours before adding **134a**. This control experiment resulted in an incomplete reaction. Five more equivalents iodine loading further shortened the reaction time only by one hour, but the reduced time did not satisfactorily compensate the consumption. Thus, the preferred conditions were 10 equiv of iodine and 12 equiv of *m*CPBA in the presence of H_2O (262 equiv). A large scale reaction achieved a reasonable yield of 70%. As a comparison, 12 molar equivalents of CAN was used instead of *m*CPBA. Gratifyingly, *m*CPBA was superior than the CAN mediated iodination. Since the radical mechanism was inferred from the observations from bromination, the radical quenchers BHT and TEMPO were added to the mixture under the chosen conditions. As expected, the reaction was completely shut down, which sustained the idea of a radical mechanism. To exclude the involvement of triiodide ion, combinations of reagents to form I_3^- were used. Again, no reaction occurred (entry 13 and 14).

Table 1.4: Direct iodination of 134a



134a 134e

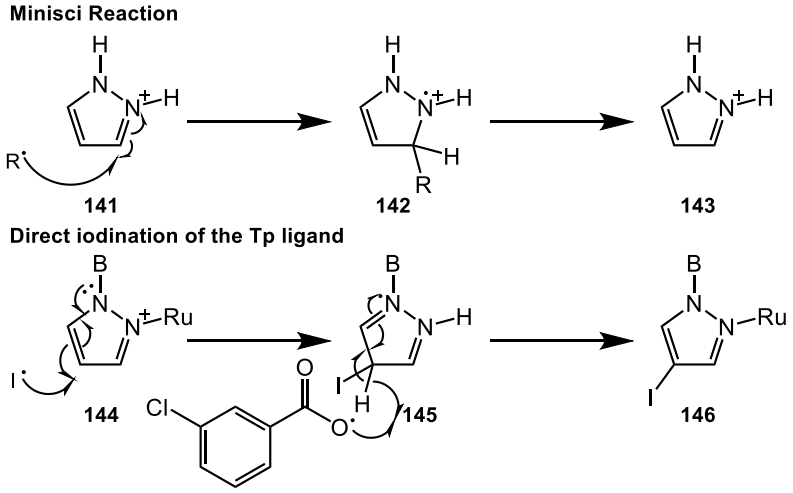
Entry	I_2 (equiv)	*m*CPBA (equiv)	Additive	Time	Result
1	10	0	-	4 h	No reaction
2	<10	<10	-	24 h	Incomplete reaction
3	10	10	-	8 h	48%
4	10	12	-	4 h	49%
5[a]	10	12	-	4 h	No product
6[b]	10	12	*m*CBA (10 equiv)	4 h	No product
7[b]	10	12	H_2O (262 equiv)	4 h	52%
8	15	12	-	3 h	53%
9[c]	10	12	-	4 h	70%
10	12	0	CAN (12 equiv)	4 h	Incomplete reaction
11	10	12	BHT (12 equiv)	4 h	trace product
12	10	12	TEMPO (12 equiv)	4 h	No product
13	10	0	KI (10 equiv) 18-crown-6 (10 equiv)	4 h	No reaction
14	10	0	TBAI	4 h	No reaction

0.124 mmol of **134a** was allowed to react in 6 mL of THF unless otherwise stated. [a]*m*CPBA (75.4%) was used unpurified from Sigma Aldrich (labelled <77%) unless otherwise stated. [b]Purified *m*CPBA (99.5%) was used. [c]Large scale reaction (x10).

Although halognation reactions of pyrzoles are not directly applicable to the direct halogenation reactions of the Tp ligands, consideration of the reaction mechanism in the halogenation of pyrazoles might help grasp the outlook of the mechanism of the direct halogenation of the Tp ligands. There is an idea that pyrazole ring is an electron rich aromatic compound and undergoes electrophilic substitution reaction at the 4 position.[17] Meanwhile, 3 position of the pyrazole is considered as the target site for a radical species in parallel with of the Minisci reaction (Scheme 1.19, top).[18] The Minisci reaction requires

that the heterocycle is protonated to increase the electrophilicity. According to the mechanism, the radical nucleophile attacks the carbon adjacent to the protonated nitrogen. The single electron moves into the nitrogen and stays on it until the C−H bond is cleaved. The direct halogenation takes place at the 4 position and shows radical behavior. Therefore, the mechanism shown at the bottom of Scheme 1. 19 incorporated some features in Minisci reaction. Specifically, the radical attacks C4, and a single electron resides on a nitrogen, followed by C−H bond cleavage,

Scheme 1.19: Minisci reaction and hypthetical radical mediated direct iodination reaction of the Tp ligand



Comparison of the ^{13}C NMR spectra of **134a**, **134c**, **134d**, and **134e** revealed distinct features. When **134c-e** were compared against **134a**, (see below 85 ppm region in Figure 1.4), the carbon peaks from the nbd ligand showed slight shifts upfield, whereas these peaks in **134c-e** are in the identical positions. This fact shows that the effect of halogenation at the Tp ligand is confined within the ligand.

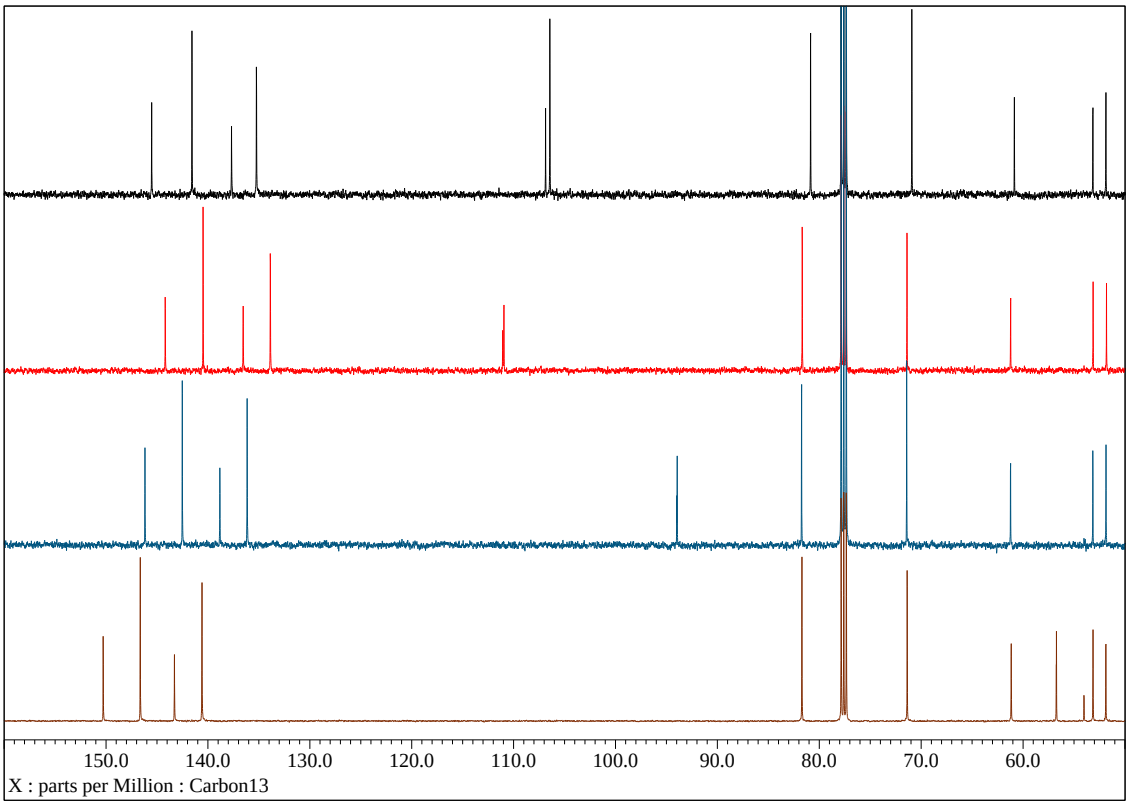


Figure 1.4: ^{13}C NMR spectra of TpRu(nbd)Cl 134a, Tp^{Cl}Ru(nbd)Cl 134c, Tp^{Br}Ru(nbd)Cl 134d, and Tp^{I}Ru(nbd)Cl 134e from top to bottom. The peak heights are adjusted to make the spectra comparable.

C4 peaks from pyrazoles generally appear in the region that spans from 90 to 110 ppm. If the C4 peak of **134a** is used as benchmark, the peaks of 1**34c** shift downfield while those from **134d** appear upfield. This phenomenon could be rationalized in terms of the electronegativity of the halogen and resonance effects. Because the electronegativity of Cl is very high, the electron density of the C4 is withdrawn to the Cl. In other words, C4 is deshielded. However, the electronegativity of the Br is not strong enough to overweigh the resonance effect of the Br to provide electron density. The net effect is the shielding of the C4. Intriguingly, such C4 peaks were not found in the middle range in ^{13}C NMR spectra of **134e**. However, two unique peaks appear at 51.8 and 61.2 ppm, which were demonstrated to correspond to C4 peaks by HMQC and HMBC. The electronegativity of iodine is 2.7 (Pauling), which is almost equal to carbon (2.6). Therefore, electron induction effects

cannot be expected. Rather, it is reasonable to think that the polarizable electron from iodine could flow into the C4 of the pyrazole and shield this carbon strongly, shifting the peaks far upfield.

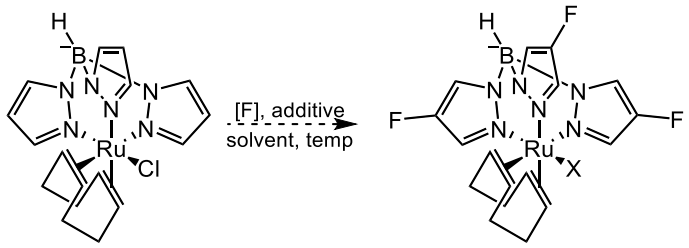
All C3 and C5 peaks from the pyrazoles appear far downfield (See above 130 ppm). The positions of the peaks vary depending on the type of the halogen, and the direction of the shift is opposite to that of C4: comparing **134a**, and **134c**, one can tell that the peaks shift to the upfield slightly while **134d** and **134e** shows these peaks downfield. Based on the NMR data, the following hypothesis was made: the chlorine substituent in the Tp^{Cl} ligand makes the C4 carbon electron deficient. This electron deficient carbon is partially positively charged. To alleviate the developing partial positive charge, the adjacent carbon atoms withdraw electron density from nitrogen to be electron rich. The upshot of the electron density redistribution shields the C3 and C5 carbons and makes the overall charge of the region (C3, C4, and C5) closer to neutral. Oppositely, Br and I increase the electron density on C4. This partial negative charge repels electron density on the adjacent carbons and deshield C3 and C5. Overall, the halogenation on Tp affects electronics of carbon-based ligands at least. However, the effects caused by the different halogens is limited to the Tp^{X} ligand.

1.4 Attempted Direct Functionalization Reactions of TpRu(nbd)Cl, 134a, and Coupling Reactions

In addition to the halogenation in the previous section, direct fluorination was attempted. Some "F^{+}" reagents, Slectfluor, NFSI and 1-Fluoro-2,4,6-trimethylpyridinium Trifluoromethanesulfonate were used to try to fluorinate the Tp ligand (Table 1.5, entries 1-4). However, none of these reagents successfully reacted. This result is consistent with the halogenation proceeding through the radical mechanism. The addition of AgF_2 turned the color of the mixture black, and reactant was consumed completely, but detectable

product was not found on TLC (entry 5). The reactant had decomposed. Xenon fluoride (XeF_2) was also used, but provided no reaction (entry 6). XeF_2 seemed to be a reasonable fluorinating reagent because a radical mechanism is accepted in some XeF_2 reactions.[19]

Table 1.5: Attempted direct fluorination of 124a



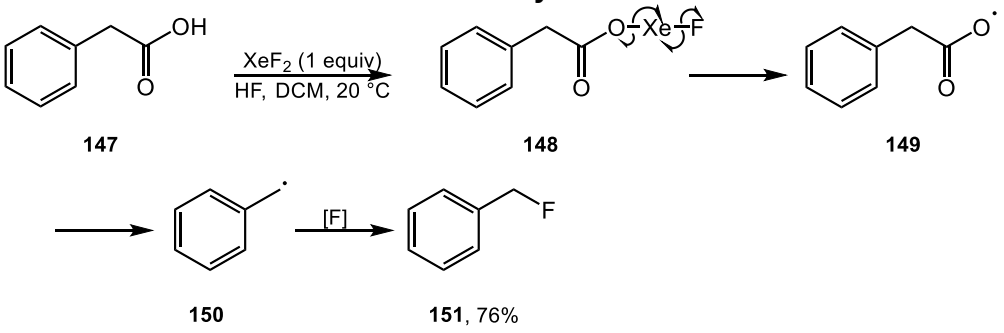
124a 124b

Entry	[F]	Additive	Solvent	Result
1	Selectfluor	-	THF or MeCN	No fluorination product
2	NFSI	*m*CPBA or CAN	DCM, THF or C_6H_6	No fluorination product
3	NFSI	BuLi	THF	No Rxn
4	$TMepyFCF_3SO_3^-$	*m*CPBA or CAN	THF	No fluorination product
5	AgF_2	-	THF	No fluorination product
6	XeF_2	-	THF, DCM, or C_6F_6	No fluorination product

One example is fluorodecarboxylation where a fluoroxenone ester was successfully isolated by DesMarteau and believed to be an active intermediate (Scheme 1.20).

However, fluorination by XeF_2 likely involves fluoride anion in other cases. One instance was the fluorination of aldehyde (Scheme 1.21).[20] In this case, fluoride anion attacked the carbonyl to make xenon fluoride ester, which made an epoxide in the following step. Another nucleophilic attack by fluoride on the less substituted carbon of the epoxide gives a rearranged product.

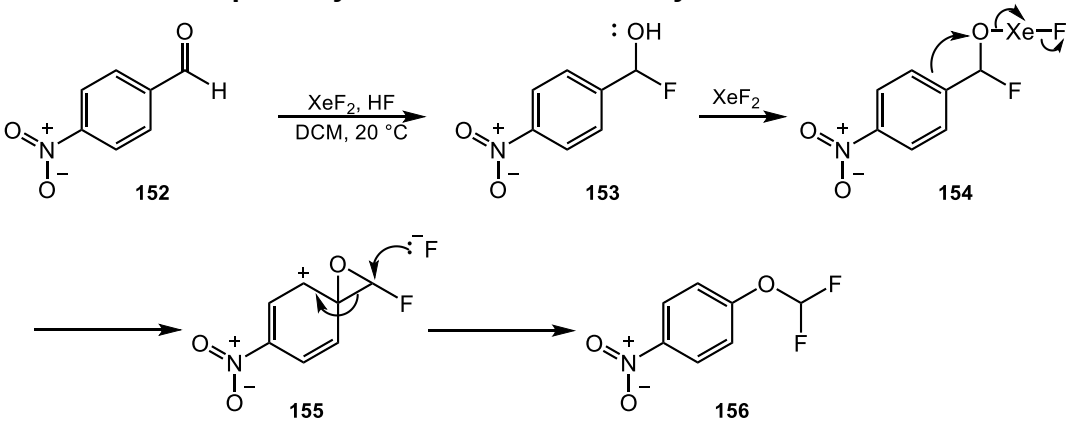
Scheme 1.20: Radical fluorination of carboxylic acid with XeF_2



147 148 149

150 **151**, 76%

Scheme 1.21: Ionic pathway in fluorination of aldehyde



152 153 154 155 156

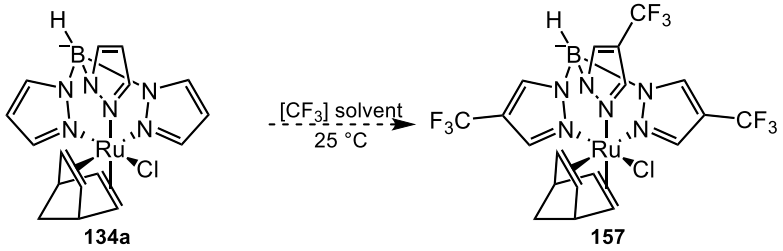
Thus, the manner XeF_2 reacts is not universal. Fluorination in the **124a** system did not work because of three possible reasons. (1) Formation of the radical is limited when the substrate has a particular functional group (carboxyl group in the above case), (2) the fluoride radical was so reactive that its lifetime was not long enough to react with the Tp complex or, (3) XeF_2 can react with solvents.

In summary, any attempt to develop direct fluorination was fruitless. While fluorine gas could potentially halogenate the Tp ligand, it may also react at different sites in **124a** or decompose the complex due to its very high reactivity.

Trifluoromethylation of **134a** was attempted with some purported radical trifluoromethylation reagents. Well-known reagents are sodium trifluoromethane sulfinate[21] and zinc trifluoromethane sulfinate.[22] Various combination of peroxides and trifluoromethylagtion reagents were examined (Table 1.6). First, the standard conditions

with *t*BuOOOH and DCM were used. Unfortunately, no reaction took place (entry 1). The solvent was switched to THF, but there was no improvement (entry 2). Using THF or DCM, the oxidizer was varied (entries 3-8). However, none of the oxidizers helped. Lastly, the trifluoromethylation reagent was switched to zinc varying the oxidizers and solvents (entries 9-11). None of the combinations above worked. Because triflinate reagents are soluble in water, it is natural to think that the radical species are born in the water. The lifetime of the CF_3 radical can be considered relatively short since radicals generally are more stable when they have electron rich substituents nearby. Therefore, the CF_3 radical could be quenched before it encountered **134a** in the organic layer.

Table 1.6: Trifluorination of 134a.



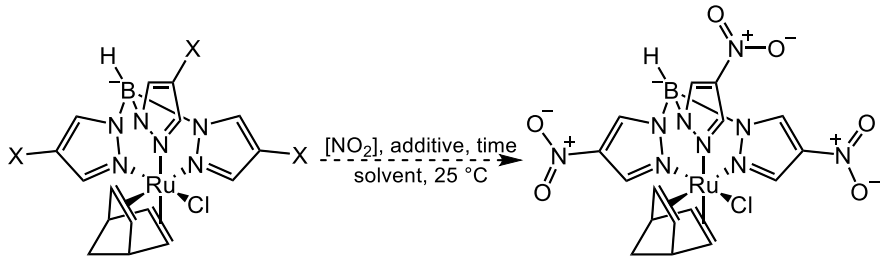
134a 157

Entry	[CF_3]	Time	Temp	Peroxide	Solvent	Yield
1	CF_3SO_2Na	28 h	25 °C	*t*BuOOH	DCM	No Rxn
2	CF_3SO_2Na	28 h	25 °C	*t*BuOOH	THF	No Rxn
3	CF_3SO_2Na	21 h	25 °C	CF_3COOOH	DCM	No Rxn
4	CF_3SO_2Na	21 h	25 °C	CF_3COOOH	THF	No Rxn
5	CF_3SO_2Na	20 h	25 °C	*m*CPBA	THF	No Rxn
6	CF_3SO_2Na	20 h	25 °C	*m*CPBA	DCM	No Rxn
7	CF_3SO_2Na	4 h	60 °C	CF_3COOOH	THF	No Rxn
8	CF_3SO_2Na	4 h	40 °C	CF_3COOOH	DCM	No Rxn
9	$(CF_3SO_2)_2Zn$	9 h	25 °C	*t*BuOOH	DCM	No Rxn
10	$(CF_3SO_2)_2Zn$	9 h	25 °C	CF_3COOOH	DCM	No Rxn
11	$(CF_3SO_2)_2Zn$	5 h	25 °C	CF_3COOOH	THF	No Rxn

Nitrogen dioxide is sometimes described as a radical species with an unpaired electron on the nitrogen. Therefore, it was proposed to nitrate the pyrazole rings of the Tp ligand. **134a** was allowed to react with an NO_2 solution in DCM (entry 1, Table 1.7). A new

compound was isolated and analyzed with NMR. It showed the proton peaks from the 4C positions of the Tp ligand, whereas the NBD peaks were replaced by two multiplet peaks (8H). The spectrum indicateed that NO_2 reacted near the ruthenium center, leaving the Tp ligand intact. Radical nitration reactions of porphyrins have been reported. When a palladium or copper porphyrin complex was treated with nitrogen dioxide, one site on the porphyrin ring was nitrated.[23] However, when the metal center was ruthenium the, nitrogen in NO_2 formed Ru-N bond.[24] Looking at the result of nitration of **134a**, it occurred to that ruthenium seems to have affinity for NO_2. Subsequently, silica-sulfuric acid catalyzed nitration of **134e** was investigated (entry 2).[25] Theoretically, this reaction forms NO_2^+ by mixing HNO_3 and H_2SO_4 adsorbed on the silica gel. However, nitrodeiodination did not occur. HNO_3 and H_2SO_4 was added to a DCM solution of **134a** instead in another trial (entry 3). This time, the complex decomposed, and the mixture became black. This meant that H_2SO_4 destroyed the complex. Li-Br exchange with BuLi followed by addition of electrophilic reagent nitronium tetrafluoroboratre, NO_2BF_4, was also examined (entry 4). No reaction occurred. The addition of NO_2BF_4 to THF violently produced bubbles, and addition of the reactant afterward did not cause any reaction (entry 5). In contrast, use of the DCM as the solvent did not destroy NO_2BF_4 before it could react with ruthenium. NO_2BF_4 consumed the ruthenium completely, but no product was visible on TLC (entry 6).

Table 1.7: Direct nitration of 134.

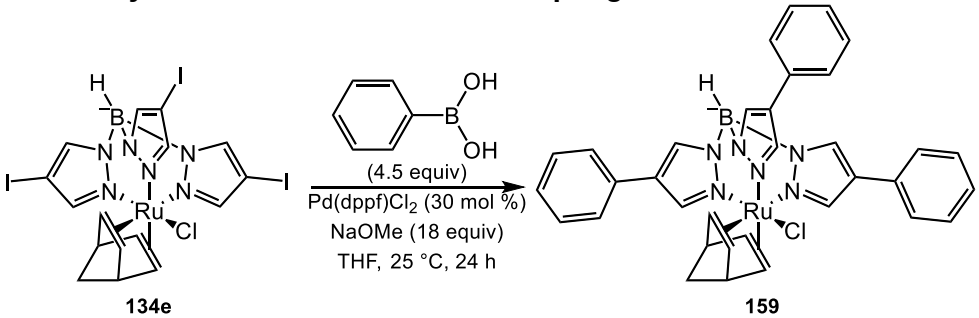


134 158

Entry	[NO_2]	X	Time	Temp	Additive	Solvent	Result
1	NO_2	H	3 h	25 °C		DCM	No nitration on Tp
2	HNO_3	I	4 h	25 °C	H_2SO_4-SiO_2	THF	No Rxn
3	HNO_3	H	24 h	25 °C	H_2SO_4	DCM	Decomposition
4	NO_2BF_4	Br	2 h	-78 to 25 °C	BuLi	THF	No Rxn
5	NO_2BF_4	I	4 h	25 °C		THF	No Rxn
6	NO_2BF_4	I	3 h	25 °C		DCM	Total conversion of reactant

Coupling reactions are used to connect organic frameworks or introduce functional groups. With **134e** in hand, it was feasible to synthesize diverse $Tp^{FG}Ru$ complexes. The most basic form of Suzuki coupling was tested at first. Phenyl boronic acid successfully added to **134e** in the presence of excess NaOEt (18 equiv) and a catalytic amount of $Pd(dppf)Cl_2$. The phenylated complex **159** could be isolated by column chromatography because it was much more polar than the reactant. However, the isolated product did not form a crystal. For this reason, further optimization of the Suzuki coupling was discontinued.

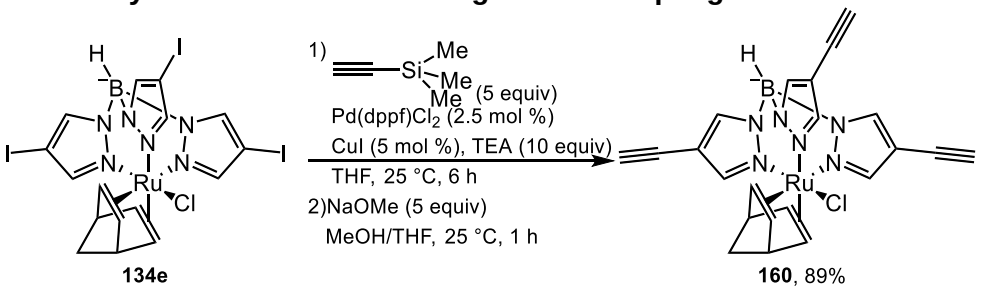
Scheme 1.22: Synthesis of 159 via Suzuki coupling.



134e 159

Another coupling partner was chosen so that the coupled product could form crystal. One way to achieve this goal is to reduce the conformational freedom of the complexes. For example, rotation of the C-C bond between the phenyl group and pyrazole ring in **159** changes the angle between these rings. One candidate was $Tp^{C\equiv CH}$(nbd)Cl, **160**, that could be formed through Sonogashira reaction(Scheme 1.23). The C-C bond rotation between the ethynyl group and the pyrazole ring does not change the shape of the complex. The complex **134e** was first coupled with trimethylsilylacetylene to give $Tp^{C\equiv CTMS}$(nbd)Cl **161** in the presence of TEA and Pd(dppf)Cl_2 (2.5%) in 6 hours at room temperature. This complex was purified with column chromatography, and the yellow solution was treated with sodium methoxide for 1 hour to deprotect the alkyne to give the target complex **160**. An orange crystal of **160** could be obtained by filtration and recrystallization.

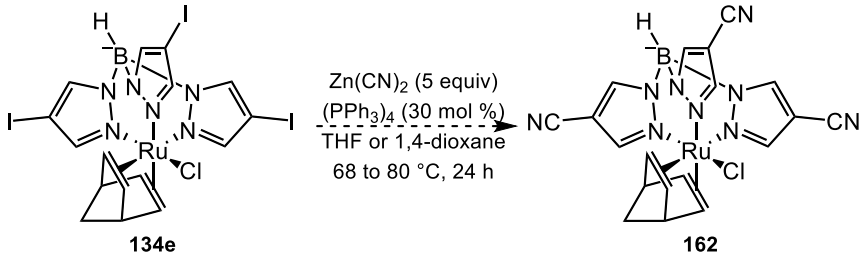
Scheme 1.23: Synthesis of 160 via Sonogahshira coupling.



134e **160**, 89%

Another functional group similar to ethynyl is the cyanide group (Scheme 1.24). In the literature, iodobenzene can be coupled with zinc cyanide in the presence of palladium.[26] This palladium coupling was applied to **134e**. This time, the palladium catalyst would not be reduced by the cyanide like copper acetylene; therefore, Pd(0) was used instead. The reaction was carried out in THF, dioxane, or DMF at 68 to 80 °C. None of these reactions made new compounds. Perhaps the low solubility of zinc cyanide did not allow the reaction.

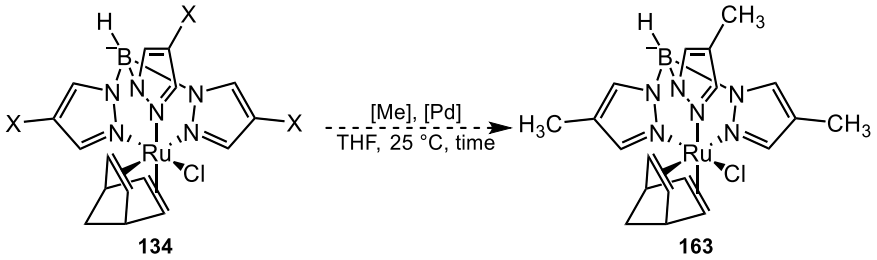
Scheme 1.24: Coupling of 134e with $Zn(CN)_2$.



134e **162**

Another relatively symmetric functional group is the methyl group. $Tp^{CH3}Ru(nbd)Cl$ **163** could be synthesized through Kumada, Negishi, or Suzuki couplings (Table 1.8). To the THF solution of **134d** was added a Grignard reagent MeMgBr in the presence of a nickel catalyst (entry 1). Although the reactant spot disappeared on TLC, no product spot was observed. The Grignard reagent was also added without the nickel complex (entry 2). Because the Kumada coupling is supposed to require a nickel catalyst, this background reaction seemed to have given undesired complex. The result was the same as with the nickel catalyst present. In the absence of a bromine substituent, on contrary, almost no reaction was obtained, probably due to the low solubility in the solvent (entry 3). The screening now moved to a milder Negishi coupling. Zinc chloride is premixed with the Grignard reagent to prepare the alkyl zinc reagent. To this solution was added the **134e**. This time, no reaction took place (entries 4-5). Similarly, Suzuki reaction with methylboronic acid did not give the product, which could be attributed to the low solubility of the boronic acid (entry 6).

Table 1.8: Attempted coupling reactions to synthesize 163.

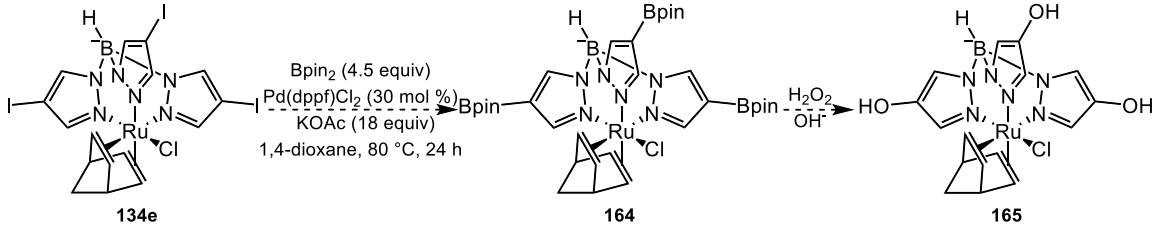


134 163

Entry	Catalyst	X	[Me], base	Time	Result
1	$Ni(PPh_3)_2Cl_2$	Br	MgBrMe, 10 equiv	2 h	Mixture, No reactant
2	-	Br	MgBrMe, 10 equiv	5 h	No reactant
3	-	H	MgBrMe, 10 equiv	5 h	Mostly No reaction
4	$Pd(PPh_3)_2Cl_2$	I	$ZnCl_2$+MgBrMe, 10 equiv	4 h	No Rxn
5	$Pd(dppf)Cl_2$	I	$ZnCl_2$+MgBrMe, 20 equiv	24 h	No Rxn
6	$Pd(PPh_3)_2Cl_2$	I	$MeB(OH)_2$ (4.5 equiv), MeONa (9.0 equiv)	29 h	No Rxn

Miyaura borylation to obtain, $Tp^{Bpin}Ru(nbd)Cl$, **164** was attempted because the peroxidation reaction could form another unprecedented complex: $Tp^{OH}Ru(nbd)Cl$, **165** (Scheme 1.25). The Miyaura borylation was carried out in THF, dioxane, DMF, and DMSO. No reaction took place in THF or dioxane regardless of whether HBpin or B_2pin_2 was used.

Scheme 1.25: Miyaura borylation of 134e to make 164 and 165.



134e 164 165

1.5 Conclusion

Unprecedented direct chlorination, bromination, and iodination reactions of Tp ligand in TpRu(diene)Cl was achieved in moderate to high yield. The mechanistic analysis first suggested that halogen molecules are good candidates to halogenate Tp ligand. Later, it was found that a radical mechanism is involved in the halogenation reaction. The weak

C-I bond of **134e** enabled a Suzuki and Sonogashira coupling to give **159** and **160** respectively. The latter gave an orange crystal that enabled full characterization of the complex with X-ray crystallography. However, fluorination, trifluorination, and nitration did not work as expected. Other coupling reactions of Tp^{I} ligand were also abandaned.

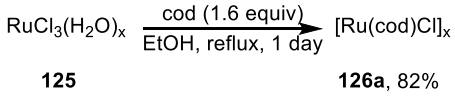
1.6 Experimental Section
Materials and Methods

All reactions were carried out in a flame-dried Shlenk flask under an Ar atmosphere. THF and toluene were purged with argon and dried over activated alumina columns and used after degassing by repetitive vacuum and Ar purges. KTp was prepared by a known procedure.[8] The synthesis of [Ru(cod)Cl]x has been reported before, but is reproduced below. TpRu(cod)Cl and TpRu(nbd)Cl were prepared by the same procedure as previously reported, but was purified differently. SO_2Cl_2 was distilled before use. NBS was recrystallized and thoroughly dried under vacuum before use. *m*CPBA was purchased from Sigma Aldrich (<77%) and used without purification unless otherwise stated. Iodometry analysis shows that the peroxy component in the unpurified *m*CPBA is 75.4%. A purified *m*CPBA was prepared by washing in benzene with 0.1M phosphate buffer 5 times and then brine. The organic layer was dried over $MgSO_4$, and the filtrate was dried under reduced pressure. (purity=99.5%). Flash column chromatography was performed on 60 Å silica gel (Sorbent technologies Inc.) unless otherwise stated. Analytical thin layer chromatography was performed on 250mm EMD silicagel/TLC plates with fluorescent detector 254 nm. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 500 spectrometer using the residual solvent peak as an internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.6 ppm for ^{13}C NMR and 400 MHz for ^{31}P NMR).

UV-Vis spectroscopy was collected on a Cary 6000 UV-vis NIR spectrophotometer over the 200-800 nm spectral range in DCM at room temperature. The crystallography

measurements were made with a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector using MoK/a radiation at 123 K. The reflections were collected using a narrow-frame algorithm with scan widths of 0.50/% in omega and phi and an exposure time of 20 s/frame at 6 cm detector distance. The data were integrated using the Bruker Apex-II program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied using SADABS. Redundant reflections were averaged. The structure was solved by direct method and refined with the program SHELXL 2014. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically with riding displacement parameters. Elemental analyses (H, C, N, Cl, Br, I) were performed by Atlantic Microlab, Inc. of Norcross, GA.

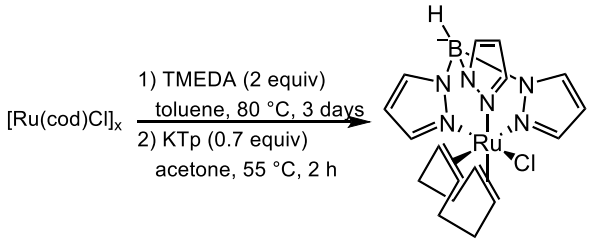
[Ru(cod)Cl]$_x$ 126a



125 **126a**, 82%

A flame dried 500 mL round-bottom flask was charged with **125** (10 g, 45.2 mmol) under inert atmosphere. Ethanol (240 mL) and 1,5-cyclooctadiene (9.5 mL, 77.1 mmol, 1.6 equiv) were added to the flask. The mixture was heated to reflux, and the mixture was kept boiled for 24 hours. The suspension was cooled to room temperature and filtered. The precipitate was rinsed with ether and dried under vacuum to give a brown powder **126a** (11.02 g, 82% yield). This powder was not characterized due to poor solubility in organic solvents.

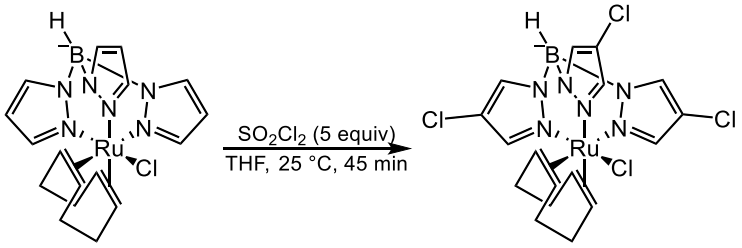
TpRu(cod)Cl 124a



126a **124a**, 25%

A flame-dried 50 mL Shlenk flask was charged with **126a** (2 g, 7.1 mmol), toluene (25 mL), and TMEDA (2.5 mL, 16.8 mmol, 2.2 equiv). The mixture was stirred in an oil bath at 80 °C for three days. Volatiles were removed under vacuum, and KTp (1.3 g, 5.2 mmol, 0.7 equiv) and acetone (13 mL) were added to the residue in a glove box. The flask was stirred in an oil bath at 55 °C for 2 hours, and the solvent was removed under reduced pressure. DCM was added to the flask and the mixture was stirred under air overnight. The DCM solution was purified via column chromatography, and the product was eluted with DCM/EtOAc=40:1. The major orange band was collected and concentrated. The residue was recrystallized from DCM/pentane over 2 days to give orange plate-like crystals **124a** (809.2 g, 25% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.13 (d, J = 2.3 Hz, 1H), 7.79 (d, J = 2.3 Hz, 1H), 7.65 (d, J = 2.3 Hz, 2H), 7.57 (d, J = 1.7 Hz, 2H), 6.32 (t, J = 2.3 Hz, 1H), 6.21 (t, J = 2.3 Hz, 2H), 4.96-4.87 (m, 2H), 4.07-3.98 (2H), 3.01-2.89 (m, 2H), 2.75-2.62 (m, 2H), 2.42 (q, J = 7.6 Hz, 2H), 2.25 (q, J = 7.4 Hz, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 30.3, 31.0, 87.6, 95.1, 106.7, 106.8, 135.4, 138.1, 142.3, 145.6.

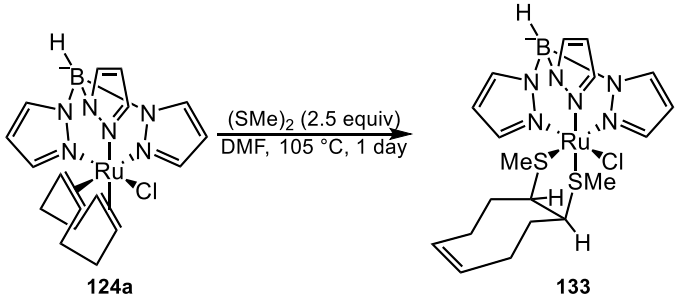
Tp^{Cl}Ru(cod)Cl 124c



124a **124c**, 92%

A flame dried 50 mL Shlenk flask was charged with **124a** (568 mg, 1.24 mmol), THF (10 mL), and SO_2Cl_2 (0.5 mL, 6.2 mmol, 5.0 equiv). The reaction was complete in 45 minutes, and the mixture was purified via column chromatography. The product was eluted with Hex/DCM/EtOAc=20:2:1. The orange fractions were collected and concentrated in a flask. The residue was recrystallized from DCM/pentane to give orange plate-like crystals **124c** that when vacuumed became an opaque solid. (698.2 mg, 100% yield) ^{1}H-NMR (500 MHz, chloroform-d) δ 8.05 (s, 1H), 7.77 (s, 1H), 7.60 (s, 2H), 7.50 (s, 2H), 4.88-4.78 (m, 2H), 4.07-3.97 (m, 2H), 2.98-2.85 (m, 2H), 2.72-2.59 (m, 2H), 2.42 (d, J = 8.6 Hz). ^{13}C-NMR (500 MHz, chloroform-d) δ 30.1, 30.6, 87.8, 95.9, 110.9, 111.1, 134.0, 136.8, 141.1, 144.2. Anal Calcd for $H_{19}C_{17}N_6BCl_4Ru$ (560.75 g/mol): H,3.42; C, 36.39; N, 14.98; Cl, 25.28; Found: H,3.40; C, 35.44; N, 14.51; Cl, 27.64.

TpRu1,2-(SMe)5, 6-COE 133

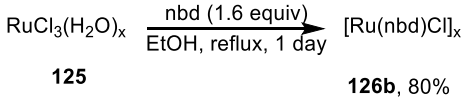


124a **133**

To the suspension of **124a** (200 mg, 0.43 mmol) in DMF (1 mL) was added dimethyl disulfide (0.1 mL, 1.11 mmol,2.6 equiv). After degassing, the mixture was heated at 100 °C for 24 hours. The mixture was purified via column chromatography. The product

was eluted with Hex/EtOAc=2:1. The yellow fractions were collected and concentrated in a flask. The compound was recrystallized from DCM/pentane to give brown crystals **133** (3.1 mg, 1.4%). Some product was lost by recrystallization. The structure of the complex was tentatively assigned by X-ray crystallography, but further characterization was not performed.

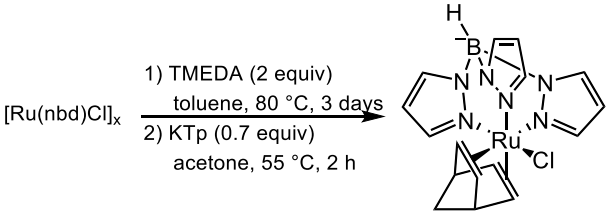
$[Ru(nbd)Cl]_x$ 126b



125 **126b**, 80%

A flame dried 500 mL round-bottom flask was charged with **125** (10 g, 45.2 mmol) under inert atmosphere. Ethanol (240 mL) and 1,5-cyclooctadiene (9.5 mL, 77.1 mmol, 1.6 equiv) were added to the flask. The mixture was heated to reflux, and the mixture was boiled 24 hours. The suspension was cooled to room temperature and filtered. The precipitate was rinsed with ether and dried under vacuum to give a reddish powder **126b** (10.10 g, 80% yield). This powder was not characterized due to poor solubility in organic solvents.

TpRu(nbd)Cl 134a

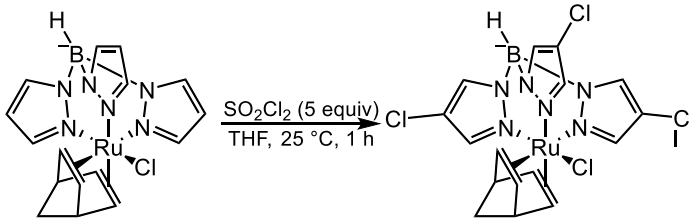


126b, 80% **134a**, 45%

A flame-dried 50 mL Shlenk flask was charged with **126b** (2 g, 7.6 mmol), toluene (25 mL), and TMEDA (2.5 mL, 16.8 mmol, 2.2 equiv). The mixture was stirred in an oil bath at 80 °C for three days. Volatiles were removed under vacuum, and KTp (1.3 g, 5.2 mmol, 0.7 equiv) and acetone (13 mL) were added to the residue in a glove box. The flask was stirred in an oil bath at 55 °C for 2 hours, and the solvent was removed under reduced pressure. DCM was added to the flask and the mixture was stirred under air overnight.

The DCM solution was purified via column chromatography, and the product was eluted with DCM/EtOAc=40:1. The major orange band was collected and concentrated. The residue was recrystallized from DCM/pentane over 2 days to give orange plate-like crystals **134a** (1.48 g, 44% yield). ^{1}H NMR (500 MHz, chloroform-d) δ 8.43 (d, J = 2.3 Hz, 1H), 7.76 (d, J = 2.3 Hz, 1H), 7.64 (d, J = 2.3 Hz, 2H), 7.30 (d, J = 2.3 Hz, 2H), 6.33 (t, J = 2.3 Hz, 1H), 6.22−6.14 (m, 2H), 5.29 (t, J = 3.4 Hz, 2H), 4.52−4.37 (m, 2H), 4.25 (dd, J = 4.6, 3.4 Hz, 2H), 1.70 (s, 2H). ^{13}C NMR (500 MHz, chloroform-d) δ51.8, 60.8, 70.9, 80.8, 106.4, 106.8, 135.2, 137.6, 141.5, 145.5.

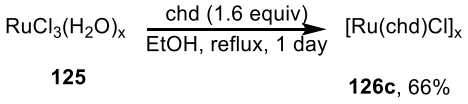
Tp^{Cl}Ru(nbd)Cl 134c



134a **134c**, 86%

A flame dried 50 mL Shlenk flask was charged with **134a** (550 mg, 1.24 mmol), THF (10 mL) and SO_2Cl_2 (0.5 mL, 6.2 mmol, 5.0 equiv). The reaction was complete in 45 minutes, and the mixture was purified via column chromatography. The product was eluted with Hex/DCM/EtOAc=16:2:1. The orange fractions were collected and concentrated in a flask. The residue was recrystallized from DCM/pentane to give orange needle crystals **134c**. (583.2 mg, 86% yield) ^{1}H-NMR (500 MHz, chloroform-d) δ8.37 (s, 1H), 7.74 (s, 1H), 7.59 (s, 2H), 7.23 (s, 2H), 5.28-5.23 (m, 2H), 4.46 (t, J = 3.4 Hz, 2H), 4.29-4.19 (m, 2H), 1.71 (d, J = 1.7 Hz, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 51.8, 61.2, 71.3, 81.6, 110.9, 111.0, 133.8, 136.5, 140.4, 144.1. Anal Calcd for $H_{35}C_{37}N_6BP_2Cl_4Ru$ (546.61 g/mol): H, 2.77; C, 35.26; N, 15.42; Cl, 26.02; Found: H, 2.77; C, 35.07; N, 15.38; Cl, 26.30.

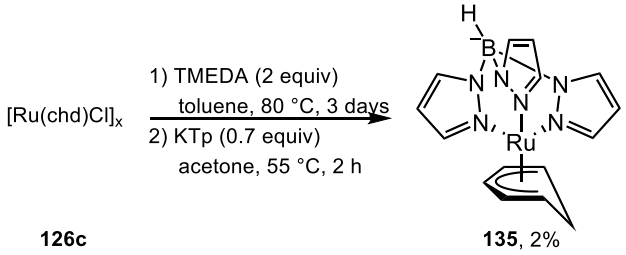
[Ru(chd)Cl]$_x$ 126c



125 **126c**, 66%

A flame dried 500 mL round-bottom flask was charged with **125** (2.0 g, 45.2 mmol) under inert atmosphere. Ethanol (48 mL) and 1,4-cyclohexadiene (1.5 mL, 15.4 mmol, 1.6 equiv) were added to the flask. The mixture was heated to reflux, and the mixture was kept boiled for 24 hours. The suspension was cooled to room temperature and filtered. The precipitate was rinsed with ether and dried under vacuum to give a brown powder **126c** (1.6 g, 66% yield). This powder was not characterized due to poor solubility in organic solvents.

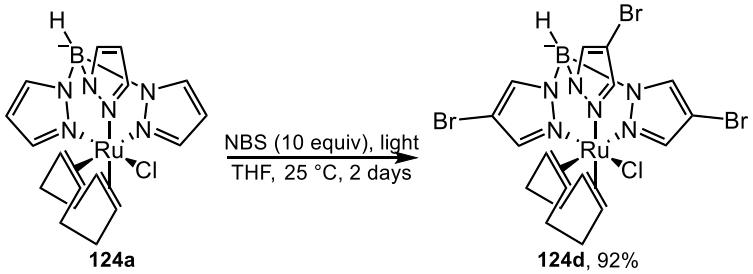
TpRuη^5-(C$_6$H$_7$)Cl 135



126c **135**, 2%

A flame dried 50 mL Shlenk flask was charged with**126c** (1.6 g, 6.36 mmol), toluene (20 mL), and TMEDA (2.0 mL). The suspension was degassed and heated to 80 °C for 3 days. The volatiles were removed under vacuum, and KTp (1.0 g) was added to the residue. Acetone was added to the residue, and the solution was heated to 55 °C over 2 hours. The mixture was purified via column chromatography, and the product was eluted with DCM/Hex=4:1. The yellow fractions were collected and concentrated in a flask. The product was recrystallized from DCM/pentane to afford light yellow crystal **135** (49.1 mg, 1.9%).

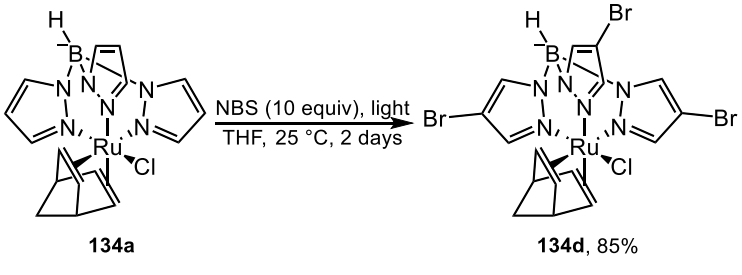
Tp^{Br}Ru(cod)Cl 124d



124a **124d**, 92%

A flame dried 50 mL Shlenk flask was charged with **124a** (568.0 mg, 1.2 mmol) under inert atmosphere. THF (80 mL) and NBS (2138 mg, 12.0 mmol, 9.7 equiv) were added to the flask. The mixture was kept stirred under light for 2 days. (670.0 mg 12.4 mmol, 10 equiv) of sodium methoxide was added, and the mixture was concentrated under reduced pressure. The residue was dissolved in DCM and purified through column chromatography with hexane/DCM/EtOAc=20:2:1. The product was recrystallized from DCM/pentane to afford orange crystal **124d**. (793.0 mg, 92% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.06 (s, 1H), 7.81 (s, 1H), 7.64 (s, 2H), 7.53 (s, 2H), 4.91-4.78 (m, 2H), 4.07-3.96 (m, 2H), 3.00-2.86 (m, 2H), 2.73-2.59 (m, 2H), 2.42 (q, J = 7.8 Hz, 2H), 2.25 (q, J = 7.4 Hz, 2H) ^{13}C-NMR (500 MHz, chloroform-d) δ 30.2, 30.6, 87.8, 93.9, 94.1, 96.0, 136.3, 139.1, 143.2, 146.1

Tp^{Br}Ru(nbd)Cl 134d

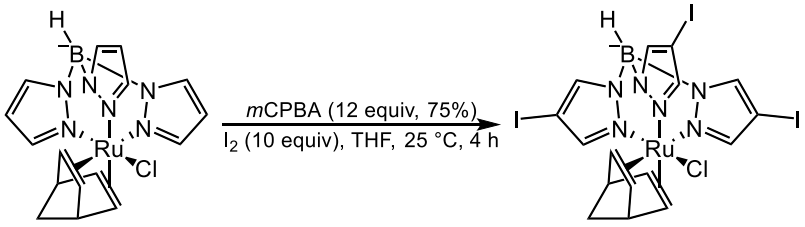


134a **134d**, 85%

A flame dried 50 mL Shlenk flask was charged with **134a** (550.1 mg, 1.2 mmol) under inert atmosphere. THF (80 mL) and NBS (2138 mg, 12.0 mmol, 9.7 equiv) were added to the flask. The mixture was kept stirred under light for 2 days. (670.0 mg, 12.4 mmol, 10 equiv) of sodium methoxide was added, and the mixture was concentrated under

reduced pressure. The residue was dissolved in DCM and purified through column chromatography with hexane/DCM/EtOAc=16:2:1. The product was recrystallized from pentane/DCM to afford orange crystal **134d**. (715.9 mg, 85% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.39 (s, 1H), 7.78 (s, 1H), 7.63 (s, 2H), 7.26 (s, 2H), 5.27 (t, J = 3.4 Hz, 2H), 4.47 (t, J = 3.7 Hz, 2H), 4.31-4.18 (m, 2H), 1.72 (s, 2H)). ^{13}C-NMR (500 MHz, chloroform-d) δ 51.8, 61.2, 71.4, 81.7, 93.9, 93.9, 136.1, 138.8, 142.5, 146.1 Anal Calcd for $H_{15}C_{16}N_6BClBr_3Ru$ (680.24 g/mol): H, 2.23; C, 28.33; N, 12.39; Cl, 5.23; Br, 35.34; Found: H,2.14; C, 28.32; N, 12.31; Cl, 5.35; Br, 35.48.

Tp^{I}Ru(nbd)Cl 134e

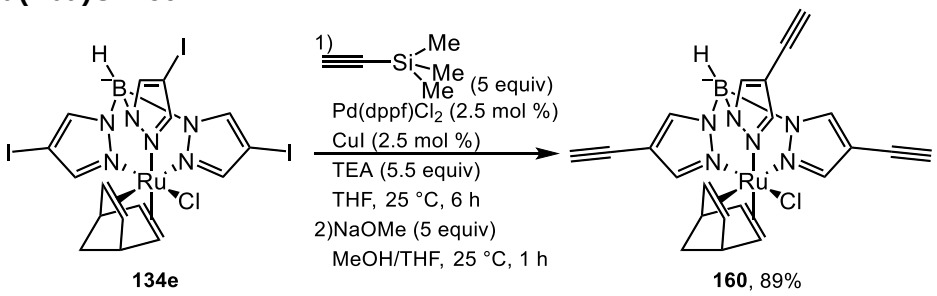


134a **134e**, 70%

A flame dried 100 mL round-bottom flask was charged with **134a** (549.9 mg, 1.2 mmol) under inert atmosphere. Iodine (3149.0 mg, 12.4 mmol, 10 equiv), *m*CPBA (3333.7 mg, 14.9 mmol, 12 equiv), and THF (60 mL) were added to the flask. The mixture was kept stirred for four hours. The mixture was washed with 20 mL of 0.775 M $Na_2S_2O_3(H_2O)_5$ solution three times and 30 mL of 0.3 M solution of $NaHCO_3$ three times. The organic layer was concentrated under diminished pressure, and the residue was purified through column chromatography with DCM as eluent. The product was recrystallized from DCM/pentane to afford orange crystal **134e** (790.6 mg, 70% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.39 (s, 1H), 7.80 (s, 1H), 7.66 (s, 2H), 7.28 (s, 2H), 5.27 (t, J =4.0 Hz, 2H), 4.46 (t, J = 3.4 Hz, 2H), 4.24 (d, J = 17.8 Hz, 2H), 1.70 (s, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 51.8, 54.0, 56.7, 61.1, 71.3, 81.7, 140.5, 143.2, 146.6, 150.2 Anal Calcd

for $H_{15}C_{16}N_6BClI_3RuCH_2Cl_2$ (904.30 g/mol): H, 1.89; C, 28.58; N, 9.29; Cl, 11.76; I, 42.10; Found: H,1.92; C, 22.78; N, 9.23; Cl, 11.83; I, 41.92.

$Tp^{C\equiv CH}Ru(nbd)Cl$ 160



134e **160**, 89%

A flame dried 10 mL round-bottom flask was charged with **134e** (712.6 mg, 0.87 mmol) under inert atmosphere. 9.5 mL of THF, CuI (4.2 mg, 0.02 mmol, 0.025 equiv), and TEA (660 mL, 4.74 mmol, 5.5 equiv) were added to the flask to completely dissolve the crystal. $Pd(dppf)Cl_2$ (15.9 mg, 0.02 mmol, 2.5 mol %) and ethynyltrimethylsilane (600 μL, 4.34 mmol, 5 equiv) were added to the flask to start the reaction. The mixture was kept stirred for six hours at room temperature. The mixture was concentrated to dryness under vacuum. The residue was dissolved in DCM and purified through column chromatography with hexane/DCM/EtOAc=20:2:1 as eluent. The product was rinsed with 12 mL THF into to a 25 mL round bottom flask. 2 mL of methanol and sodium methoxide (234 mg, 4.33 mmol, 5 equiv) were added to the flask, and the mixture was stirred for an hour. The solvent was removed under reduced pressure, and the residue was dissolved in DCM. The suspension was filtered through Celite. The product in the filtrate was recrystallized from DCM/pentane to afford orange crystal **160**. (372.1 mg, 89% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.55 (s, 1H), 7.89 (s, 1H), 7.77 (s, 2H), 7.41 (s, 2H), 5.27 (t, J = 3.7 Hz, 2H), 4.46 (t, J = 3.7 Hz, 2H), 4.31-4.17 (m, 2H), 3.06 (s, 1H), 2.94 (s, 2H), 1.71 (s, 2H) ^{13}C-NMR (500 MHz, chloroform-d) δ51.8, 61.1, 71.4, 74.3, 74.6, 79.1, 79.7, 81.7, 103.6, 103.9, 138.9, 141.2, 145.2, 148.9 Anal Calcd for $H_{18}C_{22}N_6BClRu0.15(CH_2Cl_2)$ (526.50 g/mol): H, 3.50; C, 50.53; N, 15.96; Cl, 8.75; Found: H,3.43; C, 50.78; N, 16.26; Cl, 8.78.

APPENDEX ONE: NMR Spectra

Syntheses of $Tp^{X}Ru(diene)Cl$ Complexes and Documentation of Their Thermodynamic Stability

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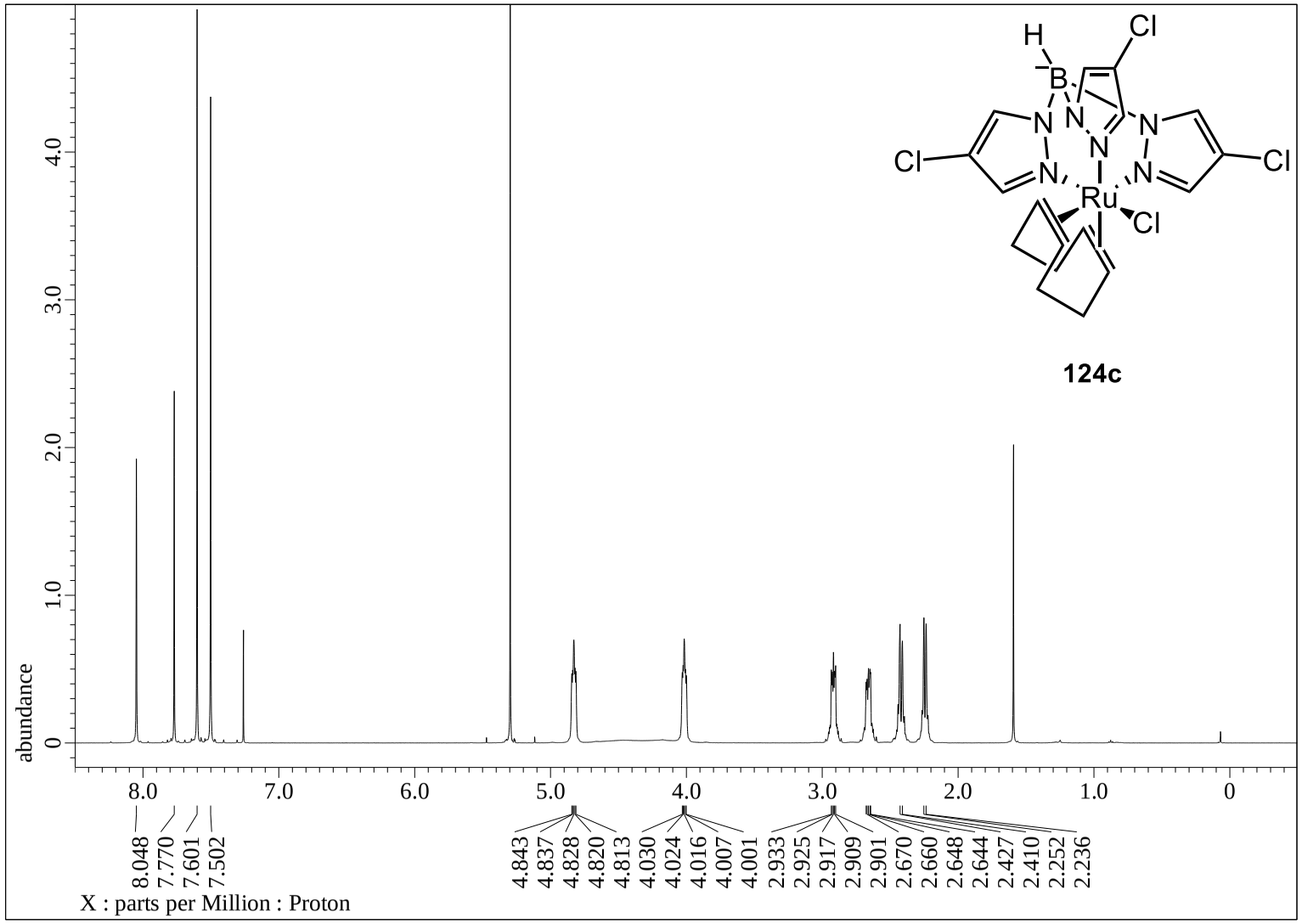

Figure A1.1: ^{1}H-NMR spectrum of 124c (500 MHz, $CDCl_3$)

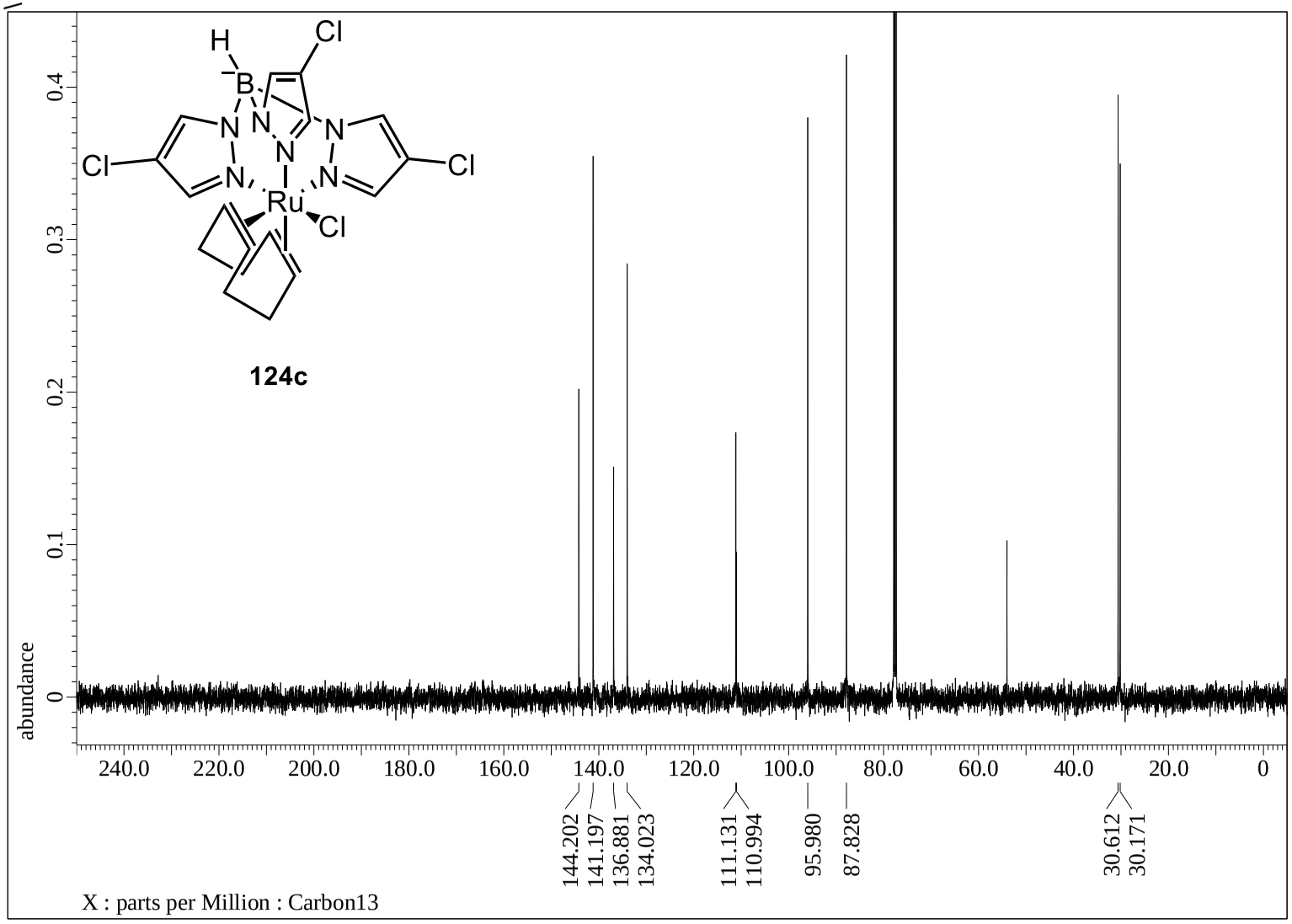

Figure A1.2: ^{13}C-NMR spectrum of 124c (500 MHz, $CDCl_3$)

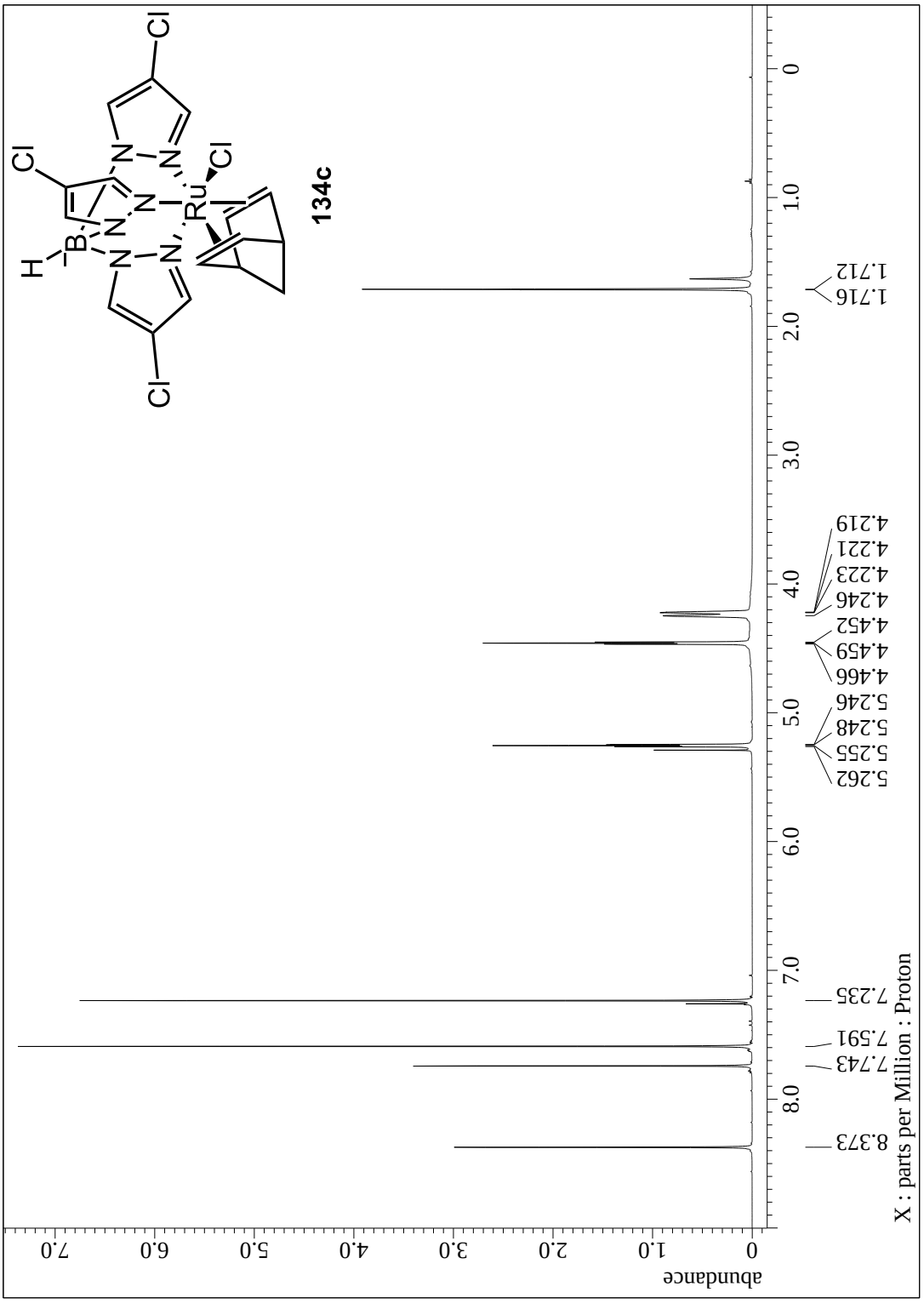

Figure A1.3: ^{1}H-NMR spectrum of 134c (500 MHz, $CDCl_3$)

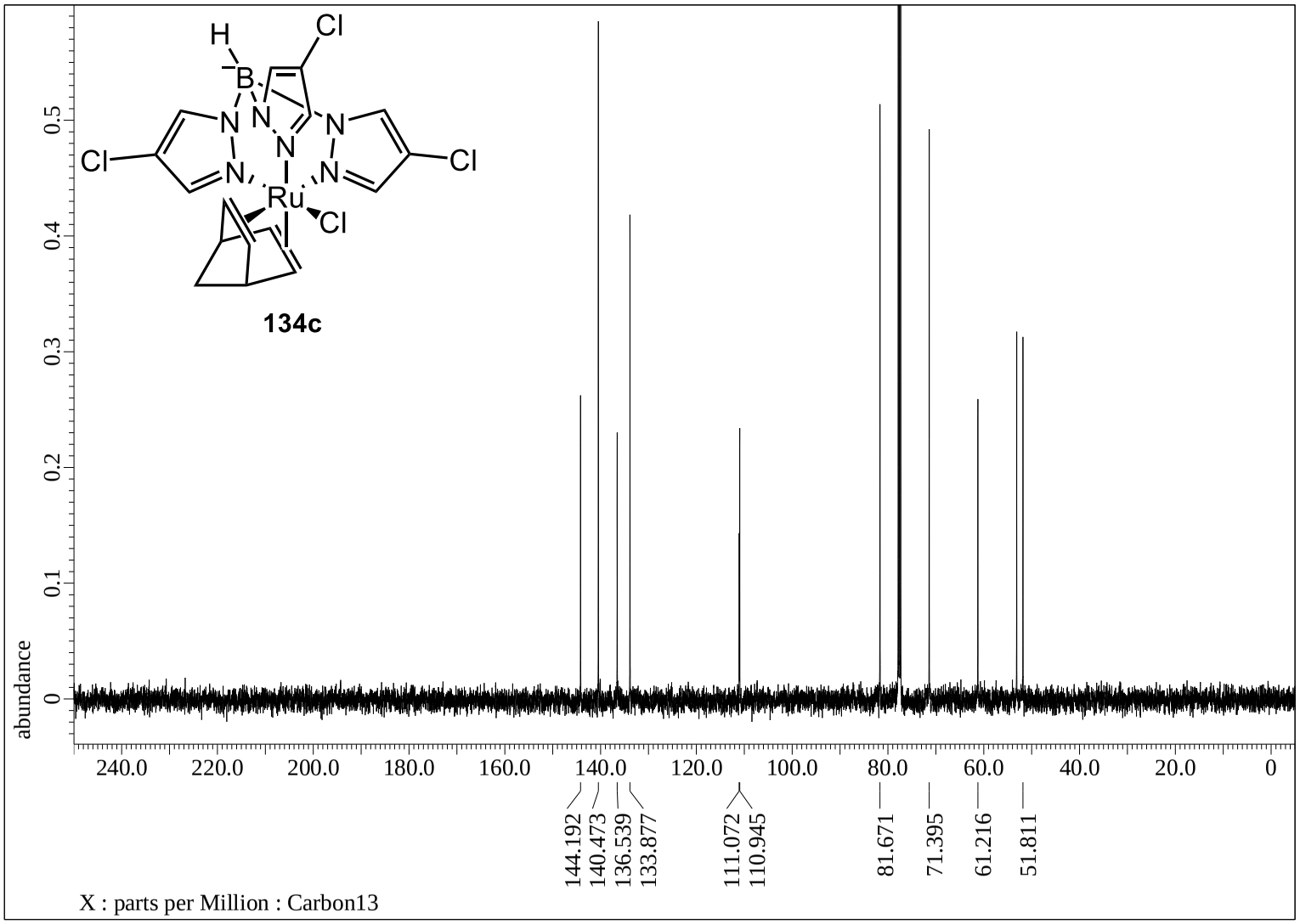

Figure A1.4: ^{13}C-NMR spectrum of 134c (500 MHz, $CDCl_3$)

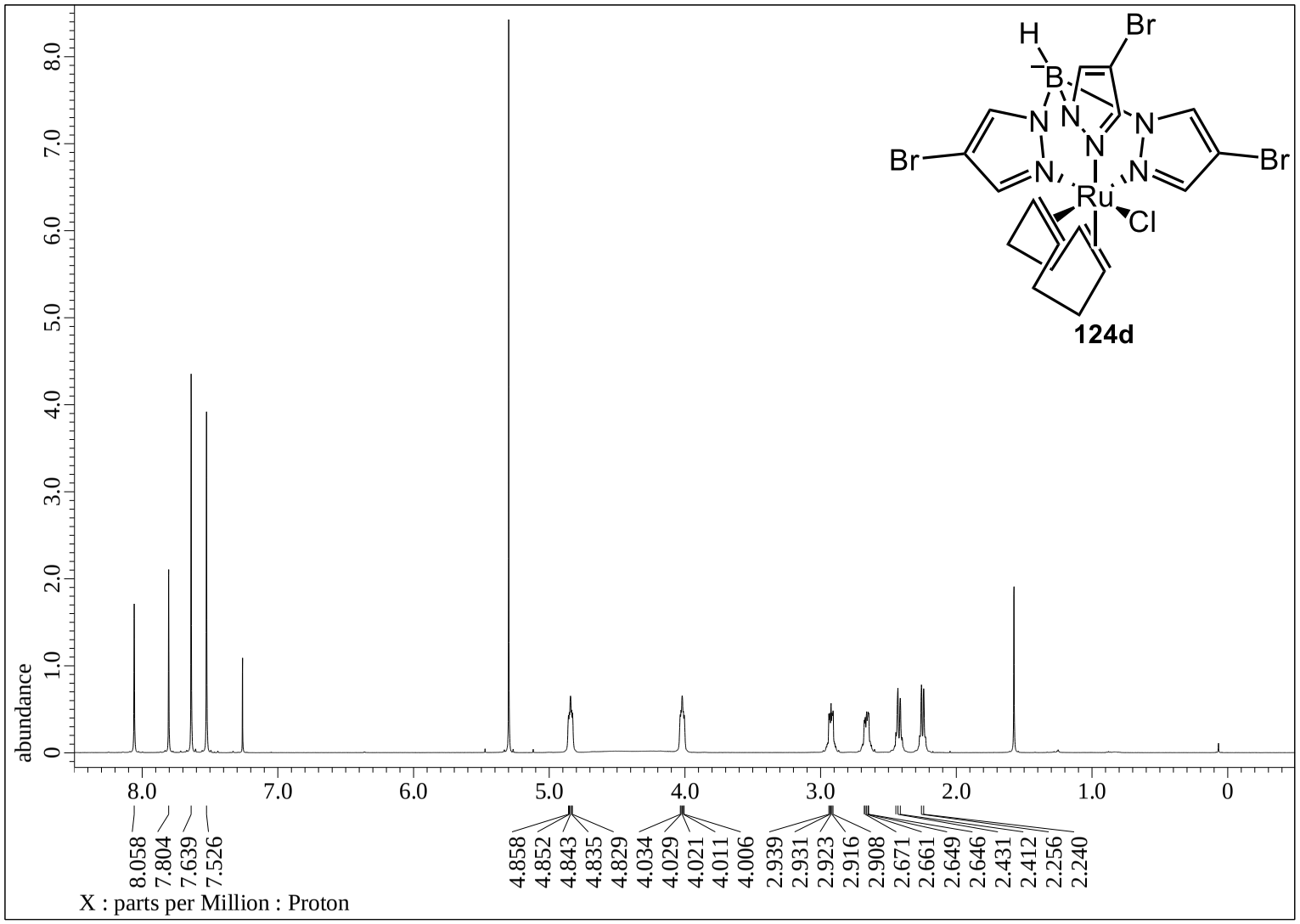

Figure A1.5: ^{1}H-NMR spectrum of 124d (500 MHz, $CDCl_3$)

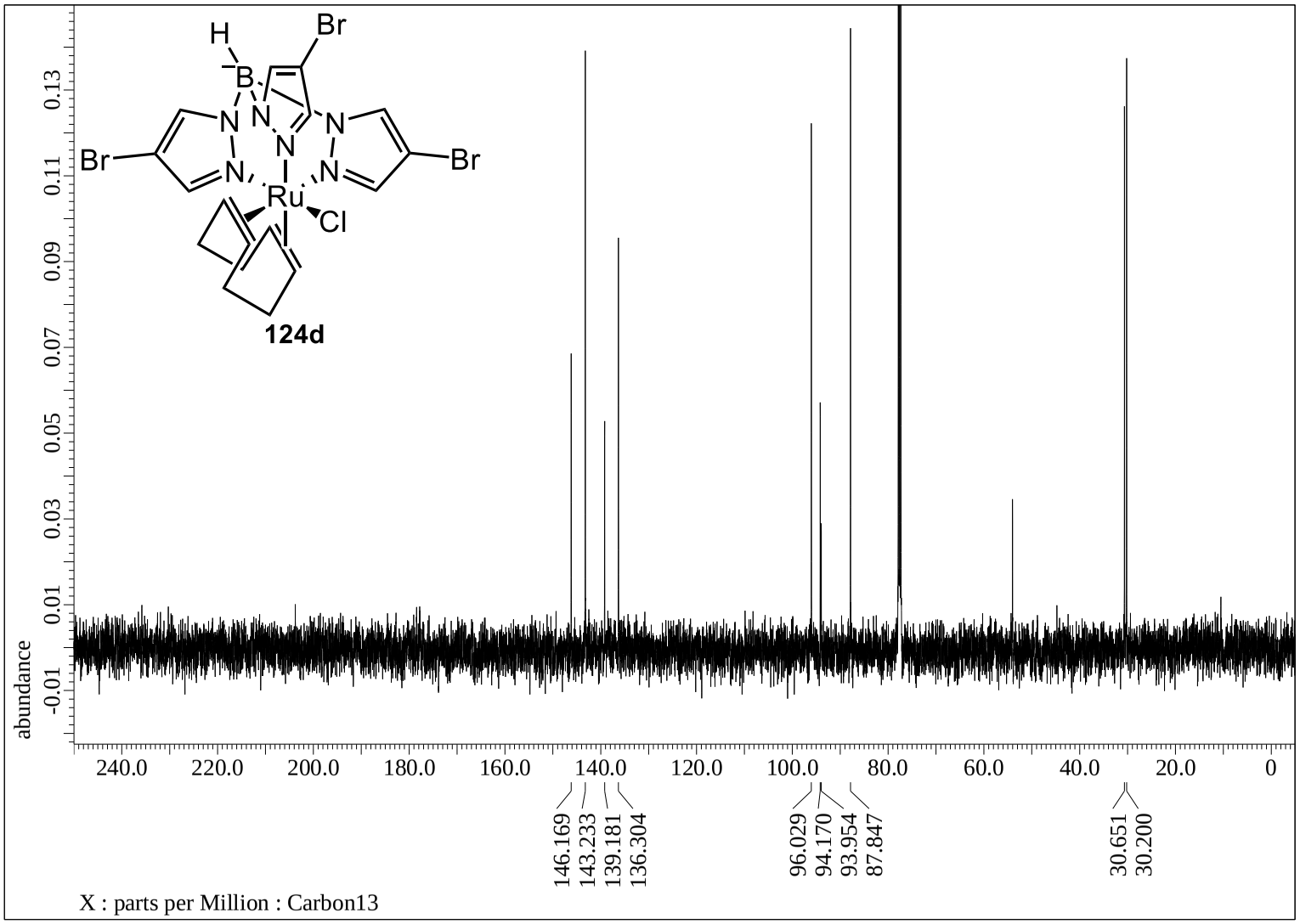

Figure A1.6: ^{13}C-NMR spectrum of 124d (500 MHz, $CDCl_3$)

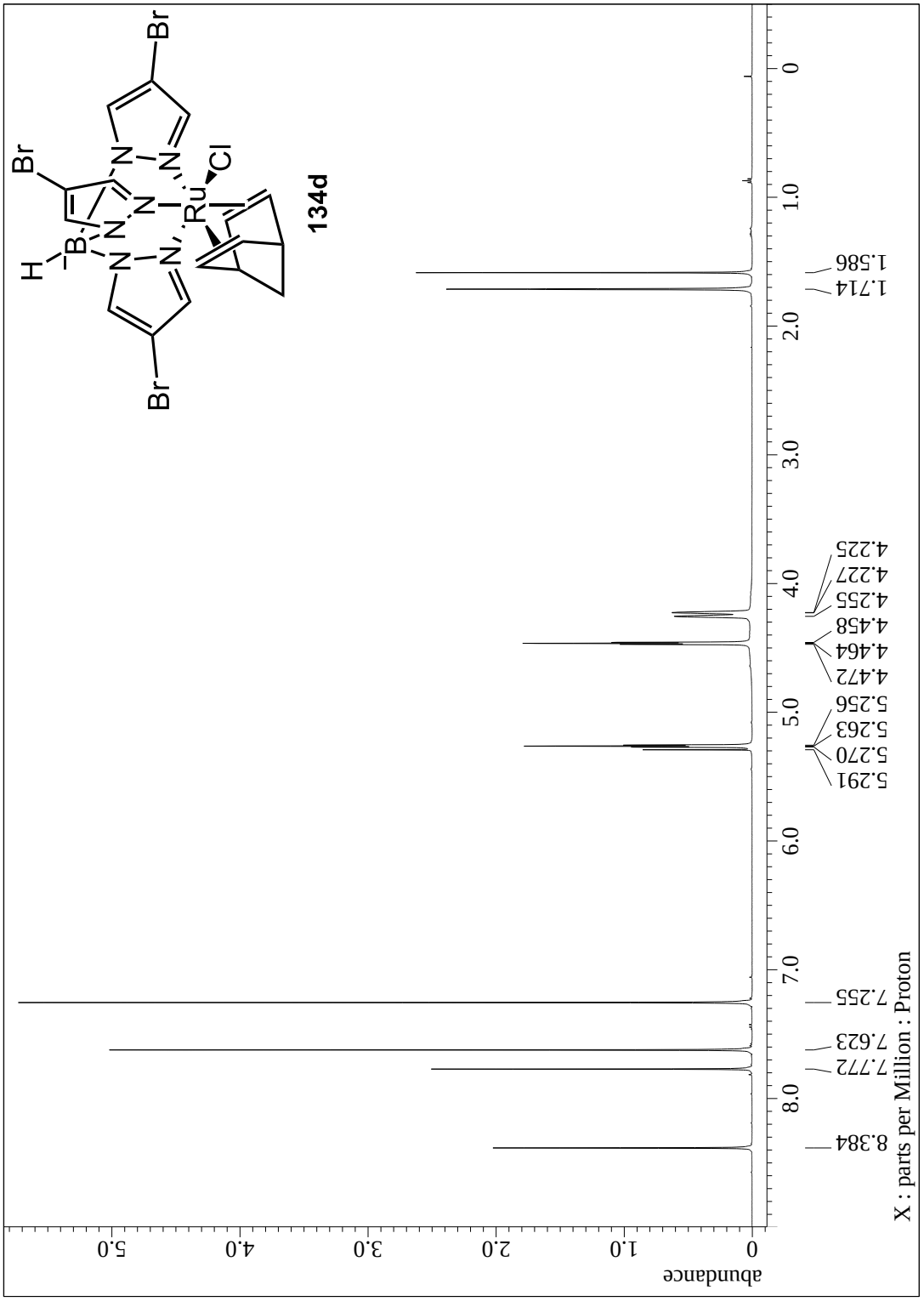

Figure A1.7: ^{1}H-NMR spectrum of 134d (500 MHz, $CDCl_3$)

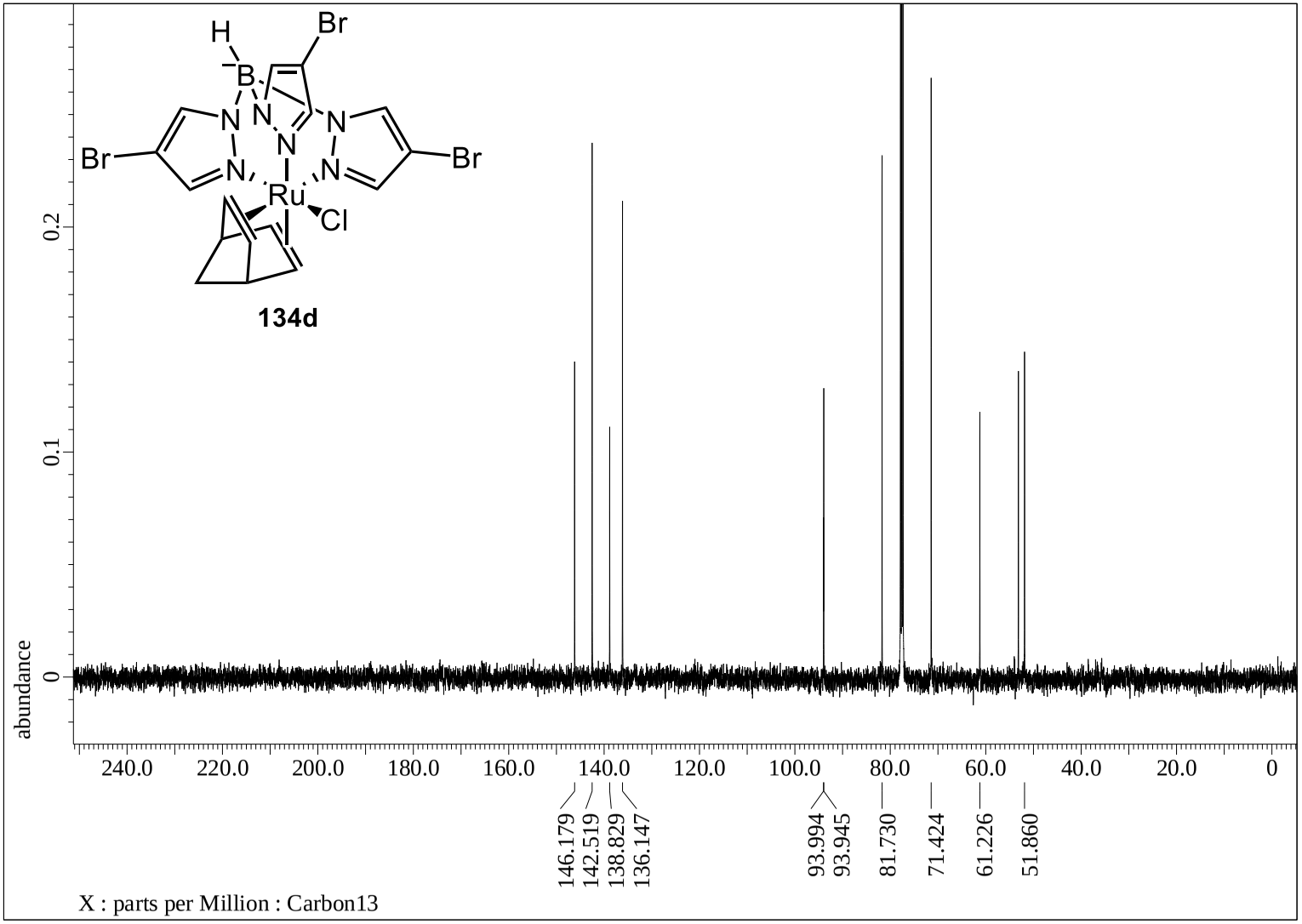

Figure A1.8: ^{13}C-NMR spectrum of 134d (500 MHz, $CDCl_3$

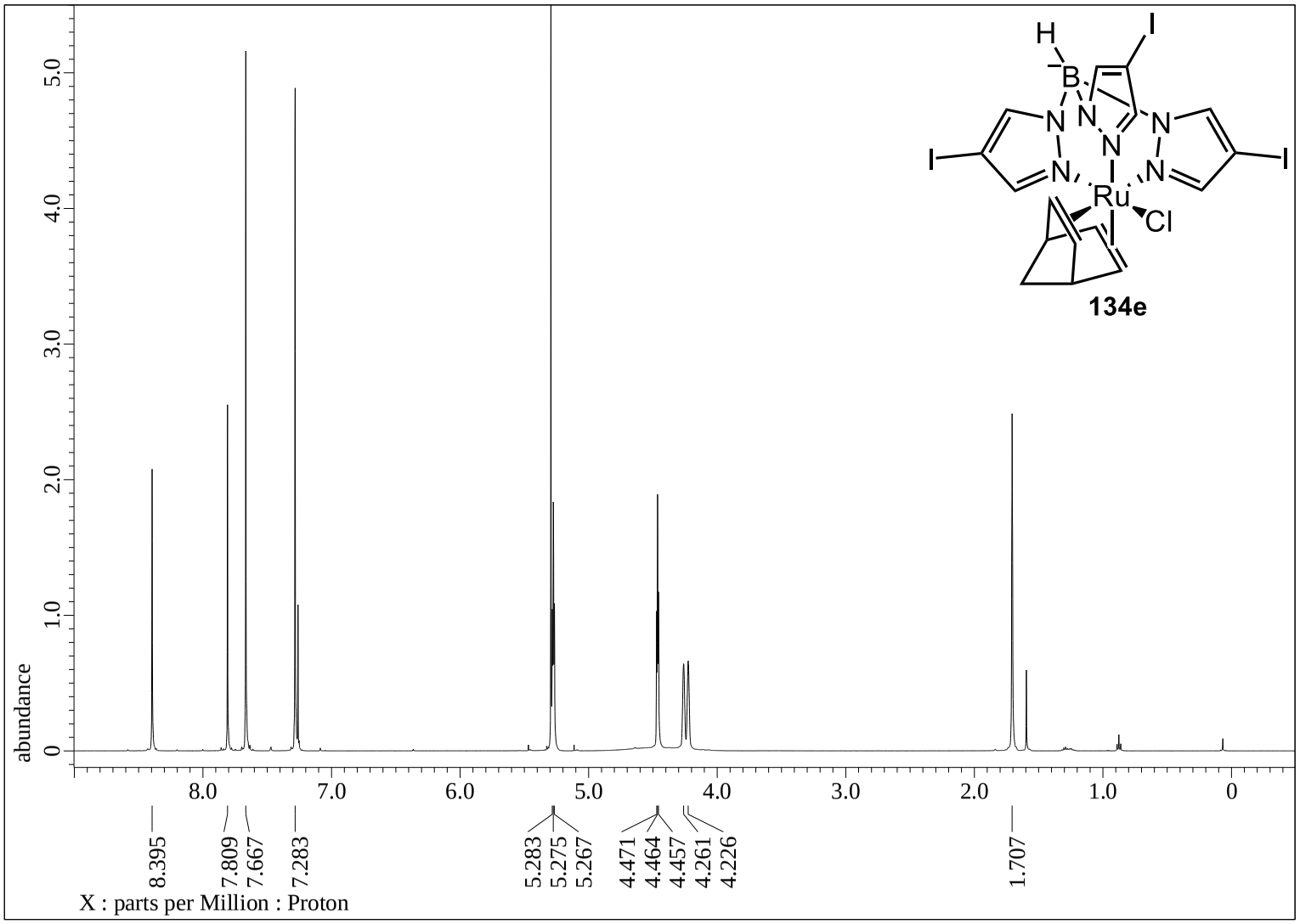

Figure A1.9: ^{1}H-NMR spectrum of 134e (500 MHz, $CDCl_3$)

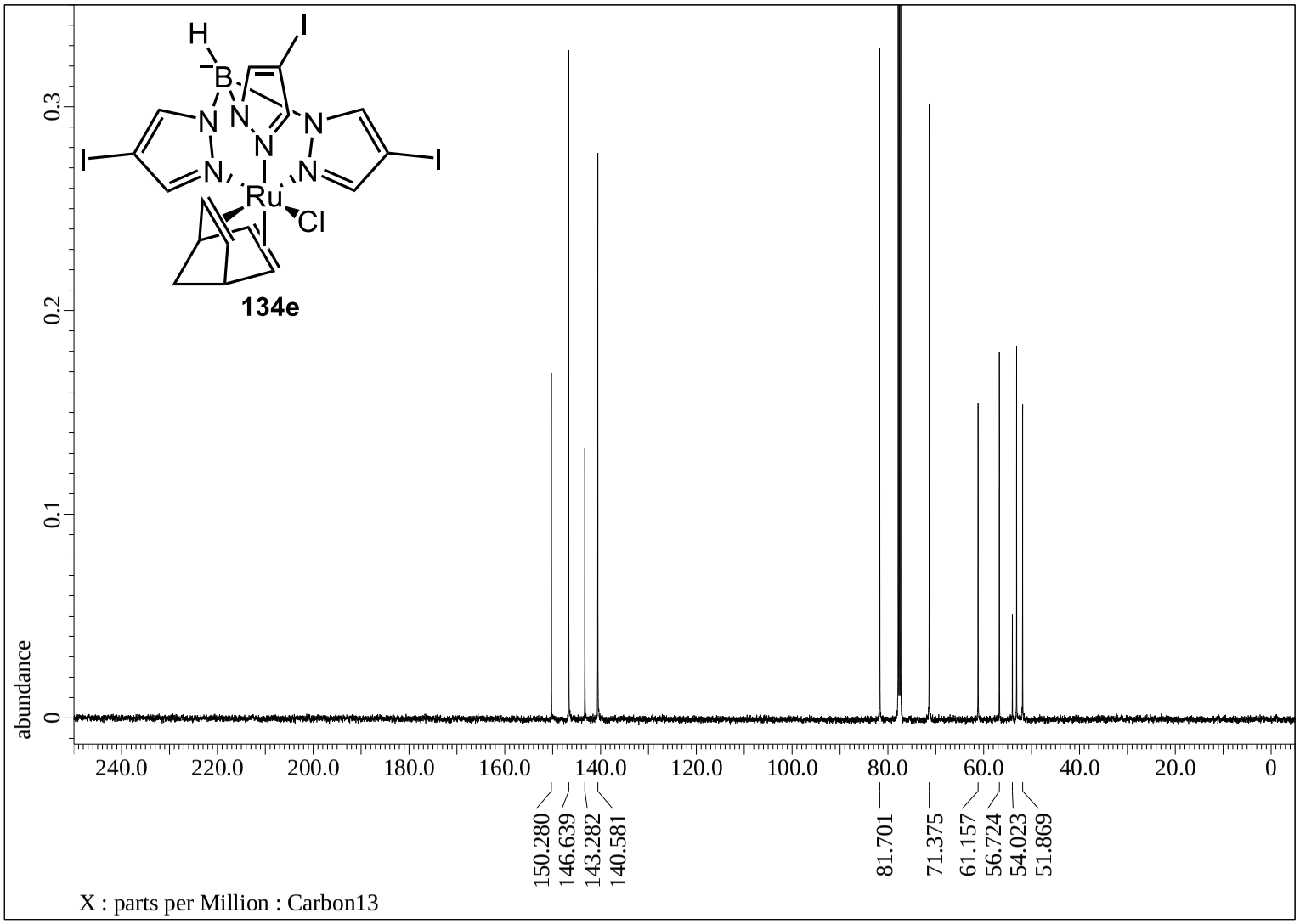

Figure A1.10: ^{13}C-NMR spectrum of 134e (500 MHz, $CDCl_3$)

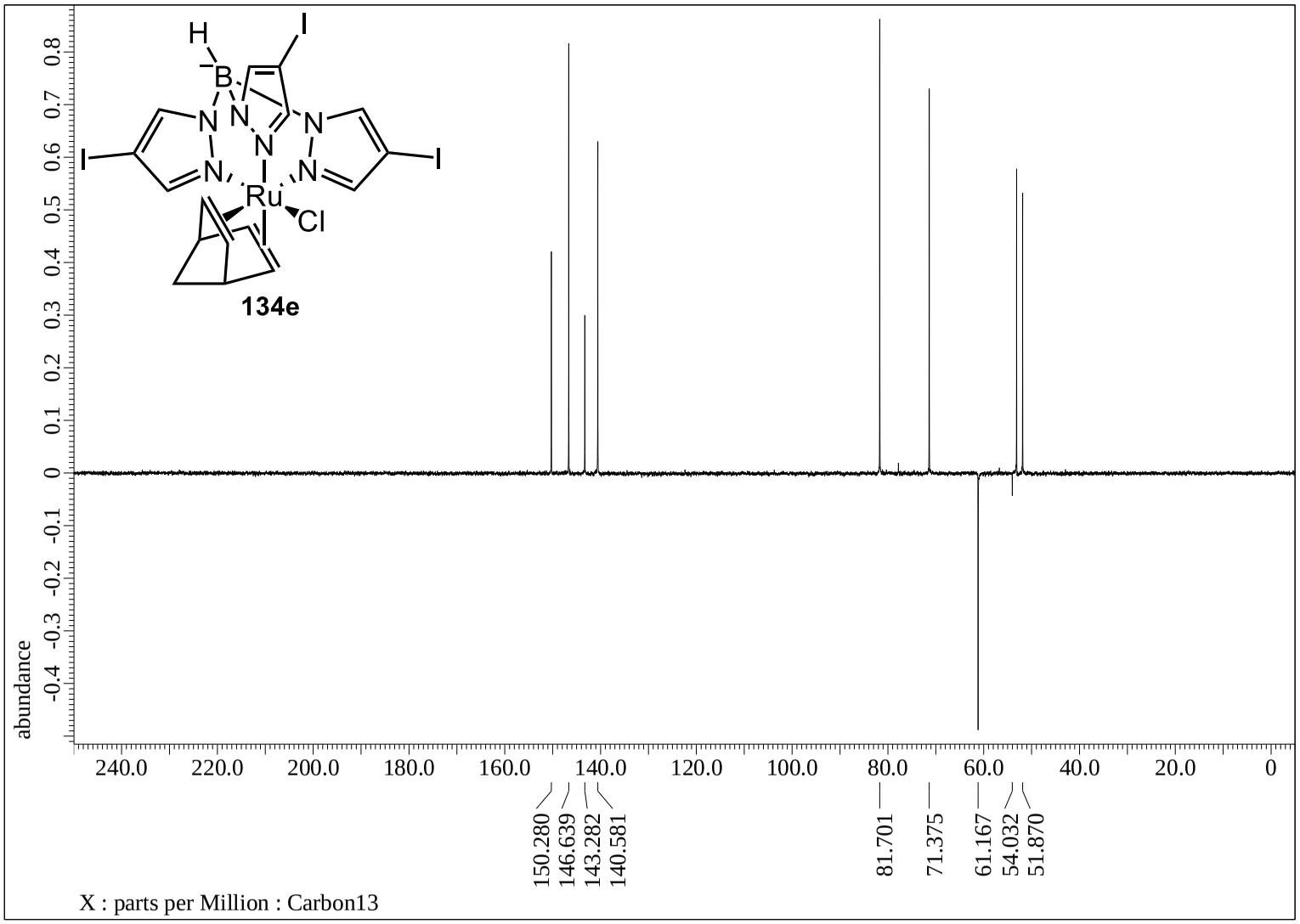

Figure A1.11. DEPT135 spectrum of 134e (500 MHz, $CDCl_3$)

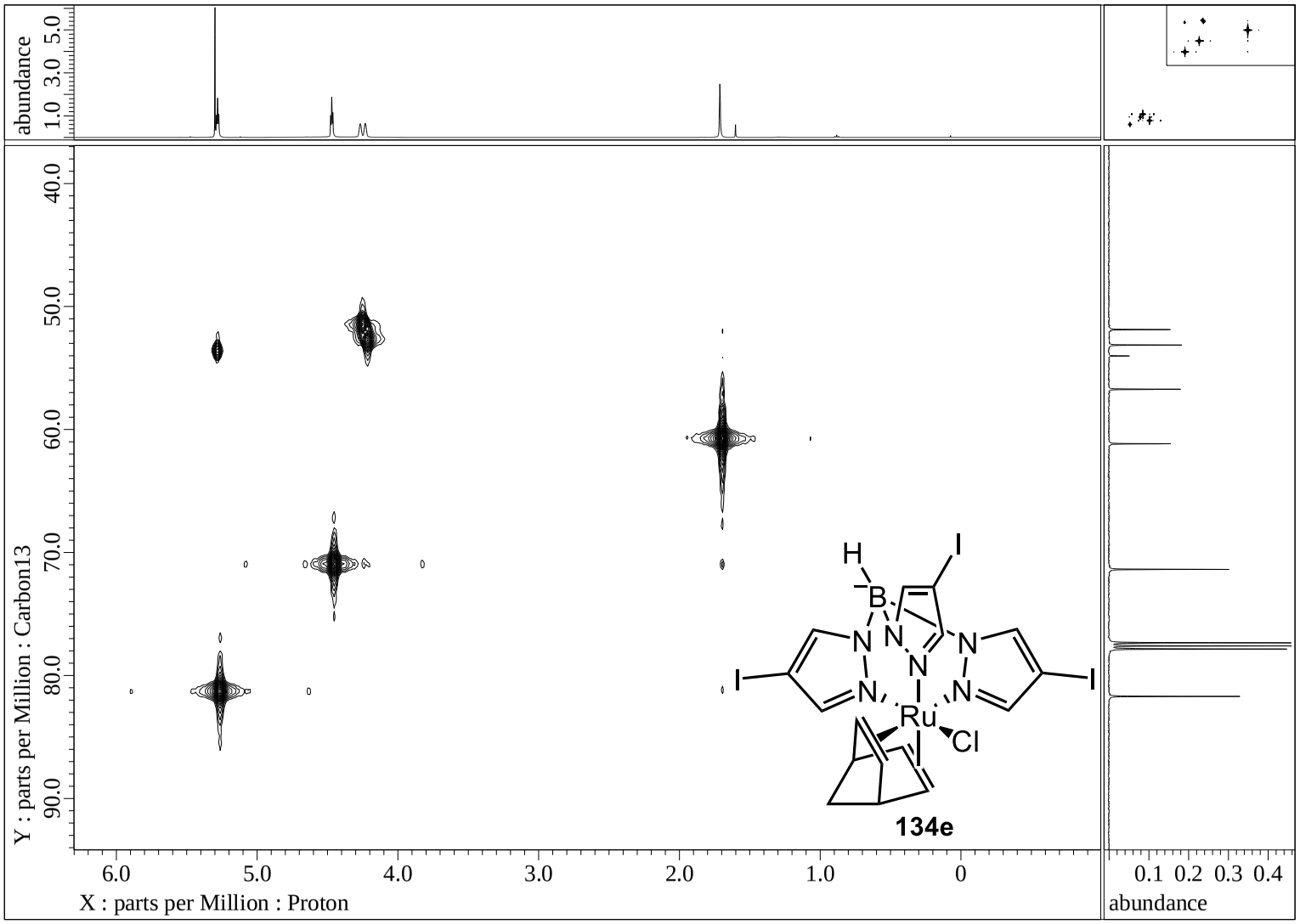

Figure A1.12 HMQC spectrum of 134e (500 MHz, $CDCl_3$)

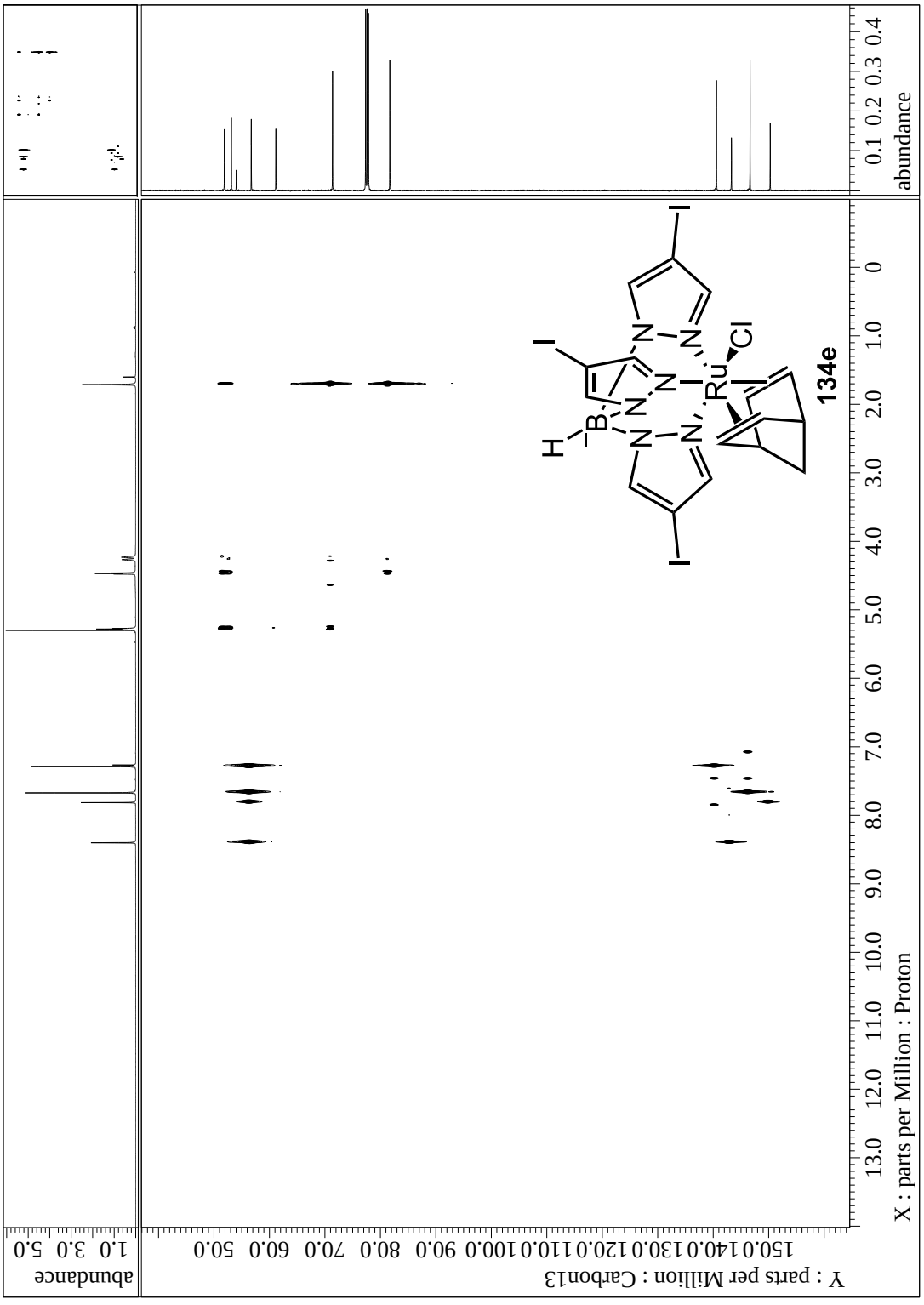

Figure A1.13 HMBC spectrum of 134e (500 MHz, $CDCl_3$)

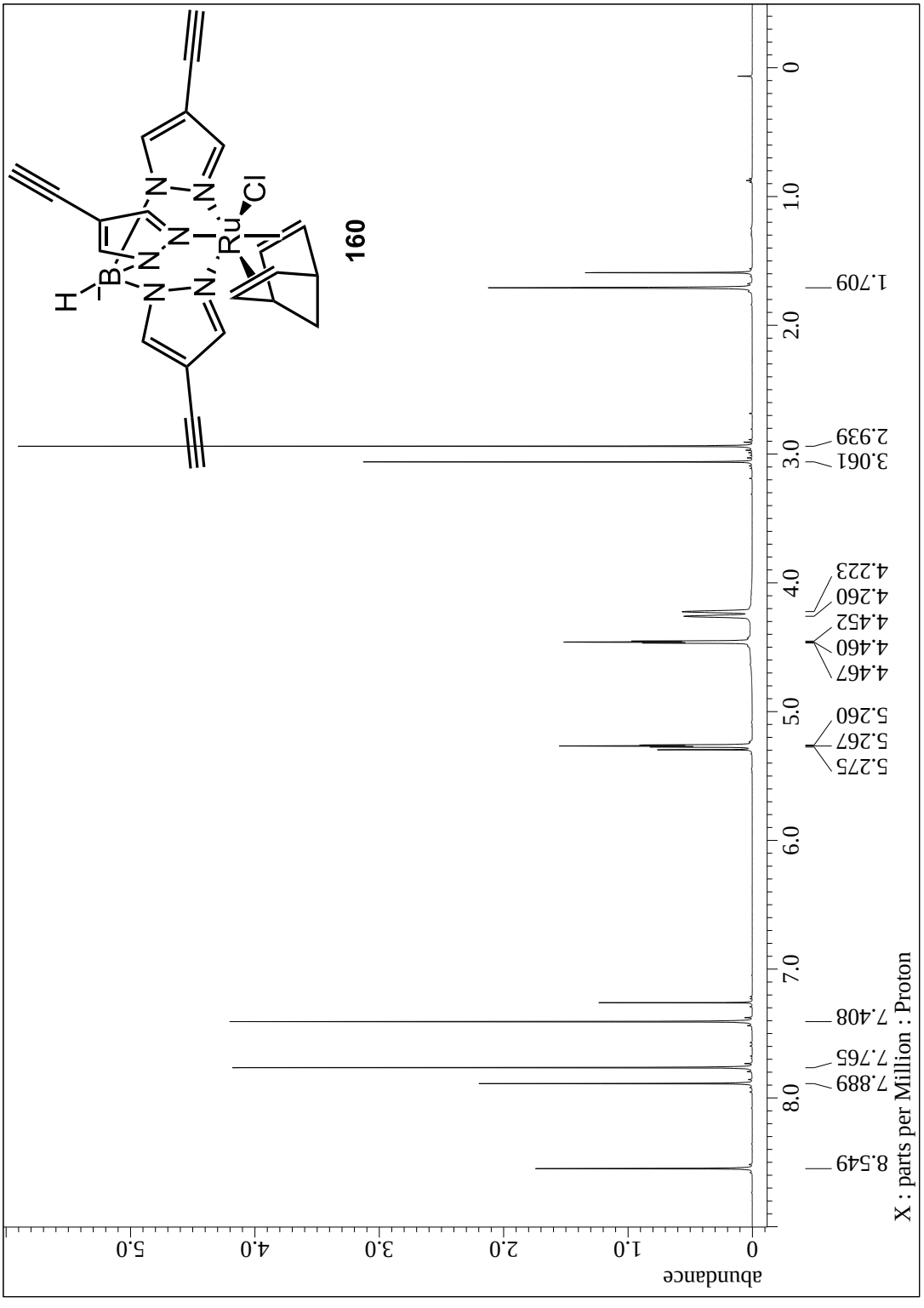

Figure A1.14: ^{1}H-NMR spectrum of 160 (500 MHz, $CDCl_3$)

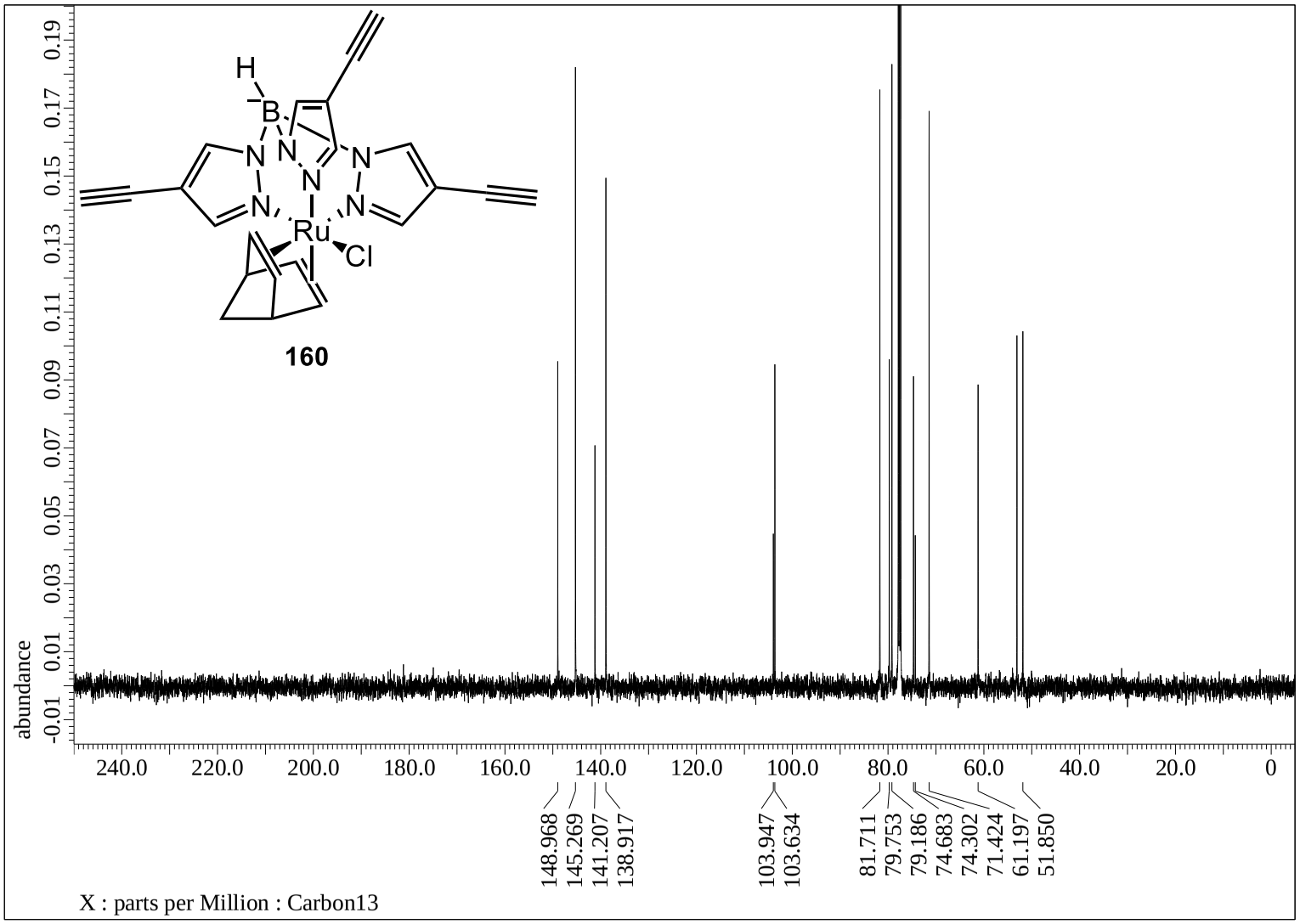

Figure A1.15: ^{13}C-NMR spectrum of 160 (500 MHz, $CDCl_3$)

APPENDEX TWO: UV-Vis Spectra

Syntheses of $Tp^{X}Ru(diene)Cl$ Complexes and Documentation of Their Thermodynamic Stability

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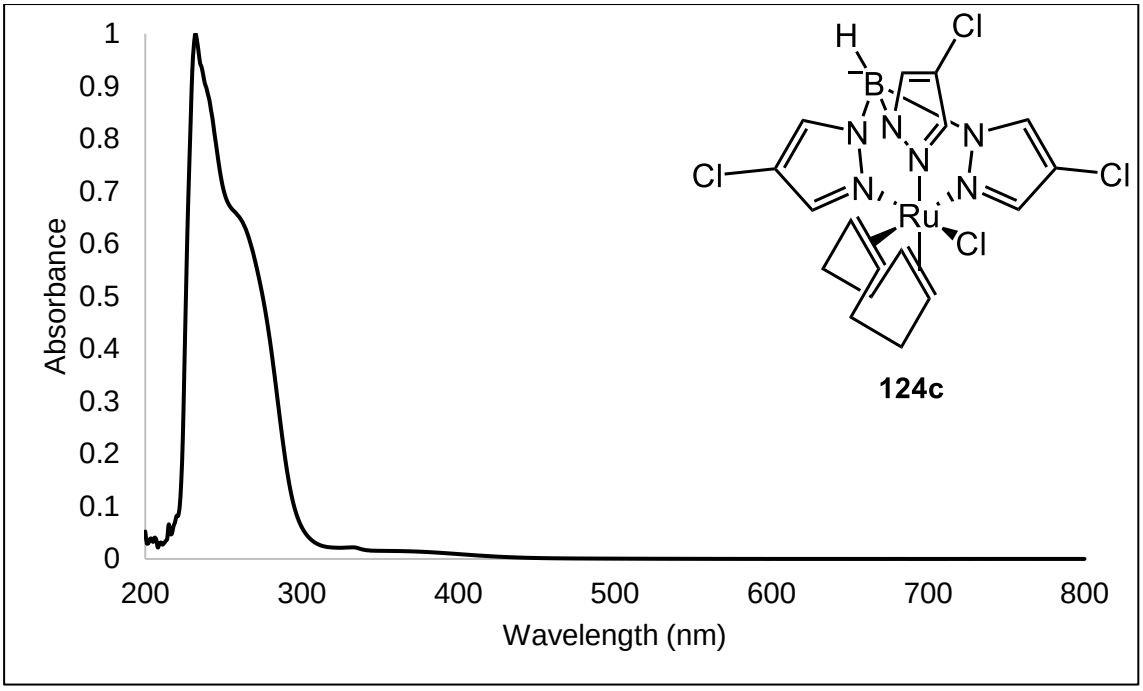

Figure A1.16: UV-Vis spectrum of 124c, ε_{231}=9.43 (L/mol cm), ε_{262}=7.38 (L/mol cm)

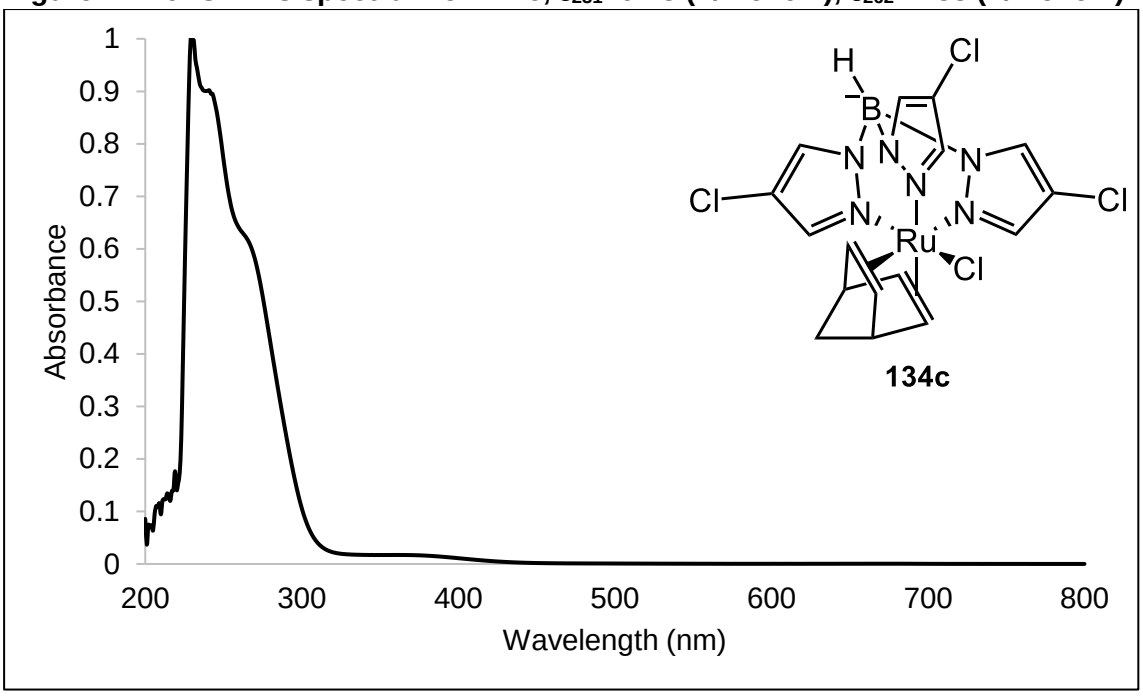

Figure A1.17: UV-Vis spectrum of 134c, ε_{231}=11.9 (L/mol cm), ε_{239}=10.5 (L/mol cm), ε_{263}=7.8 (L/mol cm)

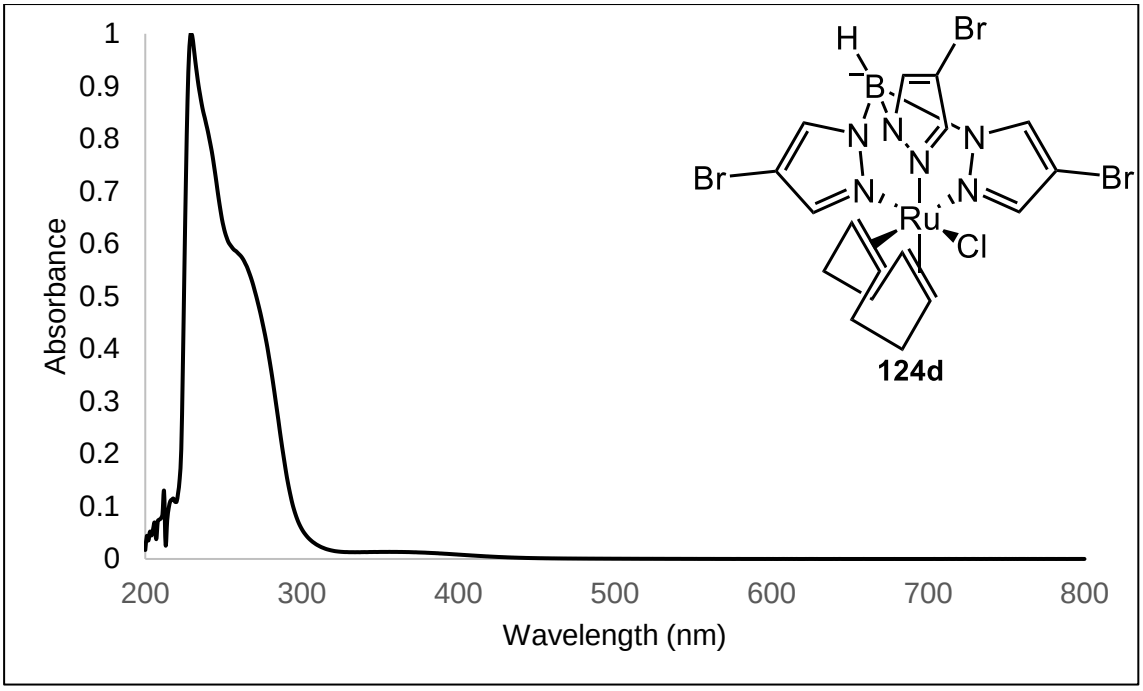

Figure A1.18: UV-Vis spectrum of 124d

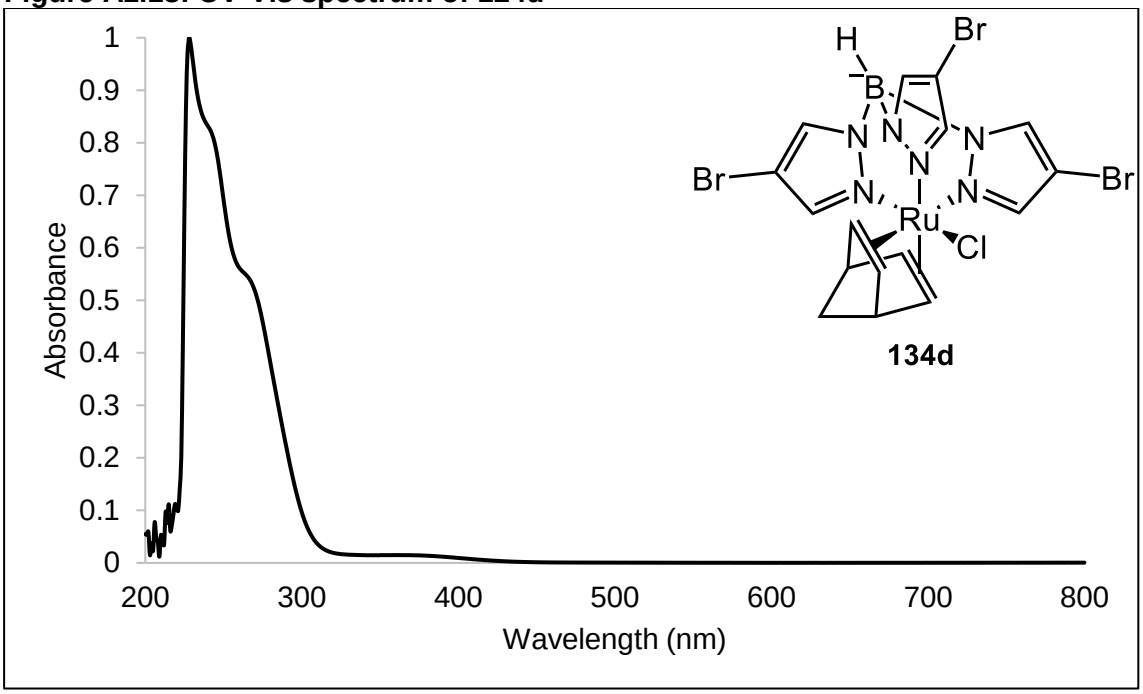

Figure A1.19: UV-Vis spectrum of 134d, ε_{228}=13.1 (L/mol cm), ε_{240}=11.0 (L/mol cm), ε_{264}=7.5 (L/mol cm)

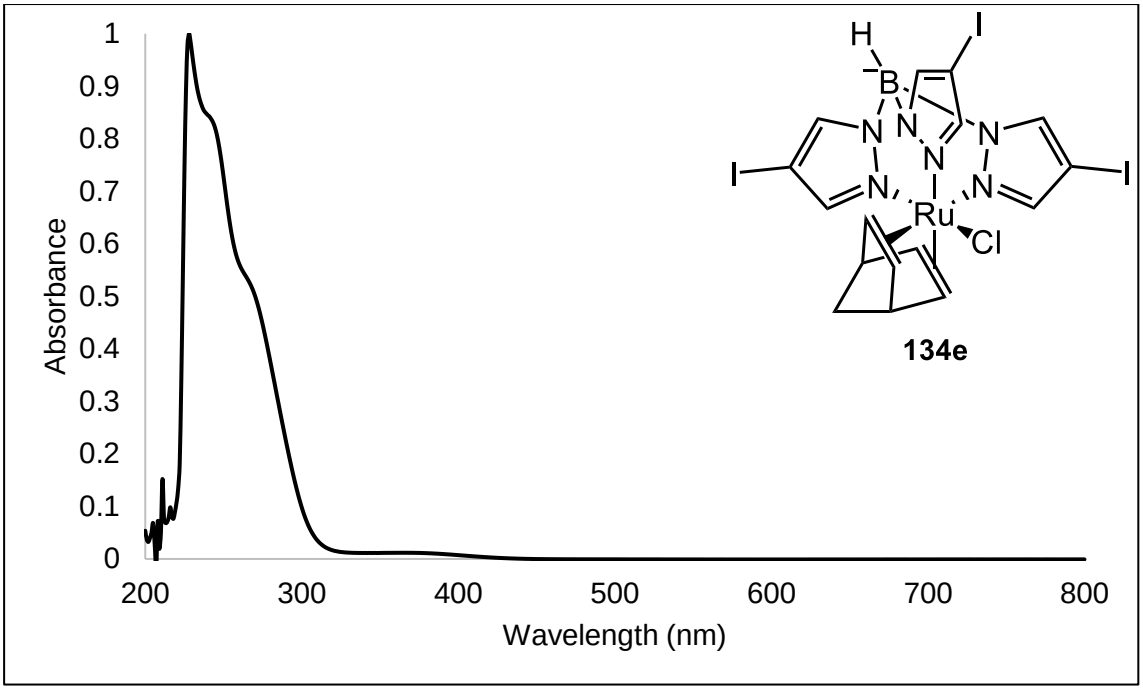

Figure A1.20: UV-Vis spectrum of 134e, ε_{228}=35.6 (L/mol cm), ε_{241}=11.7 (L/mol cm), ε_{264}=7.5 (L/mol cm)

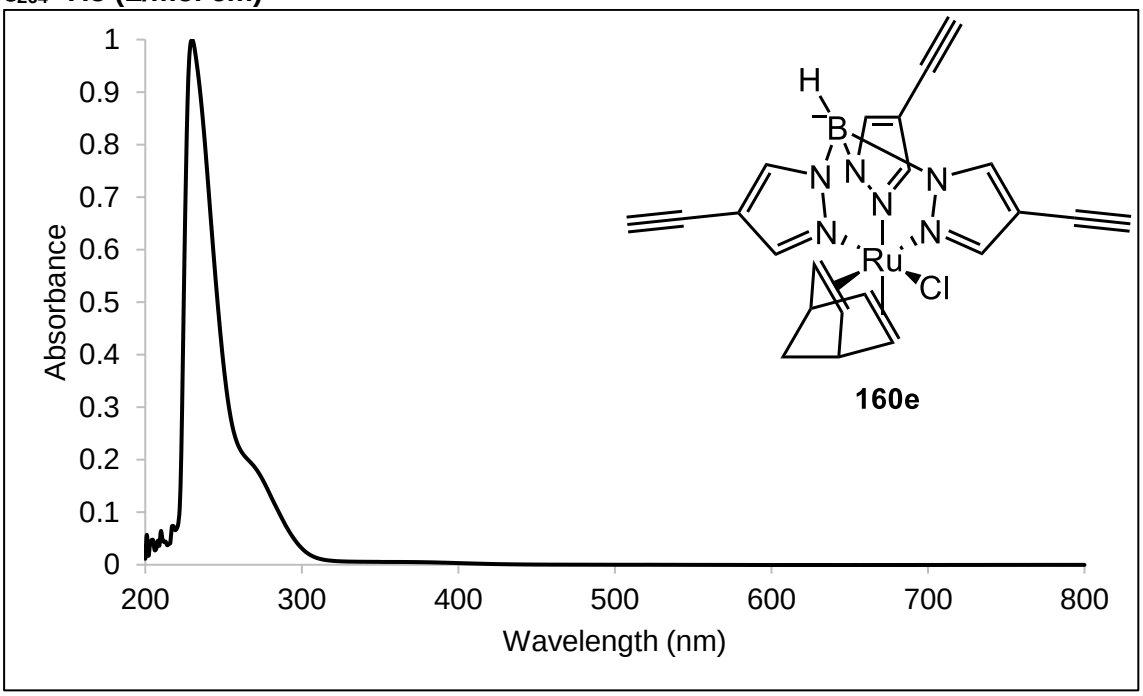

Figure A1.21: UV-Vis spectrum of 160, ε_{231}=33.5 (L/mol cm), ε_{267}=7.1 (L/mol cm)

APPENDEX THREE: Crystal Data and Structure Refinement

Syntheses of $Tp^{X}Ru(diene)Cl$ Complexes and Documentation of Their Thermodynamic Stability

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Table A1.1: Crystal data and structure refinement for $Tp^{Cl}Ru(cod)Cl$ 124c.

Identification code: $Tp^{Cl}Ru(cod)Cl$ **124c**

Empirical formula: C19 H23 B Cl7 N6 Ru

Formula weight: 695.46

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group	P -1	
Unit cell dimensions	a = 8.097(3) Å	α= 78.983(3)°.
	b = 12.711(4) Å	β= 77.289(4)°.
	c = 12.980(4) Å	γ = 88.594(3)°.
Volume	1279.1(8) $Å^3$	
Z	2	
Density (calculated)	1.806 Mg/m^3	
Absorption coefficient	1.367 mm^{-1}	
F(000)	694	
Crystal size	0.340 x 0.300 x 0.140 mm^3	
Theta range for data collection	2.081 to 27.941°.	
Index ranges	-10<=h<=10, -16<=k<=16, -17<=l<=17	
Reflections collected	28421	
Independent reflections	6109 [R(int) = 0.0179]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7456 and 0.6966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6109 / 0 / 319	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0576	
R indices (all data)	R1 = 0.0219, wR2 = 0.0580	
Largest diff. peak and hole	0.736 and -1.017 $e.Å^{-3}$	

Table A1. 2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(cod)Cl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2781(1)	2762(1)	6831(1)	10(1)
Cl(1)	5288(1)	3278(1)	5412(1)	16(1)
Cl(2)	7273(1)	-960(1)	7316(1)	26(1)
Cl(3)	-2341(1)	885(1)	10836(1)	22(1)
Cl(4)	9110(1)	3071(1)	2581(1)	50(1)
Cl(5)	7961(1)	1000(1)	3917(1)	46(1)
Cl(6)	5912(1)	6298(1)	8176(1)	30(1)
N(1)	1263(2)	2161(1)	8421(1)	13(1)
N(2)	2062(2)	2040(1)	9260(1)	13(1)
N(3)	4429(2)	3358(1)	8527(1)	13(1)
N(4)	3951(2)	3764(1)	7591(1)	13(1)
N(5)	4793(2)	1435(1)	8306(1)	13(1)
N(6)	4353(2)	1509(1)	7342(1)	13(1)
C(1)	2207(2)	1934(1)	5581(1)	15(1)
C(2)	845(2)	1758(1)	6452(1)	15(1)
C(3)	-837(2)	2314(1)	6414(1)	17(1)
C(4)	-1015(2)	3379(1)	6827(1)	18(1)
C(5)	670(2)	3922(1)	6731(1)	15(1)
C(6)	1869(2)	4138(1)	5771(1)	15(1)
C(7)	1611(2)	3854(1)	4728(1)	18(1)
C(8)	2168(2)	2721(1)	4554(1)	17(1)
C(9)	-322(2)	1776(1)	8844(1)	16(1)
C(10)	-531(2)	1426(1)	9949(1)	16(1)
C(11)	999(2)	1598(1)	10189(1)	15(1)
C(12)	4406(2)	4802(1)	7330(1)	16(1)
C(13)	5155(2)	5060(1)	8127(1)	18(1)
C(14)	5148(2)	4130(1)	8872(1)	17(1)
C(15)	5130(2)	723(1)	6882(1)	15(1)
C(16)	6054(2)	123(1)	7571(1)	15(1)

C(17)	5816(2)	591(1)	8467(1)	14(1)
C(18)	7350(3)	2206(2)	3190(2)	34(1)
B(1)	3994(2)	2192(1)	9074(1)	13(1)
C(19)	-783(5)	5378(4)	10171(4)	85(1)
Cl(7)	-790(4)	4266(2)	9539(2)	39(1)
Cl(8)	1185(4)	5592(3)	10420(4)	69(1)

Table A1.3: Bond lengths [Å] and angles [°] for Tp^{Cl}Ru(cod)Cl 124c.

Ru(1)-N(4)	2.1082(14)	C(4)-H(4AB)	0.9900
Ru(1)-N(6)	2.1133(14)	C(5)-C(6)	1.386(2)
Ru(1)-N(1)	2.1636(14)	C(5)-H(5)	1.0000
Ru(1)-C(6)	2.2277(16)	C(6)-C(7)	1.524(2)
Ru(1)-C(1)	2.2284(16)	C(6)-H(6)	1.0000
Ru(1)-C(2)	2.2373(16)	C(7)-C(8)	1.542(2)
Ru(1)-C(5)	2.2388(17)	C(7)-H(7A)	0.9900
Ru(1)-Cl(1)	2.4292(7)	C(7)-H(7AB)	0.9900
Cl(2)-C(16)	1.7152(17)	C(8)-H(8A)	0.9900
Cl(3)-C(10)	1.7177(17)	C(8)-H(8AB)	0.9900
Cl(4)-C(18)	1.765(3)	C(9)-C(10)	1.392(2)
Cl(5)-C(18)	1.761(2)	C(9)-H(9)	0.9500
Cl(6)-C(13)	1.7204(18)	C(10)-C(11)	1.374(2)
N(1)-C(9)	1.344(2)	C(11)-H(11)	0.9500
N(1)-N(2)	1.3675(19)	C(12)-C(13)	1.400(2)
N(2)-C(11)	1.348(2)	C(12)-H(12)	0.9500
N(2)-B(1)	1.541(2)	C(13)-C(14)	1.376(2)
N(3)-C(14)	1.347(2)	C(14)-H(14)	0.9500
N(3)-N(4)	1.3605(19)	C(15)-C(16)	1.396(2)
N(3)-B(1)	1.529(2)	C(15)-H(15)	0.9500
N(4)-C(12)	1.338(2)	C(16)-C(17)	1.379(2)
N(5)-C(17)	1.352(2)	C(17)-H(17)	0.9500
N(5)-N(6)	1.3613(19)	C(18)-H(18A)	0.9900
N(5)-B(1)	1.545(2)	C(18)-H(18B)	0.9900
N(6)-C(15)	1.335(2)	B(1)-H(1B)	1.10(2)
C(1)-C(2)	1.383(2)	C(19)-Cl(8)	1.731(6)
C(1)-C(8)	1.511(2)	C(19)-Cl(7)	1.765(5)
C(1)-H(1)	1.0000	C(19)-H(19A)	0.9900
C(2)-C(3)	1.526(2)	C(19)-H(19B)	0.9900
C(2)-H(2)	1.0000		
C(3)-C(4)	1.542(2)	N(4)-Ru(1)-N(6)	88.59(6)
C(3)-H(3A)	0.9900	N(4)-Ru(1)-N(1)	85.40(6)
C(3)-H(3AB)	0.9900	N(6)-Ru(1)-N(1)	80.96(5)
C(4)-C(5)	1.514(2)	N(4)-Ru(1)-C(6)	93.20(6)
C(4)-H(4A)	0.9900	N(6)-Ru(1)-C(6)	159.45(6)

N(1)-Ru(1)-C(6)	119.59(6)	C(17)-N(5)-N(6)	109.98(13)
N(4)-Ru(1)-C(1)	161.45(6)	C(17)-N(5)-B(1)	129.81(14)
N(6)-Ru(1)-C(1)	92.03(6)	N(6)-N(5)-B(1)	119.92(13)
N(1)-Ru(1)-C(1)	113.00(6)	C(15)-N(6)-N(5)	107.33(13)
C(6)-Ru(1)-C(1)	79.91(6)	C(15)-N(6)-Ru(1)	132.93(11)
N(4)-Ru(1)-C(2)	161.68(6)	N(5)-N(6)-Ru(1)	119.70(10)
N(6)-Ru(1)-C(2)	97.84(6)	C(2)-C(1)-C(8)	122.87(15)
N(1)-Ru(1)-C(2)	78.75(6)	C(2)-C(1)-Ru(1)	72.31(9)
C(6)-Ru(1)-C(2)	86.78(6)	C(8)-C(1)-Ru(1)	111.19(11)
C(1)-Ru(1)-C(2)	36.08(6)	C(2)-C(1)-H(1)	114.4
N(4)-Ru(1)-C(5)	90.47(6)	C(8)-C(1)-H(1)	114.4
N(6)-Ru(1)-C(5)	164.38(6)	Ru(1)-C(1)-H(1)	114.4
N(1)-Ru(1)-C(5)	83.42(6)	C(1)-C(2)-C(3)	121.56(15)
C(6)-Ru(1)-C(5)	36.17(6)	C(1)-C(2)-Ru(1)	71.61(9)
C(1)-Ru(1)-C(5)	93.79(6)	C(3)-C(2)-Ru(1)	113.89(11)
C(2)-Ru(1)-C(5)	78.72(6)	C(1)-C(2)-H(2)	114.3
N(4)-Ru(1)-Cl(1)	81.55(4)	C(3)-C(2)-H(2)	114.3
N(6)-Ru(1)-Cl(1)	82.36(4)	Ru(1)-C(2)-H(2)	114.3
N(1)-Ru(1)-Cl(1)	159.02(4)	C(2)-C(3)-C(4)	114.63(13)
C(6)-Ru(1)-Cl(1)	77.67(5)	C(2)-C(3)-H(3A)	108.6
C(1)-Ru(1)-Cl(1)	80.17(5)	C(4)-C(3)-H(3A)	108.6
C(2)-Ru(1)-Cl(1)	116.22(5)	C(2)-C(3)-H(3AB)	108.6
C(5)-Ru(1)-Cl(1)	112.92(5)	C(4)-C(3)-H(3AB)	108.6
C(9)-N(1)-N(2)	106.00(13)	H(3A)-C(3)-H(3AB)	107.6
C(9)-N(1)-Ru(1)	136.78(11)	C(5)-C(4)-C(3)	113.13(14)
N(2)-N(1)-Ru(1)	117.02(10)	C(5)-C(4)-H(4A)	109.0
C(11)-N(2)-N(1)	110.66(13)	C(3)-C(4)-H(4A)	109.0
C(11)-N(2)-B(1)	126.70(14)	C(5)-C(4)-H(4AB)	109.0
N(1)-N(2)-B(1)	121.56(13)	C(3)-C(4)-H(4AB)	109.0
C(14)-N(3)-N(4)	110.56(13)	H(4A)-C(4)-H(4AB)	107.8
C(14)-N(3)-B(1)	129.49(14)	C(6)-C(5)-C(4)	122.39(15)
N(4)-N(3)-B(1)	119.75(13)	C(6)-C(5)-Ru(1)	71.48(9)
C(12)-N(4)-N(3)	107.00(13)	C(4)-C(5)-Ru(1)	112.99(11)
C(12)-N(4)-Ru(1)	132.72(11)	C(6)-C(5)-H(5)	114.3
N(3)-N(4)-Ru(1)	120.27(10)	C(4)-C(5)-H(5)	114.3

Ru(1)-C(5)-H(5)	114.3	C(12)-C(13)-Cl(6)	126.84(14)
C(5)-C(6)-C(7)	123.21(15)	N(3)-C(14)-C(13)	107.04(15)
C(5)-C(6)-Ru(1)	72.35(9)	N(3)-C(14)-H(14)	126.5
C(7)-C(6)-Ru(1)	112.65(11)	C(13)-C(14)-H(14)	126.5
C(5)-C(6)-H(6)	113.9	N(6)-C(15)-C(16)	109.14(14)
C(7)-C(6)-H(6)	113.9	N(6)-C(15)-H(15)	125.4
Ru(1)-C(6)-H(6)	113.9	C(16)-C(15)-H(15)	125.4
C(6)-C(7)-C(8)	115.14(13)	C(17)-C(16)-C(15)	106.36(14)
C(6)-C(7)-H(7A)	108.5	C(17)-C(16)-Cl(2)	127.82(13)
C(8)-C(7)-H(7A)	108.5	C(15)-C(16)-Cl(2)	125.80(13)
C(6)-C(7)-H(7AB)	108.5	N(5)-C(17)-C(16)	107.16(14)
C(8)-C(7)-H(7AB)	108.5	N(5)-C(17)-H(17)	126.4
H(7A)-C(7)-H(7AB)	107.5	C(16)-C(17)-H(17)	126.4
C(1)-C(8)-C(7)	114.08(14)	Cl(5)-C(18)-Cl(4)	111.23(12)
C(1)-C(8)-H(8A)	108.7	Cl(5)-C(18)-H(18A)	109.4
C(7)-C(8)-H(8A)	108.7	Cl(4)-C(18)-H(18A)	109.4
C(1)-C(8)-H(8AB)	108.7	Cl(5)-C(18)-H(18B)	109.4
C(7)-C(8)-H(8AB)	108.7	Cl(4)-C(18)-H(18B)	109.4
H(8A)-C(8)-H(8AB)	107.6	H(18A)-C(18)-H(18B)	108.0
N(1)-C(9)-C(10)	109.77(14)	N(3)-B(1)-N(2)	107.57(13)
N(1)-C(9)-H(9)	125.1	N(3)-B(1)-N(5)	109.95(13)
C(10)-C(9)-H(9)	125.1	N(2)-B(1)-N(5)	106.17(13)
C(11)-C(10)-C(9)	106.33(14)	N(3)-B(1)-H(1B)	110.8(11)
C(11)-C(10)-Cl(3)	126.83(13)	N(2)-B(1)-H(1B)	110.1(11)
C(9)-C(10)-Cl(3)	126.84(13)	N(5)-B(1)-H(1B)	112.1(11)
N(2)-C(11)-C(10)	107.23(14)	Cl(8)-C(19)-Cl(7)	111.7(3)
N(2)-C(11)-H(11)	126.4	Cl(8)-C(19)-H(19A)	109.3
C(10)-C(11)-H(11)	126.4	Cl(7)-C(19)-H(19A)	109.3
N(4)-C(12)-C(13)	108.86(15)	Cl(8)-C(19)-H(19B)	109.3
N(4)-C(12)-H(12)	125.6	Cl(7)-C(19)-H(19B)	109.3
C(13)-C(12)-H(12)	125.6	H(19A)-C(19)-H(19B)	107.9
C(14)-C(13)-C(12)	106.53(15)		
C(14)-C(13)-Cl(6)	126.62(14)		

Symmetry transformations used to generate equivalent atoms:

Table A1.4: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for $Tp^{Cl}Ru(cod)Cl$ 124c. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	11(1)	10(1)	9(1)	-1(1)	-2(1)	-1(1)
Cl(1)	14(1)	18(1)	12(1)	0(1)	0(1)	-1(1)
Cl(2)	32(1)	22(1)	27(1)	-10(1)	-11(1)	14(1)
Cl(3)	18(1)	30(1)	15(1)	-2(1)	3(1)	-9(1)
Cl(4)	54(1)	43(1)	47(1)	5(1)	-9(1)	0(1)
Cl(5)	47(1)	27(1)	62(1)	-9(1)	-6(1)	1(1)
Cl(6)	54(1)	19(1)	17(1)	-2(1)	-7(1)	-18(1)
N(1)	13(1)	14(1)	11(1)	-1(1)	-2(1)	-1(1)
N(2)	14(1)	14(1)	11(1)	-1(1)	-2(1)	0(1)
N(3)	14(1)	15(1)	11(1)	-2(1)	-3(1)	-1(1)
N(4)	15(1)	13(1)	11(1)	-1(1)	-3(1)	-1(1)
N(5)	13(1)	14(1)	11(1)	-1(1)	-3(1)	0(1)
N(6)	14(1)	13(1)	11(1)	-1(1)	-3(1)	0(1)
C(1)	19(1)	13(1)	14(1)	-4(1)	-7(1)	0(1)
C(2)	18(1)	12(1)	16(1)	-2(1)	-7(1)	-2(1)
C(3)	14(1)	19(1)	19(1)	-1(1)	-6(1)	-3(1)
C(4)	14(1)	18(1)	22(1)	-2(1)	-4(1)	1(1)
C(5)	16(1)	12(1)	18(1)	-2(1)	-6(1)	3(1)
C(6)	17(1)	10(1)	18(1)	0(1)	-6(1)	1(1)
C(7)	22(1)	16(1)	15(1)	1(1)	-6(1)	2(1)
C(8)	21(1)	18(1)	13(1)	-2(1)	-5(1)	1(1)
C(9)	14(1)	17(1)	14(1)	-2(1)	-2(1)	-3(1)
C(10)	15(1)	16(1)	14(1)	-2(1)	1(1)	-3(1)
C(11)	17(1)	15(1)	11(1)	-1(1)	-1(1)	-1(1)
C(12)	20(1)	14(1)	14(1)	-2(1)	-2(1)	-3(1)
C(13)	24(1)	16(1)	14(1)	-4(1)	-1(1)	-7(1)
C(14)	19(1)	18(1)	13(1)	-4(1)	-2(1)	-5(1)
C(15)	15(1)	14(1)	15(1)	-3(1)	-3(1)	0(1)

C(16)	14(1)	13(1)	18(1)	-2(1)	-3(1)	1(1)
C(17)	12(1)	14(1)	15(1)	1(1)	-3(1)	-1(1)
C(18)	32(1)	41(1)	34(1)	-18(1)	-9(1)	10(1)
B(1)	13(1)	14(1)	13(1)	-2(1)	-3(1)	-1(1)
C(19)	72(3)	89(3)	96(3)	-31(3)	-14(2)	13(2)
Cl(7)	54(2)	30(1)	40(1)	-21(1)	-14(1)	-2(1)
Cl(8)	29(1)	108(3)	87(2)	-66(2)	-4(1)	-13(1)

Table A1.5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Cl}Ru(cod)Cl 124c.

	x	y	z	U(eq)
H(1)	2902	1286	5474	18
H(2)	732	1005	6868	18
H(3A)	-1767	1820	6849	21
H(3AB)	-977	2455	5661	21
H(4A)	-1707	3872	6414	22
H(4AB)	-1624	3240	7591	22
H(5)	623	4474	7191	18
H(6)	2529	4820	5666	18
H(7A)	2246	4383	4117	22
H(7AB)	395	3923	4715	22
H(8A)	1385	2438	4180	21
H(8AB)	3313	2773	4078	21
H(9)	-1171	1747	8448	19
H(11)	1259	1435	10880	18
H(12)	4246	5286	6706	19
H(14)	5571	4049	9509	20
H(15)	5065	592	6195	17
H(17)	6282	362	9082	17
H(18A)	6518	2567	3681	41
H(18B)	6796	2045	2628	41
H(1B)	4390(30)	2006(17)	9843(17)	16

H(19A)	-1104	6026	9706	102
H(19B)	-1636	5255	10859	102

Table A1.6: Crystal data and structure refinement for TpRu1,2-(SMe)5, 6-COE 133.

Identification code	TpRu1,2-(SMe)5, 6-COE, **133**	
Empirical formula	C20 H30 B Cl3 N6 Ru S2	
Formula weight	636.85	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 15.6430(6) Å	α= 90°.
	b = 15.5117(6) Å	β= 98.5620(10)°.
	c = 21.7922(8) Å	γ= 90°.
Volume	5228.9(3) $Å^3$	
Z	8	
Density (calculated)	1.618 Mg/m^3	
Absorption coefficient	1.088 mm^{-1}	
F(000)	2592	
Crystal size	0.35 x 0.26 x 0.16 mm^3	
Theta range for data collection	1.502 to 28.277°.	
Index ranges	-20<=h<=20, -20<=k<=20, -29<=l<=27	
Reflections collected	58456	
Independent reflections	12966 [R(int) = 0.0165]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.6993	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12966 / 612 / 605	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0607	
R indices (all data)	R1 = 0.0292, wR2 = 0.0631	
Largest diff. peak and hole	0.802 and -0.736 $e.Å^{-3}$	

Table A1.7: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for TpRu1,2-(SMe)5, 6-COE, 133. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7115(1)	2861(1)	6980(1)	13(1)
Ru(2)	2851(1)	4427(1)	7894(1)	13(1)
Cl(1)	7813(1)	1550(1)	7418(1)	19(1)
Cl(2)	2141(1)	5735(1)	7483(1)	20(1)
Cl(3)	8331(1)	1631(1)	9832(1)	45(1)
Cl(4)	6522(1)	1583(1)	9248(1)	52(1)
Cl(5)	3594(1)	5873(1)	5827(1)	42(1)
Cl(6)	1915(1)	5537(1)	5095(1)	53(1)
S(1)	8454(1)	3558(1)	7126(1)	17(1)
S(2)	7016(1)	3256(1)	7988(1)	16(1)
S(3)	2925(1)	4065(1)	6875(1)	16(1)
S(4)	1518(1)	3732(1)	7753(1)	18(1)
N(1)	7291(1)	2455(1)	6096(1)	16(1)
N(2)	6606(1)	2448(1)	5632(1)	17(1)
N(3)	6385(1)	3879(1)	6549(1)	16(1)
N(4)	5829(1)	3690(1)	6016(1)	17(1)
N(5)	5966(1)	2178(1)	6857(1)	16(1)
N(6)	5450(1)	2199(1)	6296(1)	17(1)
N(7)	3997(1)	5123(1)	8035(1)	16(1)
N(8)	4502(1)	5092(1)	8599(1)	18(1)
N(9)	3585(1)	3412(1)	8315(1)	15(1)
N(10)	4124(1)	3591(1)	8857(1)	17(1)
N(11)	2662(1)	4813(1)	8775(1)	17(1)
N(12)	3336(1)	4827(1)	9247(1)	18(1)
C(1)	7978(1)	2188(1)	5851(1)	21(1)
C(2)	7740(1)	2005(1)	5220(1)	25(1)
C(3)	6868(1)	2176(1)	5101(1)	22(1)
C(4)	6281(1)	4717(1)	6656(1)	18(1)
C(5)	5672(1)	5082(1)	6193(1)	22(1)

C(6)	5403(1)	4407(1)	5799(1)	21(1)
C(7)	5578(1)	1674(1)	7229(1)	21(1)
C(8)	4796(1)	1364(1)	6911(1)	25(1)
C(9)	4743(1)	1709(1)	6325(1)	22(1)
C(10)	8429(1)	4591(1)	6737(1)	24(1)
C(11)	5989(1)	3738(1)	8073(1)	24(1)
C(12)	8619(1)	3916(1)	7945(1)	18(1)
C(13)	9103(1)	3179(1)	8315(1)	24(1)
C(14)	9241(1)	3291(1)	9021(1)	31(1)
C(15)	9671(1)	4125(2)	9247(1)	33(1)
C(16)	9341(1)	4916(1)	9208(1)	28(1)
C(17)	8456(1)	5242(1)	8957(1)	26(1)
C(18)	7731(1)	4591(1)	8759(1)	23(1)
C(19)	7744(1)	4194(1)	8115(1)	17(1)
C(20)	4377(1)	5662(1)	7680(1)	21(1)
C(21)	5142(1)	5985(1)	8015(1)	25(1)
C(22)	5195(1)	5611(1)	8592(1)	22(1)
C(23)	3696(1)	2578(1)	8197(1)	18(1)
C(24)	4297(1)	2204(1)	8660(1)	22(1)
C(25)	4552(1)	2866(1)	9067(1)	21(1)
C(26)	1971(1)	5110(1)	8999(1)	22(1)
C(27)	2194(1)	5322(1)	9624(1)	26(1)
C(28)	3063(1)	5137(1)	9764(1)	24(1)
C(29)	3941(1)	3588(1)	6765(1)	24(1)
C(30)	1555(1)	2693(1)	8133(1)	25(1)
C(31)	1324(1)	3400(1)	6931(1)	20(1)
C(32)	823(1)	4147(1)	6578(1)	27(1)
C(33)	588(2)	4024(2)	5874(1)	34(1)
C(34)	157(2)	3165(2)	5691(1)	35(1)
C(35)	522(2)	2399(2)	5709(1)	35(1)
C(36)	1440(2)	2110(2)	5888(1)	37(1)
C(37)	2149(1)	2787(1)	6073(1)	28(1)
C(38)	2183(1)	3132(1)	6733(1)	20(1)
C(39)	7595(1)	1338(2)	9175(1)	35(1)
C(40)	2465(1)	5993(2)	5777(1)	31(1)

B(1)	5722(1)	2757(1)	5773(1)	19(1)
B(2)	4226(1)	4517(1)	9112(1)	18(1)

Table A1.8: Bond lengths [Å] and angles [°] for TpRu1,2-(SMe)5, 6-COE 133.

Ru(1)-N(5)	2.0685(14)	N(3)-N(4)	1.3750(19)
Ru(1)-N(1)	2.0850(14)	N(4)-C(6)	1.347(2)
Ru(1)-N(3)	2.0887(14)	N(4)-B(1)	1.540(2)
Ru(1)-S(2)	2.3059(4)	N(5)-C(7)	1.335(2)
Ru(1)-S(1)	2.3372(4)	N(5)-N(6)	1.361(2)
Ru(1)-Cl(1)	2.4333(4)	N(6)-C(9)	1.352(2)
Ru(2)-N(11)	2.0727(15)	N(6)-B(1)	1.541(3)
Ru(2)-N(7)	2.0759(15)	N(7)-C(20)	1.335(2)
Ru(2)-N(9)	2.0798(14)	N(7)-N(8)	1.360(2)
Ru(2)-S(3)	2.3100(4)	N(8)-C(22)	1.352(2)
Ru(2)-S(4)	2.3272(4)	N(8)-B(2)	1.542(3)
Ru(2)-Cl(2)	2.4190(4)	N(9)-C(23)	1.336(2)
Cl(3)-C(39)	1.759(2)	N(9)-N(10)	1.3741(19)
Cl(4)-C(39)	1.751(2)	N(10)-C(25)	1.353(2)
Cl(5)-C(40)	1.763(2)	N(10)-B(2)	1.540(2)
Cl(6)-C(40)	1.752(2)	N(11)-C(26)	1.333(2)
S(1)-C(10)	1.810(2)	N(11)-N(12)	1.359(2)
S(1)-C(12)	1.8483(18)	N(12)-C(28)	1.350(2)
S(2)-C(11)	1.8073(18)	N(12)-B(2)	1.541(2)
S(2)-C(19)	1.8434(18)	C(1)-C(2)	1.399(3)
S(3)-C(29)	1.8008(18)	C(1)-H(1)	0.9500
S(3)-C(38)	1.8525(18)	C(2)-C(3)	1.377(3)
S(4)-C(30)	1.809(2)	C(2)-H(2)	0.9500
S(4)-C(31)	1.8451(18)	C(3)-H(3)	0.9500
N(1)-C(1)	1.335(2)	C(4)-C(5)	1.399(2)
N(1)-N(2)	1.359(2)	C(4)-H(4)	0.9500
N(2)-C(3)	1.351(2)	C(5)-C(6)	1.378(3)
N(2)-B(1)	1.538(2)	C(5)-H(5)	0.9500
N(3)-C(4)	1.336(2)	C(6)-H(6)	0.9500

C(7)-C(8)	1.398(3)	C(22)-H(22)	0.9500
C(7)-H(7)	0.9500	C(23)-C(24)	1.400(2)
C(8)-C(9)	1.377(3)	C(23)-H(23)	0.9500
C(8)-H(8)	0.9500	C(24)-C(25)	1.376(3)
C(9)-H(9)	0.9500	C(24)-H(24)	0.9500
C(10)-H(10A)	0.9800	C(25)-H(25)	0.9500
C(10)-H(10B)	0.9800	C(26)-C(27)	1.394(3)
C(10)-H(10C)	0.9800	C(26)-H(26)	0.9500
C(11)-H(11A)	0.9800	C(27)-C(28)	1.380(3)
C(11)-H(11B)	0.9800	C(27)-H(27)	0.9500
C(11)-H(11C)	0.9800	C(28)-H(28)	0.9500
C(12)-C(13)	1.532(3)	C(29)-H(29A)	0.9800
C(12)-C(19)	1.533(2)	C(29)-H(29B)	0.9800
C(12)-H(12)	1.0000	C(29)-H(29C)	0.9800
C(13)-C(14)	1.530(3)	C(30)-H(30A)	0.9800
C(13)-H(13A)	0.9900	C(30)-H(30B)	0.9800
C(13)-H(13B)	0.9900	C(30)-H(30C)	0.9800
C(14)-C(15)	1.506(3)	C(31)-C(38)	1.529(2)
C(14)-H(14A)	0.9900	C(31)-C(32)	1.540(3)
C(14)-H(14B)	0.9900	C(31)-H(31)	1.0000
C(15)-C(16)	1.330(3)	C(32)-C(33)	1.536(3)
C(15)-H(15)	0.9500	C(32)-H(32A)	0.9900
C(16)-C(17)	1.498(3)	C(32)-H(32B)	0.9900
C(16)-H(16)	0.9500	C(33)-C(34)	1.519(3)
C(17)-C(18)	1.532(3)	C(33)-H(33A)	0.9900
C(17)-H(17A)	0.9900	C(33)-H(33B)	0.9900
C(17)-H(17B)	0.9900	C(34)-C(35)	1.317(3)
C(18)-C(19)	1.536(2)	C(34)-H(34)	0.9500
C(18)-H(18A)	0.9900	C(35)-C(36)	1.499(3)
C(18)-H(18B)	0.9900	C(35)-H(35)	0.9500
C(19)-H(19)	1.0000	C(36)-C(37)	1.537(3)
C(20)-C(21)	1.400(3)	C(36)-H(36A)	0.9900
C(20)-H(20)	0.9500	C(36)-H(36B)	0.9900
C(21)-C(22)	1.377(3)	C(37)-C(38)	1.527(3)
C(21)-H(21)	0.9500	C(37)-H(37A)	0.9900

C(37)-H(37B)	0.9900	N(7)-Ru(2)-Cl(2)	87.59(4)
C(38)-H(38)	1.0000	N(9)-Ru(2)-Cl(2)	172.25(4)
C(39)-H(39A)	0.9900	S(3)-Ru(2)-Cl(2)	86.221(15)
C(39)-H(39B)	0.9900	S(4)-Ru(2)-Cl(2)	89.237(16)
C(40)-H(40A)	0.9900	C(10)-S(1)-C(12)	100.18(9)
C(40)-H(40B)	0.9900	C(10)-S(1)-Ru(1)	112.92(6)
B(1)-H(41)	1.10(2)	C(12)-S(1)-Ru(1)	105.30(6)
B(2)-H(42)	1.10(2)	C(11)-S(2)-C(19)	101.33(9)
		C(11)-S(2)-Ru(1)	113.27(7)
N(5)-Ru(1)-N(1)	87.59(6)	C(19)-S(2)-Ru(1)	103.03(6)
N(5)-Ru(1)-N(3)	85.58(6)	C(29)-S(3)-C(38)	101.51(9)
N(1)-Ru(1)-N(3)	87.15(6)	C(29)-S(3)-Ru(2)	113.56(7)
N(5)-Ru(1)-S(2)	94.56(4)	C(38)-S(3)-Ru(2)	103.36(6)
N(1)-Ru(1)-S(2)	175.63(4)	C(30)-S(4)-C(31)	100.62(9)
N(3)-Ru(1)-S(2)	96.79(4)	C(30)-S(4)-Ru(2)	112.66(7)
N(5)-Ru(1)-S(1)	176.79(4)	C(31)-S(4)-Ru(2)	105.75(6)
N(1)-Ru(1)-S(1)	91.48(4)	C(1)-N(1)-N(2)	107.01(14)
N(3)-Ru(1)-S(1)	97.45(4)	C(1)-N(1)-Ru(1)	133.56(13)
S(2)-Ru(1)-S(1)	86.164(15)	N(2)-N(1)-Ru(1)	119.43(11)
N(5)-Ru(1)-Cl(1)	87.34(4)	C(3)-N(2)-N(1)	109.49(15)
N(1)-Ru(1)-Cl(1)	89.80(4)	C(3)-N(2)-B(1)	131.63(16)
N(3)-Ru(1)-Cl(1)	172.40(4)	N(1)-N(2)-B(1)	118.84(14)
S(2)-Ru(1)-Cl(1)	86.506(15)	C(4)-N(3)-N(4)	106.11(14)
S(1)-Ru(1)-Cl(1)	89.576(15)	C(4)-N(3)-Ru(1)	136.92(12)
N(11)-Ru(2)-N(7)	87.25(6)	N(4)-N(3)-Ru(1)	116.95(11)
N(11)-Ru(2)-N(9)	87.41(6)	C(6)-N(4)-N(3)	109.68(14)
N(7)-Ru(2)-N(9)	85.43(6)	C(6)-N(4)-B(1)	129.29(15)
N(11)-Ru(2)-S(3)	174.06(4)	N(3)-N(4)-B(1)	120.90(14)
N(7)-Ru(2)-S(3)	95.89(4)	C(7)-N(5)-N(6)	107.29(14)
N(9)-Ru(2)-S(3)	97.85(4)	C(7)-N(5)-Ru(1)	133.27(12)
N(11)-Ru(2)-S(4)	90.42(4)	N(6)-N(5)-Ru(1)	119.44(11)
N(7)-Ru(2)-S(4)	176.10(4)	C(9)-N(6)-N(5)	109.00(15)
N(9)-Ru(2)-S(4)	97.59(4)	C(9)-N(6)-B(1)	131.87(16)
S(3)-Ru(2)-S(4)	86.163(16)	N(5)-N(6)-B(1)	119.10(14)
N(11)-Ru(2)-Cl(2)	88.88(4)	C(20)-N(7)-N(8)	107.22(14)

C(20)-N(7)-Ru(2)	133.51(13)	N(5)-C(7)-C(8)	110.09(17)
N(8)-N(7)-Ru(2)	119.22(11)	N(5)-C(7)-H(7)	125.0
C(22)-N(8)-N(7)	109.17(15)	C(8)-C(7)-H(7)	125.0
C(22)-N(8)-B(2)	131.60(15)	C(9)-C(8)-C(7)	104.76(17)
N(7)-N(8)-B(2)	119.23(14)	C(9)-C(8)-H(8)	127.6
C(23)-N(9)-N(10)	106.29(14)	C(7)-C(8)-H(8)	127.6
C(23)-N(9)-Ru(2)	136.65(12)	N(6)-C(9)-C(8)	108.86(16)
N(10)-N(9)-Ru(2)	117.05(10)	N(6)-C(9)-H(9)	125.6
C(25)-N(10)-N(9)	109.42(14)	C(8)-C(9)-H(9)	125.6
C(25)-N(10)-B(2)	129.35(15)	S(1)-C(10)-H(10A)	109.5
N(9)-N(10)-B(2)	121.05(14)	S(1)-C(10)-H(10B)	109.5
C(26)-N(11)-N(12)	107.24(14)	H(10A)-C(10)-H(10B)	109.5
C(26)-N(11)-Ru(2)	132.36(13)	S(1)-C(10)-H(10C)	109.5
N(12)-N(11)-Ru(2)	120.33(11)	H(10A)-C(10)-H(10C)	109.5
C(28)-N(12)-N(11)	109.38(15)	H(10B)-C(10)-H(10C)	109.5
C(28)-N(12)-B(2)	132.53(15)	S(2)-C(11)-H(11A)	109.5
N(11)-N(12)-B(2)	118.09(14)	S(2)-C(11)-H(11B)	109.5
N(1)-C(1)-C(2)	110.13(17)	H(11A)-C(11)-H(11B)	109.5
N(1)-C(1)-H(1)	124.9	S(2)-C(11)-H(11C)	109.5
C(2)-C(1)-H(1)	124.9	H(11A)-C(11)-H(11C)	109.5
C(3)-C(2)-C(1)	104.90(16)	H(11B)-C(11)-H(11C)	109.5
C(3)-C(2)-H(2)	127.6	C(13)-C(12)-C(19)	118.16(15)
C(1)-C(2)-H(2)	127.6	C(13)-C(12)-S(1)	105.78(12)
N(2)-C(3)-C(2)	108.48(17)	C(19)-C(12)-S(1)	108.42(11)
N(2)-C(3)-H(3)	125.8	C(13)-C(12)-H(12)	108.0
C(2)-C(3)-H(3)	125.8	C(19)-C(12)-H(12)	108.0
N(3)-C(4)-C(5)	110.80(16)	S(1)-C(12)-H(12)	108.0
N(3)-C(4)-H(4)	124.6	C(14)-C(13)-C(12)	115.46(16)
C(5)-C(4)-H(4)	124.6	C(14)-C(13)-H(13A)	108.4
C(6)-C(5)-C(4)	104.70(16)	C(12)-C(13)-H(13A)	108.4
C(6)-C(5)-H(5)	127.6	C(14)-C(13)-H(13B)	108.4
C(4)-C(5)-H(5)	127.6	C(12)-C(13)-H(13B)	108.4
N(4)-C(6)-C(5)	108.70(16)	H(13A)-C(13)-H(13B)	107.5
N(4)-C(6)-H(6)	125.7	C(15)-C(14)-C(13)	114.55(18)
C(5)-C(6)-H(6)	125.7	C(15)-C(14)-H(14A)	108.6

C(13)-C(14)-H(14A)	108.6	N(8)-C(22)-H(22)	125.6
C(15)-C(14)-H(14B)	108.6	C(21)-C(22)-H(22)	125.6
C(13)-C(14)-H(14B)	108.6	N(9)-C(23)-C(24)	110.78(16)
H(14A)-C(14)-H(14B)	107.6	N(9)-C(23)-H(23)	124.6
C(16)-C(15)-C(14)	128.51(19)	C(24)-C(23)-H(23)	124.6
C(16)-C(15)-H(15)	115.7	C(25)-C(24)-C(23)	104.78(16)
C(14)-C(15)-H(15)	115.7	C(25)-C(24)-H(24)	127.6
C(15)-C(16)-C(17)	131.54(18)	C(23)-C(24)-H(24)	127.6
C(15)-C(16)-H(16)	114.2	N(10)-C(25)-C(24)	108.74(16)
C(17)-C(16)-H(16)	114.2	N(10)-C(25)-H(25)	125.6
C(16)-C(17)-C(18)	119.05(17)	C(24)-C(25)-H(25)	125.6
C(16)-C(17)-H(17A)	107.6	N(11)-C(26)-C(27)	109.97(17)
C(18)-C(17)-H(17A)	107.6	N(11)-C(26)-H(26)	125.0
C(16)-C(17)-H(17B)	107.6	C(27)-C(26)-H(26)	125.0
C(18)-C(17)-H(17B)	107.6	C(28)-C(27)-C(26)	105.14(17)
H(17A)-C(17)-H(17B)	107.0	C(28)-C(27)-H(27)	127.4
C(17)-C(18)-C(19)	114.30(16)	C(26)-C(27)-H(27)	127.4
C(17)-C(18)-H(18A)	108.7	N(12)-C(28)-C(27)	108.27(17)
C(19)-C(18)-H(18A)	108.7	N(12)-C(28)-H(28)	125.9
C(17)-C(18)-H(18B)	108.7	C(27)-C(28)-H(28)	125.9
C(19)-C(18)-H(18B)	108.7	S(3)-C(29)-H(29A)	109.5
H(18A)-C(18)-H(18B)	107.6	S(3)-C(29)-H(29B)	109.5
C(12)-C(19)-C(18)	117.88(14)	H(29A)-C(29)-H(29B)	109.5
C(12)-C(19)-S(2)	107.17(12)	S(3)-C(29)-H(29C)	109.5
C(18)-C(19)-S(2)	111.22(12)	H(29A)-C(29)-H(29C)	109.5
C(12)-C(19)-H(19)	106.7	H(29B)-C(29)-H(29C)	109.5
C(18)-C(19)-H(19)	106.7	S(4)-C(30)-H(30A)	109.5
S(2)-C(19)-H(19)	106.7	S(4)-C(30)-H(30B)	109.5
N(7)-C(20)-C(21)	110.08(17)	H(30A)-C(30)-H(30B)	109.5
N(7)-C(20)-H(20)	125.0	S(4)-C(30)-H(30C)	109.5
C(21)-C(20)-H(20)	125.0	H(30A)-C(30)-H(30C)	109.5
C(22)-C(21)-C(20)	104.75(17)	H(30B)-C(30)-H(30C)	109.5
C(22)-C(21)-H(21)	127.6	C(38)-C(31)-C(32)	117.81(16)
C(20)-C(21)-H(21)	127.6	C(38)-C(31)-S(4)	109.06(12)
N(8)-C(22)-C(21)	108.77(16)	C(32)-C(31)-S(4)	105.86(13)

C(38)-C(31)-H(31)	107.9	C(37)-C(38)-C(31)	116.88(15)
C(32)-C(31)-H(31)	107.9	C(37)-C(38)-S(3)	111.35(13)
S(4)-C(31)-H(31)	107.9	C(31)-C(38)-S(3)	107.15(12)
C(33)-C(32)-C(31)	115.77(17)	C(37)-C(38)-H(38)	107.0
C(33)-C(32)-H(32A)	108.3	C(31)-C(38)-H(38)	107.0
C(31)-C(32)-H(32A)	108.3	S(3)-C(38)-H(38)	107.0
C(33)-C(32)-H(32B)	108.3	Cl(4)-C(39)-Cl(3)	112.99(13)
C(31)-C(32)-H(32B)	108.3	Cl(4)-C(39)-H(39A)	109.0
H(32A)-C(32)-H(32B)	107.4	Cl(3)-C(39)-H(39A)	109.0
C(34)-C(33)-C(32)	113.65(18)	Cl(4)-C(39)-H(39B)	109.0
C(34)-C(33)-H(33A)	108.8	Cl(3)-C(39)-H(39B)	109.0
C(32)-C(33)-H(33A)	108.8	H(39A)-C(39)-H(39B)	107.8
C(34)-C(33)-H(33B)	108.8	Cl(6)-C(40)-Cl(5)	111.80(12)
C(32)-C(33)-H(33B)	108.8	Cl(6)-C(40)-H(40A)	109.3
H(33A)-C(33)-H(33B)	107.7	Cl(5)-C(40)-H(40A)	109.3
C(35)-C(34)-C(33)	127.6(2)	Cl(6)-C(40)-H(40B)	109.3
C(35)-C(34)-H(34)	116.2	Cl(5)-C(40)-H(40B)	109.3
C(33)-C(34)-H(34)	116.2	H(40A)-C(40)-H(40B)	107.9
C(34)-C(35)-C(36)	132.2(2)	N(2)-B(1)-N(4)	107.81(14)
C(34)-C(35)-H(35)	113.9	N(2)-B(1)-N(6)	109.11(14)
C(36)-C(35)-H(35)	113.9	N(4)-B(1)-N(6)	107.58(14)
C(35)-C(36)-C(37)	119.3(2)	N(2)-B(1)-H(41)	112.5(11)
C(35)-C(36)-H(36A)	107.5	N(4)-B(1)-H(41)	109.4(12)
C(37)-C(36)-H(36A)	107.5	N(6)-B(1)-H(41)	110.3(12)
C(35)-C(36)-H(36B)	107.5	N(10)-B(2)-N(12)	108.21(14)
C(37)-C(36)-H(36B)	107.5	N(10)-B(2)-N(8)	107.64(14)
H(36A)-C(36)-H(36B)	107.0	N(12)-B(2)-N(8)	108.39(14)
C(38)-C(37)-C(36)	114.12(18)	N(10)-B(2)-H(42)	108.9(11)
C(38)-C(37)-H(37A)	108.7	N(12)-B(2)-H(42)	111.5(11)
C(36)-C(37)-H(37A)	108.7	N(8)-B(2)-H(42)	112.0(12)
C(38)-C(37)-H(37B)	108.7		
C(36)-C(37)-H(37B)	108.7		
H(37A)-C(37)-H(37B)	107.6		

Symmetry transformations used to generate equivalent atoms:

Table A1.9: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for TpRu1,2-(SMe)5, 6-COE 133. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	12(1)	12(1)	14(1)	-1(1)	2(1)	1(1)
Ru(2)	13(1)	11(1)	14(1)	0(1)	2(1)	1(1)
Cl(1)	19(1)	15(1)	23(1)	2(1)	2(1)	4(1)
Cl(2)	21(1)	16(1)	24(1)	4(1)	5(1)	6(1)
Cl(3)	44(1)	56(1)	36(1)	-7(1)	4(1)	-10(1)
Cl(4)	32(1)	64(1)	63(1)	10(1)	14(1)	14(1)
Cl(5)	31(1)	48(1)	49(1)	4(1)	9(1)	9(1)
Cl(6)	59(1)	50(1)	47(1)	-5(1)	-8(1)	-9(1)
S(1)	15(1)	19(1)	17(1)	-1(1)	4(1)	-1(1)
S(2)	16(1)	15(1)	15(1)	-1(1)	4(1)	0(1)
S(3)	17(1)	17(1)	16(1)	-1(1)	3(1)	2(1)
S(4)	16(1)	20(1)	18(1)	0(1)	4(1)	-2(1)
N(1)	17(1)	16(1)	17(1)	-1(1)	4(1)	1(1)
N(2)	21(1)	16(1)	14(1)	-2(1)	3(1)	-1(1)
N(3)	14(1)	17(1)	16(1)	-1(1)	1(1)	1(1)
N(4)	16(1)	17(1)	18(1)	0(1)	-1(1)	1(1)
N(5)	17(1)	14(1)	17(1)	-2(1)	3(1)	0(1)
N(6)	15(1)	17(1)	20(1)	-4(1)	1(1)	0(1)
N(7)	18(1)	14(1)	17(1)	-1(1)	3(1)	0(1)
N(8)	16(1)	16(1)	20(1)	-4(1)	1(1)	-1(1)
N(9)	15(1)	14(1)	15(1)	0(1)	0(1)	1(1)
N(10)	17(1)	17(1)	15(1)	0(1)	-2(1)	2(1)
N(11)	19(1)	15(1)	17(1)	0(1)	3(1)	2(1)
N(12)	21(1)	17(1)	15(1)	-1(1)	3(1)	1(1)
C(1)	22(1)	17(1)	26(1)	-1(1)	10(1)	1(1)
C(2)	34(1)	21(1)	23(1)	-2(1)	15(1)	1(1)
C(3)	33(1)	17(1)	16(1)	-2(1)	7(1)	-2(1)
C(4)	16(1)	15(1)	24(1)	-2(1)	3(1)	1(1)
C(5)	19(1)	16(1)	30(1)	3(1)	1(1)	3(1)

C(6)	18(1)	20(1)	24(1)	5(1)	0(1)	3(1)
C(7)	23(1)	18(1)	23(1)	-3(1)	9(1)	-3(1)
C(8)	22(1)	23(1)	31(1)	-6(1)	10(1)	-7(1)
C(9)	16(1)	21(1)	29(1)	-9(1)	4(1)	-4(1)
C(10)	24(1)	24(1)	26(1)	4(1)	8(1)	-2(1)
C(11)	18(1)	27(1)	28(1)	-7(1)	9(1)	1(1)
C(12)	16(1)	20(1)	18(1)	-2(1)	1(1)	-2(1)
C(13)	19(1)	24(1)	28(1)	0(1)	-3(1)	2(1)
C(14)	35(1)	27(1)	28(1)	7(1)	-6(1)	-1(1)
C(15)	31(1)	38(1)	25(1)	2(1)	-10(1)	-7(1)
C(16)	33(1)	31(1)	19(1)	1(1)	-5(1)	-15(1)
C(17)	36(1)	21(1)	19(1)	-2(1)	2(1)	-7(1)
C(18)	28(1)	23(1)	18(1)	-4(1)	4(1)	-4(1)
C(19)	18(1)	17(1)	16(1)	-1(1)	1(1)	-2(1)
C(20)	22(1)	18(1)	24(1)	0(1)	8(1)	-1(1)
C(21)	22(1)	21(1)	34(1)	-2(1)	10(1)	-5(1)
C(22)	17(1)	20(1)	30(1)	-7(1)	3(1)	-3(1)
C(23)	19(1)	13(1)	22(1)	-2(1)	2(1)	0(1)
C(24)	22(1)	15(1)	28(1)	2(1)	2(1)	4(1)
C(25)	19(1)	21(1)	21(1)	4(1)	0(1)	3(1)
C(26)	23(1)	22(1)	21(1)	2(1)	7(1)	5(1)
C(27)	33(1)	28(1)	20(1)	0(1)	10(1)	7(1)
C(28)	33(1)	22(1)	15(1)	-1(1)	6(1)	2(1)
C(29)	19(1)	29(1)	25(1)	-5(1)	7(1)	2(1)
C(30)	25(1)	22(1)	29(1)	5(1)	7(1)	-3(1)
C(31)	18(1)	24(1)	19(1)	-1(1)	1(1)	-2(1)
C(32)	19(1)	31(1)	31(1)	2(1)	0(1)	2(1)
C(33)	35(1)	34(1)	31(1)	9(1)	-4(1)	-3(1)
C(34)	32(1)	44(1)	24(1)	7(1)	-10(1)	-11(1)
C(35)	43(1)	37(1)	22(1)	3(1)	-6(1)	-21(1)
C(36)	48(1)	30(1)	30(1)	-9(1)	0(1)	-10(1)
C(37)	30(1)	31(1)	24(1)	-9(1)	4(1)	-3(1)
C(38)	19(1)	17(1)	23(1)	-4(1)	2(1)	-2(1)
C(39)	28(1)	48(1)	29(1)	-5(1)	4(1)	3(1)
C(40)	28(1)	35(1)	30(1)	3(1)	5(1)	5(1)

B(1)	19(1)	18(1)	18(1)	-2(1)	0(1)	1(1)
B(2)	19(1)	17(1)	17(1)	-2(1)	-1(1)	0(1)

Table A1.10: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for TpRu1,2-(SMe)5, 6-COE 133.

	x	y	z	U(eq)
H(1)	8546	2131	6072	25
H(2)	8101	1806	4936	30
H(3)	6510	2114	4711	26
H(4)	6580	5025	6999	22
H(5)	5485	5665	6158	26
H(6)	4987	4443	5435	25
H(7)	5801	1545	7649	25
H(8)	4391	997	7066	30
H(9)	4283	1617	5994	27
H(10A)	8234	4511	6292	36
H(10B)	9009	4844	6800	36
H(10C)	8029	4978	6909	36
H(11A)	5901	4259	7817	35
H(11B)	5985	3890	8509	35
H(11C)	5522	3327	7940	35
H(12)	9007	4431	7980	22
H(13A)	8778	2638	8212	29
H(13B)	9675	3113	8178	29
H(14A)	8673	3256	9168	37
H(14B)	9599	2806	9210	37
H(15)	10253	4080	9442	39
H(16)	9737	5354	9369	34
H(17A)	8511	5608	8592	31
H(17B)	8266	5622	9275	31
H(18A)	7168	4882	8761	27
H(18B)	7774	4121	9069	27
H(19)	7507	4641	7804	20

H(20)	4159	5804	7262	25
H(21)	5538	6377	7875	30
H(22)	5644	5702	8930	27
H(23)	3406	2279	7846	22
H(24)	4486	1622	8688	26
H(25)	4961	2821	9434	25
H(26)	1410	5170	8767	26
H(27)	1825	5546	9895	32
H(28)	3411	5213	10156	28
H(29A)	3925	3438	6326	36
H(29B)	4040	3066	7019	36
H(29C)	4409	4000	6889	36
H(30A)	971	2451	8092	38
H(30B)	1787	2761	8573	38
H(30C)	1929	2303	7938	38
H(31)	937	2883	6896	24
H(32A)	282	4239	6754	33
H(32B)	1174	4678	6654	33
H(33A)	195	4495	5705	41
H(33B)	1121	4071	5681	41
H(34)	-447	3183	5548	42
H(35)	130	1943	5583	42
H(36A)	1603	1777	5536	44
H(36B)	1453	1705	6240	44
H(37A)	2716	2529	6031	34
H(37B)	2053	3277	5779	34
H(38)	2428	2662	7021	24
H(39A)	7751	1641	8807	42
H(39B)	7644	711	9103	42
H(40A)	2269	5713	6140	37
H(40B)	2321	6614	5788	37
H(41)	5222(14)	2739(14)	5363(10)	22
H(42)	4706(14)	4518(14)	9534(10)	21

Table A1.11: Crystal data and structure refinement for $Tp^{Cl}Ru(nbd)Cl$ 134c.

Identification code: $Tp^{Cl}Ru(nbd)Cl$ **134c**

Empirical formula: C16 H15 B Cl4 N6 Ru

Formula weight: 545.02

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.6919(6) Å	α= 90°.
	b = 11.9630(6) Å	β= 96.8470(10)°.
	c = 15.3378(8) Å	γ = 90°.
Volume	1947.82(18) $Å^3$	
Z	4	
Density (calculated)	1.859 Mg/m^3	
Absorption coefficient	1.370 mm^{-1}	
F(000)	1080	
Crystal size	0.38 x 0.24 x 0.22 mm^3	
Theta range for data collection	2.165 to 28.454°.	
Index ranges	-14<=h<=13, -16<=k<=16, -20<=l<=20	
Reflections collected	21003	
Independent reflections	4893 [R(int) = 0.0141]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.6942	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4893 / 0 / 256	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0188, wR2 = 0.0505	
R indices (all data)	R1 = 0.0191, wR2 = 0.0507	
Largest diff. peak and hole	0.534 and -0.661 $e.Å^{-3}$	

Table A1.12: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(nbd)Cl 134c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3516(1)	2455(1)	7076(1)	11(1)
Cl(1)	3836(1)	4010(1)	8084(1)	20(1)
Cl(2)	-931(1)	2725(1)	8989(1)	32(1)
Cl(3)	3166(1)	6241(1)	4576(1)	22(1)
Cl(4)	2068(1)	-938(1)	4285(1)	29(1)
N(1)	2977(1)	3726(1)	6160(1)	14(1)
N(2)	1787(1)	3738(1)	5733(1)	14(1)
N(3)	1698(1)	2498(1)	7453(1)	15(1)
N(4)	683(1)	2716(1)	6859(1)	15(1)
N(5)	2681(1)	1407(1)	6039(1)	14(1)
N(6)	1517(1)	1700(1)	5636(1)	14(1)
C(1)	2808(1)	5123(1)	5199(1)	16(1)
C(2)	3602(1)	4574(1)	5849(1)	16(1)
C(3)	1669(1)	4571(1)	5139(1)	15(1)
C(4)	-361(1)	2811(1)	7267(1)	17(1)
C(5)	6(1)	2656(1)	8154(1)	19(1)
C(6)	1301(1)	2467(1)	8246(1)	19(1)
C(7)	3015(1)	482(1)	5634(1)	16(1)
C(8)	2067(1)	194(1)	4968(1)	17(1)
C(9)	1131(1)	977(1)	4987(1)	16(1)
C(10)	5254(1)	1846(1)	6587(1)	15(1)
C(11)	5347(1)	717(1)	7076(1)	17(1)
C(12)	6434(1)	954(1)	7807(1)	20(1)
C(13)	5828(1)	2037(1)	8110(1)	18(1)
C(14)	5568(1)	2659(1)	7225(1)	16(1)
C(15)	4192(1)	803(1)	7593(1)	17(1)
C(16)	4496(1)	1614(1)	8231(1)	18(1)
B(1)	863(1)	2781(1)	5878(1)	14(1)

Table A1.13: Bond lengths [Å] and angles [°] for $Tp^{Cl}Ru(nbd)Cl$ 134c.

Ru(1)-N(3)	2.0937(13)	C(7)-H(7)	0.9500
Ru(1)-N(1)	2.1037(11)	C(8)-C(9)	1.3736(19)
Ru(1)-N(5)	2.1361(11)	C(9)-H(9)	0.9500
Ru(1)-C(14)	2.1917(14)	C(10)-C(14)	1.3924(19)
Ru(1)-C(16)	2.1919(13)	C(10)-C(11)	1.5437(19)
Ru(1)-C(10)	2.2092(13)	C(10)-H(10)	1.0000
Ru(1)-C(15)	2.2181(13)	C(11)-C(12)	1.5420(19)
Ru(1)-Cl(1)	2.4164(3)	C(11)-C(15)	1.5486(19)
Cl(2)-C(5)	1.7197(15)	C(11)-H(11)	1.0000
Cl(3)-C(1)	1.7145(14)	C(12)-C(13)	1.544(2)
Cl(4)-C(8)	1.7124(14)	C(12)-H(00A)	0.9900
N(1)-C(2)	1.3338(17)	C(12)-H(00B)	0.9900
N(1)-N(2)	1.3597(15)	C(13)-C(14)	1.5438(19)
N(2)-C(3)	1.3456(17)	C(13)-C(16)	1.5432(19)
N(2)-B(1)	1.5456(18)	C(13)-H(13)	1.0000
N(3)-C(6)	1.335(2)	C(14)-H(14)	1.0000
N(3)-N(4)	1.3563(16)	C(15)-C(16)	1.389(2)
N(4)-C(4)	1.3476(18)	C(15)-H(15)	1.0000
N(4)-B(1)	1.5414(18)	C(16)-H(16)	1.0000
N(5)-C(7)	1.3385(17)	B(1)-H(1B)	1.112(18)
N(5)-N(6)	1.3675(15)		
N(6)-C(9)	1.3455(17)	N(3)-Ru(1)-N(1)	88.67(4)
N(6)-B(1)	1.5368(18)	N(3)-Ru(1)-N(5)	84.28(4)
C(1)-C(3)	1.3786(19)	N(1)-Ru(1)-N(5)	82.51(4)
C(1)-C(2)	1.3949(18)	N(3)-Ru(1)-C(14)	156.80(5)
C(2)-H(2)	0.9500	N(1)-Ru(1)-C(14)	100.39(5)
C(3)-H(3)	0.9500	N(5)-Ru(1)-C(14)	117.88(5)
C(4)-C(5)	1.383(2)	N(3)-Ru(1)-C(16)	99.11(5)
C(4)-H(4)	0.9500	N(1)-Ru(1)-C(16)	159.73(5)
C(5)-C(6)	1.394(2)	N(5)-Ru(1)-C(16)	116.72(5)
C(6)-H(6)	0.9500	C(14)-Ru(1)-C(16)	65.86(5)
C(7)-C(8)	1.3933(18)	N(3)-Ru(1)-C(10)	161.49(5)

N(1)-Ru(1)-C(10)	100.72(5)	C(3)-C(1)-C(2)	106.27(12)
N(5)-Ru(1)-C(10)	81.23(5)	C(3)-C(1)-Cl(3)	126.23(11)
C(14)-Ru(1)-C(10)	36.89(5)	C(2)-C(1)-Cl(3)	127.49(11)
C(16)-Ru(1)-C(10)	77.47(5)	N(1)-C(2)-C(1)	108.96(12)
N(3)-Ru(1)-C(15)	101.34(5)	N(1)-C(2)-H(2)	125.5
N(1)-Ru(1)-C(15)	159.13(5)	C(1)-C(2)-H(2)	125.5
N(5)-Ru(1)-C(15)	80.36(5)	N(2)-C(3)-C(1)	107.36(11)
C(14)-Ru(1)-C(15)	77.47(5)	N(2)-C(3)-H(3)	126.3
C(16)-Ru(1)-C(15)	36.71(5)	C(1)-C(3)-H(3)	126.3
C(10)-Ru(1)-C(15)	64.96(5)	N(4)-C(4)-C(5)	106.93(12)
N(3)-Ru(1)-Cl(1)	82.52(3)	N(4)-C(4)-H(4)	126.5
N(1)-Ru(1)-Cl(1)	82.97(3)	C(5)-C(4)-H(4)	126.5
N(5)-Ru(1)-Cl(1)	160.55(3)	C(4)-C(5)-C(6)	106.48(13)
C(14)-Ru(1)-Cl(1)	77.53(4)	C(4)-C(5)-Cl(2)	127.17(12)
C(16)-Ru(1)-Cl(1)	79.57(4)	C(6)-C(5)-Cl(2)	126.33(12)
C(10)-Ru(1)-Cl(1)	114.24(4)	N(3)-C(6)-C(5)	108.84(14)
C(15)-Ru(1)-Cl(1)	116.24(4)	N(3)-C(6)-H(6)	125.6
C(2)-N(1)-N(2)	107.45(11)	C(5)-C(6)-H(6)	125.6
C(2)-N(1)-Ru(1)	132.76(9)	N(5)-C(7)-C(8)	109.46(12)
N(2)-N(1)-Ru(1)	119.72(8)	N(5)-C(7)-H(7)	125.3
C(3)-N(2)-N(1)	109.94(11)	C(8)-C(7)-H(7)	125.3
C(3)-N(2)-B(1)	129.51(11)	C(9)-C(8)-C(7)	106.52(12)
N(1)-N(2)-B(1)	119.99(10)	C(9)-C(8)-Cl(4)	127.27(11)
C(6)-N(3)-N(4)	107.51(13)	C(7)-C(8)-Cl(4)	126.19(11)
C(6)-N(3)-Ru(1)	131.06(11)	N(6)-C(9)-C(8)	107.08(12)
N(4)-N(3)-Ru(1)	120.98(9)	N(6)-C(9)-H(9)	126.5
C(4)-N(4)-N(3)	110.23(11)	C(8)-C(9)-H(9)	126.5
C(4)-N(4)-B(1)	130.96(12)	C(14)-C(10)-C(11)	105.87(11)
N(3)-N(4)-B(1)	118.78(11)	C(14)-C(10)-Ru(1)	70.88(8)
C(7)-N(5)-N(6)	106.32(11)	C(11)-C(10)-Ru(1)	97.51(8)
C(7)-N(5)-Ru(1)	136.05(9)	C(14)-C(10)-H(10)	123.1
N(6)-N(5)-Ru(1)	117.62(8)	C(11)-C(10)-H(10)	123.1
C(9)-N(6)-N(5)	110.61(11)	Ru(1)-C(10)-H(10)	123.1
C(9)-N(6)-B(1)	127.71(11)	C(12)-C(11)-C(10)	101.02(11)
N(5)-N(6)-B(1)	121.45(10)	C(12)-C(11)-C(15)	101.18(11)

C(10)-C(11)-C(15)	100.49(10)	Ru(1)-C(14)-H(14)	123.0
C(12)-C(11)-H(11)	117.1	C(16)-C(15)-C(11)	105.85(12)
C(10)-C(11)-H(11)	117.1	C(16)-C(15)-Ru(1)	70.62(8)
C(15)-C(11)-H(11)	117.1	C(11)-C(15)-Ru(1)	97.00(8)
C(11)-C(12)-C(13)	93.78(10)	C(16)-C(15)-H(15)	123.3
C(11)-C(12)-H(00A)	113.0	C(11)-C(15)-H(15)	123.3
C(13)-C(12)-H(00A)	113.0	Ru(1)-C(15)-H(15)	123.3
C(11)-C(12)-H(00B)	113.0	C(15)-C(16)-C(13)	106.61(12)
C(13)-C(12)-H(00B)	113.0	C(15)-C(16)-Ru(1)	72.67(8)
H(00A)-C(12)-H(00B)	110.4	C(13)-C(16)-Ru(1)	96.39(8)
C(14)-C(13)-C(16)	101.06(10)	C(15)-C(16)-H(16)	122.8
C(14)-C(13)-C(12)	100.30(11)	C(13)-C(16)-H(16)	122.8
C(16)-C(13)-C(12)	100.85(12)	Ru(1)-C(16)-H(16)	122.8
C(14)-C(13)-H(13)	117.2	N(6)-B(1)-N(4)	107.91(11)
C(16)-C(13)-H(13)	117.2	N(6)-B(1)-N(2)	105.75(11)
C(12)-C(13)-H(13)	117.2	N(4)-B(1)-N(2)	109.56(11)
C(10)-C(14)-C(13)	106.49(12)	N(6)-B(1)-H(1B)	110.8(10)
C(10)-C(14)-Ru(1)	72.24(8)	N(4)-B(1)-H(1B)	112.2(9)
C(13)-C(14)-Ru(1)	96.38(8)	N(2)-B(1)-H(1B)	110.4(10)
C(10)-C(14)-H(14)	123.0		
C(13)-C(14)-H(14)	123.0		

Symmetry transformations used to generate equivalent atoms:

Table A1.14: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Cl}Ru(nbd)Cl$ 134c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	11(1)	13(1)	9(1)	0(1)	0(1)	1(1)
Cl(1)	19(1)	22(1)	16(1)	-7(1)	-3(1)	4(1)
Cl(2)	20(1)	57(1)	20(1)	-2(1)	9(1)	1(1)
Cl(3)	25(1)	18(1)	22(1)	7(1)	3(1)	-2(1)
Cl(4)	28(1)	27(1)	32(1)	-17(1)	6(1)	-3(1)

N(1)	14(1)	14(1)	14(1)	0(1)	-1(1)	0(1)
N(2)	14(1)	14(1)	13(1)	0(1)	-1(1)	1(1)
N(3)	14(1)	20(1)	12(1)	1(1)	1(1)	2(1)
N(4)	13(1)	18(1)	14(1)	0(1)	0(1)	1(1)
N(5)	14(1)	14(1)	13(1)	1(1)	0(1)	0(1)
N(6)	14(1)	15(1)	13(1)	0(1)	-1(1)	-1(1)
C(1)	20(1)	14(1)	14(1)	2(1)	3(1)	1(1)
C(2)	16(1)	15(1)	16(1)	0(1)	1(1)	0(1)
C(3)	17(1)	15(1)	13(1)	0(1)	1(1)	3(1)
C(4)	15(1)	20(1)	18(1)	-2(1)	2(1)	0(1)
C(5)	17(1)	26(1)	17(1)	-2(1)	6(1)	0(1)
C(6)	17(1)	25(1)	14(1)	1(1)	4(1)	2(1)
C(7)	18(1)	15(1)	16(1)	-1(1)	4(1)	-1(1)
C(8)	20(1)	16(1)	15(1)	-3(1)	4(1)	-4(1)
C(9)	18(1)	16(1)	13(1)	0(1)	2(1)	-4(1)
C(10)	14(1)	18(1)	14(1)	1(1)	3(1)	2(1)
C(11)	18(1)	18(1)	16(1)	2(1)	1(1)	4(1)
C(12)	19(1)	26(1)	16(1)	2(1)	0(1)	7(1)
C(13)	16(1)	25(1)	13(1)	0(1)	0(1)	4(1)
C(14)	12(1)	22(1)	14(1)	1(1)	2(1)	1(1)
C(15)	19(1)	18(1)	16(1)	7(1)	2(1)	3(1)
C(16)	18(1)	24(1)	11(1)	5(1)	1(1)	5(1)
B(1)	15(1)	15(1)	13(1)	0(1)	0(1)	0(1)

Table A1.15: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Cl}Ru(nbd)Cl 134c.

	x	y	z	U(eq)
H(2)	4452	4771	6040	19
H(3)	936	4746	4750	18
H(4)	-1191	2956	6996	21
H(6)	1818	2337	8784	22
H(7)	3781	83	5778	19
H(9)	358	1004	4612	19

H(10)	5423	1931	5963	18
H(11)	5416	29	6715	21
H(00A)	7248	1087	7577	24
H(00B)	6528	368	8266	24
H(13)	6299	2452	8611	22
H(14)	5989	3379	7102	19
H(15)	3617	161	7671	21
H(16)	4165	1603	8814	21
H(1B)	-44(17)	2899(16)	5453(12)	17

Table A1.16: Crystal data and structure refinement for $Tp^{Br}Ru(cod)Cl$ 124d.

Identification code $Tp^{Br}Ru(cod)Cl$ **124d**

Empirical formula C18.50 H22 B Br4 Cl3 N6 Ru

Formula weight 866.29

Temperature 173(2) K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group P -1

Unit cell dimensions	a = 8.2057(9) Å	α= 79.564(2)°
	b = 12.9007(13) Å	β= 76.899(2)°.
	c = 13.3325(14) Å	γ = 88.301(2)°.
Volume		1351.8(2) $Å^3$
Z		2
Density (calculated)		2.128 Mg/m^3
Absorption coefficient		6.809 mm^{-1}
F(000)		830
Crystal size		0.180 x 0.120 x 0.050 mm^3
Theta range for data collection		1.594 to 28.186°.
Index ranges		-10<=h<=10, -17<=k<=17, -17<=l<=17
Reflections collected		34402
Independent reflections		6636 [R(int) = 0.0224]
Completeness to theta = 25.242°		99.9 %
Absorption correction		Empirical
Max. and min. transmission		0.7457 and 0.4982
Refinement method		Full-matrix least-squares on F^2
Data / restraints / parameters		6636 / 0 / 319
Goodness-of-fit on F^2		1.027
Final R indices [I>2sigma(I)]		R1 = 0.0259, wR2 = 0.0661
R indices (all data)		R1 = 0.0291, wR2 = 0.0684
Largest diff. peak and hole		1.188 and -1.192 $e.Å^{-3}$

Table A1.17: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(cod)Cl 124d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2754(1)	2807(1)	6885(1)	15(1)
Br(1)	5376(1)	3342(1)	5434(1)	25(1)
Br(2)	7468(1)	-885(1)	7232(1)	35(1)
Br(3)	5956(1)	6392(1)	8166(1)	43(1)
Br(4)	-2394(1)	866(1)	10875(1)	30(1)
Cl(1)	9084(2)	2909(1)	2745(1)	81(1)
Cl(2)	7811(2)	930(1)	4047(1)	83(1)
Cl(3)	-1128(7)	4393(6)	9592(5)	113(3)
Cl(4)	1009(8)	5795(3)	10154(6)	101(2)
N(1)	4770(3)	1505(2)	8295(2)	18(1)
N(2)	4327(3)	1575(2)	7361(2)	18(1)
N(3)	2072(3)	2098(2)	9248(2)	19(1)
N(4)	1274(3)	2209(2)	8439(2)	18(1)
N(5)	4398(3)	3396(2)	8525(2)	19(1)
N(6)	3895(3)	3796(2)	7632(2)	19(1)
C(1)	652(3)	3940(2)	6819(2)	22(1)
C(2)	-1006(3)	3403(2)	6922(2)	27(1)
C(3)	-813(4)	2360(2)	6500(2)	27(1)
C(4)	859(3)	1816(2)	6513(2)	22(1)
C(5)	2195(4)	1997(2)	5654(2)	22(1)
C(6)	2116(4)	2773(2)	4669(2)	26(1)
C(7)	1575(4)	3887(2)	4859(2)	27(1)
C(8)	1830(3)	4159(2)	5876(2)	21(1)
C(9)	4346(4)	4815(2)	7378(2)	23(1)
C(10)	5125(4)	5066(2)	8130(2)	26(1)
C(11)	5139(3)	4153(2)	8851(2)	23(1)
C(12)	1034(3)	1654(2)	10150(2)	22(1)
C(13)	-467(3)	1471(2)	9927(2)	23(1)
C(14)	-279(3)	1817(2)	8858(2)	22(1)

C(15)	5809(3)	689(2)	8429(2)	20(1)
C(16)	6057(3)	233(2)	7549(2)	21(1)
C(17)	5119(3)	814(2)	6897(2)	20(1)
C(18)	7309(6)	2092(4)	3291(4)	61(1)
C(19)	-697(12)	5365(8)	10120(10)	66(3)
B(1)	3976(4)	2248(2)	9053(2)	19(1)

Table A1.18: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(cod)Cl.

Ru(1)-N(6)	2.110(2)	N(5)-C(11)	1.349(3)
Ru(1)-N(2)	2.116(2)	N(5)-N(6)	1.357(3)
Ru(1)-N(4)	2.168(2)	N(5)-B(1)	1.533(4)
Ru(1)-C(8)	2.228(3)	N(6)-C(9)	1.338(3)
Ru(1)-C(5)	2.233(3)	C(1)-C(8)	1.390(4)
Ru(1)-C(1)	2.234(3)	C(1)-C(2)	1.512(4)
Ru(1)-C(4)	2.235(3)	C(1)-H(1)	1.0000
Ru(1)-Br(1)	2.5623(4)	C(2)-C(3)	1.540(4)
Br(2)-C(16)	1.871(3)	C(2)-H(00A)	0.9900
Br(3)-C(10)	1.874(3)	C(2)-H(00B)	0.9900
Br(4)-C(13)	1.875(3)	C(3)-C(4)	1.525(4)
Cl(1)-C(18)	1.759(5)	C(3)-H(00C)	0.9900
Cl(2)-C(18)	1.743(6)	C(3)-H(00D)	0.9900
Cl(3)-Cl(4)#1	0.409(12)	C(4)-C(5)	1.385(4)
Cl(3)-C(19)	1.627(10)	C(4)-H(4)	1.0000
Cl(4)-Cl(3)#1	0.409(12)	C(5)-C(6)	1.513(4)
Cl(4)-C(19)	1.534(11)	C(5)-H(5)	1.0000
N(1)-C(15)	1.348(3)	C(6)-C(7)	1.539(4)
N(1)-N(2)	1.361(3)	C(6)-H(00E)	0.9900
N(1)-B(1)	1.543(3)	C(6)-H(00G)	0.9900
N(2)-C(17)	1.330(3)	C(7)-C(8)	1.519(4)
N(3)-C(12)	1.347(3)	C(7)-H(7A)	0.9900
N(3)-N(4)	1.368(3)	C(7)-H(7B)	0.9900
N(3)-B(1)	1.537(4)	C(8)-H(8)	1.0000
N(4)-C(14)	1.344(3)	C(9)-C(10)	1.392(4)

C(9)-H(9)	0.9500	C(8)-Ru(1)-C(4)	86.77(10)
C(10)-C(11)	1.380(4)	C(5)-Ru(1)-C(4)	36.11(10)
C(11)-H(11)	0.9500	C(1)-Ru(1)-C(4)	78.81(10)
C(12)-C(13)	1.367(4)	N(6)-Ru(1)-Br(1)	81.29(6)
C(12)-H(12)	0.9500	N(2)-Ru(1)-Br(1)	81.98(6)
C(13)-C(14)	1.389(4)	N(4)-Ru(1)-Br(1)	158.17(6)
C(14)-H(14)	0.9500	C(8)-Ru(1)-Br(1)	78.20(7)
C(15)-C(16)	1.378(4)	C(5)-Ru(1)-Br(1)	80.40(7)
C(15)-H(15)	0.9500	C(1)-Ru(1)-Br(1)	113.52(7)
C(16)-C(17)	1.394(4)	C(4)-Ru(1)-Br(1)	116.50(7)
C(17)-H(17)	0.9500	Cl(4)#1-Cl(3)-C(19)	85.0(14)
C(18)-H(18A)	0.9900	Cl(3)#1-Cl(4)-C(19)	103.7(17)
C(18)-H(18B)	0.9900	C(15)-N(1)-N(2)	110.0(2)
C(19)-H(19A)	0.9900	C(15)-N(1)-B(1)	129.8(2)
C(19)-H(19B)	0.9900	N(2)-N(1)-B(1)	119.9(2)
B(1)-H(1B)	1.09(3)	C(17)-N(2)-N(1)	107.3(2)
		C(17)-N(2)-Ru(1)	132.87(18)
N(6)-Ru(1)-N(2)	88.67(8)	N(1)-N(2)-Ru(1)	119.75(16)
N(6)-Ru(1)-N(4)	85.22(8)	C(12)-N(3)-N(4)	110.3(2)
N(2)-Ru(1)-N(4)	80.62(8)	C(12)-N(3)-B(1)	126.8(2)
N(6)-Ru(1)-C(8)	93.17(9)	N(4)-N(3)-B(1)	121.6(2)
N(2)-Ru(1)-C(8)	159.57(9)	C(14)-N(4)-N(3)	106.0(2)
N(4)-Ru(1)-C(8)	119.81(9)	C(14)-N(4)-Ru(1)	136.80(18)
N(6)-Ru(1)-C(5)	161.35(9)	N(3)-N(4)-Ru(1)	117.00(15)
N(2)-Ru(1)-C(5)	92.25(9)	C(11)-N(5)-N(6)	110.5(2)
N(4)-Ru(1)-C(5)	113.31(9)	C(11)-N(5)-B(1)	129.6(2)
C(8)-Ru(1)-C(5)	79.66(10)	N(6)-N(5)-B(1)	119.8(2)
N(6)-Ru(1)-C(1)	90.33(9)	C(9)-N(6)-N(5)	107.1(2)
N(2)-Ru(1)-C(1)	164.12(9)	C(9)-N(6)-Ru(1)	132.50(18)
N(4)-Ru(1)-C(1)	83.51(9)	N(5)-N(6)-Ru(1)	120.28(16)
C(8)-Ru(1)-C(1)	36.30(10)	C(8)-C(1)-C(2)	122.5(3)
C(5)-Ru(1)-C(1)	93.73(10)	C(8)-C(1)-Ru(1)	71.60(15)
N(6)-Ru(1)-C(4)	161.69(9)	C(2)-C(1)-Ru(1)	113.01(18)
N(2)-Ru(1)-C(4)	97.75(9)	C(8)-C(1)-H(1)	114.2
N(4)-Ru(1)-C(4)	78.99(9)	C(2)-C(1)-H(1)	114.2

Ru(1)-C(1)-H(1)	114.2	C(6)-C(7)-H(7B)	108.4
C(1)-C(2)-C(3)	112.9(2)	H(7A)-C(7)-H(7B)	107.5
C(1)-C(2)-H(00A)	109.0	C(1)-C(8)-C(7)	123.5(2)
C(3)-C(2)-H(00A)	109.0	C(1)-C(8)-Ru(1)	72.10(15)
C(1)-C(2)-H(00B)	109.0	C(7)-C(8)-Ru(1)	113.00(18)
C(3)-C(2)-H(00B)	109.0	C(1)-C(8)-H(8)	113.8
H(00A)-C(2)-H(00B)	107.8	C(7)-C(8)-H(8)	113.8
C(4)-C(3)-C(2)	114.8(2)	Ru(1)-C(8)-H(8)	113.8
C(4)-C(3)-H(00C)	108.6	N(6)-C(9)-C(10)	109.0(2)
C(2)-C(3)-H(00C)	108.6	N(6)-C(9)-H(9)	125.5
C(4)-C(3)-H(00D)	108.6	C(10)-C(9)-H(9)	125.5
C(2)-C(3)-H(00D)	108.6	C(11)-C(10)-C(9)	106.7(2)
H(00C)-C(3)-H(00D)	107.5	C(11)-C(10)-Br(3)	126.8(2)
C(5)-C(4)-C(3)	121.4(2)	C(9)-C(10)-Br(3)	126.5(2)
C(5)-C(4)-Ru(1)	71.86(15)	N(5)-C(11)-C(10)	106.7(2)
C(3)-C(4)-Ru(1)	113.62(18)	N(5)-C(11)-H(11)	126.6
C(5)-C(4)-H(4)	114.3	C(10)-C(11)-H(11)	126.6
C(3)-C(4)-H(4)	114.3	N(3)-C(12)-C(13)	107.6(2)
Ru(1)-C(4)-H(4)	114.3	N(3)-C(12)-H(12)	126.2
C(4)-C(5)-C(6)	122.5(3)	C(13)-C(12)-H(12)	126.2
C(4)-C(5)-Ru(1)	72.03(15)	C(12)-C(13)-C(14)	106.3(2)
C(6)-C(5)-Ru(1)	111.52(18)	C(12)-C(13)-Br(4)	126.9(2)
C(4)-C(5)-H(5)	114.5	C(14)-C(13)-Br(4)	126.8(2)
C(6)-C(5)-H(5)	114.5	N(4)-C(14)-C(13)	109.8(2)
Ru(1)-C(5)-H(5)	114.5	N(4)-C(14)-H(14)	125.1
C(5)-C(6)-C(7)	114.1(2)	C(13)-C(14)-H(14)	125.1
C(5)-C(6)-H(00E)	108.7	N(1)-C(15)-C(16)	107.1(2)
C(7)-C(6)-H(00E)	108.7	N(1)-C(15)-H(15)	126.4
C(5)-C(6)-H(00G)	108.7	C(16)-C(15)-H(15)	126.4
C(7)-C(6)-H(00G)	108.7	C(15)-C(16)-C(17)	106.3(2)
H(00E)-C(6)-H(00G)	107.6	C(15)-C(16)-Br(2)	127.7(2)
C(8)-C(7)-C(6)	115.4(2)	C(17)-C(16)-Br(2)	125.9(2)
C(8)-C(7)-H(7A)	108.4	N(2)-C(17)-C(16)	109.2(2)
C(6)-C(7)-H(7A)	108.4	N(2)-C(17)-H(17)	125.4
C(8)-C(7)-H(7B)	108.4	C(16)-C(17)-H(17)	125.4

Cl(2)-C(18)-Cl(1)	111.2(2)	Cl(3)-C(19)-H(19B)	104.9
Cl(2)-C(18)-H(18A)	109.4	H(19A)-C(19)-H(19B)	105.8
Cl(1)-C(18)-H(18A)	109.4	N(5)-B(1)-N(3)	107.7(2)
Cl(2)-C(18)-H(18B)	109.4	N(5)-B(1)-N(1)	109.7(2)
Cl(1)-C(18)-H(18B)	109.4	N(3)-B(1)-N(1)	106.3(2)
H(18A)-C(18)-H(18B)	108.0	N(5)-B(1)-H(1B)	112.0(17)
Cl(4)-C(19)-Cl(3)	129.5(7)	N(3)-B(1)-H(1B)	108.8(18)
Cl(4)-C(19)-H(19A)	104.9	N(1)-B(1)-H(1B)	112.0(17)
Cl(3)-C(19)-H(19A)	104.9		
Cl(4)-C(19)-H(19B)	104.9		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2

Table A1.19: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Br}Ru(cod)Cl$ 124d. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	16(1)	14(1)	13(1)	-1(1)	-2(1)	-3(1)
Br(1)	23(1)	28(1)	21(1)	-1(1)	0(1)	-3(1)
Br(2)	41(1)	28(1)	37(1)	-9(1)	-9(1)	15(1)
Br(3)	76(1)	28(1)	26(1)	-4(1)	-9(1)	-27(1)
Br(4)	26(1)	38(1)	21(1)	-2(1)	5(1)	-13(1)
Cl(1)	79(1)	71(1)	87(1)	3(1)	-19(1)	5(1)
Cl(2)	73(1)	51(1)	115(1)	-22(1)	9(1)	3(1)
Cl(3)	56(2)	202(7)	107(3)	-99(4)	-13(2)	-22(3)
Cl(4)	110(3)	47(2)	182(6)	-39(2)	-94(4)	5(2)
N(1)	18(1)	18(1)	16(1)	0(1)	-4(1)	-2(1)
N(2)	20(1)	18(1)	16(1)	-1(1)	-3(1)	-2(1)
N(3)	19(1)	20(1)	15(1)	-1(1)	-2(1)	-3(1)
N(4)	18(1)	20(1)	16(1)	-1(1)	-2(1)	-2(1)
N(5)	21(1)	20(1)	17(1)	-4(1)	-3(1)	-4(1)
N(6)	20(1)	18(1)	18(1)	-2(1)	-2(1)	-4(1)
C(1)	21(1)	20(1)	26(1)	-2(1)	-5(1)	3(1)

C(2)	18(1)	29(1)	31(1)	1(1)	-4(1)	1(1)
C(3)	21(1)	32(1)	27(1)	0(1)	-6(1)	-8(1)
C(4)	27(1)	20(1)	22(1)	-3(1)	-8(1)	-8(1)
C(5)	29(1)	20(1)	19(1)	-5(1)	-8(1)	-2(1)
C(6)	30(1)	29(1)	18(1)	-2(1)	-7(1)	-2(1)
C(7)	31(2)	26(1)	21(1)	2(1)	-7(1)	0(1)
C(8)	23(1)	17(1)	23(1)	2(1)	-7(1)	0(1)
C(9)	30(1)	18(1)	20(1)	-3(1)	-3(1)	-4(1)
C(10)	34(2)	21(1)	21(1)	-6(1)	0(1)	-11(1)
C(11)	26(1)	26(1)	18(1)	-7(1)	-3(1)	-8(1)
C(12)	24(1)	22(1)	15(1)	-1(1)	0(1)	-3(1)
C(13)	22(1)	23(1)	19(1)	-1(1)	2(1)	-6(1)
C(14)	20(1)	24(1)	21(1)	-3(1)	-2(1)	-5(1)
C(15)	16(1)	19(1)	22(1)	2(1)	-4(1)	-4(1)
C(16)	20(1)	17(1)	25(1)	-2(1)	-3(1)	-1(1)
C(17)	21(1)	18(1)	21(1)	-3(1)	-3(1)	-1(1)
C(18)	49(2)	84(3)	60(3)	-45(3)	-15(2)	18(2)
C(19)	54(5)	59(5)	97(8)	-44(5)	-23(5)	11(4)
B(1)	19(1)	19(1)	17(1)	-2(1)	-2(1)	-2(1)

Table A1.20: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Br}Ru(cod)Cl 124d.

	x	y	z	U(eq)
H(1)	602	4482	7274	27
H(00A)	-1706	3886	6535	32
H(00B)	-1595	3260	7669	32
H(00C)	-1721	1870	6921	33
H(00D)	-960	2502	5771	33
H(4)	764	1074	6906	27
H(5)	2894	1364	5533	26
H(00E)	1320	2498	4320	31
H(00G)	3233	2822	4186	31

H(7A)	2207	4407	4270	32
H(7B)	374	3965	4851	32
H(8)	2472	4830	5780	25
H(9)	4164	5290	6782	28
H(11)	5585	4073	9458	28
H(12)	1297	1497	10819	26
H(14)	-1122	1782	8480	26
H(15)	6282	469	9020	24
H(17)	5054	686	6227	24
H(18A)	6452	2474	3733	73
H(18B)	6829	1920	2723	73
H(19A)	-1272	5980	9801	79
H(19B)	-1307	5193	10861	79
H(1B)	4350(40)	2050(30)	9800(30)	23

Table A1.21: Crystal data and structure refinement for $Tp^{Br}Ru(nbd)Cl$ 134d.

Identification code: $Tp^{Br}Ru(nbd)Cl$ **134d**		
Empirical formula: C16 H15 B Br3 Cl N6 Ru		
Formula weight: 678.40		
Temperature:	123(2) K	
Wavelength:0.71073 Å		
Crystal system: Monoclinic		
Space group	P 21/n	
Unit cell dimensions	a = 10.8913(3) Å	α= 90°.
	b = 12.1716(4) Å	β= 97.7630(10)°.
	c = 15.5435(5) Å	γ = 90°.
Volume	2041.63(11) $Å^3$	
Z	4	
Density (calculated)	2.207 Mg/m^3	
Absorption coefficient	6.786 mm^{-1}	
F(000)	1296	
Crystal size	0.200 x 0.160 x 0.140 mm^3	
Theta range for data collection	2.133 to 28.307°.	
Index ranges	-14<=h<=14, -15<=k<=16, -17<=l<=20	
Reflections collected	26129	
Independent reflections	5069 [R(int) = 0.0121]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.5821	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5069 / 2 / 276	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0148, wR2 = 0.0367	
R indices (all data)	R1 = 0.0158, wR2 = 0.0371	
Largest diff. peak and hole	0.466 and -0.574 $e.Å^{-3}$	

Table A1.22: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(nbd)Cl 134d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3431(1)	7548(1)	7106(1)	10(1)
Br(1)	2033(1)	10864(1)	4183(2)	25(1)
Br(1B)	2160(20)	11050(19)	4440(20)	20(3)
Br(2)	-1002(3)	7112(3)	9011(2)	24(1)
Br(2B)	-1038(5)	7268(11)	9026(3)	31(1)
Br(3)	3205(1)	3776(1)	4548(1)	20(1)
Cl(1)	3756(1)	6037(1)	8120(1)	19(1)
N(1)	2601(1)	8561(1)	6065(1)	13(1)
N(2)	1450(1)	8269(1)	5663(1)	13(1)
N(3)	1643(1)	7501(1)	7459(1)	14(1)
N(4)	651(1)	7257(1)	6862(1)	13(1)
N(5)	1744(1)	6271(1)	5761(1)	13(1)
N(6)	2911(1)	6289(1)	6203(1)	13(1)
C(1)	2936(1)	9448(1)	5646(1)	15(1)
C(2)	2010(1)	9714(1)	4974(1)	16(1)
C(3)	1078(1)	8957(1)	5001(1)	14(1)
C(4)	-372(1)	7132(1)	7256(1)	16(1)
C(5)	-16(1)	7293(1)	8132(1)	18(1)
C(6)	1254(1)	7517(1)	8236(1)	17(1)
C(7)	1650(1)	5464(1)	5164(1)	14(1)
C(8)	2778(1)	4940(1)	5233(1)	14(1)
C(9)	3543(1)	5474(1)	5895(1)	15(1)
C(10)	4390(1)	8392(1)	8249(1)	17(1)
C(11)	4087(1)	9177(1)	7610(1)	17(1)
C(12)	5224(1)	9259(1)	7112(1)	16(1)
C(13)	6291(2)	9039(1)	7847(1)	20(1)
C(14)	5703(1)	7978(1)	8149(1)	17(1)
C(15)	5452(1)	7354(1)	7277(1)	15(1)
C(16)	5140(1)	8142(1)	6639(1)	15(1)

B(1)	825(2)	7199(1)	5897(1)	13(1)

Table A1.23: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(nbd)Cl 134d.

Ru(1)-N(3)	2.0935(13)	C(4)-H(4)	0.9500
Ru(1)-N(6)	2.1034(12)	C(5)-C(6)	1.398(2)
Ru(1)-N(1)	2.1356(12)	C(6)-H(6)	0.9500
Ru(1)-C(10)	2.1901(15)	C(7)-C(8)	1.376(2)
Ru(1)-C(15)	2.1935(14)	C(7)-H(7)	0.9500
Ru(1)-C(16)	2.2088(14)	C(8)-C(9)	1.394(2)
Ru(1)-C(11)	2.2147(15)	C(9)-H(9)	0.9500
Ru(1)-Cl(1)	2.4160(4)	C(10)-C(11)	1.385(2)
Br(1)-C(2)	1.8657(16)	C(10)-C(14)	1.544(2)
Br(1B)-C(2)	1.844(11)	C(10)-H(10)	1.0000
Br(2)-C(5)	1.861(3)	C(11)-C(12)	1.549(2)
Br(2B)-C(5)	1.894(6)	C(11)-H(11)	1.0000
Br(3)-C(8)	1.8683(15)	C(12)-C(13)	1.539(2)
N(1)-C(1)	1.3369(19)	C(12)-C(16)	1.543(2)
N(1)-N(2)	1.3701(17)	C(12)-H(12)	1.0000
N(2)-C(3)	1.3466(19)	C(13)-C(14)	1.543(2)
N(2)-B(1)	1.535(2)	C(13)-H(13A)	0.9900
N(3)-C(6)	1.333(2)	C(13)-H(13B)	0.9900
N(3)-N(4)	1.3587(17)	C(14)-C(15)	1.545(2)
N(4)-C(4)	1.3502(19)	C(14)-H(14)	1.0000
N(4)-B(1)	1.539(2)	C(15)-C(16)	1.389(2)
N(5)-C(7)	1.3458(19)	C(15)-H(15)	1.0000
N(5)-N(6)	1.3611(16)	C(16)-H(16)	1.0000
N(5)-B(1)	1.542(2)	B(1)-H(1B)	1.107(19)
N(6)-C(9)	1.3330(19)		
C(1)-C(2)	1.389(2)	N(3)-Ru(1)-N(6)	88.77(5)
C(1)-H(1)	0.9500	N(3)-Ru(1)-N(1)	84.30(5)
C(2)-C(3)	1.375(2)	N(6)-Ru(1)-N(1)	82.31(5)
C(3)-H(3)	0.9500	N(3)-Ru(1)-C(10)	99.17(5)
C(4)-C(5)	1.379(2)	N(6)-Ru(1)-C(10)	159.83(6)

N(1)-Ru(1)-C(10)	116.76(6)	C(7)-N(5)-N(6)	109.82(12)
N(3)-Ru(1)-C(15)	156.75(5)	C(7)-N(5)-B(1)	129.67(12)
N(6)-Ru(1)-C(15)	100.24(5)	N(6)-N(5)-B(1)	119.86(12)
N(1)-Ru(1)-C(15)	117.96(5)	C(9)-N(6)-N(5)	107.41(12)
C(10)-Ru(1)-C(15)	65.90(6)	C(9)-N(6)-Ru(1)	132.56(10)
N(3)-Ru(1)-C(16)	161.75(5)	N(5)-N(6)-Ru(1)	119.85(9)
N(6)-Ru(1)-C(16)	100.47(5)	N(1)-C(1)-C(2)	109.66(14)
N(1)-Ru(1)-C(16)	81.43(5)	N(1)-C(1)-H(1)	125.2
C(10)-Ru(1)-C(16)	77.43(6)	C(2)-C(1)-H(1)	125.2
C(15)-Ru(1)-C(16)	36.78(6)	C(3)-C(2)-C(1)	106.55(13)
N(3)-Ru(1)-C(11)	101.51(5)	C(3)-C(2)-Br(1B)	135.8(10)
N(6)-Ru(1)-C(11)	158.89(5)	C(1)-C(2)-Br(1B)	116.3(12)
N(1)-Ru(1)-C(11)	80.46(5)	C(3)-C(2)-Br(1)	126.76(13)
C(10)-Ru(1)-C(11)	36.66(6)	C(1)-C(2)-Br(1)	126.69(13)
C(15)-Ru(1)-C(11)	77.46(6)	Br(1B)-C(2)-Br(1)	14.4(13)
C(16)-Ru(1)-C(11)	64.97(6)	N(2)-C(3)-C(2)	107.04(13)
N(3)-Ru(1)-Cl(1)	82.42(4)	N(2)-C(3)-H(3)	126.5
N(6)-Ru(1)-Cl(1)	83.30(4)	C(2)-C(3)-H(3)	126.5
N(1)-Ru(1)-Cl(1)	160.57(3)	N(4)-C(4)-C(5)	107.02(13)
C(10)-Ru(1)-Cl(1)	79.45(4)	N(4)-C(4)-H(4)	126.5
C(15)-Ru(1)-Cl(1)	77.47(4)	C(5)-C(4)-H(4)	126.5
C(16)-Ru(1)-Cl(1)	114.08(4)	C(4)-C(5)-C(6)	106.43(13)
C(11)-Ru(1)-Cl(1)	116.07(4)	C(4)-C(5)-Br(2)	126.53(15)
C(1)-N(1)-N(2)	106.28(12)	C(6)-C(5)-Br(2)	126.79(15)
C(1)-N(1)-Ru(1)	136.05(10)	C(4)-C(5)-Br(2B)	127.45(19)
N(2)-N(1)-Ru(1)	117.62(9)	C(6)-C(5)-Br(2B)	126.1(2)
C(3)-N(2)-N(1)	110.47(12)	Br(2)-C(5)-Br(2B)	5.9(4)
C(3)-N(2)-B(1)	127.70(13)	N(3)-C(6)-C(5)	108.90(14)
N(1)-N(2)-B(1)	121.28(12)	N(3)-C(6)-H(6)	125.5
C(6)-N(3)-N(4)	107.50(12)	C(5)-C(6)-H(6)	125.5
C(6)-N(3)-Ru(1)	131.11(11)	N(5)-C(7)-C(8)	107.49(13)
N(4)-N(3)-Ru(1)	120.65(9)	N(5)-C(7)-H(7)	126.3
C(4)-N(4)-N(3)	110.14(12)	C(8)-C(7)-H(7)	126.3
C(4)-N(4)-B(1)	130.90(13)	C(7)-C(8)-C(9)	106.24(13)
N(3)-N(4)-B(1)	118.93(12)	C(7)-C(8)-Br(3)	126.56(12)

C(9)-C(8)-Br(3)	127.17(11)	C(13)-C(14)-C(10)	100.66(13)
N(6)-C(9)-C(8)	109.03(13)	C(13)-C(14)-C(15)	100.15(12)
N(6)-C(9)-H(9)	125.5	C(10)-C(14)-C(15)	101.05(11)
C(8)-C(9)-H(9)	125.5	C(13)-C(14)-H(14)	117.3
C(11)-C(10)-C(14)	106.68(13)	C(10)-C(14)-H(14)	117.3
C(11)-C(10)-Ru(1)	72.63(9)	C(15)-C(14)-H(14)	117.3
C(14)-C(10)-Ru(1)	96.44(9)	C(16)-C(15)-C(14)	106.52(13)
C(11)-C(10)-H(10)	122.8	C(16)-C(15)-Ru(1)	72.21(8)
C(14)-C(10)-H(10)	122.8	C(14)-C(15)-Ru(1)	96.28(9)
Ru(1)-C(10)-H(10)	122.8	C(16)-C(15)-H(15)	123.0
C(10)-C(11)-C(12)	105.91(13)	C(14)-C(15)-H(15)	123.0
C(10)-C(11)-Ru(1)	70.71(9)	Ru(1)-C(15)-H(15)	123.0
C(12)-C(11)-Ru(1)	97.06(9)	C(15)-C(16)-C(12)	106.00(13)
C(10)-C(11)-H(11)	123.2	C(15)-C(16)-Ru(1)	71.01(8)
C(12)-C(11)-H(11)	123.2	C(12)-C(16)-Ru(1)	97.51(9)
Ru(1)-C(11)-H(11)	123.2	C(15)-C(16)-H(16)	123.1
C(13)-C(12)-C(16)	100.98(13)	C(12)-C(16)-H(16)	123.1
C(13)-C(12)-C(11)	101.06(12)	Ru(1)-C(16)-H(16)	123.1
C(16)-C(12)-C(11)	100.42(11)	N(2)-B(1)-N(4)	107.97(12)
C(13)-C(12)-H(12)	117.1	N(2)-B(1)-N(5)	105.85(12)
C(16)-C(12)-H(12)	117.1	N(4)-B(1)-N(5)	109.55(12)
C(11)-C(12)-H(12)	117.1	N(2)-B(1)-H(1B)	111.5(10)
C(12)-C(13)-C(14)	93.96(12)	N(4)-B(1)-H(1B)	111.5(10)
C(12)-C(13)-H(13A)	112.9	N(5)-B(1)-H(1B)	110.2(10)
C(14)-C(13)-H(13A)	112.9		
C(12)-C(13)-H(13B)	112.9		
C(14)-C(13)-H(13B)	112.9		
H(13A)-C(13)-H(13B)	110.3		

Symmetry transformations used to generate equivalent atoms:

Table A1.24: Anisotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Br}Ru(nbd)Cl$ 134d. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	10(1)	12(1)	8(1)	0(1)	1(1)	-2(1)
Br(1)	26(1)	23(1)	27(1)	15(1)	7(1)	4(1)
Br(1B)	25(4)	24(4)	12(7)	6(4)	8(4)	0(3)
Br(2)	19(1)	37(1)	19(1)	1(1)	11(1)	-4(1)
Br(2B)	14(1)	65(2)	16(1)	1(1)	6(1)	2(1)
Br(3)	21(1)	18(1)	21(1)	-7(1)	2(1)	3(1)
Cl(1)	18(1)	21(1)	16(1)	7(1)	-3(1)	-5(1)
N(1)	13(1)	14(1)	12(1)	-1(1)	1(1)	0(1)
N(2)	12(1)	14(1)	12(1)	0(1)	0(1)	1(1)
N(3)	12(1)	20(1)	12(1)	-1(1)	1(1)	-2(1)
N(4)	11(1)	16(1)	12(1)	0(1)	0(1)	-1(1)
N(5)	12(1)	14(1)	12(1)	0(1)	0(1)	-1(1)
N(6)	12(1)	13(1)	13(1)	1(1)	-1(1)	-1(1)
C(1)	17(1)	14(1)	15(1)	0(1)	6(1)	1(1)
C(2)	18(1)	15(1)	14(1)	3(1)	6(1)	4(1)
C(3)	16(1)	15(1)	12(1)	1(1)	3(1)	5(1)
C(4)	13(1)	17(1)	17(1)	2(1)	3(1)	0(1)
C(5)	15(1)	24(1)	15(1)	2(1)	5(1)	-1(1)
C(6)	15(1)	25(1)	13(1)	-1(1)	4(1)	-2(1)
C(7)	14(1)	15(1)	12(1)	0(1)	1(1)	-3(1)
C(8)	18(1)	12(1)	14(1)	-1(1)	4(1)	-1(1)
C(9)	14(1)	14(1)	16(1)	1(1)	1(1)	1(1)
C(10)	16(1)	23(1)	11(1)	-5(1)	2(1)	-6(1)
C(11)	19(1)	17(1)	14(1)	-7(1)	3(1)	-4(1)
C(12)	18(1)	18(1)	14(1)	-1(1)	2(1)	-6(1)
C(13)	18(1)	25(1)	15(1)	-1(1)	1(1)	-9(1)
C(14)	14(1)	23(1)	13(1)	1(1)	0(1)	-4(1)
C(15)	10(1)	22(1)	15(1)	-1(1)	2(1)	-1(1)
C(16)	12(1)	19(1)	14(1)	-1(1)	4(1)	-3(1)

B(1)	13(1)	15(1)	12(1)	0(1)	1(1)	0(1)

Table A1.25: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Br}Ru(nbd)Cl 134d.

	x	y	z	U(eq)
H(1)	3692	9837	5787	18
H(3)	316	8926	4624	17
H(4)	-1184	6965	6981	19
H(6)	1758	7658	8772	21
H(7)	935	5289	4767	16
H(9)	4380	5287	6095	18
H(10)	4063	8410	8819	20
H(11)	3519	9808	7674	20
H(12)	5289	9931	6750	20
H(13A)	6378	9622	8296	23
H(13B)	7093	8908	7632	23
H(14)	6168	7578	8653	20
H(15)	5869	6646	7166	18
H(16)	5305	8051	6026	18
H(1B)	-67(18)	7066(16)	5477(12)	16

Table A1.26: Crystal data and structure refinement for Tp^{I}Ru(nbd)Cl 134e.

Identification code: Tp^{I}Ru(nbd)Cl **134e**	
Empirical formula: C17H17BCl3I3N6Ru	
Formula weight: 904.29	
Temperature/K: 123(2)	
Crystal system: monoclinic	
Space group: P21/n	
a/Å: 21.409(4) b/Å: 10.2148(19): c/Å 24.770(5)	
α/°: 90 β/°: 107.833(2) γ/°: 90	
Volume/Å3: 5156.7(17) Z: 8 ρcalcg/cm3: 2.330 μ/mm 1: 4.529 F(000): 3360.0	
Crystal size/mm3	0.240 × 0.080 × 0.020
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.536 to 56.72
Index ranges	-28 ≤ h ≤ 28, -13 ≤ k ≤ 13, -32 ≤ l ≤ 33
Reflections collected	67426
Independent reflections	12867 [Rint = 0.0251, Rsigma = 0.0194]
Data/restraints/parameters	12867/808/651
Goodness-of-fit on F2	1.021
Final R indexes [I>=2σ (I)]	R1 = 0.0206, wR2 = 0.0400
Final R indexes [all data]	R1 = 0.0283, wR2 = 0.0422
Largest diff. peak/hole / e Å-3	0.71/-0.53

Table A1.27: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic isplacement Parameters (Å^2×10^3) for Tp^{i}Ru(nbd)Cl 134e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	3269(4)	3157(12)	4299(13)	98(5)
Cl^{2_1}	4209(5)	1465(18)	5065(5)	107(4)
C^{1_1}	3427(10)	1544(15)	4557(13)	40.5(15)
Cl^{1_2}	3316.9(16)	3281(3)	4521.9(16)	71.3(8)
Cl^{2_2}	4196.4(18)	1267(3)	5130.6(16)	59.4(9)
C^{1_2}	3526(4)	1634(6)	4532(4)	40.5(15)
Cl^{1_3}	1528(11)	-988(19)	5286(8)	91(5)
Cl^{2_3}	2366(4)	1219(13)	5380(5)	45.7(16)
C^{1_3}	1943(18)	270(30)	5747(9)	52.9(15)
Cl^{1_4}	2402(3)	958(7)	5363(2)	72.9(15)
Cl^{2_4}	1724.9(10)	-1432(4)	5476.1(15)	48.9(8)
C^{1_4}	1863(8)	228(11)	5673(5)	52.9(15)
I^{1}	11675.6(2)	5199.6(2)	3387.5(2)	19.64(4)
I^{2A}	9628(2)	13518(2)	3845.3(10)	32.9(3)
I^{2B}	9524(4)	13471(6)	3857(3)	35.1(7)
I^{3A}	7835.4(4)	4896.2(15)	4661.5(7)	30.05(18)
I^{3B}	7882(3)	5189(10)	4788(4)	30.2(8)
I^{4}	6592.9(2)	7711.4(2)	3118.5(2)	19.91(4)
I^{5A}	2891.8(13)	7861.1(10)	4618.7(7)	22.1(2)
I^{5B}	3036(5)	7917(7)	4673(3)	29.8(9)
I^{6A}	4429.2(12)	-597.8(11)	3556.8(5)	36.4(2)
I^{6B}	4303(9)	-493(11)	3597(5)	41.1(14)
Ru^{1}	8887.1(2)	7841.7(2)	2910.8(2)	12.91(4)
Ru^{2}	3788.1(2)	5149.5(2)	2706.5(2)	11.46(4)

Cl^{1}	7866.7(3)	8973.7(6)	2844.9(3)	20.66(12)
Cl^{2}	2759.6(3)	4123.4(6)	2686.9(3)	19.76(11)
N^{1}	9198.8(10)	7229.9(19)	4158.3(8)	17.2(4)
N^{2}	8761.0(9)	6987.4(19)	3637.6(8)	17.1(4)
N^{3}	9853.3(9)	7057.2(19)	3249.5(8)	13.8(4)
N^{4}	10170.1(9)	7246.4(19)	3815.3(8)	15.7(4)
N^{5}	9675.6(9)	9366.7(19)	3952.1(8)	15.7(4)
N^{6}	9290.4(9)	9496.4(19)	3404.1(8)	15.4(4)
N^{7}	5111.5(9)	5645.7(19)	3570.8(8)	16.4(4)
N^{8}	4768.2(9)	5883.8(19)	3014.7(8)	14.4(4)
N^{9}	4603.1(10)	3536(2)	3707.6(8)	17.4(4)
N^{10}	4184.1(9)	3455.3(19)	3169.2(8)	15.8(4)
N^{11}	4180.1(10)	5679(2)	3963.2(8)	17.0(4)
N^{12}	3724.6(9)	5996.4(19)	3462.1(8)	14.7(4)
C^{1}	9218.8(12)	8090(2)	2148.3(10)	18.7(5)
C^{2}	9077.9(12)	6678(3)	1923.3(10)	22.0(5)
C^{3}	8451.6(13)	6893(3)	1413.7(11)	26.9(6)
C^{4}	8090.9(12)	7644(3)	1768.8(11)	22.3(5)
C^{5}	8171.2(12)	6681(2)	2265.9(11)	21.4(5)
C^{6}	8779.8(12)	6095(2)	2366.2(10)	20.0(5)
C^{7}	8611.6(12)	8687(2)	2049.6(10)	19.0(5)
C^{8}	8282.4(12)	6244(2)	3715.1(11)	21.0(5)
C^{9}	8411.2(12)	6003(3)	4295.9(11)	22.2(5)
C^{10}	8991.3(12)	6626(2)	4560.3(11)	21.2(5)
C^{11}	10275.1(11)	6383(2)	3049.9(10)	16.4(5)
C^{12}	10856.8(11)	6144(2)	3479.4(10)	16.5(5)
C^{13}	10773.4(11)	6705(2)	3957.4(10)	17.1(5)

C^{14}	9209.1(11)	10776(2)	3298.9(10)	18.3(5)
C^{15}	9554.2(12)	11486(2)	3778.5(11)	20.9(5)
C^{16}	9846.5(12)	10559(2)	4183.9(10)	19.6(5)
C^{17}	4068.4(11)	4866(2)	1924.6(9)	17.2(5)
C^{18}	3934.7(12)	6281(2)	1697.7(10)	19.0(5)
C^{19}	3289.0(13)	6086(3)	1209.8(10)	23.4(5)
C^{20}	2944.2(12)	5369(2)	1586.9(10)	18.9(5)
C^{21}	3061.8(12)	6347(2)	2081.9(10)	17.7(5)
C^{22}	3675.1(11)	6897(2)	2157(1)	17.1(5)
C^{23}	3458.1(11)	4304(2)	1851.1(9)	17.0(5)
C^{24}	5169.4(11)	6584(2)	2802.9(10)	15.7(4)
C^{25}	5769.6(11)	6789(2)	3218.1(11)	18.2(5)
C^{26}	5715.3(11)	6184(2)	3700.3(10)	18.2(5)
C^{27}	4010.9(13)	6219(2)	4395.9(10)	20.9(5)
C^{28}	3429.7(12)	6884(2)	4168.7(10)	18.8(5)
C^{29}	3267.5(11)	6730(2)	3581.5(10)	16.2(4)
C^{30}	4756.3(12)	2321(2)	3920.1(11)	21.2(5)
C^{31}	4421.1(12)	1431(2)	3513.9(11)	20.7(5)
C^{32}	4065.9(12)	2189(2)	3051.3(10)	18.1(5)
B^{1}	9838.8(13)	7977(3)	4198.8(11)	17.3(5)
B^{2}	4797.7(13)	4903(3)	3963.2(11)	18.0(5)

Table A1.28: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{i}Ru(nbd)Cl$ 134e. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	30(3)	62(4)	206(13)	57(6)	44(4)	-3(2)
Cl^{2_1}	45(4)	236(13)	42(3)	19(5)	18(3)	3(5)

C^{1_1}	28(3)	50(2)	46(2)	-7.3(17)	15(2)	-10.4(17)
Cl^{1_2}	75.3(18)	41.8(10)	83.3(19)	-5.3(12)	4.2(12)	-3.1(8)
Cl^{2_2}	55.7(15)	61.6(18)	46.2(14)	-1.7(8)	-6.1(11)	-3.4(8)
C^{1_2}	28(3)	50(2)	46(2)	-7.3(17)	15(2)	-10.4(17)
Cl^{1_3}	107(9)	96(7)	92(7)	-44(6)	65(7)	-58(7)
Cl^{2_3}	62(4)	44(4)	34(2)	-22(2)	18(2)	-2.5(19)
C^{1_3}	61(4)	58(2)	44(3)	-10(2)	22(3)	20(2)
Cl^{1_4}	139(3)	50(2)	34.2(12)	-12.6(13)	34.0(14)	-9.4(16)
Cl^{2_4}	33.2(10)	68.6(14)	43.0(12)	-13.1(9)	8.6(8)	0.8(9)
C^{1_4}	61(4)	58(2)	44(3)	-10(2)	22(3)	20(2)
I^{1}	14.60(7)	16.77(7)	27.06(8)	-2.83(6)	5.66(6)	3.76(6)
I^{2A}	47.9(8)	15.0(3)	31.0(3)	-1.81(19)	5.1(4)	-3.0(3)
I^{2B}	47.6(14)	11.4(9)	42.2(12)	-4.4(6)	7.7(8)	2.0(8)
I^{3A}	27.73(17)	37.6(4)	28.1(3)	11.7(3)	13.5(2)	-6.03(18)
I^{3B}	28.2(13)	39.1(19)	27.6(18)	11.6(11)	15.0(13)	-5.6(12)
I^{4}	13.63(7)	16.60(8)	27.81(8)	-1.09(6)	3.85(6)	-3.19(6)
I^{5A}	31.9(5)	20.8(2)	18.3(2)	-0.86(14)	14.8(3)	3.4(2)
I^{5B}	34.1(15)	36.8(16)	21.9(12)	-8.3(10)	13.6(11)	3.4(11)
I^{6A}	57.2(5)	13.52(17)	33.5(2)	4.57(14)	6.7(2)	2.8(2)
I^{6B}	65(2)	7.5(19)	52(4)	7.2(15)	20(2)	-0.8(15)
Ru^{1}	10.51(8)	12.59(9)	15.63(9)	1.79(7)	4.02(7)	-0.85(6)
Ru^{2}	11.16(8)	11.39(8)	11.59(8)	-0.45(6)	3.12(6)	0.66(6)
Cl^{1}	13.6(3)	21.2(3)	28.2(3)	5.9(2)	7.7(2)	3.1(2)
Cl^{2}	15.8(3)	19.5(3)	25.4(3)	-3.8(2)	8.4(2)	-4.0(2)
N^{1}	18.2(9)	16.4(10)	18.5(10)	3.9(8)	7.8(8)	3.3(8)

N^{2}	14.7(9)	16.6(10)	20.5(10)	5.5(8)	6.1(8)	2.2(7)
N^{3}	12.3(8)	14.4(9)	14.2(9)	-0.1(7)	3.4(7)	-0.5(7)
N^{4}	14.2(9)	16.8(10)	15.4(9)	0.0(7)	3.8(7)	1.0(7)
N^{5}	18.0(9)	14.8(9)	15.0(9)	-0.9(7)	6.1(8)	0.1(7)
N^{6}	15.8(9)	16(1)	15.3(9)	0.7(7)	6.3(7)	0.3(7)
N^{7}	13.7(9)	18.5(10)	14.3(9)	0.9(8)	0.5(7)	0.8(7)
N^{8}	12.4(9)	16.8(10)	13.0(9)	-0.1(7)	2.2(7)	0.7(7)
N^{9}	19.2(10)	17.5(10)	14.2(9)	2.9(7)	3.2(8)	2.5(8)
N^{10}	16.6(9)	16.0(9)	13.7(9)	0.9(7)	3.2(7)	0.7(7)
N^{11}	20(1)	17(1)	13.6(9)	1.2(7)	4.9(8)	1.0(8)
N^{12}	15.4(9)	16.1(9)	12.4(9)	0.5(7)	4.1(7)	-1.6(7)
C^{1}	18.7(11)	23.3(12)	15.2(11)	1.7(9)	6.7(9)	-4.0(9)
C^{2}	20.0(12)	25.9(13)	17.7(12)	-5.5(10)	2.4(9)	-1.2(10)
C^{3}	24.6(13)	31.9(15)	19.5(12)	-3.3(11)	-0.2(10)	-2.9(11)
C^{4}	18.8(12)	24.0(13)	20.4(12)	2.1(10)	0.3(9)	-4.1(10)
C^{5}	19.3(12)	17.6(12)	23.7(12)	-0.3(9)	1.2(10)	-7.8(9)
C^{6}	20.8(12)	15.5(11)	20.9(12)	-2.8(9)	2.2(9)	-4.3(9)
C^{7}	20.1(11)	18.7(12)	17.1(11)	3.9(9)	4.0(9)	-3.4(9)
C^{8}	15.0(11)	21.7(13)	27.9(13)	8.5(10)	9(1)	2.0(9)
C^{9}	20.3(12)	22.3(13)	28.5(13)	10.5(10)	14.3(10)	3.3(10)
C^{10}	25.2(12)	21.5(12)	20.0(12)	6.9(10)	11.4(10)	4.8(10)
C^{11}	16.8(11)	13.9(11)	19.1(11)	-3.1(9)	6.3(9)	-0.6(8)
C^{12}	13.2(10)	13.3(11)	23.6(12)	-0.5(9)	6.4(9)	0.7(8)
C^{13}	14.4(10)	15.3(11)	20.6(11)	2.0(9)	4.1(9)	1.3(8)
C^{14}	16.0(11)	19.4(12)	20.7(12)	2.8(9)	7.5(9)	1.6(9)
C^{15}	23.8(12)	17.3(12)	24.5(12)	-2.0(9)	11.6(10)	-1.3(9)
C^{16}	23.3(12)	17.7(12)	19.6(12)	-3.6(9)	9.3(10)	-1.2(9)

C^{17}	19.3(11)	20.5(12)	11.8(10)	-1.5(9)	4.8(9)	3.4(9)
C^{18}	19.8(12)	21.7(12)	15.3(11)	2.3(9)	5.3(9)	0.8(9)
C^{19}	27.3(13)	25.5(13)	14.5(11)	1(1)	2.1(10)	2(1)
C^{20}	17.0(11)	19.1(12)	17.2(11)	-1.4(9)	0.0(9)	1.9(9)
C^{21}	17.9(11)	14.8(11)	17.6(11)	1.7(9)	1.1(9)	5.4(9)
C^{22}	21.1(11)	12.9(11)	15.2(11)	2.9(8)	2.6(9)	2.3(9)
C^{23}	19.8(11)	18.4(11)	10.9(10)	-3.2(8)	2.0(9)	3.0(9)
C^{24}	15.8(11)	13.2(11)	17.6(11)	0.1(9)	4.3(9)	1.3(8)
C^{25}	13.5(10)	14.0(11)	26.6(12)	-1.4(9)	5.2(9)	0.0(8)
C^{26}	15.4(11)	16.5(11)	19.7(11)	-1.1(9)	1.1(9)	0.7(9)
C^{27}	29.8(13)	19.4(12)	14.1(11)	-0.2(9)	8(1)	-2(1)
C^{28}	27.9(12)	14.5(11)	17.3(11)	-1.6(9)	11.9(10)	-2.3(9)
C^{29}	17.2(11)	15.3(11)	18.0(11)	-1.1(9)	8.4(9)	-0.7(8)
C^{30}	24.7(12)	17.6(12)	21.1(12)	6.4(9)	6.6(10)	2.9(9)
C^{31}	24.8(13)	16.2(11)	22.2(12)	3.7(9)	8.8(10)	1.5(9)
C^{32}	19.4(11)	15.9(11)	20.5(11)	-0.3(9)	8.5(9)	-0.2(9)
B^{1}	15.9(12)	19.8(13)	16.8(12)	0.1(10)	6(1)	1.9(10)
B^{2}	18.7(12)	18.0(13)	15.2(12)	2.6(10)	2(1)	1(1)

Table A1.29: Bond Lengths for Tp^{i}Ru(nbd)Cl 134e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.762(10)	N^{5}	N^{6}	1.362(3)
Cl^{2_1}	C^{1_1}	1.762(10)	N^{5}	B^{1}	1.542(3)
Cl^{1_2}	C^{1_2}	1.738(7)	N^{6}	C^{14}	1.334(3)
Cl^{2_2}	C^{1_2}	1.759(5)	N^{7}	C^{26}	1.350(3)
Cl^{1_3}	C^{1_3}	1.769(10)	N^{7}	N^{8}	1.370(3)
Cl^{2_3}	C^{1_3}	1.757(10)	N^{7}	B^{2}	1.540(3)
Cl^{1_4}	C^{1_4}	1.739(7)	N^{8}	C^{24}	1.342(3)

Cl2_4	C1_4	1.764(8)	N9	C30	1.349(3)
I1	C12	2.074(2)	N9	N10	1.363(3)
I2A	C15	2.084(3)	N9	B2	1.537(3)
I2B	C15	2.040(7)	N10	C32	1.333(3)
I3A	C9	2.074(2)	N11	C27	1.350(3)
I3B	C9	2.076(6)	N11	N12	1.362(3)
I4	C25	2.079(2)	N11	B2	1.542(3)
I5A	C28	2.086(3)	N12	C29	1.336(3)
I5B	C28	2.008(7)	C1	C7	1.388(3)
I6A	C31	2.075(3)	C1	C2	1.542(3)
I6B	C31	2.001(10)	C2	C6	1.548(3)
Ru1	N2	2.0914(19)	C2	C3	1.550(3)
Ru1	N6	2.109(2)	C3	C4	1.541(4)
Ru1	N3	2.1359(19)	C4	C5	1.544(3)
Ru1	C5	2.192(2)	C4	C7	1.545(3)
Ru1	C6	2.206(2)	C5	C6	1.386(3)
Ru1	C7	2.208(2)	C8	C9	1.401(3)
Ru1	C1	2.227(2)	C9	C10	1.371(4)
Ru1	Cl1	2.4328(7)	C11	C12	1.390(3)
Ru2	N12	2.1037(19)	C12	C13	1.375(3)
Ru2	N10	2.1052(19)	C14	C15	1.395(3)
Ru2	N8	2.1371(19)	C15	C16	1.382(4)
Ru2	C23	2.195(2)	C17	C23	1.387(3)
Ru2	C21	2.199(2)	C17	C18	1.545(3)
Ru2	C22	2.213(2)	C18	C22	1.545(3)
Ru2	C17	2.215(2)	C18	C19	1.545(3)
Ru2	Cl2	2.4257(7)	C19	C20	1.541(3)

N^{1}	C^{10}	1.357(3)	C^{20}	C^{21}	1.541(3)
N^{1}	N^{2}	1.365(3)	C^{20}	C^{23}	1.544(3)
N^{1}	B^{1}	1.545(3)	C^{21}	C^{22}	1.387(3)
N^{2}	C^{8}	1.336(3)	C^{24}	C^{25}	1.394(3)
N^{3}	C^{11}	1.345(3)	C^{25}	C^{26}	1.381(3)
N^{3}	N^{4}	1.371(3)	C^{27}	C^{28}	1.377(4)
N^{4}	C^{13}	1.349(3)	C^{28}	C^{29}	1.397(3)
N^{4}	B^{1}	1.541(3)	C^{30}	C^{31}	1.383(4)
N^{5}	C^{16}	1.349(3)	C^{31}	C^{32}	1.399(3)

Table A1.30: Bond Angles for Tp^{i}Ru(nbd)Cl 134e.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl^{1_1}	C^{1_1}	Cl^{2_1}	109.7(9)	C^{27}	N^{11}	B^{2}	130.5(2)
Cl^{1_2}	C^{1_2}	Cl^{2_2}	111.0(5)	N^{12}	N^{11}	B^{2}	119.79(18)
Cl^{2_3}	C^{1_3}	Cl^{1_3}	107.7(9)	C^{29}	N^{12}	N^{11}	107.47(18)
Cl^{1_4}	C^{1_4}	Cl^{2_4}	111.5(6)	C^{29}	N^{12}	Ru^{2}	132.77(16)
N^{2}	Ru^{1}	N^{6}	88.48(8)	N^{11}	N^{12}	Ru^{2}	119.32(14)
N^{2}	Ru^{1}	N^{3}	82.54(7)	C^{7}	C^{1}	C^{2}	106.2(2)
N^{6}	Ru^{1}	N^{3}	84.13(7)	C^{7}	C^{1}	Ru^{1}	71.01(13)
N^{2}	Ru^{1}	C^{5}	98.97(9)	C^{2}	C^{1}	Ru^{1}	97.02(15)
N^{6}	Ru^{1}	C^{5}	157.84(9)	C^{1}	C^{2}	C^{6}	100.46(19)
N^{3}	Ru^{1}	C^{5}	117.41(9)	C^{1}	C^{2}	C^{3}	100.8(2)
N^{2}	Ru^{1}	C^{6}	99.91(9)	C^{6}	C^{2}	C^{3}	101.0(2)
N^{6}	Ru^{1}	C^{6}	161.78(8)	C^{4}	C^{3}	C^{2}	93.75(19)
N^{3}	Ru^{1}	C^{6}	81.01(8)	C^{3}	C^{4}	C^{5}	100.7(2)
C^{5}	Ru^{1}	C^{6}	36.73(9)	C^{3}	C^{4}	C^{7}	100.5(2)
N^{2}	Ru^{1}	C^{7}	158.18(8)	C^{5}	C^{4}	C^{7}	101.05(19)
N^{6}	Ru^{1}	C^{7}	100.78(8)	C^{6}	C^{5}	C^{4}	106.7(2)

N^{3}	Ru^{1}	C^{7}	117.81(8)	C^{6}	C^{5}	Ru^{1}	72.18(14)
C^{5}	Ru^{1}	C^{7}	65.61(9)	C^{4}	C^{5}	Ru^{1}	96.84(15)
C^{6}	Ru^{1}	C^{7}	77.21(9)	C^{5}	C^{6}	C^{2}	106.0(2)
N^{2}	Ru^{1}	C^{1}	159.49(8)	C^{5}	C^{6}	Ru^{1}	71.10(14)
N^{6}	Ru^{1}	C^{1}	102.70(8)	C^{2}	C^{6}	Ru^{1}	97.67(15)
N^{3}	Ru^{1}	C^{1}	81.60(8)	C^{1}	C^{7}	C^{4}	106.5(2)
C^{5}	Ru^{1}	C^{1}	77.11(9)	C^{1}	C^{7}	Ru^{1}	72.49(14)
C^{6}	Ru^{1}	C^{1}	64.78(9)	C^{4}	C^{7}	Ru^{1}	96.17(15)
C^{7}	Ru^{1}	C^{1}	36.49(9)	N^{2}	C^{8}	C^{9}	109.2(2)
N^{2}	Ru^{1}	Cl^{1}	84.61(5)	C^{10}	C^{9}	C^{8}	105.9(2)
N^{6}	Ru^{1}	Cl^{1}	81.83(5)	C^{10}	C^{9}	I^{3A}	128.12(19)
N^{3}	Ru^{1}	Cl^{1}	161.17(5)	C^{8}	C^{9}	I^{3A}	126.0(2)
C^{5}	Ru^{1}	Cl^{1}	78.17(7)	C^{10}	C^{9}	I^{3B}	118.9(3)
C^{6}	Ru^{1}	Cl^{1}	114.85(7)	C^{8}	C^{9}	I^{3B}	134.6(3)
C^{7}	Ru^{1}	Cl^{1}	77.32(7)	I^{3A}	C^{9}	I^{3B}	11.7(3)
C^{1}	Ru^{1}	Cl^{1}	113.71(7)	N^{1}	C^{10}	C^{9}	108.2(2)
N^{12}	Ru^{2}	N^{10}	88.78(7)	N^{3}	C^{11}	C^{12}	110.7(2)
N^{12}	Ru^{2}	N^{8}	82.06(7)	C^{13}	C^{12}	C^{11}	105.3(2)
N^{10}	Ru^{2}	N^{8}	84.63(7)	C^{13}	C^{12}	I^{1}	128.70(18)
N^{12}	Ru^{2}	C^{23}	158.63(8)	C^{11}	C^{12}	I^{1}	125.96(17)
N^{10}	Ru^{2}	C^{23}	99.14(8)	N^{4}	C^{13}	C^{12}	108.2(2)
N^{8}	Ru^{2}	C^{23}	118.26(8)	N^{6}	C^{14}	C^{15}	109.9(2)
N^{12}	Ru^{2}	C^{21}	99.95(8)	C^{16}	C^{15}	C^{14}	105.5(2)
N^{10}	Ru^{2}	C^{21}	157.01(8)	C^{16}	C^{15}	I^{2B}	129.2(3)
N^{8}	Ru^{2}	C^{21}	117.48(8)	C^{14}	C^{15}	I^{2B}	125.0(3)
C^{23}	Ru^{2}	C^{21}	65.84(9)	C^{16}	C^{15}	I^{2A}	128.2(2)
N^{12}	Ru^{2}	C^{22}	100.99(8)	C^{14}	C^{15}	I^{2A}	126.4(2)

N^{10}	Ru^{2}	C^{22}	161.45(8)	I^{2B}	C^{15}	I^{2A}	6.5(2)
N^{8}	Ru^{2}	C^{22}	81.20(8)	N^{5}	C^{16}	C^{15}	107.8(2)
C^{23}	Ru^{2}	C^{22}	77.39(9)	C^{23}	C^{17}	C^{18}	106.1(2)
C^{21}	Ru^{2}	C^{22}	36.65(9)	C^{23}	C^{17}	Ru^{2}	70.88(13)
N^{12}	Ru^{2}	C^{17}	160.08(8)	C^{18}	C^{17}	Ru^{2}	97.26(14)
N^{10}	Ru^{2}	C^{17}	101.36(8)	C^{22}	C^{18}	C^{17}	100.47(18)
N^{8}	Ru^{2}	C^{17}	81.89(8)	C^{22}	C^{18}	C^{19}	101.02(19)
C^{23}	Ru^{2}	C^{17}	36.67(9)	C^{17}	C^{18}	C^{19}	100.71(19)
C^{21}	Ru^{2}	C^{17}	77.29(9)	C^{20}	C^{19}	C^{18}	93.85(18)
C^{22}	Ru^{2}	C^{17}	64.88(9)	C^{19}	C^{20}	C^{21}	100.51(19)
N^{12}	Ru^{2}	Cl^{2}	83.68(5)	C^{19}	C^{20}	C^{23}	100.39(19)
N^{10}	Ru^{2}	Cl^{2}	82.38(6)	C^{21}	C^{20}	C^{23}	101.43(18)
N^{8}	Ru^{2}	Cl^{2}	160.87(5)	C^{22}	C^{21}	C^{20}	106.7(2)
C^{23}	Ru^{2}	Cl^{2}	77.80(6)	C^{22}	C^{21}	Ru^{2}	72.22(13)
C^{21}	Ru^{2}	Cl^{2}	77.55(7)	C^{20}	C^{21}	Ru^{2}	96.15(14)
C^{22}	Ru^{2}	Cl^{2}	114.12(6)	C^{21}	C^{22}	C^{18}	106.0(2)
C^{17}	Ru^{2}	Cl^{2}	114.42(6)	C^{21}	C^{22}	Ru^{2}	71.12(13)
C^{10}	N^{1}	N^{2}	109.1(2)	C^{18}	C^{22}	Ru^{2}	97.34(14)
C^{10}	N^{1}	B^{1}	131.3(2)	C^{17}	C^{23}	C^{20}	106.5(2)
N^{2}	N^{1}	B^{1}	119.34(18)	C^{17}	C^{23}	Ru^{2}	72.45(13)
C^{8}	N^{2}	N^{1}	107.62(19)	C^{20}	C^{23}	Ru^{2}	96.24(14)
C^{8}	N^{2}	Ru^{1}	131.90(17)	N^{8}	C^{24}	C^{25}	110.3(2)
N^{1}	N^{2}	Ru^{1}	120.35(14)	C^{26}	C^{25}	C^{24}	105.6(2)
C^{11}	N^{3}	N^{4}	105.69(18)	C^{26}	C^{25}	I^{4}	127.19(18)
C^{11}	N^{3}	Ru^{1}	136.59(16)	C^{24}	C^{25}	I^{4}	127.15(18)
N^{4}	N^{3}	Ru^{1}	117.72(13)	N^{7}	C^{26}	C^{25}	107.8(2)
C^{13}	N^{4}	N^{3}	110.09(18)	N^{11}	C^{27}	C^{28}	107.8(2)

C^{13}	N^{4}	B^{1}	128.5(2)	C^{27}	C^{28}	C^{29}	106.0(2)
N^{3}	N^{4}	B^{1}	121.42(18)	C^{27}	C^{28}	I^{5B}	120.2(3)
C^{16}	N^{5}	N^{6}	109.82(19)	C^{29}	C^{28}	I^{5B}	133.6(3)
C^{16}	N^{5}	B^{1}	131.6(2)	C^{27}	C^{28}	I^{5A}	126.51(19)
N^{6}	N^{5}	B^{1}	118.62(19)	C^{29}	C^{28}	I^{5A}	127.47(19)
C^{14}	N^{6}	N^{5}	107.04(19)	I^{5B}	C^{28}	I^{5A}	8.2(3)
C^{14}	N^{6}	Ru^{1}	131.78(16)	N^{12}	C^{29}	C^{28}	109.2(2)
N^{5}	N^{6}	Ru^{1}	121.00(14)	N^{9}	C^{30}	C^{31}	108.1(2)
C^{26}	N^{7}	N^{8}	110.25(19)	C^{30}	C^{31}	C^{32}	105.2(2)
C^{26}	N^{7}	B^{2}	128.5(2)	C^{30}	C^{31}	I^{6B}	128.7(4)
N^{8}	N^{7}	B^{2}	121.26(18)	C^{32}	C^{31}	I^{6B}	125.0(4)
C^{24}	N^{8}	N^{7}	106.10(18)	C^{30}	C^{31}	I^{6A}	128.69(19)
C^{24}	N^{8}	Ru^{2}	136.34(16)	C^{32}	C^{31}	I^{6A}	126.06(19)
N^{7}	N^{8}	Ru^{2}	117.54(14)	I^{6B}	C^{31}	I^{6A}	9.1(6)
C^{30}	N^{9}	N^{10}	109.6(2)	N^{10}	C^{32}	C^{31}	109.8(2)
C^{30}	N^{9}	B^{2}	132.2(2)	N^{4}	B^{1}	N^{5}	107.02(19)
N^{10}	N^{9}	B^{2}	118.16(18)	N^{4}	B^{1}	N^{1}	106.7(2)
C^{32}	N^{10}	N^{9}	107.27(19)	N^{5}	B^{1}	N^{1}	109.89(19)
C^{32}	N^{10}	Ru^{2}	131.34(16)	N^{9}	B^{2}	N^{7}	107.65(19)
N^{9}	N^{10}	Ru^{2}	121.18(15)	N^{9}	B^{2}	N^{11}	110.0(2)
C^{27}	N^{11}	N^{12}	109.58(19)	N^{7}	B^{2}	N^{11}	106.67(19)

Table A1.31: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Tp^{I}Ru(nbd)Cl 134e.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	3408	941	4239	49
H^{1AB_1}	3089	1271	4731	49
H^{1A_2}	3639	1419	4184	49

H^{1AB_2}	3145	1091	4538	49
H^{1A_3}	1625	821	5862	63
H^{1AB_3}	2256	-110	6092	63
H^{1A_4}	1440	705	5556	63
H^{1AB_4}	2046	291	6091	63
H^{1}	9625	8580	2154	22
H^{2}	9447	6187	1849	26
H^{3A}	8532	7434	1110	32
H^{3AB}	8231	6065	1255	32
H^{4}	7637	7961	1568	27
H^{5}	7791	6231	2340	26
H^{6}	8878	5188	2521	24
H^{7}	8541	9646	1974	23
H^{8}	7913	5928	3423	25
H^{10}	9210	6634	4957	25
H^{11}	10187	6107	2668	20
H^{13}	11087	6711	4324	20
H^{14}	8954	11148	2949	22
H^{16}	10119	10732	4559	24
H^{17}	4462	4352	1915	21
H^{18}	4300	6746	1605	23
H^{19A}	3073	6922	1056	28
H^{19B}	3344	5530	900	28
H^{20}	2483	5073	1403	23
H^{21}	2698	6822	2172	21
H^{22}	3794	7801	2309	21
H^{23}	3371	3347	1779	20

H^{24}	5060	6895	2424	19
H^{26}	6044	6153	4059	22
H^{27}	4250	6153	4787	25
H^{29}	2892	7090	3310	19
H^{30}	5044	2113	4285	25
H^{32}	3783	1852	2705	22
H^{1B}	10188(14)	8010(30)	4667(12)	26(8)
H^{2B}	5139(13)	4840(30)	4387(12)	23(7)

Table A1.32: Atomic Occupancy for Tp^{i}Ru(nbd)Cl 134e.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Cl^{1_1}	0.270(18)	Cl^{2_1}	0.270(18)	C^{1_1}	0.270(18)
H^{1A_1}	0.270(18)	H^{1AB_1}	0.270(18)	Cl^{1_2}	0.730(18)
Cl^{2_2}	0.730(18)	C^{1_2}	0.730(18)	H^{1A_2}	0.730(18)
H^{1AB_2}	0.730(18)	Cl^{1_3}	0.306(18)	Cl^{2_3}	0.306(18)
C^{1_3}	0.306(18)	H^{1A_3}	0.306(18)	H^{1AB_3}	0.306(18)
Cl^{1_4}	0.694(18)	Cl^{2_4}	0.694(18)	C^{1_4}	0.694(18)
H^{1A_4}	0.694(18)	H^{1AB_4}	0.694(18)	I^{2A}	0.74(2)
I^{2B}	0.26(2)	I^{3A}	0.881(8)	I^{3B}	0.119(8)
I^{5A}	0.853(12)	I^{5B}	0.147(12)	I^{6A}	0.918(14)
I^{6B}	0.082(14)				

Table A1.33: Crystal data and structure refinement for $Tp^{C\equiv CH}$(nbd)Cl 160.

Identification code: $Tp^{C\equiv CH}$(nbd)Cl **160**	
Empirical formula: C23.5H21BCl4N6Ru	
Formula weight: 641.14	
Temperature/K :123(2)	
Crystal system: orthorhombic	
Space group: Pbca	
a/Å: 14.6424(9) b/Å: 16.9129(10) c/Å: 22.1075(13)	
α/°: 90 β/°: 90 γ/°: 90	
Volume/Å3: 5474.8(6)	
Z: 8 ρcalcg/cm3: 1.556 μ/mm 1: 0.988	
F(000) 2568.0	
Crystal size/mm3	0.200 × 0.150 × 0.050
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.684 to 55.992
Index ranges	-19 ≤ h ≤ 19, -22 ≤ k ≤ 22, -28 ≤ l ≤ 29
Reflections collected	63676
Independent reflections	6599 [Rint = 0.0187, Rsigma = 0.0102]
Data/restraints/parameters	6599/189/421
Goodness-of-fit on F2	1.068
Final R indexes [I>=2σ (I)]	R1 = 0.0379, wR2 = 0.1021
Final R indexes [all data]	R1 = 0.0460, wR2 = 0.1118
Largest diff. peak/hole / e Å-3	1.07/-0.83

Table A1.34: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp$^{C\equiv CH}$(nbd)Cl 160. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	4472(8)	1942(7)	2908(5)	56(2)
Cl^{2_1}	3880(20)	392(14)	3290(17)	58.3(18)
C^{1_1}	4590(50)	1220(20)	3480(20)	107(3)
Cl^{1_2}	5459(7)	-631(6)	5840(6)	63(3)
Cl^{2_2}	5450(20)	640(15)	5030(12)	89(7)
C^{1_2}	5230(50)	-388(18)	5077(11)	104(14)
Cl^{1_3}	5275(6)	1375(5)	3708(4)	81(2)
Cl^{2_3}	3820(5)	902(7)	2970(4)	93(3)
C^{1_3}	4430(20)	1756(8)	3219(17)	107(3)
Cl^{1_4}	3983(2)	-276(2)	4355(3)	110.1(17)
Cl^{2_4}	5094(7)	784(4)	5067(4)	122(3)
C^{1_4}	5095(6)	-26(6)	4561(5)	67(3)
Cl^{1_5}	3725(10)	253(6)	3297(8)	58.3(18)
Cl^{2_5}	3939(4)	1931(4)	2973(3)	69.5(17)
C^{1_5}	3850(40)	947(7)	2711(8)	107(3)
Cl^{1_6}	5003(2)	1780.3(17)	3597.0(12)	70.5(7)
Cl^{2_6}	3379(2)	1538(2)	2875.8(12)	85.3(9)
C^{1_6}	4456(7)	1145(7)	3077(6)	107(3)
Ru^{1}	5464.8(2)	1451.4(2)	827.5(2)	16.58(8)
Cl^{1}	6218.0(5)	1464.1(3)	1808.0(3)	23.12(14)
N^{1}	4409.2(16)	1441.6(12)	166.3(10)	20.8(4)
N^{6}	4661.5(14)	584.1(12)	1250.6(10)	18.9(4)
N^{4}	4643.3(15)	2330.0(13)	1216.7(10)	21.2(4)
N^{2}	3522.9(16)	1408.0(12)	376.9(11)	23.3(5)
N^{3}	3736.5(15)	2196.7(13)	1310.8(10)	22.7(4)
N^{5}	3750.3(15)	703.4(13)	1337.2(10)	21.6(4)
C^{5}	2780(3)	1276(3)	-1717.5(18)	55.9(11)
C^{3}	4353(2)	1435.0(15)	-435.7(12)	24.7(5)
C^{15}	3910(2)	-1828.1(19)	2272.2(15)	36.7(7)
C^{16}	6704.4(17)	752.1(14)	645.6(12)	20.6(5)
C^{10}	3898(2)	4789(2)	2171.3(16)	42.9(8)
C^{8}	3357(2)	2833.2(16)	1574.0(12)	25.5(5)
C^{11}	4867.7(17)	-111.3(14)	1499.0(11)	19.8(5)
C^{12}	4072.9(18)	-459.3(15)	1741.3(11)	22.4(5)
C^{21}	7359(2)	1463.5(15)	585.2(13)	24.9(5)
C^{20}	6681.4(18)	2158.9(15)	636.4(12)	23.0(5)
C^{22}	7535(2)	1454.9(17)	-103.1(13)	29.0(6)
C^{7}	4031(2)	3397.2(16)	1662.5(12)	26.3(6)
C^{6}	4831(2)	3045.0(15)	1428.3(11)	23.0(5)
C^{19}	6152.5(19)	2143.7(15)	114.4(12)	23.4(5)

C^{14}	3988.9(19)	-1204.5(17)	2037.2(13)	27.0(6)
C^{13}	3385.0(19)	83.0(16)	1624.7(12)	24.2(5)
C^{17}	6176.2(18)	743.0(15)	124.2(12)	22.7(5)
C^{2}	3436(2)	1384.6(16)	-621.0(14)	29.1(6)
C^{18}	6505(2)	1446.2(15)	-265.0(13)	24.9(5)
C^{1}	2943(2)	1369.5(15)	-90.8(13)	27.3(6)
C^{9}	3950(2)	4158.3(18)	1937.4(13)	31.3(6)
C^{4}	3090(2)	1337(2)	-1223.0(15)	37.6(7)
B^{1}	3299(2)	1436.3(17)	1057.9(15)	23.5(6)

Table A1.35: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{C≡CH}$(nbd)Cl 160. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	26(4)	84(6)	57(6)	-4(5)	4(4)	-13(4)
Cl^{2_1}	61(6)	55(4)	59(2)	-24(3)	28(3)	-13(3)
C^{1_1}	113(6)	115(5)	91(6)	-1(4)	2(5)	-17(4)
Cl^{1_2}	55(6)	38(5)	95(8)	-11(5)	8(5)	-7(4)
Cl^{2_2}	93(15)	103(13)	72(11)	-12(9)	-1(10)	-46(10)
C^{1_2}	90(40)	108(16)	108(14)	8(10)	-10(14)	-45(16)
Cl^{1_3}	81(5)	90(5)	72(4)	-6(4)	-34(4)	-22(4)
Cl^{2_3}	48(3)	153(7)	79(5)	-72(5)	-8(3)	12(4)
C^{1_3}	113(6)	115(5)	91(6)	-1(4)	2(5)	-17(4)
Cl^{1_4}	57.3(18)	77(2)	196(5)	-65(3)	40(2)	-22.3(16)
Cl^{2_4}	182(9)	79(3)	104(4)	-31(3)	53(5)	-63(4)
C^{1_4}	66(6)	56(6)	80(7)	0(5)	3(5)	-18(5)
Cl^{1_5}	61(6)	55(4)	59(2)	-24(3)	28(3)	-13(3)
Cl^{2_5}	36(3)	94(4)	79(4)	43(3)	-1(3)	-16(3)
C^{1_5}	113(6)	115(5)	91(6)	-1(4)	2(5)	-17(4)
Cl^{1_6}	83.1(19)	68.5(16)	59.9(14)	24.7(12)	-6.5(13)	-5.6(14)
Cl^{2_6}	85(2)	124(3)	46.6(13)	-4.3(14)	14.3(13)	-18.7(19)
C^{1_6}	113(6)	115(5)	91(6)	-1(4)	2(5)	-17(4)
Ru^{1}	21.84(12)	12.72(11)	15.20(12)	-0.60(6)	1.45(7)	-0.28(6)
Cl^{1}	30.9(3)	20.4(3)	18.0(3)	-1.5(2)	-1.9(2)	1.2(2)
N^{1}	26.6(11)	16.6(10)	19.2(11)	-0.8(7)	0.8(9)	1.1(8)
N^{6}	21.3(10)	16.9(10)	18.6(10)	0.5(8)	2.5(8)	-0.4(8)
N^{4}	26.6(11)	17.7(10)	19.2(10)	-0.2(8)	0.4(8)	3.7(8)
N^{2}	24.8(11)	19.7(10)	25.4(11)	-0.6(8)	-2.8(9)	2.9(8)
N^{3}	25.8(11)	21.5(10)	20.8(10)	-2.4(8)	2.6(8)	4.6(8)
N^{5}	20.9(10)	21.2(10)	22.9(10)	1.2(8)	3.7(8)	1.7(8)
C^{5}	56(2)	77(3)	34.7(18)	-15.7(19)	-16.4(17)	24(2)
C^{3}	35.5(14)	20.1(12)	18.6(12)	-2.5(9)	-1.6(11)	5(1)
C^{15}	42.5(18)	30.7(15)	37.1(16)	12.4(13)	-8.9(14)	-11.0(13)
C^{16}	22.2(12)	16.4(11)	23.4(12)	-2.6(9)	4.5(10)	0.5(9)

C^{10}	51(2)	34.5(16)	43.4(18)	-18.8(14)	-20.6(16)	17.4(15)
C^{8}	30.1(13)	26.2(13)	20.3(12)	-2.1(10)	-1.2(10)	9.3(11)
C^{11}	22.4(12)	18.8(11)	18.1(11)	0.4(9)	1.3(9)	-0.2(9)
C^{12}	26.5(13)	22.2(12)	18.5(11)	2.4(9)	1.1(10)	-3.9(10)
C^{21}	26.7(13)	24.4(13)	23.4(13)	-1.2(10)	3.5(11)	-4.3(10)
C^{20}	27.4(13)	17.9(11)	23.8(12)	-0.4(9)	5(1)	-6.7(10)
C^{22}	30.8(14)	29.7(14)	26.6(14)	-2.7(11)	8.2(12)	-6.1(11)
C^{7}	35.3(15)	24.1(12)	19.4(12)	-3.3(10)	-4.9(11)	10.0(11)
C^{6}	31.7(13)	17.8(11)	19.5(12)	-3.0(9)	-3.2(10)	4(1)
C^{19}	31.1(13)	17.8(11)	21.5(12)	2.8(9)	4.2(10)	-5(1)
C^{14}	27.5(14)	28.4(14)	25.1(13)	4.5(11)	-3.0(11)	-3.6(11)
C^{13}	24.7(12)	23.9(12)	23.9(12)	2.3(10)	3.2(10)	-2.6(10)
C^{17}	27.3(13)	18.0(11)	22.8(12)	-4.3(9)	5.7(10)	0.9(10)
C^{2}	36.3(15)	24.6(13)	26.6(14)	-5.2(10)	-6.5(12)	9.8(11)
C^{18}	33.0(14)	22.1(12)	19.6(12)	-1.3(9)	2.3(11)	-3.1(10)
C^{1}	29.5(14)	22.0(12)	30.3(14)	-3.7(10)	-6.9(11)	7(1)
C^{9}	34.9(15)	30.4(15)	28.5(14)	-7.0(11)	-8.5(12)	11.7(12)
C^{4}	40.2(18)	41.5(17)	31.0(16)	-6.7(13)	-7.7(13)	16.5(14)
B^{1}	25.3(14)	20.4(13)	24.8(14)	1.2(11)	-1.8(12)	2.5(11)

Table A1.36: Bond Lengths for $Tp^{C\equiv CH}$(nbd)Cl 160.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.773(9)	N^{2}	C^{1}	1.340(4)
Cl^{2_1}	C^{1_1}	1.789(9)	N^{2}	B^{1}	1.542(4)
Cl^{1_2}	C^{1_2}	1.768(9)	N^{3}	C^{8}	1.344(3)
Cl^{2_2}	C^{1_2}	1.771(9)	N^{3}	B^{1}	1.542(4)
Cl^{1_3}	C^{1_3}	1.762(9)	N^{5}	C^{13}	1.338(3)
Cl^{2_3}	C^{1_3}	1.789(9)	N^{5}	B^{1}	1.534(4)
Cl^{1_4}	C^{1_4}	1.744(7)	C^{5}	C^{4}	1.188(5)
Cl^{2_4}	C^{1_4}	1.768(8)	C^{3}	C^{2}	1.406(4)
Cl^{1_5}	C^{1_5}	1.759(9)	C^{15}	C^{14}	1.181(4)
Cl^{2_5}	C^{1_5}	1.766(9)	C^{16}	C^{17}	1.388(4)
Cl^{1_6}	C^{1_6}	1.766(8)	C^{16}	C^{21}	1.544(4)
Cl^{2_6}	C^{1_6}	1.768(8)	C^{10}	C^{9}	1.187(4)
Ru^{1}	N^{4}	2.096(2)	C^{8}	C^{7}	1.387(4)
Ru^{1}	N^{6}	2.100(2)	C^{11}	C^{12}	1.410(3)
Ru^{1}	N^{1}	2.127(2)	C^{12}	C^{13}	1.386(4)
Ru^{1}	C^{20}	2.187(3)	C^{12}	C^{14}	1.425(4)
Ru^{1}	C^{16}	2.203(2)	C^{21}	C^{20}	1.543(4)
Ru^{1}	C^{19}	2.207(2)	C^{21}	C^{22}	1.543(4)
Ru^{1}	C^{17}	2.222(2)	C^{20}	C^{19}	1.390(4)
Ru^{1}	Cl^{1}	2.4321(7)	C^{22}	C^{18}	1.550(4)
N^{1}	C^{3}	1.333(4)	C^{7}	C^{6}	1.411(4)
N^{1}	N^{2}	1.380(3)	C^{7}	C^{9}	1.429(4)

N^{6}	C^{11}	1.333(3)	C^{19}	C^{18}	1.537(4)
N^{6}	N^{5}	1.363(3)	C^{17}	C^{18}	1.545(4)
N^{4}	C^{6}	1.325(3)	C^{2}	C^{1}	1.377(4)
N^{4}	N^{3}	1.363(3)	C^{2}	C^{4}	1.427(4)

Table A1.37: Bond Angles for $Tp^{C\equiv CH}(nbd)Cl$ 160.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl^{1_1}	C^{1_1}	Cl^{2_1}	108.2(11)	C^{8}	N^{3}	N^{4}	109.7(2)
Cl^{1_2}	C^{1_2}	Cl^{2_2}	104.5(11)	C^{8}	N^{3}	B^{1}	130.8(2)
Cl^{1_3}	C^{1_3}	Cl^{2_3}	104.1(7)	N^{4}	N^{3}	B^{1}	119.2(2)
Cl^{1_4}	C^{1_4}	Cl^{2_4}	110.6(6)	C^{13}	N^{5}	N^{6}	110.0(2)
Cl^{1_5}	C^{1_5}	Cl^{2_5}	113.2(9)	C^{13}	N^{5}	B^{1}	130.7(2)
Cl^{1_6}	C^{1_6}	Cl^{2_6}	109.8(5)	N^{6}	N^{5}	B^{1}	119.0(2)
N^{4}	Ru^{1}	N^{6}	89.48(9)	N^{1}	C^{3}	C^{2}	110.5(3)
N^{4}	Ru^{1}	N^{1}	82.57(8)	C^{17}	C^{16}	C^{21}	106.4(2)
N^{6}	Ru^{1}	N^{1}	83.90(8)	C^{17}	C^{16}	Ru^{1}	72.45(15)
N^{4}	Ru^{1}	C^{20}	99.14(9)	C^{21}	C^{16}	Ru^{1}	96.25(16)
N^{6}	Ru^{1}	C^{20}	157.57(9)	N^{3}	C^{8}	C^{7}	108.5(2)
N^{1}	Ru^{1}	C^{20}	117.60(9)	N^{6}	C^{11}	C^{12}	109.8(2)
N^{4}	Ru^{1}	C^{16}	158.13(9)	C^{13}	C^{12}	C^{11}	104.7(2)
N^{6}	Ru^{1}	C^{16}	99.65(9)	C^{13}	C^{12}	C^{14}	127.4(2)
N^{1}	Ru^{1}	C^{16}	117.96(9)	C^{11}	C^{12}	C^{14}	127.9(3)
C^{20}	Ru^{1}	C^{16}	65.64(10)	C^{20}	C^{21}	C^{22}	100.8(2)
N^{4}	Ru^{1}	C^{19}	100.31(9)	C^{20}	C^{21}	C^{16}	100.9(2)
N^{6}	Ru^{1}	C^{19}	160.80(9)	C^{22}	C^{21}	C^{16}	100.4(2)
N^{1}	Ru^{1}	C^{19}	81.07(9)	C^{19}	C^{20}	C^{21}	106.5(2)
C^{20}	Ru^{1}	C^{19}	36.88(10)	C^{19}	C^{20}	Ru^{1}	72.33(15)
C^{16}	Ru^{1}	C^{19}	77.21(10)	C^{21}	C^{20}	Ru^{1}	96.95(15)
N^{4}	Ru^{1}	C^{17}	159.76(9)	C^{21}	C^{22}	C^{18}	93.8(2)
N^{6}	Ru^{1}	C^{17}	101.40(9)	C^{8}	C^{7}	C^{6}	104.4(2)
N^{1}	Ru^{1}	C^{17}	81.70(9)	C^{8}	C^{7}	C^{9}	128.4(3)
C^{20}	Ru^{1}	C^{17}	77.18(10)	C^{6}	C^{7}	C^{9}	127.3(3)
C^{16}	Ru^{1}	C^{17}	36.56(10)	N^{4}	C^{6}	C^{7}	110.1(3)
C^{19}	Ru^{1}	C^{17}	64.68(10)	C^{20}	C^{19}	C^{18}	106.3(2)
N^{4}	Ru^{1}	Cl^{1}	83.58(6)	C^{20}	C^{19}	Ru^{1}	70.79(15)
N^{6}	Ru^{1}	Cl^{1}	82.14(6)	C^{18}	C^{19}	Ru^{1}	97.81(16)
N^{1}	Ru^{1}	Cl^{1}	160.37(6)	C^{15}	C^{14}	C^{12}	178.6(3)
C^{20}	Ru^{1}	Cl^{1}	78.34(7)	N^{5}	C^{13}	C^{12}	108.5(2)
C^{16}	Ru^{1}	Cl^{1}	78.10(7)	C^{16}	C^{17}	C^{18}	106.3(2)
C^{19}	Ru^{1}	Cl^{1}	115.15(7)	C^{16}	C^{17}	Ru^{1}	70.99(14)
C^{17}	Ru^{1}	Cl^{1}	114.57(7)	C^{18}	C^{17}	Ru^{1}	96.94(15)
C^{3}	N^{1}	N^{2}	106.2(2)	C^{1}	C^{2}	C^{3}	104.7(3)
C^{3}	N^{1}	Ru^{1}	137.0(2)	C^{1}	C^{2}	C^{4}	127.3(3)
N^{2}	N^{1}	Ru^{1}	116.85(17)	C^{3}	C^{2}	C^{4}	127.9(3)

C^{11}	N^{6}	N^{5}	107.1(2)	C^{19}	C^{18}	C^{17}	100.5(2)
C^{11}	N^{6}	Ru^{1}	132.31(17)	C^{19}	C^{18}	C^{22}	101.2(2)
N^{5}	N^{6}	Ru^{1}	120.49(16)	C^{17}	C^{18}	C^{22}	100.5(2)
C^{6}	N^{4}	N^{3}	107.4(2)	N^{2}	C^{1}	C^{2}	108.9(3)
C^{6}	N^{4}	Ru^{1}	132.28(19)	C^{10}	C^{9}	C^{7}	178.8(3)
N^{3}	N^{4}	Ru^{1}	120.30(16)	C^{5}	C^{4}	C^{2}	177.6(5)
C^{1}	N^{2}	N^{1}	109.8(2)	N^{5}	B^{1}	N^{2}	106.0(2)
C^{1}	N^{2}	B^{1}	128.3(2)	N^{5}	B^{1}	N^{3}	110.4(2)
N^{1}	N^{2}	B^{1}	121.9(2)	N^{2}	B^{1}	N^{3}	107.0(2)

Table A1.38: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Tp$^{C\equiv CH}$(nbd)Cl 160.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	4400	1440	3877	128
H^{1AB_1}	5235	1049	3513	128
H^{1A_2}	4587	-506	4972	124
H^{1AB_2}	5636	-687	4801	124
H^{1A_3}	4716	2035	2872	128
H^{1AB_3}	4025	2127	3435	128
H^{1A_4}	5451	113	4195	81
H^{1AB_4}	5393	-485	4756	81
H^{1A_5}	3322	907	2435	128
H^{1AB_5}	4407	816	2476	128
H^{1A_6}	4376	615	3260	128
H^{1AB_6}	4839	1086	2710	128
H^{5}	2532	1227	-2113	67
H^{3}	4861	1461	-702	30
H^{15}	3846	-2329	2461	44
H^{16}	6864	262	876	25
H^{10}	3856	5293	2358	51
H^{8}	2732	2888	1681	31
H^{11}	5461	-338	1511	24
H^{21}	7906	1473	856	30
H^{20}	6828	2658	858	28
H^{22A}	7860	974	-240	35
H^{22B}	7853	1935	-248	35
H^{6}	5417	3285	1423	28
H^{19}	5880	2630	-69	28
H^{13}	2760	24	1731	29
H^{17}	5916	248	-53	27
H^{18}	6341	1440	-704	30
H^{1}	2296	1337	-61	33
$H^{1'}$	2520(20)	1438(18)	1137(16)	28

Table A1.39: Atomic Occupancy for $Tp^{C\equiv CH}$(nbd)Cl 160.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl^{1_1}	0.1	Cl^{2_1}	0.1	C^{1_1}	0.1
H^{1A_1}	0.1	H^{1AB_1}	0.1	Cl^{1_2}	0.1
Cl^{2_2}	0.1	C^{1_2}	0.1	H^{1A_2}	0.1
H^{1AB_2}	0.1	Cl^{1_3}	0.2	Cl^{2_3}	0.2
C^{1_3}	0.2	H^{1A_3}	0.2	H^{1AB_3}	0.2
Cl^{1_4}	0.4	Cl^{2_4}	0.4	C^{1_4}	0.4
H^{1A_4}	0.4	H^{1AB_4}	0.4	Cl^{1_5}	0.2
Cl^{2_5}	0.2	C^{1_5}	0.2	H^{1A_5}	0.2
H^{1AB_5}	0.2	Cl^{1_6}	0.5	Cl^{2_6}	0.5
C^{1_6}	0.5	H^{1A_6}	0.5	H^{1AB_6}	0.5

CHAPTER 2: Ligand Exchange Reactions of $Tp^{X}Ru(diene)Cl$ to Mono- and Di-phosphine Complexes and their Oxidation Potentials

(Hattori, H.; Koo, H. D.; May, A. J. Direct Chlorination of Trispyrazolyl Borate Ligands in Tp-Ruthenium Complexes *Organometallics* **2017**, *36*, 4707−4712.)

2.1 Background

One crucial structural motif of the catalytic intermediate in propargylic substitution reaction is allenylidene.[6] Allenylidene is characterized by three serial double bonds stretching from the metal center. It belongs to the cumulenylidene family.[27] The cumulenylidenes with longer double bonds are rarer, and the longest cumulenyliedene known to date is Heptahexanylidene, **206**.[28]

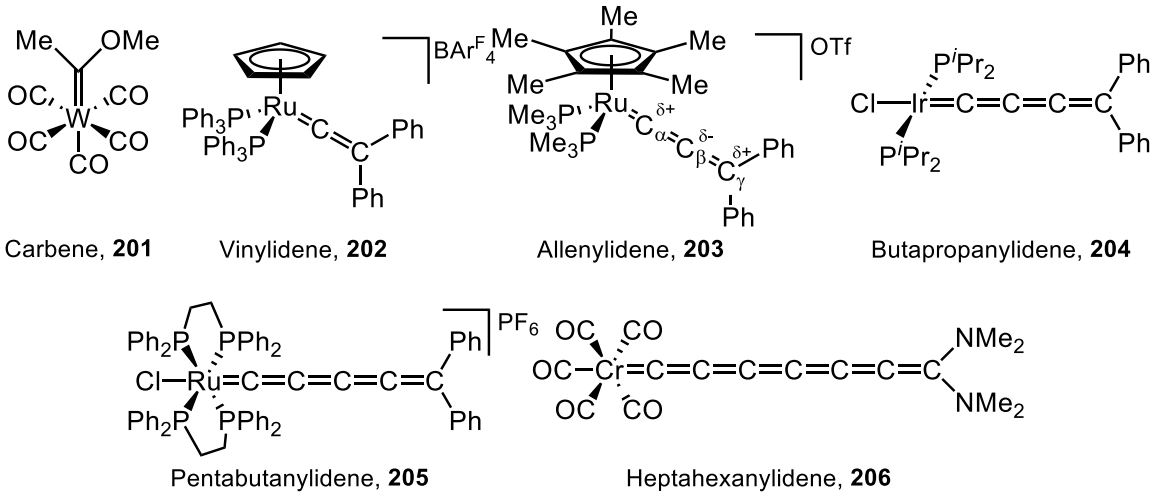


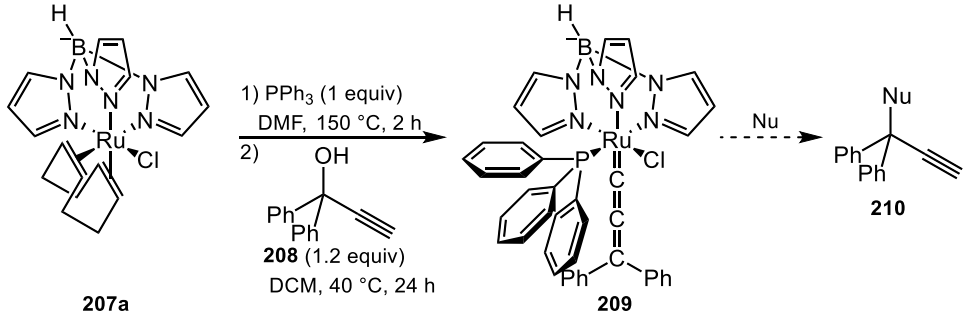
Figure 2.1: Cumulenylidenes

Charge-separated forms of the cumulenylidenes (described as localized positive and negative charges on segregated carbons) are more stable with an odd number of carbon atoms in the cumulenylidene.[29] As is consistent with this fact, perhaps, those cumulenylidenes found in catalysis are often carbenes[30] and allenylidenes.[31]

If cumulenylidene compounds were inspected carefully, one would notice that the complexes in figure 2.1 have strong donors such as carbonato or phosphine ligands. Because the ultimate goal of the project is to develop a propargylic substitution reaction catalyst, syntheses of complexes capable of forming an allenylidene might help. Because phosphine ligated TpRu complex was demonstrated to be able to form an allenylidene

complex **209** by treating a TpRu complex **207a** with a propargylic alcohol **208** (Scheme 2.1),[32] use of these complexes in catalysis could lead to a propargylic substitution reaction to form **210**. Thus, ligand exchange reactions of Tp^{X}Ru(diene)Cl were undertaken to prepare a variety of TpRu phosphine complexes.

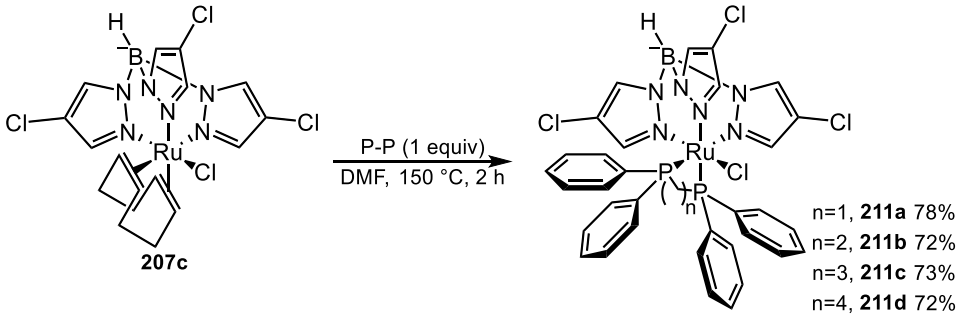
Scheme 2.1: TpRuPPh$_3$(allenylidene)Cl complex 209



2.2 Ligand Exchange Reactions to Synthesize Mono- and Di-phosphine Complexes

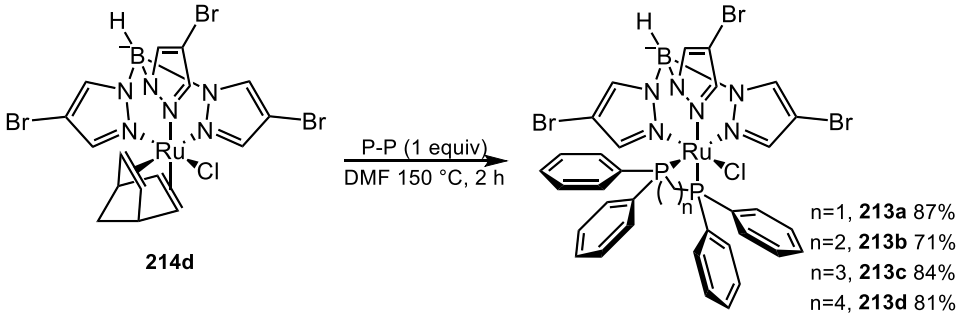
Although complex **207a** is stable over a moderate temperature range (25 to 80 °C), it is known that the cod ligand dissociates at very high temperatures, and new ligands can coordinate to the ruthenium. [33] Therefore, **207a** was allowed to react with diphosphinoalkane (Scheme 2.2). Overall, Tp^{Cl}Ru(P-P)Cl complexes **211** were synthesized in 70-80% having up to four carbons between two phosphines. All of these compounds readily crystalized to give light yellow crystals. These complexes were only slightly soluble in DCM and did not dissolve in other organic solvents at room temperature. When there were five carbons between the phosphines, the product did not crystallize. Among these complexes, **211b** and **211d** were more soluble in DCM and were easier to purify and handle. In an attempt to compare the chemical and physical properties of **211** and TpRu(P-P)Cl **212**, TpRu(dppe)Cl **212b** was synthesized under parallel conditions. However, these complexes were barely soluble in any of the organic solvents, which precluded some measurements such as CV or UV-Vis spectroscopy. Hence, these complexes were not prepared for the comparison of data.

Scheme 2.2: Syntheses of $Tp^{Cl}Ru(P\text{-}P)Cl$ complexes 211.



Next, diphosphine complexes **213a-d** were synthesized under the same conditions, but starting from another precursor (**214d**, Scheme 2.3). The syntheses were successful to afford the products in 70-80% yield. The physical properties of **213a-d** were indistinguishable from **211a-d** (color, solubility, e.t.c).

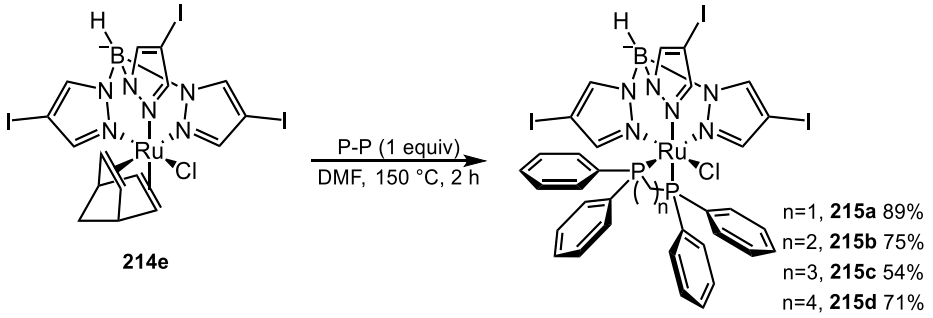
Scheme 2.3: Syntheses of 213a-d from 214d.



The iodinated Tp complex **214e** was used in the same reaction to make the di-phosphine complexes **215a-d** (Scheme 2.4). As was the case previously, the yield of **215a** in dppm exchange are slightly higher than those of **215b-d**. In contrast to air-stable complexes **215a-b**, **215c** and **215d** were unique in that they were slowly oxidized in solution. Additionally, **215c** was a sticky solid, which made isolation tricky. As a result, these complexes gave lower yields than the chloro- and bromo-equivalents **211c** and **213c**. Ru(III) mono-phosphine complex **216a** was also made via a known method.[12] The diene complex **207a** or **214a** was heated to 150 °C in DMF with PPh_3 (Scheme 2.5). Then, the solvent was removed before CCl_4 was added to the residue in order to oxidize the

ruthenium. The complex was stable enough for purification through column chromatography.

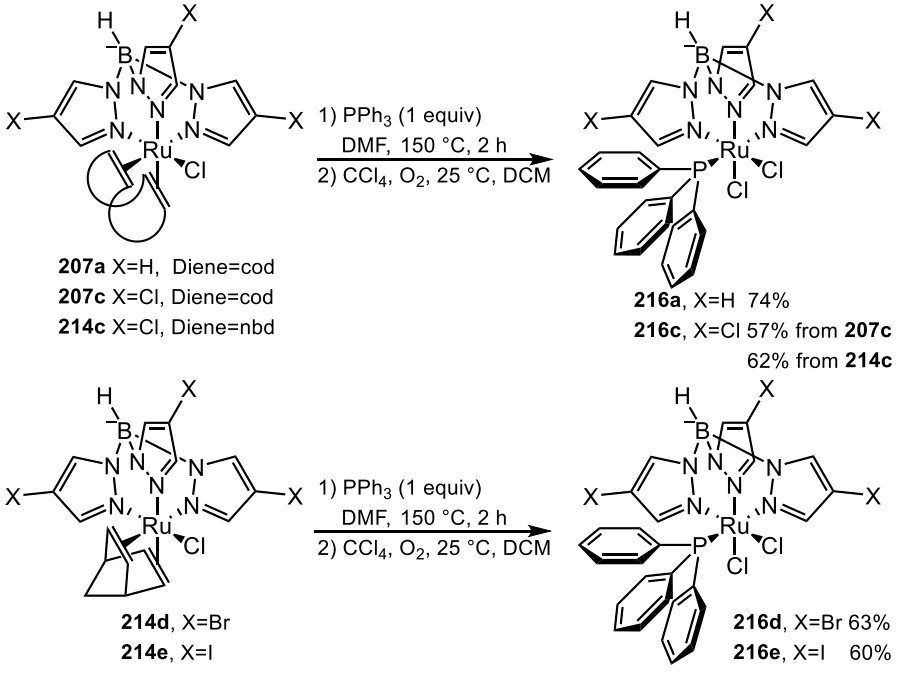
Scheme 2.4: Syntheses of 215a-d from 214e



214e

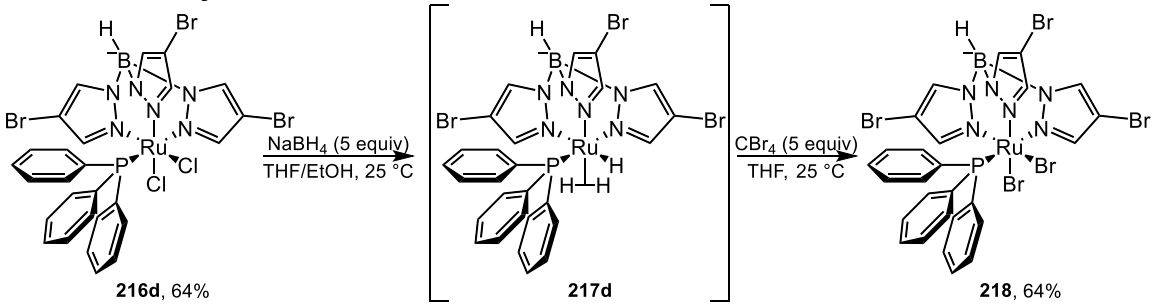
The same procedure was applied to complexes **207c** and **214c**. Regardless of the starting diene ligand, the desired product **216c** was obtained. The yield was 57% from **207c** while the yield was 62% from **214c**. Overall, the yield of the reaction averaged about 60% regardless of the halogen substituent on the Tp ligand. The color of **216a** was much brighter red while for the halogenated complexes **216c-e** the color was much darker. The crystals of **216c** were needle-like, while **216d-e** made beautiful block-shaped crystals.

Scheme 2.5: Syntheses of Ru(III) complexes, 216



If **216** works as a catalyst, at least one of the chloro ligands has to be dissociated from the metal center. However, possessing two chloro ligands, one of these ligands is not necessarily removed selectively. Also, the chloro ligand might be difficult to dissociate under some mild reactions. Therefore, a reaction was designed to replace the halogen ligands (Scheme 2.6). Because CCl_4 can oxidize weakly coordinated Ru(II) complexes, giving an additional chloro ligand to the product, carbon tetrabromide and iodide should react in similar manners to give Ru-Br and Ru-I bonds. **216a** is known to be easily reduced by $NaBH_4$ to form $TpRuPPh_3(H_2)H$, **217** (Scheme 2.6).[12] The addition of $NaBH_4$ to the solution of **216d** turned the mixture yellow. Addition of 5 molar equivalents of CBr_4 indeed changed the color to black. Purification with column chromatography gave a dark green compound, which gave a dark green block-shaped crystal. The complex **218** was characterized with X-ray crystallography as expected. The synthesis was repeated starting from **216d** to obtain $Tp^{Br}RuPPh_3I_2$, **219**. However, this complex did not give any crystal.

Scheme 2.6: Synthesis of 218

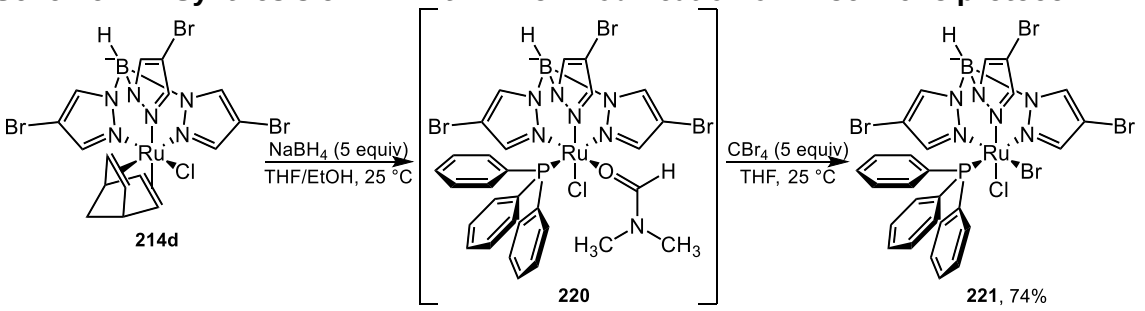


216d, 64% **217d** **218**, 64%

While both halogen ligands are replaced by the above method, it is theoretically possible to synthesize complexes that have two different halo ligands on ruthenium. Heating TpRu(cod)Cl **207a** with triphenyl phosphine gives a known complex $TpRuPPh_3(dmf)Cl$ **220** (Scheme 2.7).[34] This intermediary complex keeps the chloro-ligand on the ruthenium. Consequently, CX_4 oxidation would add only one halo-ligand to the ruthenium at the DMF coordination site. In practice, instead of the second step of the

Kirschner's protocol, CBr_4 and THF were added to the putative **220**. The mixture became purple, and a dark purple crystal of **221** was obtained after purification and recrystallization.

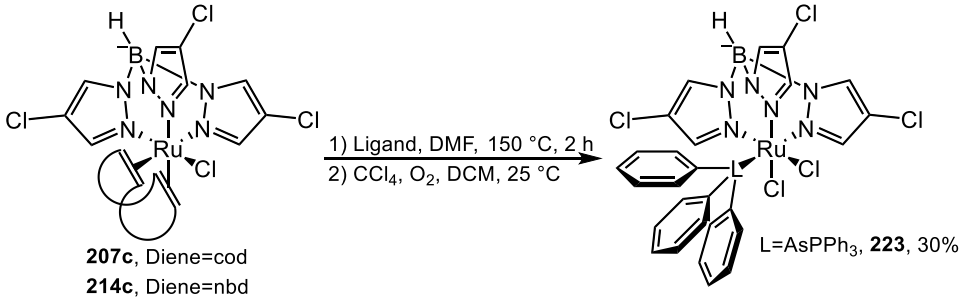
Scheme 2.7: Synthesis of 221 with minor modification of Kirschner's protocol



Triphenyl phosphine ligand was switched to other ligands in order to access the properties of these homologous complexes. At the beginning, **207c** was allowed to react with PCy_3, and then carbon tetrachloride to give a red complex (entry 1, Table 2.1). The red complex was expected to be $Tp^{Cl}RuPCy_3Cl_2$ **222**, but the analysis by NMR nor crystallography was impossible because the complex was paramagnetic and did not form a single crystal. Next, tris-(pentafluorophenyl)phosphine was utilized in the reaction. This time, the mixture became brown in the first step, and following oxidation did not change the color of the mixture. TLC analysis showed complex mixture of spots (entry 2). A big spot of the phosphine indicates that the phosphine did not ligate to the ruthenium, which in turn would be due to the electron withdrawing fluorine atoms that make the phosphorous a weaker donor. The complex **207c** was heated with NPh_3 in DMF to give a mixture of dim color. (entry 3). Addition of CCl_4 to the yellowish green residue after drying of the mixture gave a light blue solution. Purification with column chromatography eluted blue liquid that did not form crystal. The lone pair on the nitrogen in NPh_3 is delocalized into the phenyl rings.[35] The first step of the reactions discolored the mixture presumable because the lone pair is not available for the coordination. $AsPh_3$ was chosen to react with **214c**. The following oxidation reaction gave a stable complex $TpRuAsPh_3Cl_2$, **223**, but in much lower

yield of 30% (entry 4). The appearance of the crystal did not show much difference from **216c**. The reactions with $SbPh_3$ gave an orange solution in the first step (entry 4). Addition of CCl_4 turned the color green. Though less common, some ruthenium complexes possessing $AsPh_3$ or $SbPh_3$ were synthesized.[36] Therefore, rather than the coordination problem, the decomposition of the complexes seemed to explain the low yield. The reaction of **207c** with $BiPh_3$ turned the mixture black. The following addition of CCl_4 did not change the color, and no product was isolated (entry 6). This time, the reason for the failure could be attributed to the low coordination of $BiPh_3$ as the Kelen group's interpreted the negative Hammett−Taft as delocalization of the lone pair on bismuth into a phenyl ring.[37]

Table 2.1: Synthesis of 223.



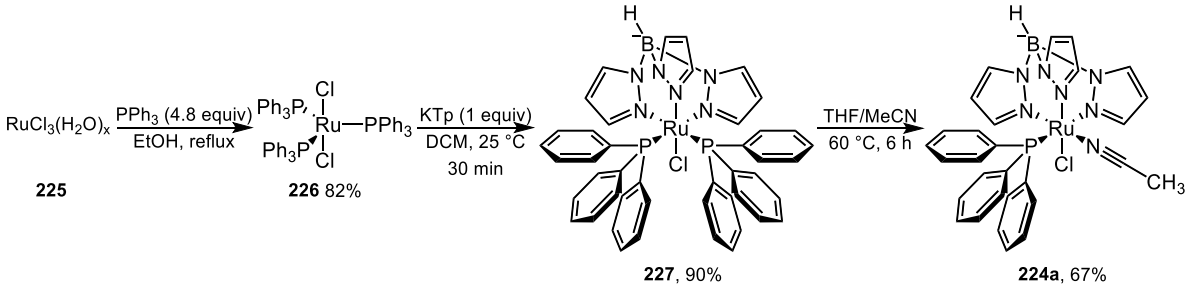
207c, Diene=cod
214c, Diene=nbd

Entry	Reactant	Ligand	Result
1	**207c**	PCy_3	Red liquid that does not crystalizes
2	**207c**	$PAr^{F5}{}_3$	Decomposition of the comlex
3	**214c**	NPh_3	Decomposition of the comlex
4	**214c**	$AsPh_3$	**223**, 30%
5	**214c**	$SbPh_3$	Decomposition of the comlex
6	**214c**	$BiPh_3$	Decomposition of the comlex

$TpRuPPh_3(MeCN)Cl$, (**224a**) is another Tp phosphine complex that was synthesized in 1997s (Scheme 2.8).[38] Later, it was reported to be a catalyst that facilitates the rearrangement of epoxyalkanes to furans.[39] The synthesis of **224a** starts from treating $RuCl_3(H_2O)_x$, (**225**) with PPh_3. Tp coordinates to the resulting $Ru(PPh_3)_3Cl_2$ (**226**), to afford

TpRu(PPh_3)$_2$Cl (**227**) (Scheme 2.8). One of the PPh_3 ligands is replaced by MeCN to give the catalyst. Unfortunately, none of these complexes were synthesized through a direct halogenation methodology. Therefore, a new condition had to be devised to reach **224**.

Scheme 2.8: Synthesis of 224a through the known route



Our library of the complexes includes **216**, which happened to be similar to **224** (Figure 2.2). The main differences between these complexes are the oxidation state of the ruthenium and acetonitrile ligand. The Kirschner's group added zinc and acetonitrile to **216a**, which gave a cationic ruthenium complex [TpRuPPh_3(MeCN)$_2$]$_2$$ZnCl_4$, **228**. Because the target complex is neutral, the use of ionic reagents may be entirely avoided or a counterion to precipitate ionic species should be added. One solution is to reduce **216** with $NaBH_4$ to TpRuPPh_3(H_2)H **217a**, so it would have a seemingly weak L type ligand (H_2) ligand and an X type ligand (H). Acetonitrile ligand is another L type ligand, and therefore could easily replace the H_2 to give **229**. The reagent has to be chosen so that the hydride ligand is exchanged with a chloro ligand as well as precipitate Na^+ as a salt. A reagent that fulfills these criteria is HCl. The proton of the acid could react with the hydride forming a hydrogen gas. The chloride ion can associate with the sodium ion in the mixture, and the NaCl would precipitate. Additionally, any unreacted $NaBH_4$ could be quenched.

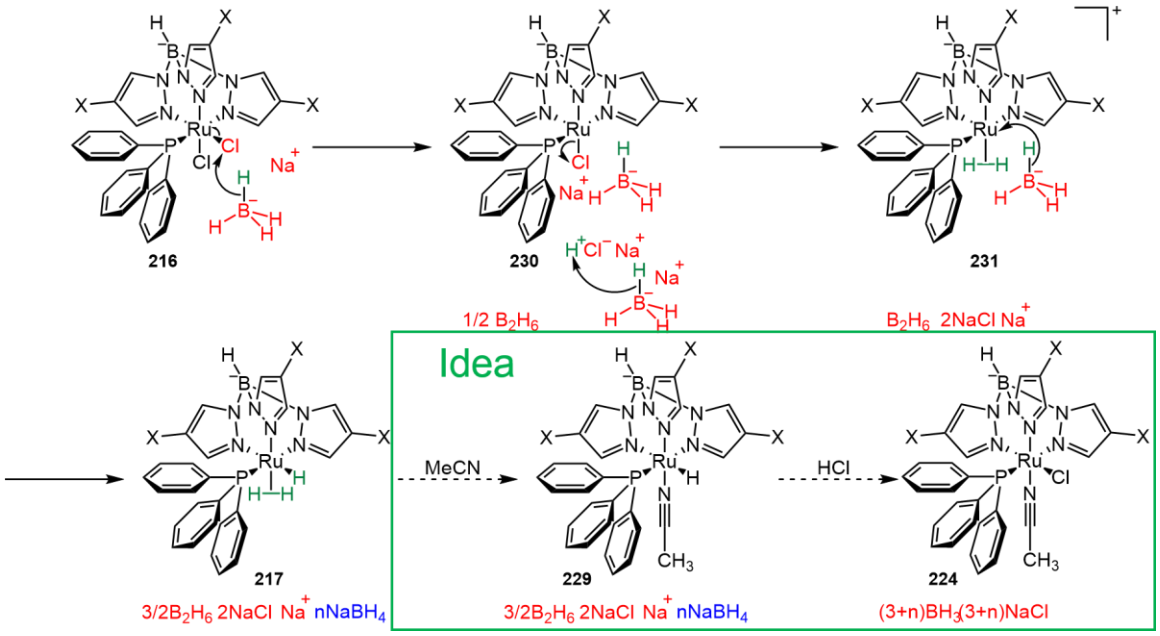
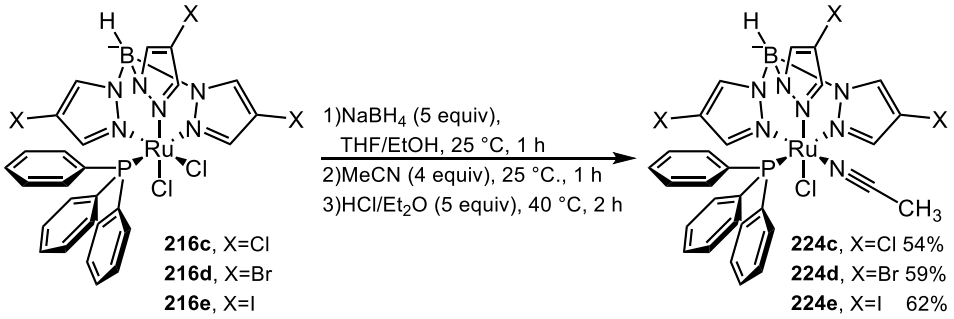


Figure 2.2: Hypothetical components of the mixture and choice of reagents

The plan was put into practice. The ruthenium was reduced over 1 hour with $NaBH_4$ in the first step (Scheme 31). Then, acetonitrile was added to the yellow solution of **217**, and the mixture was stirred for another 1 hour at room temperature. Once the HCl solution was added to the mixture, the mixture was heated at 40 °C for 2 hours to remove any HCl This heating was indispensable to obtain the product. Otherwise, the addition of DCM discolored the mixture, and no crystal was formed. The Tp^{Cl} and Tp^{Br} complexes **224c** and **224d** were purified by means of recrystallization, which gave light yellow crystals. On the other hand, the Tp^{I} counterpart **224e** was purified through a neutral alumina column and precipitated by adding hexane to a DCM solution because it did not readily form the crystal. The powdery product was light brown. These complexes were slightly air sensitive in solution, but were insensitive in the solid phase. The product yields averaged 60% overall and were satisfactory.

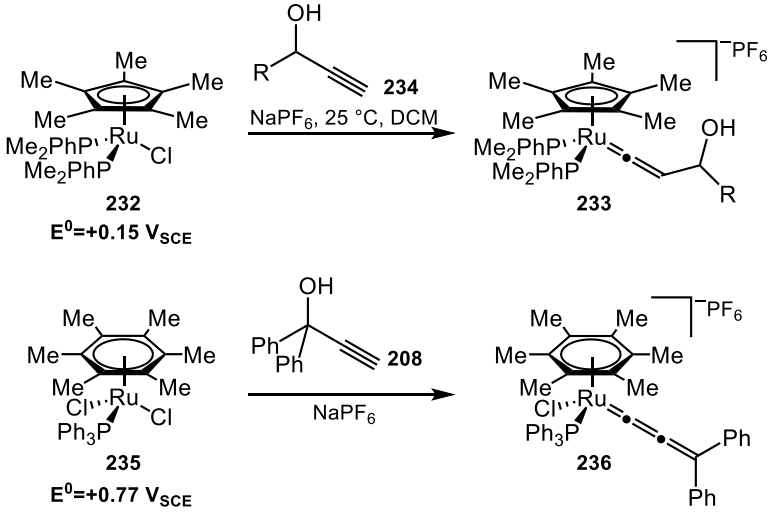
Scheme 2.9: Syntheses of 224c-e via a new synthetic route



2.3 Oxidation Potentials of the Tp Ruthenium Complexes

Since the presence of allenylidenes in propargylic substitution reactions has been observed,[40] modulating the relative stability of the allenylidene ligand might change the speed of the overall reaction. The Dixneuf group correlated the oxidation potential of similar ruthenium complexes to the ease of allenylidene formation (Scheme 2.10).[41] However, because the structures of the tridentate ligands and the substrates being compared were different, the correlation between the oxidation potentials of the complex to the stability of the allenylidene is not straightforward. To deepen the understanding of the interplay of oxidation potential and catalysis, the complexes obtained so far were analyzed with cyclic voltammetry (CV).

Scheme 2.10: Comparison of allenylidene formation in similar ruthenium complexes and their oxidation potentials.



The oxidation potentials of **207a**, **207c**, **214a**, and **214c** were obtained via CV and compared (Figure 2.3). When a complex is reversibly oxidized, symmetric broad peaks appear along the voltage, axis which was the case with the voltammogram of **207a**. On the other hand, when the complex is irreversibly oxidized or reduced, asymmetric peaks appear, which was the case with **207c**. The voltammogram (second from the top) shows a zigzag curve in the bottom half of the loop, which indicates that the complex was decomposing. In short, chlorinating the Tp ligand made the complex vulnerable to voltage.

The oxidation potentials of **207a** (0.81 V) and **214a**, (0.82 V) are the same, but comparison of **214a** and **214c** (1.22 V) revealed that the latter shows a higher oxidation potential than the former by 0.4 V. This means that **214c** resists oxidation better than **214a**.

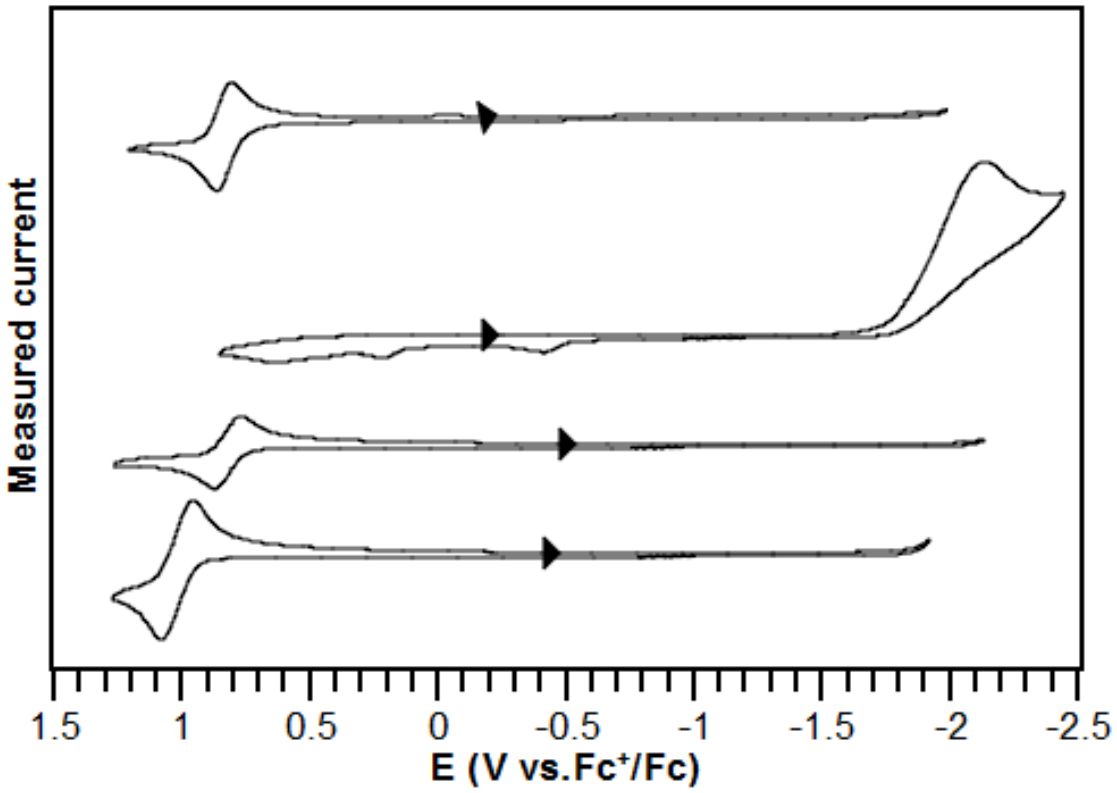


Figure 2.3: Cyclic voltammogram (CV) of TpRu(cod)Cl (207a), Tp^{Cl}Ru(cod)Cl (207c), TpRu(nbd)Cl (214a), and Tp^{Cl}Ru(nbd)Cl (214c) from to top to bottom[42]

Next, the influence that the type of halogen that was added to the Tp ligand had on the oxidation potential was benchmarked with $Tp^{X}RuPPh_3Cl_2$ **216** (Figure 2.4). Each of

these CVs shows a reversible peak. Overall, the complexes had much lower oxidation potentials than the Ru(II) diene complexes in Figure 2.3. The peak was considered to represent a Ru(II)/Ru(III) redox pair rather than a Ru(III)/Ru(IV) pair because electron removal from more highly charged species is tougher due to the stronger Coulombic force and TpRu(IV) complex is unknown. The trend was that halogenated complexes had higher oxidation potentials than their non-halogenated Tp counterparts by 0.17 V. The electronegative chlorine substituents on Tp^{Cl} were expected to reduce the electron density on Tp, resulting in weaker coordination to the ruthenium. Because less electron density is donated to the ruthenium, removing an electron from the electron deficient source should be harder. Interestingly, the type of halogen did not change the oxidation potential at all.

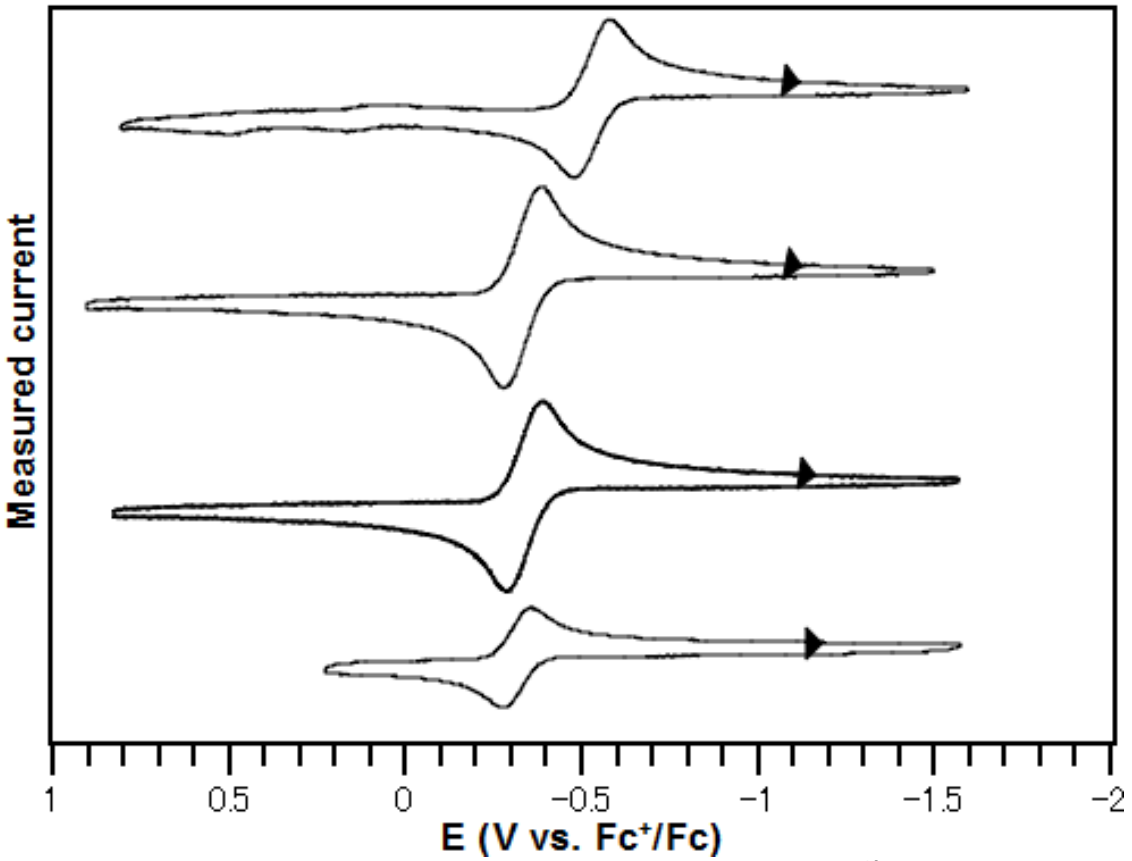


Figure 2.4: Cyclic voltammogram of $TpRuPPh_3Cl_2$ (216a), $Tp^{Cl}RuPPh_3Cl_2$ (216c), $Tp^{Br}RuPPh_3Cl_2$ (216d), and $Tp^{I}RuPPh_3Cl_2$ (216e) from top to bottom[42]

Figure 2.5 shows the CVs of $Tp^{Cl}Ru(P\text{-}P)Cl$ (**211a-d)**. The main focus here is how the linker size affected the coordination of the phosphorus. Coordination of the ligand usually means that an electron is donated from the ligand to the metal to increase the electron density of the metal. This donation would depend on how effectively the ligand can coordinate to the ruthenium. Theoretically, introduction of distortion into the linker would disturb the effective coordination of the phosphorus to ruthenium, which should be reflected on the CV. However, **211a-d** show a reversible peak around 0.3 V. It seems that the linker size between the phosphines did not distort P-P ligation.

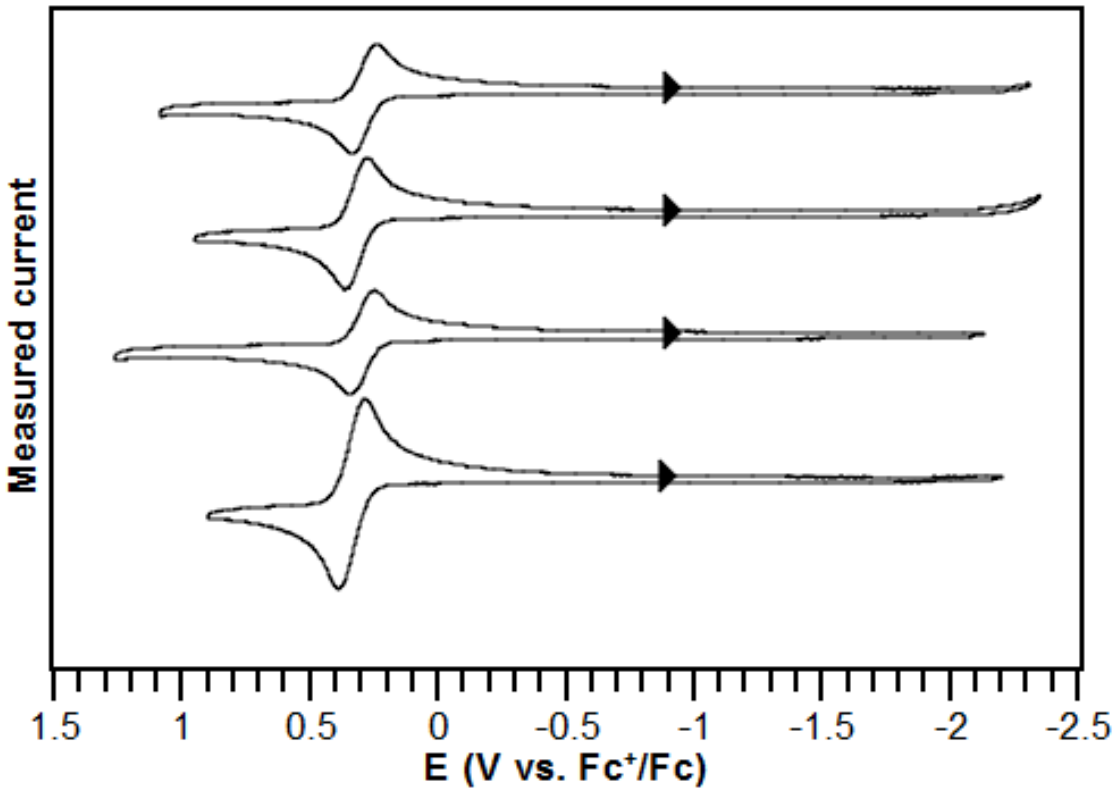


Figure 2.5: Cyclic voltammogram of $Tp^{Cl}Ru(dppm)Cl$ (211a), $Tp^{Cl}Ru(dppe)Cl$ (211b), $Tp^{Cl}Ru(dppp)Cl$ (211c), and $Tp^{Cl}Ru(dppb)Cl$ (211d) from top to bottom[42]

The last discussion of the oxidation potential is on $TpRuPPh_3(MeCN)Cl$ **224a**, and $Tp^{X}RuPPh_3(MeCN)Cl$ **224c-e** (Figure 2.6). Each of the CVs here also shows a reversible peak. The positions of the peaks are very similar to those from $Tp^{X}Ru(P\text{-}P)Cl$. One way to interpret the data is that PPh_2R and MeCN ligands are similarly good σ donors that

switching these ligands did not change the electron density on the ruthenium. The trend of the oxidation potentials here also shows that those for $Tp^{X}Ru$ complexes are higher than those for TpRu complexes, but the type of the halogen does not matter.

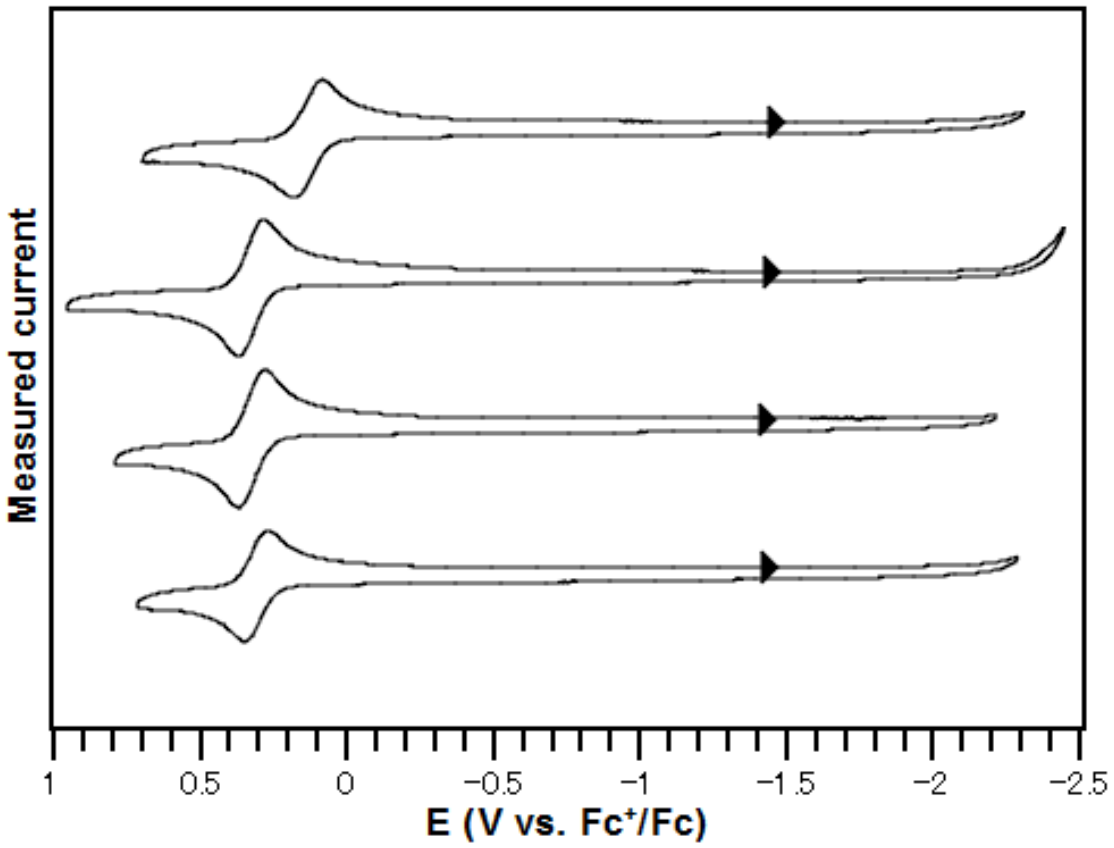


Figure 2.6: Cyclic voltammogram of $TpRuPPh_3(MeCN)Cl$ 224a, $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c, $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d, and $Tp^{I}RuPPh_3(MeCN)Cl$ 224e[42]

2.4 Conclusion

$Tp^{X}Ru(diene)Cl$ complexes successfully underwent ligand exchange reactions to afford mono-phosphine and di-phosphine complexes in reasonable to high product yields. A general trend of $Tp^{X}Ru$ complexes having higher oxidation potentials than TpRu complexes was revealed regardless of the ligands on ruthenium. However, halogen

substituents on the Tp ligand were not powerful enough to impart distinct oxidation potentials to the ruthenium.

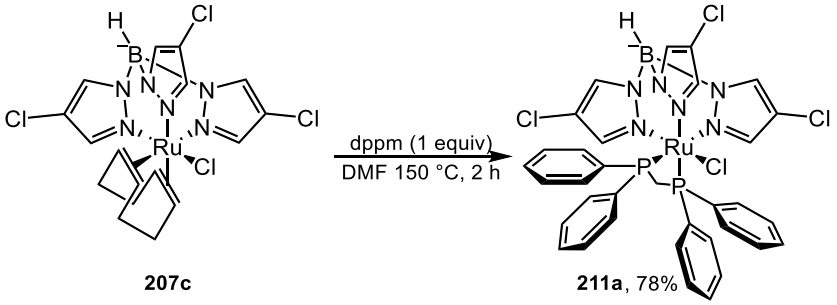
2.5 Experimental Section

Materials and Methods

All reactions were carried out in a flame-dried Shlenk flask under an Ar atmosphere. THF and acetonitrile were purged with argon and dried over activated alumina columns and used after degassing by repetitive vacuum and Ar purges. $TpRuPPh_3(MeCN)Cl$ was synthesized as reported.[38] The rest of the reagents are commercially available and were degassed before usage as necessary. Flash column chromatography was performed on 60 Å silica gel (Sorbent technologies Inc.) unless otherwise stated. Aluminum oxide (activated, neutral Brockmann I) was purchased from Sigma Aldrich. Analytical thin layer chromatography was performed on 250mm EMD silicagel/TLC plates with fluorescent detector (254 nm). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 500 spectrometer using the residual solvent peak as an internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.6 ppm for ^{13}C NMR and 400 MHz for ^{31}P NMR). The crystallography measurements were made with a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector using MoK/a radiation at 123 K. The reflections were collected using a narrow-frame algorithm with scan widths of 0.50/% in omega and phi and an exposure time of 20 s/frame at 6 cm detector distance. The data were integrated using the Bruker Apex-II program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied using SADABS. Redundant reflections were averaged. The structure was solved by direct method and refined with the program SHELXL 2014. All non-hydrogen atoms were refined

anisotropically. The hydrogen atoms were refined isotropically with riding displacement parameters. UV-Vis spectroscopy was collected on a Cary 6000 UV-vis NIR spectrophotometer over the 200-800 nm spectral range in DCM at room temperature. Cyclic Voltammetry (CV) measurements were performed at the scan rate of 0.1 V/s with a CH Instruments 602E potentiostat interfaced with a nitrogen glove box via wire feedthroughs. Samples were dissolved in DCM with 0.1 M $TBAPF_6$ as a supporting electrolyte. A 3 mm diameter glassy carbon working electrode, platinum wire counter electrode, and a silver wire pseudoreference electrode were used. Elemental analyses (H, C, N, Cl, Br, I) were performed by Atlantic Microlab, Inc. of Norcross, GA.

$Tp^{Cl}Ru(dppm)Cl$ 211a

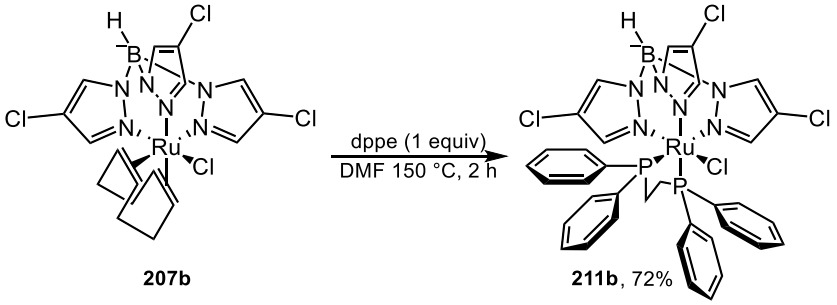


207c **211a**, 78%

A flame-dried 10 mL Schlenk flask was charged with **207c** (245.0 mg, 0.46 mmol) and 1,1-bis(diphenylphosphino)methane (168.1 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent as removed under vacuum. The residue was recrystallized form DCM pentane to give yellow needle-like crystals **211a** (295.1 mg, 78% yield). ^{1}H NMR (500 MHz, chloroform-d) δ 7.83−7.74 (m, 4H), 7.68 (d, J = 14.9 Hz, 2H), 7.50 (s, 1H), 7.48−7.36 (m, 8H), 7.31 (t, J = 7.4 Hz, 2H), 7.25−7.13 (m, 4H), 7.08 (dd, J = 10.6, 6.6 Hz, 4H), 5.27−5.15 (m, 1H), 5.10 (d, J = 14.3 Hz, 1H), 5.00−4.88 (m, 1H), 4.28 (s, 1H). ^{13}C NMR (500 MHz, chloroform-d) δ 48.2−48.5 (t, J_{C-P} = 83 Hz), 107.5, 110.2, 128.8, 128.8, 128.8, 128.9, 128.9, 130.2, 130.7,

131.4−131.7 (t, J_{C-P} = 73 Hz), 132.9, 133.3, 133.4, 133.4, 133.7, 134.3−134.6 (t, J_{C-P} = 78 Hz), 134.8, 142.7, 146.8. ^{31}P NMR (400 MHz, chloroform-d) δ 8.2 Anal. Calcd for $H_{29}C_{34}N_6BP_2Cl_4Ru$ (840.65 g/mol): H, 3.49; C, 48.77; N, 10.03; Cl, 16.94; Found: H, 3.59; C, 48.87; N, 10.11; Cl, 16.79.

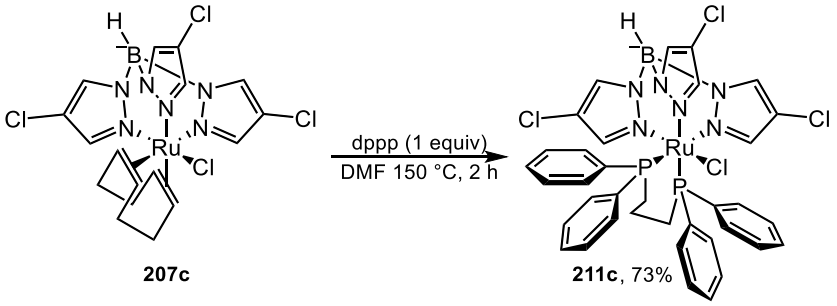
Tp^{Cl}Ru(dppe)Cl 211b



207b **211b**, 72%

A flame-dried 10 mL Schlenk flask was charged with **207c** (245.0 mg, 0.46 mmol) and 1,2-bis(diphenylphosphino)ethane (174.1 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 12:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needles **211b** (269.2 mg, 72% yield). ^{1}H NMR (500 MHz, chloroform-d) δ 7.67 (s, 2H), 7.57 (t, J = 8.0 Hz, 4H), 7.44 (s, 1H), 7.43−7.31 (m, 6H), 7.23 (t, J = 7.4 Hz, 2H), 7.12−7.03 (m, 6H), 6.72 (t, J = 8.0 Hz, 4H), 4.86 (s, 1H), 4.72−3.98 (1H), 3.20−2.99 (m, 2H), 2.94−2.77 (m, 2H). ^{13}C NMR (500 MHz, chloroform-d) δ 29.2−29.5 (t, J_{C-P} = 93 Hz), 108, 110.2, 128.2−128.3, 128.7, 130, 130.3, 131.4− 131.8 (m), 132.7, 133.5, 133.9, 134.1, 136.1−136.4 (m), 142.7, 147. ^{31}P NMR (400 MHz, chloroform-d) δ 70.7 Anal. Calcd for $H_{31}C_{35}N_6BP_2Cl_4Ru$ (854.78 g/mol): H, 3.67; C, 49.38; N, 9.87; Cl, 16.65; Found: H, 3.73; C, 49.12; N, 9.85; Cl, 16.38.

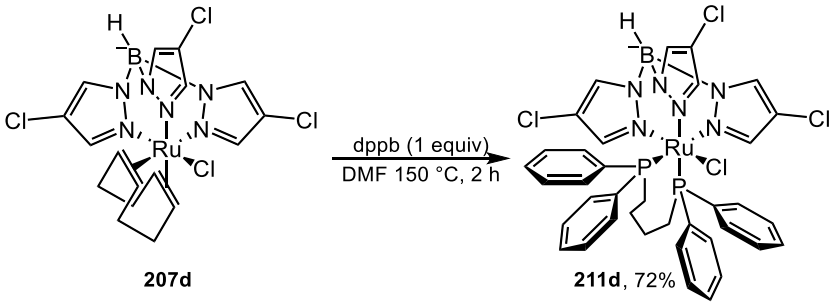
Tp^{Cl}Ru(dppp)Cl 211c



207c **211c**, 73%

A flame-dried 10 mL Schlenk flask was charged with **207c** (245.0 mg, 0.46 mmol) and 1,3-bis(diphenylphosphino)propane (181.0 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was recrystallized form DCM pentane to give yellow needle-like crystals **211c**. (276.3 mg, 73% yield). ^{1}H NMR (500 MHz, chloroform-d) δ 7.71 (t, J = 8.0 Hz, 4H), 7.55 (s, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.35−7.27 (m, 5H), 7.19 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.4 Hz, 4H), 6.55 (t, J = 7.7 Hz, 4H), 6.33 (s, 2H), 4.81 (s, 1H), 4.63−3.82 (1H), 3.00 (td, J = 15.8, 7.1 Hz, 2H), 2.79 (t, J = 12.9 Hz, 3H), 2.21 (q, J = 12.8 Hz, 1H). ^{13}C NMR (500 MHz, chloroform-d) δ 21.2, 28.9−29.2 (t, J_{C-P} = 59 Hz), 108.2, 109.6, 127.9−128, 128.5, 129.8, 131.0−131.3 (t, J_{C-P} = 73.5 Hz), 132.3, 133.3, 134.1, 134.2, 135.5−135.9 (t, J_{C-P} = 83 Hz), 143.1, 148.3. ^{31}P NMR (400 MHz, chloroform-d) δ 34.1 Anal. Calcd for $H_{33}C_{36}N_6BP_2Cl_4Ru$ (868.90 g/mol): H, 3.84; C, 50.00; N, 9.71; Cl, 16.39; Found: H, 3.90; C, 49.53; N, 9.69; Cl, 17.51.

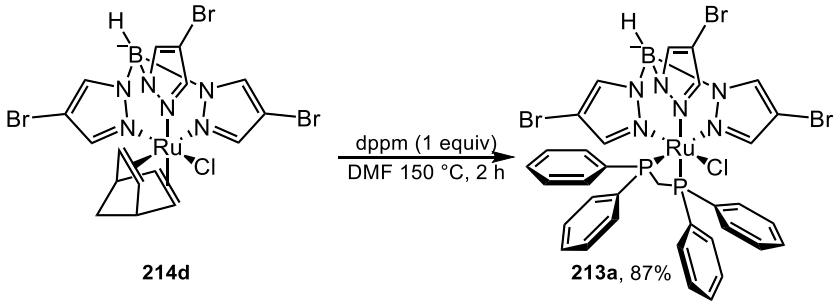
Tp^{Cl}Ru(dppb)Cl 211d



207d **211d**, 72%

A flame-dried 10 mL Schlenk flask was charged with **207c** (245.0 mg, 0.46 mmol) and 1,4-bis-(diphenylphosphino)butane (186.7 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 16:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needle **211d** (278.1 mg, 72.0% yield). ^{1}H NMR (500 MHz, chloroform-d) δ7.62 (s, 4H), 7.53 (d, J = 10.9 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 8.0 Hz, 5H), 7.22−7.11 (m, 2H), 6.99 (t, J = 7.7 Hz, 4H), 6.60−6.40 (m, 6H), 5.55 (s, 1H), 4.54−3.83 (1H), 2.87 (d, J = 10.9 Hz, 2H), 2.77−2.54 (m, 4H), 2.18 (d, J = 5.7 Hz, 2H). ^{13}C NMR (500 MHz, chloroform-d) 23.1, 27.8−28.0 (t, J_{C-P} = 49 Hz), 108.5, 109.7, 127.7−127.8, 128.2, 129.6, 132.5, 133.2−133.5 (t, J_{C-P} = 73.5 Hz), 133.7, 134.2, 134.4, 137.6−137.9 (t, J_{C-P} = 76 Hz), 143.8, 148.6. ^{31}P NMR (400 MHz, chloroform-d) δ 35.9 Anal. Calcd for $H_{35}C_{37}N_6BP_2Cl_4Ru$ (883.03 g/mol): H, 4.01; C, 50.5; N, 9.56; Cl, 16.12; Found: H, 4.07; C, 50.61; N, 9.55; Cl, 16.03.

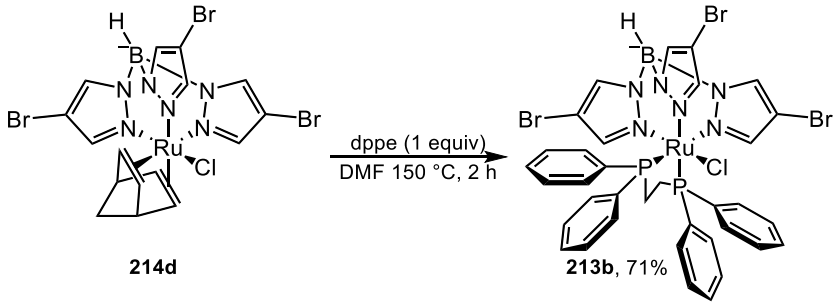
Tp^{Br}Ru(dppm)Cl 213a



214d **213a**, 87%

A flame dried 10 mL Shlenk flask was charged with Tp^{Br}Ru(nbd)Cl (297.1 mg, 0.44 mmol) under inert atmosphere. 1,1-bis(diphenylphosphino)methane (168.0 mg, 0.44 mmol, 1 equiv), and degassed DMF (4.0 mL) were added to the flask. The mixture was stirred at 150 °C for two hours. The solvent was removed under vacuum, and the residue was recrystallized from DCM/pentane to afford yellow crystal (368.7 mg, 87% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 7.84-7.73 (4H), 7.73-7.66 (2H), 7.57-7.49 (1H), 7.46-7.36 (8H), 7.35-7.27 (2H), 7.22-7.13 (4H), 7.12-6.99 (4H), 5.27-5.16 (1H), 5.09-5.02 (1H), 4.98-4.87 (1H). ^{13}C-NMR (500 MHz, chloroform-d) δ 47.9-48.3 (*t*, J_{C-P}=86 Hz), 90.3, 93.3, 128.8-128.9 (*m*, 2C), 130.2, 130.7, 131.3-131.6 (*t*, J_{C-P}=86 Hz), 132.9, 133.3-133.4 (*t*, J_{C-P}=19.5 Hz), 134.2-134.6 (*t*, J_{C-P}=78.25 Hz), 136, 137.1, 144.7, 148.8. ^{31}P-NMR (400 MHz, chloroform-d) δ 8.0. Anal Calcd for $H_{29}C_{34}N_6BP_2ClBr_3Ru$ (974.28 g/mol): H, 3.01; C, 42.07; N, 8.66; Cl, 3.65; Br, 24.70; Found: H,2.84; C, 42.20; N, 8.92; Cl, 3.54; Br, 24.46.

Tp^{Br}Ru(dppe)Cl 213b

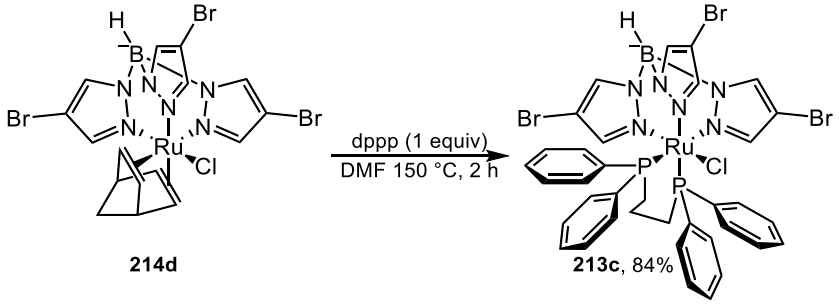


214d **213b**, 71%

A flame-dried 10 mL Schlenk flask was charged with **214**d (297.1 mg, 0.44 mmol) and 1,2-bis(diphenylphosphino)ethane (174.0 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was

added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 12:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needle **213b** (309.2 mg, 71% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 7.71 (s, 2H), 7.56 (t, J = 8.0 Hz, 4H), 7.47 (s, 1H), 7.39 (dt, J = 18.5, 7.0 Hz, 6H), 7.23 (t, J = 7.4 Hz, 2H), 7.10 (s, 2H), 7.07 (t, J = 7.4 Hz, 4H), 6.71 (t, J = 8.0 Hz, 4H), 4.85 (s, 1H), 4.73-4.09 (1H), 3.19-3.01 (m, 2H), 2.95-2.78 (m, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 29.1-29.4 (*t*, J_{C-P}=85.75 Hz), 90.8, 93.3, 128.3, 128.3, 128.7, 130, 130.3, 131.4-131.7 (*m*, 1C), 132.7, 133.5, 136.0-136.4 (*m*, 1C), 136.2, 136.4, 144.7, 149.1 ^{31}P-NMR (400 MHz, chloroform-d) δ 70.5. $H_{31}C_{35}N_6BP_2ClBr_3Ru$-0.1 ($CH_2Cl_2$) (993.16 g/mol): H, 3.17; C, 42.44; N, 8.46; Cl, 4.28; Br, 24.13; Found: H, 3.15; C, 42.45; N, 8.36; Cl, 4.36; Br, 23.93.

Tp^{Br}Ru(dppp)Cl 213c

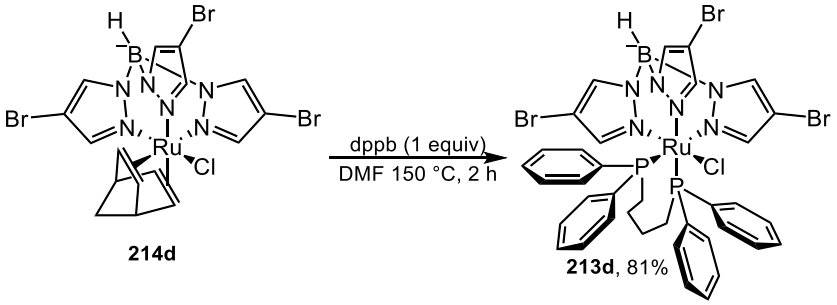


214d **213c**, 84%

A flame-dried 10 mL Schlenk flask was charged with **214d** (297.1 mg, 0.44 mmol) and 1,3-bis(diphenylphosphino)propane (181.3 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent as removed under vacuum. The residue was recrystallized form DCM pentane to give yellow crystals **213c**. (367.2 mg, 84% yield) ^{1}H-NMR (500 MHz, chloroform-d) δ 7.73 (d,

J = 31.5 Hz, 4H), 7.56 (d, J = 11.5 Hz, 2H), 7.34 (dt, J = 36.3, 7.7 Hz, 7H), 7.24-7.13 (m, 2H), 7.03 (t, J = 7.4 Hz, 4H), 6.53 (s, 4H), 6.30 (d, J = 11.5 Hz, 2H), 4.81 (s, 1H), 4.27 (s, 1H), 3.12-2.69 (m, 5H), 2.21 (td, J = 25.3, 13.0 Hz, 1H) ^{13}C-NMR (500 MHz, chloroform-d) δ 21.2, 28.8-29.0 (*t*, J_{C-P}=58.75 Hz), 91.1, 92.8, 127.9, 128.5, 129.8, 129.9, 130.9-131.2 (*t*, J_{C-P}=73.5 Hz), 132.3, 134.2, 135.5-135.8 (*t*, J_{C-P}=78.25 Hz), 135.6 136.3, 145.2, 150.3. ^{31}P-NMR (400 MHz, chloroform-d) δ 33.9. $H_{33}C_{36}N_6BP_2ClBr_3Ru$ (1002.53 g/mol): H, 3.33; C, 42.38; N, 8.41; Cl, 3.55; Br, 24.01; Found: H, 3.29; C, 41.75; N, 7.95; Cl, 7.51; Br, 23.33.

Tp^{Br}Ru(dppb)Cl 213d

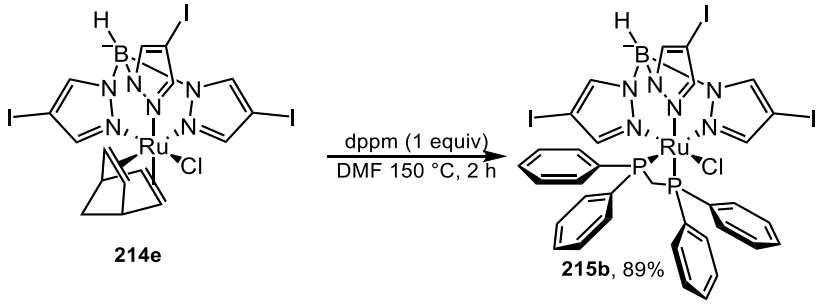


214d **213d**, 81%

A flame-dried 10 mL Schlenk flask was charged with **213d** (297.1 mg, 0.44 mmol) and 1,4-bis-(diphenylphosphino)butane (186.6 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 16:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needle **214d** (358.2 mg, 81.0% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 7.59 (d, J = 14.3 Hz, 6H), 7.37 (t, J = 6.9 Hz, 3H), 7.29 (t, J = 7.4 Hz, 3H), 7.16 (t, J = 7.2 Hz, 2H), 6.98 (t, J = 7.4 Hz, 4H), 6.47 (d, J = 30.9 Hz, 6H), 5.54 (s, 1H), 5.29 (d, J = 7.2 Hz, 1H), 4.65-3.68 (m, 1H), 2.98-2.81 (m, 2H), 2.81-2.54 (m, 4H), 2.18 (d, J = 7.4 Hz, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 23.2, 27.6-27.8 (*t*, J_{C-P}=29 Hz), 91.4, 92.8, 127.7-

127.8 (*t*, J_{C-P}=17.25 Hz), 128.2-128.3 (*t*, J_{C-P}=14.75 Hz), 129.6, 129.6, 132.5, 133.0-133.3 (*t*, J_{C-P}=73.25 Hz), 134.2, 136, 136.6, 137.6-137.9 (*t*, J_{C-P}=73.5 Hz), 145.8, 150.5. ^{31}P-NMR (400 MHz, chloroform-d) δ 35.8. $H_{35}C_{37}N_6BP_2ClBr_3Ru$ (1016.65 g/mol): H, 3.48; C, 43.87; N, 8.30; Cl, 3.50; Br, 23.70; Found: H, 3.59; C, 43.80; N, 8.25; Cl, 3.60; Br, 23.77.

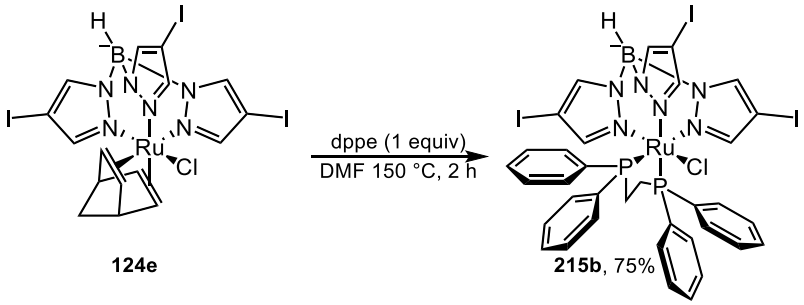
Tp^{I}Ru(dppm)Cl 215a



214e **215b**, 89%

A flame dried 10 mL Shlenk flask was charged with **214e** (358.7 mg, 0.44 mmol) under inert atmosphere. 1,1-bis(diphenylphosphino)methane (168.0 mg, 0.44 mmol, 1 equiv), and degassed DMF (4.0 mL) were added to the flask. The mixture was stirred at 150 °C for two hours. The solvent was removed under vacuum, and the residue was recrystallized from DCM/pentane to afford yellow crystal **215a** (415.4 mg, 89% yield). ^{1}H-NMR δ 7.84-7.75 (m, 4H), 7.73 (s, 2H), 7.56 (s, 1H), 7.45 (s, 2H), 7.44-7.36 (m, 6H), 7.31 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 7.7 Hz, 4H), 7.06 (dd, J = 10.3, 6.9 Hz, 4H), 5.27-5.17 (m, 1H), 5.03 (s, 1H), 4.97-4.87 (m, 1H), 4.73-4.25 (1H) ^{13}C-NMR (500 MHz, chloroform-d) δ 47.6-48.0 (*t*, J_{C-P}=85.8 Hz), 52.8, 56.2, 128.7-128.8 (*t*, J_{C-P}=19.5 Hz), 128.8-128.9 (*t*, J_{C-P}=19.5 Hz), 130.2, 130.7, 131.3-131.6 (*t*, J_{C-P}=75.8 Hz), 132.9, 133.4, 134.2-134.5 (*t*, J_{C-P}=75.8 Hz), 140.5, 141.6, 148.8, 153.2. ^{31}P-NMR (400 MHz, chloroform-d) δ 7.8. Anal Calcd for $H_{29}C_{34}N_6BP_2ClI_3Ru$-0.85($CH_2Cl_2$) (1183.82 g/mol): H, 2.61; C, 35.36; N, 7.10; Cl, 8.08; I, 32.16; Found: H,2.63; C, 35.64; N, 7.16; Cl, 7.92; I, 32.08.

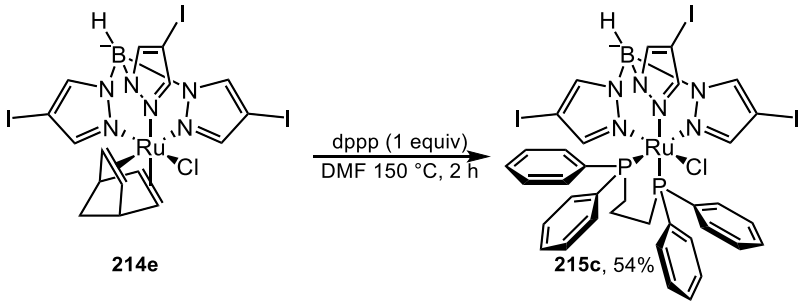
Tp^{I}Ru(dppe)Cl 215b



124e **215b**, 75%

A flame dried 10 mL Shlenk flask was charged with **214e** (358.7 mg, 0.44 mmol) and 1,2-bis(diphenylphosphino)ethane (174.3 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 12:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needles **215b** (341.5 mg, 75% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ 7.76 (d, J = 17.8 Hz, 2H), 7.62-7.45 (m, 5H), 7.44-7.30 (m, 6H), 7.22 (t, J = 7.4 Hz, 2H), 7.12-6.98 (m, 6H), 6.68 (t, J = 7.7 Hz, 4H), 4.86-4.80 (1H), 4.73-4.13 (1H), 3.22-2.76 (m, 4H). ^{13}C-NMR (500 MHz, chloroform-d) δ 28.9-29.2 (*t*, J_{C-P}=83.0 Hz), 54.0, 56.2, 128.2, 128.6, 129.9, 130.3, 131.4-131.7 (*t*, J_{C-P}=63.5 Hz), 132.7, 133.5, 135.9-136.2 (*t*, J_{C-P}=78.3 Hz), 140.6, 141.0, 148.9, 153.4. ^{31}P-NMR (400 MHz, chloroform-d) δ 70.1. $H_{31}C_{35}N_6BP_2ClI_3Ru$-0.25($CH_2Cl_2$) (1146.89 g/mol): H, 2.77; C, 36.91; N, 7.32; Cl, 4.63; I, 33.19; Found: H, 2.77; C, 37.06; N, 7.37; Cl, 4.57; I, 33.25.

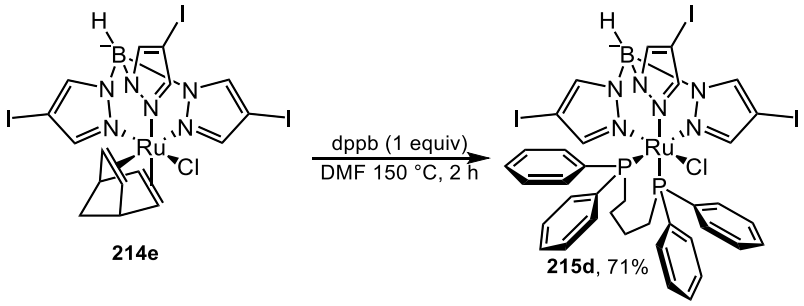
Tp^{I}Ru(dppp)Cl 215c



214e **215c**, 54%

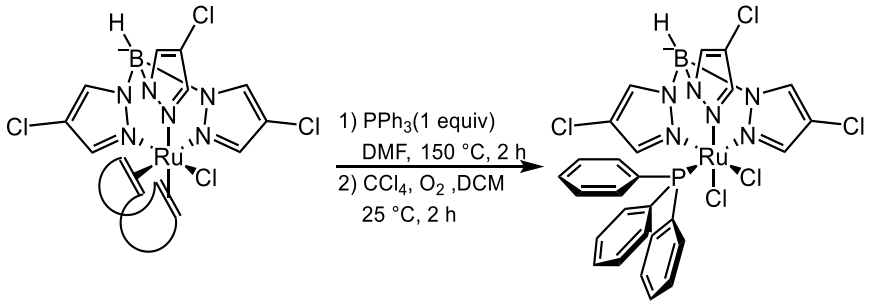
A flame-dried 10 mL Schlenk flask was charged with **214e** (358.7 mg, 0.44 mmol) and 1,3-bis(diphenylphosphino)propane (180.4 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent as removed under vacuum. The residue was recrystallized form degassed DCM/pentane in the absence of oxygen. The fluffy yellow solid **215c** was suspended in diethyl ether and trapped on a glass frit. (266.7 mg, 54% yield) ^{1}H-NMR (500 MHz, chloroform-d) 7.69 (s, 4H), 7.61 (s, 2H), 7.48-7.14 (m, 10H), 7.02 (t, J = 7.4 Hz, 4H), 6.51 (s, 4H), 6.30 (d, J = 10.3 Hz, 2H), 4.83 (s, 1H), 4.30 (s, 1H), 3.11-2.94 (m, 2H), 2.94-2.72 (m, 3H), 2.23 (q, J = 12.4 Hz, 1H). ^{13}C-NMR (500 MHz, chloroform-d) δ 21.2, 28.6-28.8 (*t*, $J_{C\text{-}P}$=59.0 Hz), 53.8, 55.8, 127.9, 128.4, 129.7, 130, 131.0-131.3 (*t*, $J_{C\text{-}P}$=71.0 Hz), 132.4, 134.2, 135.4-135.8 (*t*, $J_{C\text{-}P}$=78.3 Hz), 140.3, 140.8, 149.4, 154.0. ^{31}P-NMR (400 MHz, chloroform-d) δ 33.8. $H_{33}C_{36}N_6BP_2ClI_3Ru$ (1139.69 g/mol): H, 2.92; C, 37.90; N, 7.37; Cl, 3.11; I, 33.40; Found: H, 2.89; C, 38.80; N, 7.33; Cl, 3.68; I, 31.91.

Tp^{I}Ru(dppb)Cl 215d



A flame-dried 10 mL Schlenk flask was charged with **214e** (358.7 mg, 0.44 mmol) and 1,4-bis-(diphenylphosphino)butane (186.6 mg, 0.46 mmol, 1.0 equiv). DMF (4 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent was removed under vacuum. The residue was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 16:2:1. The yellow fractions were collected, the solvent was removed and the product was recrystallized from DCM/pentane to give light yellow needles **215d** (341.6 mg, 71% yield). ^{1}H-NMR (500 MHz, chloroform-d) δ. ^{1}H-NMR (500 MHz, chloroform-d) δ 7.59 (d, J = 16.0 Hz, 6H), 7.37 (q, J = 7.4 Hz, 3H), 7.30 (t, J = 7.7 Hz, 4H), 7.16 (t, J = 7.2 Hz, 2H), 6.97 (t, J = 7.7 Hz, 4H), 6.43 (d, J = 33.8 Hz, 6H), 5.53 (s, 1H), 4.32 (s, 1H), 2.91 (d, J = 10.3 Hz, 2H), 2.79-2.55 (m, 4H), 2.19 (s, 2H). ^{13}C-NMR (500 MHz, chloroform-d) δ 23.2, 27.5-27.7 (*t*, J_{C-P}=49.0 Hz), 55.9, 127.7, 127.7, 128.2, 129.5, 129.7, 132.6, 133-133.3 (*t*, J_{C-P}=73.5 Hz), 134.2, 137.6-137.9 (*t*, J_{C-P}=73.5 Hz), 140.7, 141.1, 150.0, 154.7. ^{31}P-NMR (400 MHz, chloroform-d) δ 35.6. $H_{35}C_{37}N_6BP_2ClI_3Ru$-0.75($CH_2Cl_2$) (1217.40 g/mol): H, 3.02; C, 37.24; N, 6.90; Cl, 7.28; Br, 31.27; Found: H, 2.92; C, 37.02; N, 6.77; Cl, 7.32; I, 31.25.

$Tp^{Cl}RuPPh_3Cl_2$ 216c

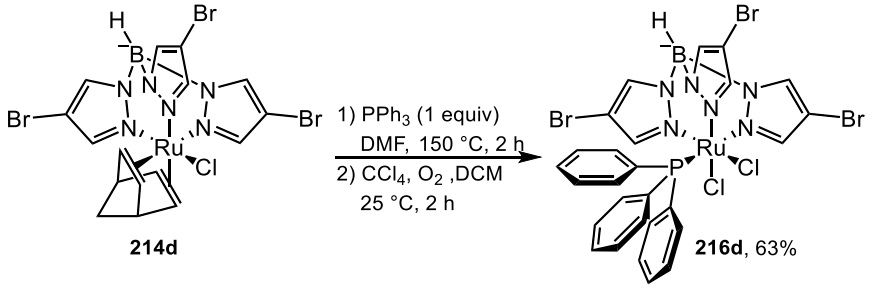


207c or **214c**

216c 57% from **207c**
62% from **214c**

Either **207c** (245.0 mg, 0.44 mmol) or **214c** (238.8 mg, 0.44 mmol) and PPh_3 (114.6 mg, 0.44 mmol, 1.0 equiv) were added to a flame-dried 10 mL Schlenk flask. DMF (4.0 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent as removed under vacuum. CCl_4 (1 mL) and DCM (3 mL) were added to the flask. After overnight, the mixture was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 20:2:1. The red fractions were collected and recrystallized from DCM/pentane to give dark red needles **216c** (181.1 mg, 57% yield from **207c**) (20 mg, 62% yield from **214c**). Anal. Calcd for $H_{22}C_{27}N_6BPCl_5Ru$ (750.63 g/mol): H, 2.95; C, 43.2; N, 11.2; Cl, 23.62; Found: H, 2.96; C, 43.43; N, 11.18; Cl, 23.45.

$Tp^{Br}RuPPh_3Cl_2$ 216d



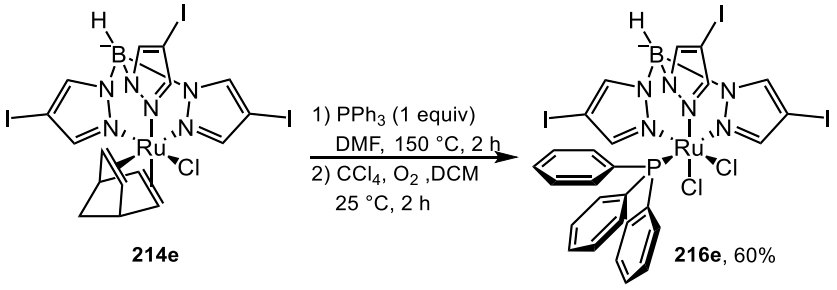
214d

216d, 63%

A flame dried 10 mL Shlenk flask was charged with **214d** (297.4 mg, 0.44 mmol) under inert atmosphere. Triphenyl phosphine (114.6 mg, 0.44 mmol, 1 equiv), and degassed DMF (4.0 mL) were added to the flask. The mixture was stirred at 150 °C for 2

hours. The solvent was removed under vacuum at room temperature. CCl_4 (1 mL) and DCM (3 mL) was added to the residue, and the solution was stirred overnight under air. The mixture was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 20:2:1. The red fractions were collected and recrystallized from DCM/pentane to give dark red crystal **216d** (245.4 mg, 63% yield). $H_{22}C_{27}N_6BPCl_2Br_3Ru$ (886.93 g/mol): H, 2.51; C, 36.69; N, 9.51; Cl, 8.02; Br, 27.14; Found: H, 2.41; C, 36.52; N, 9.45; Cl, 8.18; Br, 27.33.

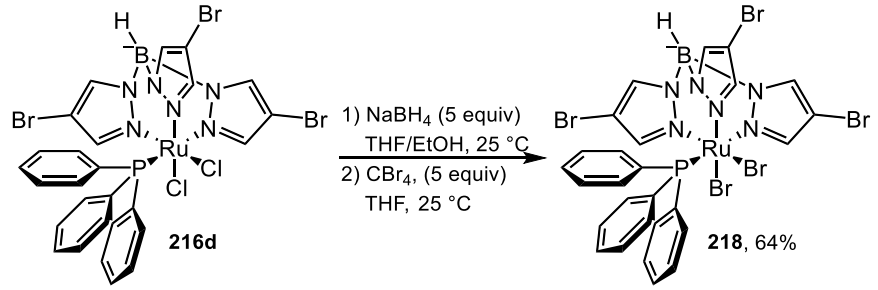
Tp^{I}RuPPh$_3$Cl$_2$ 216e



214e **216e**, 60%

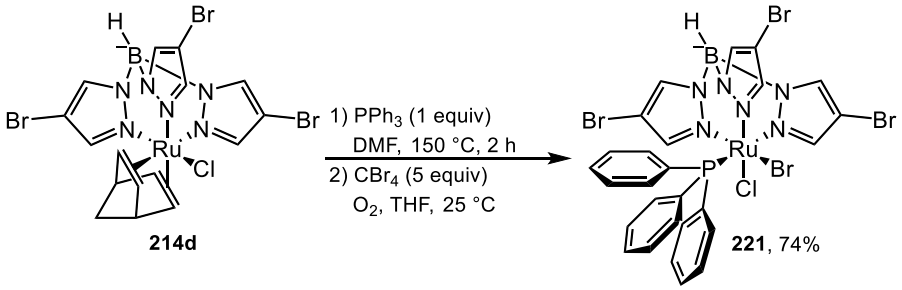
A flame dried 10 mL Shlenk flask was charged with **214e** (358.9 mg, 0.44 mmol) under inert atmosphere. Triphenyl phosphine (114.6 mg, 0.44 mmol, 1 equiv), and degassed DMF (4.0 mL) were added to the flask. The mixture was stirred at 150 °C for 2 hours. The solvent was removed under vacuum at room temperature. CCl_4 (1 mL) and DCM (3 mL) was added to the residue, and the solution was stirred overnight under air. The mixture was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 20:2:1. The red fractions were collected and recrystallized from DCM/pentane to give dark red crystal **216e** (266.1 mg, 60% yield). $H_{22}C_{27}N_6BPCl_2I_3Ru$-$0.25(CH_2Cl_2)$ (1046.21 g/mol): H, 2.17; C, 31.28; N, 8.03; Cl, 8.47; I, 36.39; Found: H, 2.16; C, 31.38; N, 8.05; Cl, 8.44; I, 36.20.

$Tp^{Br}RuPPh_3Br_2$ 218



To a mixture of THF (7.5 mL) and EtOH (1.5 mL) in a 10 mL flame-dried flask was added **216d** (290.5 mg, 0.33 mmol) to dissolve it. After through degassing, $NaBH_4$ (63.4 mg, 1.64 mmol, 5 equiv) was added to the solution. CBr_4 (543.3 mg, 1.64 mmol, 5 equiv) was added to the mixture after 2 hours of stirring, and the mixture was stirred for another 2 hours under exposure to air. The mixture was purified via column chromatography, and the product was eluted with eluent: Hex:DCM:EtOAc=20:2:1. The dark green fractions were collected and recrystallized from DCM/pentane to give dark green block crystal **218** (203.0 mg, 64%). The structure of the complex was tentatively assigned by X-ray crystallography, but further characterization was not performed.

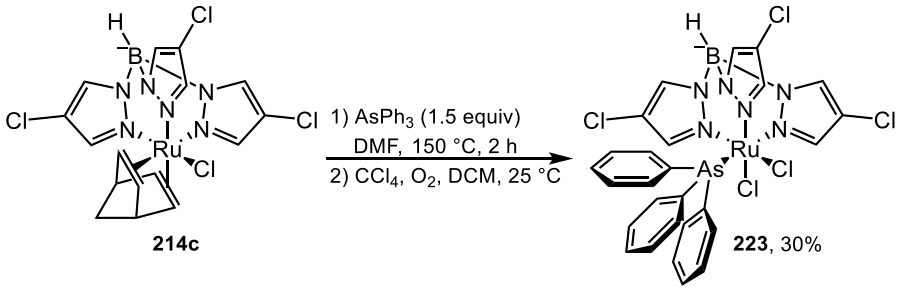
$Tp^{Br}RuPPh_3ClBr$ 221



A flame dried 10 mL Shlenk flask was charged with **214d** (297.3 mg, 0.44 mmol) under inert atmosphere. PPh_3 (114.6 mg, 0.44 mmol, 1 equiv), and degassed DMF (4.0 mL) were added to the flask. The mixture was stirred at 150 °C for 2 hours. The solvent was removed under vacuum at room temperature. CBr_4 (543.0 mg, 1.64 mmol, 4 equiv) and DCM (3 mL) was added to the residue, and the solution was stirred overnight under

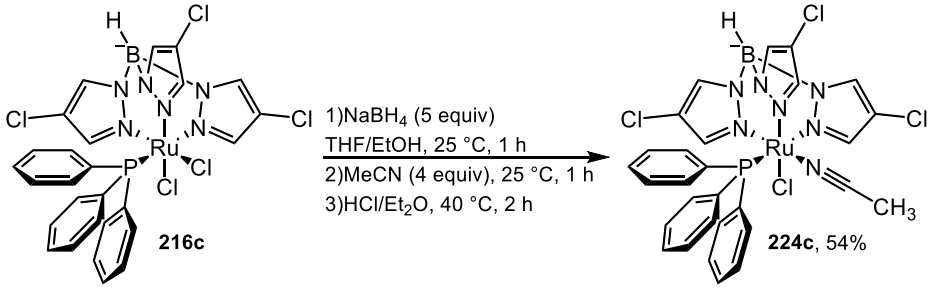
air. The mixture was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 20:2:1. The red fractions were collected and recrystallized from DCM/pentane to give purple crystal **221** (245.4 mg, 74% yield).

$Tp^{Cl}RuAsPh_3Cl_2$ 223



To a flame-dried 10 mL Schlenk flask were added **214c** (238.6 mg, 0.44 mmol) and $AsPh_3$ (200.6 mg, 0.66 mmol, 1.5 equiv). DMF (4.0 mL) was added to the flask, and the suspension was slowly heated to 150 °C. The temperature was maintained for 2 h. The mixture was then cooled to room temperature, and the solvent as removed under vacuum. CCl_4 (1 mL) and DCM (3 mL) were added to the flask. After overnight, the mixture was purified via column chromatography, and the product was eluted with Hex:DCM:EtOAc = 20:2:1. The red fractions were collected and recrystallized from DCM/pentane to give dark red needles **223** (103.9 mg, 30% yield)

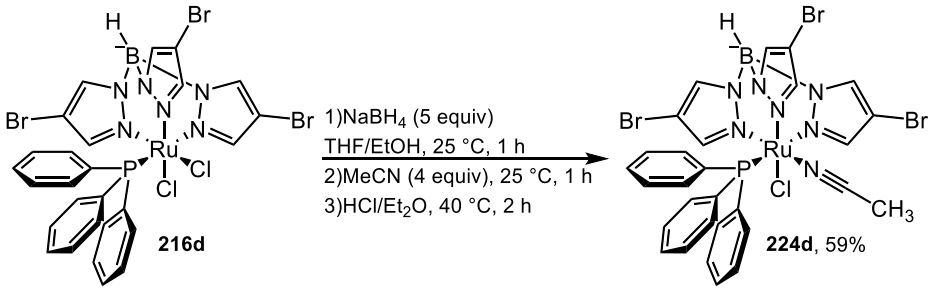
$Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c



A flame dried 50 mL Shlenk flask was charged with **216c** (358.4 mg, 0.46 mmol) under argon flow. Tetrahydrofuran (12 mL) and ethanol (2 mol) were added to the flask to dissolve the crystal. After through degassing, sodium borohydride (90.6 mg, 2.4 mmol, 5.0

equiv) was added to the solution, and the mixture was stirred for an hour. Acetonitrile (0.1 mL) was added to the flask, and the mixture was stirred for another one hour. 2M Hydrochloric acid in ether (3.6 mL, 7.2 mmol) was added to the mixture, and the mixture was heated to 40 °C. The mixture was stirred for another 2 hours and the volatile was removed under vacuum. The residue was dissolved in DCM (30 mL) and sonicated. The suspension was filtered through Celite into a 100 mL Shlenk flask, and additional DCM was poured onto the Celite to rinse off the product. The volume of the filtrate was reduced to about 10 mL, and degassed pentane (90 mL) was mounted to the top of the DCM layer. The layer was partitioned for 2 days, and the supernatant was disposed. The stained crystal was recrystallized again to form light yellow crystal **224c** (201.8 mg, 54%). ^{1}H-NMR (500 MHz, chloroform-d) δ 7.98 (s, 1H), 7.57 (d, J = 5.7 Hz, 3H), 7.47-7.21 (m, 15H), 6.62 (s, 1H), 6.26 (s, 1H), 4.20 (s, 1H), 2.25 (s, 3H). ^{13}C-NMR (500 MHz, chloroform-d) δ 5.1, 109.6, 109.8, 110.3 (*d*, $J_{C\text{-}P}$=20 Hz), 123, 128.3-128.4 (*t*, $J_{C\text{-}P}$=34.5 Hz), 130, 133.4, 133.7, 134.0, 134.6-134.7 (*d*, $J_{C\text{-}P}$=39 Hz), 141.0, 144.0, 144.9 ^{31}P-NMR (400 MHz, chloroform-d) δ 49.4. $H_{25}C_{29}N_7BPCl_4Ru$-0.25CH_2Cl_2 (777.47 g/mol): H, 3.31; C, 45.19; N, 12.61; Cl, 20.52; Found: H, 3.33; C, 44.96; N, 12.45; Cl, 20.34.

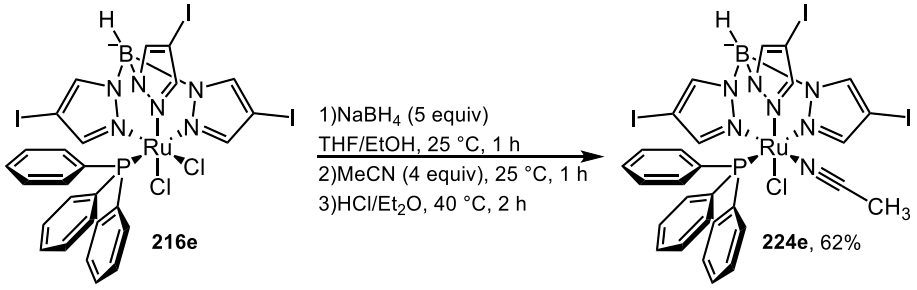
Tp^{Br}RuPPh$_3$(MeCN)Cl 224d



A flame dried 50 mL Shlenk flask was charged with **216d** (425.5 mg, 0.46 mmol) under argon flow. Tetrahydrofuran (12 mL) and ethanol (2 mL) were added to the flask to dissolve the crystal. After through degassing, sodium borohydride (90.6 mg, 2.4 mmol, 5.0 equiv) was added to the solution, and the mixture was stirred for an hour. Acetonitrile (0.1

mL) was added to the flask, and the mixture was stirred for another one hour. 2M Hydrochloric acid in ether (3.6 mL, 7.2 mmol) was added to the mixture, and the mixture was heated to 40 °C. The mixture was stirred for another 2 hours and the volatile was removed under vacuum. The residue was dissolved in DCM (30 mL) and sonicated. The suspension was filtered through Celite into a 100 mL Shlenk flask, and additional DCM was poured onto the Celite to rinse off the product. The volume of the filtrate was reduced to about 20 mL, and degassed pentane (80 mL) was mounted to the top of the DCM layer. The layer was partitioned for 2 days, and the supernatant was disposed. The stained crystal was recrystallized again to form light yellow crystal **224d** (253.8 mg, 59%). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.00 (s, 1H), 7.60 (d, J = 5.7 Hz, 3H), 7.52-7.04 (m, 15H), 6.60 (s, 1H), 6.22 (s, 1H), 4.31 (s, 1H), 2.26 (s, 3H). ^{13}C-NMR (500 MHz, chloroform-d) δ 5.2, 92.4, 92.8, 93.4, 123.1, 128.3 (*d*, J_{C-P}=39 Hz), 130, 133.6, 133.9, 134.7 (*d*, J_{C-P}=39 Hz), 135.6, 137 (*d*, J_{C-P}=19.5 Hz), 142.9, 146, 146. ^{31}P-NMR (400 MHz, chloroform-d) δ 49.3. $H_{25}C_{29}N_7BPClBr_3Ru$-0.1($CH_2Cl_2$) (889.60 g/mol): H, 2.82; C, 38.92; N, 10.92; Cl, 4.73; Br, 26.69; Found: H, 2.88; C, 38.80; N, 10.79; Cl, 4.84; Br, 26.39.

Tp^{I}RuPPh$_3$(MeCN)Cl 224e



A flame dried 50 mL Shlenk flask was charged with **216e** (425.5 mg, 0.46 mmol) under argon flow. Tetrahydrofuran (12 mL) and ethanol (2 mL) were added to the flask to dissolve the crystal. After through degassing, sodium borohydride (90.6 mg, 2.4 mmol, 5.0 equiv) was added to the solution, and the mixture was stirred for an hour. Acetonitrile (0.1

mL) was added to the flask, and the mixture was stirred for another one hour. 2M Hydrochloric acid in ether (3.6 mL, 7.2 mmol) was added to the mixture, and the mixture was heated to 40 °C. The mixture was stirred for another 2 hours and the volatile was removed under vacuum. The residue was dissolved in DCM (30 mL) and sonicated. The mixture was purified via neutral alumina column chromatography, and eluted with Hex:DCM:EtOAc=6:2:1 (332.8 mg, 62%). The yellow fractions were collected through glass frit into 500 mL round-bottom flask, and the solvent was removed from the filtrate under reduced pressure. Any orange precipitate on the glass frit was rinsed with copious amount of DCM into the receiver flask to combine with the previous filtrate. The volume of DCM solution was reduced to about 5 to 10 % of the volume of the flask, and pentane was poured through the glass frit into the DCM solution to fill about 80% of the flask. The mixture was stirred with rotavap for 10 minutes, and the precipitate was collected on another glass frit. The precipitate was rinsed with DCM (3 to 4 mL) dried under vacuum to give beige precipitate **224e** (332.8 mg, 62%). ^{1}H-NMR (500 MHz, chloroform-d) δ 8.03 (s, 1H), 7.63 (d, J = 2.3 Hz, 3H), 7.53-7.16 (m, 15H), 6.56 (s, 1H), 6.18 (s, 1H), 4.36 (s, 1H), 2.29 (s, 3H). ^{13}C-NMR (500 MHz, chloroform-d) δ 5.3, 54.9, 55.6, 56.2, 123.1, 128.2-128.3 (*d*, J_{C-P}=39 Hz), 130.0, 133.7, 134.0, 134.6-134.7 (*d*, J_{C-P}=39 Hz), 140.1, 141.5 (*d*, J_{C-P}=24 Hz), 147, 150.1, 151. ^{31}P-NMR (400 MHz, chloroform-d) δ 49.0. $H_{25}C_{29}N_7BPClI_3Ru\text{-}CH_2Cl_2$ (1115.50 g/mol): H, 2.44; C, 32.30; N, 8.79; Cl, 9.53; I, 34.13; Found: H, 2.49; C, 32.80; N, 8.67; Cl, 9.60; I, 33.67.

APPENDEX FOUR: NMR Spectra

Ligand exchange reactions of $Tp^{X}Ru(diene)Cl$ to mono- and di-phosphine complexes and their oxidation potentials.

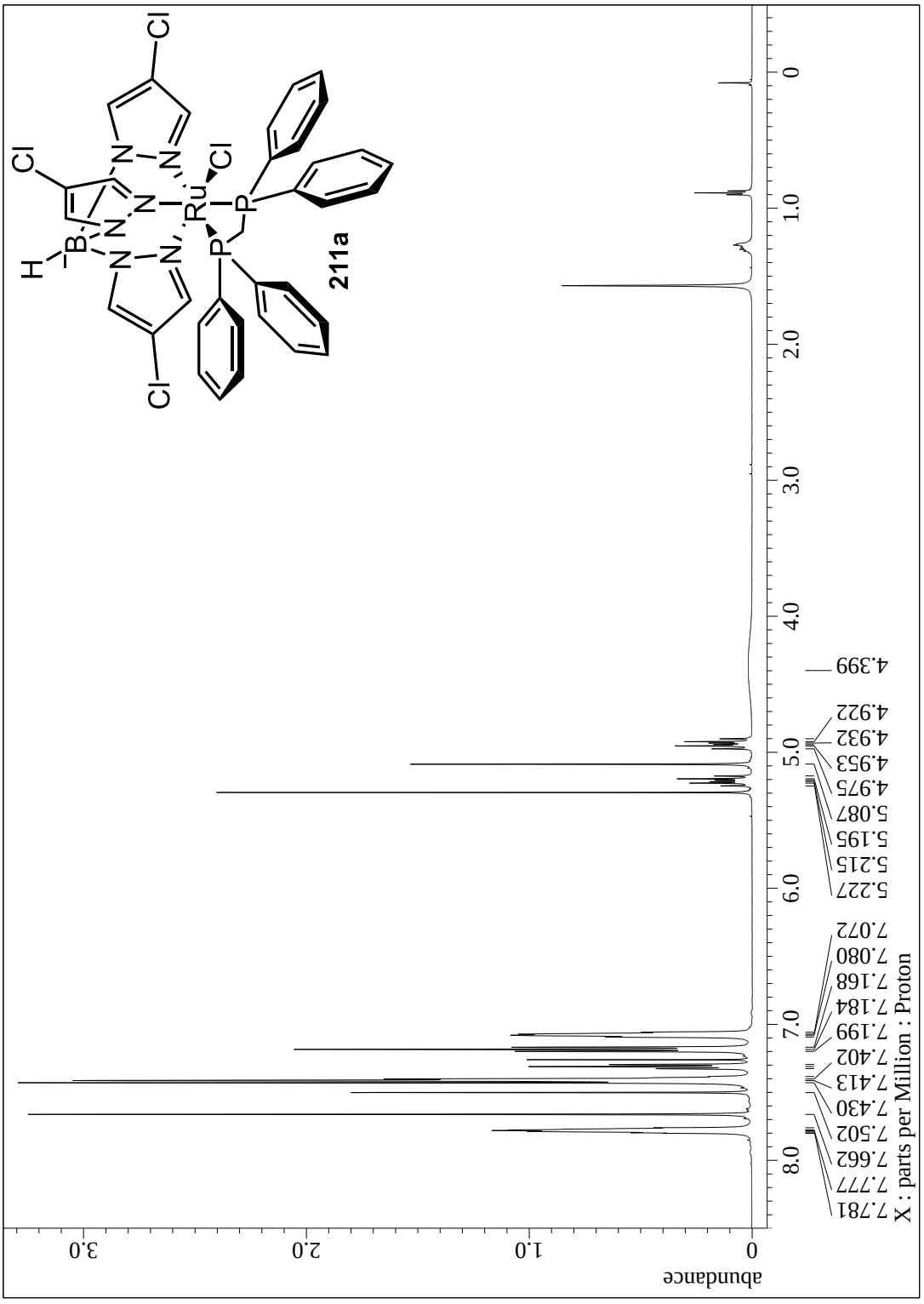


Figure A2.1: ^{1}H-NMR spectrum of 211a (500 MHz, $CDCl_3$)

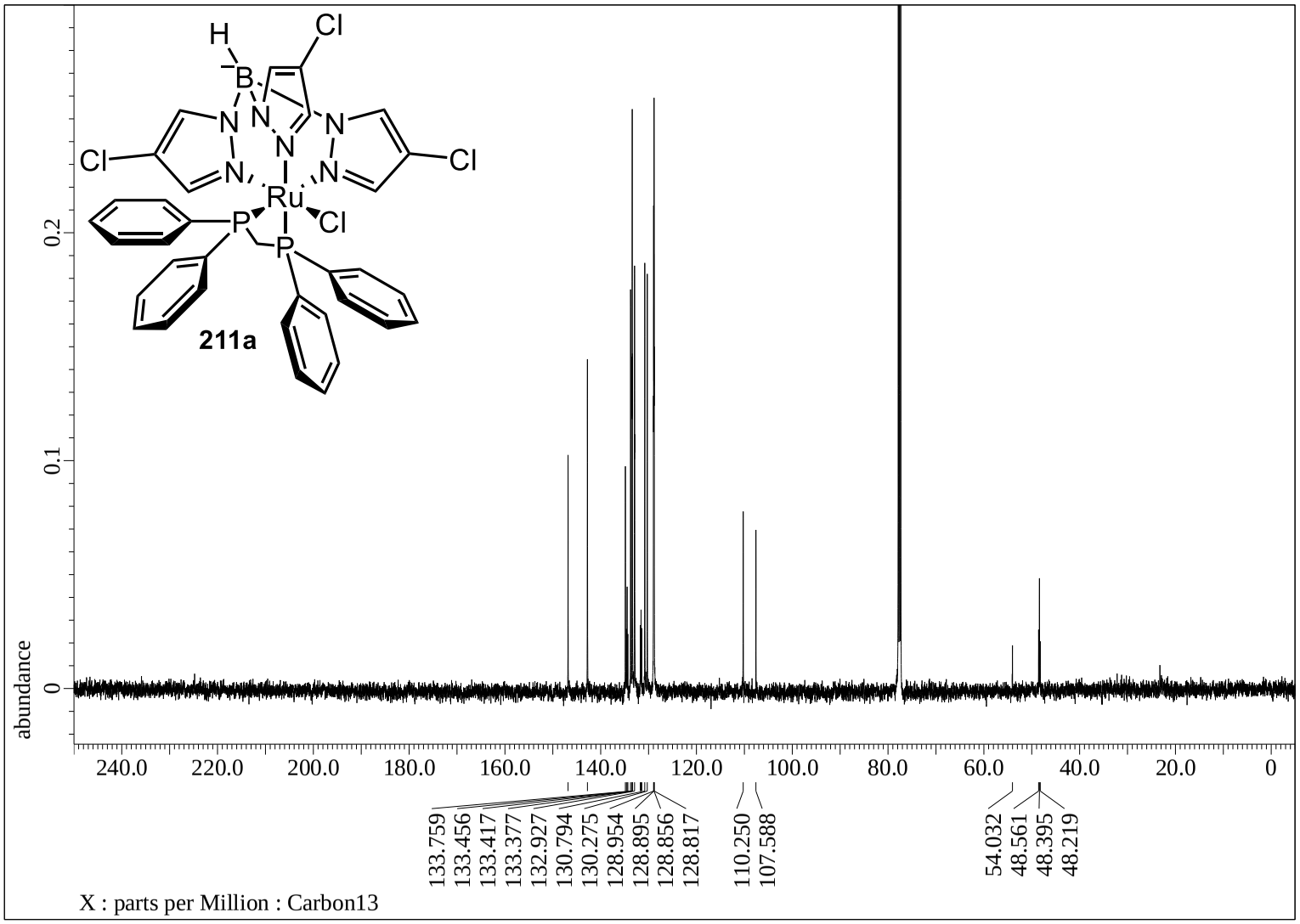


Figure A2.2: ^{13}C-NMR spectrum of 211a (500 MHz, $CDCl_3$)

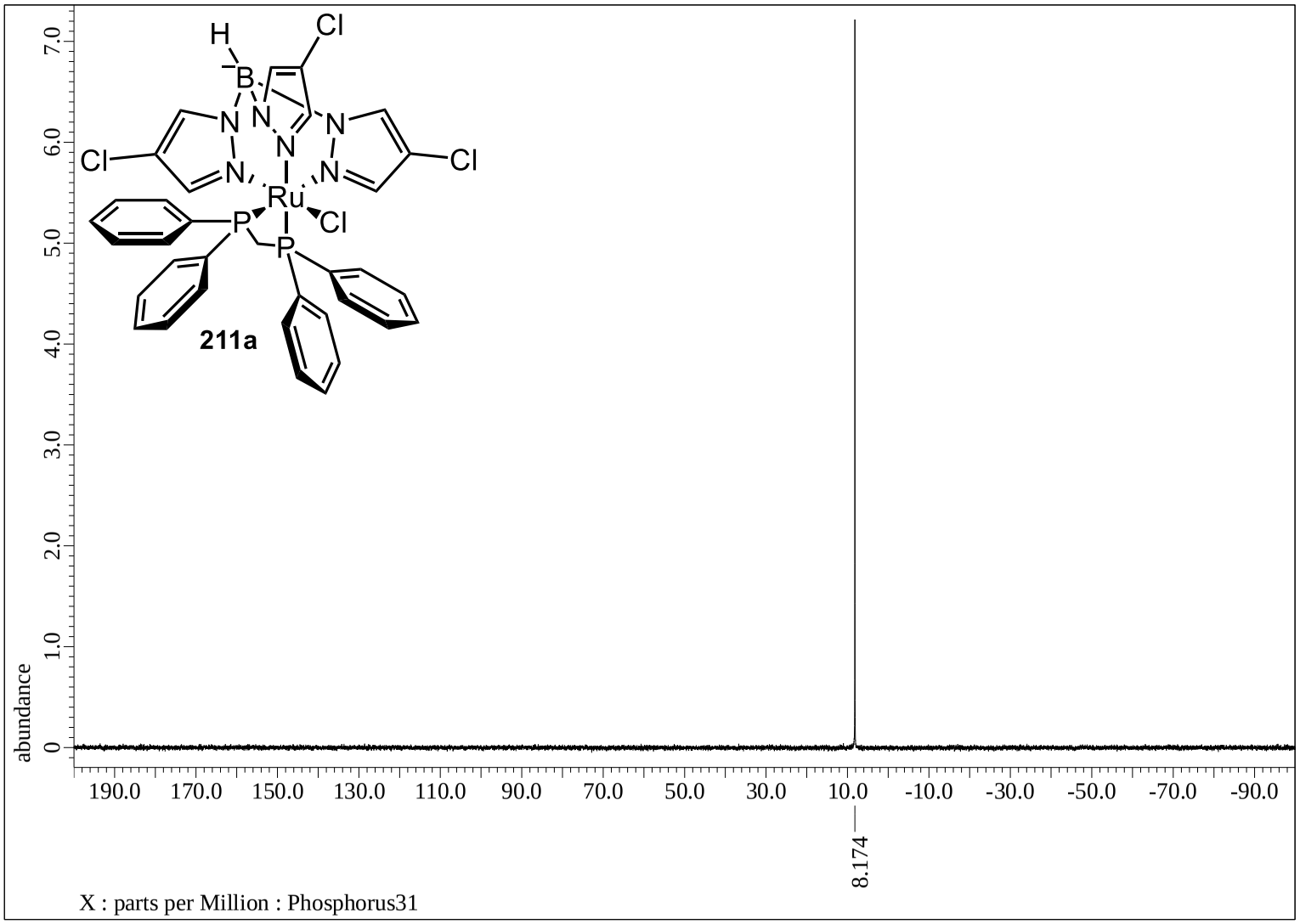


Figure A2.3: ^{31}P-NMR spectrum of 211a (400 MHz, $CDCl_3$)

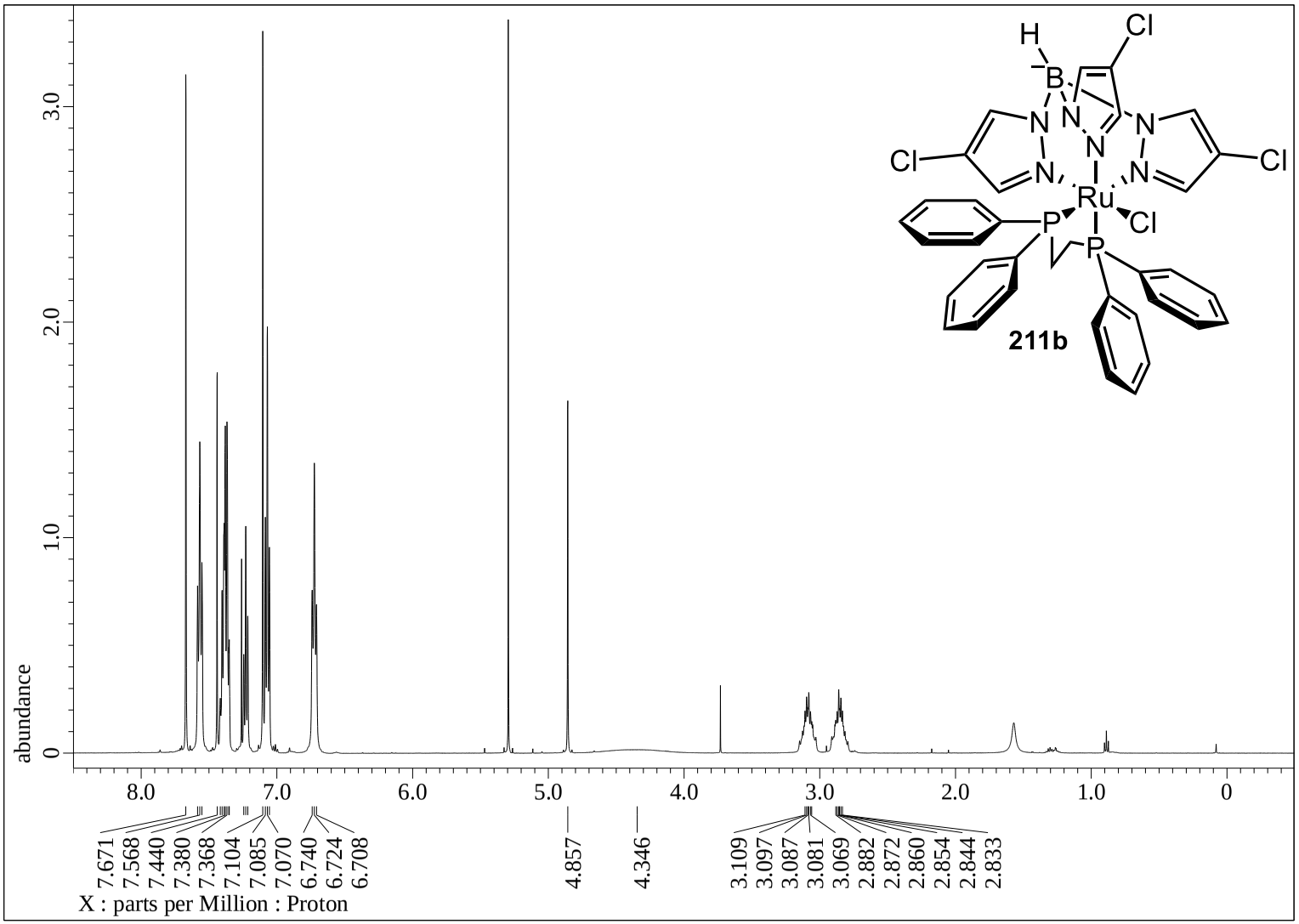


Figure A2.4: ^{1}H-NMR spectrum of 211b (500 MHz, $CDCl_3$)

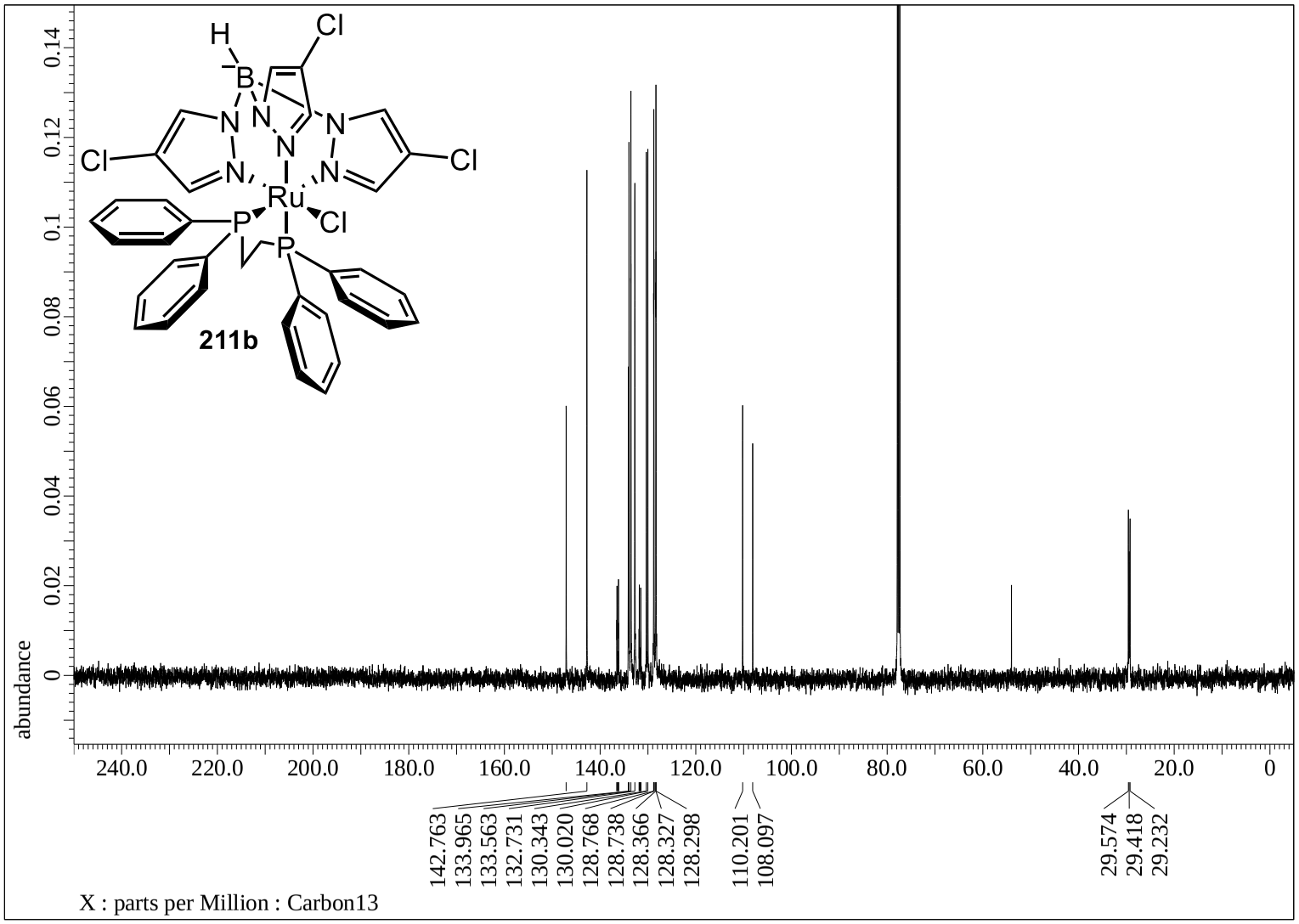


Figure A2.5: ^{13}C-NMR spectrum of 211b (500 MHz, $CDCl_3$)

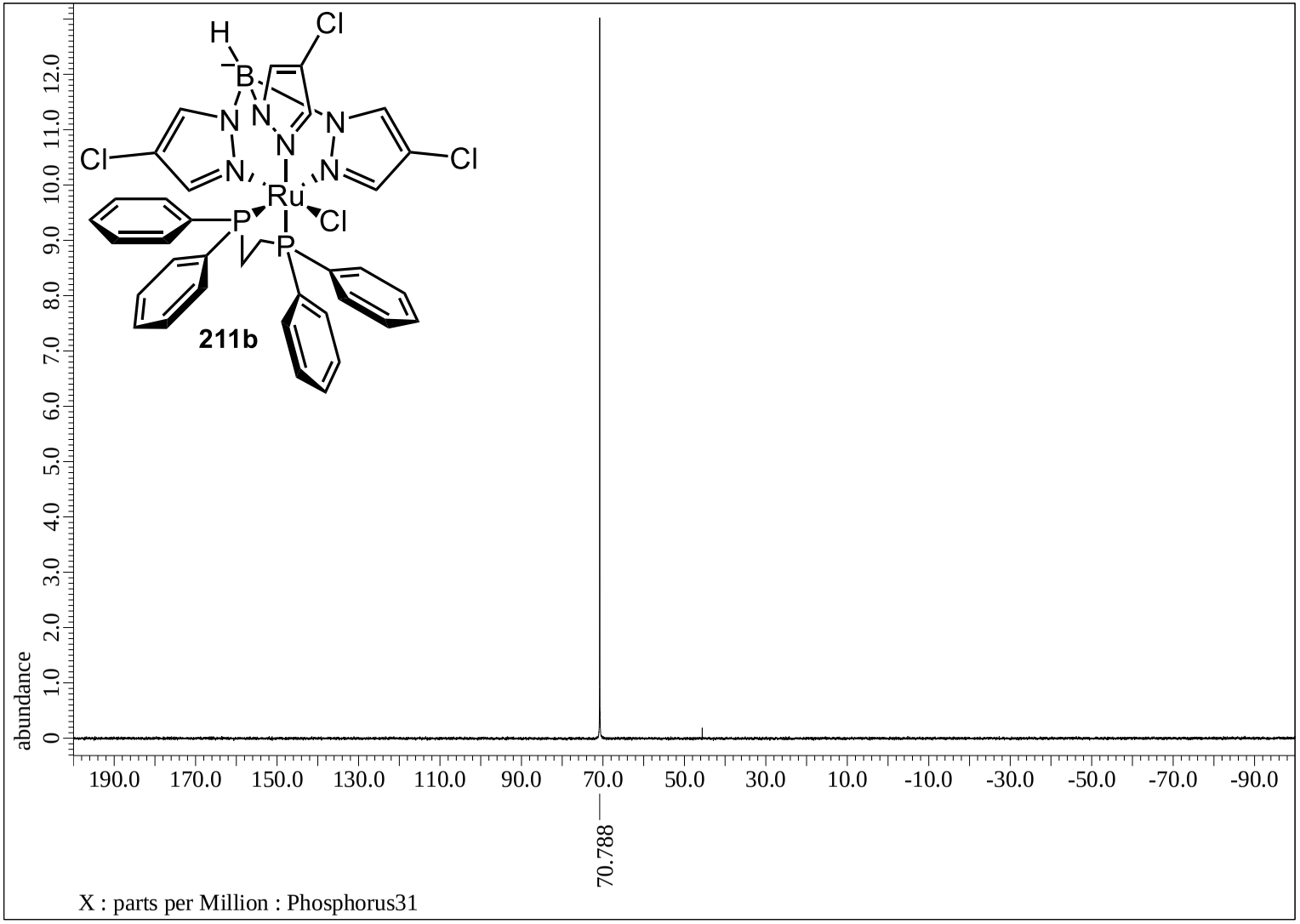


Figure A2.6: ^{31}P-NMR spectrum of 211b (400 MHz, $CDCl_3$)

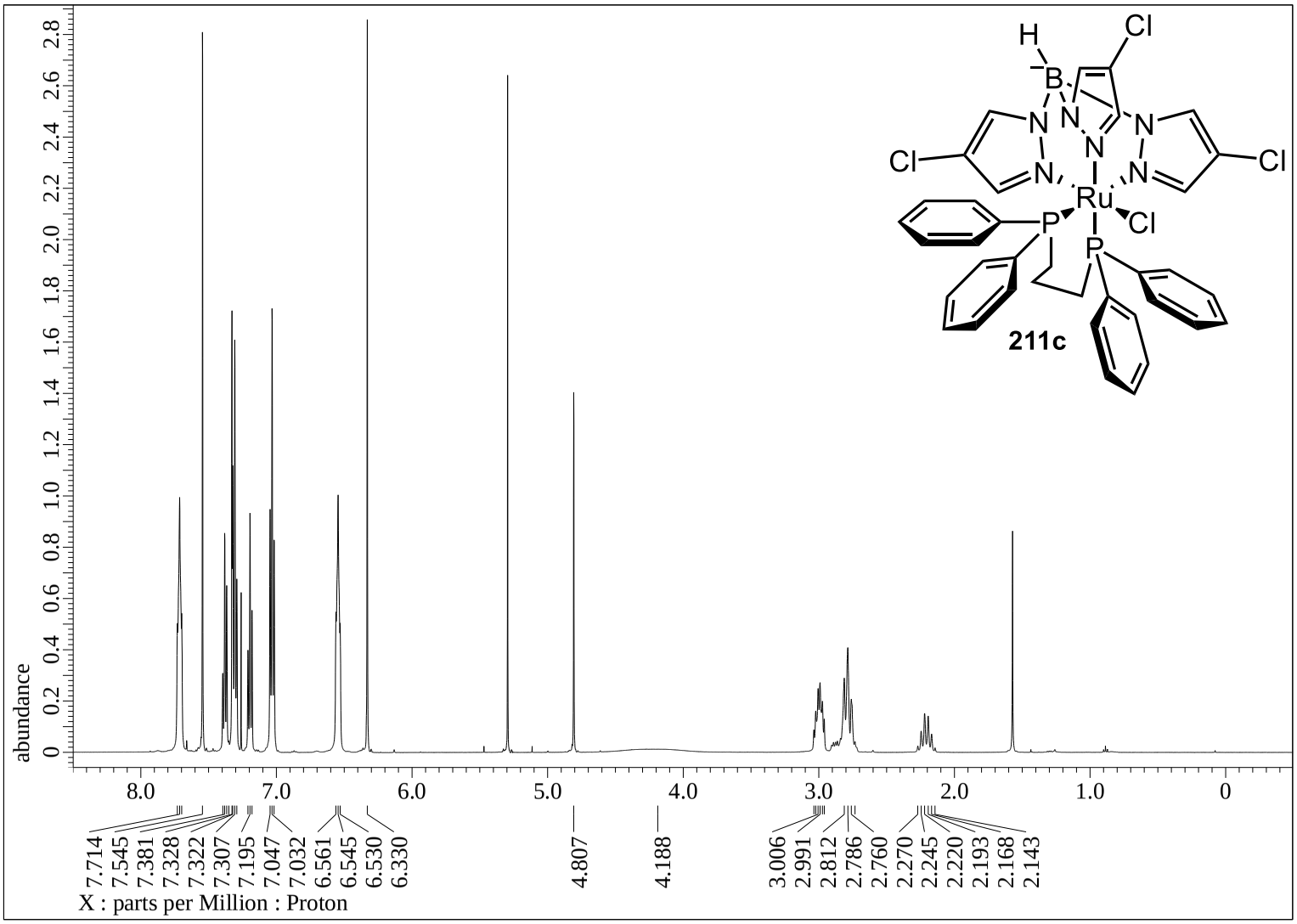


Figure A2.7: ^{1}H-NMR spectrum of 211c (500 MHz, $CDCl_3$)

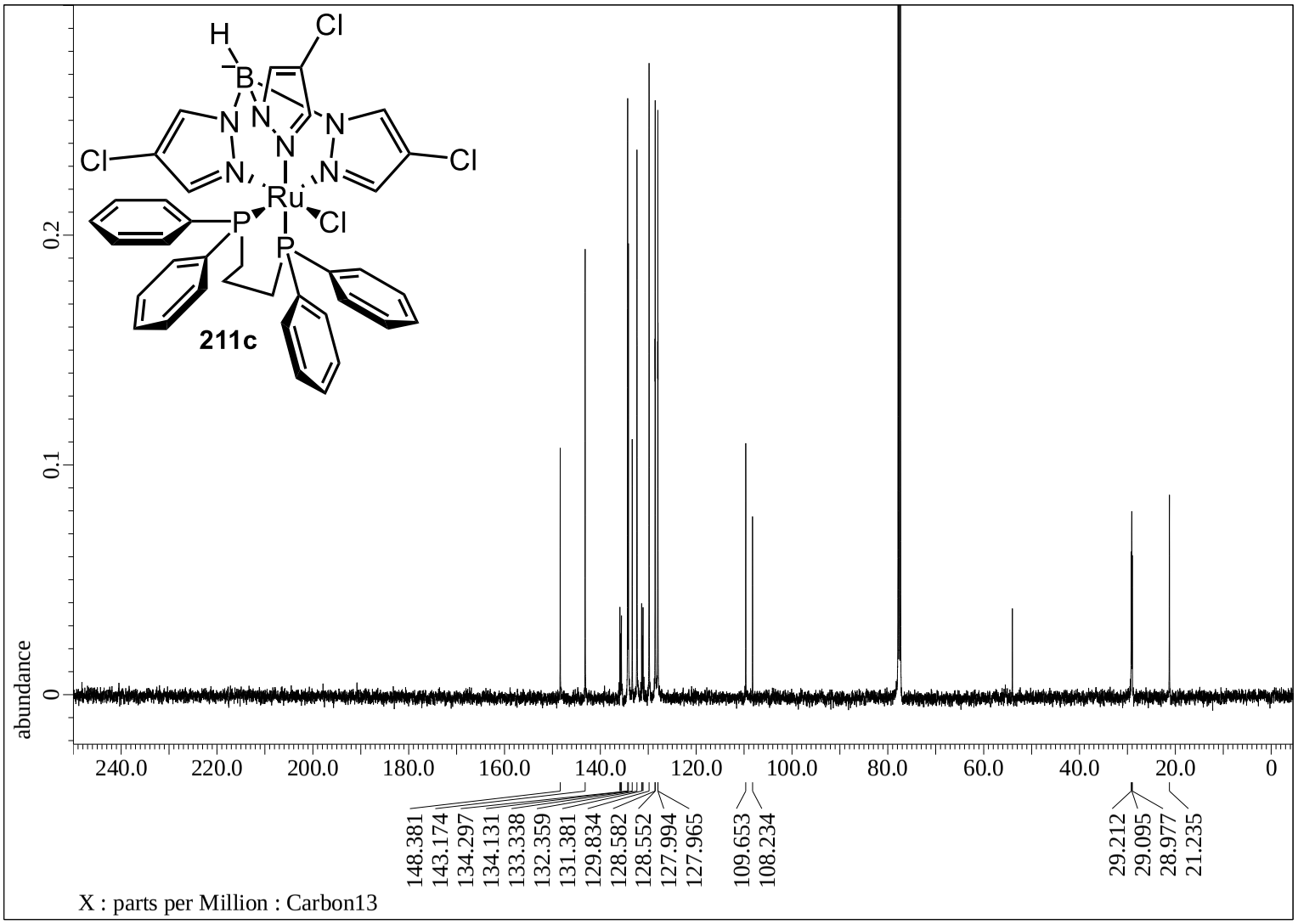


Figure A2.8: ^{13}C-NMR spectrum of 211c (500 MHz, $CDCl_3$)

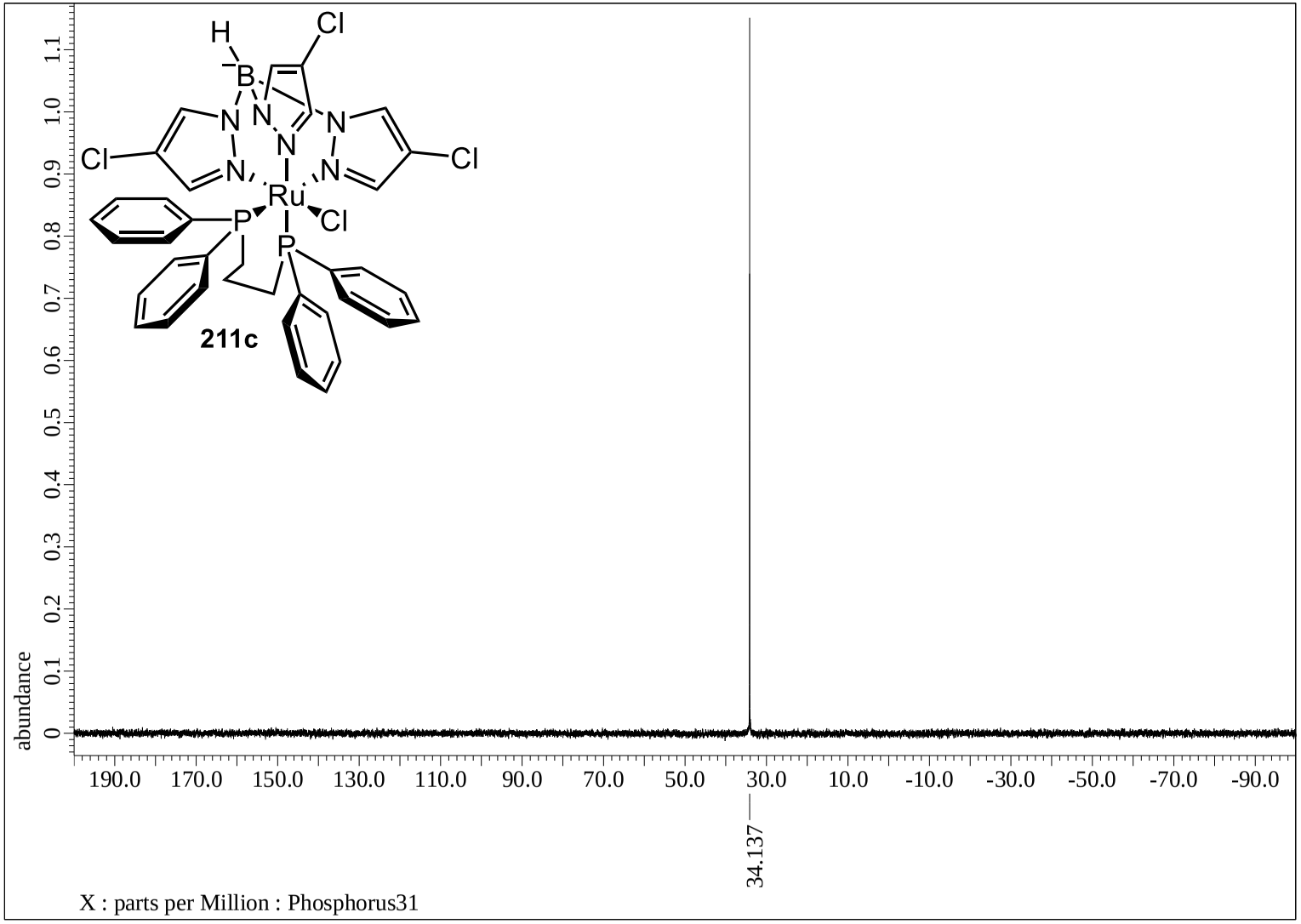


Figure A2.9: ^{31}P-NMR spectrum of 211c (400 MHz, $CDCl_3$)

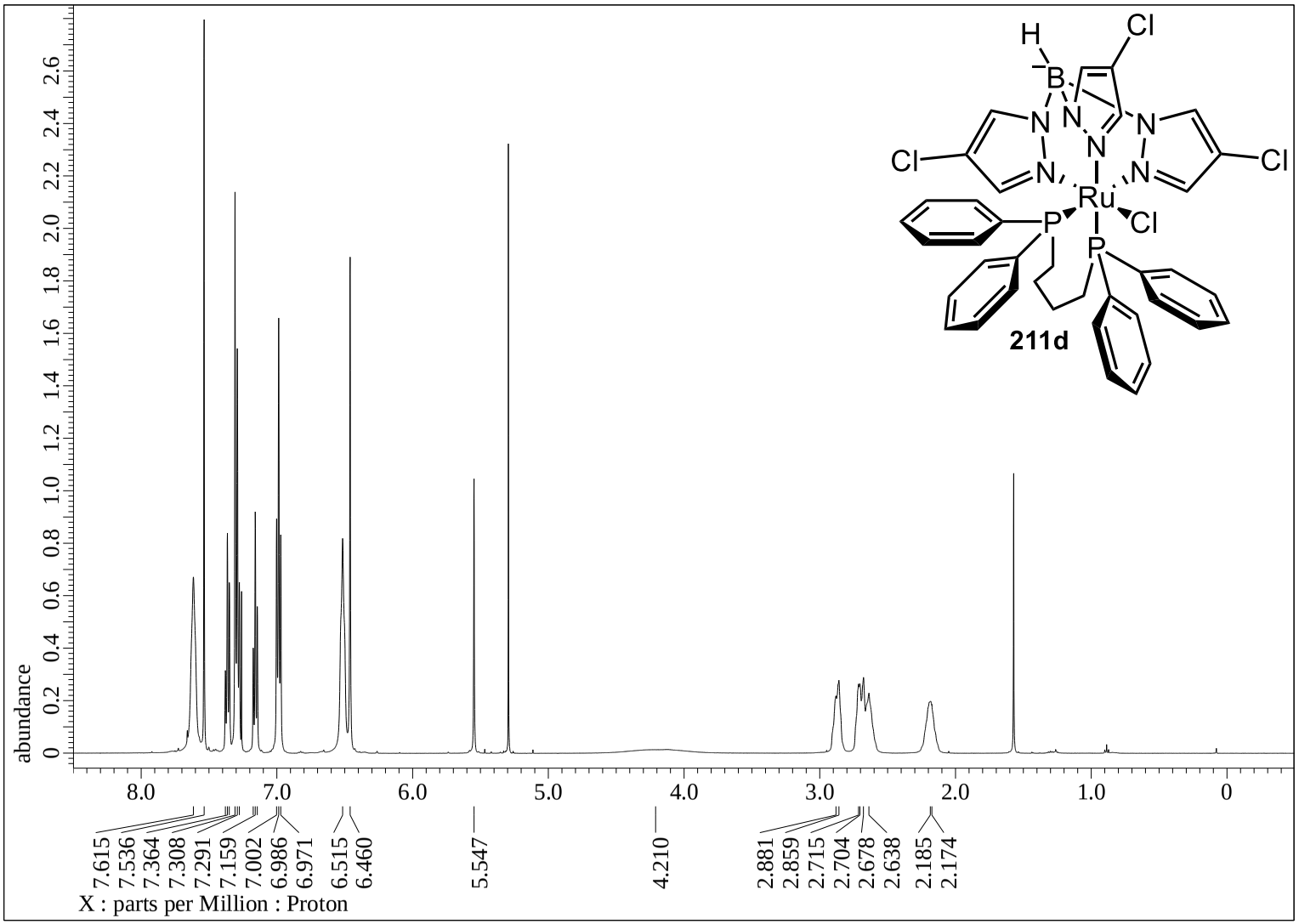


Figure A2.10: ^{1}H-NMR spectrum of 211d (500 MHz, $CDCl_3$)

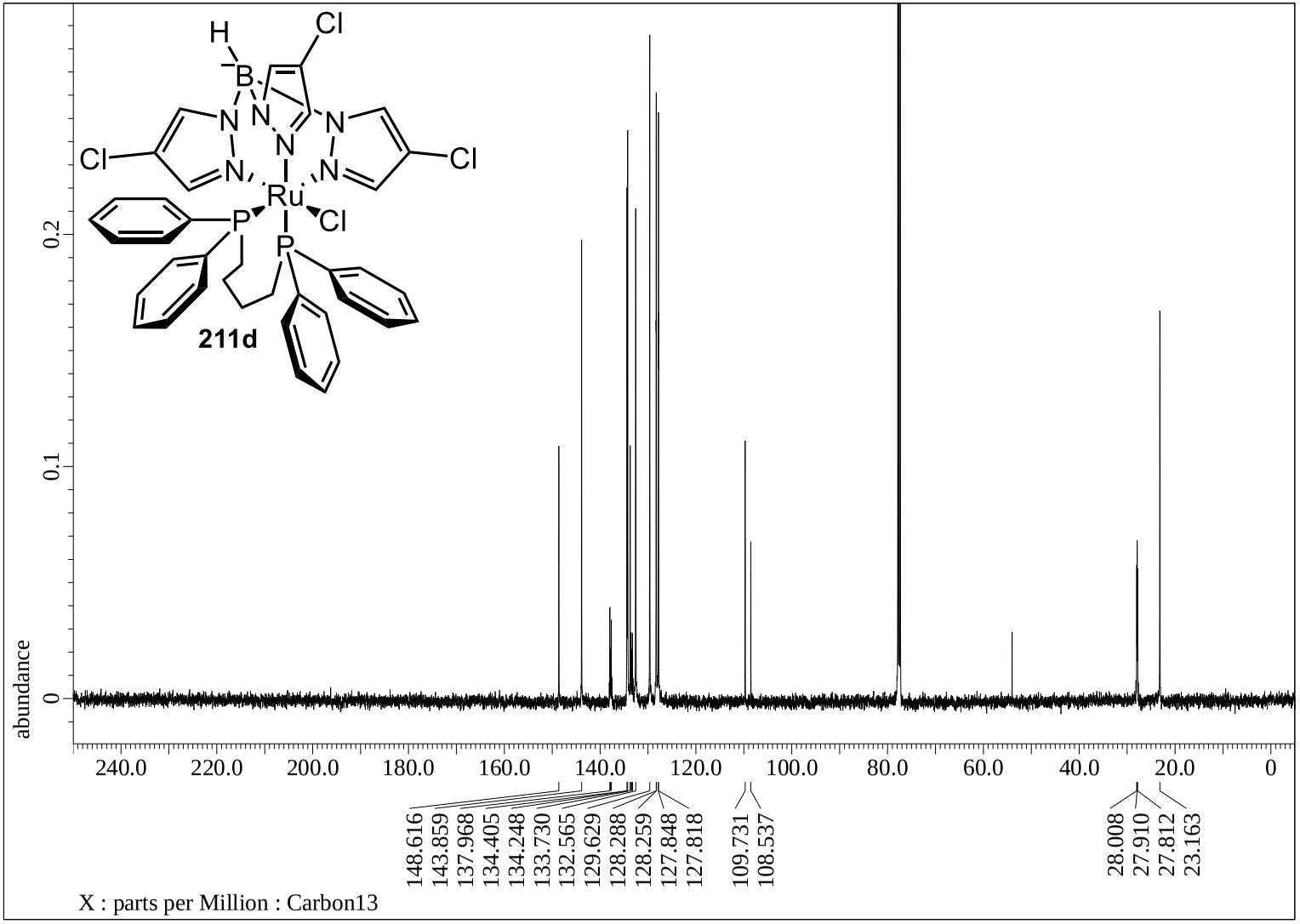


Figure A2.11: ^{13}C-NMR spectrum of 211d (500 MHz, $CDCl_3$)

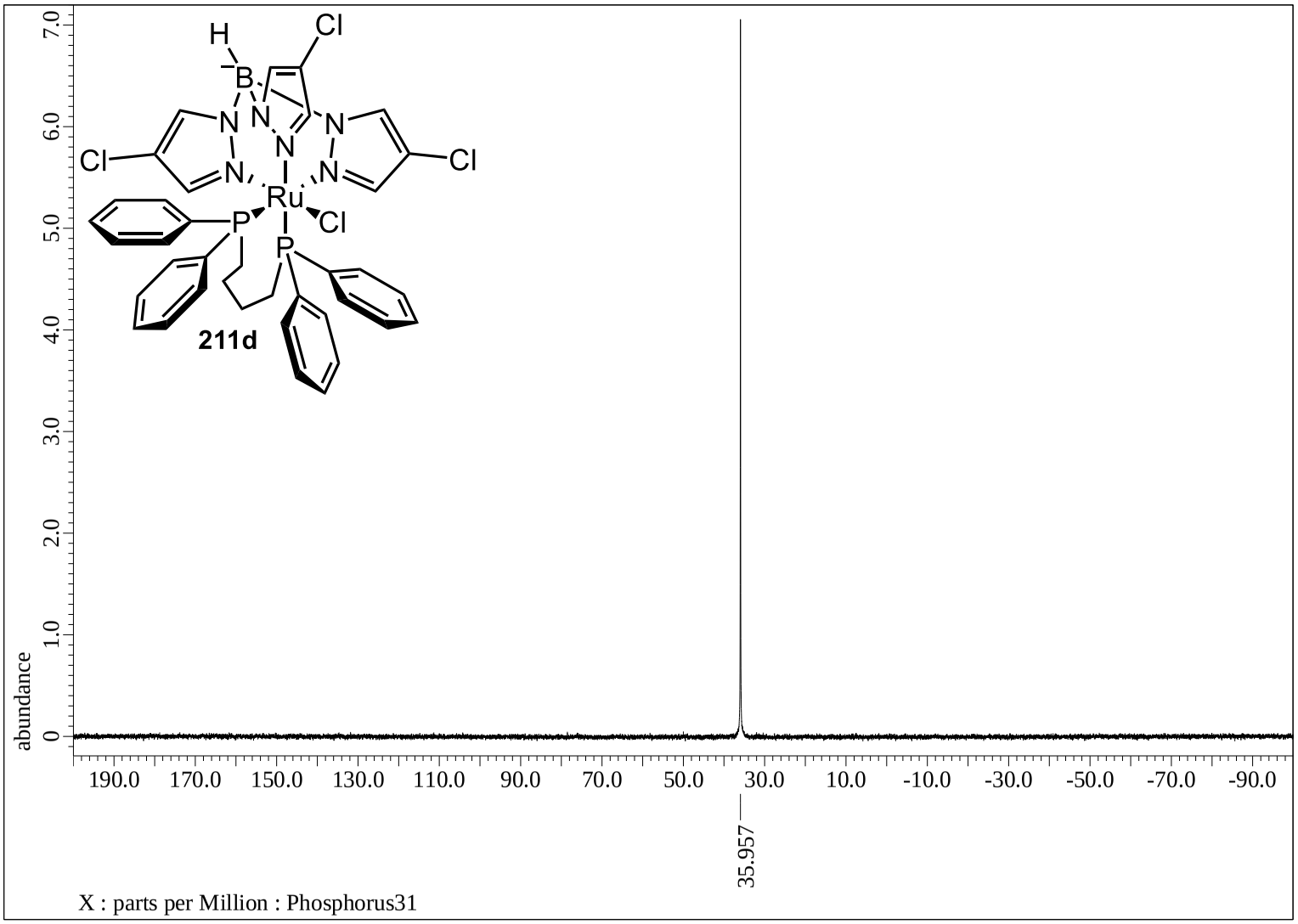


Figure A2.12: ^{31}P-NMR spectrum of 211d (400 MHz, $CDCl_3$)

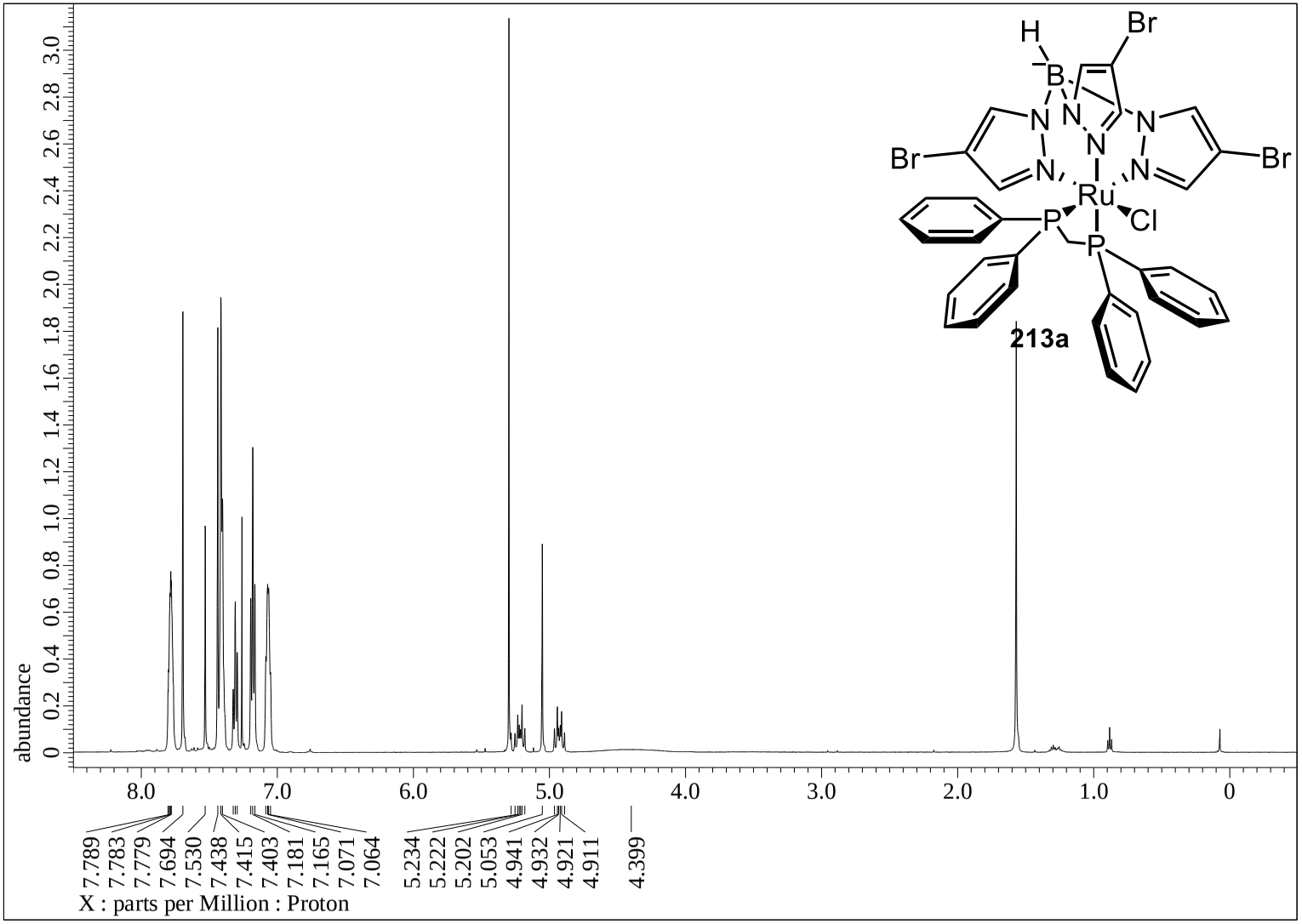


Figure A2.13: ^{1}H-NMR spectrum of 213a (500 MHz, $CDCl_3$)

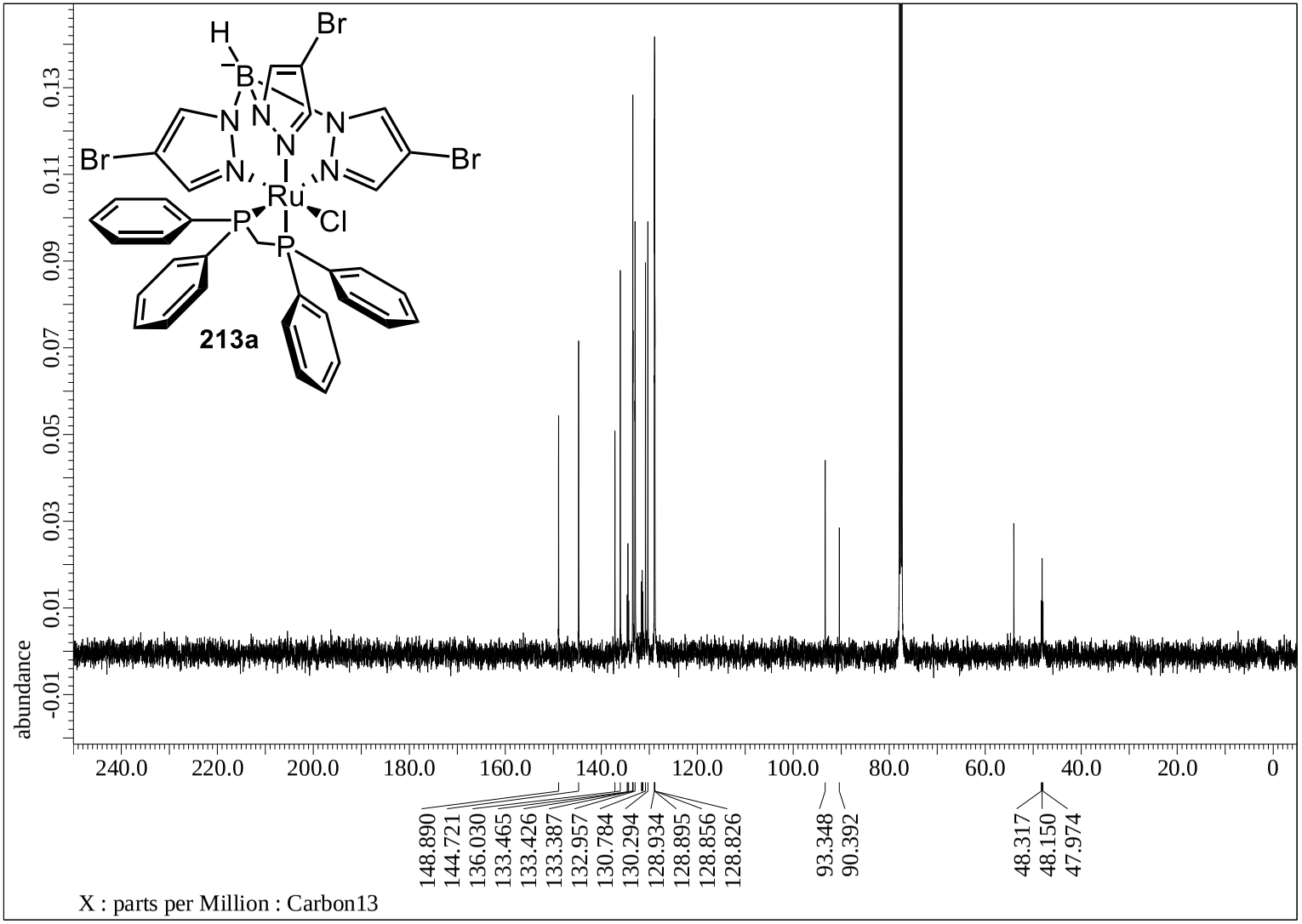


Figure A2.14: ^{13}C-NMR spectrum of 213a (500 MHz, $CDCl_3$)

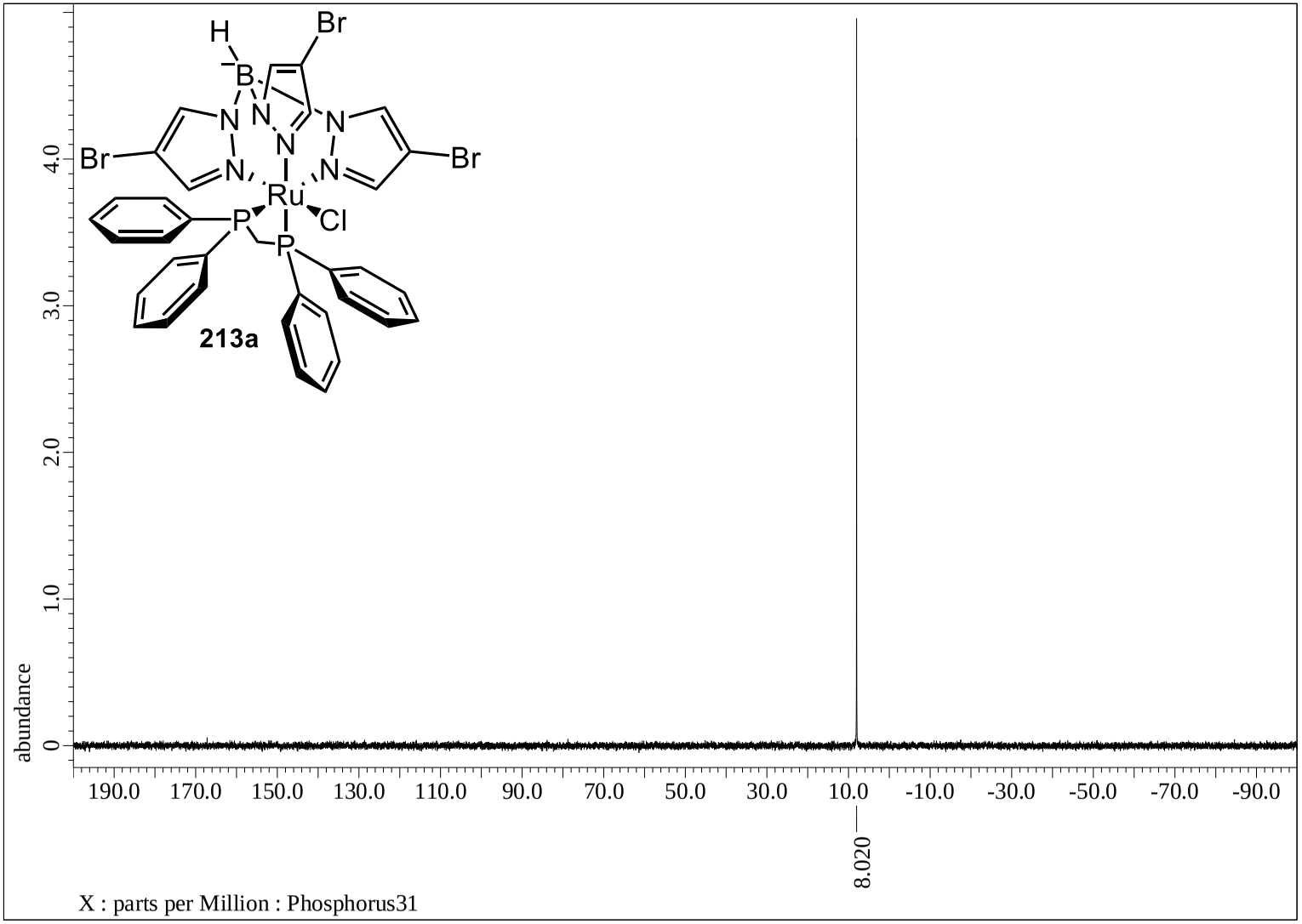


Figure A2.15: ^{31}P-NMR spectrum of 213a (400 MHz, $CDCl_3$)

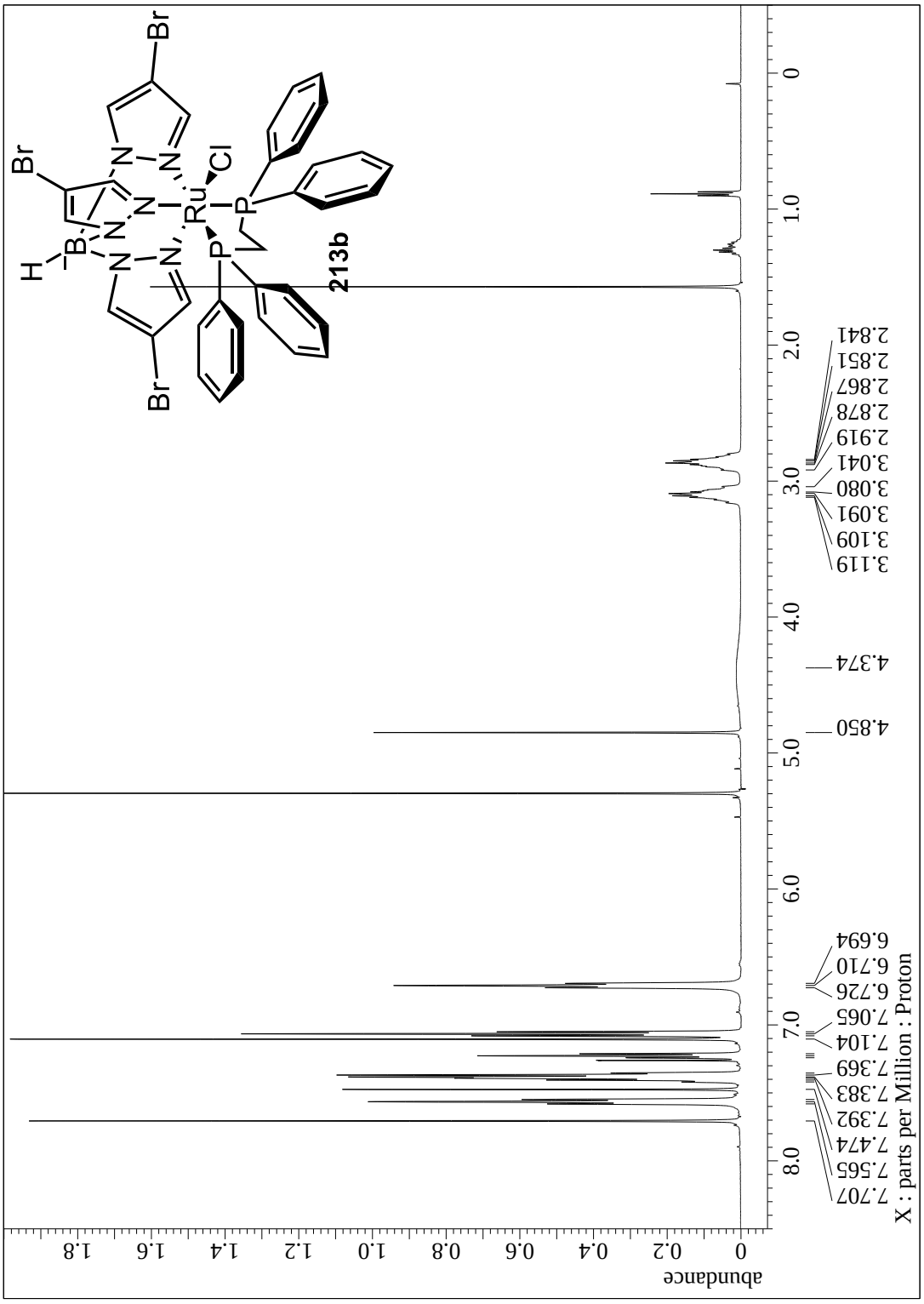


Figure A2.16: ^{1}H-NMR spectrum of 213b (500 MHz, $CDCl_3$)

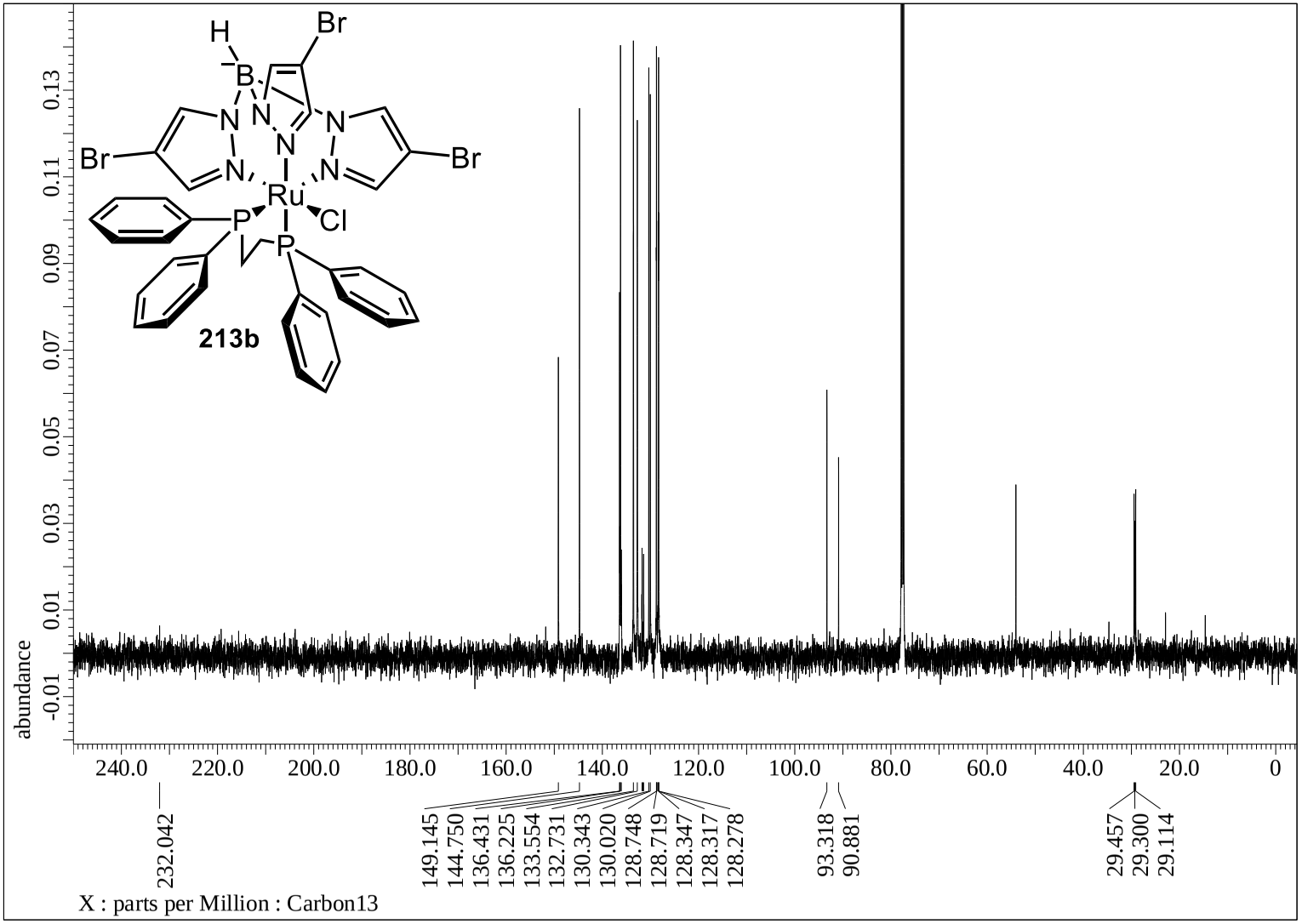


Figure A2.17: ^{13}C-NMR spectrum of 213b (500 MHz, $CDCl_3$)

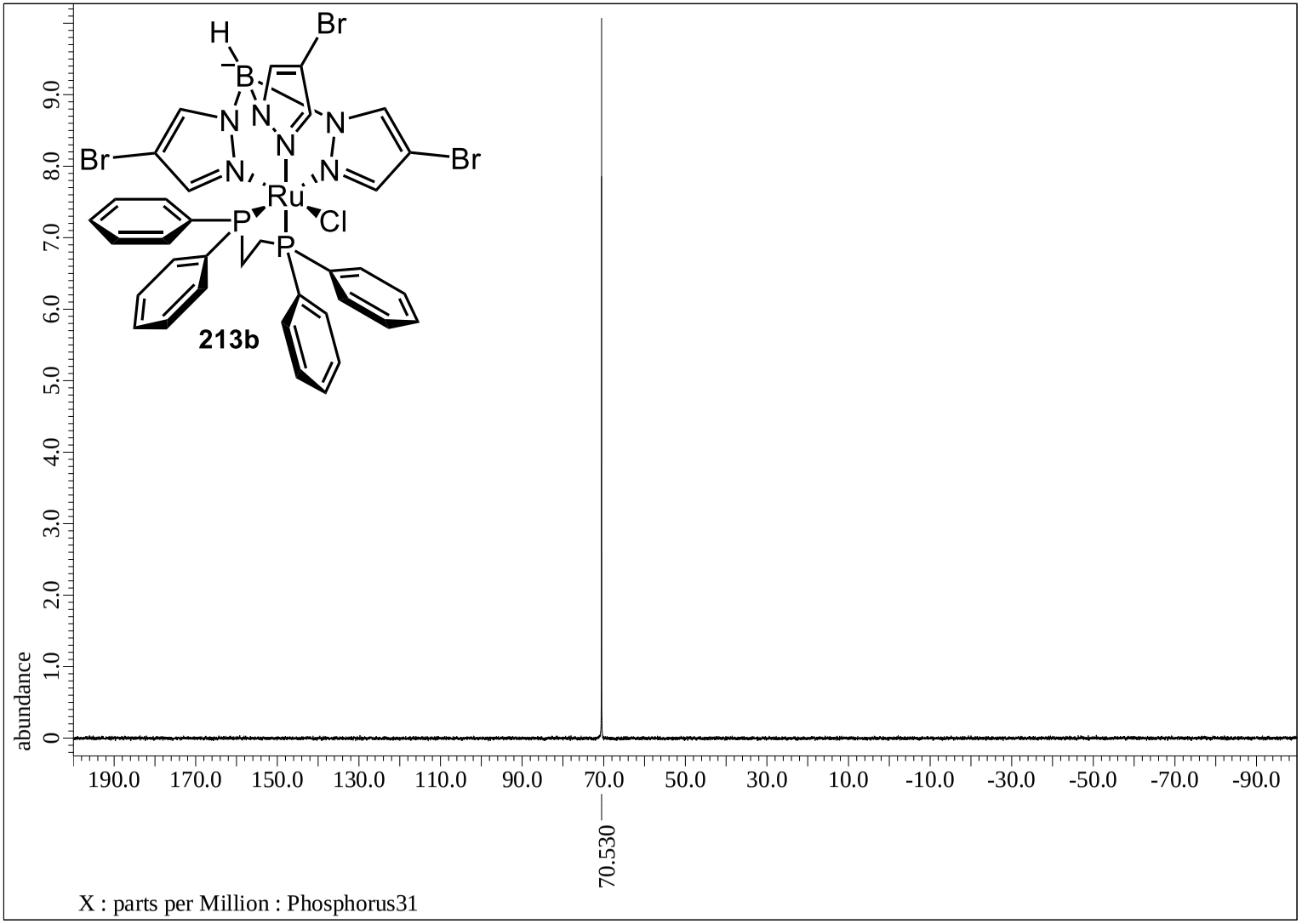


Figure A2.18: ^{31}P-NMR spectrum of 213b (400 MHz, $CDCl_3$)

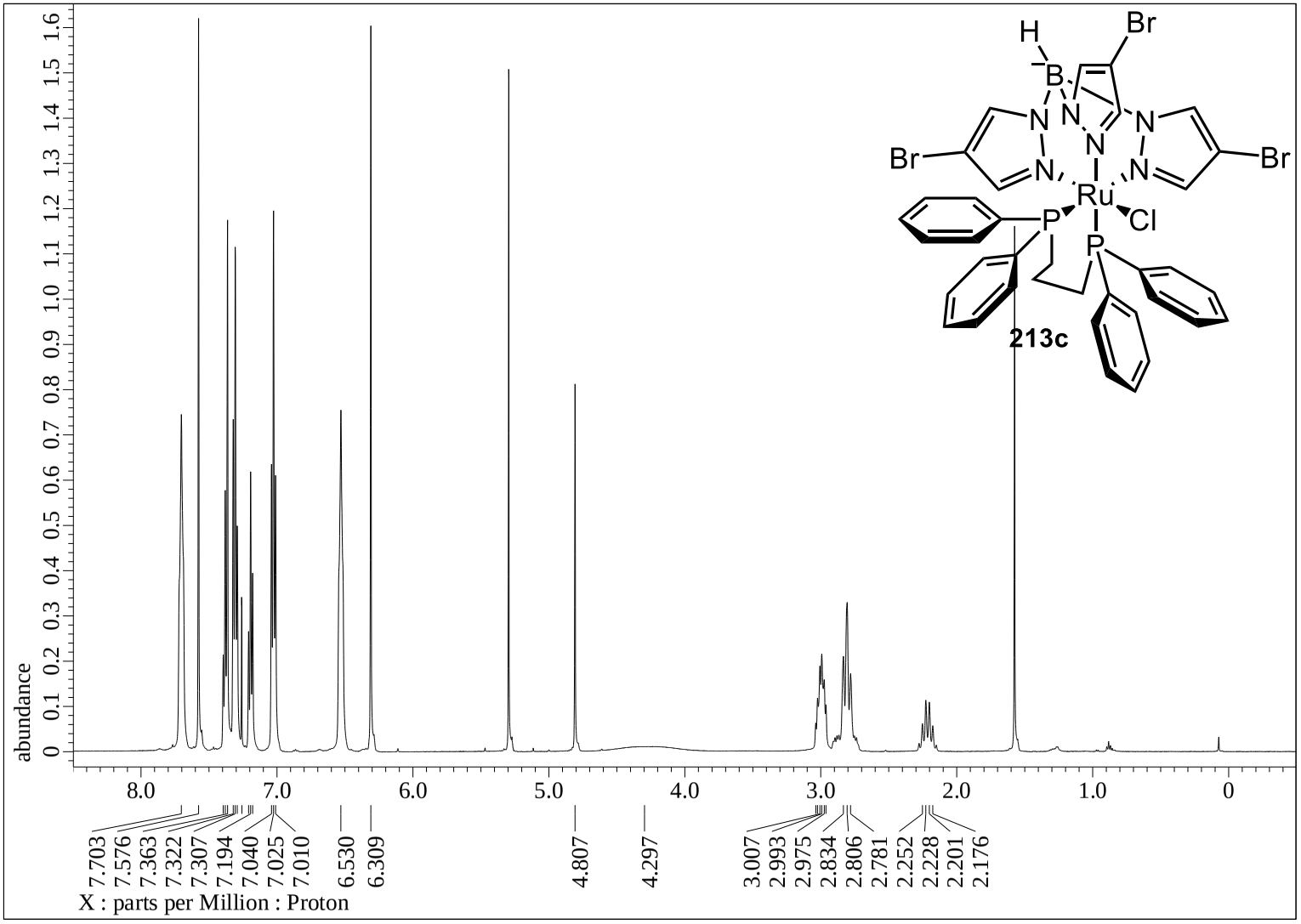


Figure A2.19: ^{1}H-NMR spectrum of 213c (500 MHz, $CDCl_3$)

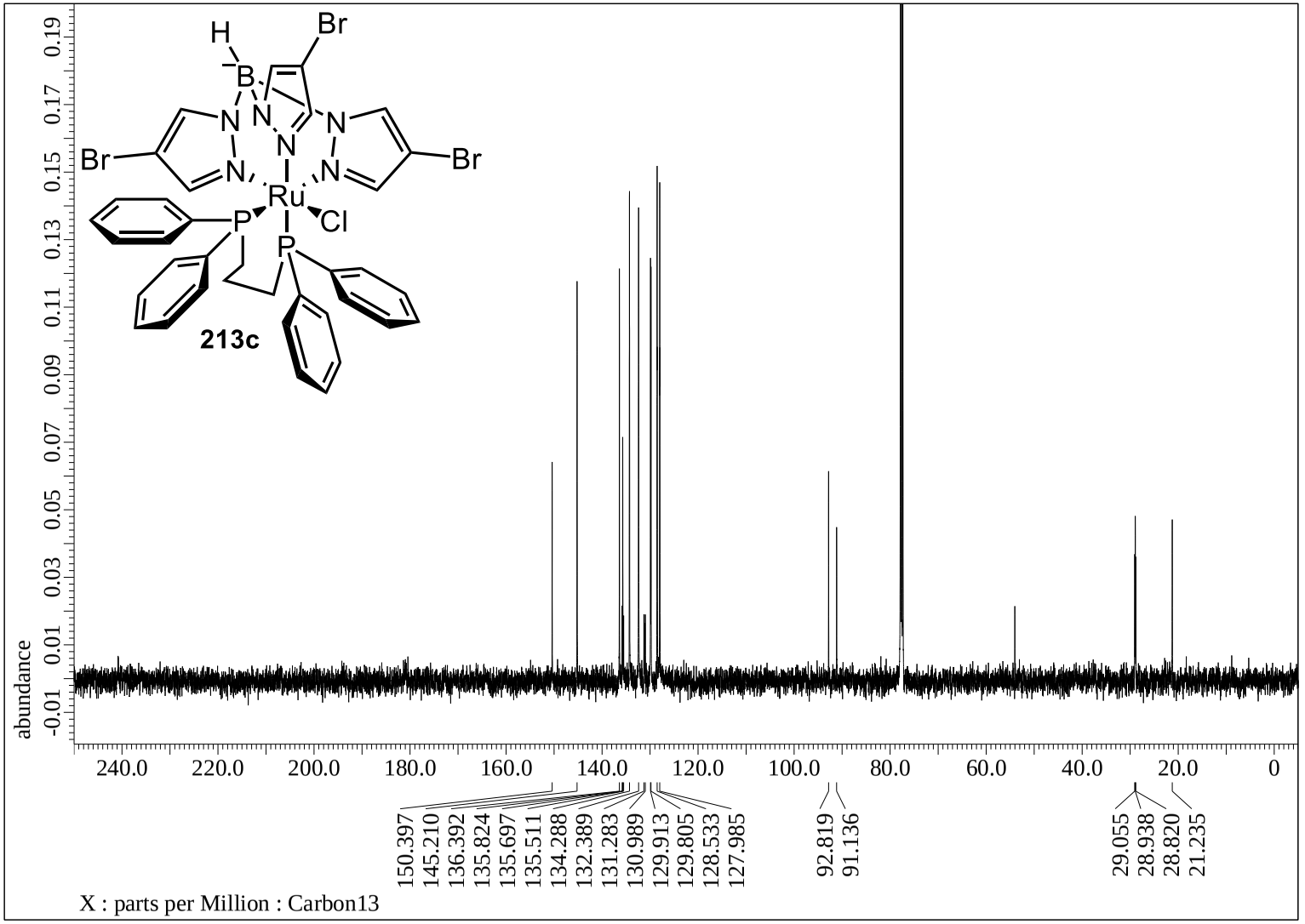


Figure A2.20: ^{13}C-NMR spectrum of 213c (500 MHz, $CDCl_3$)

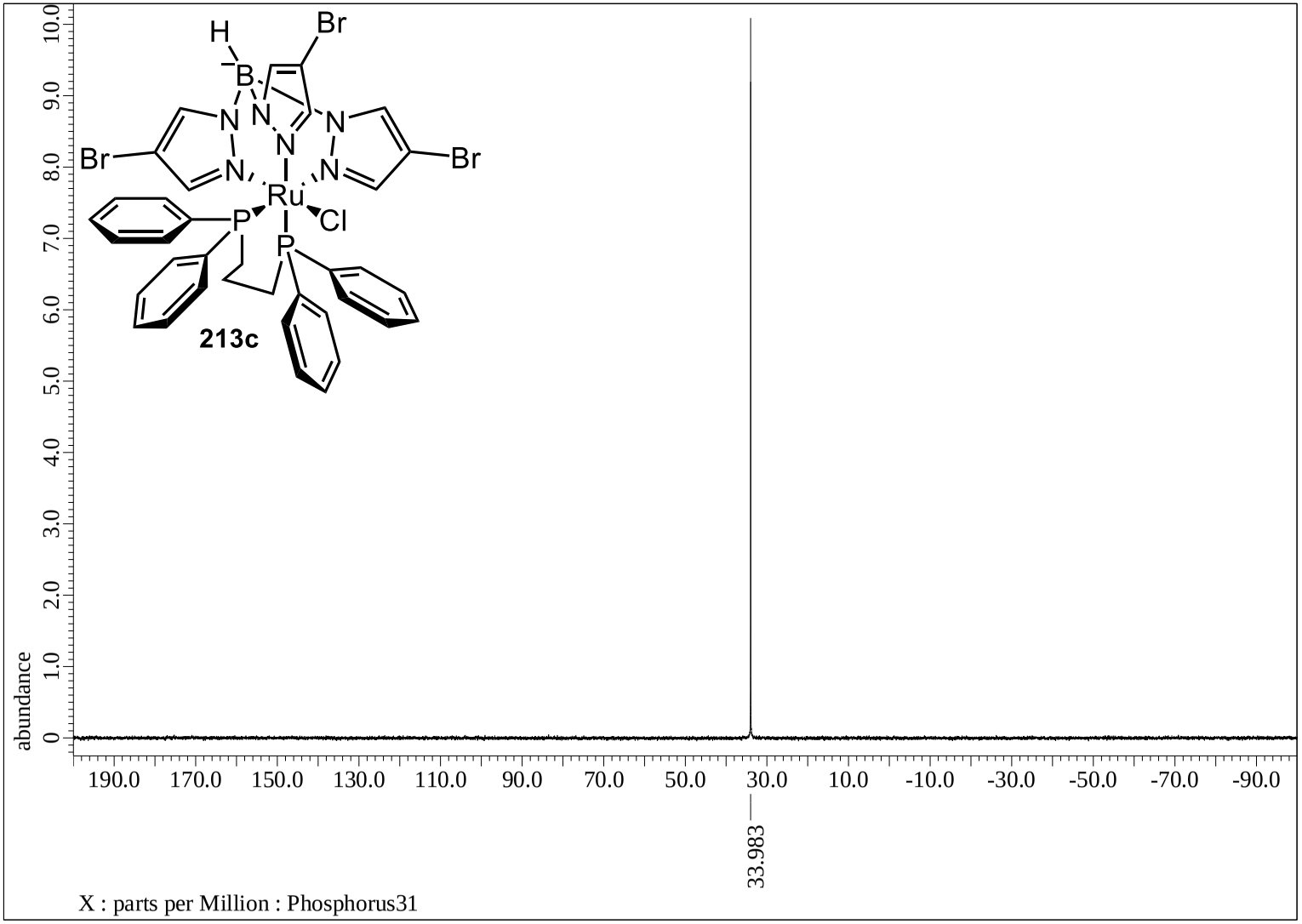


Figure A2.21: ^{31}P-NMR spectrum of 213c (400 MHz, $CDCl_3$)

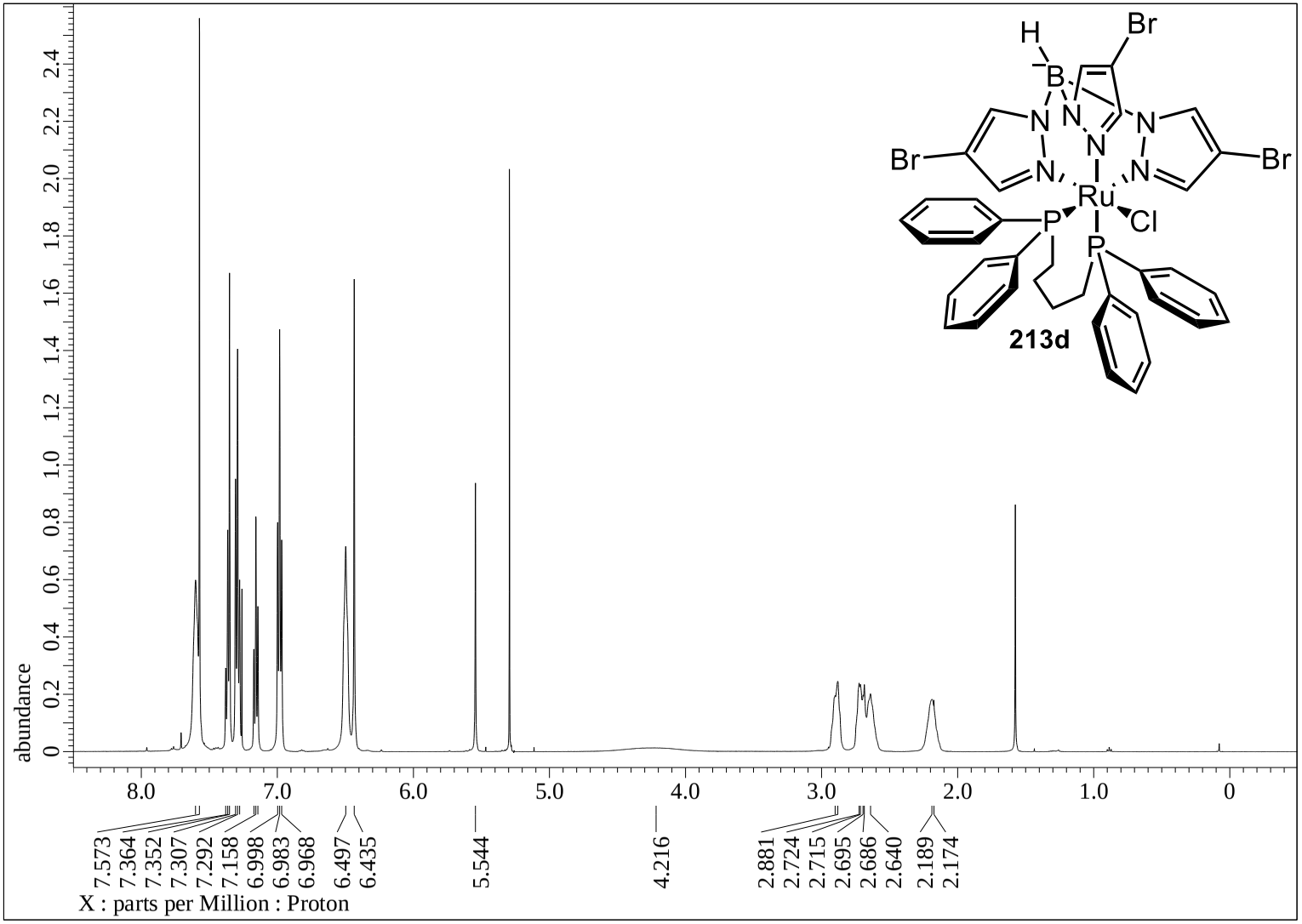


Figure A2.22: ^{1}H-NMR spectrum of 213d (500 MHz, $CDCl_3$)

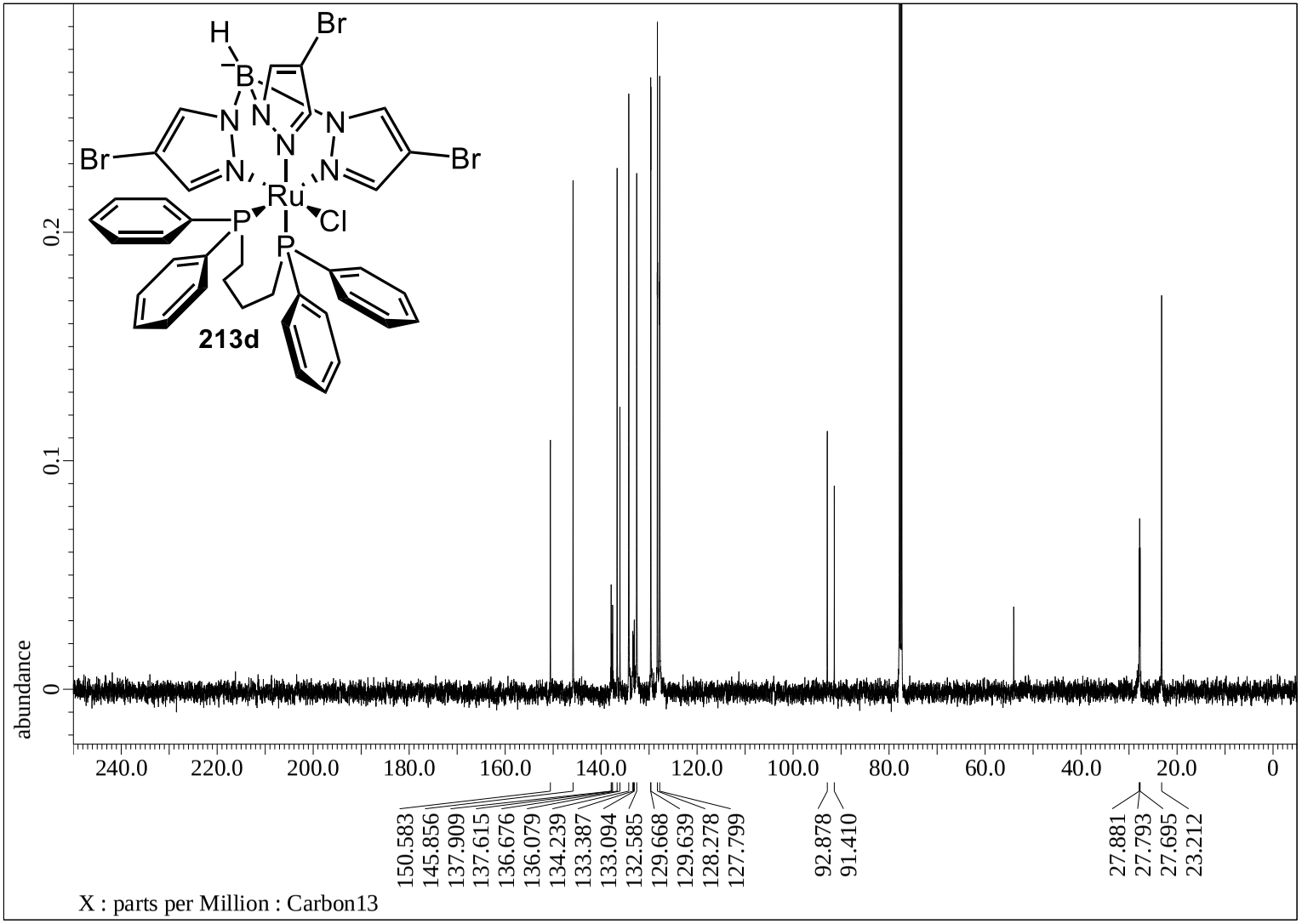


Figure A2.23: ^{13}C-NMR spectrum of 213d (500 MHz, $CDCl_3$)

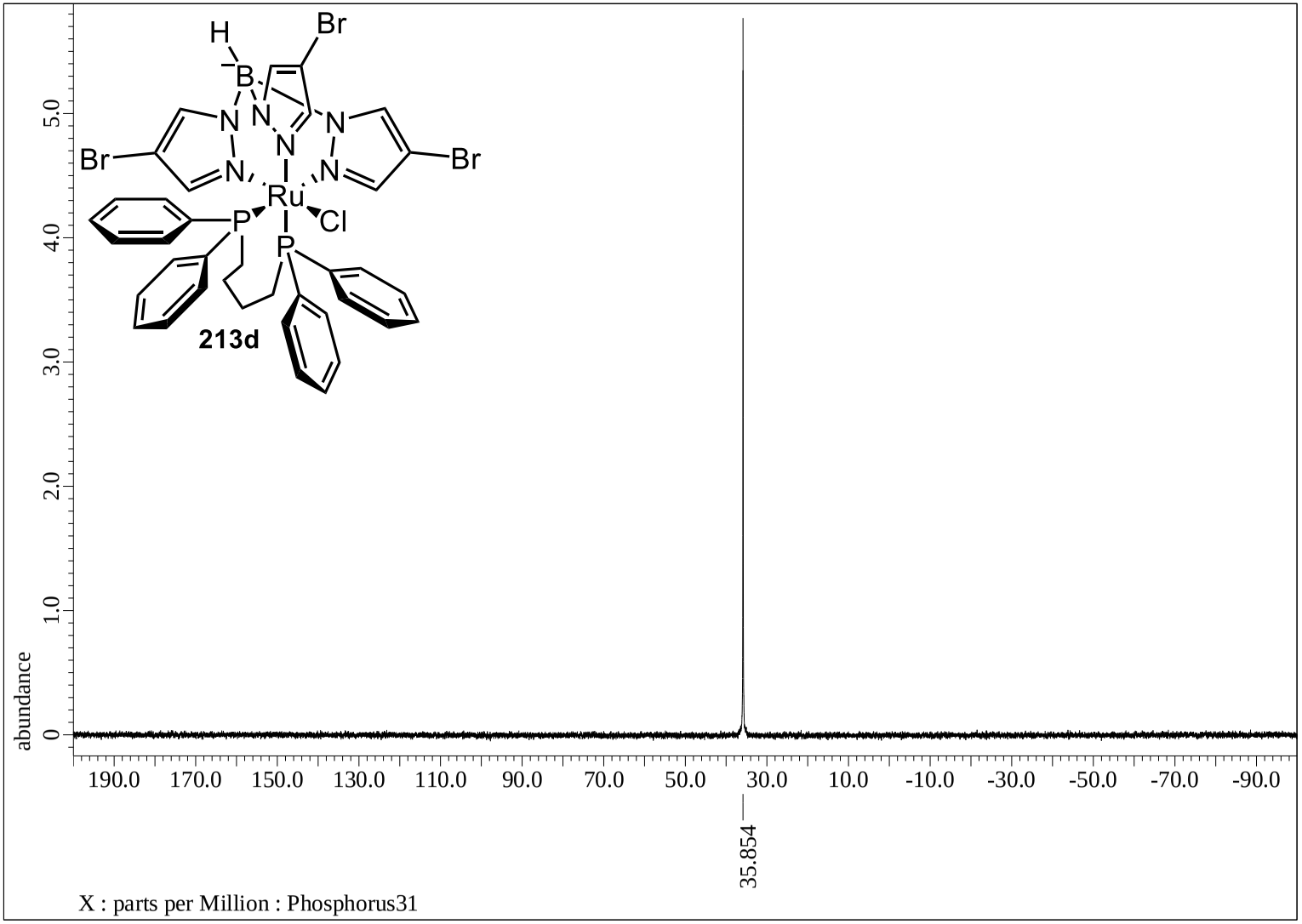


Figure A2.24: ^{31}P-NMR spectrum of 213d (400 MHz, $CDCl_3$)

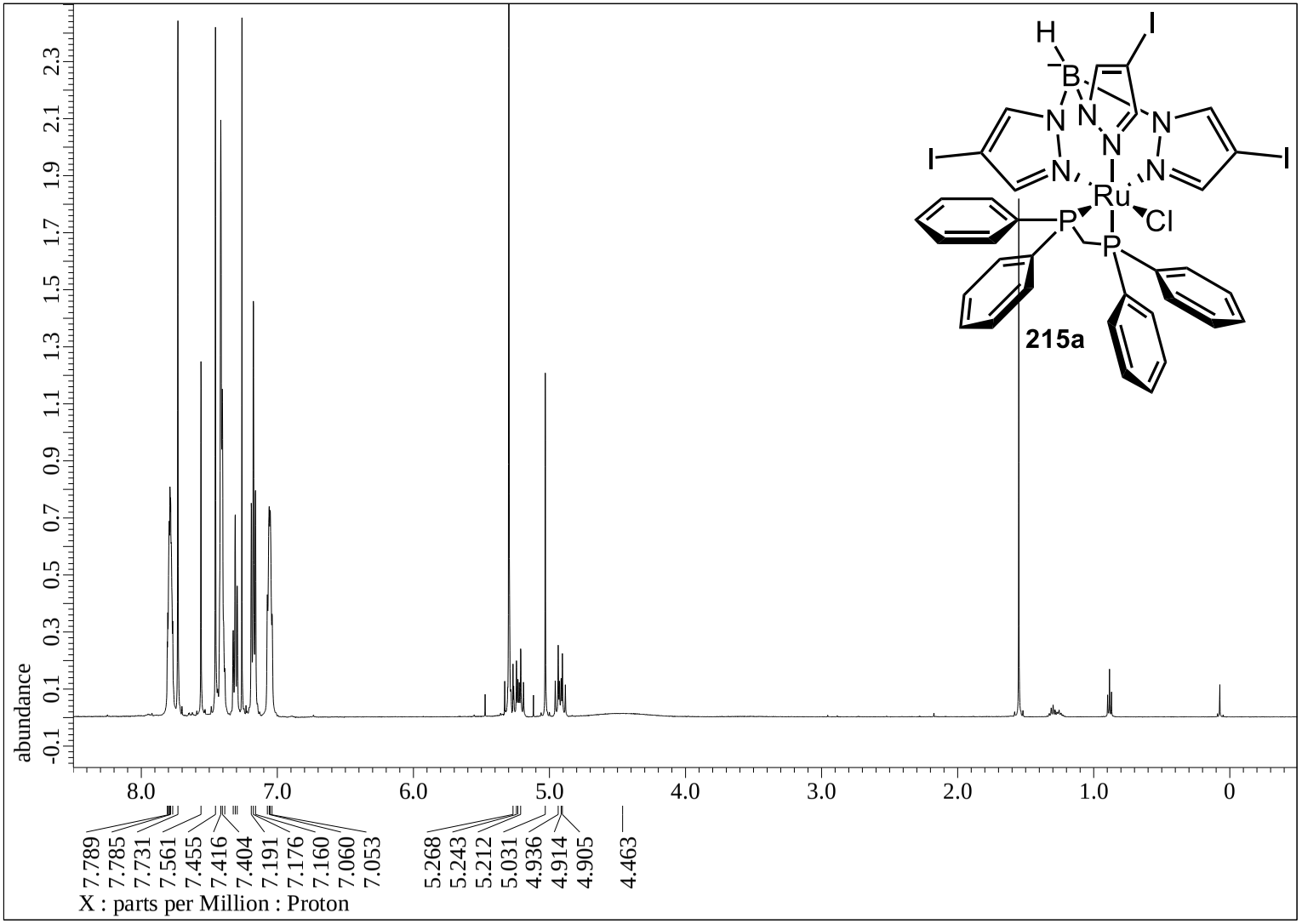


Figure A2.25: ^{1}H-NMR spectrum of 215a (500 MHz, $CDCl_3$)

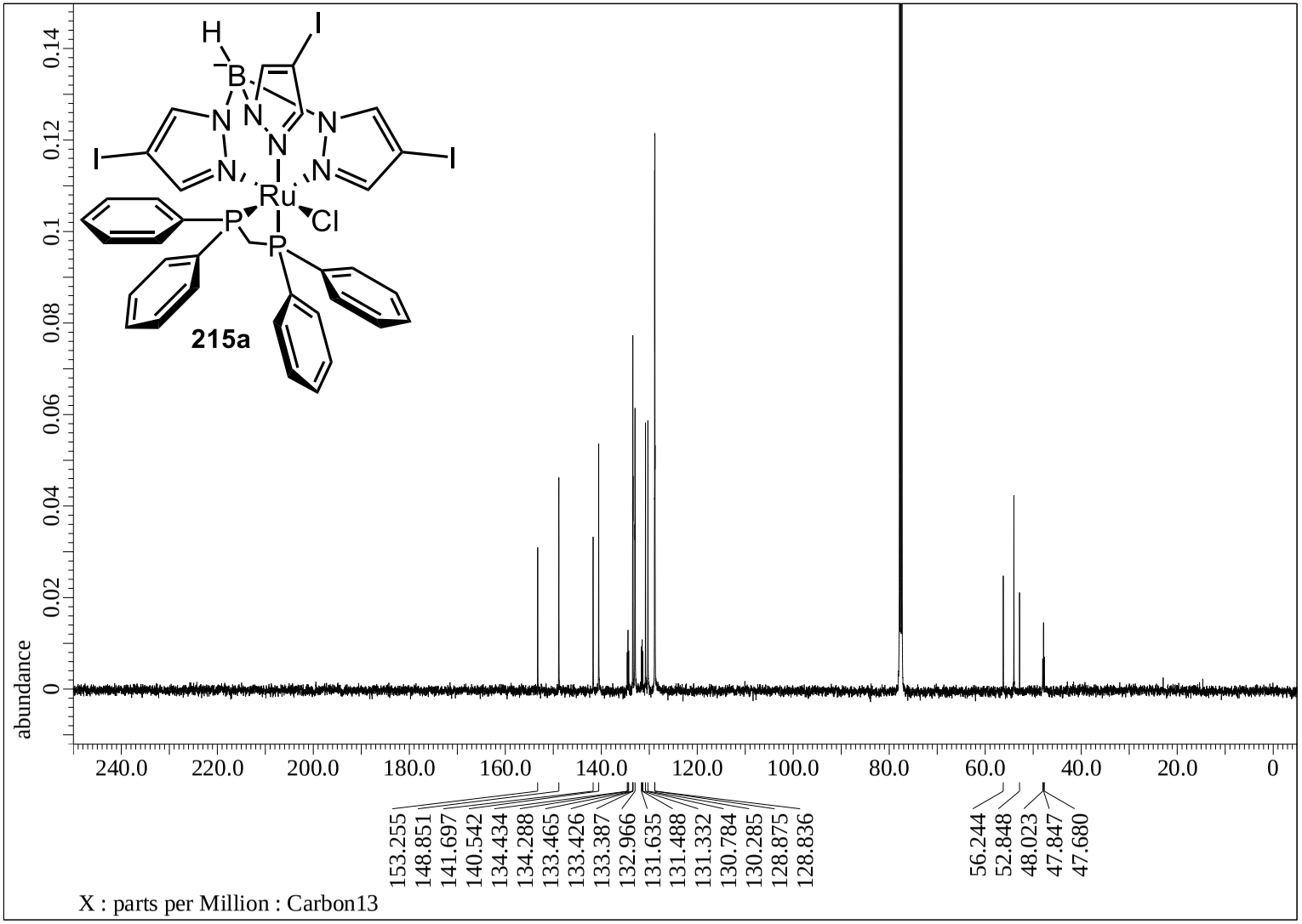


Figure A2.26: ^{13}C-NMR spectrum of 215a (500 MHz, $CDCl_3$)

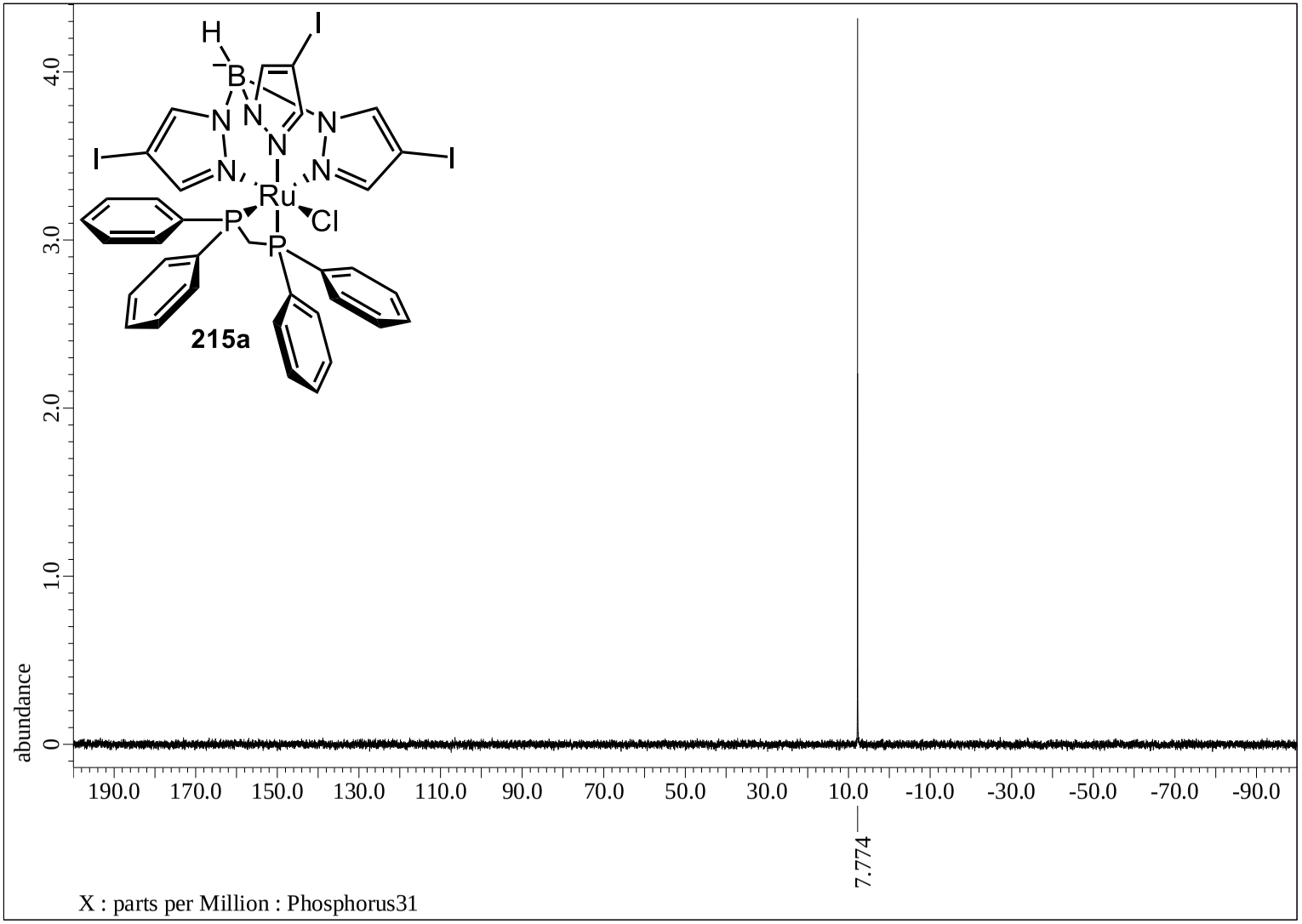


Figure A2.27: ^{31}P-NMR spectrum of 215a (400 MHz, $CDCl_3$)

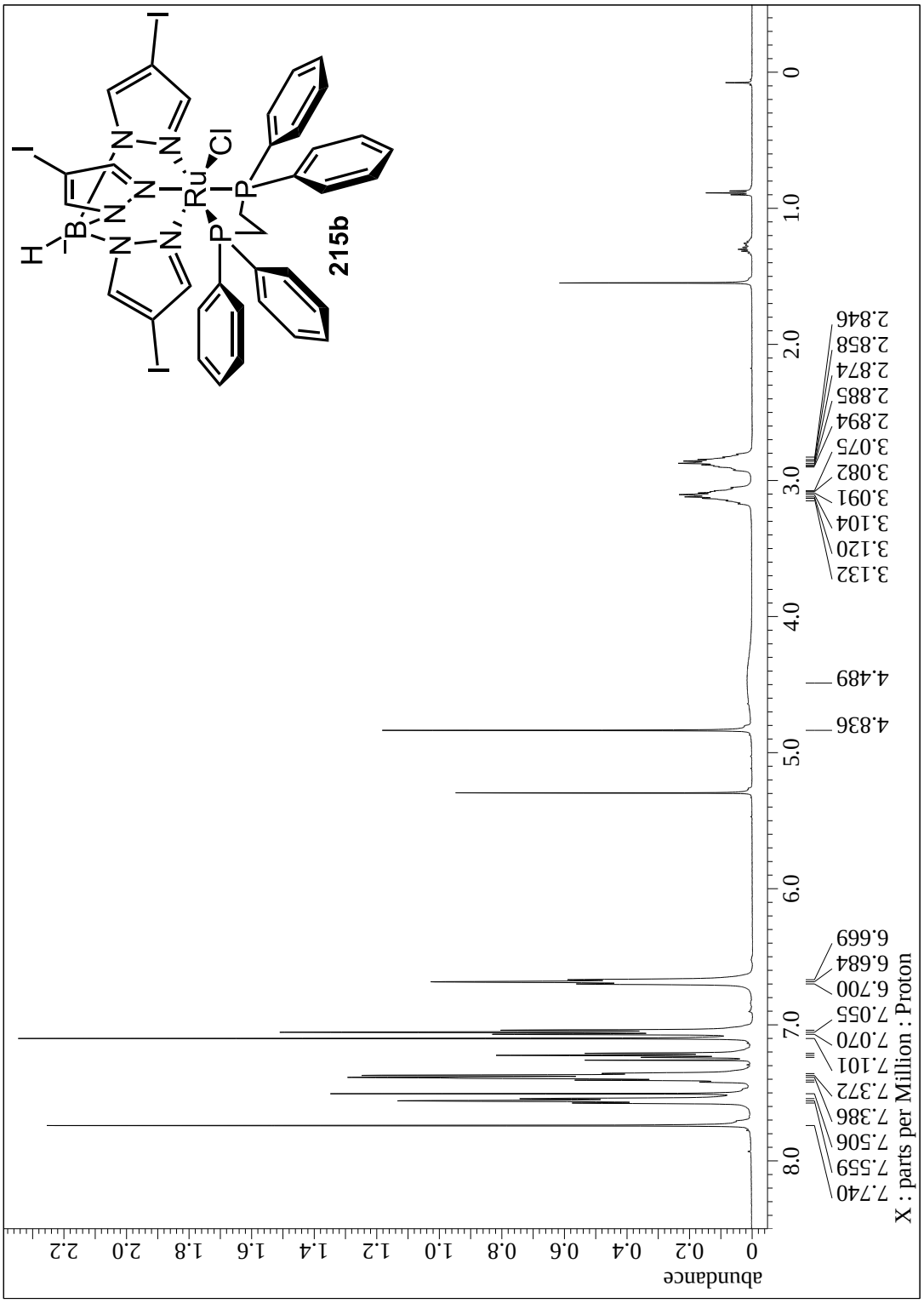


Figure A2.28: ^{1}H-NMR spectrum of 215b (500 MHz, $CDCl_3$)

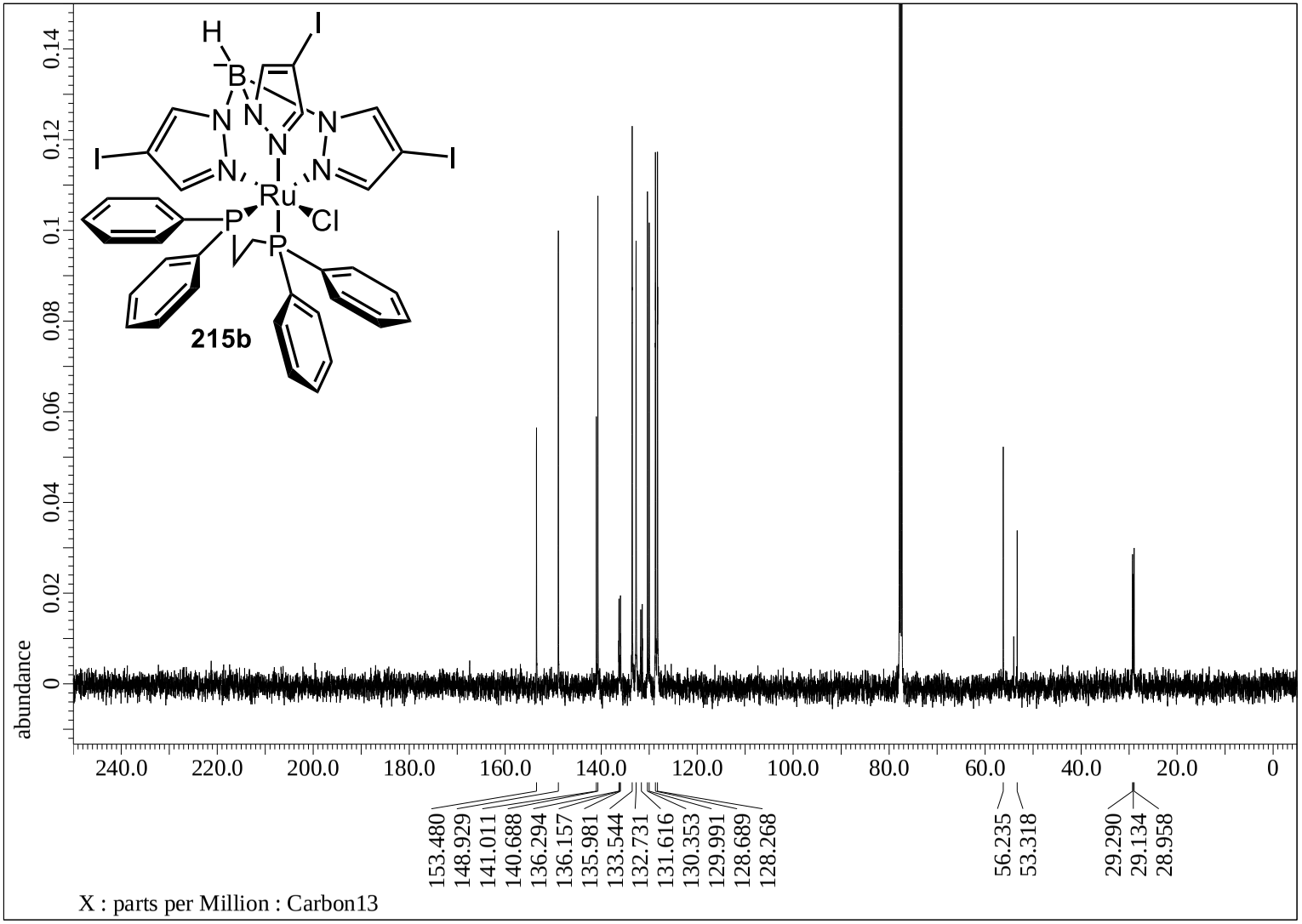


Figure A2.29: ^{13}C-NMR spectrum of 215b (500 MHz, $CDCl_3$)

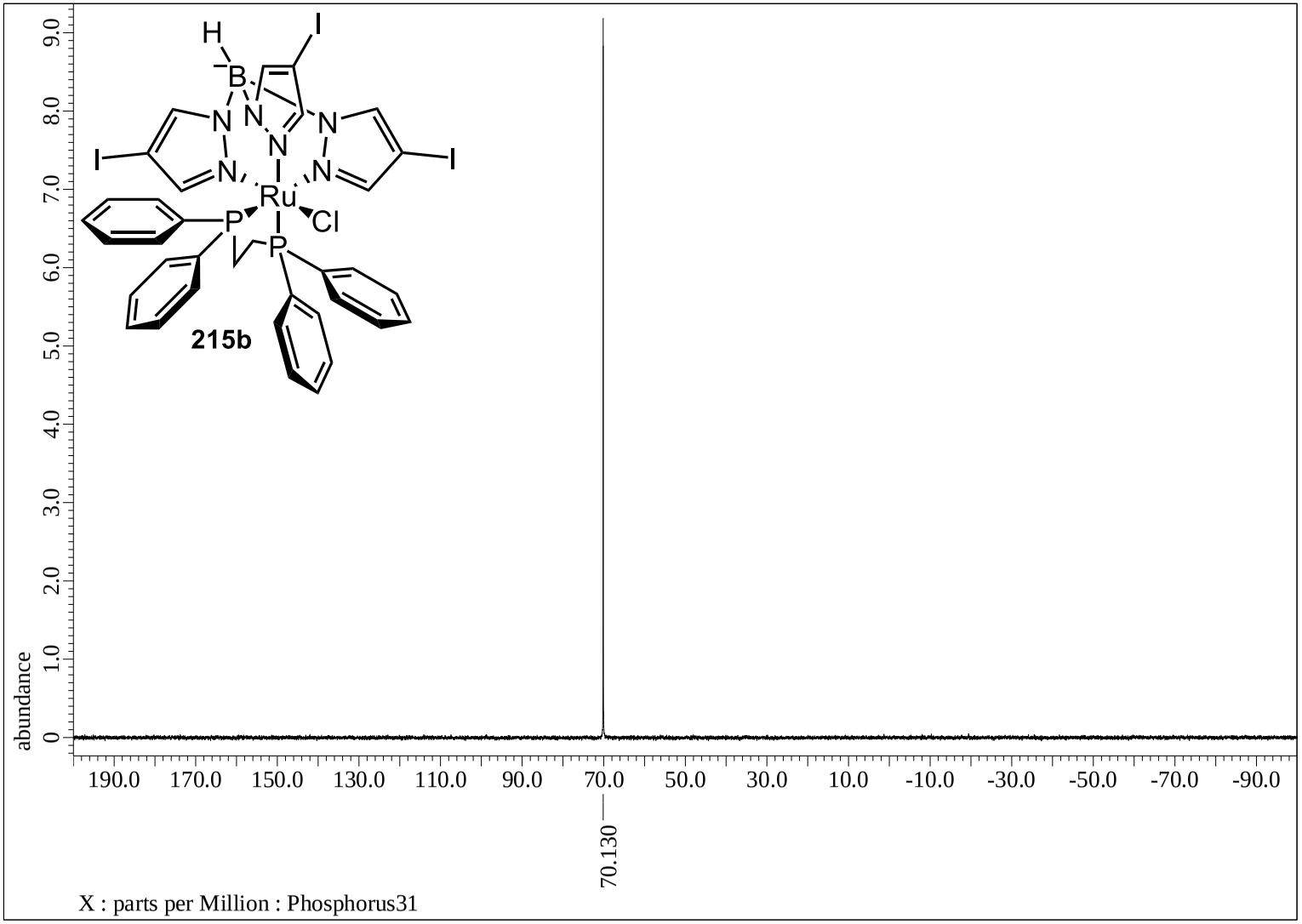


Figure A2.30: ^{31}P-NMR spectrum of 215b (400 MHz, $CDCl_3$)

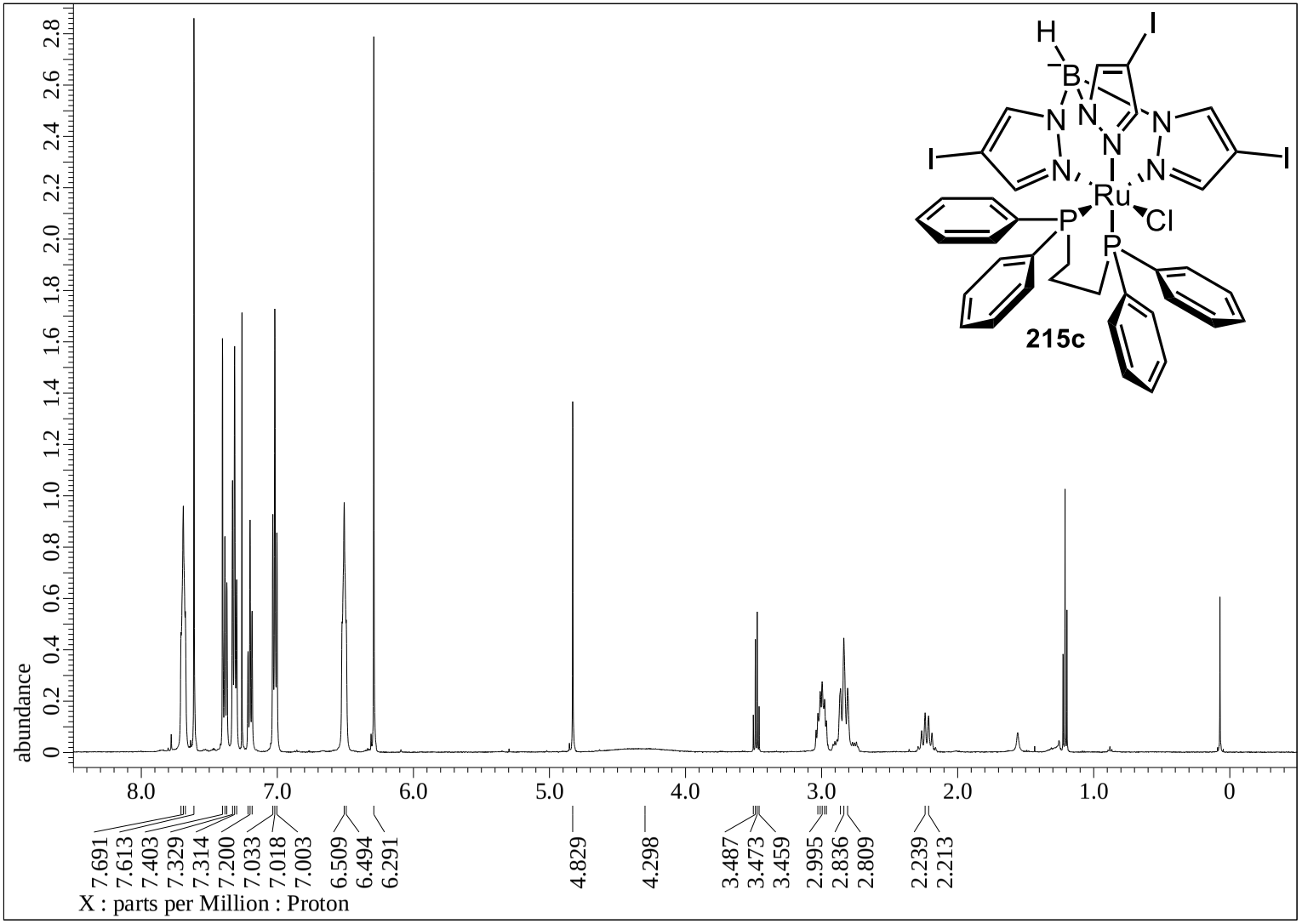


Figure A2.31: ^{1}H-NMR spectrum of 215c (500 MHz, $CDCl_3$)

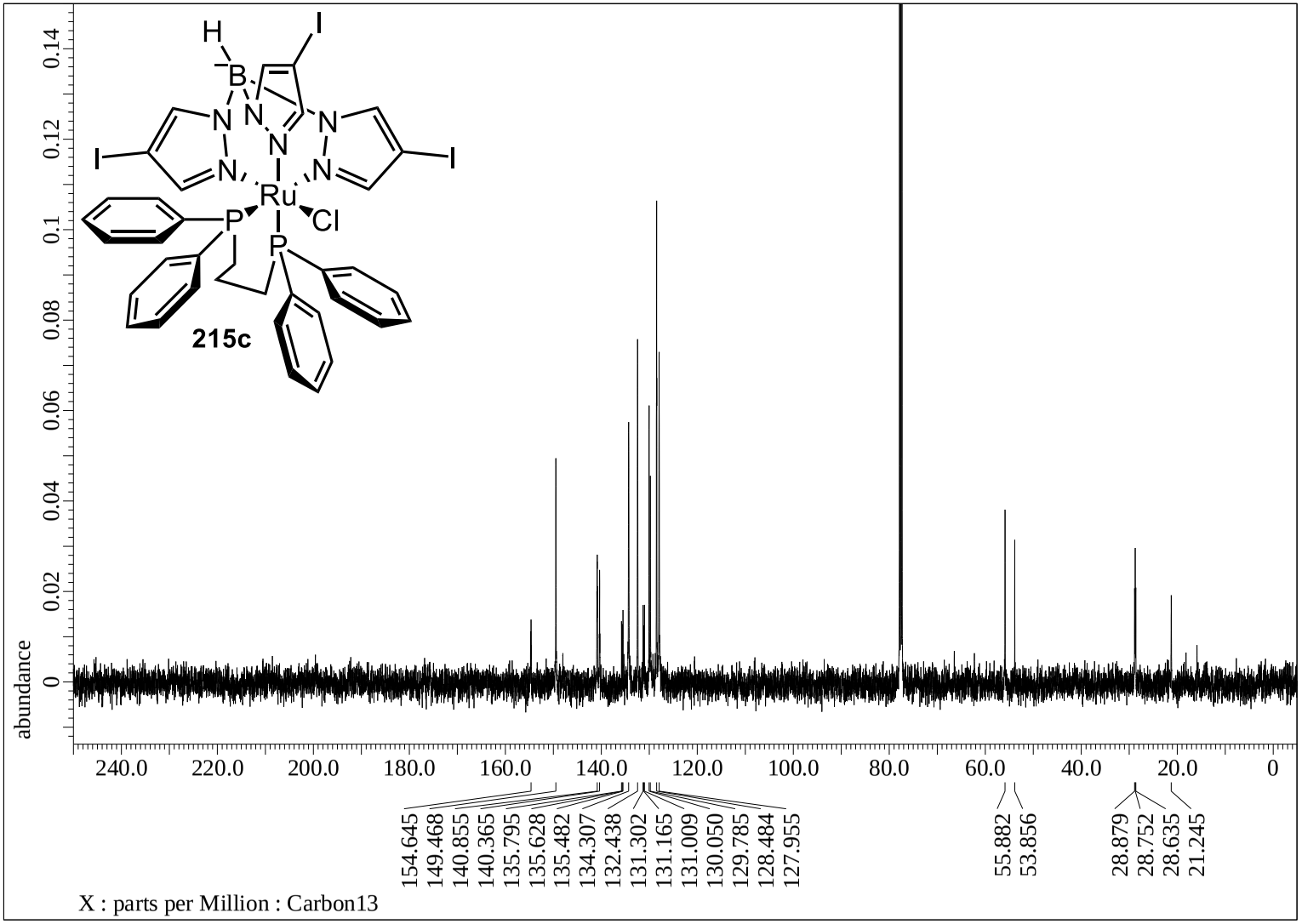


Figure A2.32: ^{13}C-NMR spectrum of 215c (500 MHz, $CDCl_3$)

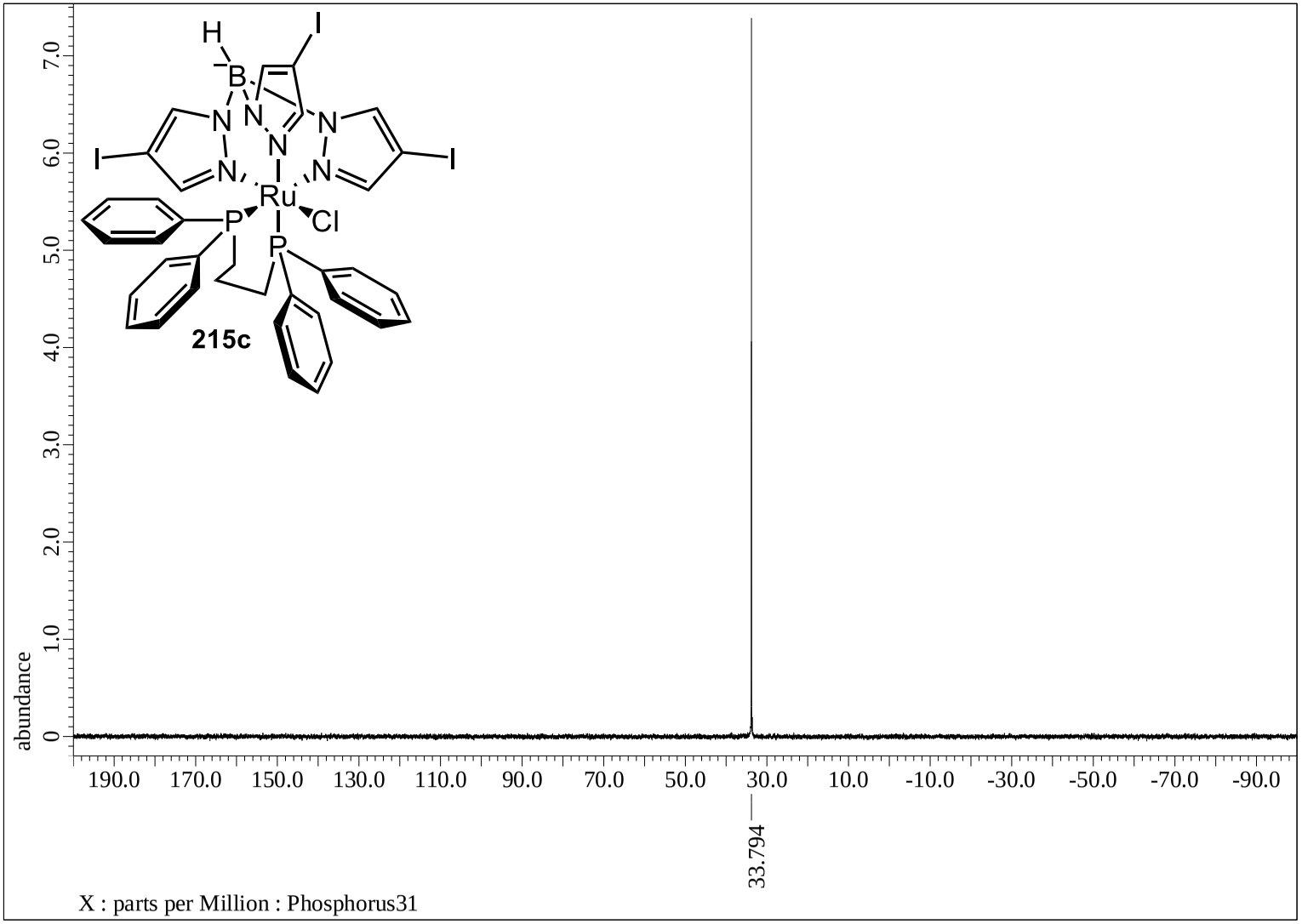


Figure A2.33: ^{31}P-NMR spectrum of 215c (400 MHz, $CDCl_3$)

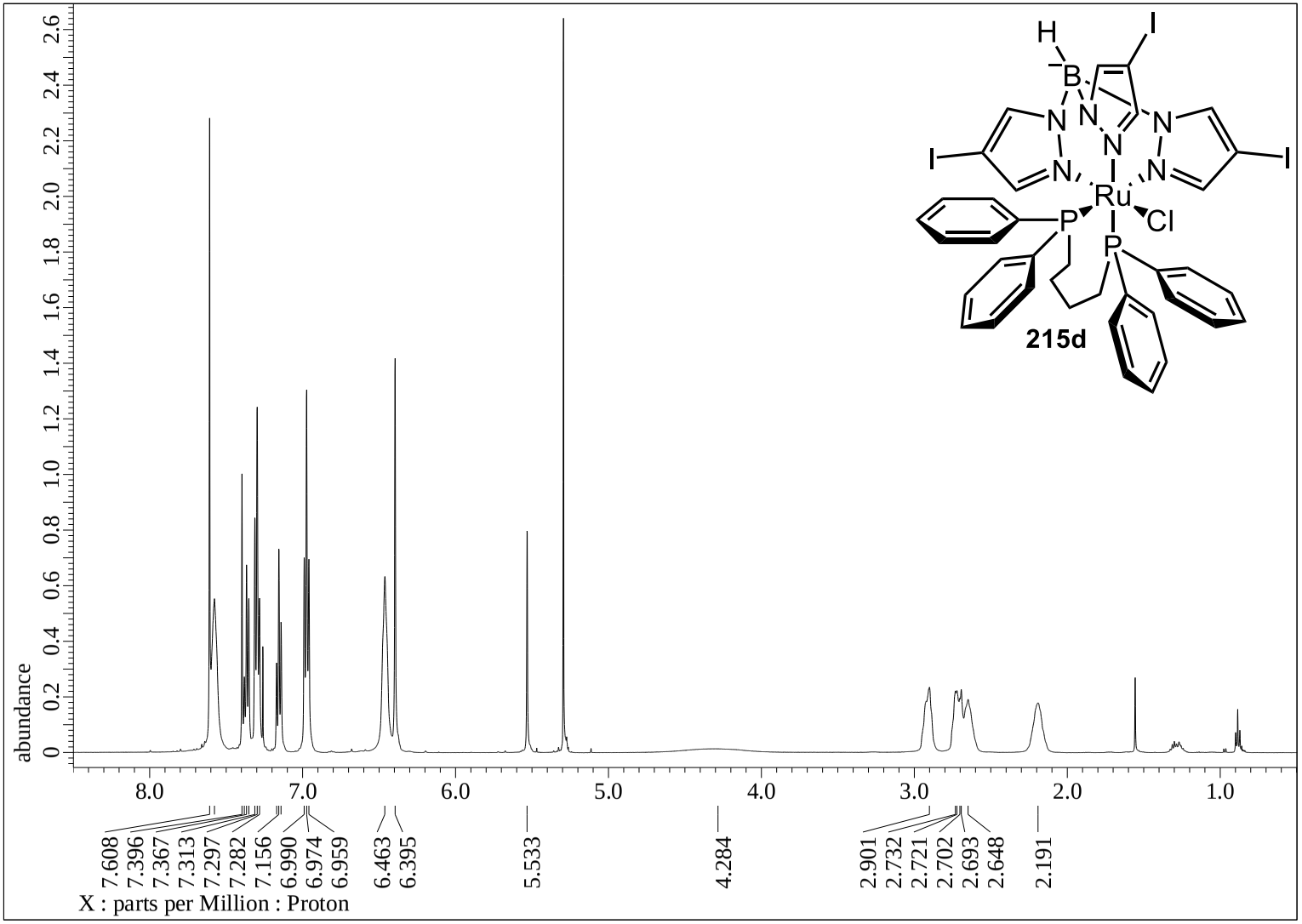


Figure A2.34: ^{1}H-NMR spectrum of 215d (500 MHz, $CDCl_3$)

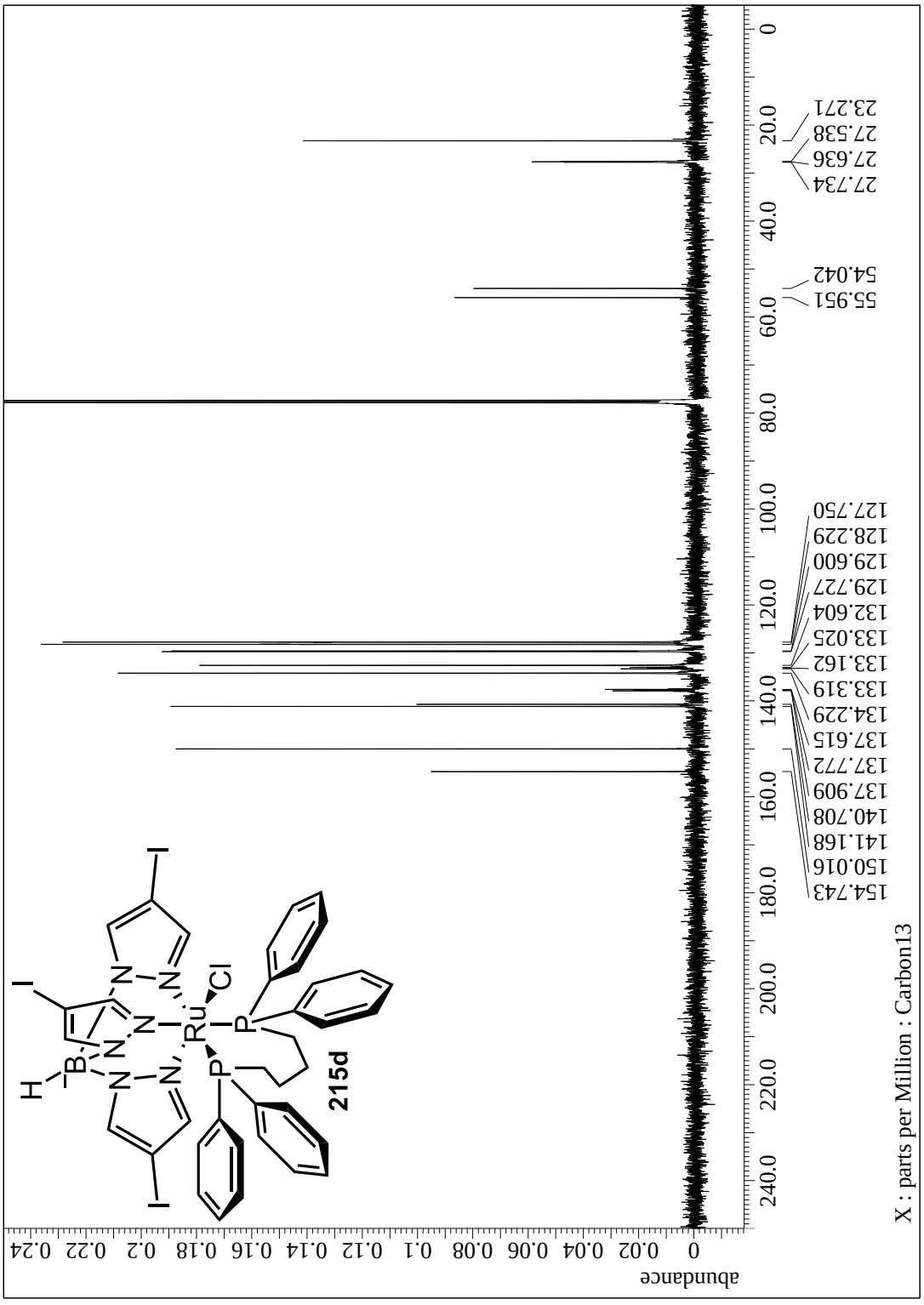


Figure A2.35: ^{13}C-NMR spectrum of 215d (500 MHz, $CDCl_3$)

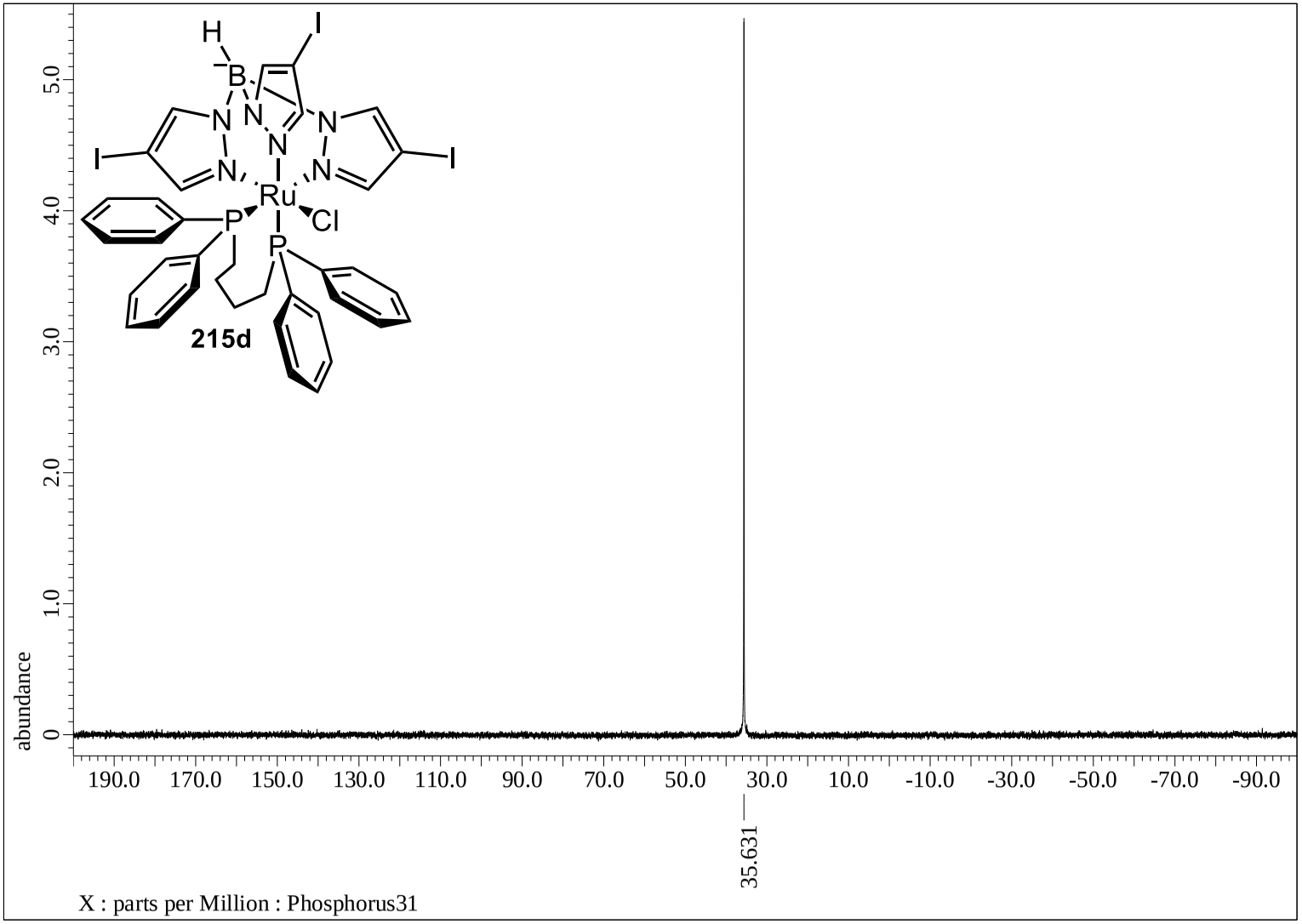


Figure A2.36: ^{31}P-NMR spectrum of 215d (400 MHz, $CDCl_3$)

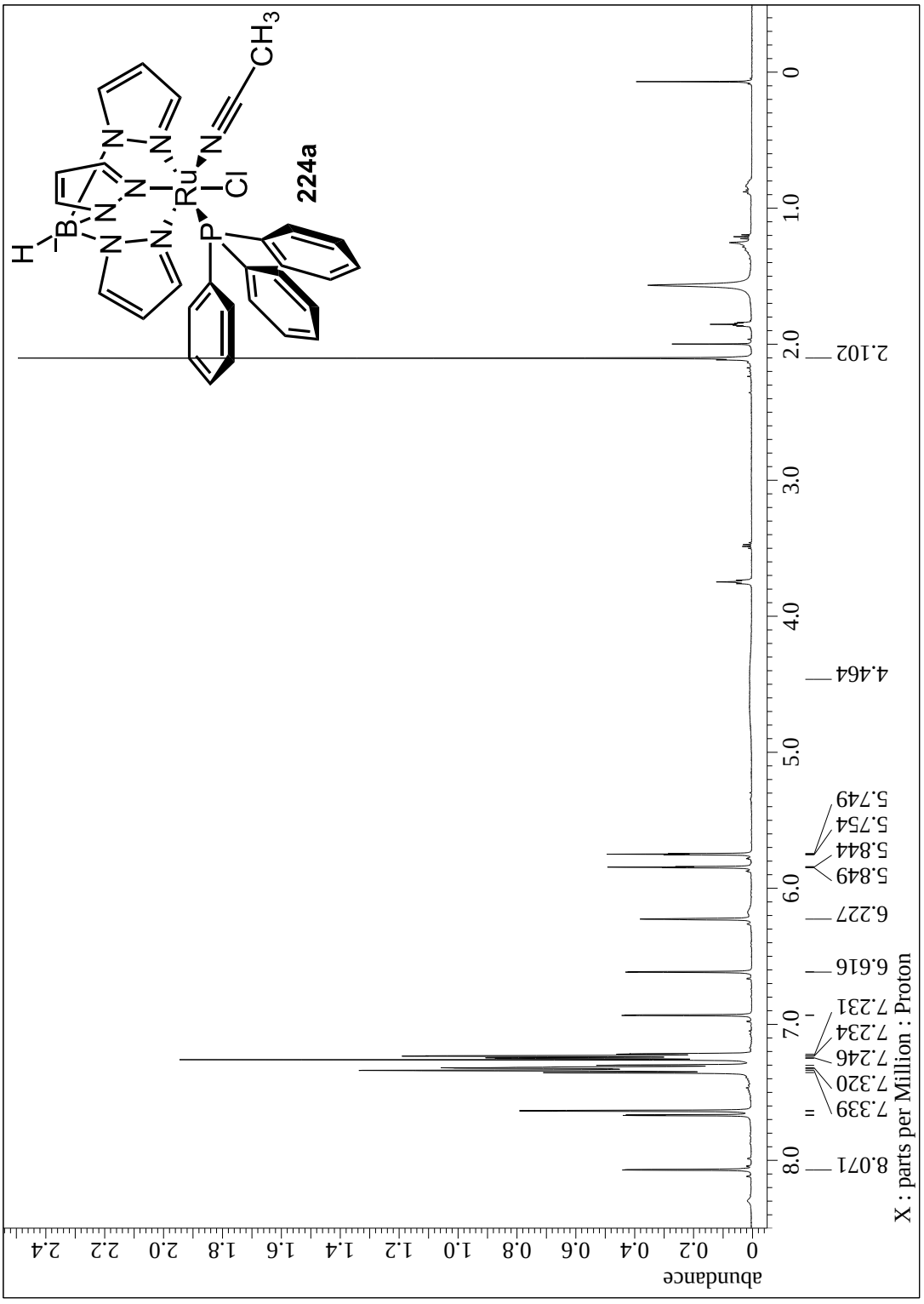


Figure A2.37: ^{1}H-NMR spectrum of 224a (500 MHz, $CDCl_3$)

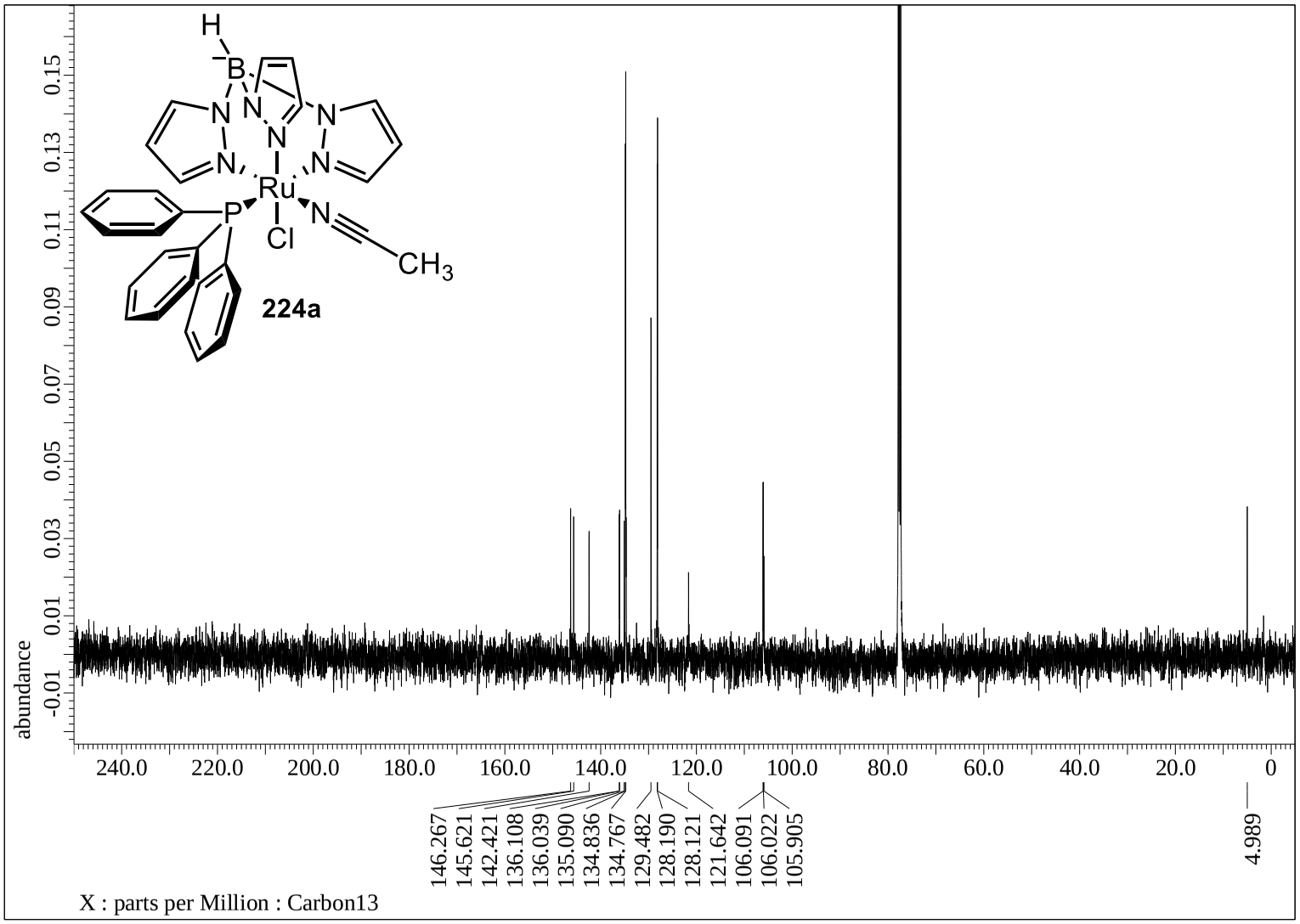


Figure A2.37: ^{1}H-NMR spectrum of 224a (500 MHz, $CDCl_3$)

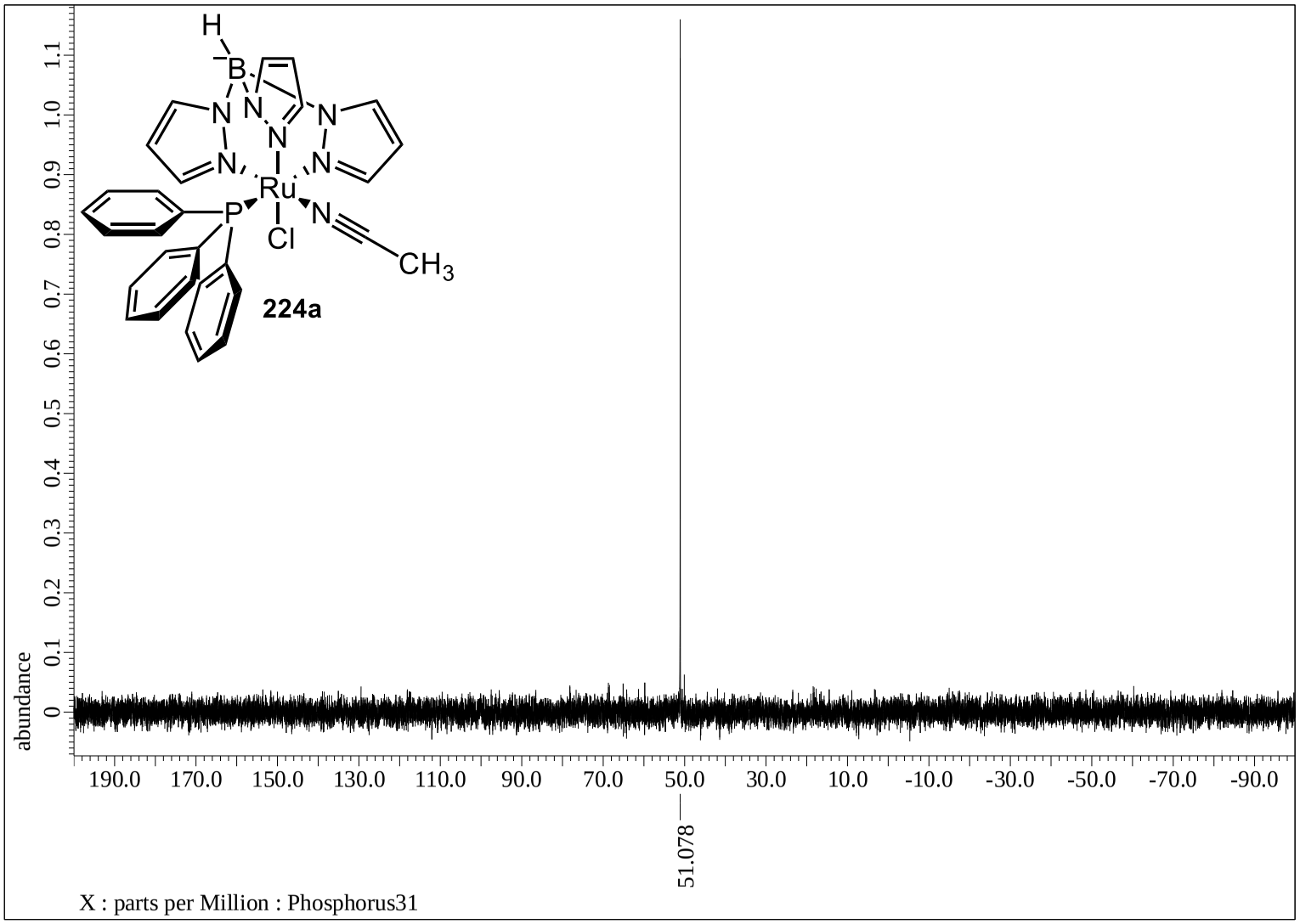


Figure A2.39: ^{31}P-NMR spectrum of 224a (400 MHz, $CDCl_3$)

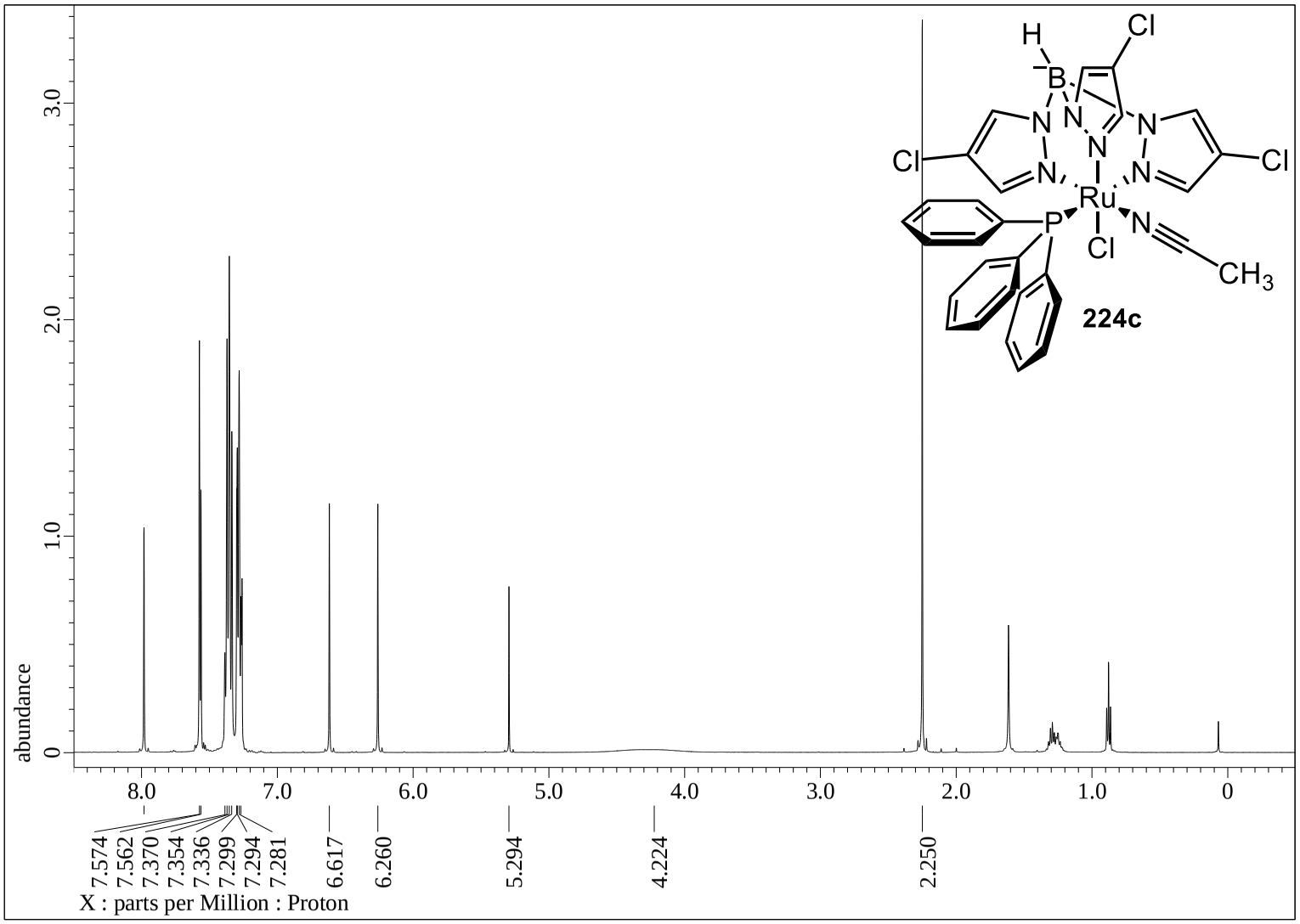


Figure A2.40: ^{1}H-NMR spectrum of 224c (500 MHz, $CDCl_3$)

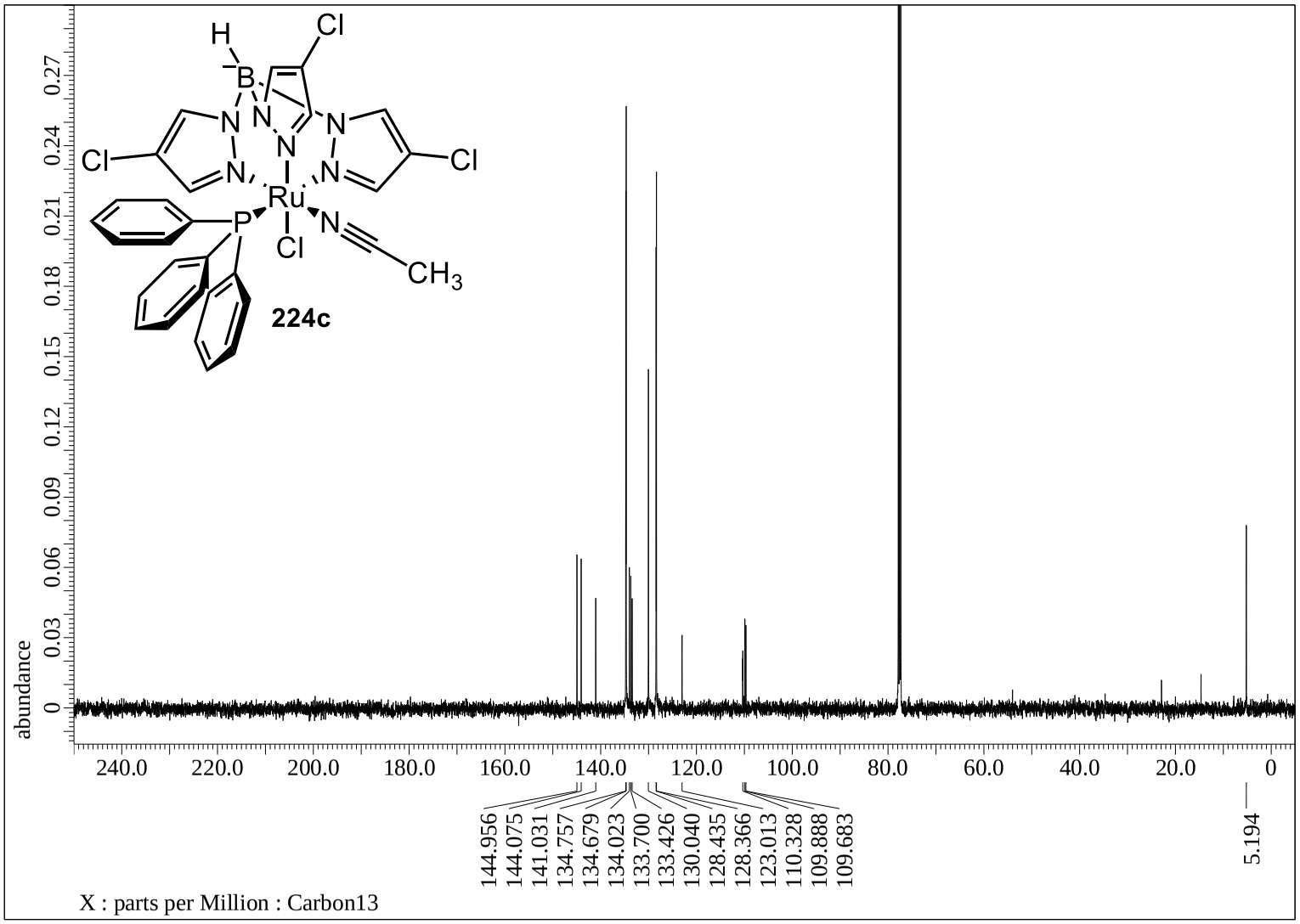


Figure A2.41: ^{13}C-NMR spectrum of 224c (500 MHz, $CDCl_3$)

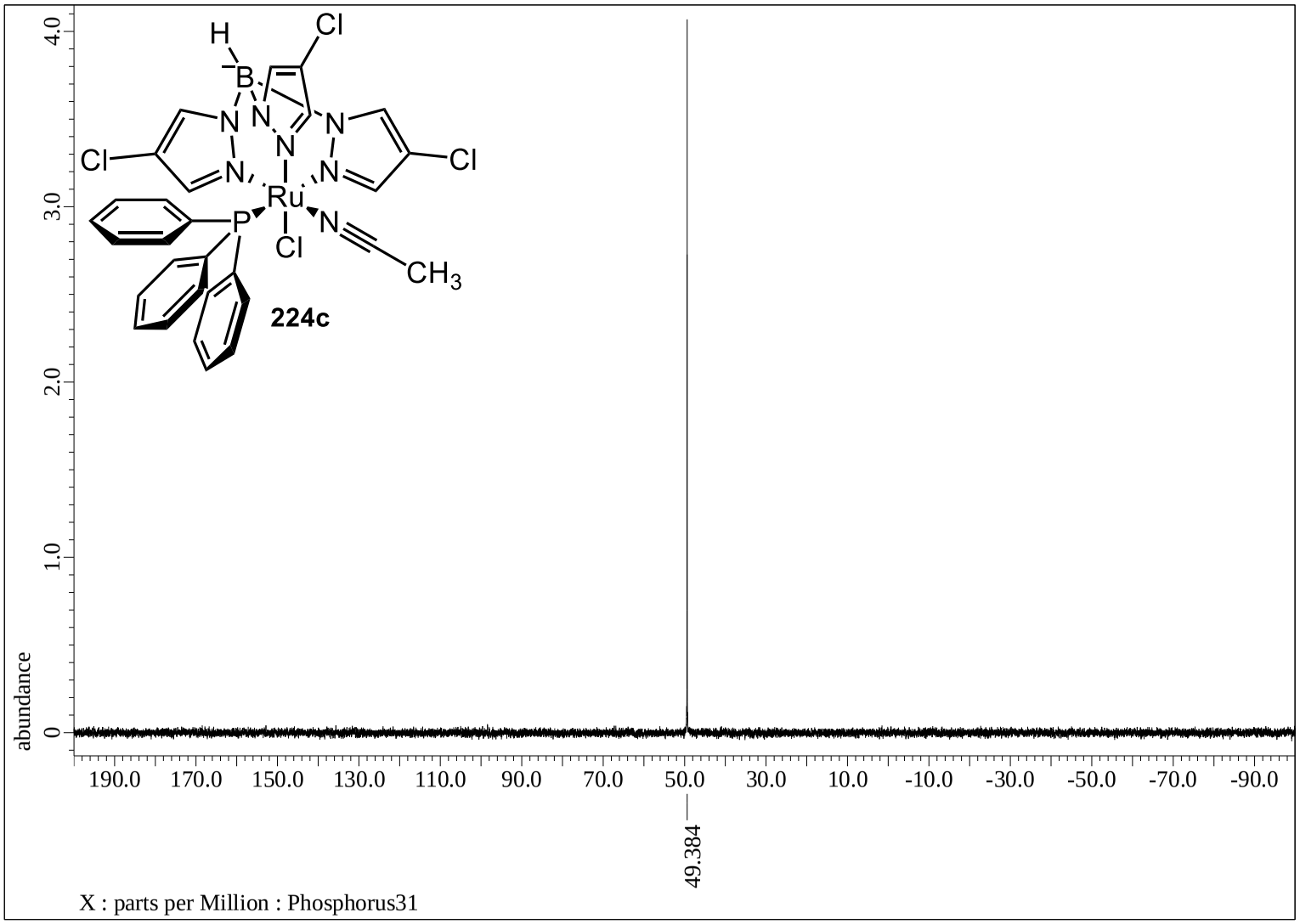


Figure A2.42: ^{31}P-NMR spectrum of 224c (400 MHz, $CDCl_3$)

Figure A2.43: ^{1}H-NMR spectrum of 224d (500 MHz, $CDCl_3$)

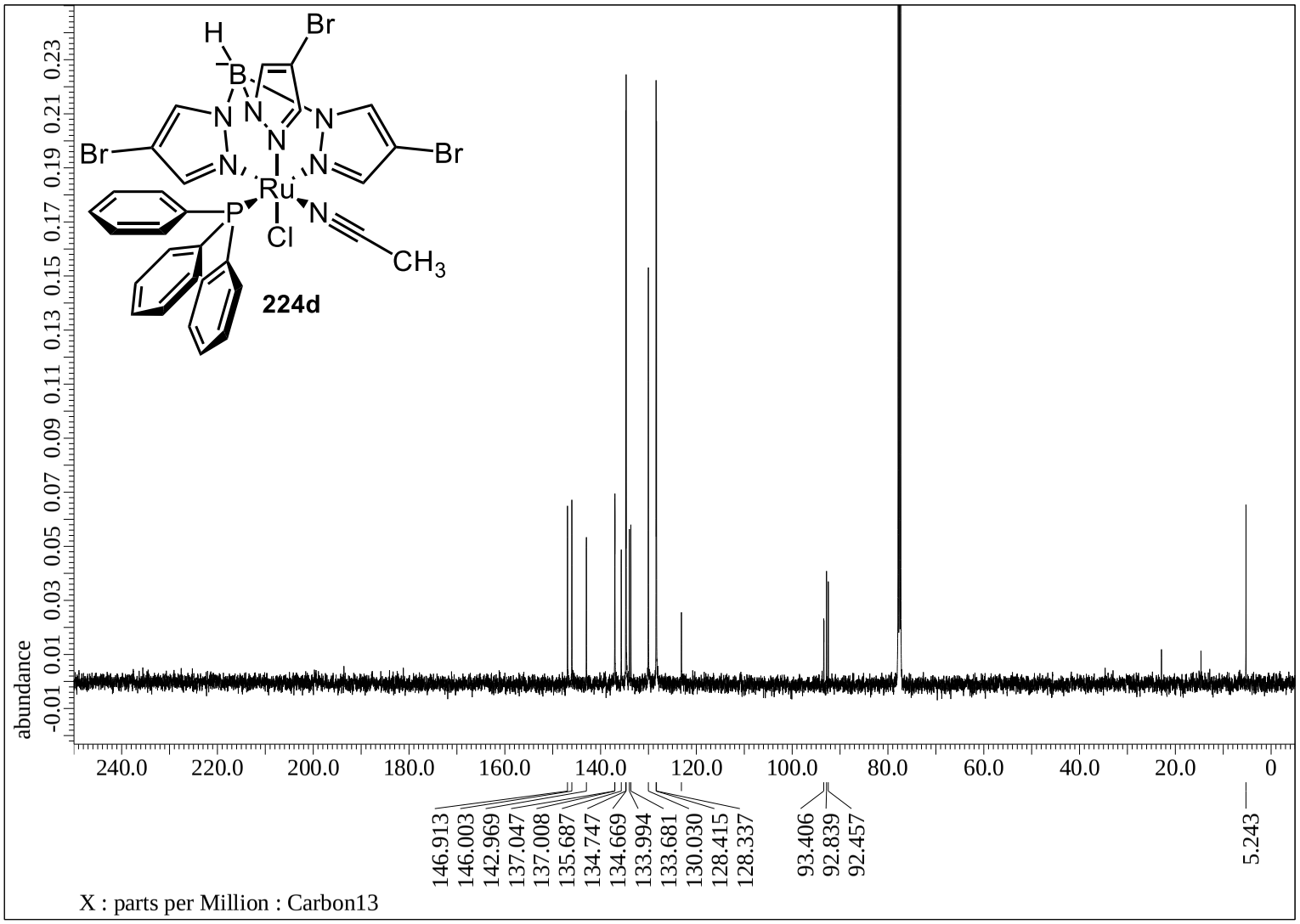


Figure A2.44: ^{13}C-NMR spectrum of 224d (500 MHz, $CDCl_3$)

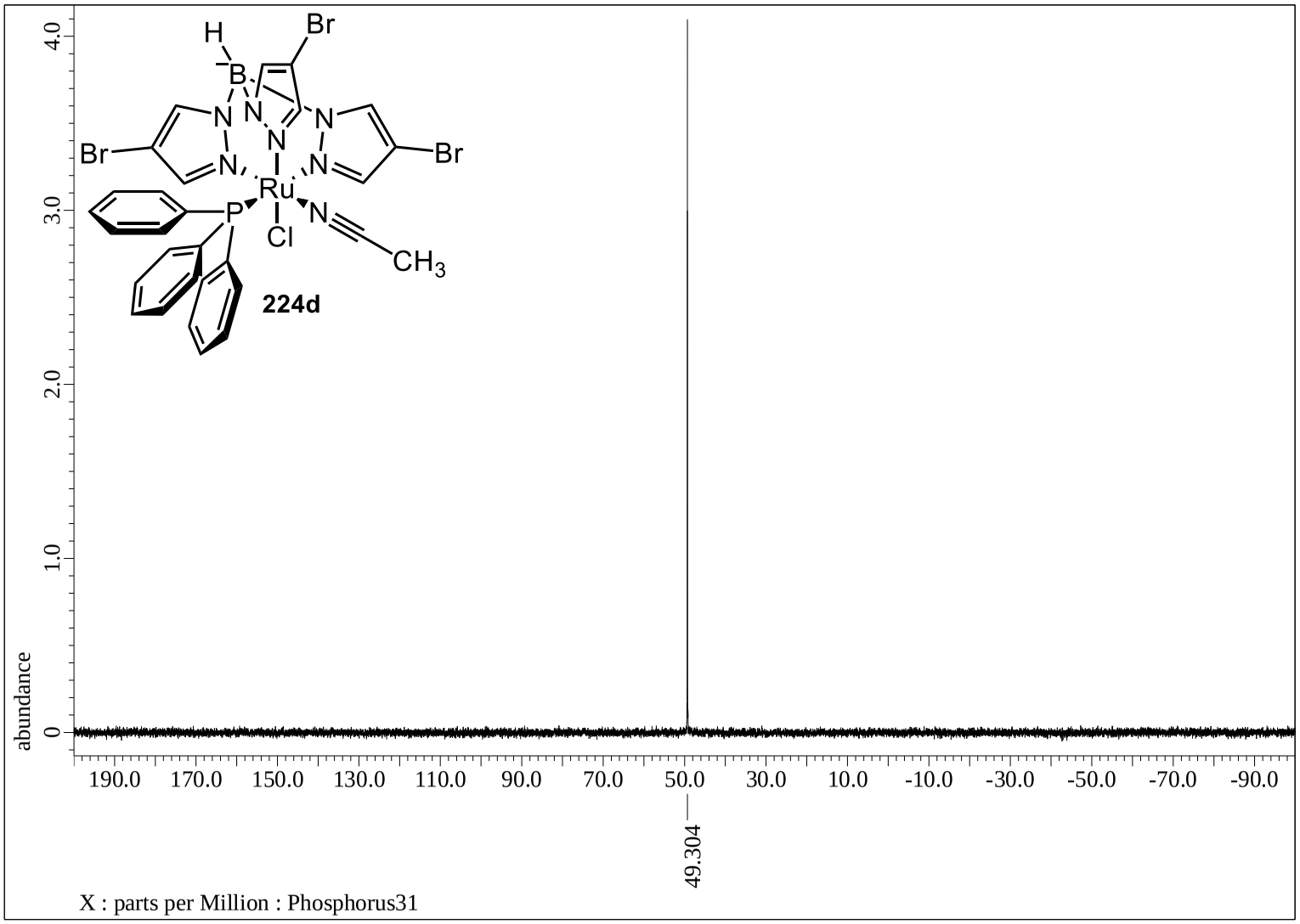


Figure A2.45: ^{31}P-NMR spectrum of 224d (400 MHz, $CDCl_3$)

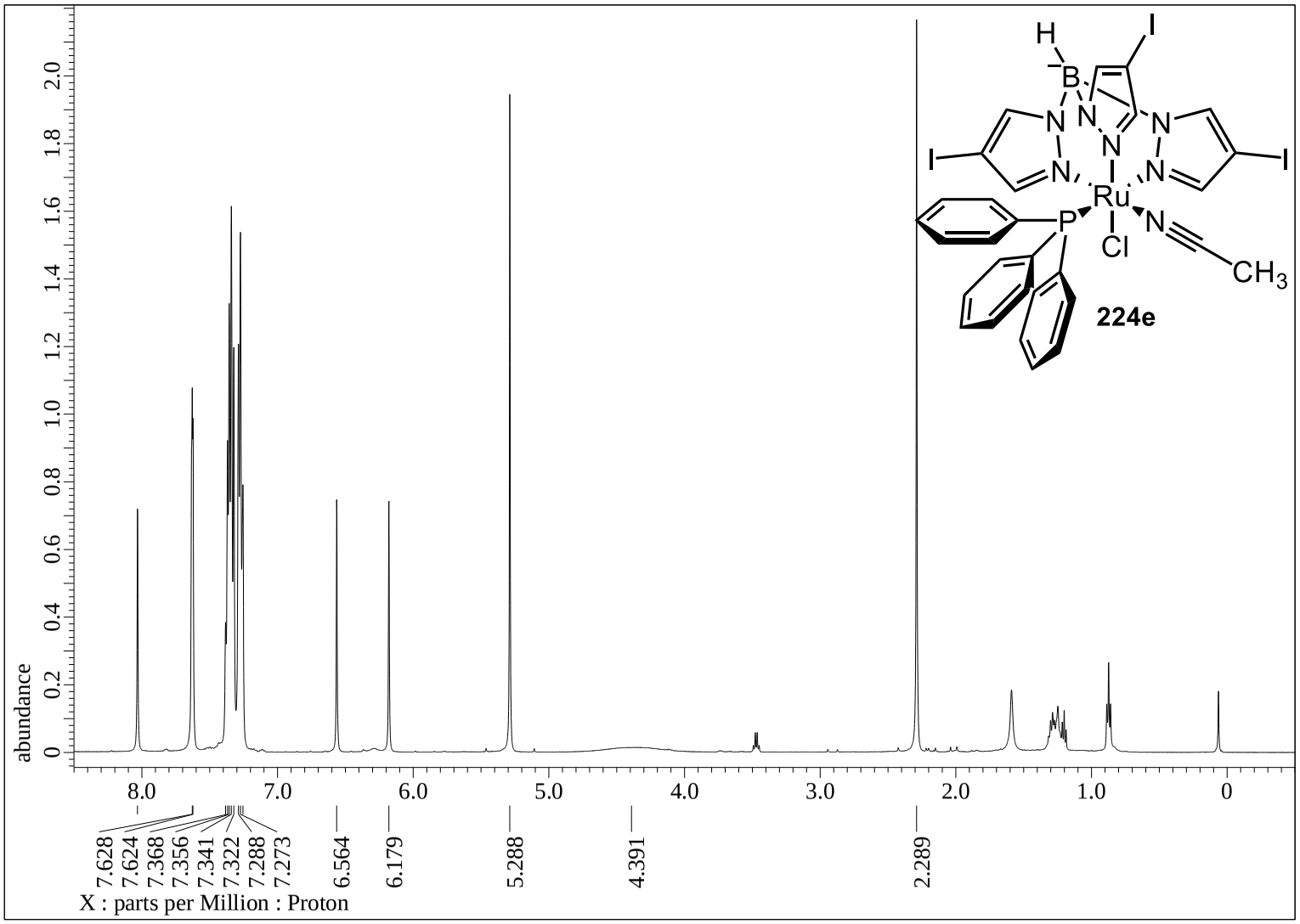


Figure A2.46: ^{1}H-NMR spectrum of 224e (500 MHz, $CDCl_3$)

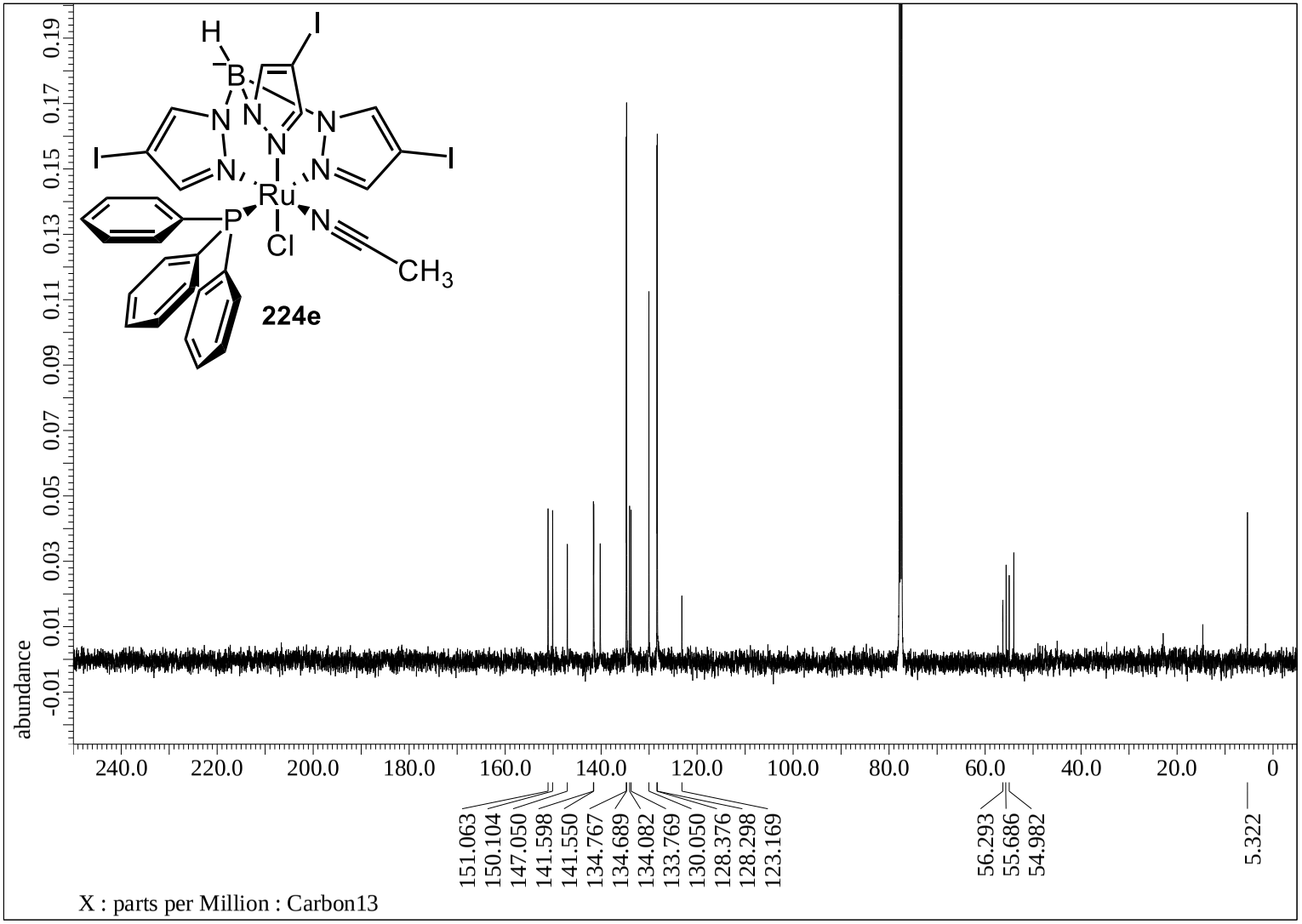


Figure A2.47: ^{13}C-NMR spectrum of 224e (500 MHz, $CDCl_3$)

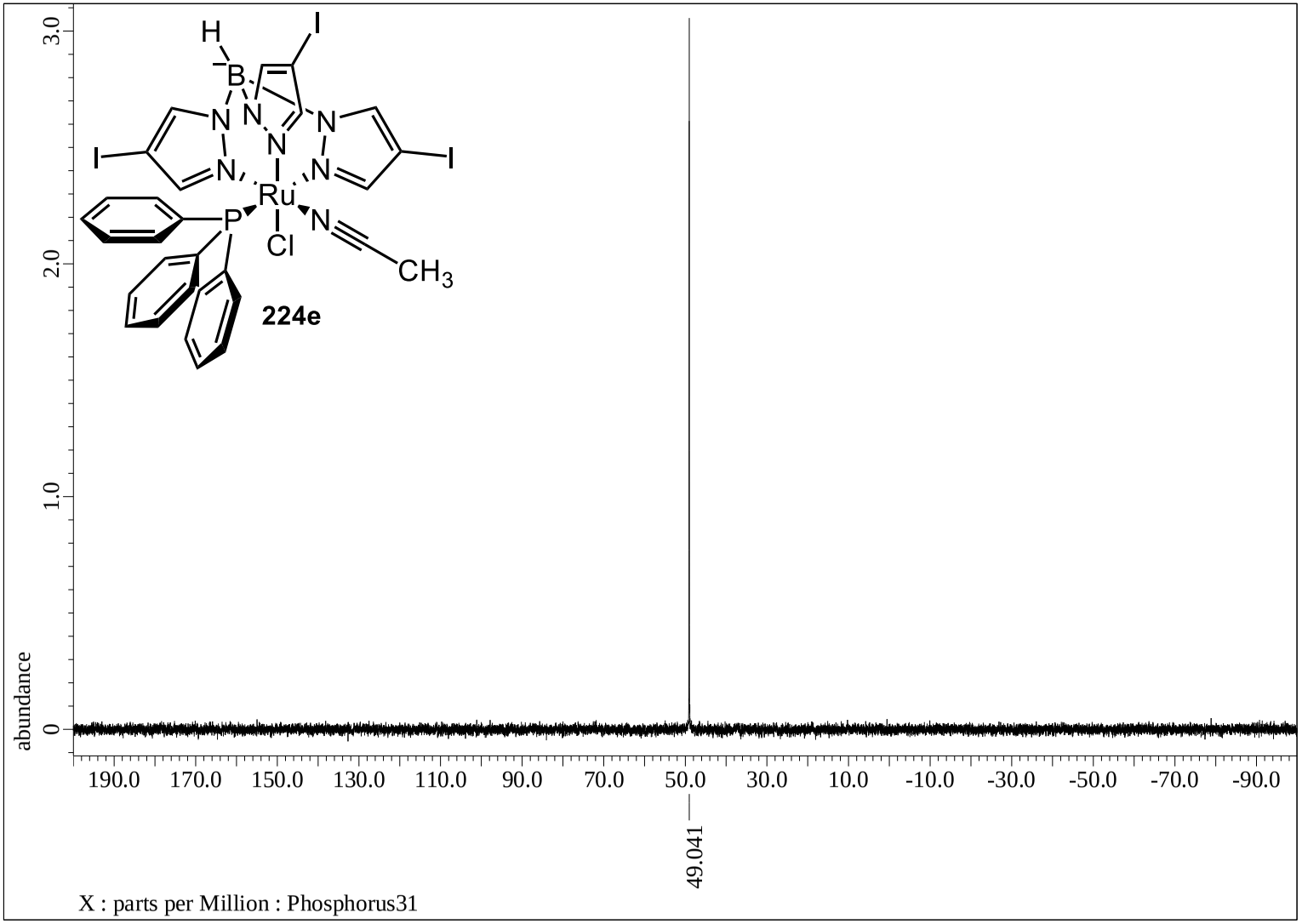


Figure A2.48: ^{31}P-NMR spectrum of 224e (400 MHz, $CDCl_3$)

APPENDEX FIVE: UV-Vis Spectra

Ligand exchange reactions of $Tp^{X}Ru(diene)Cl$ to mono- and di-phosphine complexes and their oxidation potentials.

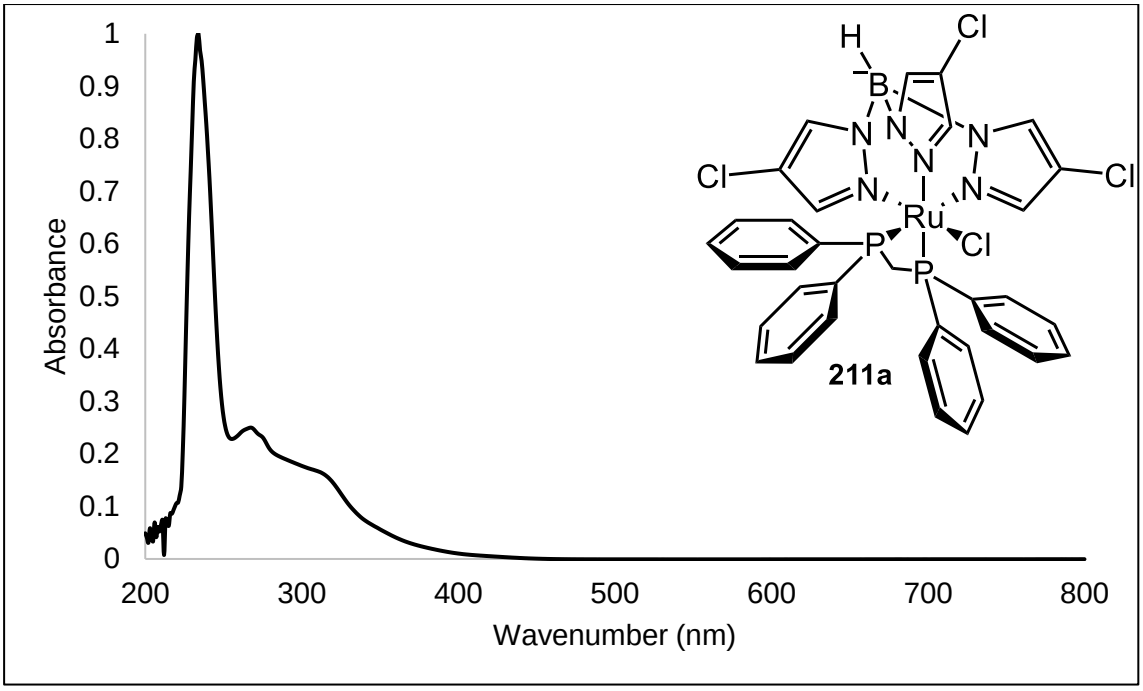


Figure A2.49: UV-Vis spectrum of 211a, ε_{236}=20.2 (L/mol cm) , ε_{268}=11.4 (L/mol cm), ε_{306}=7.8 (L/mol cm)

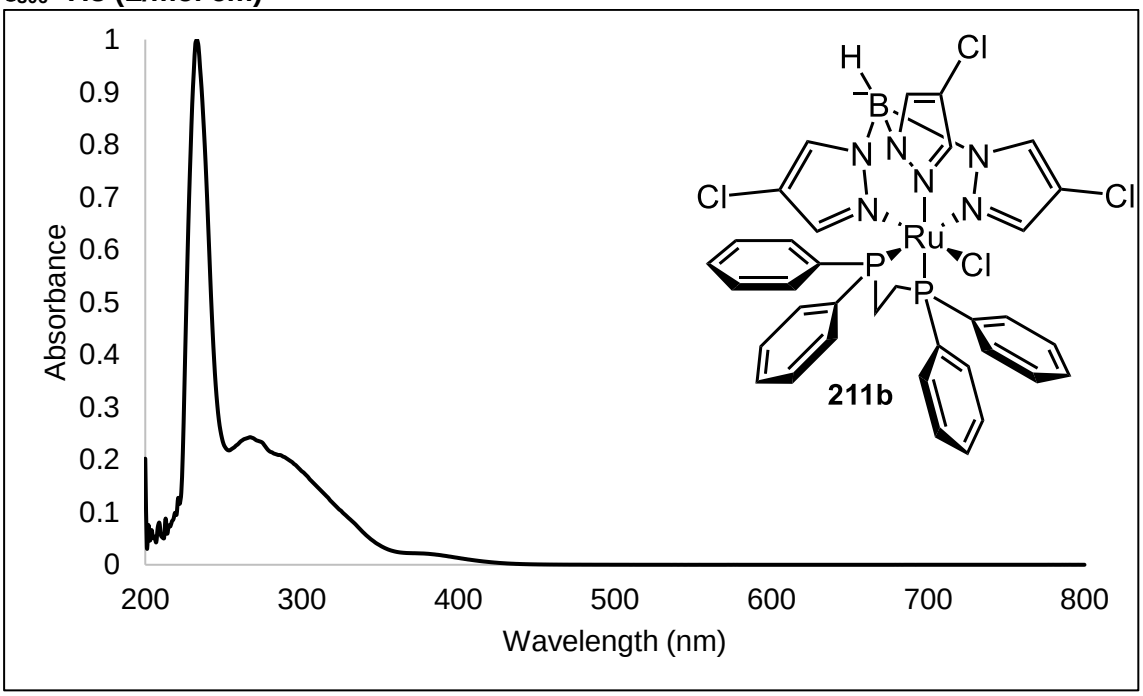


Figure A2.50: UV-Vis spectrum of 211b, ε_{232}=31.7 (L/mol cm) , ε_{283}=8.1 (L/mol cm)

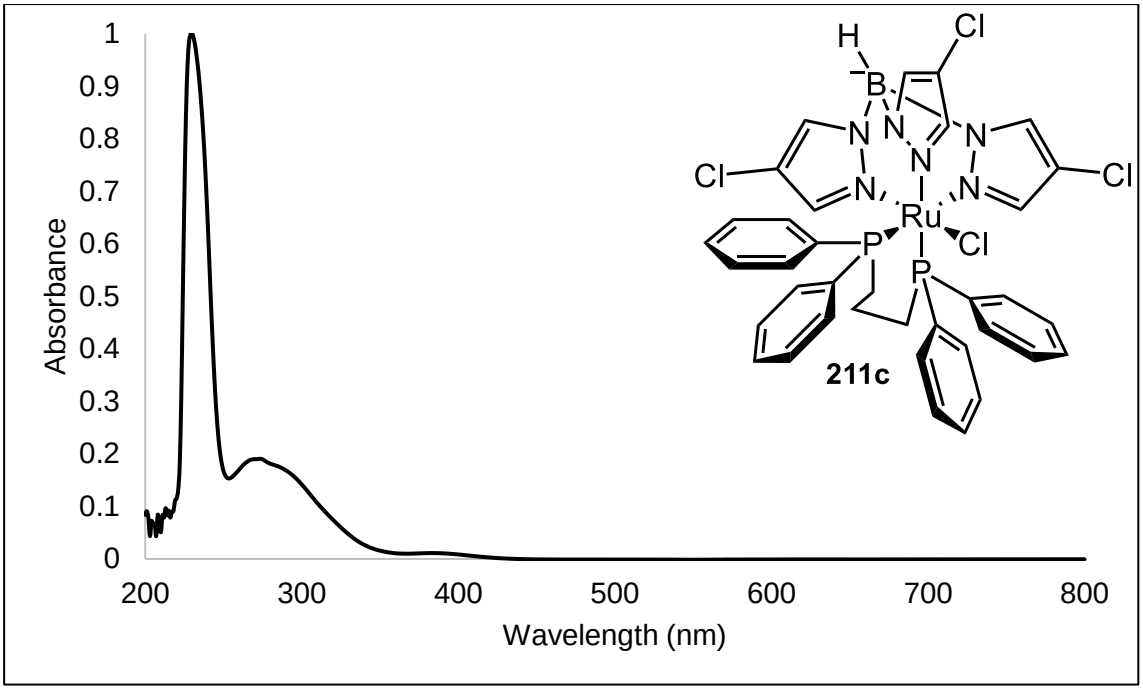


Figure A2.51: UV-Vis spectrum of 211c, ε_{235}=16.7 (L/mol cm) , ε_{274}=9.8 (L/mol cm)

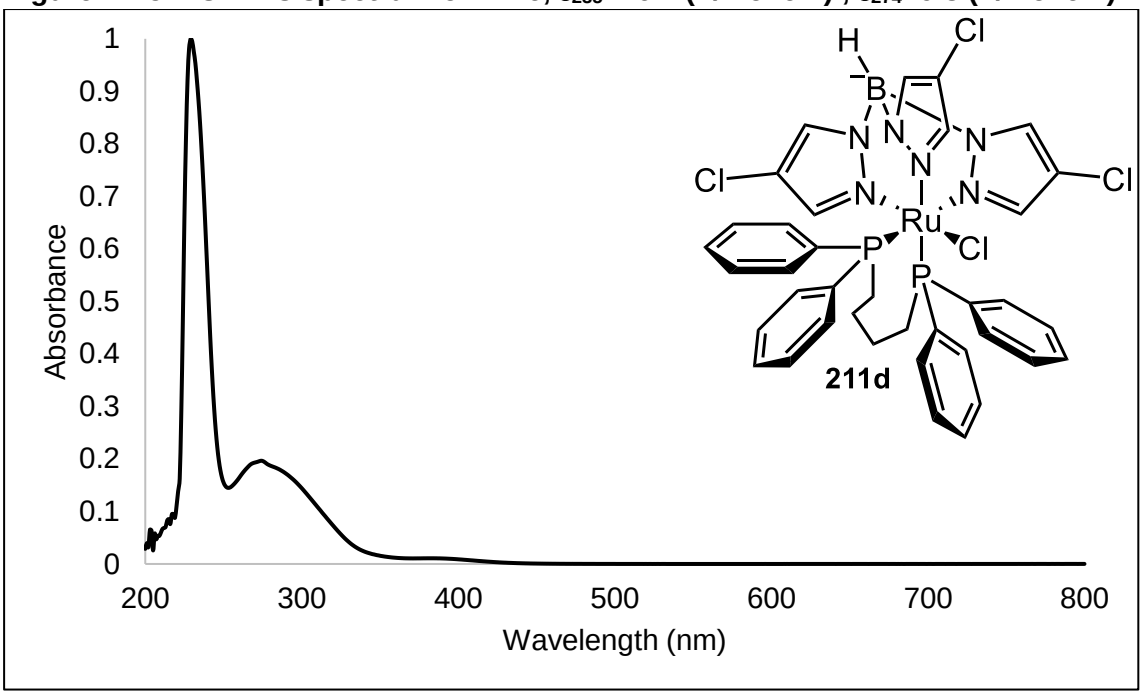


Figure A2.52: UV-Vis spectrum of 211d, ε_{239}=13.1 (L/mol cm), ε_{274}=10.2 (L/mol cm)

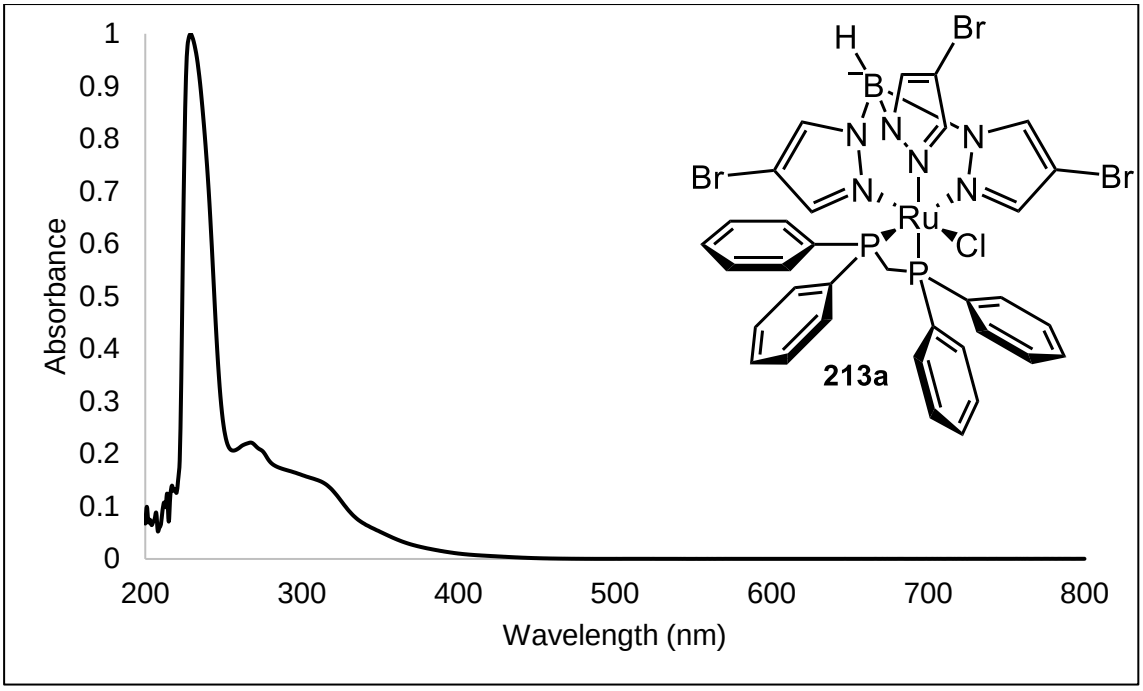


Figure A2.53: UV-Vis spectrum of 213a, ε_{239}=27.0 (L/mol cm) , ε_{268}=10.8 (L/mol cm) ε_{307}=7.5 (L/mol cm)

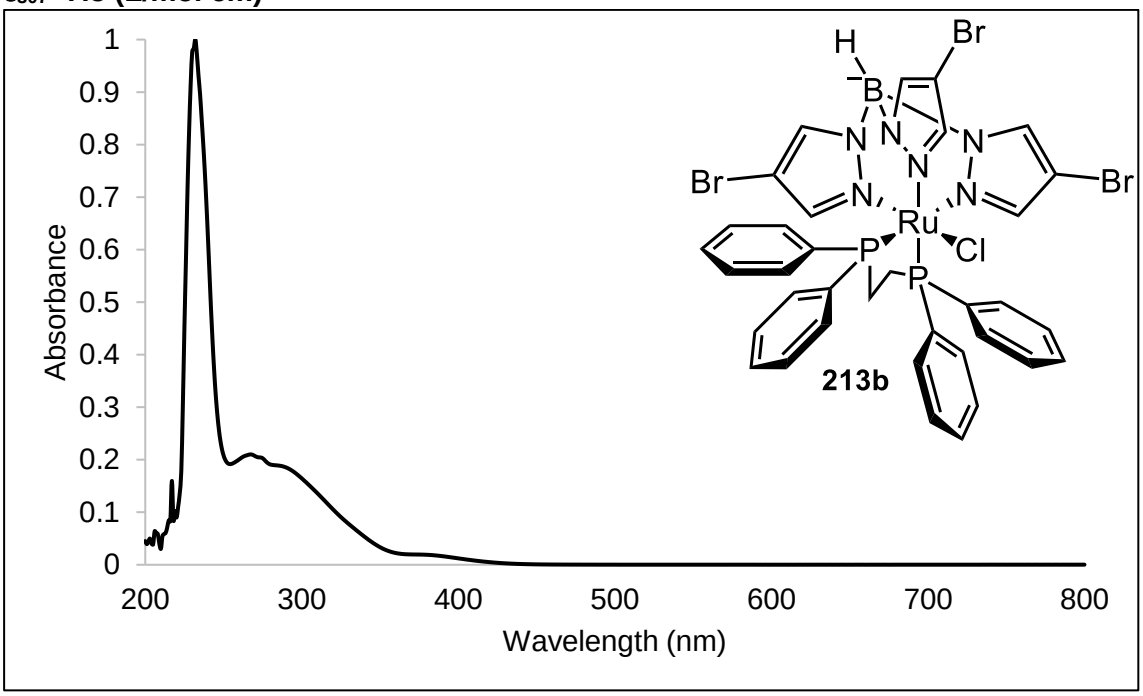


Figure A2.54: UV-Vis spectrum of 213b, ε_{236}=20.2 (L/mol cm) , ε_{268}=9.1 (L/mol cm), ε_{282}=8.4 (L/mol cm)

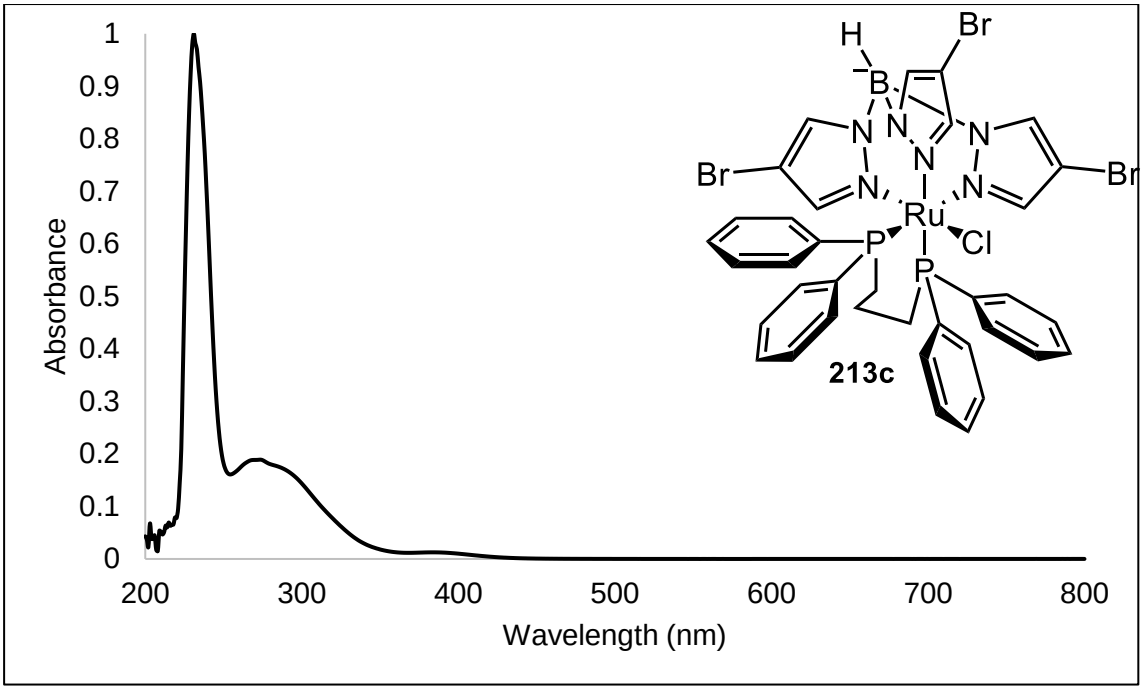


Figure A2.55: UV-Vis spectrum of 213c, ε_{238}=24.0 (L/mol cm), ε_{268}=9.6 (L/mol cm), ε_{283}=9.1 (L/mol cm)

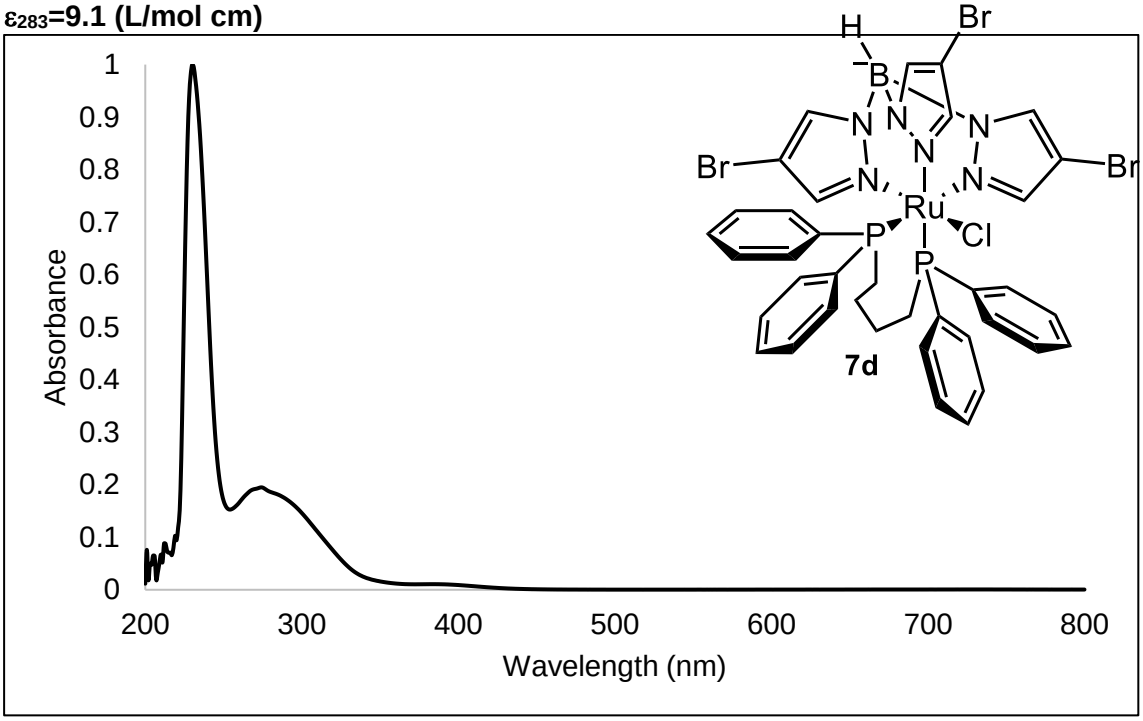


Figure A2.56: UV-Vis spectrum of 213d, ε_{235}=24.96 (L/mol cm), ε_{275}=10.2 (L/mol cm)

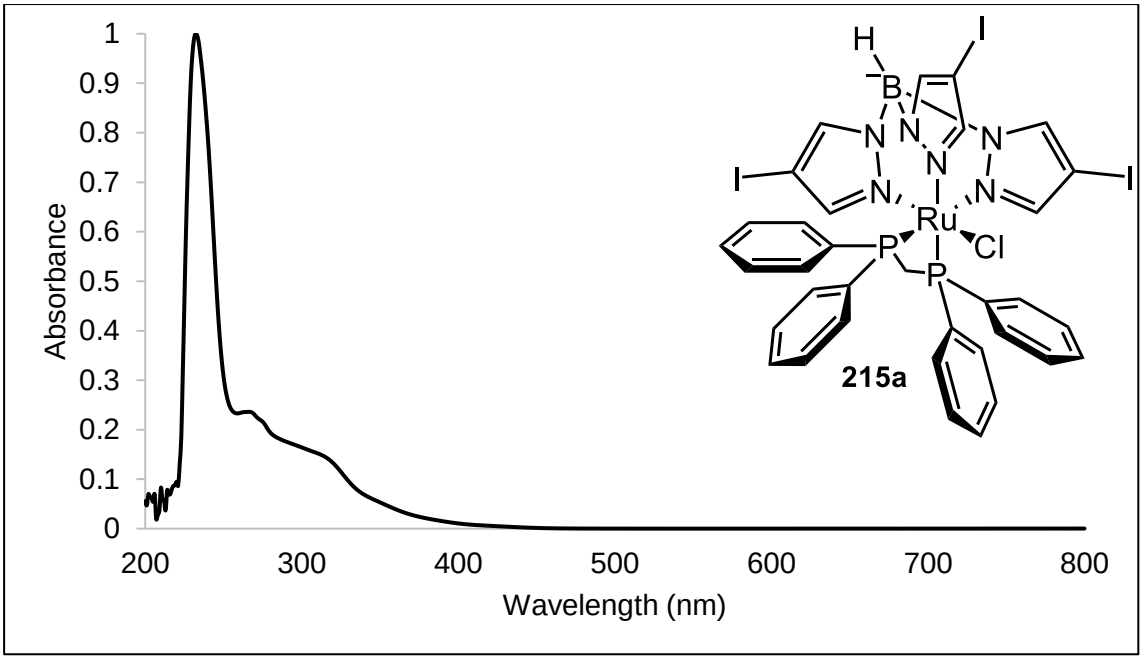


Figure A2.57: UV-Vis spectrum of 215a, ε_{231}=47.9 (L/mol cm), ε_{266}=12.2 (L/mol cm)

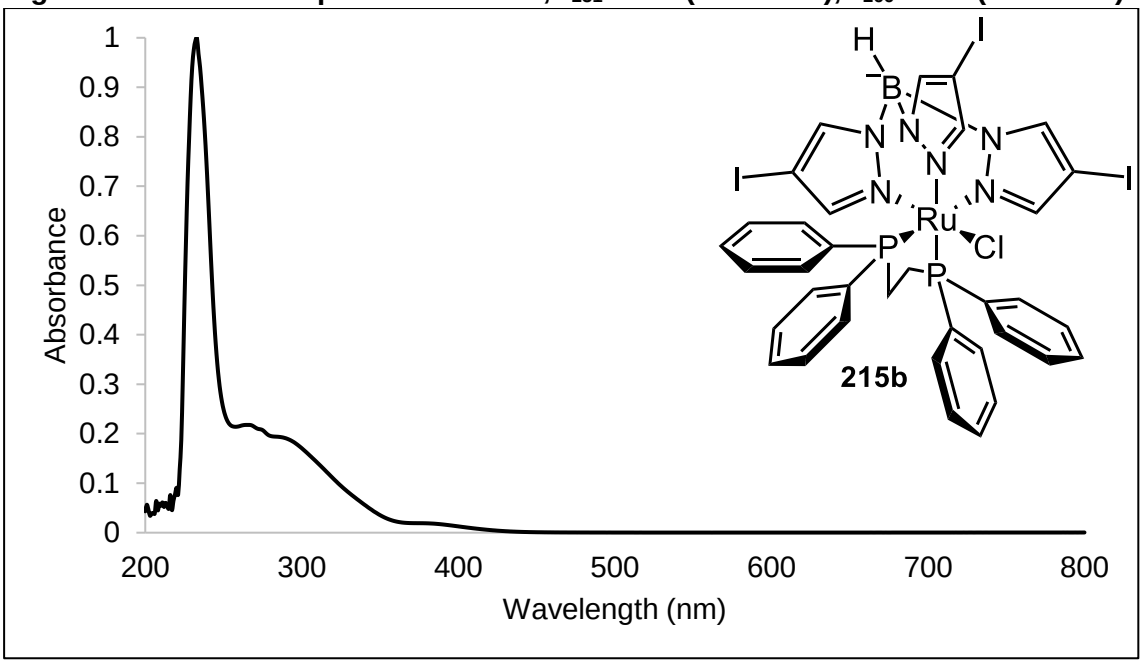


Figure A2.58: UV-Vis spectrum of 215b, ε_{230}=39.3 (L/mol cm), ε_{266}=9.1 (L/mol cm), ε_{284}=9.1 (L/mol cm)

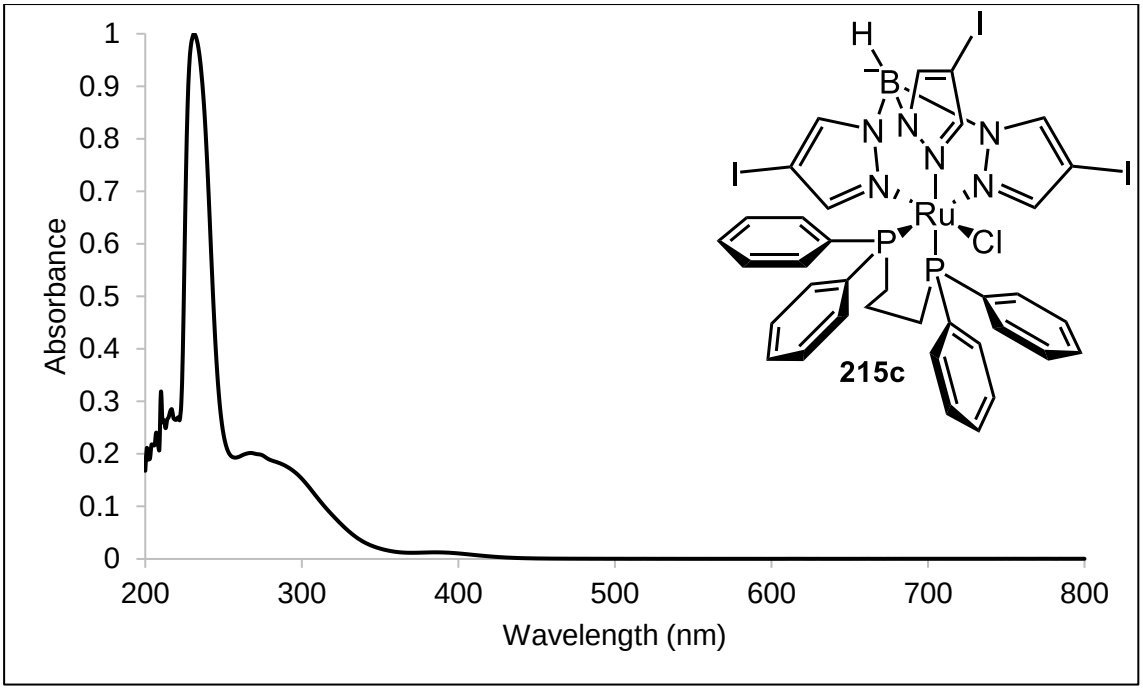


Figure A2.59: UV-Vis spectrum of 215c, ε_{233}=51.9 (L/mol cm), ε_{267}=9.7 (L/mol cm), ε_{283}=8.8 (L/mol cm)

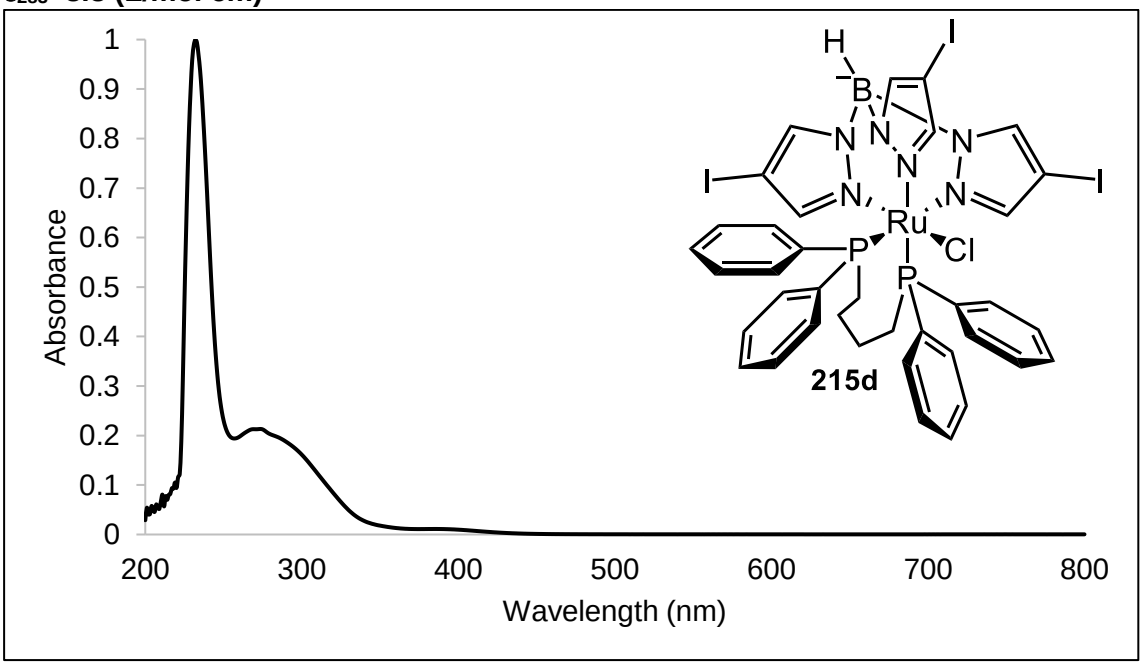


Figure A2.60: UV-Vis spectrum of 215d, ε_{230}=50.3 (L/mol cm), ε_{272}=10.4 (L/mol cm)

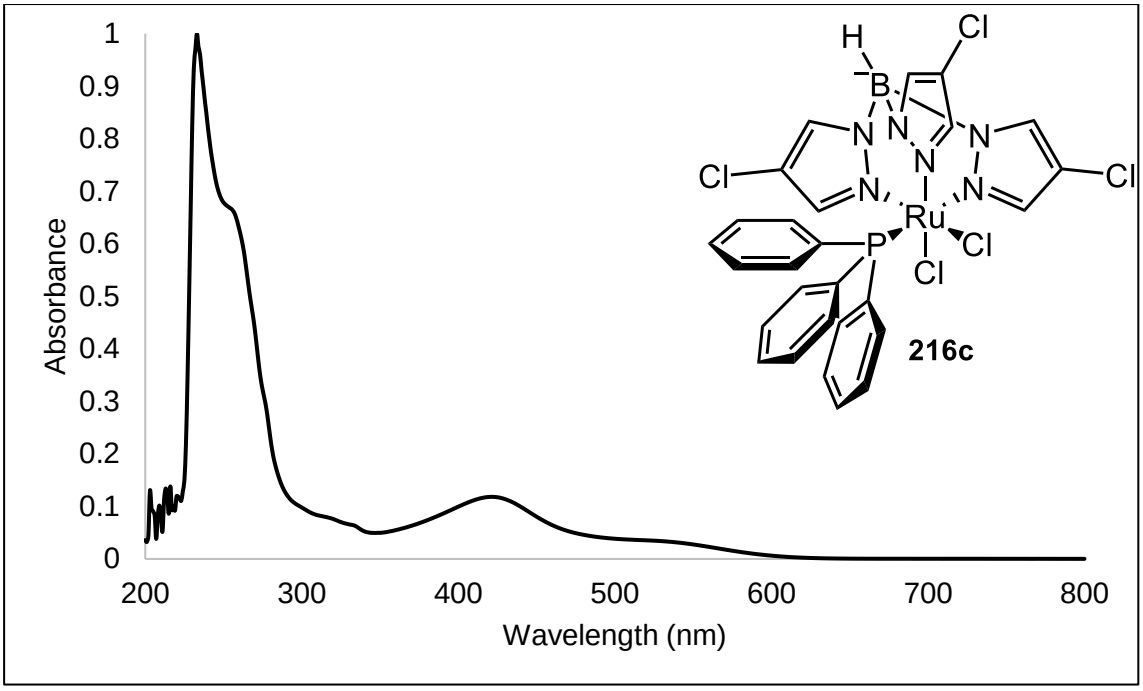


Figure A2.61: UV-Vis spectrum of 216c, ε_{231}=27.7 (L/mol cm) , ε_{255}=21.3 (L/mol cm) , ε_{313}=1.9 (L/mol cm) , ε_{422}=3.8 (L/mol cm)

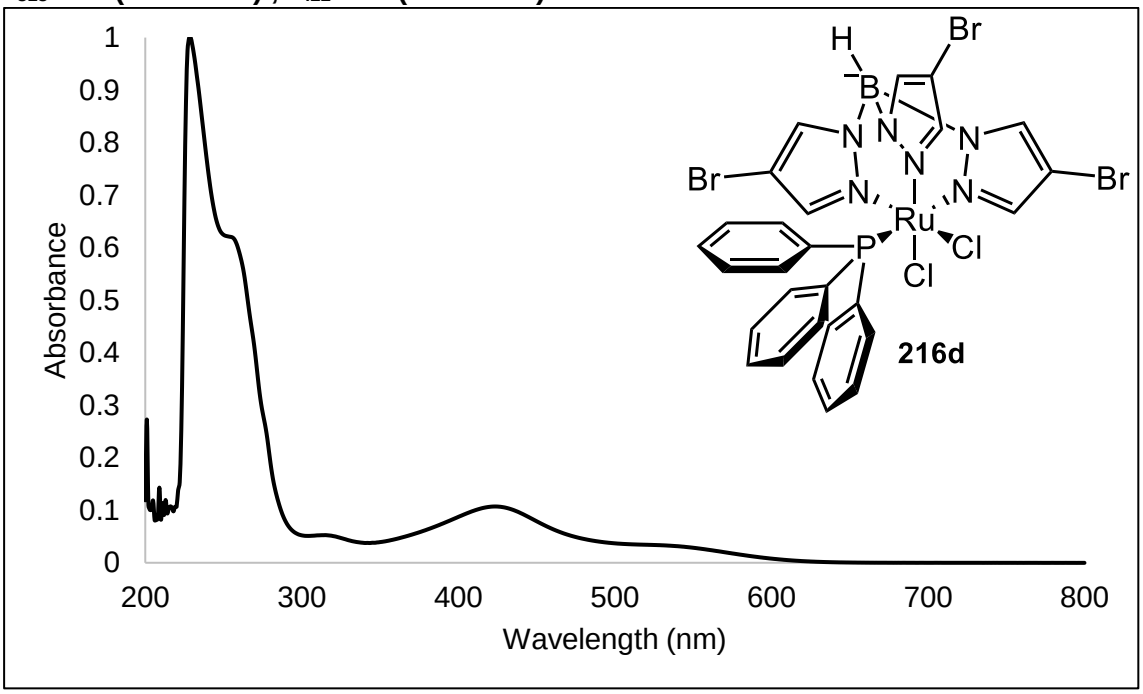


Figure A2.62: UV-Vis spectrum of 216d, ε_{233}=29.7 (L/mol cm), ε_{252}=22.2 (L/mol cm), ε_{312}=2.0 (L/mol cm), ε_{424}=3.9 (L/mol cm), ε_{525}=3.9 (L/mol cm)

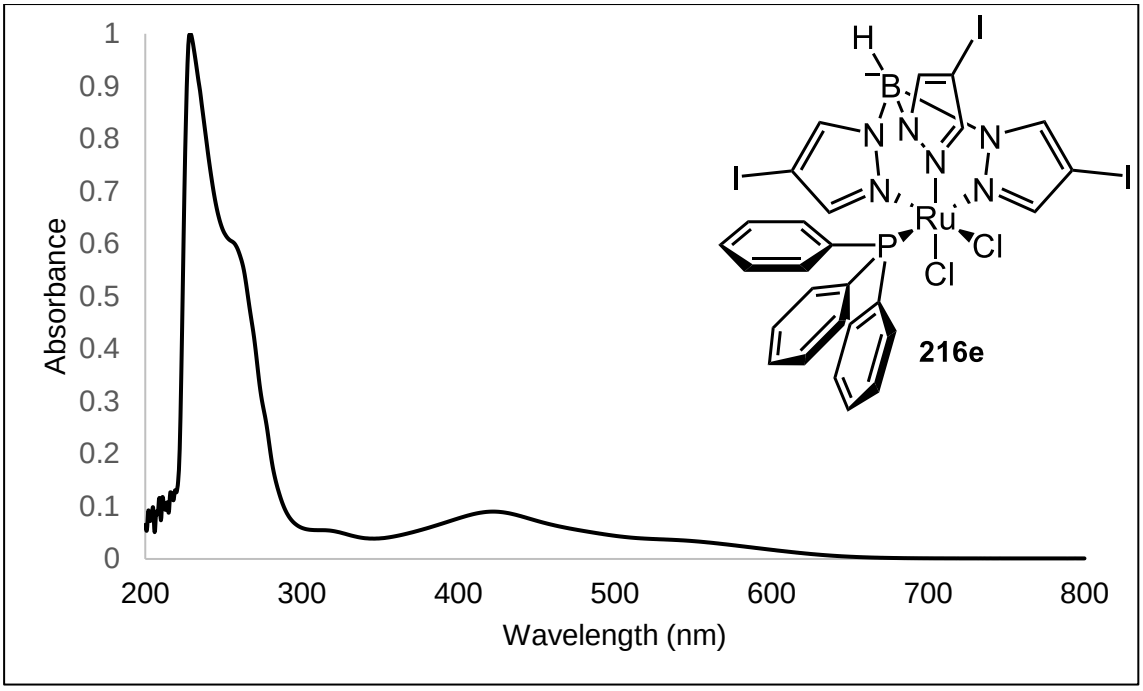


Figure A2.63: UV-Vis spectrum of 26e, ε_{227}=13.3 (L/mol cm), ε_{241}=26.9 (L/mol cm), ε_{256}=21.9 (L/mol cm), ε_{313}=2.0 (L/mol cm), ε_{422}=3.3 (L/mol cm), ε_{531}=1.3 (L/mol cm)

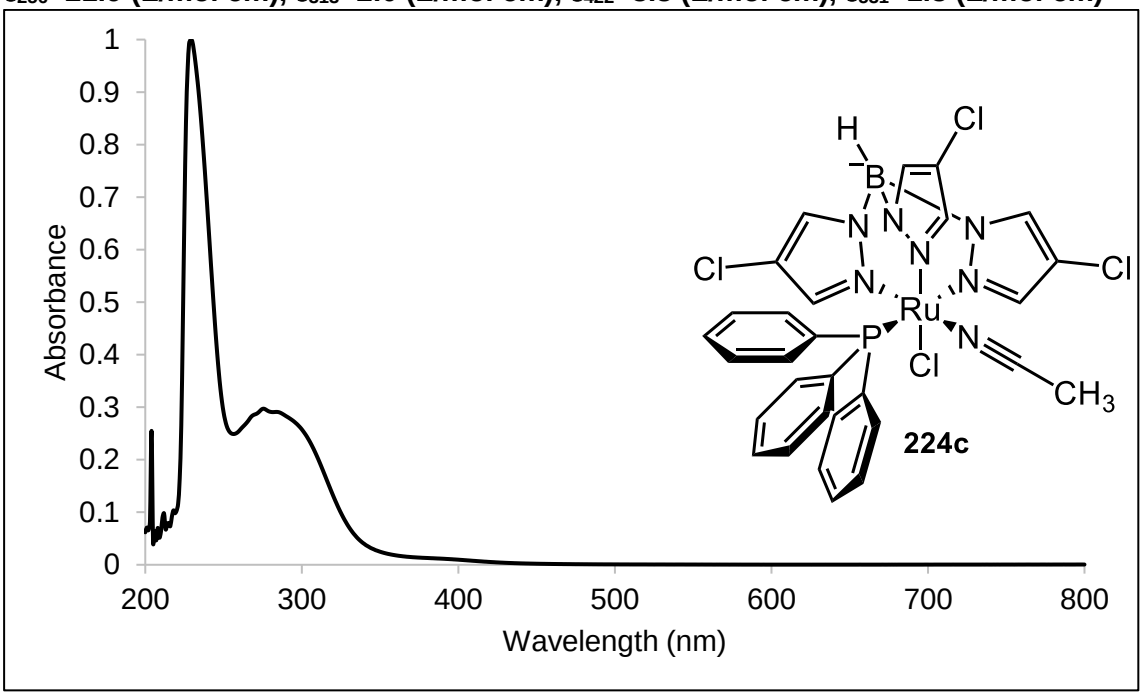


Figure A2.64: UV-Vis spectrum of 224c, ε_{230}=27.2 (L/mol cm), ε_{276}=8.8 (L/mol cm)

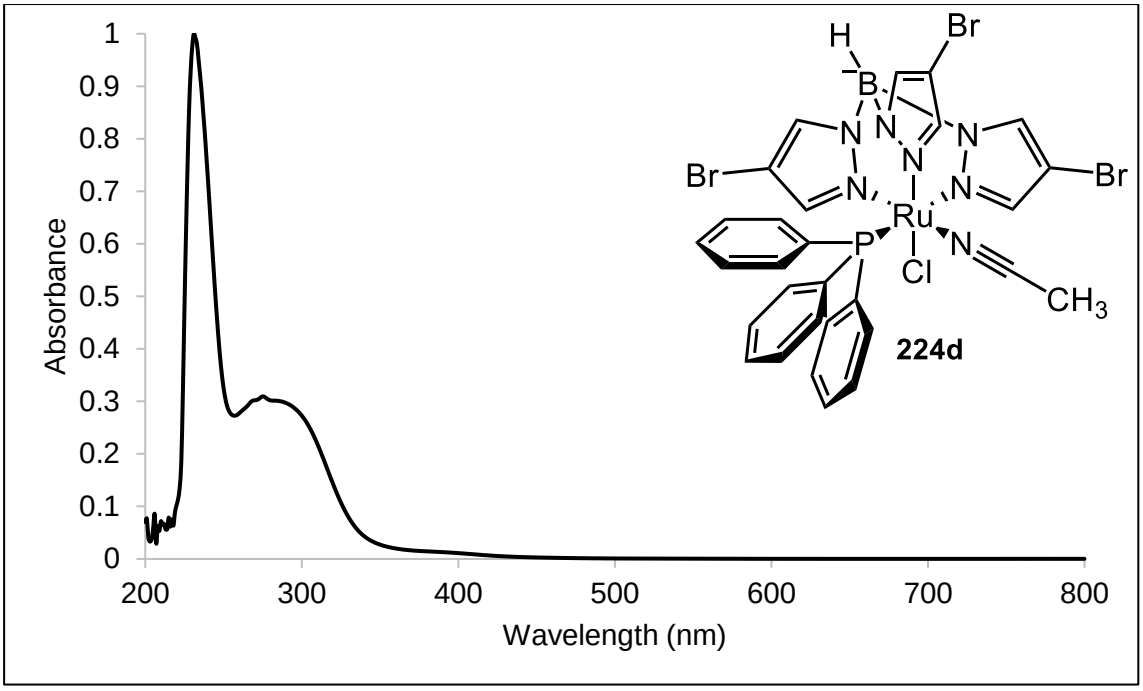


Figure A2.65: UV-Vis spectrum of 224d, ε_{229}=30.0 (L/mol cm), ε_{275}=11.0 (L/mol cm)

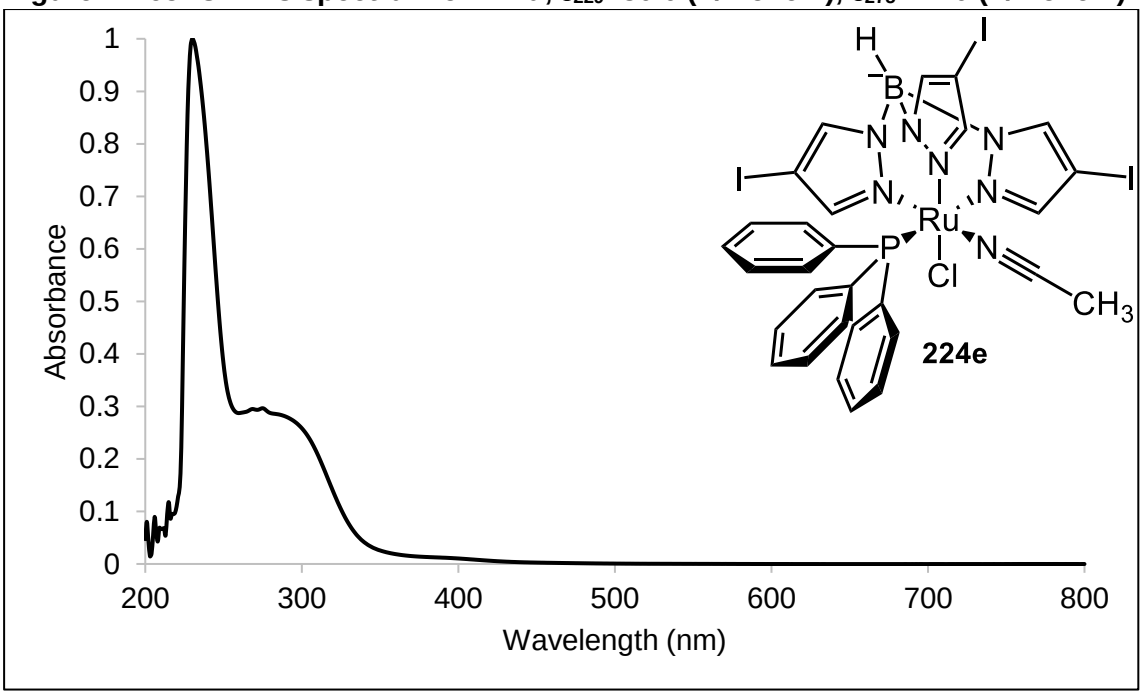


Figure A2.66: UV-Vis spectrum of 224e, ε_{229}=35.0 (L/mol cm), ε_{275}=11.2 (L/mol cm)

APPENDEX SIX: Crystal Data and Structure Refinement

Ligand exchange reactions of $Tp^{X}Ru(diene)Cl$ to mono- and di-phosphine complexes and their oxidation potentials.

Table A2.1: Crystal data and structure refinement for $Tp^{Cl}Ru(dppm)Cl$ 211a.

Identification code: $Tp^{Cl}Ru(dppm)Cl$ **211a**

Empirical formula: C74 H63 B2 Cl9 N12 P4 Ru2

Formula weight: 1787.05

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P -1

Unit cell dimensions	a = 10.2143(7) Å	α= 96.393(2)°.
	b = 11.6336(8) Å	β= 90.614(2)°.
	c = 18.0989(12) Å	γ = 115.8180(10)°.
Volume	1919.7(2) $Å^3$	
Z	1	
Density (calculated)	1.546 Mg/m^3	
Absorption coefficient	0.842 mm^{-1}	
F(000)	902	
Crystal size	0.300 x 0.080 x 0.060 mm^3	
Theta range for data collection	1.961 to 27.931°.	
Index ranges	-13<=h<=13, -15<=k<=15, -23<=l<=23	
Reflections collected	47922	
Independent reflections	9190 [R(int) = 0.0300]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7456 and 0.6838	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9190 / 122 / 499	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0557	
R indices (all data)	R1 = 0.0376, wR2 = 0.0589	
Largest diff. peak and hole	0.658 and -0.416 $e.Å^{-3}$	

Table A2.2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) Tp^{Cl}Ru(dppm)Cl 211a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl11	-418(2)	1532(2)	969(1)	68(1)
C11	-33(6)	510(5)	313(3)	44(1)
C21	-1111(11)	-299(10)	-210(6)	61(3)
C31	-852(9)	-1094(6)	-735(3)	75(2)
C41	553(10)	-1023(7)	-717(4)	70(2)
C51	1578(8)	-245(6)	-207(3)	60(2)
C61	1316(9)	566(10)	336(5)	41(2)
Ru(1)	3357(1)	6050(1)	2649(1)	12(1)
C(1)	2940(2)	7872(2)	818(1)	19(1)
Cl(1)	4614(1)	10526(1)	1019(1)	35(1)
N(1)	2671(2)	6890(2)	1221(1)	16(1)
P(1)	3594(1)	4808(1)	3483(1)	14(1)
B(1)	1789(2)	5422(2)	1014(1)	17(1)
Cl(2)	5236(1)	3157(1)	334(1)	28(1)
N(2)	3425(2)	7348(2)	1896(1)	15(1)
P(2)	5720(1)	7035(1)	3116(1)	14(1)
C(2)	3890(2)	8987(2)	1249(1)	22(1)
N(5)	644(2)	4891(2)	1592(1)	16(1)
C(5)	4344(2)	3937(2)	813(1)	20(1)
N(4)	3679(2)	4994(2)	1719(1)	16(1)
Cl(4)	2697(1)	7374(1)	3544(1)	18(1)
C(4)	3267(2)	4191(2)	517(1)	19(1)
N(3)	2870(2)	4827(2)	1070(1)	16(1)
Cl(3)	-3081(1)	3164(1)	2442(1)	29(1)
C(3)	4160(2)	8621(2)	1921(1)	19(1)
N(6)	1115(2)	4985(2)	2314(1)	15(1)
C(6)	4572(2)	4444(2)	1561(1)	18(1)
C(9)	-65(2)	4409(2)	2690(1)	17(1)
C(8)	-1308(2)	3947(2)	2204(1)	19(1)

C(7)	-829(2)	4262(2)	1516(1)	20(1)
C(10)	5562(2)	5838(2)	3748(1)	18(1)
C(11)	3391(2)	3188(2)	3187(1)	17(1)
C(12)	2226(2)	2366(2)	2686(1)	25(1)
C(13)	1887(3)	1065(2)	2545(1)	33(1)
C(15)	3913(2)	1398(2)	3368(1)	29(1)
C(14)	2723(3)	581(2)	2888(1)	33(1)
C(16)	4235(2)	2693(2)	3526(1)	23(1)
C(17)	2625(2)	4540(2)	4346(1)	16(1)
C(18)	1699(2)	3299(2)	4496(1)	22(1)
C(19)	880(2)	3114(2)	5119(1)	25(1)
C(20)	944(2)	4159(2)	5592(1)	23(1)
C(21)	1875(2)	5388(2)	5457(1)	23(1)
C(22)	2708(2)	5586(2)	4838(1)	20(1)
C(23)	6477(2)	8622(2)	3674(1)	18(1)
C(24)	6218(2)	8788(2)	4421(1)	29(1)
C(25)	6684(2)	10019(2)	4810(1)	33(1)
C(26)	7403(2)	11085(2)	4457(1)	31(1)
C(27)	7686(3)	10938(2)	3713(1)	34(1)
C(28)	7235(2)	9715(2)	3326(1)	26(1)
C(29)	7199(2)	7204(2)	2514(1)	16(1)
C(30)	8456(2)	7140(2)	2774(1)	21(1)
C(31)	9600(2)	7346(2)	2317(1)	26(1)
C(32)	9509(2)	7646(2)	1606(1)	27(1)
C(33)	8270(2)	7718(2)	1342(1)	25(1)
C(34)	7109(2)	7480(2)	1790(1)	20(1)

Table A2.3: Bond lengths [Å] and angles [°] for Tp^{Cl}Ru(dppm)Cl 211a.

Cl11-C41#1	0.667(6)	C11-C41#1	1.166(10)
Cl11-C31#1	1.631(10)	C11-C21#1	1.305(13)
Cl11-C11	1.755(6)	C11-C61	1.351(8)
Cl11-C51#1	1.874(6)	C11-C21	1.368(8)
C11-C31#1	1.095(8)	C11-C51#1	1.476(9)

C11-C11#1	1.571(12)	N(5)-C(7)	1.353(2)
C11-C61#1	1.696(10)	N(5)-N(6)	1.364(2)
C21-C31	1.361(10)	C(5)-C(4)	1.374(3)
C21-H21	0.9500	C(5)-C(6)	1.389(3)
C31-C41	1.400(9)	N(4)-C(6)	1.340(2)
C31-H31	0.9500	N(4)-N(3)	1.374(2)
C41-C51	1.318(8)	C(4)-N(3)	1.348(2)
C41-H41	0.9500	C(4)-H(4)	0.9500
C51-C61	1.395(9)	Cl(3)-C(8)	1.7215(19)
C51-H51	0.9500	C(3)-H(3)	0.9500
C61-H61	0.9500	N(6)-C(9)	1.334(2)
Ru(1)-N(4)	2.0870(16)	C(6)-H(6)	0.9500
Ru(1)-N(6)	2.1159(15)	C(9)-C(8)	1.397(3)
Ru(1)-N(2)	2.1243(16)	C(9)-H(9)	0.9500
Ru(1)-P(2)	2.2769(5)	C(8)-C(7)	1.372(3)
Ru(1)-P(1)	2.2818(5)	C(7)-H(7)	0.9500
Ru(1)-Cl(4)	2.4129(5)	C(10)-H(10A)	0.9900
C(1)-N(1)	1.353(2)	C(10)-H(10B)	0.9900
C(1)-C(2)	1.376(3)	C(11)-C(12)	1.394(3)
C(1)-H(1)	0.9500	C(11)-C(16)	1.397(3)
Cl(1)-C(2)	1.716(2)	C(12)-C(13)	1.390(3)
N(1)-N(2)	1.358(2)	C(12)-H(12)	0.9500
N(1)-B(1)	1.542(3)	C(13)-C(14)	1.384(3)
P(1)-C(11)	1.8214(19)	C(13)-H(13)	0.9500
P(1)-C(17)	1.8400(19)	C(15)-C(14)	1.386(3)
P(1)-C(10)	1.8604(18)	C(15)-C(16)	1.389(3)
B(1)-N(5)	1.543(3)	C(15)-H(15)	0.9500
B(1)-N(3)	1.545(3)	C(14)-H(14)	0.9500
B(1)-H(101)	1.09(2)	C(16)-H(16)	0.9500
Cl(2)-C(5)	1.7231(19)	C(17)-C(22)	1.396(3)
N(2)-C(3)	1.333(2)	C(17)-C(18)	1.399(3)
P(2)-C(29)	1.8258(19)	C(18)-C(19)	1.393(3)
P(2)-C(23)	1.8308(19)	C(18)-H(18)	0.9500
P(2)-C(10)	1.8546(19)	C(19)-C(20)	1.383(3)
C(2)-C(3)	1.395(3)	C(19)-H(19)	0.9500

C(20)-C(21)	1.380(3)	C31#1-C11-C21#1	68.4(6)
C(20)-H(20)	0.9500	C41#1-C11-C21#1	144.6(7)
C(21)-C(22)	1.393(3)	C31#1-C11-C61	54.0(6)
C(21)-H(21)	0.9500	C41#1-C11-C61	130.5(6)
C(22)-H(22)	0.9500	C21#1-C11-C61	14.8(6)
C(23)-C(24)	1.388(3)	C31#1-C11-C21	175.5(8)
C(23)-C(28)	1.395(3)	C41#1-C11-C21	106.7(6)
C(24)-C(25)	1.395(3)	C21#1-C11-C21	108.1(6)
C(24)-H(24)	0.9500	C61-C11-C21	122.6(7)
C(25)-C(26)	1.371(3)	C31#1-C11-C51#1	134.8(8)
C(25)-H(25)	0.9500	C41#1-C11-C51#1	58.4(5)
C(26)-C(27)	1.387(3)	C21#1-C11-C51#1	155.7(6)
C(26)-H(26)	0.9500	C61-C11-C51#1	170.5(6)
C(27)-C(28)	1.388(3)	C21-C11-C51#1	48.2(5)
C(27)-H(27)	0.9500	C31#1-C11-C11#1	124.2(8)
C(28)-H(28)	0.9500	C41#1-C11-C11#1	158.1(7)
C(29)-C(34)	1.395(3)	C21#1-C11-C11#1	55.9(5)
C(29)-C(30)	1.398(3)	C61-C11-C11#1	70.5(5)
C(30)-C(31)	1.389(3)	C21-C11-C11#1	52.2(5)
C(30)-H(30)	0.9500	C51#1-C11-C11#1	100.2(5)
C(31)-C(32)	1.382(3)	C31#1-C11-C61#1	171.5(8)
C(31)-H(31)	0.9500	C41#1-C11-C61#1	110.0(6)
C(32)-C(33)	1.388(3)	C21#1-C11-C61#1	104.5(6)
C(32)-H(32)	0.9500	C61-C11-C61#1	119.2(5)
C(33)-C(34)	1.387(3)	C21-C11-C61#1	4.0(7)
C(33)-H(33)	0.9500	C51#1-C11-C61#1	51.6(4)
C(34)-H(34)	0.9500	C11#1-C11-C61#1	48.7(4)
		C31#1-C11-Cl11	65.1(6)
C41#1-Cl11-C31#1	58.3(9)	C41#1-C11-Cl11	12.6(4)
C41#1-Cl11-C11	22.3(9)	C21#1-C11-Cl11	133.5(5)
C31#1-Cl11-C11	37.5(3)	C61-C11-Cl11	119.0(4)
C41#1-Cl11-C51#1	27.5(8)	C21-C11-Cl11	118.4(6)
C31#1-Cl11-C51#1	85.2(3)	C51#1-C11-Cl11	70.3(4)
C11-Cl11-C51#1	47.9(3)	C11#1-C11-Cl11	170.5(5)
C31#1-C11-C41#1	76.5(6)	C61#1-C11-Cl11	121.9(5)

C31-C21-C11	120.3(8)	N(2)-N(1)-B(1)	118.81(15)
C31-C21-H21	119.9	C(11)-P(1)-C(17)	99.93(9)
C11-C21-H21	119.9	C(11)-P(1)-C(10)	106.97(9)
C21-C31-C41	117.0(6)	C(17)-P(1)-C(10)	107.79(8)
C21-C31-H31	121.5	C(11)-P(1)-Ru(1)	121.43(6)
C41-C31-H31	121.5	C(17)-P(1)-Ru(1)	123.09(6)
C51-C41-C31	122.0(7)	C(10)-P(1)-Ru(1)	96.24(6)
C51-C41-H41	119.0	N(1)-B(1)-N(5)	109.27(15)
C31-C41-H41	119.0	N(1)-B(1)-N(3)	106.93(15)
C41-C51-C61	121.2(7)	N(5)-B(1)-N(3)	108.00(16)
C41-C51-H51	119.4	N(1)-B(1)-H(101)	111.0(11)
C61-C51-H51	119.4	N(5)-B(1)-H(101)	110.1(11)
C11-C61-C51	116.8(6)	N(3)-B(1)-H(101)	111.4(11)
C11-C61-H61	121.6	C(3)-N(2)-N(1)	107.26(15)
C51-C61-H61	121.6	C(3)-N(2)-Ru(1)	132.63(13)
N(4)-Ru(1)-N(6)	84.98(6)	N(1)-N(2)-Ru(1)	120.01(12)
N(4)-Ru(1)-N(2)	84.97(6)	C(29)-P(2)-C(23)	101.31(9)
N(6)-Ru(1)-N(2)	87.18(6)	C(29)-P(2)-C(10)	108.02(9)
N(4)-Ru(1)-P(2)	96.50(4)	C(23)-P(2)-C(10)	107.59(9)
N(6)-Ru(1)-P(2)	173.14(4)	C(29)-P(2)-Ru(1)	120.75(6)
N(2)-Ru(1)-P(2)	99.61(4)	C(23)-P(2)-Ru(1)	121.47(6)
N(4)-Ru(1)-P(1)	95.03(5)	C(10)-P(2)-Ru(1)	96.57(6)
N(6)-Ru(1)-P(1)	100.05(4)	C(1)-C(2)-C(3)	106.16(17)
N(2)-Ru(1)-P(1)	172.75(4)	C(1)-C(2)-Cl(1)	127.73(16)
P(2)-Ru(1)-P(1)	73.174(17)	C(3)-C(2)-Cl(1)	126.11(16)
N(4)-Ru(1)-Cl(4)	168.24(4)	C(7)-N(5)-N(6)	109.92(15)
N(6)-Ru(1)-Cl(4)	87.89(4)	C(7)-N(5)-B(1)	131.38(16)
N(2)-Ru(1)-Cl(4)	85.34(4)	N(6)-N(5)-B(1)	118.64(14)
P(2)-Ru(1)-Cl(4)	91.687(17)	C(4)-C(5)-C(6)	106.63(16)
P(1)-Ru(1)-Cl(4)	95.420(18)	C(4)-C(5)-Cl(2)	125.94(16)
N(1)-C(1)-C(2)	107.32(17)	C(6)-C(5)-Cl(2)	127.43(16)
N(1)-C(1)-H(1)	126.3	C(6)-N(4)-N(3)	106.70(15)
C(2)-C(1)-H(1)	126.3	C(6)-N(4)-Ru(1)	135.80(13)
C(1)-N(1)-N(2)	109.94(15)	N(3)-N(4)-Ru(1)	117.42(11)
C(1)-N(1)-B(1)	131.07(16)	N(3)-C(4)-C(5)	107.51(17)

N(3)-C(4)-H(4)	126.2	C(14)-C(13)-C(12)	120.2(2)
C(5)-C(4)-H(4)	126.2	C(14)-C(13)-H(13)	119.9
C(4)-N(3)-N(4)	109.80(15)	C(12)-C(13)-H(13)	119.9
C(4)-N(3)-B(1)	127.95(16)	C(14)-C(15)-C(16)	120.0(2)
N(4)-N(3)-B(1)	122.03(15)	C(14)-C(15)-H(15)	120.0
N(2)-C(3)-C(2)	109.32(17)	C(16)-C(15)-H(15)	120.0
N(2)-C(3)-H(3)	125.3	C(13)-C(14)-C(15)	120.0(2)
C(2)-C(3)-H(3)	125.3	C(13)-C(14)-H(14)	120.0
C(9)-N(6)-N(5)	107.19(15)	C(15)-C(14)-H(14)	120.0
C(9)-N(6)-Ru(1)	132.69(13)	C(15)-C(16)-C(11)	120.4(2)
N(5)-N(6)-Ru(1)	119.90(11)	C(15)-C(16)-H(16)	119.8
N(4)-C(6)-C(5)	109.36(17)	C(11)-C(16)-H(16)	119.8
N(4)-C(6)-H(6)	125.3	C(22)-C(17)-C(18)	118.30(18)
C(5)-C(6)-H(6)	125.3	C(22)-C(17)-P(1)	120.18(15)
N(6)-C(9)-C(8)	109.10(17)	C(18)-C(17)-P(1)	121.31(15)
N(6)-C(9)-H(9)	125.4	C(19)-C(18)-C(17)	120.72(19)
C(8)-C(9)-H(9)	125.4	C(19)-C(18)-H(18)	119.6
C(7)-C(8)-C(9)	106.51(16)	C(17)-C(18)-H(18)	119.6
C(7)-C(8)-Cl(3)	127.69(15)	C(20)-C(19)-C(18)	120.35(19)
C(9)-C(8)-Cl(3)	125.80(16)	C(20)-C(19)-H(19)	119.8
N(5)-C(7)-C(8)	107.28(16)	C(18)-C(19)-H(19)	119.8
N(5)-C(7)-H(7)	126.4	C(21)-C(20)-C(19)	119.39(19)
C(8)-C(7)-H(7)	126.4	C(21)-C(20)-H(20)	120.3
P(2)-C(10)-P(1)	94.01(8)	C(19)-C(20)-H(20)	120.3
P(2)-C(10)-H(10A)	112.9	C(20)-C(21)-C(22)	120.80(19)
P(1)-C(10)-H(10A)	112.9	C(20)-C(21)-H(21)	119.6
P(2)-C(10)-H(10B)	112.9	C(22)-C(21)-H(21)	119.6
P(1)-C(10)-H(10B)	112.9	C(21)-C(22)-C(17)	120.39(19)
H(10A)-C(10)-H(10B)	110.3	C(21)-C(22)-H(22)	119.8
C(12)-C(11)-C(16)	119.09(18)	C(17)-C(22)-H(22)	119.8
C(12)-C(11)-P(1)	118.62(15)	C(24)-C(23)-C(28)	118.41(19)
C(16)-C(11)-P(1)	121.63(15)	C(24)-C(23)-P(2)	122.28(16)
C(13)-C(12)-C(11)	120.3(2)	C(28)-C(23)-P(2)	119.06(15)
C(13)-C(12)-H(12)	119.9	C(23)-C(24)-C(25)	120.8(2)
C(11)-C(12)-H(12)	119.9	C(23)-C(24)-H(24)	119.6

C(25)-C(24)-H(24)	119.6	C(31)-C(30)-H(30)	119.8
C(26)-C(25)-C(24)	120.2(2)	C(29)-C(30)-H(30)	119.8
C(26)-C(25)-H(25)	119.9	C(32)-C(31)-C(30)	119.78(19)
C(24)-C(25)-H(25)	119.9	C(32)-C(31)-H(31)	120.1
C(25)-C(26)-C(27)	119.8(2)	C(30)-C(31)-H(31)	120.1
C(25)-C(26)-H(26)	120.1	C(31)-C(32)-C(33)	120.34(19)
C(27)-C(26)-H(26)	120.1	C(31)-C(32)-H(32)	119.8
C(26)-C(27)-C(28)	120.2(2)	C(33)-C(32)-H(32)	119.8
C(26)-C(27)-H(27)	119.9	C(34)-C(33)-C(32)	120.1(2)
C(28)-C(27)-H(27)	119.9	C(34)-C(33)-H(33)	120.0
C(27)-C(28)-C(23)	120.6(2)	C(32)-C(33)-H(33)	120.0
C(27)-C(28)-H(28)	119.7	C(33)-C(34)-C(29)	120.18(18)
C(23)-C(28)-H(28)	119.7	C(33)-C(34)-H(34)	119.9
C(34)-C(29)-C(30)	119.20(17)	C(29)-C(34)-H(34)	119.9
C(34)-C(29)-P(2)	119.06(14)		
C(30)-C(29)-P(2)	121.63(15)		
C(31)-C(30)-C(29)	120.40(19)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z

Table A2.4: Anisotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppm)Cl. 211a The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl11	58(1)	63(1)	85(2)	8(1)	-5(1)	28(1)
C11	48(3)	29(3)	41(3)	15(2)	-14(2)	2(2)
C21	60(4)	44(5)	44(4)	20(3)	-29(3)	-13(4)
C31	101(5)	44(4)	42(3)	17(3)	-22(3)	-5(3)
C41	127(5)	29(4)	33(4)	-2(3)	-20(3)	17(4)
C51	98(5)	41(3)	45(3)	10(3)	-12(3)	33(3)
C61	43(3)	26(4)	39(4)	6(3)	-23(3)	4(3)
Ru(1)	12(1)	13(1)	12(1)	1(1)	1(1)	6(1)
C(1)	24(1)	22(1)	17(1)	7(1)	5(1)	15(1)

Cl(1)	50(1)	19(1)	36(1)	11(1)	4(1)	13(1)
N(1)	18(1)	19(1)	14(1)	3(1)	2(1)	11(1)
P(1)	13(1)	14(1)	13(1)	2(1)	1(1)	5(1)
B(1)	18(1)	19(1)	15(1)	3(1)	1(1)	9(1)
Cl(2)	43(1)	23(1)	30(1)	10(1)	20(1)	23(1)
N(2)	16(1)	17(1)	14(1)	2(1)	2(1)	8(1)
P(2)	13(1)	14(1)	14(1)	2(1)	1(1)	5(1)
C(2)	26(1)	19(1)	25(1)	8(1)	7(1)	14(1)
N(5)	16(1)	18(1)	15(1)	1(1)	-1(1)	7(1)
C(5)	26(1)	15(1)	22(1)	6(1)	11(1)	11(1)
N(4)	16(1)	16(1)	15(1)	3(1)	2(1)	6(1)
Cl(4)	21(1)	19(1)	16(1)	0(1)	2(1)	11(1)
C(4)	27(1)	14(1)	14(1)	2(1)	6(1)	8(1)
N(3)	19(1)	17(1)	12(1)	2(1)	2(1)	8(1)
Cl(3)	13(1)	35(1)	35(1)	11(1)	4(1)	5(1)
C(3)	19(1)	16(1)	22(1)	2(1)	2(1)	9(1)
N(6)	15(1)	16(1)	14(1)	1(1)	1(1)	7(1)
C(6)	18(1)	15(1)	22(1)	6(1)	6(1)	9(1)
C(9)	17(1)	18(1)	18(1)	3(1)	3(1)	8(1)
C(8)	14(1)	17(1)	26(1)	4(1)	2(1)	5(1)
C(7)	16(1)	19(1)	23(1)	1(1)	-2(1)	7(1)
C(10)	14(1)	18(1)	19(1)	6(1)	0(1)	5(1)
C(11)	20(1)	15(1)	17(1)	4(1)	6(1)	8(1)
C(12)	30(1)	20(1)	25(1)	-1(1)	-1(1)	12(1)
C(13)	36(1)	23(1)	34(1)	-6(1)	-1(1)	9(1)
C(15)	30(1)	26(1)	42(1)	15(1)	15(1)	18(1)
C(14)	39(1)	19(1)	45(1)	5(1)	15(1)	15(1)
C(16)	21(1)	24(1)	26(1)	7(1)	6(1)	10(1)
C(17)	14(1)	21(1)	14(1)	4(1)	1(1)	8(1)
C(18)	22(1)	20(1)	20(1)	2(1)	2(1)	5(1)
C(19)	21(1)	24(1)	24(1)	8(1)	5(1)	3(1)
C(20)	22(1)	36(1)	17(1)	9(1)	6(1)	16(1)
C(21)	30(1)	28(1)	17(1)	3(1)	4(1)	19(1)
C(22)	24(1)	19(1)	18(1)	4(1)	1(1)	10(1)
C(23)	15(1)	16(1)	22(1)	-1(1)	-2(1)	5(1)

C(24)	29(1)	22(1)	24(1)	-1(1)	5(1)	2(1)
C(25)	33(1)	30(1)	26(1)	-8(1)	3(1)	7(1)
C(26)	31(1)	23(1)	37(1)	-8(1)	-8(1)	13(1)
C(27)	42(1)	19(1)	36(1)	4(1)	-3(1)	8(1)
C(28)	33(1)	20(1)	23(1)	3(1)	-1(1)	9(1)
C(29)	14(1)	13(1)	19(1)	3(1)	2(1)	5(1)
C(30)	19(1)	19(1)	25(1)	6(1)	0(1)	8(1)
C(31)	17(1)	23(1)	41(1)	5(1)	4(1)	10(1)
C(32)	23(1)	21(1)	37(1)	4(1)	14(1)	9(1)
C(33)	29(1)	23(1)	20(1)	4(1)	7(1)	8(1)
C(34)	19(1)	19(1)	21(1)	3(1)	2(1)	7(1)

Table A2.5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppm)Cl 211a.

	x	y	z	U(eq)
H21	-2044	-305	-207	74
H31	-1591	-1672	-1098	90
H41	773	-1552	-1083	84
H51	2513	-235	-208	72
H61	2051	1131	705	49
H(1)	2546	7805	329	23
H(101)	1250(20)	5190(20)	458(12)	20
H(4)	2874	3960	15	22
H(3)	4773	9191	2331	23
H(6)	5254	4405	1907	21
H(9)	-60	4326	3206	21
H(7)	-1421	4073	1069	24
H(10A)	5753	6207	4280	21
H(10B)	6178	5393	3617	21
H(12)	1663	2696	2440	30
H(13)	1078	505	2213	40
H(15)	4508	1071	3588	35
H(14)	2482	-310	2794	40

H(16)	5033	3244	3867	27
H(18)	1629	2574	4168	26
H(19)	274	2265	5221	30
H(20)	353	4033	6005	28
H(21)	1949	6107	5791	27
H(22)	3336	6438	4750	24
H(24)	5716	8055	4670	35
H(25)	6503	10118	5321	40
H(26)	7705	11922	4720	38
H(27)	8191	11675	3468	41
H(28)	7443	9622	2818	31
H(30)	8527	6955	3267	25
H(31)	10442	7281	2492	32
H(32)	10299	7803	1296	32
H(33)	8217	7932	855	30
H(34)	6250	7505	1603	24

Table A2.6: Crystal data and structure refinement for $Tp^{Cl}Ru(dppe)Cl$ 211b.

Identification code: $Tp^{Cl}Ru(dppe)Cl$ **211b**

Empirical formula: C41 H36 B Cl5 N6 P2 Ru

Formula weight: 963.83

Temperature: 223(2) K

Wavelength: 0.71073 Å

Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.5862(4) Å	α= 90°.
	b = 15.5491(5) Å	β= 98.7790(10)°.
	c = 26.1072(9) Å	γ = 90°.
Volume	4247.1(3) $Å^3$	
Z	4	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	0.798 mm^{-1}	
F(000)	1952	
Crystal size	0.30 x 0.28 x 0.14 mm^3	
Theta range for data collection	1.986 to 28.318°.	
Index ranges	-12<=h<=14, -20<=k<=20, -34<=l<=30	
Reflections collected	51181	
Independent reflections	10555 [R(int) = 0.0174]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10555 / 595 / 634	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0733	
R indices (all data)	R1 = 0.0397, wR2 = 0.0793	
Largest diff. peak and hole	0.687 and -0.498 $e.Å^{-3}$	

Table A2.7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppe)Cl 211b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3935(1)	7089(1)	6820(1)	29(1)
Cl(1)	6448(1)	9568(1)	8407(1)	62(1)
Cl(2)	8249(1)	6853(1)	5614(1)	77(1)
Cl(3)	153(1)	9125(1)	5432(1)	74(1)
Cl(4)	5395(1)	6169(1)	7371(1)	42(1)
P(1)	2438(1)	6799(1)	7337(1)	31(1)
P(2)	2996(1)	5992(1)	6317(1)	33(1)
N(1)	4827(2)	8144(1)	7267(1)	35(1)
N(2)	5159(2)	8852(1)	7006(1)	38(1)
N(3)	5409(2)	7277(1)	6361(1)	37(1)
N(4)	5683(2)	8091(1)	6223(1)	40(1)
N(5)	2885(2)	8007(1)	6353(1)	33(1)
N(6)	3509(2)	8716(1)	6215(1)	40(1)
C(1)	5224(2)	8285(1)	7766(1)	40(1)
C(2)	5805(2)	9090(1)	7832(1)	43(1)
C(3)	5757(2)	9426(1)	7345(1)	42(1)
C(4)	6217(2)	6749(2)	6173(1)	42(1)
C(5)	7018(2)	7235(2)	5911(1)	49(1)
C(6)	6670(2)	8075(2)	5950(1)	49(1)
C(7)	1677(2)	8055(1)	6114(1)	37(1)
C(8)	1532(2)	8800(1)	5820(1)	46(1)
C(9)	2690(3)	9204(1)	5891(1)	49(1)
C(10)	935(2)	7399(1)	7231(1)	35(1)
C(11)	992(2)	8294(1)	7183(1)	40(1)
C(12)	-114(2)	8784(2)	7122(1)	55(1)
C(13)	-1276(3)	8398(2)	7106(1)	70(1)
C(14)	-1361(2)	7517(2)	7150(1)	68(1)
C(15)	-260(2)	7014(2)	7211(1)	49(1)
C(16)	2842(2)	6873(1)	8047(1)	37(1)

C(17)	2565(2)	7615(2)	8308(1)	46(1)
C(18)	2914(3)	7695(2)	8841(1)	58(1)
C(19)	3546(3)	7037(2)	9120(1)	62(1)
C(20)	3825(3)	6298(2)	8871(1)	65(1)
C(21)	3486(3)	6210(2)	8339(1)	55(1)
C(22)	1999(2)	5666(1)	7219(1)	42(1)
C(23)	1698(2)	5520(1)	6633(1)	44(1)
C(24)	3922(2)	5049(1)	6167(1)	38(1)
C(25)	4530(2)	4541(1)	6570(1)	48(1)
C(26)	5247(3)	3833(2)	6471(1)	56(1)
C(27)	5380(3)	3627(2)	5970(1)	65(1)
C(28)	4781(3)	4118(2)	5567(1)	72(1)
C(29)	4047(3)	4826(2)	5662(1)	58(1)
C(30)	2231(2)	6284(1)	5663(1)	41(1)
C(31)	2872(2)	6844(2)	5375(1)	48(1)
C(32)	2357(3)	7067(2)	4873(1)	60(1)
C(33)	1198(3)	6728(2)	4652(1)	74(1)
C(34)	550(3)	6174(2)	4930(1)	71(1)
C(35)	1064(2)	5947(2)	5436(1)	55(1)
B(1)	4942(2)	8854(2)	6410(1)	41(1)
Cl13	746(16)	6301(7)	9763(7)	136(5)
C13	-548(11)	6151(8)	9300(4)	54(6)
C23	-515(16)	6436(18)	8809(6)	68(7)
C33	-1552(17)	6327(12)	8437(5)	53(4)
C43	-2640(14)	5952(13)	8561(5)	56(4)
C53	-2680(12)	5645(11)	9059(6)	56(4)
C63	-1592(15)	5709(12)	9419(5)	51(4)
Cl12	-102(11)	5965(6)	9949(2)	161(4)
C12	-803(8)	6094(7)	9323(3)	60(5)
C22	-95(10)	6391(9)	8967(4)	52(3)
C32	-686(13)	6513(8)	8466(4)	59(3)
C42	-1945(15)	6306(17)	8328(5)	66(5)
C52	-2661(15)	6040(30)	8690(7)	77(7)
C62	-2076(11)	5887(14)	9193(5)	77(4)
Cl11	1091(4)	6311(2)	9624(2)	86(1)

C11	-408(8)	6161(5)	9272(3)	55(2)
C21	-653(10)	6421(8)	8760(3)	65(3)
C31	-1896(13)	6331(11)	8500(4)	87(4)
C41	-2783(11)	5936(14)	8742(6)	108(5)
C51	-2534(10)	5674(10)	9253(6)	106(4)
C61	-1331(9)	5826(8)	9520(4)	72(2)

Table A2.8 Bond lengths [Å] and angles [°] for Tp^{Cl}Ru(dppe)Cl 211b.

Ru(1)-N(5)	2.0845(15)	N(6)-C(9)	1.349(3)
Ru(1)-N(3)	2.1289(16)	N(6)-B(1)	1.540(3)
Ru(1)-N(1)	2.1466(17)	C(1)-C(2)	1.393(3)
Ru(1)-P(1)	2.2780(5)	C(1)-H(1)	0.9400
Ru(1)-P(2)	2.2854(5)	C(2)-C(3)	1.368(3)
Ru(1)-Cl(4)	2.4128(5)	C(3)-H(3)	0.9400
Cl(1)-C(2)	1.720(2)	C(4)-C(5)	1.390(3)
Cl(2)-C(5)	1.722(2)	C(4)-H(4)	0.9400
Cl(3)-C(8)	1.721(2)	C(5)-C(6)	1.366(3)
P(1)-C(10)	1.830(2)	C(6)-H(6)	0.9400
P(1)-C(22)	1.836(2)	C(7)-C(8)	1.387(3)
P(1)-C(16)	1.841(2)	C(7)-H(7)	0.9400
P(2)-C(30)	1.831(2)	C(8)-C(9)	1.364(4)
P(2)-C(24)	1.839(2)	C(9)-H(9)	0.9400
P(2)-C(23)	1.858(2)	C(10)-C(15)	1.394(3)
N(1)-C(1)	1.325(3)	C(10)-C(11)	1.400(3)
N(1)-N(2)	1.368(2)	C(11)-C(12)	1.386(3)
N(2)-C(3)	1.346(3)	C(11)-H(11)	0.9400
N(2)-B(1)	1.539(3)	C(12)-C(13)	1.364(4)
N(3)-C(4)	1.331(3)	C(12)-H(12)	0.9400
N(3)-N(4)	1.359(2)	C(13)-C(14)	1.378(5)
N(4)-C(6)	1.352(3)	C(13)-H(13)	0.9400
N(4)-B(1)	1.542(3)	C(14)-C(15)	1.393(4)
N(5)-C(7)	1.337(3)	C(14)-H(14)	0.9400
N(5)-N(6)	1.362(2)	C(15)-H(15)	0.9400

C(16)-C(17)	1.393(3)	C(34)-C(35)	1.395(4)
C(16)-C(21)	1.397(3)	C(34)-H(34)	0.9400
C(17)-C(18)	1.391(3)	C(35)-H(35)	0.9400
C(17)-H(17)	0.9400	B(1)-H(101)	1.11(2)
C(18)-C(19)	1.370(4)	Cl13-C13	1.700(7)
C(18)-H(18)	0.9400	C13-C23	1.361(5)
C(19)-C(20)	1.375(4)	C13-C63	1.377(9)
C(19)-H(19)	0.9400	C23-C33	1.361(11)
C(20)-C(21)	1.389(4)	C23-H23	0.9400
C(20)-H(20)	0.9400	C33-C43	1.373(11)
C(21)-H(21)	0.9400	C33-H33	0.9400
C(22)-C(23)	1.531(3)	C43-C53	1.390(10)
C(22)-H(22A)	0.9800	C43-H43	0.9400
C(22)-H(22B)	0.9800	C53-C63	1.374(10)
C(23)-H(23A)	0.9800	C53-H53	0.9400
C(23)-H(23B)	0.9800	C63-H63	0.9400
C(24)-C(29)	1.387(3)	Cl12-C12	1.700(6)
C(24)-C(25)	1.393(3)	C12-C22	1.362(5)
C(25)-C(26)	1.384(3)	C12-C62	1.377(9)
C(25)-H(25)	0.9400	C22-C32	1.375(10)
C(26)-C(27)	1.374(4)	C22-H22	0.9400
C(26)-H(26)	0.9400	C32-C42	1.365(11)
C(27)-C(28)	1.374(4)	C32-H32	0.9400
C(27)-H(27)	0.9400	C42-C52	1.362(12)
C(28)-C(29)	1.392(3)	C42-H42	0.9400
C(28)-H(28)	0.9400	C52-C62	1.384(11)
C(29)-H(29)	0.9400	C52-H52	0.9400
C(30)-C(35)	1.388(3)	C62-H62	0.9400
C(30)-C(31)	1.394(3)	Cl11-C11	1.725(8)
C(31)-C(32)	1.384(3)	C11-C61	1.355(8)
C(31)-H(31)	0.9400	C11-C21	1.382(8)
C(32)-C(33)	1.378(5)	C21-C31	1.393(9)
C(32)-H(32)	0.9400	C21-H21	0.9400
C(33)-C(34)	1.375(5)	C31-C41	1.357(10)
C(33)-H(33)	0.9400	C31-H31	0.9400

C41-C51	1.382(10)	N(2)-N(1)-Ru(1)	118.00(13)
C41-H41	0.9400	C(3)-N(2)-N(1)	109.75(17)
C51-C61	1.376(9)	C(3)-N(2)-B(1)	130.22(17)
C51-H51	0.9400	N(1)-N(2)-B(1)	119.74(16)
C61-H61	0.9400	C(4)-N(3)-N(4)	107.59(16)
		C(4)-N(3)-Ru(1)	133.63(14)
N(5)-Ru(1)-N(3)	87.01(6)	N(4)-N(3)-Ru(1)	118.74(12)
N(5)-Ru(1)-N(1)	86.87(7)	C(6)-N(4)-N(3)	109.61(17)
N(3)-Ru(1)-N(1)	84.37(6)	C(6)-N(4)-B(1)	130.65(18)
N(5)-Ru(1)-P(1)	97.18(5)	N(3)-N(4)-B(1)	119.64(16)
N(3)-Ru(1)-P(1)	175.72(5)	C(7)-N(5)-N(6)	107.41(16)
N(1)-Ru(1)-P(1)	96.73(4)	C(7)-N(5)-Ru(1)	134.26(13)
N(5)-Ru(1)-P(2)	91.65(5)	N(6)-N(5)-Ru(1)	118.19(13)
N(3)-Ru(1)-P(2)	94.03(5)	C(9)-N(6)-N(5)	109.29(18)
N(1)-Ru(1)-P(2)	177.88(5)	C(9)-N(6)-B(1)	129.40(18)
P(1)-Ru(1)-P(2)	84.958(18)	N(5)-N(6)-B(1)	121.28(16)
N(5)-Ru(1)-Cl(4)	171.93(5)	N(1)-C(1)-C(2)	109.72(19)
N(3)-Ru(1)-Cl(4)	87.64(5)	N(1)-C(1)-H(1)	125.1
N(1)-Ru(1)-Cl(4)	86.59(5)	C(2)-C(1)-H(1)	125.1
P(1)-Ru(1)-Cl(4)	88.291(18)	C(3)-C(2)-C(1)	106.1(2)
P(2)-Ru(1)-Cl(4)	94.752(19)	C(3)-C(2)-Cl(1)	126.78(18)
C(10)-P(1)-C(22)	105.79(10)	C(1)-C(2)-Cl(1)	127.16(19)
C(10)-P(1)-C(16)	100.55(9)	N(2)-C(3)-C(2)	107.65(18)
C(22)-P(1)-C(16)	104.09(10)	N(2)-C(3)-H(3)	126.2
C(10)-P(1)-Ru(1)	118.50(7)	C(2)-C(3)-H(3)	126.2
C(22)-P(1)-Ru(1)	105.75(7)	N(3)-C(4)-C(5)	108.7(2)
C(16)-P(1)-Ru(1)	120.57(7)	N(3)-C(4)-H(4)	125.7
C(30)-P(2)-C(24)	99.96(10)	C(5)-C(4)-H(4)	125.7
C(30)-P(2)-C(23)	105.07(11)	C(6)-C(5)-C(4)	106.99(19)
C(24)-P(2)-C(23)	103.59(9)	C(6)-C(5)-Cl(2)	126.48(18)
C(30)-P(2)-Ru(1)	116.23(7)	C(4)-C(5)-Cl(2)	126.50(19)
C(24)-P(2)-Ru(1)	121.24(7)	N(4)-C(6)-C(5)	107.13(19)
C(23)-P(2)-Ru(1)	108.99(7)	N(4)-C(6)-H(6)	126.4
C(1)-N(1)-N(2)	106.81(17)	C(5)-C(6)-H(6)	126.4
C(1)-N(1)-Ru(1)	135.10(14)	N(5)-C(7)-C(8)	108.8(2)

N(5)-C(7)-H(7)	125.6	C(18)-C(19)-C(20)	119.7(2)
C(8)-C(7)-H(7)	125.6	C(18)-C(19)-H(19)	120.1
C(9)-C(8)-C(7)	106.7(2)	C(20)-C(19)-H(19)	120.1
C(9)-C(8)-Cl(3)	127.53(18)	C(19)-C(20)-C(21)	120.9(3)
C(7)-C(8)-Cl(3)	125.7(2)	C(19)-C(20)-H(20)	119.5
N(6)-C(9)-C(8)	107.75(19)	C(21)-C(20)-H(20)	119.5
N(6)-C(9)-H(9)	126.1	C(20)-C(21)-C(16)	120.2(3)
C(8)-C(9)-H(9)	126.1	C(20)-C(21)-H(21)	119.9
C(15)-C(10)-C(11)	118.4(2)	C(16)-C(21)-H(21)	119.9
C(15)-C(10)-P(1)	123.36(17)	C(23)-C(22)-P(1)	108.58(14)
C(11)-C(10)-P(1)	118.17(15)	C(23)-C(22)-H(22A)	110.0
C(12)-C(11)-C(10)	120.6(2)	P(1)-C(22)-H(22A)	110.0
C(12)-C(11)-H(11)	119.7	C(23)-C(22)-H(22B)	110.0
C(10)-C(11)-H(11)	119.7	P(1)-C(22)-H(22B)	110.0
C(13)-C(12)-C(11)	120.2(3)	H(22A)-C(22)-H(22B)	108.4
C(13)-C(12)-H(12)	119.9	C(22)-C(23)-P(2)	109.28(14)
C(11)-C(12)-H(12)	119.9	C(22)-C(23)-H(23A)	109.8
C(12)-C(13)-C(14)	120.4(2)	P(2)-C(23)-H(23A)	109.8
C(12)-C(13)-H(13)	119.8	C(22)-C(23)-H(23B)	109.8
C(14)-C(13)-H(13)	119.8	P(2)-C(23)-H(23B)	109.8
C(13)-C(14)-C(15)	120.3(3)	H(23A)-C(23)-H(23B)	108.3
C(13)-C(14)-H(14)	119.9	C(29)-C(24)-C(25)	118.4(2)
C(15)-C(14)-H(14)	119.9	C(29)-C(24)-P(2)	122.24(17)
C(14)-C(15)-C(10)	120.1(3)	C(25)-C(24)-P(2)	119.35(16)
C(14)-C(15)-H(15)	120.0	C(26)-C(25)-C(24)	120.8(2)
C(10)-C(15)-H(15)	120.0	C(26)-C(25)-H(25)	119.6
C(17)-C(16)-C(21)	117.8(2)	C(24)-C(25)-H(25)	119.6
C(17)-C(16)-P(1)	120.65(16)	C(27)-C(26)-C(25)	120.2(2)
C(21)-C(16)-P(1)	121.44(18)	C(27)-C(26)-H(26)	119.9
C(18)-C(17)-C(16)	121.3(2)	C(25)-C(26)-H(26)	119.9
C(18)-C(17)-H(17)	119.4	C(28)-C(27)-C(26)	119.8(2)
C(16)-C(17)-H(17)	119.4	C(28)-C(27)-H(27)	120.1
C(19)-C(18)-C(17)	120.0(3)	C(26)-C(27)-H(27)	120.1
C(19)-C(18)-H(18)	120.0	C(27)-C(28)-C(29)	120.5(2)
C(17)-C(18)-H(18)	120.0	C(27)-C(28)-H(28)	119.8

C(29)-C(28)-H(28)	119.8	C23-C33-H33	120.1
C(24)-C(29)-C(28)	120.3(2)	C43-C33-H33	120.1
C(24)-C(29)-H(29)	119.9	C33-C43-C53	120.9(9)
C(28)-C(29)-H(29)	119.9	C33-C43-H43	119.6
C(35)-C(30)-C(31)	118.6(2)	C53-C43-H43	119.6
C(35)-C(30)-P(2)	122.88(19)	C63-C53-C43	118.1(9)
C(31)-C(30)-P(2)	118.48(18)	C63-C53-H53	120.9
C(32)-C(31)-C(30)	121.0(3)	C43-C53-H53	120.9
C(32)-C(31)-H(31)	119.5	C53-C63-C13	120.0(8)
C(30)-C(31)-H(31)	119.5	C53-C63-H63	120.0
C(33)-C(32)-C(31)	119.7(3)	C13-C63-H63	120.0
C(33)-C(32)-H(32)	120.1	C22-C12-C62	122.0(6)
C(31)-C(32)-H(32)	120.1	C22-C12-Cl12	119.4
C(34)-C(33)-C(32)	120.2(3)	C62-C12-Cl12	118.5(6)
C(34)-C(33)-H(33)	119.9	C12-C22-C32	118.6(7)
C(32)-C(33)-H(33)	119.9	C12-C22-H22	120.7
C(33)-C(34)-C(35)	120.2(3)	C32-C22-H22	120.7
C(33)-C(34)-H(34)	119.9	C42-C32-C22	120.1(9)
C(35)-C(34)-H(34)	119.9	C42-C32-H32	119.9
C(30)-C(35)-C(34)	120.2(3)	C22-C32-H32	119.9
C(30)-C(35)-H(35)	119.9	C52-C42-C32	120.9(9)
C(34)-C(35)-H(35)	119.9	C52-C42-H42	119.6
N(2)-B(1)-N(6)	108.68(17)	C32-C42-H42	119.6
N(2)-B(1)-N(4)	108.21(18)	C42-C52-C62	119.7(10)
N(6)-B(1)-N(4)	108.16(18)	C42-C52-H52	120.2
N(2)-B(1)-H(101)	109.9(11)	C62-C52-H52	120.2
N(6)-B(1)-H(101)	112.1(11)	C12-C62-C52	118.3(8)
N(4)-B(1)-H(101)	109.7(11)	C12-C62-H62	120.9
C23-C13-C63	120.8(6)	C52-C62-H62	120.9
C23-C13-Cl13	119.4	C61-C11-C21	122.1(7)
C63-C13-Cl13	119.7(6)	C61-C11-Cl11	117.9(6)
C13-C23-C33	119.8(8)	C21-C11-Cl11	119.8(6)
C13-C23-H23	120.1	C11-C21-C31	117.8(7)
C33-C23-H23	120.1	C11-C21-H21	121.1
C23-C33-C43	119.9(9)	C31-C21-H21	121.1

C41-C31-C21	119.2(7)	C41-C51-H51	121.2
C41-C31-H31	120.4	C11-C61-C51	120.2(7)
C21-C31-H31	120.4	C11-C61-H61	119.9
C31-C41-C51	122.7(8)	C51-C61-H61	119.9
C31-C41-H41	118.7		
C51-C41-H41	118.7		
C61-C51-C41	117.6(8)		
C61-C51-H51	121.2		

Symmetry transformations used to generate equivalent atoms:

Table A2.9 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Cl}Ru(dppe)Cl$ 211b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	28(1)	25(1)	37(1)	5(1)	12(1)	2(1)
Cl(1)	50(1)	68(1)	67(1)	-20(1)	0(1)	-4(1)
Cl(2)	62(1)	87(1)	96(1)	-10(1)	53(1)	6(1)
Cl(3)	87(1)	55(1)	69(1)	7(1)	-28(1)	19(1)
Cl(4)	38(1)	36(1)	53(1)	10(1)	7(1)	6(1)
P(1)	30(1)	29(1)	36(1)	3(1)	12(1)	0(1)
P(2)	35(1)	28(1)	40(1)	0(1)	14(1)	1(1)
N(1)	33(1)	29(1)	45(1)	4(1)	13(1)	-2(1)
N(2)	37(1)	29(1)	50(1)	3(1)	16(1)	-1(1)
N(3)	35(1)	34(1)	46(1)	3(1)	17(1)	0(1)
N(4)	43(1)	34(1)	49(1)	6(1)	23(1)	-2(1)
N(5)	37(1)	27(1)	36(1)	4(1)	14(1)	6(1)
N(6)	50(1)	28(1)	44(1)	10(1)	16(1)	4(1)
C(1)	32(1)	42(1)	45(1)	3(1)	8(1)	3(1)
C(2)	31(1)	44(1)	54(1)	-8(1)	9(1)	2(1)
C(3)	33(1)	31(1)	64(1)	-6(1)	16(1)	-1(1)
C(4)	36(1)	41(1)	53(1)	-2(1)	17(1)	3(1)
C(5)	38(1)	60(1)	54(1)	-5(1)	24(1)	1(1)

C(6)	47(1)	53(1)	52(1)	4(1)	26(1)	-7(1)
C(7)	42(1)	33(1)	36(1)	0(1)	9(1)	8(1)
C(8)	60(1)	38(1)	38(1)	2(1)	-1(1)	16(1)
C(9)	71(2)	33(1)	43(1)	12(1)	12(1)	11(1)
C(10)	31(1)	45(1)	30(1)	-4(1)	9(1)	3(1)
C(11)	40(1)	45(1)	37(1)	-3(1)	8(1)	10(1)
C(12)	56(2)	63(2)	44(1)	-7(1)	3(1)	27(1)
C(13)	46(2)	97(2)	64(2)	-18(2)	2(1)	31(2)
C(14)	28(1)	114(3)	63(2)	-19(2)	7(1)	-1(1)
C(15)	35(1)	67(2)	45(1)	-9(1)	11(1)	-7(1)
C(16)	31(1)	44(1)	37(1)	8(1)	11(1)	-1(1)
C(17)	47(1)	49(1)	41(1)	0(1)	4(1)	3(1)
C(18)	62(2)	68(2)	43(1)	-6(1)	4(1)	-2(1)
C(19)	60(2)	85(2)	38(1)	6(1)	0(1)	-9(1)
C(20)	66(2)	75(2)	51(2)	26(1)	3(1)	5(1)
C(21)	60(2)	55(1)	51(1)	13(1)	13(1)	10(1)
C(22)	47(1)	31(1)	53(1)	1(1)	26(1)	-6(1)
C(23)	43(1)	36(1)	57(1)	-8(1)	23(1)	-11(1)
C(24)	42(1)	27(1)	50(1)	1(1)	21(1)	0(1)
C(25)	59(1)	34(1)	52(1)	2(1)	16(1)	7(1)
C(26)	62(2)	36(1)	72(2)	10(1)	19(1)	12(1)
C(27)	79(2)	37(1)	90(2)	11(1)	49(2)	21(1)
C(28)	112(2)	50(1)	68(2)	7(1)	56(2)	26(2)
C(29)	82(2)	45(1)	53(1)	8(1)	33(1)	20(1)
C(30)	43(1)	37(1)	43(1)	-6(1)	9(1)	10(1)
C(31)	57(1)	45(1)	44(1)	-1(1)	16(1)	11(1)
C(32)	80(2)	60(2)	43(1)	1(1)	20(1)	23(1)
C(33)	86(2)	92(2)	42(1)	-7(1)	6(1)	39(2)
C(34)	58(2)	91(2)	60(2)	-26(2)	-3(1)	18(2)
C(35)	50(1)	58(1)	56(2)	-14(1)	9(1)	7(1)
B(1)	45(1)	29(1)	53(1)	6(1)	21(1)	-1(1)
Cl13	95(6)	200(9)	97(7)	-43(5)	-33(5)	-9(5)
C13	57(7)	57(14)	46(7)	-8(7)	4(5)	6(7)
C23	87(9)	58(14)	57(7)	1(7)	9(6)	-4(9)
C33	82(8)	38(6)	41(6)	2(5)	14(5)	8(6)

C43	74(7)	60(8)	33(6)	5(5)	2(4)	8(5)
C53	55(6)	73(8)	41(6)	10(5)	5(4)	0(5)
C63	61(6)	50(7)	40(6)	-2(5)	2(4)	13(5)
Cl12	184(9)	225(8)	67(3)	27(4)	-1(4)	22(7)
C12	67(7)	59(11)	53(6)	-7(6)	9(5)	2(6)
C22	52(6)	51(6)	49(6)	-3(5)	-6(4)	0(5)
C32	67(6)	52(6)	53(6)	-6(5)	-4(5)	10(5)
C42	58(7)	81(10)	55(7)	-29(7)	-6(5)	14(6)
C52	71(8)	98(15)	62(8)	-29(8)	10(6)	11(8)
C62	71(7)	102(12)	60(7)	-20(7)	15(5)	-5(7)
Cl11	72(1)	81(2)	106(2)	-21(1)	17(1)	-10(1)
C11	70(4)	39(5)	59(4)	-13(3)	21(3)	3(3)
C21	101(5)	37(5)	61(5)	-6(4)	27(4)	3(4)
C31	109(6)	85(7)	65(6)	-17(5)	6(5)	20(5)
C41	96(6)	131(12)	97(8)	-23(7)	11(5)	-3(6)
C51	90(6)	128(9)	99(8)	-24(6)	10(5)	-17(5)
C61	83(5)	74(5)	62(5)	-13(4)	25(4)	-16(4)

Table A2.10 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Cl}Ru(dppe)Cl 211b.

	x	y	z	U(eq)
H(1)	5128	7900	8035	47
H(3)	6083	9963	7262	50
H(4)	6242	6148	6212	51
H(6)	7047	8553	5813	58
H(7)	1032	7649	6141	44
H(9)	2883	9728	5741	58
H(11)	1789	8566	7192	48
H(12)	-63	9385	7092	66
H(13)	-2022	8734	7064	84
H(14)	-2165	7256	7139	82
H(15)	-324	6413	7238	58
H(17)	2133	8071	8119	55

H(18)	2716	8200	9010	70
H(19)	3788	7092	9480	74
H(20)	4250	5845	9065	77
H(21)	3691	5702	8174	65
H(22A)	2706	5293	7369	50
H(22B)	1250	5525	7382	50
H(101)	5300(20)	9466(14)	6265(8)	38(6)
H(23A)	881	5792	6496	52
H(23B)	1627	4903	6560	52
H(25)	4452	4681	6914	57
H(26)	5644	3493	6746	67
H(27)	5881	3153	5903	78
H(28)	4866	3974	5224	87
H(29)	3634	5155	5384	69
H(31)	3666	7073	5523	58
H(32)	2797	7448	4683	72
H(33)	849	6876	4311	88
H(34)	-242	5947	4779	85
H(35)	620	5566	5623	65
H23	223	6707	8728	81
H33	-1524	6508	8096	64
H43	-3367	5902	8307	67
H53	-3430	5400	9147	68
H63	-1561	5451	9746	61
H22	780	6509	9062	62
H32	-223	6740	8217	71
H42	-2323	6346	7979	79
H52	-3547	5965	8599	92
H62	-2536	5646	9438	92
H21	-2	6650	8593	78
H31	-2117	6542	8160	104
H41	-3601	5836	8554	130
H51	-3164	5401	9413	127
H61	-1147	5698	9875	86

Table A2.11: Crystal data and structure refinement for $Tp^{Cl}Ru(dppp)Cl$ 211c.

Identification code	$Tp^{Cl}Ru(dppp)Cl$ **211c**	
Empirical formula	C36 H33 B Cl4 N6 P2 Ru	
Formula weight	865.30	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 16.8721(10) Å	α= 90°.
	b = 21.8378(13) Å	β= 90°.
	c = 10.1191(6) Å	γ = 90°.
Volume	3728.4(4) $Å^3$	
Z	4	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	0.829 mm^{-1}	
F(000)	1752	
Crystal size	0.300 x 0.270 x 0.220 mm^3	
Theta range for data collection	2.347 to 28.372°.	
Index ranges	-22<=h<=18, -25<=k<=29, -13<=l<=13	
Reflections collected	45561	
Independent reflections	4786 [R(int) = 0.0139]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.7078	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4786 / 0 / 243	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0535	
R indices (all data)	R1 = 0.0214, wR2 = 0.0540	
Largest diff. peak and hole	0.412 and -0.486 $e.Å^{-3}$	

Table A2.12: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppp)Cl 211c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3001(1)	2500	6226(1)	11(1)
Cl(1)	592(1)	4480(1)	5713(1)	28(1)
Cl(2)	4730(1)	2500	1185(1)	28(1)
Cl(3)	2375(1)	2500	8379(1)	18(1)
P(1)	3871(1)	3269(1)	6792(1)	13(1)
N(1)	2115(1)	3144(1)	5656(1)	14(1)
N(2)	1757(1)	3071(1)	4458(1)	16(1)
N(3)	3377(1)	2500	4277(2)	13(1)
N(4)	2825(1)	2500	3291(2)	15(1)
C(1)	3466(1)	3909(1)	7765(1)	16(1)
C(2)	3386(1)	4503(1)	7276(1)	20(1)
C(3)	3042(1)	4960(1)	8042(2)	26(1)
C(4)	2778(1)	4834(1)	9305(2)	28(1)
C(5)	2871(1)	4249(1)	9815(2)	27(1)
C(6)	3212(1)	3791(1)	9059(1)	22(1)
C(7)	4321(1)	3680(1)	5401(1)	16(1)
C(8)	5130(1)	3804(1)	5316(2)	26(1)
C(9)	5435(1)	4135(1)	4256(2)	35(1)
C(10)	4942(1)	4349(1)	3274(2)	32(1)
C(11)	4135(1)	4226(1)	3334(2)	25(1)
C(12)	3830(1)	3889(1)	4383(1)	19(1)
C(13)	4715(1)	3078(1)	7845(1)	18(1)
C(14)	5170(1)	2500	7464(2)	20(1)
C(15)	1776(1)	3625(1)	6243(1)	17(1)
C(16)	1200(1)	3866(1)	5402(2)	19(1)
C(17)	1199(1)	3508(1)	4289(1)	19(1)
C(18)	3184(1)	2500	2097(2)	18(1)
C(19)	3986(1)	2500	2329(2)	17(1)
C(20)	4085(1)	2500	3692(2)	14(1)

B(1)	1936(1)	2500	3611(2)	16(1)

Table A2.13: Bond lengths [Å] and angles [°] for Tp^{Cl}Ru(dppp)Cl 211c.

Ru(1)-N(3)	2.0718(15)	C(7)-C(8)	1.3941(19)
Ru(1)-N(1)	2.1310(11)	C(7)-C(12)	1.3985(19)
Ru(1)-N(1)#1	2.1310(11)	C(8)-C(9)	1.391(2)
Ru(1)-P(1)	2.3040(3)	C(8)-H(8)	0.9500
Ru(1)-P(1)#1	2.3040(3)	C(9)-C(10)	1.378(3)
Ru(1)-Cl(3)	2.4216(5)	C(9)-H(9)	0.9500
Cl(1)-C(16)	1.7163(14)	C(10)-C(11)	1.389(2)
Cl(2)-C(19)	1.7080(19)	C(10)-H(10)	0.9500
P(1)-C(13)	1.8263(13)	C(11)-C(12)	1.3897(19)
P(1)-C(7)	1.8336(13)	C(11)-H(11)	0.9500
P(1)-C(1)	1.8401(13)	C(12)-H(12)	0.9500
N(1)-C(15)	1.3361(17)	C(13)-C(14)	1.5272(18)
N(1)-N(2)	1.3636(15)	C(13)-H(13A)	0.9900
N(2)-C(17)	1.3516(17)	C(13)-H(13B)	0.9900
N(2)-B(1)	1.5439(17)	C(14)-C(13)#1	1.5272(18)
N(3)-C(20)	1.333(2)	C(14)-H(14A)	0.9900
N(3)-N(4)	1.365(2)	C(14)-H(14B)	0.9900
N(4)-C(18)	1.352(2)	C(15)-C(16)	1.3951(19)
N(4)-B(1)	1.534(3)	C(15)-H(15)	0.9500
C(1)-C(2)	1.3950(19)	C(16)-C(17)	1.371(2)
C(1)-C(6)	1.4014(19)	C(17)-H(17)	0.9500
C(2)-C(3)	1.392(2)	C(18)-C(19)	1.372(3)
C(2)-H(2)	0.9500	C(18)-H(18)	0.9500
C(3)-C(4)	1.382(2)	C(19)-C(20)	1.389(2)
C(3)-H(3)	0.9500	C(20)-H(20)	0.9500
C(4)-C(5)	1.386(2)	B(1)-N(2)#1	1.5438(17)
C(4)-H(4)	0.9500	B(1)-H(1B)	1.23(3)
C(5)-C(6)	1.384(2)		
C(5)-H(5)	0.9500	N(3)-Ru(1)-N(1)	87.55(4)
C(6)-H(6)	0.9500	N(3)-Ru(1)-N(1)#1	87.55(4)

N(1)-Ru(1)-N(1)#1	82.56(6)	C(3)-C(2)-H(2)	119.7
N(3)-Ru(1)-P(1)	92.38(3)	C(1)-C(2)-H(2)	119.7
N(1)-Ru(1)-P(1)	91.90(3)	C(4)-C(3)-C(2)	120.43(15)
N(1)#1-Ru(1)-P(1)	174.46(3)	C(4)-C(3)-H(3)	119.8
N(3)-Ru(1)-P(1)#1	92.38(3)	C(2)-C(3)-H(3)	119.8
N(1)-Ru(1)-P(1)#1	174.46(3)	C(3)-C(4)-C(5)	119.46(14)
N(1)#1-Ru(1)-P(1)#1	91.90(3)	C(3)-C(4)-H(4)	120.3
P(1)-Ru(1)-P(1)#1	93.638(17)	C(5)-C(4)-H(4)	120.3
N(3)-Ru(1)-Cl(3)	171.98(4)	C(6)-C(5)-C(4)	120.48(15)
N(1)-Ru(1)-Cl(3)	86.42(3)	C(6)-C(5)-H(5)	119.8
N(1)#1-Ru(1)-Cl(3)	86.42(3)	C(4)-C(5)-H(5)	119.8
P(1)-Ru(1)-Cl(3)	93.101(12)	C(5)-C(6)-C(1)	120.73(14)
P(1)#1-Ru(1)-Cl(3)	93.101(12)	C(5)-C(6)-H(6)	119.6
C(13)-P(1)-C(7)	103.72(6)	C(1)-C(6)-H(6)	119.6
C(13)-P(1)-C(1)	98.66(6)	C(8)-C(7)-C(12)	118.09(13)
C(7)-P(1)-C(1)	101.13(6)	C(8)-C(7)-P(1)	123.23(11)
C(13)-P(1)-Ru(1)	118.36(5)	C(12)-C(7)-P(1)	118.68(10)
C(7)-P(1)-Ru(1)	115.46(4)	C(9)-C(8)-C(7)	120.68(14)
C(1)-P(1)-Ru(1)	116.73(4)	C(9)-C(8)-H(8)	119.7
C(15)-N(1)-N(2)	107.23(11)	C(7)-C(8)-H(8)	119.7
C(15)-N(1)-Ru(1)	134.38(9)	C(10)-C(9)-C(8)	120.61(15)
N(2)-N(1)-Ru(1)	118.33(8)	C(10)-C(9)-H(9)	119.7
C(17)-N(2)-N(1)	109.87(11)	C(8)-C(9)-H(9)	119.7
C(17)-N(2)-B(1)	129.51(13)	C(9)-C(10)-C(11)	119.61(15)
N(1)-N(2)-B(1)	120.06(12)	C(9)-C(10)-H(10)	120.2
C(20)-N(3)-N(4)	106.69(14)	C(11)-C(10)-H(10)	120.2
C(20)-N(3)-Ru(1)	134.20(12)	C(10)-C(11)-C(12)	119.89(14)
N(4)-N(3)-Ru(1)	119.11(12)	C(10)-C(11)-H(11)	120.1
C(18)-N(4)-N(3)	110.29(15)	C(12)-C(11)-H(11)	120.1
C(18)-N(4)-B(1)	128.82(16)	C(11)-C(12)-C(7)	121.10(13)
N(3)-N(4)-B(1)	120.88(15)	C(11)-C(12)-H(12)	119.5
C(2)-C(1)-C(6)	118.17(13)	C(7)-C(12)-H(12)	119.5
C(2)-C(1)-P(1)	123.48(10)	C(14)-C(13)-P(1)	115.72(11)
C(6)-C(1)-P(1)	118.34(10)	C(14)-C(13)-H(13A)	108.4
C(3)-C(2)-C(1)	120.68(14)	P(1)-C(13)-H(13A)	108.4

C(14)-C(13)-H(13B)	108.4	N(4)-C(18)-C(19)	106.81(16)
P(1)-C(13)-H(13B)	108.4	N(4)-C(18)-H(18)	126.6
H(13A)-C(13)-H(13B)	107.4	C(19)-C(18)-H(18)	126.6
C(13)#1-C(14)-C(13)	111.46(16)	C(18)-C(19)-C(20)	106.78(17)
C(13)#1-C(14)-H(14A)	109.3	C(18)-C(19)-Cl(2)	127.51(15)
C(13)-C(14)-H(14A)	109.3	C(20)-C(19)-Cl(2)	125.71(15)
C(13)#1-C(14)-H(14B)	109.3	N(3)-C(20)-C(19)	109.42(16)
C(13)-C(14)-H(14B)	109.3	N(3)-C(20)-H(20)	125.3
H(14A)-C(14)-H(14B)	108.0	C(19)-C(20)-H(20)	125.3
N(1)-C(15)-C(16)	108.95(12)	N(4)-B(1)-N(2)#1	107.97(10)
N(1)-C(15)-H(15)	125.5	N(4)-B(1)-N(2)	107.97(10)
C(16)-C(15)-H(15)	125.5	N(2)#1-B(1)-N(2)	107.80(16)
C(17)-C(16)-C(15)	106.64(12)	N(4)-B(1)-H(1B)	110.6(12)
C(17)-C(16)-Cl(1)	126.53(11)	N(2)#1-B(1)-H(1B)	111.2(6)
C(15)-C(16)-Cl(1)	126.81(12)	N(2)-B(1)-H(1B)	111.2(6)
N(2)-C(17)-C(16)	107.30(12)		
N(2)-C(17)-H(17)	126.3		
C(16)-C(17)-H(17)	126.3		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z

Table A2.14: Anisotropic displacement parameters ($Å^2$x 10^3)for Tp^{Cl}Ru(dppp)Cl 211c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	10(1)	11(1)	11(1)	0	0(1)	0
Cl(1)	25(1)	18(1)	41(1)	4(1)	6(1)	10(1)
Cl(2)	21(1)	48(1)	16(1)	0	6(1)	0
Cl(3)	19(1)	20(1)	15(1)	0	4(1)	0
P(1)	13(1)	12(1)	12(1)	0(1)	-1(1)	-1(1)
N(1)	12(1)	14(1)	17(1)	1(1)	-1(1)	1(1)
N(2)	13(1)	16(1)	17(1)	2(1)	-2(1)	1(1)
N(3)	13(1)	13(1)	12(1)	0	-2(1)	0

N(4)	14(1)	19(1)	12(1)	0	-3(1)	0
C(1)	15(1)	16(1)	17(1)	-4(1)	-2(1)	-2(1)
C(2)	22(1)	17(1)	21(1)	-2(1)	-2(1)	-1(1)
C(3)	30(1)	17(1)	31(1)	-5(1)	-3(1)	3(1)
C(4)	27(1)	26(1)	31(1)	-13(1)	2(1)	2(1)
C(5)	28(1)	31(1)	22(1)	-8(1)	5(1)	-4(1)
C(6)	26(1)	20(1)	20(1)	-3(1)	2(1)	-4(1)
C(7)	18(1)	14(1)	16(1)	0(1)	1(1)	-2(1)
C(8)	19(1)	31(1)	28(1)	8(1)	0(1)	-3(1)
C(9)	22(1)	43(1)	41(1)	14(1)	7(1)	-6(1)
C(10)	34(1)	33(1)	30(1)	12(1)	10(1)	-2(1)
C(11)	31(1)	23(1)	21(1)	6(1)	1(1)	1(1)
C(12)	20(1)	17(1)	19(1)	1(1)	0(1)	-2(1)
C(13)	19(1)	17(1)	18(1)	0(1)	-7(1)	-2(1)
C(14)	15(1)	21(1)	22(1)	0	-5(1)	0
C(15)	14(1)	14(1)	22(1)	0(1)	3(1)	0(1)
C(16)	14(1)	14(1)	29(1)	5(1)	3(1)	3(1)
C(17)	14(1)	18(1)	25(1)	6(1)	-2(1)	2(1)
C(18)	20(1)	21(1)	13(1)	0	0(1)	0
C(19)	18(1)	20(1)	13(1)	0	2(1)	0
C(20)	13(1)	15(1)	15(1)	0	0(1)	0
B(1)	14(1)	18(1)	17(1)	0	-3(1)	0

Table A2.15: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppp)Cl 211c.

	x	y	z	U(eq)
H(2)	3569	4596	6411	24
H(3)	2987	5362	7694	31
H(4)	2534	5145	9820	34
H(5)	2700	4162	10689	32
H(6)	3274	3393	9421	26

H(8)	5477	3661	5989	31
H(9)	5988	4213	4209	42
H(10)	5152	4580	2560	39
H(11)	3792	4371	2659	30
H(12)	3280	3799	4409	22
H(13A)	5088	3428	7838	22
H(13B)	4521	3030	8763	22
H(14A)	5266	2500	6499	23
H(14B)	5691	2500	7914	23
H(15)	1906	3778	7094	20
H(17)	867	3558	3537	23
H(18)	2931	2500	1259	22
H(20)	4580	2500	4137	17
H(1B)	1542(15)	2500	2590(30)	19

Table A2.16: Crystal data and structure refinement for $Tp^{Cl}Ru(dppb)Cl$ 211d.

Identification code: $Tp^{Cl}Ru(dppb)Cl$ **211d**

Empirical formula: C37 H35 B Cl4 N6 P2 Ru

Formula weight: 879.33

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group	P 21/c	
Unit cell dimensions	a = 11.9255(8) Å	α= 90°.
	b = 20.3366(14) Å	β= 103.368(2)°.
	c = 15.9734(11) Å	γ = 90°.
Volume	3769.0(4) $Å^3$	
Z	4	
Density (calculated)	1.550 Mg/m^3	
Absorption coefficient	0.822 mm^{-1}	
F(000)	1784	
Crystal size	0.280 x 0.240 x 0.080 mm^3	
Theta range for data collection	1.649 to 28.442°.	
Index ranges	-15<=h<=15, -27<=k<=27, -21<=l<=21	
Reflections collected	49022	
Independent reflections	9480 [R(int) = 0.0187]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.7012	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9480 / 0 / 463	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0611	
R indices (all data)	R1 = 0.0284, wR2 = 0.0633	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.849 and -0.451 $e.Å^{-3}$	

Table A2.17: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppb)Cl 211d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	6522(1)	6583(1)	2972(1)	12(1)
Cl(1)	5968(1)	7645(1)	3405(1)	19(1)
Cl(2)	4517(1)	5997(1)	5972(1)	27(1)
Cl(3)	10764(1)	7360(1)	5563(1)	34(1)
Cl(4)	7276(1)	4061(1)	1404(1)	33(1)
P(1)	7317(1)	7079(1)	1937(1)	14(1)
P(2)	4617(1)	6459(1)	2163(1)	13(1)
N(1)	6624(1)	5666(1)	4502(1)	19(1)
N(2)	6011(1)	6179(1)	4067(1)	16(1)
N(3)	8507(1)	6104(1)	4378(1)	20(1)
N(4)	8123(1)	6651(1)	3898(1)	18(1)
N(5)	7529(1)	5241(1)	3339(1)	18(1)
N(6)	7049(1)	5658(1)	2683(1)	15(1)
C(1)	6345(1)	7411(1)	976(1)	19(1)
C(2)	5522(1)	6896(1)	461(1)	20(1)
C(3)	4271(1)	7041(1)	447(1)	21(1)
C(4)	3985(1)	7073(1)	1334(1)	19(1)
C(5)	4185(1)	5653(1)	1681(1)	16(1)
C(6)	3360(2)	5578(1)	912(1)	22(1)
C(7)	3035(2)	4957(1)	583(1)	28(1)
C(8)	3525(2)	4400(1)	1023(1)	26(1)
C(9)	4310(1)	4464(1)	1800(1)	22(1)
C(10)	4635(1)	5086(1)	2131(1)	19(1)
C(11)	3517(1)	6533(1)	2806(1)	17(1)
C(12)	3043(1)	5977(1)	3101(1)	21(1)
C(13)	2237(2)	6038(1)	3605(1)	28(1)
C(14)	1892(2)	6650(1)	3812(1)	31(1)
C(15)	2346(2)	7208(1)	3519(1)	28(1)
C(16)	3158(1)	7153(1)	3021(1)	22(1)

C(17)	8315(1)	6567(1)	1499(1)	18(1)
C(18)	8302(2)	6555(1)	624(1)	22(1)
C(19)	9095(2)	6174(1)	318(1)	30(1)
C(20)	9913(2)	5810(1)	880(1)	33(1)
C(21)	9948(2)	5825(1)	1752(1)	29(1)
C(22)	9150(1)	6195(1)	2061(1)	22(1)
C(23)	8217(1)	7818(1)	2252(1)	17(1)
C(24)	9403(2)	7811(1)	2327(1)	23(1)
C(25)	10046(2)	8383(1)	2516(1)	31(1)
C(26)	9522(2)	8970(1)	2641(1)	32(1)
C(27)	8345(2)	8983(1)	2569(1)	30(1)
C(28)	7694(2)	8413(1)	2374(1)	24(1)
C(29)	8816(1)	7148(1)	4232(1)	20(1)
C(30)	9649(1)	6919(1)	4936(1)	24(1)
C(31)	9430(2)	6261(1)	5013(1)	24(1)
C(32)	6235(2)	5529(1)	5213(1)	22(1)
C(33)	5353(1)	5958(1)	5229(1)	20(1)
C(34)	5246(1)	6362(1)	4510(1)	18(1)
C(35)	7703(2)	4645(1)	3018(1)	22(1)
C(36)	7343(1)	4682(1)	2138(1)	20(1)
C(37)	6951(1)	5323(1)	1953(1)	17(1)
B(1)	7766(2)	5472(1)	4279(1)	20(1)

Table A2.18: Bond lengths [Å] and angles [°] for Tp^{Cl}Ru(dppb)Cl 211d.

Ru(1)-N(6)	2.0690(12)	P(1)-C(1)	1.8259(16)
Ru(1)-N(4)	2.1318(13)	P(1)-C(17)	1.8370(16)
Ru(1)-N(2)	2.1441(12)	P(1)-C(23)	1.8474(16)
Ru(1)-P(1)	2.3181(4)	P(2)-C(5)	1.8339(15)
Ru(1)-P(2)	2.3530(4)	P(2)-C(4)	1.8488(16)
Ru(1)-Cl(1)	2.4064(4)	P(2)-C(11)	1.8494(16)
Cl(2)-C(33)	1.7187(16)	N(1)-C(32)	1.352(2)
Cl(3)-C(30)	1.7197(17)	N(1)-N(2)	1.3670(18)
Cl(4)-C(36)	1.7130(16)	N(1)-B(1)	1.536(2)

N(2)-C(34)	1.331(2)	C(13)-C(14)	1.375(3)
N(3)-C(31)	1.351(2)	C(13)-H(13)	0.9500
N(3)-N(4)	1.3689(18)	C(14)-C(15)	1.384(3)
N(3)-B(1)	1.546(2)	C(14)-H(14)	0.9500
N(4)-C(29)	1.336(2)	C(15)-C(16)	1.394(2)
N(5)-C(35)	1.352(2)	C(15)-H(15)	0.9500
N(5)-N(6)	1.3659(17)	C(16)-H(16)	0.9500
N(5)-B(1)	1.536(2)	C(17)-C(18)	1.395(2)
N(6)-C(37)	1.3321(19)	C(17)-C(22)	1.398(2)
C(1)-C(2)	1.537(2)	C(18)-C(19)	1.395(2)
C(1)-H(1A)	0.9900	C(18)-H(18)	0.9500
C(1)-H(1B)	0.9900	C(19)-C(20)	1.379(3)
C(2)-C(3)	1.516(2)	C(19)-H(19)	0.9500
C(2)-H(2A)	0.9900	C(20)-C(21)	1.384(3)
C(2)-H(2B)	0.9900	C(20)-H(20)	0.9500
C(3)-C(4)	1.533(2)	C(21)-C(22)	1.389(2)
C(3)-H(3A)	0.9900	C(21)-H(21)	0.9500
C(3)-H(3B)	0.9900	C(22)-H(22)	0.9500
C(4)-H(4A)	0.9900	C(23)-C(24)	1.391(2)
C(4)-H(4B)	0.9900	C(23)-C(28)	1.396(2)
C(5)-C(6)	1.393(2)	C(24)-C(25)	1.388(2)
C(5)-C(10)	1.398(2)	C(24)-H(24)	0.9500
C(6)-C(7)	1.389(2)	C(25)-C(26)	1.383(3)
C(6)-H(6)	0.9500	C(25)-H(25)	0.9500
C(7)-C(8)	1.387(3)	C(26)-C(27)	1.382(3)
C(7)-H(7)	0.9500	C(26)-H(26)	0.9500
C(8)-C(9)	1.378(2)	C(27)-C(28)	1.391(2)
C(8)-H(8)	0.9500	C(27)-H(27)	0.9500
C(9)-C(10)	1.390(2)	C(28)-H(28)	0.9500
C(9)-H(9)	0.9500	C(29)-C(30)	1.397(2)
C(10)-H(10)	0.9500	C(29)-H(29)	0.9500
C(11)-C(12)	1.394(2)	C(30)-C(31)	1.375(3)
C(11)-C(16)	1.400(2)	C(31)-H(31)	0.9500
C(12)-C(13)	1.394(2)	C(32)-C(33)	1.372(2)
C(12)-H(12)	0.9500	C(32)-H(32)	0.9500

C(33)-C(34)	1.393(2)	C(32)-N(1)-N(2)	109.72(13)
C(34)-H(34)	0.9500	C(32)-N(1)-B(1)	129.53(14)
C(35)-C(36)	1.374(2)	N(2)-N(1)-B(1)	118.46(12)
C(35)-H(35)	0.9500	C(34)-N(2)-N(1)	107.11(12)
C(36)-C(37)	1.393(2)	C(34)-N(2)-Ru(1)	133.33(11)
C(37)-H(37)	0.9500	N(1)-N(2)-Ru(1)	119.16(9)
B(1)-H(1)	1.19(2)	C(31)-N(3)-N(4)	109.74(14)
		C(31)-N(3)-B(1)	128.37(14)
N(6)-Ru(1)-N(4)	86.77(5)	N(4)-N(3)-B(1)	120.53(13)
N(6)-Ru(1)-N(2)	89.54(5)	C(29)-N(4)-N(3)	107.12(13)
N(4)-Ru(1)-N(2)	80.61(5)	C(29)-N(4)-Ru(1)	134.28(11)
N(6)-Ru(1)-P(1)	92.34(4)	N(3)-N(4)-Ru(1)	117.79(10)
N(4)-Ru(1)-P(1)	91.03(4)	C(35)-N(5)-N(6)	109.90(12)
N(2)-Ru(1)-P(1)	171.33(4)	C(35)-N(5)-B(1)	129.44(13)
N(6)-Ru(1)-P(2)	94.86(4)	N(6)-N(5)-B(1)	120.65(12)
N(4)-Ru(1)-P(2)	169.70(4)	C(37)-N(6)-N(5)	106.88(12)
N(2)-Ru(1)-P(2)	89.22(4)	C(37)-N(6)-Ru(1)	133.68(10)
P(1)-Ru(1)-P(2)	99.049(15)	N(5)-N(6)-Ru(1)	119.19(9)
N(6)-Ru(1)-Cl(1)	176.24(4)	C(2)-C(1)-P(1)	113.67(11)
N(4)-Ru(1)-Cl(1)	90.22(4)	C(2)-C(1)-H(1A)	108.8
N(2)-Ru(1)-Cl(1)	87.75(4)	P(1)-C(1)-H(1A)	108.8
P(1)-Ru(1)-Cl(1)	89.966(14)	C(2)-C(1)-H(1B)	108.8
P(2)-Ru(1)-Cl(1)	87.704(14)	P(1)-C(1)-H(1B)	108.8
C(1)-P(1)-C(17)	103.32(7)	H(1A)-C(1)-H(1B)	107.7
C(1)-P(1)-C(23)	98.29(7)	C(3)-C(2)-C(1)	112.31(13)
C(17)-P(1)-C(23)	100.27(7)	C(3)-C(2)-H(2A)	109.1
C(1)-P(1)-Ru(1)	118.40(5)	C(1)-C(2)-H(2A)	109.1
C(17)-P(1)-Ru(1)	115.63(5)	C(3)-C(2)-H(2B)	109.1
C(23)-P(1)-Ru(1)	117.87(5)	C(1)-C(2)-H(2B)	109.1
C(5)-P(2)-C(4)	105.94(7)	H(2A)-C(2)-H(2B)	107.9
C(5)-P(2)-C(11)	98.01(7)	C(2)-C(3)-C(4)	115.07(13)
C(4)-P(2)-C(11)	96.81(7)	C(2)-C(3)-H(3A)	108.5
C(5)-P(2)-Ru(1)	117.91(5)	C(4)-C(3)-H(3A)	108.5
C(4)-P(2)-Ru(1)	120.19(5)	C(2)-C(3)-H(3B)	108.5
C(11)-P(2)-Ru(1)	113.91(5)	C(4)-C(3)-H(3B)	108.5

H(3A)-C(3)-H(3B)	107.5	C(13)-C(14)-H(14)	120.1
C(3)-C(4)-P(2)	119.50(11)	C(15)-C(14)-H(14)	120.1
C(3)-C(4)-H(4A)	107.4	C(14)-C(15)-C(16)	120.36(16)
P(2)-C(4)-H(4A)	107.4	C(14)-C(15)-H(15)	119.8
C(3)-C(4)-H(4B)	107.4	C(16)-C(15)-H(15)	119.8
P(2)-C(4)-H(4B)	107.4	C(15)-C(16)-C(11)	120.31(16)
H(4A)-C(4)-H(4B)	107.0	C(15)-C(16)-H(16)	119.8
C(6)-C(5)-C(10)	118.19(14)	C(11)-C(16)-H(16)	119.8
C(6)-C(5)-P(2)	122.69(12)	C(18)-C(17)-C(22)	118.35(15)
C(10)-C(5)-P(2)	118.95(12)	C(18)-C(17)-P(1)	122.23(13)
C(7)-C(6)-C(5)	120.72(15)	C(22)-C(17)-P(1)	119.37(12)
C(7)-C(6)-H(6)	119.6	C(17)-C(18)-C(19)	120.64(17)
C(5)-C(6)-H(6)	119.6	C(17)-C(18)-H(18)	119.7
C(8)-C(7)-C(6)	120.18(16)	C(19)-C(18)-H(18)	119.7
C(8)-C(7)-H(7)	119.9	C(20)-C(19)-C(18)	120.26(17)
C(6)-C(7)-H(7)	119.9	C(20)-C(19)-H(19)	119.9
C(9)-C(8)-C(7)	119.88(15)	C(18)-C(19)-H(19)	119.9
C(9)-C(8)-H(8)	120.1	C(19)-C(20)-C(21)	119.72(17)
C(7)-C(8)-H(8)	120.1	C(19)-C(20)-H(20)	120.1
C(8)-C(9)-C(10)	119.97(15)	C(21)-C(20)-H(20)	120.1
C(8)-C(9)-H(9)	120.0	C(20)-C(21)-C(22)	120.35(18)
C(10)-C(9)-H(9)	120.0	C(20)-C(21)-H(21)	119.8
C(9)-C(10)-C(5)	120.95(15)	C(22)-C(21)-H(21)	119.8
C(9)-C(10)-H(10)	119.5	C(21)-C(22)-C(17)	120.66(16)
C(5)-C(10)-H(10)	119.5	C(21)-C(22)-H(22)	119.7
C(12)-C(11)-C(16)	118.47(15)	C(17)-C(22)-H(22)	119.7
C(12)-C(11)-P(2)	121.16(12)	C(24)-C(23)-C(28)	118.38(14)
C(16)-C(11)-P(2)	120.36(12)	C(24)-C(23)-P(1)	121.99(12)
C(11)-C(12)-C(13)	120.69(16)	C(28)-C(23)-P(1)	119.53(12)
C(11)-C(12)-H(12)	119.7	C(25)-C(24)-C(23)	120.63(16)
C(13)-C(12)-H(12)	119.7	C(25)-C(24)-H(24)	119.7
C(14)-C(13)-C(12)	120.28(17)	C(23)-C(24)-H(24)	119.7
C(14)-C(13)-H(13)	119.9	C(26)-C(25)-C(24)	120.63(17)
C(12)-C(13)-H(13)	119.9	C(26)-C(25)-H(25)	119.7
C(13)-C(14)-C(15)	119.88(16)	C(24)-C(25)-H(25)	119.7

C(27)-C(26)-C(25)	119.31(16)	C(32)-C(33)-Cl(2)	127.73(12)
C(27)-C(26)-H(26)	120.3	C(34)-C(33)-Cl(2)	125.81(13)
C(25)-C(26)-H(26)	120.3	N(2)-C(34)-C(33)	109.36(14)
C(26)-C(27)-C(28)	120.40(17)	N(2)-C(34)-H(34)	125.3
C(26)-C(27)-H(27)	119.8	C(33)-C(34)-H(34)	125.3
C(28)-C(27)-H(27)	119.8	N(5)-C(35)-C(36)	107.36(14)
C(27)-C(28)-C(23)	120.64(16)	N(5)-C(35)-H(35)	126.3
C(27)-C(28)-H(28)	119.7	C(36)-C(35)-H(35)	126.3
C(23)-C(28)-H(28)	119.7	C(35)-C(36)-C(37)	106.24(14)
N(4)-C(29)-C(30)	109.22(15)	C(35)-C(36)-Cl(4)	127.84(13)
N(4)-C(29)-H(29)	125.4	C(37)-C(36)-Cl(4)	125.75(13)
C(30)-C(29)-H(29)	125.4	N(6)-C(37)-C(36)	109.60(14)
C(31)-C(30)-C(29)	106.36(15)	N(6)-C(37)-H(37)	125.2
C(31)-C(30)-Cl(3)	126.36(14)	C(36)-C(37)-H(37)	125.2
C(29)-C(30)-Cl(3)	127.24(14)	N(5)-B(1)-N(1)	109.42(13)
N(3)-C(31)-C(30)	107.57(15)	N(5)-B(1)-N(3)	109.05(13)
N(3)-C(31)-H(31)	126.2	N(1)-B(1)-N(3)	106.20(13)
C(30)-C(31)-H(31)	126.2	N(5)-B(1)-H(1)	108.8(10)
N(1)-C(32)-C(33)	107.35(14)	N(1)-B(1)-H(1)	113.1(10)
N(1)-C(32)-H(32)	126.3	N(3)-B(1)-H(1)	110.2(10)
C(33)-C(32)-H(32)	126.3		
C(32)-C(33)-C(34)	106.45(14)		

Symmetry transformations used to generate equivalent atoms:

Table A2.19: Anisotropic displacement parameters ($Å^2$x 10^3) for Tp^{Cl}Ru(dppb)Cl 211d. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	12(1)	12(1)	0(1)	3(1)	0(1)
Cl(1)	24(1)	14(1)	21(1)	-3(1)	9(1)	-1(1)
Cl(2)	38(1)	27(1)	21(1)	0(1)	17(1)	-5(1)
Cl(3)	21(1)	48(1)	30(1)	-15(1)	1(1)	-8(1)
Cl(4)	48(1)	21(1)	26(1)	-7(1)	1(1)	13(1)

P(1)	16(1)	13(1)	15(1)	1(1)	5(1)	0(1)
P(2)	14(1)	13(1)	13(1)	0(1)	3(1)	0(1)
N(1)	22(1)	18(1)	15(1)	3(1)	3(1)	1(1)
N(2)	19(1)	15(1)	14(1)	1(1)	3(1)	0(1)
N(3)	19(1)	23(1)	16(1)	0(1)	1(1)	1(1)
N(4)	17(1)	20(1)	15(1)	-1(1)	3(1)	-1(1)
N(5)	19(1)	16(1)	16(1)	2(1)	2(1)	4(1)
N(6)	15(1)	14(1)	16(1)	2(1)	3(1)	1(1)
C(1)	21(1)	18(1)	18(1)	5(1)	5(1)	0(1)
C(2)	25(1)	21(1)	14(1)	1(1)	4(1)	-2(1)
C(3)	23(1)	22(1)	16(1)	6(1)	0(1)	-2(1)
C(4)	19(1)	17(1)	21(1)	4(1)	3(1)	2(1)
C(5)	18(1)	15(1)	17(1)	-2(1)	7(1)	-2(1)
C(6)	27(1)	19(1)	19(1)	2(1)	2(1)	-3(1)
C(7)	37(1)	25(1)	19(1)	-3(1)	1(1)	-9(1)
C(8)	35(1)	18(1)	28(1)	-6(1)	11(1)	-8(1)
C(9)	22(1)	16(1)	29(1)	2(1)	9(1)	0(1)
C(10)	18(1)	18(1)	20(1)	0(1)	6(1)	-2(1)
C(11)	14(1)	21(1)	16(1)	-2(1)	3(1)	0(1)
C(12)	21(1)	23(1)	22(1)	-2(1)	8(1)	-2(1)
C(13)	26(1)	33(1)	29(1)	0(1)	13(1)	-5(1)
C(14)	22(1)	43(1)	30(1)	-5(1)	14(1)	1(1)
C(15)	24(1)	31(1)	29(1)	-7(1)	8(1)	8(1)
C(16)	20(1)	22(1)	23(1)	-2(1)	5(1)	2(1)
C(17)	18(1)	14(1)	23(1)	-2(1)	9(1)	-3(1)
C(18)	22(1)	24(1)	23(1)	-4(1)	9(1)	-4(1)
C(19)	31(1)	35(1)	30(1)	-11(1)	16(1)	-5(1)
C(20)	25(1)	30(1)	48(1)	-15(1)	17(1)	-2(1)
C(21)	20(1)	22(1)	43(1)	-3(1)	7(1)	2(1)
C(22)	21(1)	19(1)	26(1)	-2(1)	7(1)	-1(1)
C(23)	20(1)	15(1)	17(1)	0(1)	6(1)	-3(1)
C(24)	21(1)	19(1)	31(1)	-2(1)	6(1)	-1(1)
C(25)	20(1)	26(1)	46(1)	-4(1)	7(1)	-6(1)
C(26)	31(1)	20(1)	47(1)	-5(1)	11(1)	-9(1)
C(27)	35(1)	16(1)	43(1)	-4(1)	16(1)	-3(1)

C(28)	24(1)	18(1)	32(1)	-1(1)	13(1)	-2(1)
C(29)	19(1)	25(1)	19(1)	-5(1)	7(1)	-3(1)
C(30)	15(1)	35(1)	21(1)	-8(1)	4(1)	-3(1)
C(31)	19(1)	35(1)	18(1)	-2(1)	1(1)	2(1)
C(32)	30(1)	20(1)	16(1)	3(1)	5(1)	-3(1)
C(33)	26(1)	20(1)	15(1)	-1(1)	8(1)	-6(1)
C(34)	20(1)	18(1)	15(1)	-2(1)	4(1)	-3(1)
C(35)	25(1)	17(1)	23(1)	1(1)	4(1)	6(1)
C(36)	22(1)	17(1)	22(1)	-2(1)	4(1)	4(1)
C(37)	18(1)	16(1)	18(1)	0(1)	4(1)	0(1)
B(1)	21(1)	20(1)	17(1)	2(1)	3(1)	2(1)

Table A2.20: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Cl}Ru(dppb)Cl 211d.

	x	y	z	U(eq)
H(1A)	5884	7769	1149	23
H(1B)	6810	7604	598	23
H(2A)	5621	6885	-138	24
H(2B)	5726	6456	717	24
H(3A)	3785	6697	103	25
H(3B)	4060	7467	152	25
H(4A)	3137	7044	1243	23
H(4B)	4215	7513	1578	23
H(6)	3015	5956	610	26
H(7)	2476	4912	56	34
H(8)	3320	3976	788	32
H(9)	4629	4084	2111	26
H(10)	5171	5126	2670	22
H(12)	3272	5552	2958	25
H(13)	1926	5655	3806	34
H(14)	1342	6690	4155	37
H(15)	2102	7630	3659	33
H(16)	3470	7538	2826	26

H(18)	7749	6809	232	27
H(19)	9071	6166	-281	36
H(20)	10450	5550	670	39
H(21)	10520	5582	2142	34
H(22)	9172	6195	2659	27
H(24)	9776	7410	2248	28
H(25)	10854	8371	2559	37
H(26)	9966	9360	2774	39
H(27)	7979	9385	2654	36
H(28)	6884	8428	2323	28
H(29)	8752	7587	4025	24
H(31)	9852	5969	5435	29
H(32)	6520	5197	5625	26
H(34)	4711	6712	4360	21
H(35)	8017	4269	3342	26
H(37)	6658	5495	1392	20
H(1)	8265(17)	5049(10)	4729(12)	23

Table A2.21: Crystal data and structure refinement for $Tp^{Br}Ru(dppm)Cl$ 213a.

Identification code: $Tp^{Br}Ru(dppm)Cl$ **213a**

Empirical formula: C40 H34 B Br3 Cl2 N6 P2 Ru

Formula weight: 1083.18

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group	P 21/c	
Unit cell dimensions	a = 10.3676(6) Å	α= 90°.
	b = 18.4514(10) Å	β= 91.0840(10)°.
	c = 21.9342(13) Å	γ = 90°.
Volume	4195.2(4) $Å^3$	
Z	4	
Density (calculated)	1.715 Mg/m^3	
Absorption coefficient	3.473 mm^{-1}	
F(000)	2136	
Crystal size	0.410 x 0.050 x 0.040 mm^3	
Theta range for data collection	1.857 to 28.387°.	
Index ranges	-13<=h<=13, -24<=k<=24, -29<=l<=29	
Reflections collected	54995	
Independent reflections	10493 [R(int) = 0.0221]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.5401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10493 / 1060 / 628	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0237, wR2 = 0.0516	
R indices (all data)	R1 = 0.0308, wR2 = 0.0542	
Largest diff. peak and hole	0.765 and -0.565 $e.Å^{-3}$	

Table A2.22: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppm)Cl 213a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl13	1081(7)	5575(5)	5507(5)	81(3)
C13	63(13)	5628(7)	6103(7)	55(4)
C23	503(14)	5507(8)	6690(6)	60(4)
C33	-319(19)	5565(18)	7177(7)	70(6)
C43	-1601(17)	5731(12)	7065(7)	55(4)
C53	-2027(15)	5865(16)	6478(7)	46(4)
C63	-1232(13)	5783(17)	5989(6)	36(4)
Cl12	647(5)	5508(3)	5399(2)	95(2)
C12	84(9)	5518(5)	6129(4)	53(2)
C22	-1119(10)	5788(8)	6253(5)	64(3)
C32	-1544(10)	5796(7)	6847(5)	73(3)
C42	-757(10)	5546(8)	7314(5)	57(3)
C52	464(8)	5271(4)	7190(3)	50(2)
C62	876(7)	5256(4)	6600(3)	42(2)
Cl11	1372(2)	5421(2)	6024(2)	74(1)
C11	-32(6)	5600(4)	6408(4)	35(2)
C21	-1117(8)	5811(10)	6087(4)	35(3)
C31	-2248(8)	5935(9)	6397(4)	29(2)
C41	-2254(6)	5859(4)	7027(3)	34(2)
C51	-1158(9)	5644(7)	7340(4)	42(2)
C61	-11(7)	5515(6)	7037(4)	38(2)
Ru(1)	2824(1)	7987(1)	3859(1)	13(1)
Br(1)	304(1)	7328(1)	1384(1)	31(1)
Br(2)	6334(1)	5496(1)	4575(1)	37(1)
Br(3)	-2157(1)	7394(1)	5166(1)	23(1)
Cl(1)	1537(1)	9027(1)	3584(1)	20(1)
P(1)	3621(1)	8496(1)	4723(1)	16(1)
P(2)	4686(1)	8570(1)	3614(1)	15(1)
N(1)	788(2)	6841(1)	4087(1)	18(1)

N(2)	1163(1)	7524(1)	4243(1)	17(1)
N(3)	2111(2)	7499(1)	3025(1)	17(1)
N(4)	1716(2)	6794(1)	3045(1)	17(1)
N(5)	3719(2)	6998(1)	4037(1)	16(1)
N(6)	3021(2)	6376(1)	3948(1)	18(1)
C(1)	6054(2)	8054(1)	3339(1)	17(1)
C(2)	5814(2)	7450(1)	2976(1)	22(1)
C(3)	6833(2)	7045(1)	2758(1)	28(1)
C(4)	8089(2)	7246(1)	2895(1)	32(1)
C(5)	8343(2)	7852(1)	3249(1)	30(1)
C(6)	7327(2)	8253(1)	3475(1)	24(1)
C(7)	4825(2)	9387(1)	3151(1)	20(1)
C(8)	5645(2)	9953(1)	3320(1)	31(1)
C(9)	5849(3)	10530(1)	2926(1)	39(1)
C(10)	5253(2)	10545(1)	2364(1)	38(1)
C(11)	4428(3)	9992(1)	2192(1)	42(1)
C(12)	4210(2)	9414(1)	2585(1)	30(1)
C(13)	2769(2)	9247(1)	5074(1)	21(1)
C(14)	2659(2)	9912(1)	4777(1)	25(1)
C(15)	1875(2)	10452(1)	5012(1)	31(1)
C(16)	1187(2)	10328(1)	5533(1)	32(1)
C(17)	1287(2)	9669(1)	5830(1)	32(1)
C(18)	2079(2)	9131(1)	5604(1)	26(1)
C(19)	4112(2)	7946(1)	5373(1)	22(1)
C(20)	5132(2)	8168(1)	5756(1)	31(1)
C(21)	5514(2)	7745(2)	6248(1)	43(1)
C(22)	4878(3)	7110(2)	6371(1)	46(1)
C(23)	3857(3)	6886(1)	6003(1)	41(1)
C(24)	3471(2)	7303(1)	5501(1)	29(1)
C(25)	5117(2)	8860(1)	4400(1)	20(1)
C(26)	280(2)	7788(1)	4615(1)	18(1)
C(27)	-681(2)	7271(1)	4695(1)	19(1)
C(28)	-338(2)	6680(1)	4358(1)	20(1)
C(29)	1127(2)	6615(1)	2511(1)	19(1)
C(30)	1142(2)	7217(1)	2144(1)	21(1)

C(31)	1760(2)	7758(1)	2481(1)	19(1)
C(32)	3736(2)	5797(1)	4116(1)	22(1)
C(33)	4917(2)	6048(1)	4315(1)	22(1)
C(34)	4874(2)	6799(1)	4259(1)	19(1)
B(1)	1656(2)	6396(1)	3662(1)	19(1)

Table A2.23: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(dppm)Cl 213a.

Cl13-C13	1.698(14)	C11-C61	1.387(9)
C13-C23	1.377(11)	C21-C31	1.386(8)
C13-C63	1.390(11)	C21-H21	0.9500
C23-C33	1.382(12)	C31-C41	1.389(8)
C23-H23	0.9500	C31-H31	0.9500
C33-C43	1.381(12)	C41-C51	1.375(8)
C33-H33	0.9500	C41-H41	0.9500
C43-C53	1.376(12)	C51-C61	1.393(9)
C43-H43	0.9500	C51-H51	0.9500
C53-C63	1.374(11)	C61-H61	0.9500
C53-H53	0.9500	Ru(1)-N(5)	2.0801(15)
C63-H63	0.9500	Ru(1)-N(2)	2.1105(15)
Cl12-C12	1.716(10)	Ru(1)-N(3)	2.1566(15)
C12-C22	1.376(10)	Ru(1)-P(1)	2.2574(5)
C12-C62	1.393(9)	Ru(1)-P(2)	2.2838(5)
C22-C32	1.383(10)	Ru(1)-Cl(1)	2.4075(5)
C22-H22	0.9500	Br(1)-C(30)	1.8752(19)
C32-C42	1.376(10)	Br(2)-C(33)	1.8687(19)
C32-H32	0.9500	Br(3)-C(27)	1.8756(19)
C42-C52	1.396(9)	P(1)-C(19)	1.815(2)
C42-H42	0.9500	P(1)-C(13)	1.8216(19)
C52-C62	1.372(8)	P(1)-C(25)	1.8430(19)
C52-H52	0.9500	P(1)-P(2)	2.6939(7)
C62-H62	0.9500	P(2)-C(1)	1.8193(18)
Cl11-C11	1.728(7)	P(2)-C(7)	1.8252(19)
C11-C21	1.373(9)	P(2)-C(25)	1.8531(19)

N(1)-C(28)	1.352(2)	C(13)-C(18)	1.394(3)
N(1)-N(2)	1.361(2)	C(14)-C(15)	1.390(3)
N(1)-B(1)	1.543(3)	C(14)-H(14)	0.9500
N(2)-C(26)	1.331(2)	C(15)-C(16)	1.379(3)
N(3)-C(31)	1.330(2)	C(15)-H(15)	0.9500
N(3)-N(4)	1.366(2)	C(16)-C(17)	1.383(3)
N(4)-C(29)	1.352(2)	C(16)-H(16)	0.9500
N(4)-B(1)	1.543(3)	C(17)-C(18)	1.386(3)
N(5)-C(34)	1.336(2)	C(17)-H(17)	0.9500
N(5)-N(6)	1.368(2)	C(18)-H(18)	0.9500
N(6)-C(32)	1.348(2)	C(19)-C(24)	1.392(3)
N(6)-B(1)	1.537(3)	C(19)-C(20)	1.399(3)
C(1)-C(2)	1.390(3)	C(20)-C(21)	1.383(3)
C(1)-C(6)	1.396(3)	C(20)-H(20)	0.9500
C(2)-C(3)	1.386(3)	C(21)-C(22)	1.373(4)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-C(4)	1.381(3)	C(22)-C(23)	1.383(4)
C(3)-H(3)	0.9500	C(22)-H(22)	0.9500
C(4)-C(5)	1.384(3)	C(23)-C(24)	1.395(3)
C(4)-H(4)	0.9500	C(23)-H(23)	0.9500
C(5)-C(6)	1.387(3)	C(24)-H(24)	0.9500
C(5)-H(5)	0.9500	C(25)-H(25A)	0.9900
C(6)-H(6)	0.9500	C(25)-H(25B)	0.9900
C(7)-C(12)	1.386(3)	C(26)-C(27)	1.394(3)
C(7)-C(8)	1.393(3)	C(26)-H(26)	0.9500
C(8)-C(9)	1.390(3)	C(27)-C(28)	1.368(3)
C(8)-H(8)	0.9500	C(28)-H(28)	0.9500
C(9)-C(10)	1.368(4)	C(29)-C(30)	1.372(3)
C(9)-H(9)	0.9500	C(29)-H(29)	0.9500
C(10)-C(11)	1.380(4)	C(30)-C(31)	1.391(3)
C(10)-H(10)	0.9500	C(31)-H(31)	0.9500
C(11)-C(12)	1.391(3)	C(32)-C(33)	1.372(3)
C(11)-H(11)	0.9500	C(32)-H(32)	0.9500
C(12)-H(12)	0.9500	C(33)-C(34)	1.390(3)
C(13)-C(14)	1.393(3)	C(34)-H(34)	0.9500

B(1)-H(1B)	1.09(2)	C52-C62-C12	120.2(7)
		C52-C62-H62	119.9
C23-C13-C63	120.2(10)	C12-C62-H62	119.9
C23-C13-Cl13	120.8(9)	C21-C11-C61	122.7(6)
C63-C13-Cl13	119.0(10)	C21-C11-Cl11	119.5(6)
C13-C23-C33	120.8(10)	C61-C11-Cl11	117.8(6)
C13-C23-H23	119.6	C11-C21-C31	119.1(7)
C33-C23-H23	119.6	C11-C21-H21	120.4
C43-C33-C23	119.1(10)	C31-C21-H21	120.4
C43-C33-H33	120.5	C21-C31-C41	119.4(7)
C23-C33-H33	120.5	C21-C31-H31	120.3
C53-C43-C33	119.8(10)	C41-C31-H31	120.3
C53-C43-H43	120.1	C51-C41-C31	120.5(6)
C33-C43-H43	120.1	C51-C41-H41	119.8
C63-C53-C43	121.6(10)	C31-C41-H41	119.8
C63-C53-H53	119.2	C41-C51-C61	121.0(7)
C43-C53-H53	119.2	C41-C51-H51	119.5
C53-C63-C13	118.3(10)	C61-C51-H51	119.5
C53-C63-H63	120.8	C11-C61-C51	117.3(6)
C13-C63-H63	120.8	C11-C61-H61	121.4
C22-C12-C62	120.2(8)	C51-C61-H61	121.4
C22-C12-Cl12	121.0(7)	N(5)-Ru(1)-N(2)	86.25(6)
C62-C12-Cl12	118.8(7)	N(5)-Ru(1)-N(3)	86.42(6)
C12-C22-C32	119.8(8)	N(2)-Ru(1)-N(3)	84.29(6)
C12-C22-H22	120.1	N(5)-Ru(1)-P(1)	93.02(4)
C32-C22-H22	120.1	N(2)-Ru(1)-P(1)	97.06(4)
C42-C32-C22	120.1(8)	N(3)-Ru(1)-P(1)	178.51(4)
C42-C32-H32	119.9	N(5)-Ru(1)-P(2)	94.65(4)
C22-C32-H32	119.9	N(2)-Ru(1)-P(2)	169.82(4)
C32-C42-C52	120.3(8)	N(3)-Ru(1)-P(2)	105.89(4)
C32-C42-H42	119.8	P(1)-Ru(1)-P(2)	72.769(17)
C52-C42-H42	119.8	N(5)-Ru(1)-Cl(1)	171.54(4)
C62-C52-C42	119.4(7)	N(2)-Ru(1)-Cl(1)	88.32(4)
C62-C52-H52	120.3	N(3)-Ru(1)-Cl(1)	86.59(4)
C42-C52-H52	120.3	P(1)-Ru(1)-Cl(1)	94.080(17)

P(2)-Ru(1)-Cl(1)	91.838(17)	N(6)-N(5)-Ru(1)	118.41(11)
C(19)-P(1)-C(13)	102.94(9)	C(32)-N(6)-N(5)	109.82(15)
C(19)-P(1)-C(25)	106.25(9)	C(32)-N(6)-B(1)	128.85(16)
C(13)-P(1)-C(25)	107.66(9)	N(5)-N(6)-B(1)	121.24(14)
C(19)-P(1)-Ru(1)	121.32(7)	C(2)-C(1)-C(6)	119.39(17)
C(13)-P(1)-Ru(1)	119.87(6)	C(2)-C(1)-P(2)	118.50(14)
C(25)-P(1)-Ru(1)	97.30(6)	C(6)-C(1)-P(2)	122.10(15)
C(19)-P(1)-P(2)	128.64(6)	C(3)-C(2)-C(1)	120.10(19)
C(13)-P(1)-P(2)	123.59(7)	C(3)-C(2)-H(2)	120.0
C(25)-P(1)-P(2)	43.36(6)	C(1)-C(2)-H(2)	120.0
Ru(1)-P(1)-P(2)	54.066(15)	C(4)-C(3)-C(2)	120.1(2)
C(1)-P(2)-C(7)	100.23(8)	C(4)-C(3)-H(3)	120.0
C(1)-P(2)-C(25)	106.47(9)	C(2)-C(3)-H(3)	120.0
C(7)-P(2)-C(25)	105.02(9)	C(3)-C(4)-C(5)	120.5(2)
C(1)-P(2)-Ru(1)	119.98(6)	C(3)-C(4)-H(4)	119.7
C(7)-P(2)-Ru(1)	126.61(6)	C(5)-C(4)-H(4)	119.7
C(25)-P(2)-Ru(1)	96.11(6)	C(4)-C(5)-C(6)	119.6(2)
C(1)-P(2)-P(1)	127.42(6)	C(4)-C(5)-H(5)	120.2
C(7)-P(2)-P(1)	125.60(6)	C(6)-C(5)-H(5)	120.2
C(25)-P(2)-P(1)	43.06(6)	C(5)-C(6)-C(1)	120.34(19)
Ru(1)-P(2)-P(1)	53.164(14)	C(5)-C(6)-H(6)	119.8
C(28)-N(1)-N(2)	109.77(15)	C(1)-C(6)-H(6)	119.8
C(28)-N(1)-B(1)	131.75(15)	C(12)-C(7)-C(8)	118.68(18)
N(2)-N(1)-B(1)	118.48(14)	C(12)-C(7)-P(2)	119.28(15)
C(26)-N(2)-N(1)	107.29(15)	C(8)-C(7)-P(2)	121.67(16)
C(26)-N(2)-Ru(1)	132.17(12)	C(9)-C(8)-C(7)	120.5(2)
N(1)-N(2)-Ru(1)	120.44(11)	C(9)-C(8)-H(8)	119.8
C(31)-N(3)-N(4)	107.04(15)	C(7)-C(8)-H(8)	119.8
C(31)-N(3)-Ru(1)	134.08(13)	C(10)-C(9)-C(8)	120.2(2)
N(4)-N(3)-Ru(1)	117.95(11)	C(10)-C(9)-H(9)	119.9
C(29)-N(4)-N(3)	109.66(15)	C(8)-C(9)-H(9)	119.9
C(29)-N(4)-B(1)	128.25(16)	C(9)-C(10)-C(11)	120.0(2)
N(3)-N(4)-B(1)	119.91(14)	C(9)-C(10)-H(10)	120.0
C(34)-N(5)-N(6)	106.79(14)	C(11)-C(10)-H(10)	120.0
C(34)-N(5)-Ru(1)	134.71(12)	C(10)-C(11)-C(12)	120.2(2)

C(10)-C(11)-H(11)	119.9	C(22)-C(23)-C(24)	120.0(2)
C(12)-C(11)-H(11)	119.9	C(22)-C(23)-H(23)	120.0
C(7)-C(12)-C(11)	120.4(2)	C(24)-C(23)-H(23)	120.0
C(7)-C(12)-H(12)	119.8	C(19)-C(24)-C(23)	119.9(2)
C(11)-C(12)-H(12)	119.8	C(19)-C(24)-H(24)	120.0
C(14)-C(13)-C(18)	119.05(18)	C(23)-C(24)-H(24)	120.0
C(14)-C(13)-P(1)	120.65(15)	P(1)-C(25)-P(2)	93.58(8)
C(18)-C(13)-P(1)	119.78(15)	P(1)-C(25)-H(25A)	113.0
C(15)-C(14)-C(13)	120.1(2)	P(2)-C(25)-H(25A)	113.0
C(15)-C(14)-H(14)	119.9	P(1)-C(25)-H(25B)	113.0
C(13)-C(14)-H(14)	119.9	P(2)-C(25)-H(25B)	113.0
C(16)-C(15)-C(14)	120.3(2)	H(25A)-C(25)-H(25B)	110.4
C(16)-C(15)-H(15)	119.9	N(2)-C(26)-C(27)	109.10(16)
C(14)-C(15)-H(15)	119.9	N(2)-C(26)-H(26)	125.4
C(15)-C(16)-C(17)	120.0(2)	C(27)-C(26)-H(26)	125.4
C(15)-C(16)-H(16)	120.0	C(28)-C(27)-C(26)	106.49(16)
C(17)-C(16)-H(16)	120.0	C(28)-C(27)-Br(3)	128.13(14)
C(16)-C(17)-C(18)	120.1(2)	C(26)-C(27)-Br(3)	125.37(15)
C(16)-C(17)-H(17)	120.0	N(1)-C(28)-C(27)	107.35(16)
C(18)-C(17)-H(17)	120.0	N(1)-C(28)-H(28)	126.3
C(17)-C(18)-C(13)	120.4(2)	C(27)-C(28)-H(28)	126.3
C(17)-C(18)-H(18)	119.8	N(4)-C(29)-C(30)	107.50(16)
C(13)-C(18)-H(18)	119.8	N(4)-C(29)-H(29)	126.2
C(24)-C(19)-C(20)	119.13(19)	C(30)-C(29)-H(29)	126.2
C(24)-C(19)-P(1)	120.46(16)	C(29)-C(30)-C(31)	106.20(16)
C(20)-C(19)-P(1)	120.41(16)	C(29)-C(30)-Br(1)	126.85(15)
C(21)-C(20)-C(19)	120.3(2)	C(31)-C(30)-Br(1)	126.48(15)
C(21)-C(20)-H(20)	119.8	N(3)-C(31)-C(30)	109.59(17)
C(19)-C(20)-H(20)	119.8	N(3)-C(31)-H(31)	125.2
C(22)-C(21)-C(20)	120.2(2)	C(30)-C(31)-H(31)	125.2
C(22)-C(21)-H(21)	119.9	N(6)-C(32)-C(33)	107.56(16)
C(20)-C(21)-H(21)	119.9	N(6)-C(32)-H(32)	126.2
C(21)-C(22)-C(23)	120.4(2)	C(33)-C(32)-H(32)	126.2
C(21)-C(22)-H(22)	119.8	C(32)-C(33)-C(34)	106.34(17)
C(23)-C(22)-H(22)	119.8	C(32)-C(33)-Br(2)	127.17(15)

C(34)-C(33)-Br(2)	126.44(15)	N(4)-B(1)-N(1)	108.08(15)
N(5)-C(34)-C(33)	109.49(17)	N(6)-B(1)-H(1B)	111.5(12)
N(5)-C(34)-H(34)	125.3	N(4)-B(1)-H(1B)	109.7(11)
C(33)-C(34)-H(34)	125.3	N(1)-B(1)-H(1B)	111.0(12)
N(6)-B(1)-N(4)	108.46(15)		
N(6)-B(1)-N(1)	108.01(15)		

Symmetry transformations used to generate equivalent atoms:

Table A2.24: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Br}Ru(dppm)Cl$ 213a. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl13	46(3)	55(3)	142(8)	38(4)	23(4)	30(2)
C13	42(6)	32(9)	90(8)	9(6)	-12(5)	-5(5)
C23	62(9)	27(8)	90(8)	5(6)	-19(6)	-20(6)
C33	73(10)	58(14)	79(8)	-2(7)	-20(6)	-22(8)
C43	78(10)	38(9)	48(7)	-10(6)	-13(6)	-17(7)
C53	60(8)	27(9)	51(7)	-11(6)	-5(6)	-10(7)
C63	40(6)	16(7)	51(7)	-7(5)	-8(5)	-6(5)
Cl12	127(4)	92(3)	64(2)	41(2)	-19(2)	33(3)
C12	68(5)	22(4)	70(5)	6(4)	-27(4)	-3(3)
C22	70(6)	21(5)	101(6)	1(5)	-23(4)	3(4)
C32	67(6)	37(5)	113(7)	-11(6)	-14(5)	9(4)
C42	43(5)	38(5)	89(6)	-23(4)	-1(4)	-2(5)
C52	52(4)	36(4)	62(4)	-16(3)	-10(3)	-8(3)
C62	38(4)	29(4)	58(4)	-5(3)	-9(3)	-1(3)
Cl11	29(1)	75(2)	118(3)	-32(2)	22(1)	-1(1)
C11	19(3)	28(4)	59(4)	-13(3)	3(3)	-5(2)
C21	23(4)	30(7)	52(5)	-7(5)	8(3)	-5(4)
C31	21(3)	29(4)	37(3)	1(3)	-3(3)	1(3)
C41	27(3)	42(4)	33(3)	-2(3)	0(3)	3(3)
C51	35(4)	48(5)	43(4)	-9(3)	-13(3)	14(4)

C61	25(4)	30(4)	58(4)	-18(3)	-12(3)	5(3)
Ru(1)	12(1)	12(1)	16(1)	0(1)	0(1)	-2(1)
Br(1)	34(1)	39(1)	20(1)	-5(1)	-9(1)	7(1)
Br(2)	29(1)	25(1)	57(1)	5(1)	-18(1)	6(1)
Br(3)	16(1)	31(1)	21(1)	1(1)	3(1)	-5(1)
Cl(1)	18(1)	17(1)	26(1)	1(1)	1(1)	2(1)
P(1)	15(1)	17(1)	17(1)	-2(1)	2(1)	-3(1)
P(2)	14(1)	15(1)	17(1)	0(1)	2(1)	-2(1)
N(1)	16(1)	16(1)	22(1)	-1(1)	0(1)	-4(1)
N(2)	16(1)	15(1)	19(1)	-1(1)	0(1)	-3(1)
N(3)	15(1)	16(1)	20(1)	-1(1)	-1(1)	0(1)
N(4)	16(1)	15(1)	20(1)	-3(1)	-2(1)	0(1)
N(5)	18(1)	14(1)	18(1)	0(1)	-1(1)	-3(1)
N(6)	18(1)	14(1)	20(1)	0(1)	-2(1)	-1(1)
C(1)	15(1)	19(1)	16(1)	4(1)	2(1)	0(1)
C(2)	19(1)	24(1)	21(1)	0(1)	1(1)	0(1)
C(3)	29(1)	29(1)	27(1)	-4(1)	6(1)	6(1)
C(4)	23(1)	43(1)	30(1)	3(1)	6(1)	12(1)
C(5)	15(1)	46(1)	29(1)	3(1)	-1(1)	2(1)
C(6)	19(1)	32(1)	22(1)	0(1)	0(1)	-3(1)
C(7)	18(1)	17(1)	26(1)	2(1)	7(1)	1(1)
C(8)	36(1)	24(1)	33(1)	1(1)	5(1)	-10(1)
C(9)	46(1)	24(1)	47(1)	1(1)	18(1)	-11(1)
C(10)	46(1)	24(1)	46(1)	14(1)	20(1)	4(1)
C(11)	44(1)	44(1)	37(1)	19(1)	1(1)	-1(1)
C(12)	30(1)	30(1)	30(1)	9(1)	1(1)	-6(1)
C(13)	17(1)	21(1)	24(1)	-8(1)	1(1)	-3(1)
C(14)	23(1)	21(1)	31(1)	-5(1)	1(1)	-5(1)
C(15)	26(1)	20(1)	45(1)	-9(1)	-5(1)	-2(1)
C(16)	21(1)	32(1)	43(1)	-18(1)	-1(1)	2(1)
C(17)	23(1)	40(1)	33(1)	-13(1)	6(1)	-1(1)
C(18)	23(1)	29(1)	26(1)	-7(1)	3(1)	-3(1)
C(19)	22(1)	28(1)	17(1)	-1(1)	3(1)	4(1)
C(20)	27(1)	46(1)	20(1)	-3(1)	2(1)	0(1)
C(21)	34(1)	75(2)	21(1)	2(1)	-3(1)	8(1)

C(22)	49(2)	66(2)	24(1)	15(1)	2(1)	20(1)
C(23)	51(2)	41(1)	31(1)	14(1)	8(1)	9(1)
C(24)	32(1)	31(1)	23(1)	4(1)	4(1)	2(1)
C(25)	17(1)	22(1)	20(1)	-4(1)	2(1)	-6(1)
C(26)	16(1)	19(1)	18(1)	0(1)	-1(1)	-2(1)
C(27)	15(1)	25(1)	17(1)	3(1)	1(1)	-3(1)
C(28)	17(1)	21(1)	22(1)	4(1)	-1(1)	-6(1)
C(29)	15(1)	22(1)	21(1)	-7(1)	-2(1)	3(1)
C(30)	18(1)	29(1)	16(1)	-5(1)	-2(1)	5(1)
C(31)	16(1)	23(1)	19(1)	0(1)	1(1)	3(1)
C(32)	26(1)	16(1)	25(1)	2(1)	-4(1)	1(1)
C(33)	22(1)	21(1)	25(1)	3(1)	-5(1)	3(1)
C(34)	18(1)	21(1)	18(1)	0(1)	-1(1)	-1(1)
B(1)	18(1)	16(1)	23(1)	-2(1)	-3(1)	-2(1)

Table A2.25: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Br}Ru(dppm)Cl 213a.

	x	y	z	U(eq)
H23	1381	5381	6762	72
H33	-6	5492	7582	84
H43	-2186	5752	7393	66
H53	-2893	6018	6409	55
H63	-1558	5832	5584	43
H22	-1657	5970	5933	77
H32	-2381	5974	6934	87
H42	-1047	5561	7722	68
H52	1006	5097	7512	60
H62	1703	5066	6511	50
H21	-1093	5871	5657	42
H31	-3013	6071	6181	35
H41	-3020	5956	7243	41
H51	-1182	5582	7770	51

H61	753	5375	7251	45
H(2)	4952	7315	2876	26
H(3)	6667	6629	2513	34
H(4)	8783	6965	2746	38
H(5)	9209	7991	3338	36
H(6)	7497	8665	3723	29
H(8)	6068	9945	3708	37
H(9)	6403	10916	3047	46
H(10)	5408	10935	2093	46
H(11)	4007	10005	1804	50
H(12)	3636	9037	2464	36
H(14)	3120	9998	4414	30
H(15)	1813	10908	4812	37
H(16)	643	10696	5689	39
H(17)	813	9585	6190	38
H(18)	2151	8681	5811	31
H(20)	5566	8611	5678	37
H(21)	6218	7894	6502	52
H(22)	5141	6824	6711	56
H(23)	3418	6447	6091	49
H(24)	2771	7148	5247	34
H(25A)	5904	8619	4564	24
H(25B)	5191	9393	4442	24
H(26)	302	8256	4797	22
H(28)	-804	6238	4320	24
H(29)	769	6156	2408	23
H(31)	1909	8238	2343	23
H(32)	3471	5304	4100	27
H(34)	5559	7120	4363	23
H(1B)	1270(20)	5850(12)	3593(10)	23

Table A2.26: Crystal data and structure refinement for $Tp^{Br}Ru(dppe)Cl$ 213b.

Identification code: $Tp^{Br}Ru(dppe)Cl$ **213b**

Empirical formula: C41 H36 B Br3 Cl2 N6 P2 Ru

Formula weight: 1097.21

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 21.3784(19) Å	α= 90°.
	b = 15.4131(13) Å	β= 105.6960(10)°.
	c = 26.810(2) Å	γ = 90°.
Volume	8504.5(13) $Å^3$	
Z	8	
Density (calculated)	1.714 Mg/m^3	
Absorption coefficient	3.427 mm^{-1}	
F(000)	4336	
Crystal size	0.240 x 0.220 x 0.180 mm^3	
Theta range for data collection	2.658 to 28.424°.	
Index ranges	-28<=h<=28, -20<=k<=20, -35<=l<=35	
Reflections collected	130118	
Independent reflections	21342 [R(int) = 0.0175]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.6278	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21342 / 320 / 1115	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0499	
R indices (all data)	R1 = 0.0292, wR2 = 0.0540	
Largest diff. peak and hole	0.583 and -0.631 $e.Å^{-3}$	

Table A2.27: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppe)Cl 213b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(12)	4888(2)	8899(1)	4971(1)	67(1)
C12	4988(3)	8868(4)	4352(3)	32(2)
C22	4462(3)	8594(6)	3961(2)	26(1)
C32	4529(3)	8512(3)	3466(2)	32(1)
C42	5119(3)	8704(4)	3369(2)	39(1)
C52	5631(3)	9009(6)	3756(3)	51(2)
C62	5567(3)	9094(4)	4256(2)	50(2)
Cl(11)	4472(3)	8778(2)	4834(2)	84(2)
C11	4845(4)	8859(5)	4331(3)	26(2)
C21	4537(4)	8557(8)	3848(3)	36(2)
C31	4851(5)	8593(4)	3463(2)	37(2)
C41	5463(5)	8921(6)	3562(3)	40(2)
C51	5769(3)	9245(5)	4049(4)	45(2)
C61	5463(3)	9210(5)	4440(3)	34(2)
Ru(1)	1421(1)	7055(1)	6835(1)	13(1)
Ru(2)	6423(1)	7124(1)	6904(1)	12(1)
Br(1)	1006(1)	9658(1)	8445(1)	27(1)
Br(2)	2726(2)	9137(2)	5508(1)	38(1)
Br(2B)	2775(2)	9077(2)	5484(1)	26(1)
Br(3)	-1403(2)	6831(1)	5547(1)	30(1)
Br(3B)	-1366(2)	6807(2)	5509(1)	43(1)
Br(4)	6039(1)	9714(1)	8535(1)	25(1)
Br(5)	3603(1)	6722(2)	5649(1)	40(1)
Br(5B)	3591(1)	6733(1)	5685(1)	20(1)
Br(6)	7470(2)	9159(2)	5387(1)	26(1)
Br(6B)	7541(2)	9167(3)	5421(1)	43(1)
Cl(1)	939(1)	6130(1)	7360(1)	19(1)
Cl(2)	6025(1)	6196(1)	7480(1)	18(1)
Cl(4)	4224(1)	6339(1)	9560(1)	43(1)

P(1)	1626(1)	5932(1)	6346(1)	15(1)
P(2)	2419(1)	6744(1)	7379(1)	14(1)
P(3)	7450(1)	6845(1)	7401(1)	13(1)
P(4)	6610(1)	6008(1)	6401(1)	14(1)
N(1)	909(1)	8839(1)	6999(1)	19(1)
N(2)	1205(1)	8131(1)	7268(1)	17(1)
N(3)	1737(1)	7965(1)	6388(1)	16(1)
N(4)	1375(1)	8702(1)	6243(1)	19(1)
N(5)	470(1)	7260(1)	6346(1)	17(1)
N(6)	277(1)	8084(1)	6196(1)	19(1)
N(7)	5893(1)	8893(1)	7083(1)	16(1)
N(8)	6219(1)	8197(1)	7347(1)	15(1)
N(9)	5218(1)	8096(1)	6312(1)	17(1)
N(10)	5445(1)	7283(1)	6459(1)	16(1)
N(11)	6275(1)	8754(1)	6282(1)	17(1)
N(12)	6668(1)	8044(1)	6423(1)	15(1)
C(1)	1074(1)	4998(1)	6171(1)	18(1)
C(2)	968(1)	4466(1)	6561(1)	22(1)
C(3)	563(1)	3746(1)	6441(1)	27(1)
C(4)	255(1)	3552(1)	5927(1)	30(1)
C(5)	357(1)	4071(1)	5537(1)	33(1)
C(6)	763(1)	4791(1)	5655(1)	27(1)
C(7)	1707(1)	6216(1)	5703(1)	20(1)
C(8)	2149(1)	5802(1)	5483(1)	26(1)
C(9)	2176(1)	6020(2)	4984(1)	34(1)
C(10)	1766(1)	6650(2)	4703(1)	35(1)
C(11)	1320(1)	7058(1)	4914(1)	30(1)
C(12)	1289(1)	6838(1)	5412(1)	24(1)
C(13)	2558(1)	6859(1)	8083(1)	17(1)
C(14)	2863(1)	7603(1)	8339(1)	23(1)
C(15)	2928(1)	7731(1)	8864(1)	28(1)
C(16)	2695(1)	7115(1)	9144(1)	28(1)
C(17)	2402(1)	6371(1)	8900(1)	29(1)
C(18)	2329(1)	6243(1)	8372(1)	24(1)
C(19)	3139(1)	7295(1)	7289(1)	18(1)

C(20)	3715(1)	6855(1)	7297(1)	25(1)
C(21)	4261(1)	7309(2)	7251(1)	36(1)
C(22)	4235(1)	8205(2)	7194(1)	39(1)
C(23)	3666(1)	8651(1)	7177(1)	31(1)
C(24)	3122(1)	8200(1)	7227(1)	23(1)
C(25)	2549(1)	5583(1)	7276(1)	19(1)
C(26)	2414(1)	5426(1)	6690(1)	20(1)
C(27)	-30(1)	6734(1)	6146(1)	20(1)
C(28)	-552(1)	7229(1)	5861(1)	24(1)
C(29)	-346(1)	8079(1)	5901(1)	23(1)
C(30)	1645(1)	9197(1)	5939(1)	23(1)
C(31)	2189(1)	8766(1)	5886(1)	21(1)
C(32)	2231(1)	8005(1)	6172(1)	18(1)
C(33)	786(1)	9434(1)	7330(1)	20(1)
C(34)	1011(1)	9104(1)	7822(1)	20(1)
C(35)	1266(1)	8283(1)	7768(1)	19(1)
C(36)	7648(1)	6963(1)	8109(1)	16(1)
C(37)	7921(1)	7735(1)	8346(1)	20(1)
C(38)	8039(1)	7852(1)	8879(1)	24(1)
C(39)	7889(1)	7202(1)	9183(1)	27(1)
C(40)	7622(1)	6432(1)	8954(1)	30(1)
C(41)	7500(1)	6309(1)	8422(1)	25(1)
C(42)	8127(1)	7424(1)	7252(1)	17(1)
C(43)	8684(1)	7004(1)	7190(1)	25(1)
C(44)	9186(1)	7483(2)	7080(1)	36(1)
C(45)	9134(1)	8373(2)	7026(1)	37(1)
C(46)	8583(1)	8799(1)	7078(1)	29(1)
C(47)	8082(1)	8328(1)	7192(1)	20(1)
C(48)	6640(1)	6296(1)	5745(1)	19(1)
C(49)	7088(1)	5946(1)	5509(1)	25(1)
C(50)	7067(1)	6165(2)	4999(1)	32(1)
C(51)	6599(1)	6734(1)	4723(1)	33(1)
C(52)	6149(1)	7085(1)	4953(1)	28(1)
C(53)	6167(1)	6866(1)	5459(1)	22(1)
C(54)	6064(1)	5067(1)	6251(1)	17(1)

C(55)	5725(1)	4844(1)	5745(1)	26(1)
C(56)	5313(1)	4126(1)	5651(1)	30(1)
C(57)	5236(1)	3623(1)	6056(1)	26(1)
C(58)	5575(1)	3830(1)	6560(1)	24(1)
C(59)	5981(1)	4550(1)	6657(1)	21(1)
C(60)	4960(1)	6728(1)	6272(1)	19(1)
C(61)	4413(1)	7191(1)	5999(1)	21(1)
C(62)	4591(1)	8054(1)	6033(1)	20(1)
C(63)	5775(1)	9483(1)	7419(1)	18(1)
C(64)	6036(1)	9159(1)	7911(1)	18(1)
C(65)	6305(1)	8352(1)	7850(1)	18(1)
C(66)	7123(1)	8093(1)	6165(1)	17(1)
C(67)	7019(1)	8833(1)	5858(1)	21(1)
C(68)	6482(1)	9240(1)	5938(1)	22(1)
C(69)	7416(1)	5519(1)	6712(1)	19(1)
C(70)	7596(1)	5690(1)	7298(1)	18(1)
C(77)	4863(1)	6140(1)	9285(1)	26(1)
C(78)	5421(1)	5763(2)	9582(1)	38(1)
C(79)	5918(1)	5608(2)	9353(1)	60(1)
C(80)	5849(2)	5839(2)	8840(1)	66(1)
C(81)	5285(2)	6215(2)	8555(1)	53(1)
C(82)	4782(1)	6369(1)	8772(1)	36(1)
B(1)	743(1)	8851(1)	6402(1)	20(1)
B(2)	5671(1)	8886(1)	6484(1)	18(1)

Table A2.28: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(dppe)Cl 213b.

Cl12-C12	1.728(7)	C42-C52	1.373(7)
C12-C62	1.376(7)	C42-H42	0.9500
C12-C22	1.380(7)	C52-C62	1.388(7)
C22-C32	1.379(5)	C52-H52	0.9500
C22-H22	0.9500	C62-H62	0.9500
C32-C42	1.386(6)	Cl11-C11	1.748(9)
C32-H32	0.9500	C11-C21	1.368(9)

C11-C61	1.384(9)	P(1)-C(26)	1.8590(17)
C21-C31	1.377(9)	P(2)-C(19)	1.8310(17)
C21-H21	0.9500	P(2)-C(13)	1.8369(17)
C31-C41	1.359(9)	P(2)-C(25)	1.8441(17)
C31-H31	0.9500	P(3)-C(42)	1.8343(17)
C41-C51	1.385(8)	P(3)-C(36)	1.8398(17)
C41-H41	0.9500	P(3)-C(70)	1.8414(17)
C51-C61	1.380(7)	P(4)-C(48)	1.8301(17)
C51-H51	0.9500	P(4)-C(54)	1.8372(17)
C61-H61	0.9500	P(4)-C(69)	1.8587(17)
Ru(1)-N(3)	2.0746(14)	N(1)-C(33)	1.350(2)
Ru(1)-N(5)	2.1245(14)	N(1)-N(2)	1.3663(19)
Ru(1)-N(2)	2.1441(14)	N(1)-B(1)	1.544(2)
Ru(1)-P(2)	2.2841(4)	N(2)-C(35)	1.332(2)
Ru(1)-P(1)	2.2852(4)	N(3)-C(32)	1.336(2)
Ru(1)-Cl(1)	2.4197(4)	N(3)-N(4)	1.3704(19)
Ru(2)-N(12)	2.0786(13)	N(4)-C(30)	1.354(2)
Ru(2)-N(10)	2.1228(14)	N(4)-B(1)	1.541(2)
Ru(2)-N(8)	2.1476(13)	N(5)-C(27)	1.333(2)
Ru(2)-P(3)	2.2784(4)	N(5)-N(6)	1.3622(19)
Ru(2)-P(4)	2.2881(4)	N(6)-C(29)	1.351(2)
Ru(2)-Cl(2)	2.4209(4)	N(6)-B(1)	1.549(2)
Br(1)-C(34)	1.8790(17)	N(7)-C(63)	1.351(2)
Br(2)-C(31)	1.817(4)	N(7)-N(8)	1.3667(18)
Br(2B)-C(31)	1.921(4)	N(7)-B(2)	1.546(2)
Br(3)-C(28)	1.890(3)	N(8)-C(65)	1.334(2)
Br(3B)-C(28)	1.860(3)	N(9)-C(62)	1.349(2)
Br(4)-C(64)	1.8785(16)	N(9)-N(10)	1.3622(18)
Br(5)-C(61)	1.877(3)	N(9)-B(2)	1.547(2)
Br(5B)-C(61)	1.870(3)	N(10)-C(60)	1.333(2)
Br(6)-C(67)	1.852(4)	N(11)-C(68)	1.354(2)
Br(6B)-C(67)	1.893(4)	N(11)-N(12)	1.3685(18)
Cl(4)-C(77)	1.745(2)	N(11)-B(2)	1.541(2)
P(1)-C(7)	1.8328(18)	N(12)-C(66)	1.339(2)
P(1)-C(1)	1.8401(17)	C(1)-C(2)	1.395(2)

C(1)-C(6)	1.400(2)	C(20)-H(20)	0.9500
C(2)-C(3)	1.390(2)	C(21)-C(22)	1.388(4)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-C(4)	1.388(3)	C(22)-C(23)	1.388(3)
C(3)-H(3)	0.9500	C(22)-H(22)	0.9500
C(4)-C(5)	1.381(3)	C(23)-C(24)	1.392(2)
C(4)-H(4)	0.9500	C(23)-H(23)	0.9500
C(5)-C(6)	1.391(3)	C(24)-H(24)	0.9500
C(5)-H(5)	0.9500	C(25)-C(26)	1.536(2)
C(6)-H(6)	0.9500	C(25)-H(25A)	0.9900
C(7)-C(8)	1.395(3)	C(25)-H(25B)	0.9900
C(7)-C(12)	1.396(3)	C(26)-H(26A)	0.9900
C(8)-C(9)	1.398(3)	C(26)-H(26B)	0.9900
C(8)-H(8)	0.9500	C(27)-C(28)	1.397(2)
C(9)-C(10)	1.386(3)	C(27)-H(27)	0.9500
C(9)-H(9)	0.9500	C(28)-C(29)	1.377(3)
C(10)-C(11)	1.385(3)	C(29)-H(29)	0.9500
C(10)-H(10)	0.9500	C(30)-C(31)	1.378(3)
C(11)-C(12)	1.395(3)	C(30)-H(30)	0.9500
C(11)-H(11)	0.9500	C(31)-C(32)	1.391(2)
C(12)-H(12)	0.9500	C(32)-H(32)	0.9500
C(13)-C(18)	1.397(2)	C(33)-C(34)	1.374(3)
C(13)-C(14)	1.403(2)	C(33)-H(33)	0.9500
C(14)-C(15)	1.391(3)	C(34)-C(35)	1.400(2)
C(14)-H(14)	0.9500	C(35)-H(35)	0.9500
C(15)-C(16)	1.385(3)	C(36)-C(37)	1.399(2)
C(15)-H(15)	0.9500	C(36)-C(41)	1.401(2)
C(16)-C(17)	1.383(3)	C(37)-C(38)	1.393(2)
C(16)-H(16)	0.9500	C(37)-H(37)	0.9500
C(17)-C(18)	1.394(3)	C(38)-C(39)	1.383(3)
C(17)-H(17)	0.9500	C(38)-H(38)	0.9500
C(18)-H(18)	0.9500	C(39)-C(40)	1.387(3)
C(19)-C(20)	1.400(2)	C(39)-H(39)	0.9500
C(19)-C(24)	1.403(2)	C(40)-C(41)	1.392(3)
C(20)-C(21)	1.395(3)	C(40)-H(40)	0.9500

C(41)-H(41)	0.9500	C(60)-H(60)	0.9500
C(42)-C(47)	1.403(2)	C(61)-C(62)	1.379(2)
C(42)-C(43)	1.403(2)	C(62)-H(62)	0.9500
C(43)-C(44)	1.398(3)	C(63)-C(64)	1.379(2)
C(43)-H(43)	0.9500	C(63)-H(63)	0.9500
C(44)-C(45)	1.380(3)	C(64)-C(65)	1.399(2)
C(44)-H(44)	0.9500	C(65)-H(65)	0.9500
C(45)-C(46)	1.388(3)	C(66)-C(67)	1.390(2)
C(45)-H(45)	0.9500	C(66)-H(66)	0.9500
C(46)-C(47)	1.394(2)	C(67)-C(68)	1.375(3)
C(46)-H(46)	0.9500	C(68)-H(68)	0.9500
C(47)-H(47)	0.9500	C(69)-C(70)	1.536(2)
C(48)-C(49)	1.392(2)	C(69)-H(69A)	0.9900
C(48)-C(53)	1.401(2)	C(69)-H(69B)	0.9900
C(49)-C(50)	1.399(3)	C(70)-H(70A)	0.9900
C(49)-H(49)	0.9500	C(70)-H(70B)	0.9900
C(50)-C(51)	1.385(3)	C(77)-C(78)	1.372(3)
C(50)-H(50)	0.9500	C(77)-C(82)	1.386(3)
C(51)-C(52)	1.387(3)	C(78)-C(79)	1.384(4)
C(51)-H(51)	0.9500	C(78)-H(78)	0.9500
C(52)-C(53)	1.387(2)	C(79)-C(80)	1.390(5)
C(52)-H(52)	0.9500	C(79)-H(79)	0.9500
C(53)-H(53)	0.9500	C(80)-C(81)	1.369(5)
C(54)-C(59)	1.396(2)	C(80)-H(80)	0.9500
C(54)-C(55)	1.399(2)	C(81)-C(82)	1.375(4)
C(55)-C(56)	1.395(3)	C(81)-H(81)	0.9500
C(55)-H(55)	0.9500	C(82)-H(82)	0.9500
C(56)-C(57)	1.381(3)	B(1)-H(101)	1.10(2)
C(56)-H(56)	0.9500	B(2)-H(102)	1.13(2)
C(57)-C(58)	1.386(3)		
C(57)-H(57)	0.9500	C62-C12-C22	121.6(6)
C(58)-C(59)	1.390(2)	C62-C12-Cl12	121.6(5)
C(58)-H(58)	0.9500	C22-C12-Cl12	116.8(5)
C(59)-H(59)	0.9500	C32-C22-C12	119.0(5)
C(60)-C(61)	1.396(2)	C32-C22-H22	120.5

C12-C22-H22	120.5	N(5)-Ru(1)-P(2)	175.98(4)
C22-C32-C42	119.8(5)	N(2)-Ru(1)-P(2)	96.74(4)
C22-C32-H32	120.1	N(3)-Ru(1)-P(1)	92.14(4)
C42-C32-H32	120.1	N(5)-Ru(1)-P(1)	93.36(4)
C52-C42-C32	120.8(5)	N(2)-Ru(1)-P(1)	177.79(4)
C52-C42-H42	119.6	P(2)-Ru(1)-P(1)	85.229(15)
C32-C42-H42	119.6	N(3)-Ru(1)-Cl(1)	172.34(4)
C42-C52-C62	119.7(5)	N(5)-Ru(1)-Cl(1)	87.69(4)
C42-C52-H52	120.2	N(2)-Ru(1)-Cl(1)	87.32(4)
C62-C52-H52	120.2	P(2)-Ru(1)-Cl(1)	88.651(16)
C12-C62-C52	119.1(5)	P(1)-Ru(1)-Cl(1)	93.747(16)
C12-C62-H62	120.5	N(12)-Ru(2)-N(10)	86.94(5)
C52-C62-H62	120.5	N(12)-Ru(2)-N(8)	86.55(5)
C21-C11-C61	121.4(7)	N(10)-Ru(2)-N(8)	84.53(5)
C21-C11-Cl11	120.3(7)	N(12)-Ru(2)-P(3)	97.28(4)
C61-C11-Cl11	118.3(6)	N(10)-Ru(2)-P(3)	175.41(4)
C11-C21-C31	119.3(7)	N(8)-Ru(2)-P(3)	97.50(4)
C11-C21-H21	120.4	N(12)-Ru(2)-P(4)	91.88(4)
C31-C21-H21	120.4	N(10)-Ru(2)-P(4)	93.32(4)
C41-C31-C21	120.4(6)	N(8)-Ru(2)-P(4)	177.40(4)
C41-C31-H31	119.8	P(3)-Ru(2)-P(4)	84.750(15)
C21-C31-H31	119.8	N(12)-Ru(2)-Cl(2)	171.99(4)
C31-C41-C51	120.3(6)	N(10)-Ru(2)-Cl(2)	87.98(4)
C31-C41-H41	119.9	N(8)-Ru(2)-Cl(2)	86.82(4)
C51-C41-H41	119.9	P(3)-Ru(2)-Cl(2)	88.023(16)
C61-C51-C41	120.1(6)	P(4)-Ru(2)-Cl(2)	94.579(16)
C61-C51-H51	119.9	C(7)-P(1)-C(1)	99.46(8)
C41-C51-H51	119.9	C(7)-P(1)-C(26)	105.30(8)
C51-C61-C11	118.4(6)	C(1)-P(1)-C(26)	103.37(8)
C51-C61-H61	120.8	C(7)-P(1)-Ru(1)	116.17(6)
C11-C61-H61	120.8	C(1)-P(1)-Ru(1)	121.98(6)
N(3)-Ru(1)-N(5)	87.08(5)	C(26)-P(1)-Ru(1)	108.75(5)
N(3)-Ru(1)-N(2)	86.64(5)	C(19)-P(2)-C(13)	100.52(7)
N(5)-Ru(1)-N(2)	84.74(5)	C(19)-P(2)-C(25)	105.24(8)
N(3)-Ru(1)-P(2)	96.73(4)	C(13)-P(2)-C(25)	104.99(8)

C(19)-P(2)-Ru(1)	119.43(6)	N(8)-N(7)-B(2)	120.16(13)
C(13)-P(2)-Ru(1)	119.98(5)	C(65)-N(8)-N(7)	107.17(13)
C(25)-P(2)-Ru(1)	105.12(5)	C(65)-N(8)-Ru(2)	134.70(11)
C(42)-P(3)-C(36)	101.66(7)	N(7)-N(8)-Ru(2)	118.02(10)
C(42)-P(3)-C(70)	105.10(8)	C(62)-N(9)-N(10)	109.86(14)
C(36)-P(3)-C(70)	104.43(8)	C(62)-N(9)-B(2)	130.68(14)
C(42)-P(3)-Ru(2)	118.26(5)	N(10)-N(9)-B(2)	119.44(13)
C(36)-P(3)-Ru(2)	120.07(5)	C(60)-N(10)-N(9)	107.51(13)
C(70)-P(3)-Ru(2)	105.72(5)	C(60)-N(10)-Ru(2)	133.19(11)
C(48)-P(4)-C(54)	99.62(8)	N(9)-N(10)-Ru(2)	119.30(10)
C(48)-P(4)-C(69)	105.13(8)	C(68)-N(11)-N(12)	109.87(14)
C(54)-P(4)-C(69)	103.59(7)	C(68)-N(11)-B(2)	128.78(14)
C(48)-P(4)-Ru(2)	116.21(6)	N(12)-N(11)-B(2)	121.24(13)
C(54)-P(4)-Ru(2)	121.29(6)	C(66)-N(12)-N(11)	106.93(13)
C(69)-P(4)-Ru(2)	109.20(5)	C(66)-N(12)-Ru(2)	134.32(11)
C(33)-N(1)-N(2)	109.96(14)	N(11)-N(12)-Ru(2)	118.54(10)
C(33)-N(1)-B(1)	129.95(14)	C(2)-C(1)-C(6)	118.47(16)
N(2)-N(1)-B(1)	120.04(13)	C(2)-C(1)-P(1)	119.47(13)
C(35)-N(2)-N(1)	107.14(13)	C(6)-C(1)-P(1)	122.05(13)
C(35)-N(2)-Ru(1)	134.78(11)	C(3)-C(2)-C(1)	120.75(17)
N(1)-N(2)-Ru(1)	118.01(10)	C(3)-C(2)-H(2)	119.6
C(32)-N(3)-N(4)	106.93(13)	C(1)-C(2)-H(2)	119.6
C(32)-N(3)-Ru(1)	134.48(11)	C(4)-C(3)-C(2)	120.15(18)
N(4)-N(3)-Ru(1)	118.53(11)	C(4)-C(3)-H(3)	119.9
C(30)-N(4)-N(3)	109.70(14)	C(2)-C(3)-H(3)	119.9
C(30)-N(4)-B(1)	129.20(14)	C(5)-C(4)-C(3)	119.71(17)
N(3)-N(4)-B(1)	121.02(13)	C(5)-C(4)-H(4)	120.1
C(27)-N(5)-N(6)	107.59(13)	C(3)-C(4)-H(4)	120.1
C(27)-N(5)-Ru(1)	133.37(11)	C(4)-C(5)-C(6)	120.43(18)
N(6)-N(5)-Ru(1)	119.01(10)	C(4)-C(5)-H(5)	119.8
C(29)-N(6)-N(5)	109.87(14)	C(6)-C(5)-H(5)	119.8
C(29)-N(6)-B(1)	130.53(15)	C(5)-C(6)-C(1)	120.48(18)
N(5)-N(6)-B(1)	119.42(13)	C(5)-C(6)-H(6)	119.8
C(63)-N(7)-N(8)	110.09(13)	C(1)-C(6)-H(6)	119.8
C(63)-N(7)-B(2)	129.56(14)	C(8)-C(7)-C(12)	118.86(17)

C(8)-C(7)-P(1)	122.33(14)	C(20)-C(19)-C(24)	118.50(16)
C(12)-C(7)-P(1)	118.73(14)	C(20)-C(19)-P(2)	122.70(14)
C(7)-C(8)-C(9)	120.23(19)	C(24)-C(19)-P(2)	118.76(13)
C(7)-C(8)-H(8)	119.9	C(21)-C(20)-C(19)	120.57(19)
C(9)-C(8)-H(8)	119.9	C(21)-C(20)-H(20)	119.7
C(10)-C(9)-C(8)	120.28(19)	C(19)-C(20)-H(20)	119.7
C(10)-C(9)-H(9)	119.9	C(22)-C(21)-C(20)	120.0(2)
C(8)-C(9)-H(9)	119.9	C(22)-C(21)-H(21)	120.0
C(11)-C(10)-C(9)	120.01(18)	C(20)-C(21)-H(21)	120.0
C(11)-C(10)-H(10)	120.0	C(21)-C(22)-C(23)	120.30(19)
C(9)-C(10)-H(10)	120.0	C(21)-C(22)-H(22)	119.9
C(10)-C(11)-C(12)	119.9(2)	C(23)-C(22)-H(22)	119.9
C(10)-C(11)-H(11)	120.1	C(22)-C(23)-C(24)	119.8(2)
C(12)-C(11)-H(11)	120.1	C(22)-C(23)-H(23)	120.1
C(11)-C(12)-C(7)	120.74(19)	C(24)-C(23)-H(23)	120.1
C(11)-C(12)-H(12)	119.6	C(23)-C(24)-C(19)	120.83(18)
C(7)-C(12)-H(12)	119.6	C(23)-C(24)-H(24)	119.6
C(18)-C(13)-C(14)	118.00(16)	C(19)-C(24)-H(24)	119.6
C(18)-C(13)-P(2)	121.45(13)	C(26)-C(25)-P(2)	108.22(11)
C(14)-C(13)-P(2)	120.40(13)	C(26)-C(25)-H(25A)	110.1
C(15)-C(14)-C(13)	121.19(17)	P(2)-C(25)-H(25A)	110.1
C(15)-C(14)-H(14)	119.4	C(26)-C(25)-H(25B)	110.1
C(13)-C(14)-H(14)	119.4	P(2)-C(25)-H(25B)	110.1
C(16)-C(15)-C(14)	119.95(18)	H(25A)-C(25)-H(25B)	108.4
C(16)-C(15)-H(15)	120.0	C(25)-C(26)-P(1)	109.62(11)
C(14)-C(15)-H(15)	120.0	C(25)-C(26)-H(26A)	109.7
C(17)-C(16)-C(15)	119.70(17)	P(1)-C(26)-H(26A)	109.7
C(17)-C(16)-H(16)	120.2	C(25)-C(26)-H(26B)	109.7
C(15)-C(16)-H(16)	120.2	P(1)-C(26)-H(26B)	109.7
C(16)-C(17)-C(18)	120.62(18)	H(26A)-C(26)-H(26B)	108.2
C(16)-C(17)-H(17)	119.7	N(5)-C(27)-C(28)	108.79(15)
C(18)-C(17)-H(17)	119.7	N(5)-C(27)-H(27)	125.6
C(17)-C(18)-C(13)	120.53(17)	C(28)-C(27)-H(27)	125.6
C(17)-C(18)-H(18)	119.7	C(29)-C(28)-C(27)	106.64(15)
C(13)-C(18)-H(18)	119.7	C(29)-C(28)-Br(3B)	127.48(16)

C(27)-C(28)-Br(3B)	125.87(16)	C(39)-C(38)-H(38)	119.8
C(29)-C(28)-Br(3)	126.37(15)	C(37)-C(38)-H(38)	119.8
C(27)-C(28)-Br(3)	126.67(15)	C(38)-C(39)-C(40)	119.40(17)
Br(3B)-C(28)-Br(3)	4.5(2)	C(38)-C(39)-H(39)	120.3
N(6)-C(29)-C(28)	107.11(15)	C(40)-C(39)-H(39)	120.3
N(6)-C(29)-H(29)	126.4	C(39)-C(40)-C(41)	120.80(18)
C(28)-C(29)-H(29)	126.4	C(39)-C(40)-H(40)	119.6
N(4)-C(30)-C(31)	107.42(15)	C(41)-C(40)-H(40)	119.6
N(4)-C(30)-H(30)	126.3	C(40)-C(41)-C(36)	120.29(17)
C(31)-C(30)-H(30)	126.3	C(40)-C(41)-H(41)	119.9
C(30)-C(31)-C(32)	106.35(15)	C(36)-C(41)-H(41)	119.9
C(30)-C(31)-Br(2)	125.65(18)	C(47)-C(42)-C(43)	118.52(16)
C(32)-C(31)-Br(2)	127.99(19)	C(47)-C(42)-P(3)	118.33(13)
C(30)-C(31)-Br(2B)	129.28(17)	C(43)-C(42)-P(3)	123.14(14)
C(32)-C(31)-Br(2B)	124.31(17)	C(44)-C(43)-C(42)	120.36(19)
Br(2)-C(31)-Br(2B)	4.0(2)	C(44)-C(43)-H(43)	119.8
N(3)-C(32)-C(31)	109.60(15)	C(42)-C(43)-H(43)	119.8
N(3)-C(32)-H(32)	125.2	C(45)-C(44)-C(43)	120.2(2)
C(31)-C(32)-H(32)	125.2	C(45)-C(44)-H(44)	119.9
N(1)-C(33)-C(34)	107.38(15)	C(43)-C(44)-H(44)	119.9
N(1)-C(33)-H(33)	126.3	C(44)-C(45)-C(46)	120.40(19)
C(34)-C(33)-H(33)	126.3	C(44)-C(45)-H(45)	119.8
C(33)-C(34)-C(35)	106.28(15)	C(46)-C(45)-H(45)	119.8
C(33)-C(34)-Br(1)	126.89(13)	C(45)-C(46)-C(47)	119.83(19)
C(35)-C(34)-Br(1)	126.79(14)	C(45)-C(46)-H(46)	120.1
N(2)-C(35)-C(34)	109.23(15)	C(47)-C(46)-H(46)	120.1
N(2)-C(35)-H(35)	125.4	C(46)-C(47)-C(42)	120.70(18)
C(34)-C(35)-H(35)	125.4	C(46)-C(47)-H(47)	119.7
C(37)-C(36)-C(41)	118.36(15)	C(42)-C(47)-H(47)	119.7
C(37)-C(36)-P(3)	120.23(13)	C(49)-C(48)-C(53)	118.54(16)
C(41)-C(36)-P(3)	121.32(13)	C(49)-C(48)-P(4)	123.32(14)
C(38)-C(37)-C(36)	120.81(16)	C(53)-C(48)-P(4)	118.07(13)
C(38)-C(37)-H(37)	119.6	C(48)-C(49)-C(50)	120.50(18)
C(36)-C(37)-H(37)	119.6	C(48)-C(49)-H(49)	119.8
C(39)-C(38)-C(37)	120.34(17)	C(50)-C(49)-H(49)	119.8

C(51)-C(50)-C(49)	120.15(19)	C(60)-C(61)-Br(5B)	126.54(15)
C(51)-C(50)-H(50)	119.9	C(62)-C(61)-Br(5)	127.18(15)
C(49)-C(50)-H(50)	119.9	C(60)-C(61)-Br(5)	126.43(16)
C(50)-C(51)-C(52)	119.87(18)	Br(5B)-C(61)-Br(5)	3.31(17)
C(50)-C(51)-H(51)	120.1	N(9)-C(62)-C(61)	107.27(15)
C(52)-C(51)-H(51)	120.1	N(9)-C(62)-H(62)	126.4
C(51)-C(52)-C(53)	120.11(19)	C(61)-C(62)-H(62)	126.4
C(51)-C(52)-H(52)	119.9	N(7)-C(63)-C(64)	107.16(14)
C(53)-C(52)-H(52)	119.9	N(7)-C(63)-H(63)	126.4
C(52)-C(53)-C(48)	120.83(18)	C(64)-C(63)-H(63)	126.4
C(52)-C(53)-H(53)	119.6	C(63)-C(64)-C(65)	106.37(15)
C(48)-C(53)-H(53)	119.6	C(63)-C(64)-Br(4)	126.25(13)
C(59)-C(54)-C(55)	118.32(16)	C(65)-C(64)-Br(4)	127.36(13)
C(59)-C(54)-P(4)	119.17(13)	N(8)-C(65)-C(64)	109.20(15)
C(55)-C(54)-P(4)	122.51(13)	N(8)-C(65)-H(65)	125.4
C(56)-C(55)-C(54)	120.40(17)	C(64)-C(65)-H(65)	125.4
C(56)-C(55)-H(55)	119.8	N(12)-C(66)-C(67)	109.27(15)
C(54)-C(55)-H(55)	119.8	N(12)-C(66)-H(66)	125.4
C(57)-C(56)-C(55)	120.48(17)	C(67)-C(66)-H(66)	125.4
C(57)-C(56)-H(56)	119.8	C(68)-C(67)-C(66)	106.75(15)
C(55)-C(56)-H(56)	119.8	C(68)-C(67)-Br(6)	126.32(17)
C(56)-C(57)-C(58)	119.73(17)	C(66)-C(67)-Br(6)	126.74(18)
C(56)-C(57)-H(57)	120.1	C(68)-C(67)-Br(6B)	128.94(18)
C(58)-C(57)-H(57)	120.1	C(66)-C(67)-Br(6B)	124.32(18)
C(57)-C(58)-C(59)	120.09(17)	Br(6)-C(67)-Br(6B)	4.61(17)
C(57)-C(58)-H(58)	120.0	N(11)-C(68)-C(67)	107.18(15)
C(59)-C(58)-H(58)	120.0	N(11)-C(68)-H(68)	126.4
C(58)-C(59)-C(54)	120.97(16)	C(67)-C(68)-H(68)	126.4
C(58)-C(59)-H(59)	119.5	C(70)-C(69)-P(4)	109.57(11)
C(54)-C(59)-H(59)	119.5	C(70)-C(69)-H(69A)	109.8
N(10)-C(60)-C(61)	108.97(15)	P(4)-C(69)-H(69A)	109.8
N(10)-C(60)-H(60)	125.5	C(70)-C(69)-H(69B)	109.8
C(61)-C(60)-H(60)	125.5	P(4)-C(69)-H(69B)	109.8
C(62)-C(61)-C(60)	106.39(15)	H(69A)-C(69)-H(69B)	108.2
C(62)-C(61)-Br(5B)	126.98(14)	C(69)-C(70)-P(3)	108.30(11)

C(69)-C(70)-H(70A)	110.0	C(82)-C(81)-H(81)	119.7
P(3)-C(70)-H(70A)	110.0	C(81)-C(82)-C(77)	118.4(2)
C(69)-C(70)-H(70B)	110.0	C(81)-C(82)-H(82)	120.8
P(3)-C(70)-H(70B)	110.0	C(77)-C(82)-H(82)	120.8
H(70A)-C(70)-H(70B)	108.4	N(4)-B(1)-N(1)	108.22(14)
C(78)-C(77)-C(82)	122.6(2)	N(4)-B(1)-N(6)	108.40(14)
C(78)-C(77)-Cl(4)	119.22(17)	N(1)-B(1)-N(6)	107.85(14)
C(82)-C(77)-Cl(4)	118.21(17)	N(4)-B(1)-H(101)	111.8(11)
C(77)-C(78)-C(79)	118.0(2)	N(1)-B(1)-H(101)	110.6(11)
C(77)-C(78)-H(78)	121.0	N(6)-B(1)-H(101)	109.9(11)
C(79)-C(78)-H(78)	121.0	N(11)-B(2)-N(7)	108.31(14)
C(78)-C(79)-C(80)	120.3(3)	N(11)-B(2)-N(9)	107.95(13)
C(78)-C(79)-H(79)	119.8	N(7)-B(2)-N(9)	107.83(13)
C(80)-C(79)-H(79)	119.8	N(11)-B(2)-H(102)	112.2(10)
C(81)-C(80)-C(79)	120.2(2)	N(7)-B(2)-H(102)	110.5(10)
C(81)-C(80)-H(80)	119.9	N(9)-B(2)-H(102)	110.0(11)
C(79)-C(80)-H(80)	119.9		
C(80)-C(81)-C(82)	120.5(3)		
C(80)-C(81)-H(81)	119.7		

Symmetry transformations used to generate equivalent atoms:

Table A2.29: Anisotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppe)Cl 213b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl12	107(2)	72(1)	23(1)	-2(1)	19(1)	8(1)
C12	35(3)	35(3)	25(2)	3(2)	6(2)	3(2)
C22	35(2)	20(2)	28(2)	4(2)	16(2)	1(2)
C32	47(3)	21(2)	29(2)	4(1)	15(2)	2(2)
C42	41(3)	40(3)	45(3)	19(2)	29(2)	17(2)
C52	28(3)	71(5)	56(4)	26(4)	13(3)	13(2)
C62	27(2)	67(4)	50(4)	22(3)	2(2)	5(2)

Cl11	121(3)	73(2)	88(2)	38(1)	77(3)	22(2)
C11	29(3)	21(3)	28(3)	14(2)	7(2)	10(2)
C21	43(4)	25(3)	32(4)	4(3)	-3(3)	-4(3)
C31	54(5)	24(3)	30(3)	0(2)	6(3)	5(4)
C41	53(5)	35(3)	41(4)	-2(3)	28(4)	4(4)
C51	33(3)	49(4)	58(4)	-1(3)	21(3)	12(3)
C61	32(3)	36(3)	30(3)	1(2)	1(2)	6(2)
Ru(1)	12(1)	11(1)	14(1)	1(1)	2(1)	0(1)
Ru(2)	12(1)	10(1)	13(1)	1(1)	2(1)	0(1)
Br(1)	28(1)	27(1)	29(1)	-10(1)	14(1)	-3(1)
Br(2)	59(1)	25(1)	46(1)	8(1)	39(1)	1(1)
Br(2B)	34(1)	23(1)	25(1)	7(1)	18(1)	2(1)
Br(3)	16(1)	27(1)	39(1)	4(1)	-5(1)	-2(1)
Br(3B)	20(1)	60(1)	39(1)	10(1)	-11(1)	-11(1)
Br(4)	27(1)	26(1)	23(1)	-6(1)	11(1)	0(1)
Br(5)	24(1)	44(1)	42(1)	3(1)	-9(1)	-8(1)
Br(5B)	11(1)	20(1)	26(1)	1(1)	-1(1)	-2(1)
Br(6)	38(1)	25(1)	19(1)	3(1)	17(1)	-7(1)
Br(6B)	69(2)	25(1)	49(1)	7(1)	42(1)	-2(1)
Cl(1)	19(1)	18(1)	20(1)	2(1)	7(1)	-1(1)
Cl(2)	21(1)	15(1)	20(1)	4(1)	8(1)	0(1)
Cl(4)	39(1)	42(1)	51(1)	-8(1)	20(1)	2(1)
P(1)	15(1)	13(1)	16(1)	-1(1)	2(1)	0(1)
P(2)	13(1)	13(1)	15(1)	0(1)	2(1)	0(1)
P(3)	13(1)	13(1)	13(1)	0(1)	2(1)	0(1)
P(4)	14(1)	13(1)	14(1)	-1(1)	2(1)	0(1)
N(1)	17(1)	14(1)	24(1)	0(1)	3(1)	2(1)
N(2)	16(1)	14(1)	20(1)	0(1)	3(1)	2(1)
N(3)	17(1)	13(1)	17(1)	2(1)	2(1)	0(1)
N(4)	22(1)	14(1)	20(1)	4(1)	2(1)	2(1)
N(5)	16(1)	15(1)	17(1)	1(1)	2(1)	2(1)
N(6)	16(1)	17(1)	21(1)	2(1)	0(1)	3(1)
N(7)	17(1)	13(1)	20(1)	1(1)	4(1)	2(1)
N(8)	16(1)	13(1)	17(1)	2(1)	4(1)	2(1)
N(9)	16(1)	15(1)	18(1)	2(1)	2(1)	2(1)

N(10)	16(1)	14(1)	18(1)	2(1)	4(1)	1(1)
N(11)	21(1)	13(1)	16(1)	2(1)	3(1)	1(1)
N(12)	17(1)	12(1)	14(1)	2(1)	2(1)	-1(1)
C(1)	16(1)	13(1)	23(1)	-1(1)	2(1)	1(1)
C(2)	25(1)	18(1)	23(1)	-1(1)	4(1)	-2(1)
C(3)	30(1)	17(1)	33(1)	3(1)	7(1)	-4(1)
C(4)	26(1)	18(1)	38(1)	0(1)	-3(1)	-6(1)
C(5)	37(1)	26(1)	26(1)	1(1)	-9(1)	-9(1)
C(6)	31(1)	21(1)	22(1)	3(1)	-3(1)	-6(1)
C(7)	23(1)	21(1)	18(1)	-5(1)	6(1)	-8(1)
C(8)	24(1)	30(1)	24(1)	-8(1)	8(1)	-6(1)
C(9)	31(1)	48(1)	25(1)	-16(1)	13(1)	-15(1)
C(10)	40(1)	48(1)	18(1)	-5(1)	7(1)	-22(1)
C(11)	34(1)	32(1)	19(1)	1(1)	-1(1)	-14(1)
C(12)	27(1)	24(1)	20(1)	-2(1)	3(1)	-7(1)
C(13)	14(1)	19(1)	16(1)	1(1)	1(1)	2(1)
C(14)	26(1)	21(1)	22(1)	-1(1)	6(1)	-4(1)
C(15)	32(1)	28(1)	22(1)	-5(1)	4(1)	-4(1)
C(16)	26(1)	40(1)	16(1)	-1(1)	4(1)	2(1)
C(17)	28(1)	38(1)	21(1)	7(1)	6(1)	-5(1)
C(18)	24(1)	26(1)	21(1)	3(1)	3(1)	-6(1)
C(19)	15(1)	23(1)	14(1)	-3(1)	3(1)	-5(1)
C(20)	19(1)	35(1)	22(1)	-6(1)	5(1)	0(1)
C(21)	19(1)	63(2)	26(1)	-12(1)	9(1)	-5(1)
C(22)	29(1)	63(2)	27(1)	-11(1)	13(1)	-25(1)
C(23)	39(1)	35(1)	20(1)	-4(1)	9(1)	-21(1)
C(24)	24(1)	25(1)	19(1)	-2(1)	5(1)	-8(1)
C(25)	18(1)	14(1)	22(1)	0(1)	0(1)	3(1)
C(26)	17(1)	18(1)	25(1)	-6(1)	3(1)	3(1)
C(27)	17(1)	22(1)	19(1)	1(1)	3(1)	-2(1)
C(28)	16(1)	31(1)	21(1)	1(1)	-1(1)	-2(1)
C(29)	18(1)	26(1)	21(1)	4(1)	-1(1)	5(1)
C(30)	30(1)	16(1)	22(1)	5(1)	4(1)	-1(1)
C(31)	27(1)	19(1)	19(1)	2(1)	8(1)	-4(1)
C(32)	20(1)	16(1)	17(1)	1(1)	4(1)	-3(1)

C(33)	16(1)	14(1)	29(1)	-4(1)	7(1)	-1(1)
C(34)	17(1)	19(1)	26(1)	-6(1)	8(1)	-2(1)
C(35)	17(1)	19(1)	22(1)	-2(1)	6(1)	-1(1)
C(36)	14(1)	20(1)	15(1)	0(1)	3(1)	1(1)
C(37)	22(1)	21(1)	19(1)	-1(1)	5(1)	-1(1)
C(38)	25(1)	25(1)	21(1)	-6(1)	5(1)	-2(1)
C(39)	29(1)	37(1)	15(1)	-1(1)	6(1)	5(1)
C(40)	35(1)	34(1)	20(1)	6(1)	7(1)	-4(1)
C(41)	30(1)	24(1)	20(1)	2(1)	4(1)	-5(1)
C(42)	14(1)	22(1)	13(1)	-2(1)	1(1)	-3(1)
C(43)	20(1)	34(1)	21(1)	-6(1)	6(1)	0(1)
C(44)	22(1)	58(1)	30(1)	-11(1)	13(1)	-6(1)
C(45)	33(1)	54(1)	28(1)	-9(1)	15(1)	-23(1)
C(46)	35(1)	32(1)	18(1)	-3(1)	6(1)	-16(1)
C(47)	22(1)	23(1)	15(1)	-1(1)	3(1)	-7(1)
C(48)	21(1)	17(1)	17(1)	-3(1)	4(1)	-6(1)
C(49)	22(1)	31(1)	22(1)	-6(1)	5(1)	-4(1)
C(50)	30(1)	45(1)	25(1)	-11(1)	13(1)	-11(1)
C(51)	39(1)	44(1)	16(1)	-2(1)	6(1)	-18(1)
C(52)	34(1)	26(1)	18(1)	1(1)	-2(1)	-9(1)
C(53)	26(1)	19(1)	19(1)	-2(1)	3(1)	-4(1)
C(54)	16(1)	12(1)	22(1)	-1(1)	1(1)	1(1)
C(55)	28(1)	21(1)	22(1)	3(1)	-4(1)	-4(1)
C(56)	31(1)	24(1)	26(1)	0(1)	-8(1)	-7(1)
C(57)	22(1)	17(1)	35(1)	1(1)	-1(1)	-5(1)
C(58)	28(1)	16(1)	28(1)	4(1)	7(1)	-1(1)
C(59)	22(1)	18(1)	21(1)	0(1)	2(1)	0(1)
C(60)	17(1)	19(1)	19(1)	0(1)	4(1)	-1(1)
C(61)	14(1)	26(1)	21(1)	-1(1)	1(1)	-1(1)
C(62)	17(1)	22(1)	19(1)	2(1)	1(1)	4(1)
C(63)	16(1)	14(1)	24(1)	-2(1)	6(1)	0(1)
C(64)	17(1)	17(1)	21(1)	-4(1)	7(1)	-2(1)
C(65)	16(1)	18(1)	20(1)	2(1)	5(1)	1(1)
C(66)	20(1)	17(1)	15(1)	-2(1)	5(1)	-5(1)
C(67)	27(1)	18(1)	17(1)	1(1)	9(1)	-5(1)

C(68)	32(1)	15(1)	19(1)	4(1)	7(1)	-2(1)
C(69)	17(1)	17(1)	20(1)	-5(1)	1(1)	3(1)
C(70)	17(1)	15(1)	20(1)	0(1)	0(1)	3(1)
C(77)	29(1)	21(1)	30(1)	-7(1)	9(1)	-4(1)
C(78)	34(1)	35(1)	40(1)	-3(1)	1(1)	-2(1)
C(79)	32(1)	57(2)	89(2)	-16(2)	11(1)	5(1)
C(80)	59(2)	66(2)	91(2)	-37(2)	50(2)	-21(2)
C(81)	82(2)	43(1)	48(2)	-15(1)	40(2)	-26(1)
C(82)	53(1)	22(1)	32(1)	-2(1)	8(1)	-7(1)
B(1)	20(1)	14(1)	24(1)	1(1)	2(1)	3(1)
B(2)	19(1)	14(1)	19(1)	2(1)	3(1)	1(1)

Table A2.30: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Br}Ru(dppe)Cl 213b.

	x	y	z	U(eq)
H22	4060	8465	4032	31
H32	4172	8325	3192	38
H42	5169	8623	3031	46
H52	6027	9162	3683	62
H62	5918	9304	4527	59
H21	4110	8324	3778	43
H31	4639	8387	3125	45
H41	5681	8928	3297	48
H51	6190	9492	4113	54
H61	5671	9423	4777	41
H(2)	1175	4596	6914	27
H(3)	497	3387	6710	32
H(4)	-25	3063	5845	36
H(5)	148	3937	5186	40
H(6)	830	5144	5384	32
H(8)	2432	5371	5674	31
H(9)	2478	5736	4836	40

H(10)	1790	6801	4365	42
H(11)	1037	7487	4721	36
H(12)	979	7115	5554	29
H(14)	3027	8027	8150	28
H(15)	3134	8240	9031	34
H(16)	2735	7202	9502	33
H(17)	2249	5943	9094	35
H(18)	2121	5732	8209	29
H(20)	3733	6242	7335	30
H(21)	4650	7006	7258	43
H(22)	4609	8513	7166	47
H(23)	3648	9263	7132	37
H(24)	2735	8508	7219	27
H(25A)	3003	5420	7454	23
H(25B)	2254	5226	7418	23
H(26A)	2399	4795	6619	24
H(26B)	2768	5680	6563	24
H(27)	-30	6123	6190	24
H(29)	-594	8570	5750	27
H(30)	1489	9740	5789	28
H(32)	2561	7578	6208	21
H(33)	581	9981	7239	24
H(35)	1453	7897	8044	23
H(37)	8026	8186	8141	24
H(38)	8224	8380	9034	29
H(39)	7969	7283	9546	32
H(40)	7520	5984	9162	36
H(41)	7315	5779	8270	30
H(43)	8720	6391	7222	30
H(44)	9564	7196	7043	43
H(45)	9477	8695	6952	45
H(46)	8547	9411	7036	34
H(47)	7707	8622	7229	25
H(49)	7411	5555	5696	30
H(50)	7375	5923	4840	39

H(51)	6586	6884	4377	40
H(52)	5827	7475	4765	33
H(53)	5855	7107	5613	26
H(55)	5776	5183	5462	31
H(56)	5083	3981	5305	36
H(57)	4953	3136	5991	32
H(58)	5529	3480	6840	29
H(59)	6207	4693	7004	25
H(60)	4983	6117	6318	22
H(62)	4321	8530	5886	24
H(63)	5554	10020	7332	21
H(65)	6516	7974	8124	21
H(66)	7464	7686	6189	21
H(68)	6293	9765	5781	26
H(69A)	7401	4886	6646	23
H(69B)	7749	5774	6562	23
H(70A)	8059	5547	7455	22
H(70B)	7328	5323	7463	22
H(78)	5465	5612	9933	46
H(79)	6309	5343	9548	72
H(80)	6194	5736	8686	79
H(81)	5241	6371	8204	64
H(82)	4388	6625	8574	44
H(101)	508(10)	9467(14)	6248(8)	24
H(102)	5403(10)	9503(13)	6333(8)	21

Table A2.31: Crystal data and structure refinement for $Tp^{Br}Ru(dppp)Cl$ 213c.

Identification code: $Tp^{Br}Ru(dppp)Cl$ **213c**		
Empirical formula: C44.33 H43.27 B Br3 Cl2.04 N6 P2 Ru		
Formula weight: 1145.79		
Temperature: 123(2) K		
Wavelength: 0.71073 Å		
Crystal system: Triclinic		
Space group	P -1	
Unit cell dimensions	a = 14.3839(10) Å	α= 100.274(2)°.
	b = 15.3216(11) Å	β= 91.466(2)°.
	c = 21.9229(15) Å	γ = 102.412(2)°.
Volume	4632.6(6) $Å^3$	
Z	4	
Density (calculated)	1.643 Mg/m^3	
Absorption coefficient	3.152 mm^{-1}	
F(000)	2279.5	
Crystal size	0.420 x 0.060 x 0.010 mm^3	
Theta range for data collection	0.946 to 28.084°.	
Index ranges	-19<=h<=19, -20<=k<=20, -28<=l<=28	
Reflections collected	114892	
Independent reflections	22347 [R(int) = 0.0470]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7456 and 0.5642	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22347 / 2849 / 1282	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0675	
R indices (all data)	R1 = 0.0542, wR2 = 0.0760	
Largest diff. peak and hole	0.908 and -0.824 $e.Å^{-3}$	

Table A2.32: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppp)Cl 213c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C16	8423(5)	7944(4)	11373(3)	54(2)
C26	8644(3)	7320(3)	10811(2)	47(1)
C36	9523(3)	7700(3)	10503(2)	41(1)
C46	9754(3)	7085(3)	9946(2)	44(1)
C56	10614(5)	7453(5)	9626(4)	86(3)
Cl15	10438(10)	7488(8)	9872(6)	93(4)
C15	9630(11)	7574(11)	10436(7)	51(8)
C25	9612(12)	8408(10)	10779(7)	42(5)
C35	8972(15)	8475(12)	11236(9)	50(6)
C45	8370(30)	7709(14)	11342(16)	51(8)
C55	8359(15)	6878(12)	10982(10)	56(6)
C65	9017(14)	6809(10)	10541(9)	56(6)
Cl14	10749(12)	8629(14)	8371(8)	88(5)
C14	10346(12)	8605(12)	7626(10)	57(5)
C24	10926(14)	8438(19)	7155(11)	60(5)
C34	10613(19)	8410(20)	6552(12)	51(5)
C44	9720(19)	8540(20)	6424(10)	56(5)
C54	9153(19)	8730(30)	6898(11)	51(6)
C64	9461(17)	8750(30)	7500(10)	49(6)
Cl13	11041(3)	8908(2)	8115(2)	95(1)
C13	10382(4)	8706(3)	7406(3)	52(1)
C23	10813(4)	8445(4)	6872(4)	60(2)
C33	10284(5)	8289(4)	6315(3)	61(2)
C43	9357(5)	8394(5)	6292(3)	56(2)
C53	8938(5)	8628(6)	6824(3)	48(2)
C63	9462(4)	8795(6)	7395(3)	42(1)
Cl12	9149(11)	6444(8)	5079(6)	174(6)
C12	8779(12)	5426(9)	4576(6)	76(5)
C22	9439(9)	4951(10)	4363(8)	78(4)

C32	9169(10)	4140(11)	3949(9)	79(4)
C42	8223(11)	3782(9)	3762(7)	53(4)
C52	7575(11)	4281(14)	3968(11)	62(5)
C62	7837(11)	5066(13)	4407(11)	79(6)
Cl11	9048(2)	6443(2)	5110(1)	58(1)
C11	8684(5)	5478(5)	4531(4)	50(2)
C21	9310(5)	5269(6)	4099(4)	66(3)
C31	9026(6)	4494(7)	3650(5)	78(3)
C41	8127(6)	3949(6)	3614(4)	56(2)
C51	7527(6)	4169(7)	4065(5)	42(2)
C61	7784(5)	4963(6)	4500(5)	42(2)
Ru(1)	7187(1)	2411(1)	7022(1)	16(1)
Ru(2)	5632(1)	7433(1)	8249(1)	15(1)
Br(1)	9231(5)	6415(4)	7306(3)	44(1)
Br(1B)	9150(5)	6434(4)	7411(3)	38(1)
Br(2)	3505(1)	3181(1)	6028(1)	26(1)
Br(3)	8881(1)	415(1)	4861(1)	47(1)
Br(4)	3804(1)	8263(1)	5935(1)	36(1)
Br(5)	6613(1)	11304(1)	9710(1)	35(1)
Br(6)	2440(1)	5549(1)	9590(1)	48(1)
Cl(1)	7013(1)	8089(1)	7751(1)	22(1)
Cl(2)	6509(1)	3039(1)	7951(1)	21(1)
P(1)	6280(1)	997(1)	7083(1)	17(1)
P(2)	8483(1)	2247(1)	7589(1)	19(1)
P(3)	5573(1)	6013(1)	7660(1)	16(1)
P(4)	6585(1)	7202(1)	9041(1)	17(1)
N(1)	7723(2)	1956(2)	6185(1)	20(1)
N(2)	7718(2)	2435(2)	5717(1)	24(1)
N(3)	6271(2)	3053(2)	5973(1)	22(1)
N(4)	6063(2)	2718(1)	6504(1)	20(1)
N(5)	7879(2)	3985(2)	6358(1)	24(1)
N(6)	7901(2)	3758(1)	6933(1)	20(1)
N(7)	4778(2)	7796(1)	7564(1)	20(1)
N(8)	4061(2)	8215(2)	7760(1)	24(1)
N(9)	5639(2)	8775(1)	8720(1)	19(1)

N(10)	4795(2)	9038(2)	8802(1)	23(1)
N(11)	4383(2)	7002(2)	8657(1)	20(1)
N(12)	3699(2)	7504(2)	8688(1)	23(1)
C(1)	9465(2)	1970(2)	7131(1)	23(1)
C(2)	9856(2)	1225(2)	7169(1)	31(1)
C(3)	10586(2)	1039(2)	6794(2)	41(1)
C(4)	10942(2)	1599(2)	6391(2)	42(1)
C(5)	10566(2)	2345(2)	6349(1)	36(1)
C(6)	9823(2)	2525(2)	6708(1)	26(1)
C(7)	9109(2)	3258(2)	8147(1)	22(1)
C(8)	9995(2)	3773(2)	8052(1)	29(1)
C(9)	10415(2)	4574(2)	8456(2)	42(1)
C(10)	9945(2)	4875(2)	8967(2)	47(1)
C(11)	9075(2)	4367(2)	9072(1)	40(1)
C(12)	8655(2)	3569(2)	8673(1)	29(1)
C(13)	6233(2)	149(2)	6373(1)	21(1)
C(14)	6472(2)	-688(2)	6371(1)	29(1)
C(15)	6514(2)	-1263(2)	5811(2)	39(1)
C(16)	6317(2)	-1024(2)	5251(2)	41(1)
C(17)	6064(2)	-206(2)	5250(1)	34(1)
C(18)	6027(2)	379(2)	5804(1)	25(1)
C(19)	5003(2)	911(2)	7217(1)	20(1)
C(20)	4291(2)	594(2)	6741(1)	26(1)
C(21)	3341(2)	568(2)	6851(2)	33(1)
C(22)	3085(2)	855(2)	7446(2)	35(1)
C(23)	3786(2)	1173(2)	7926(1)	33(1)
C(24)	4737(2)	1207(2)	7816(1)	26(1)
C(25)	6618(2)	452(2)	7706(1)	24(1)
C(26)	7681(2)	474(2)	7776(1)	25(1)
C(27)	8276(2)	1403(2)	8094(1)	25(1)
C(28)	8326(2)	4506(2)	7330(1)	25(1)
C(29)	8587(2)	5217(2)	7010(2)	31(1)
C(30)	8294(2)	4872(2)	6401(1)	31(1)
C(31)	8100(2)	1248(2)	5966(1)	23(1)
C(32)	8338(2)	1270(2)	5360(1)	29(1)

C(33)	8095(2)	2029(2)	5213(1)	29(1)
C(34)	5150(2)	2723(2)	6594(1)	20(1)
C(35)	4766(2)	3054(2)	6117(1)	22(1)
C(36)	5483(2)	3258(2)	5734(1)	24(1)
C(37)	4448(2)	5176(2)	7655(1)	18(1)
C(38)	4413(2)	4303(2)	7763(1)	23(1)
C(39)	3538(2)	3695(2)	7761(1)	30(1)
C(40)	2698(2)	3950(2)	7642(1)	32(1)
C(41)	2725(2)	4815(2)	7528(1)	30(1)
C(42)	3591(2)	5427(2)	7542(1)	24(1)
C(43)	5715(2)	5973(2)	6823(1)	19(1)
C(44)	4955(2)	5632(2)	6379(1)	23(1)
C(45)	5087(2)	5685(2)	5756(1)	31(1)
C(46)	5968(2)	6057(2)	5573(1)	32(1)
C(47)	6734(2)	6375(2)	6009(1)	28(1)
C(48)	6612(2)	6338(2)	6633(1)	23(1)
C(49)	7514(2)	8205(2)	9402(1)	23(1)
C(50)	8297(2)	8500(2)	9067(1)	30(1)
C(51)	8934(2)	9325(2)	9284(2)	40(1)
C(52)	8798(3)	9867(2)	9838(2)	45(1)
C(53)	8063(3)	9565(2)	10187(2)	40(1)
C(54)	7423(2)	8734(2)	9974(1)	29(1)
C(55)	6004(2)	6898(2)	9732(1)	20(1)
C(56)	5357(2)	7400(2)	9997(1)	25(1)
C(57)	4943(2)	7230(2)	10540(1)	31(1)
C(58)	5146(2)	6547(2)	10824(1)	35(1)
C(59)	5767(2)	6046(2)	10562(1)	35(1)
C(60)	6194(2)	6215(2)	10019(1)	26(1)
C(61)	7304(2)	6357(2)	8843(1)	22(1)
C(62)	6721(2)	5428(2)	8511(1)	20(1)
C(63)	6496(2)	5420(2)	7823(1)	18(1)
C(64)	6329(2)	9481(2)	8985(1)	21(1)
C(65)	5926(2)	10192(2)	9253(1)	24(1)
C(66)	4960(2)	9894(2)	9126(1)	26(1)
C(67)	4802(2)	7771(2)	6952(1)	22(1)

C(68)	4099(2)	8170(2)	6756(1)	26(1)
C(69)	3649(2)	8452(2)	7276(1)	27(1)
C(70)	4052(2)	6298(2)	8930(1)	22(1)
C(71)	3161(2)	6347(2)	9140(1)	27(1)
C(72)	2956(2)	7109(2)	8982(1)	27(1)
B(1)	7318(2)	3297(2)	5803(1)	26(1)
B(2)	3879(2)	8411(2)	8457(1)	25(1)

Table A2.33: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(dppp)Cl 213c.

C16-C26	1.505(6)	C45-H45	0.9500
C16-H1A6	0.9800	C55-C65	1.376(12)
C16-H1B6	0.9800	C55-H55	0.9500
C16-H1C6	0.9800	C65-H65	0.9500
C26-C36	1.502(6)	Cl14-C14	1.709(16)
C26-H2A6	0.9900	C14-C24	1.367(12)
C26-H2B6	0.9900	C14-C64	1.370(12)
C36-C46	1.495(5)	C24-C34	1.375(12)
C36-H3A6	0.9900	C24-H24	0.9500
C36-H3B6	0.9900	C34-C44	1.372(12)
C46-C56	1.492(7)	C34-H34	0.9500
C46-H4A6	0.9900	C44-C54	1.367(12)
C46-H4B6	0.9900	C44-H44	0.9500
C56-H5A6	0.9800	C54-C64	1.374(12)
C56-H5B6	0.9800	C54-H54	0.9500
C56-H5C6	0.9800	C64-H64	0.9500
Cl15-C15	1.725(16)	Cl13-C13	1.743(5)
C15-C65	1.367(12)	C13-C63	1.359(6)
C15-C25	1.367(12)	C13-C23	1.376(6)
C25-C35	1.384(12)	C23-C33	1.378(7)
C25-H25	0.9500	C23-H23	0.9500
C35-C45	1.363(12)	C33-C43	1.378(7)
C35-H35	0.9500	C33-H33	0.9500
C45-C55	1.371(12)	C43-C53	1.354(6)

C43-H43	0.9500	Ru(2)-N(9)	2.129(2)
C53-C63	1.398(6)	Ru(2)-N(7)	2.138(2)
C53-H53	0.9500	Ru(2)-P(3)	2.3059(7)
C63-H63	0.9500	Ru(2)-P(4)	2.3072(7)
Cl12-C12	1.712(15)	Ru(2)-Cl(1)	2.4065(6)
C12-C22	1.360(11)	Br(1)-C(29)	1.859(7)
C12-C62	1.363(12)	Br(1B)-C(29)	1.906(6)
C22-C32	1.375(11)	Br(2)-C(35)	1.874(3)
C22-H22	0.9500	Br(3)-C(32)	1.871(3)
C32-C42	1.375(11)	Br(4)-C(68)	1.874(3)
C32-H32	0.9500	Br(5)-C(65)	1.871(3)
C42-C52	1.364(12)	Br(6)-C(71)	1.866(3)
C42-H42	0.9500	P(1)-C(25)	1.830(3)
C52-C62	1.375(11)	P(1)-C(13)	1.831(3)
C52-H52	0.9500	P(1)-C(19)	1.847(3)
C62-H62	0.9500	P(2)-C(27)	1.830(3)
Cl11-C11	1.741(7)	P(2)-C(1)	1.833(3)
C11-C61	1.357(8)	P(2)-C(7)	1.838(3)
C11-C21	1.367(8)	P(3)-C(63)	1.825(3)
C21-C31	1.378(8)	P(3)-C(37)	1.835(3)
C21-H21	0.9500	P(3)-C(43)	1.845(2)
C31-C41	1.373(9)	P(4)-C(61)	1.827(3)
C31-H31	0.9500	P(4)-C(55)	1.832(2)
C41-C51	1.373(9)	P(4)-C(49)	1.845(3)
C41-H41	0.9500	N(1)-C(31)	1.335(3)
C51-C61	1.378(8)	N(1)-N(2)	1.365(3)
C51-H51	0.9500	N(2)-C(33)	1.354(3)
C61-H61	0.9500	N(2)-B(1)	1.534(4)
Ru(1)-N(1)	2.0731(19)	N(3)-C(36)	1.355(3)
Ru(1)-N(4)	2.135(2)	N(3)-N(4)	1.368(3)
Ru(1)-N(6)	2.143(2)	N(3)-B(1)	1.544(4)
Ru(1)-P(2)	2.2968(7)	N(4)-C(34)	1.334(3)
Ru(1)-P(1)	2.3039(7)	N(5)-C(30)	1.347(4)
Ru(1)-Cl(2)	2.4146(6)	N(5)-N(6)	1.367(3)
Ru(2)-N(11)	2.062(2)	N(5)-B(1)	1.538(4)

N(6)-C(28)	1.328(3)	C(13)-C(18)	1.396(4)
N(7)-C(67)	1.337(3)	C(13)-C(14)	1.396(4)
N(7)-N(8)	1.367(3)	C(14)-C(15)	1.390(4)
N(8)-C(69)	1.345(3)	C(14)-H(14)	0.9500
N(8)-B(2)	1.543(4)	C(15)-C(16)	1.380(5)
N(9)-C(64)	1.333(3)	C(15)-H(15)	0.9500
N(9)-N(10)	1.364(3)	C(16)-C(17)	1.379(5)
N(10)-C(66)	1.345(3)	C(16)-H(16)	0.9500
N(10)-B(2)	1.541(4)	C(17)-C(18)	1.385(4)
N(11)-C(70)	1.331(3)	C(17)-H(17)	0.9500
N(11)-N(12)	1.367(3)	C(18)-H(18)	0.9500
N(12)-C(72)	1.349(3)	C(19)-C(20)	1.388(4)
N(12)-B(2)	1.537(4)	C(19)-C(24)	1.401(4)
C(1)-C(2)	1.391(4)	C(20)-C(21)	1.388(4)
C(1)-C(6)	1.401(4)	C(20)-H(20)	0.9500
C(2)-C(3)	1.395(4)	C(21)-C(22)	1.385(4)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-C(4)	1.374(5)	C(22)-C(23)	1.383(4)
C(3)-H(3)	0.9500	C(22)-H(22)	0.9500
C(4)-C(5)	1.381(5)	C(23)-C(24)	1.387(4)
C(4)-H(4)	0.9500	C(23)-H(23)	0.9500
C(5)-C(6)	1.389(4)	C(24)-H(24)	0.9500
C(5)-H(5)	0.9500	C(25)-C(26)	1.525(4)
C(6)-H(6)	0.9500	C(25)-H(25A)	0.9900
C(7)-C(8)	1.388(4)	C(25)-H(25B)	0.9900
C(7)-C(12)	1.400(3)	C(26)-C(27)	1.529(4)
C(8)-C(9)	1.386(4)	C(26)-H(26A)	0.9900
C(8)-H(8)	0.9500	C(26)-H(26B)	0.9900
C(9)-C(10)	1.383(4)	C(27)-H(27A)	0.9900
C(9)-H(9)	0.9500	C(27)-H(27B)	0.9900
C(10)-C(11)	1.373(5)	C(28)-C(29)	1.389(4)
C(10)-H(10)	0.9500	C(28)-H(28)	0.9500
C(11)-C(12)	1.379(4)	C(29)-C(30)	1.365(4)
C(11)-H(11)	0.9500	C(30)-H(30)	0.9500
C(12)-H(12)	0.9500	C(31)-C(32)	1.384(4)

C(31)-H(31)	0.9500	C(52)-C(53)	1.369(5)
C(32)-C(33)	1.371(4)	C(52)-H(52)	0.9500
C(33)-H(33)	0.9500	C(53)-C(54)	1.396(4)
C(34)-C(35)	1.392(4)	C(53)-H(53)	0.9500
C(34)-H(34)	0.9500	C(54)-H(54)	0.9500
C(35)-C(36)	1.366(4)	C(55)-C(60)	1.384(4)
C(36)-H(36)	0.9500	C(55)-C(56)	1.404(4)
C(37)-C(38)	1.389(4)	C(56)-C(57)	1.385(4)
C(37)-C(42)	1.397(4)	C(56)-H(56)	0.9500
C(38)-C(39)	1.395(4)	C(57)-C(58)	1.385(4)
C(38)-H(38)	0.9500	C(57)-H(57)	0.9500
C(39)-C(40)	1.380(4)	C(58)-C(59)	1.372(4)
C(39)-H(39)	0.9500	C(58)-H(58)	0.9500
C(40)-C(41)	1.384(4)	C(59)-C(60)	1.392(4)
C(40)-H(40)	0.9500	C(59)-H(59)	0.9500
C(41)-C(42)	1.385(4)	C(60)-H(60)	0.9500
C(41)-H(41)	0.9500	C(61)-C(62)	1.532(4)
C(42)-H(42)	0.9500	C(61)-H(61A)	0.9900
C(43)-C(44)	1.389(4)	C(61)-H(61B)	0.9900
C(43)-C(48)	1.398(4)	C(62)-C(63)	1.533(3)
C(44)-C(45)	1.397(4)	C(62)-H(62A)	0.9900
C(44)-H(44)	0.9500	C(62)-H(62B)	0.9900
C(45)-C(46)	1.374(4)	C(63)-H(63A)	0.9900
C(45)-H(45)	0.9500	C(63)-H(63B)	0.9900
C(46)-C(47)	1.384(4)	C(64)-C(65)	1.388(3)
C(46)-H(46)	0.9500	C(64)-H(64)	0.9500
C(47)-C(48)	1.392(3)	C(65)-C(66)	1.370(4)
C(47)-H(47)	0.9500	C(66)-H(66)	0.9500
C(48)-H(48)	0.9500	C(67)-C(68)	1.386(4)
C(49)-C(54)	1.391(4)	C(67)-H(67)	0.9500
C(49)-C(50)	1.398(4)	C(68)-C(69)	1.374(4)
C(50)-C(51)	1.388(4)	C(69)-H(69)	0.9500
C(50)-H(50)	0.9500	C(70)-C(71)	1.385(4)
C(51)-C(52)	1.387(5)	C(70)-H(70)	0.9500
C(51)-H(51)	0.9500	C(71)-C(72)	1.362(4)

C(72)-H(72)	0.9500	C65-C15-Cl15	119.9(10)
B(1)-H(1B)	1.13(3)	C25-C15-Cl15	119.8(10)
B(2)-H(2B)	1.11(3)	C15-C25-C35	119.8(10)
		C15-C25-H25	120.1
C26-C16-H1A6	109.5	C35-C25-H25	120.1
C26-C16-H1B6	109.5	C45-C35-C25	119.7(10)
H1A6-C16-H1B6	109.5	C45-C35-H35	120.1
C26-C16-H1C6	109.5	C25-C35-H35	120.1
H1A6-C16-H1C6	109.5	C35-C45-C55	120.5(10)
H1B6-C16-H1C6	109.5	C35-C45-H45	119.7
C36-C26-C16	115.0(4)	C55-C45-H45	119.7
C36-C26-H2A6	108.5	C45-C55-C65	119.5(10)
C16-C26-H2A6	108.5	C45-C55-H55	120.2
C36-C26-H2B6	108.5	C65-C55-H55	120.2
C16-C26-H2B6	108.5	C15-C65-C55	120.0(10)
H2A6-C26-H2B6	107.5	C15-C65-H65	120.0
C46-C36-C26	115.6(4)	C55-C65-H65	120.0
C46-C36-H3A6	108.4	C24-C14-C64	120.2(10)
C26-C36-H3A6	108.4	C24-C14-Cl14	118.8(10)
C46-C36-H3B6	108.4	C64-C14-Cl14	121.0(10)
C26-C36-H3B6	108.4	C14-C24-C34	119.9(10)
H3A6-C36-H3B6	107.5	C14-C24-H24	120.1
C56-C46-C36	116.6(4)	C34-C24-H24	120.1
C56-C46-H4A6	108.1	C44-C34-C24	119.9(10)
C36-C46-H4A6	108.1	C44-C34-H34	120.0
C56-C46-H4B6	108.1	C24-C34-H34	120.0
C36-C46-H4B6	108.1	C54-C44-C34	120.0(10)
H4A6-C46-H4B6	107.3	C54-C44-H44	120.0
C46-C56-H5A6	109.5	C34-C44-H44	120.0
C46-C56-H5B6	109.5	C44-C54-C64	120.0(11)
H5A6-C56-H5B6	109.5	C44-C54-H54	120.0
C46-C56-H5C6	109.5	C64-C54-H54	120.0
H5A6-C56-H5C6	109.5	C14-C64-C54	119.9(10)
H5B6-C56-H5C6	109.5	C14-C64-H64	120.0
C65-C15-C25	120.3(10)	C54-C64-H64	120.0

C63-C13-C23	122.1(5)	C52-C62-H62	120.2
C63-C13-Cl13	119.7(4)	C61-C11-C21	120.8(6)
C23-C13-Cl13	118.2(4)	C61-C11-Cl11	120.2(5)
C13-C23-C33	117.6(5)	C21-C11-Cl11	118.9(5)
C13-C23-H23	121.2	C11-C21-C31	118.7(6)
C33-C23-H23	121.2	C11-C21-H21	120.7
C43-C33-C23	121.3(5)	C31-C21-H21	120.7
C43-C33-H33	119.4	C41-C31-C21	121.7(6)
C23-C33-H33	119.4	C41-C31-H31	119.1
C53-C43-C33	120.1(5)	C21-C31-H31	119.1
C53-C43-H43	119.9	C51-C41-C31	117.8(7)
C33-C43-H43	119.9	C51-C41-H41	121.1
C43-C53-C63	119.6(5)	C31-C41-H41	121.1
C43-C53-H53	120.2	C41-C51-C61	120.9(7)
C63-C53-H53	120.2	C41-C51-H51	119.5
C13-C63-C53	119.2(4)	C61-C51-H51	119.5
C13-C63-H63	120.4	C11-C61-C51	119.5(6)
C53-C63-H63	120.4	C11-C61-H61	120.2
C22-C12-C62	119.5(10)	C51-C61-H61	120.2
C22-C12-Cl12	119.0(10)	N(1)-Ru(1)-N(4)	88.02(8)
C62-C12-Cl12	121.5(10)	N(1)-Ru(1)-N(6)	87.06(8)
C12-C22-C32	120.5(9)	N(4)-Ru(1)-N(6)	82.38(8)
C12-C22-H22	119.8	N(1)-Ru(1)-P(2)	92.58(6)
C32-C22-H22	119.8	N(4)-Ru(1)-P(2)	173.62(6)
C42-C32-C22	120.4(9)	N(6)-Ru(1)-P(2)	91.31(6)
C42-C32-H32	119.8	N(1)-Ru(1)-P(1)	94.00(6)
C22-C32-H32	119.8	N(4)-Ru(1)-P(1)	91.93(6)
C52-C42-C32	118.1(9)	N(6)-Ru(1)-P(1)	174.17(6)
C52-C42-H42	120.9	P(2)-Ru(1)-P(1)	94.37(2)
C32-C42-H42	120.9	N(1)-Ru(1)-Cl(2)	174.69(6)
C42-C52-C62	121.2(10)	N(4)-Ru(1)-Cl(2)	87.42(5)
C42-C52-H52	119.4	N(6)-Ru(1)-Cl(2)	89.65(6)
C62-C52-H52	119.4	P(2)-Ru(1)-Cl(2)	91.65(2)
C12-C62-C52	119.6(10)	P(1)-Ru(1)-Cl(2)	88.86(2)
C12-C62-H62	120.2	N(11)-Ru(2)-N(9)	87.55(8)

N(11)-Ru(2)-N(7)	86.99(8)	C(61)-P(4)-Ru(2)	117.15(9)
N(9)-Ru(2)-N(7)	82.35(8)	C(55)-P(4)-Ru(2)	117.42(9)
N(11)-Ru(2)-P(3)	93.38(6)	C(49)-P(4)-Ru(2)	114.97(9)
N(9)-Ru(2)-P(3)	174.89(6)	C(31)-N(1)-N(2)	106.46(19)
N(7)-Ru(2)-P(3)	92.68(6)	C(31)-N(1)-Ru(1)	134.40(18)
N(11)-Ru(2)-P(4)	93.70(6)	N(2)-N(1)-Ru(1)	119.14(15)
N(9)-Ru(2)-P(4)	91.57(6)	C(33)-N(2)-N(1)	110.0(2)
N(7)-Ru(2)-P(4)	173.85(6)	C(33)-N(2)-B(1)	129.1(2)
P(3)-Ru(2)-P(4)	93.38(2)	N(1)-N(2)-B(1)	120.83(19)
N(11)-Ru(2)-Cl(1)	173.05(6)	C(36)-N(3)-N(4)	109.5(2)
N(9)-Ru(2)-Cl(1)	87.31(6)	C(36)-N(3)-B(1)	129.8(2)
N(7)-Ru(2)-Cl(1)	87.69(6)	N(4)-N(3)-B(1)	119.6(2)
P(3)-Ru(2)-Cl(1)	91.33(2)	C(34)-N(4)-N(3)	107.0(2)
P(4)-Ru(2)-Cl(1)	91.12(2)	C(34)-N(4)-Ru(1)	134.35(17)
C(25)-P(1)-C(13)	104.56(12)	N(3)-N(4)-Ru(1)	118.45(16)
C(25)-P(1)-C(19)	99.56(12)	C(30)-N(5)-N(6)	109.6(2)
C(13)-P(1)-C(19)	102.24(12)	C(30)-N(5)-B(1)	129.8(2)
C(25)-P(1)-Ru(1)	117.43(9)	N(6)-N(5)-B(1)	120.1(2)
C(13)-P(1)-Ru(1)	113.45(9)	C(28)-N(6)-N(5)	107.0(2)
C(19)-P(1)-Ru(1)	117.43(8)	C(28)-N(6)-Ru(1)	134.61(18)
C(27)-P(2)-C(1)	104.09(13)	N(5)-N(6)-Ru(1)	118.09(16)
C(27)-P(2)-C(7)	100.43(12)	C(67)-N(7)-N(8)	106.9(2)
C(1)-P(2)-C(7)	101.16(12)	C(67)-N(7)-Ru(2)	134.89(18)
C(27)-P(2)-Ru(1)	117.49(10)	N(8)-N(7)-Ru(2)	118.07(15)
C(1)-P(2)-Ru(1)	115.14(9)	C(69)-N(8)-N(7)	109.8(2)
C(7)-P(2)-Ru(1)	116.15(9)	C(69)-N(8)-B(2)	129.7(2)
C(63)-P(3)-C(37)	104.54(12)	N(7)-N(8)-B(2)	120.4(2)
C(63)-P(3)-C(43)	98.61(11)	C(64)-N(9)-N(10)	107.0(2)
C(37)-P(3)-C(43)	101.79(11)	C(64)-N(9)-Ru(2)	133.48(18)
C(63)-P(3)-Ru(2)	118.11(9)	N(10)-N(9)-Ru(2)	119.47(16)
C(37)-P(3)-Ru(2)	115.36(8)	C(66)-N(10)-N(9)	109.6(2)
C(43)-P(3)-Ru(2)	115.89(8)	C(66)-N(10)-B(2)	131.1(2)
C(61)-P(4)-C(55)	103.58(12)	N(9)-N(10)-B(2)	118.6(2)
C(61)-P(4)-C(49)	100.66(12)	C(70)-N(11)-N(12)	106.7(2)
C(55)-P(4)-C(49)	100.41(12)	C(70)-N(11)-Ru(2)	133.78(18)

N(12)-N(11)-Ru(2)	119.49(16)	C(10)-C(11)-H(11)	119.4
C(72)-N(12)-N(11)	109.5(2)	C(12)-C(11)-H(11)	119.4
C(72)-N(12)-B(2)	129.7(2)	C(11)-C(12)-C(7)	120.5(3)
N(11)-N(12)-B(2)	120.6(2)	C(11)-C(12)-H(12)	119.8
C(2)-C(1)-C(6)	118.2(2)	C(7)-C(12)-H(12)	119.8
C(2)-C(1)-P(2)	123.5(2)	C(18)-C(13)-C(14)	118.5(2)
C(6)-C(1)-P(2)	118.3(2)	C(18)-C(13)-P(1)	118.5(2)
C(1)-C(2)-C(3)	120.6(3)	C(14)-C(13)-P(1)	122.8(2)
C(1)-C(2)-H(2)	119.7	C(15)-C(14)-C(13)	119.9(3)
C(3)-C(2)-H(2)	119.7	C(15)-C(14)-H(14)	120.0
C(4)-C(3)-C(2)	120.5(3)	C(13)-C(14)-H(14)	120.0
C(4)-C(3)-H(3)	119.8	C(16)-C(15)-C(14)	121.0(3)
C(2)-C(3)-H(3)	119.8	C(16)-C(15)-H(15)	119.5
C(3)-C(4)-C(5)	119.7(3)	C(14)-C(15)-H(15)	119.5
C(3)-C(4)-H(4)	120.1	C(17)-C(16)-C(15)	119.4(3)
C(5)-C(4)-H(4)	120.1	C(17)-C(16)-H(16)	120.3
C(4)-C(5)-C(6)	120.3(3)	C(15)-C(16)-H(16)	120.3
C(4)-C(5)-H(5)	119.8	C(16)-C(17)-C(18)	120.3(3)
C(6)-C(5)-H(5)	119.8	C(16)-C(17)-H(17)	119.9
C(5)-C(6)-C(1)	120.6(3)	C(18)-C(17)-H(17)	119.9
C(5)-C(6)-H(6)	119.7	C(17)-C(18)-C(13)	120.9(3)
C(1)-C(6)-H(6)	119.7	C(17)-C(18)-H(18)	119.6
C(8)-C(7)-C(12)	117.6(3)	C(13)-C(18)-H(18)	119.6
C(8)-C(7)-P(2)	123.00(19)	C(20)-C(19)-C(24)	118.1(2)
C(12)-C(7)-P(2)	119.2(2)	C(20)-C(19)-P(1)	122.5(2)
C(9)-C(8)-C(7)	121.7(2)	C(24)-C(19)-P(1)	119.4(2)
C(9)-C(8)-H(8)	119.2	C(19)-C(20)-C(21)	121.2(3)
C(7)-C(8)-H(8)	119.2	C(19)-C(20)-H(20)	119.4
C(10)-C(9)-C(8)	119.6(3)	C(21)-C(20)-H(20)	119.4
C(10)-C(9)-H(9)	120.2	C(22)-C(21)-C(20)	120.2(3)
C(8)-C(9)-H(9)	120.2	C(22)-C(21)-H(21)	119.9
C(11)-C(10)-C(9)	119.4(3)	C(20)-C(21)-H(21)	119.9
C(11)-C(10)-H(10)	120.3	C(23)-C(22)-C(21)	119.3(3)
C(9)-C(10)-H(10)	120.3	C(23)-C(22)-H(22)	120.3
C(10)-C(11)-C(12)	121.2(3)	C(21)-C(22)-H(22)	120.3

C(22)-C(23)-C(24)	120.7(3)	C(29)-C(30)-H(30)	126.2
C(22)-C(23)-H(23)	119.7	N(1)-C(31)-C(32)	109.9(2)
C(24)-C(23)-H(23)	119.7	N(1)-C(31)-H(31)	125.0
C(23)-C(24)-C(19)	120.5(3)	C(32)-C(31)-H(31)	125.0
C(23)-C(24)-H(24)	119.7	C(33)-C(32)-C(31)	106.4(2)
C(19)-C(24)-H(24)	119.7	C(33)-C(32)-Br(3)	128.2(2)
C(26)-C(25)-P(1)	114.47(18)	C(31)-C(32)-Br(3)	125.4(2)
C(26)-C(25)-H(25A)	108.6	N(2)-C(33)-C(32)	107.2(2)
P(1)-C(25)-H(25A)	108.6	N(2)-C(33)-H(33)	126.4
C(26)-C(25)-H(25B)	108.6	C(32)-C(33)-H(33)	126.4
P(1)-C(25)-H(25B)	108.6	N(4)-C(34)-C(35)	109.3(2)
H(25A)-C(25)-H(25B)	107.6	N(4)-C(34)-H(34)	125.3
C(25)-C(26)-C(27)	113.1(2)	C(35)-C(34)-H(34)	125.3
C(25)-C(26)-H(26A)	109.0	C(36)-C(35)-C(34)	106.6(2)
C(27)-C(26)-H(26A)	109.0	C(36)-C(35)-Br(2)	127.6(2)
C(25)-C(26)-H(26B)	109.0	C(34)-C(35)-Br(2)	125.83(19)
C(27)-C(26)-H(26B)	109.0	N(3)-C(36)-C(35)	107.6(2)
H(26A)-C(26)-H(26B)	107.8	N(3)-C(36)-H(36)	126.2
C(26)-C(27)-P(2)	113.93(18)	C(35)-C(36)-H(36)	126.2
C(26)-C(27)-H(27A)	108.8	C(38)-C(37)-C(42)	118.6(2)
P(2)-C(27)-H(27A)	108.8	C(38)-C(37)-P(3)	122.7(2)
C(26)-C(27)-H(27B)	108.8	C(42)-C(37)-P(3)	118.7(2)
P(2)-C(27)-H(27B)	108.8	C(37)-C(38)-C(39)	120.4(3)
H(27A)-C(27)-H(27B)	107.7	C(37)-C(38)-H(38)	119.8
N(6)-C(28)-C(29)	109.3(3)	C(39)-C(38)-H(38)	119.8
N(6)-C(28)-H(28)	125.4	C(40)-C(39)-C(38)	120.3(3)
C(29)-C(28)-H(28)	125.4	C(40)-C(39)-H(39)	119.8
C(30)-C(29)-C(28)	106.6(3)	C(38)-C(39)-H(39)	119.8
C(30)-C(29)-Br(1)	124.0(3)	C(39)-C(40)-C(41)	119.7(3)
C(28)-C(29)-Br(1)	129.4(3)	C(39)-C(40)-H(40)	120.1
C(30)-C(29)-Br(1B)	130.2(3)	C(41)-C(40)-H(40)	120.1
C(28)-C(29)-Br(1B)	123.1(3)	C(40)-C(41)-C(42)	120.1(3)
Br(1)-C(29)-Br(1B)	7.8(3)	C(40)-C(41)-H(41)	119.9
N(5)-C(30)-C(29)	107.5(2)	C(42)-C(41)-H(41)	119.9
N(5)-C(30)-H(30)	126.2	C(41)-C(42)-C(37)	120.8(3)

C(41)-C(42)-H(42)	119.6	C(49)-C(54)-C(53)	120.6(3)
C(37)-C(42)-H(42)	119.6	C(49)-C(54)-H(54)	119.7
C(44)-C(43)-C(48)	119.0(2)	C(53)-C(54)-H(54)	119.7
C(44)-C(43)-P(3)	122.48(19)	C(60)-C(55)-C(56)	118.0(2)
C(48)-C(43)-P(3)	118.4(2)	C(60)-C(55)-P(4)	123.26(19)
C(43)-C(44)-C(45)	120.0(3)	C(56)-C(55)-P(4)	118.7(2)
C(43)-C(44)-H(44)	120.0	C(57)-C(56)-C(55)	120.7(3)
C(45)-C(44)-H(44)	120.0	C(57)-C(56)-H(56)	119.6
C(46)-C(45)-C(44)	120.7(3)	C(55)-C(56)-H(56)	119.6
C(46)-C(45)-H(45)	119.6	C(56)-C(57)-C(58)	120.5(3)
C(44)-C(45)-H(45)	119.6	C(56)-C(57)-H(57)	119.8
C(45)-C(46)-C(47)	119.6(2)	C(58)-C(57)-H(57)	119.8
C(45)-C(46)-H(46)	120.2	C(59)-C(58)-C(57)	119.1(3)
C(47)-C(46)-H(46)	120.2	C(59)-C(58)-H(58)	120.5
C(46)-C(47)-C(48)	120.4(3)	C(57)-C(58)-H(58)	120.5
C(46)-C(47)-H(47)	119.8	C(58)-C(59)-C(60)	121.0(3)
C(48)-C(47)-H(47)	119.8	C(58)-C(59)-H(59)	119.5
C(47)-C(48)-C(43)	120.2(3)	C(60)-C(59)-H(59)	119.5
C(47)-C(48)-H(48)	119.9	C(55)-C(60)-C(59)	120.7(3)
C(43)-C(48)-H(48)	119.9	C(55)-C(60)-H(60)	119.7
C(54)-C(49)-C(50)	118.2(3)	C(59)-C(60)-H(60)	119.7
C(54)-C(49)-P(4)	122.3(2)	C(62)-C(61)-P(4)	113.28(18)
C(50)-C(49)-P(4)	119.2(2)	C(62)-C(61)-H(61A)	108.9
C(51)-C(50)-C(49)	120.6(3)	P(4)-C(61)-H(61A)	108.9
C(51)-C(50)-H(50)	119.7	C(62)-C(61)-H(61B)	108.9
C(49)-C(50)-H(50)	119.7	P(4)-C(61)-H(61B)	108.9
C(52)-C(51)-C(50)	120.2(3)	H(61A)-C(61)-H(61B)	107.7
C(52)-C(51)-H(51)	119.9	C(61)-C(62)-C(63)	111.5(2)
C(50)-C(51)-H(51)	119.9	C(61)-C(62)-H(62A)	109.3
C(53)-C(52)-C(51)	119.8(3)	C(63)-C(62)-H(62A)	109.3
C(53)-C(52)-H(52)	120.1	C(61)-C(62)-H(62B)	109.3
C(51)-C(52)-H(52)	120.1	C(63)-C(62)-H(62B)	109.3
C(52)-C(53)-C(54)	120.4(3)	H(62A)-C(62)-H(62B)	108.0
C(52)-C(53)-H(53)	119.8	C(62)-C(63)-P(3)	115.54(16)
C(54)-C(53)-H(53)	119.8	C(62)-C(63)-H(63A)	108.4

P(3)-C(63)-H(63A)	108.4	N(11)-C(70)-H(70)	125.2
C(62)-C(63)-H(63B)	108.4	C(71)-C(70)-H(70)	125.2
P(3)-C(63)-H(63B)	108.4	C(72)-C(71)-C(70)	106.4(2)
H(63A)-C(63)-H(63B)	107.5	C(72)-C(71)-Br(6)	127.9(2)
N(9)-C(64)-C(65)	109.3(2)	C(70)-C(71)-Br(6)	125.6(2)
N(9)-C(64)-H(64)	125.3	N(12)-C(72)-C(71)	107.8(2)
C(65)-C(64)-H(64)	125.3	N(12)-C(72)-H(72)	126.1
C(66)-C(65)-C(64)	106.2(2)	C(71)-C(72)-H(72)	126.1
C(66)-C(65)-Br(5)	129.0(2)	N(2)-B(1)-N(5)	108.6(2)
C(64)-C(65)-Br(5)	124.7(2)	N(2)-B(1)-N(3)	108.8(2)
N(10)-C(66)-C(65)	107.7(2)	N(5)-B(1)-N(3)	107.1(2)
N(10)-C(66)-H(66)	126.1	N(2)-B(1)-H(1B)	109.7(15)
C(65)-C(66)-H(66)	126.1	N(5)-B(1)-H(1B)	110.6(16)
N(7)-C(67)-C(68)	109.4(2)	N(3)-B(1)-H(1B)	111.8(15)
N(7)-C(67)-H(67)	125.3	N(12)-B(2)-N(10)	108.6(2)
C(68)-C(67)-H(67)	125.3	N(12)-B(2)-N(8)	107.9(2)
C(69)-C(68)-C(67)	106.4(2)	N(10)-B(2)-N(8)	107.7(2)
C(69)-C(68)-Br(4)	127.3(2)	N(12)-B(2)-H(2B)	110.7(16)
C(67)-C(68)-Br(4)	126.2(2)	N(10)-B(2)-H(2B)	110.6(16)
N(8)-C(69)-C(68)	107.5(2)	N(8)-B(2)-H(2B)	111.3(15)
N(8)-C(69)-H(69)	126.2		
C(68)-C(69)-H(69)	126.2		
N(11)-C(70)-C(71)	109.7(2)		

Symmetry transformations used to generate equivalent atoms:

Table A2.34: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Br}Ru(dppp)Cl$ 213c. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C16	61(4)	67(4)	40(3)	13(3)	8(3)	22(3)
C26	53(3)	41(2)	49(2)	15(2)	8(2)	9(2)
C36	32(2)	38(2)	49(3)	-4(2)	-5(2)	8(2)

C46	37(2)	40(2)	51(2)	-3(2)	0(2)	8(2)
C56	67(4)	56(4)	121(6)	-12(4)	53(4)	1(3)
Cl15	121(9)	51(5)	107(8)	15(5)	75(7)	13(5)
C15	51(11)	49(8)	54(11)	12(6)	5(9)	8(6)
C25	48(9)	42(8)	39(8)	20(6)	-3(7)	9(6)
C35	56(10)	43(8)	50(9)	14(6)	3(8)	6(7)
C45	56(12)	46(8)	51(11)	16(7)	2(10)	5(7)
C55	52(10)	52(8)	60(10)	11(7)	7(8)	5(7)
C65	59(10)	51(8)	58(10)	16(6)	9(8)	8(7)
Cl14	74(7)	94(9)	81(6)	-19(5)	-12(5)	19(6)
C14	41(7)	46(11)	73(7)	-3(6)	10(5)	-3(7)
C24	46(8)	53(11)	76(8)	4(7)	12(6)	6(7)
C34	40(8)	43(10)	66(8)	1(7)	19(6)	7(7)
C44	45(8)	53(11)	69(8)	5(7)	17(6)	10(8)
C54	46(8)	38(12)	65(8)	2(7)	15(6)	2(8)
C64	40(8)	37(12)	61(8)	-1(7)	13(6)	-2(7)
Cl13	73(2)	104(2)	101(2)	9(2)	-28(2)	16(1)
C13	55(3)	32(2)	67(3)	8(2)	12(2)	1(2)
C23	44(3)	53(3)	83(4)	9(3)	17(3)	9(2)
C33	57(4)	54(3)	74(3)	11(3)	31(3)	12(3)
C43	62(4)	50(3)	55(3)	9(2)	15(2)	7(3)
C53	42(3)	38(3)	63(3)	12(2)	15(2)	7(3)
C63	46(3)	30(3)	50(3)	10(2)	14(2)	9(2)
Cl12	237(12)	131(7)	135(8)	16(6)	30(7)	6(7)
C12	82(7)	85(7)	71(8)	30(6)	25(6)	22(6)
C22	70(7)	81(7)	83(8)	12(6)	15(6)	12(5)
C32	67(6)	84(7)	84(8)	4(6)	6(5)	21(5)
C42	64(6)	49(6)	57(7)	30(5)	5(5)	19(5)
C52	75(7)	68(7)	62(8)	38(6)	2(6)	35(5)
C62	90(7)	79(8)	79(10)	33(7)	27(6)	28(6)
Cl11	68(2)	44(1)	55(2)	-2(1)	33(1)	3(1)
C11	45(4)	48(4)	58(4)	11(3)	18(3)	10(3)
C21	49(4)	74(5)	75(5)	7(4)	22(3)	21(3)
C31	56(4)	85(5)	88(6)	-4(4)	29(4)	21(4)
C41	51(4)	63(5)	64(5)	22(4)	5(3)	23(3)

C51	45(4)	42(4)	49(4)	26(3)	7(3)	15(3)
C61	44(3)	43(3)	51(4)	29(3)	27(3)	20(3)
Ru(1)	19(1)	15(1)	14(1)	4(1)	3(1)	5(1)
Ru(2)	19(1)	15(1)	13(1)	2(1)	2(1)	6(1)
Br(1)	42(2)	24(1)	63(2)	10(1)	16(1)	-4(1)
Br(1B)	36(1)	16(1)	59(2)	2(1)	25(1)	1(1)
Br(2)	23(1)	34(1)	26(1)	8(1)	2(1)	12(1)
Br(3)	54(1)	59(1)	33(1)	-5(1)	14(1)	34(1)
Br(4)	53(1)	31(1)	24(1)	8(1)	-15(1)	6(1)
Br(5)	46(1)	20(1)	34(1)	-7(1)	-5(1)	9(1)
Br(6)	31(1)	67(1)	50(1)	31(1)	18(1)	5(1)
Cl(1)	24(1)	19(1)	22(1)	5(1)	6(1)	3(1)
Cl(2)	24(1)	20(1)	19(1)	1(1)	6(1)	6(1)
P(1)	20(1)	16(1)	17(1)	4(1)	1(1)	5(1)
P(2)	20(1)	19(1)	18(1)	3(1)	1(1)	5(1)
P(3)	19(1)	16(1)	13(1)	2(1)	2(1)	5(1)
P(4)	20(1)	17(1)	15(1)	2(1)	1(1)	6(1)
N(1)	21(1)	23(1)	17(1)	4(1)	4(1)	7(1)
N(2)	26(1)	33(1)	16(1)	8(1)	6(1)	12(1)
N(3)	24(1)	27(1)	20(1)	11(1)	6(1)	10(1)
N(4)	26(1)	20(1)	16(1)	7(1)	3(1)	9(1)
N(5)	25(1)	25(1)	29(1)	14(1)	11(1)	8(1)
N(6)	22(1)	19(1)	23(1)	8(1)	8(1)	7(1)
N(7)	24(1)	20(1)	17(1)	2(1)	-2(1)	9(1)
N(8)	27(1)	24(1)	22(1)	3(1)	-2(1)	12(1)
N(9)	20(1)	20(1)	19(1)	3(1)	2(1)	8(1)
N(10)	26(1)	21(1)	22(1)	-1(1)	0(1)	12(1)
N(11)	21(1)	23(1)	16(1)	2(1)	4(1)	9(1)
N(12)	21(1)	29(1)	20(1)	0(1)	3(1)	10(1)
C(1)	18(1)	25(1)	23(1)	-2(1)	-1(1)	5(1)
C(2)	25(2)	28(2)	40(2)	2(1)	0(1)	8(1)
C(3)	26(2)	35(2)	59(2)	-7(2)	2(2)	14(1)
C(4)	28(2)	43(2)	48(2)	-12(2)	11(1)	9(1)
C(5)	30(2)	41(2)	31(2)	-2(1)	10(1)	2(1)
C(6)	25(1)	28(2)	24(1)	1(1)	4(1)	5(1)

C(7)	23(1)	25(1)	18(1)	2(1)	0(1)	6(1)
C(8)	24(1)	33(2)	25(1)	-5(1)	4(1)	2(1)
C(9)	29(2)	43(2)	42(2)	-10(1)	11(1)	-4(1)
C(10)	37(2)	45(2)	41(2)	-21(2)	8(2)	-7(2)
C(11)	34(2)	48(2)	28(2)	-12(1)	8(1)	3(1)
C(12)	25(2)	36(2)	22(1)	1(1)	3(1)	3(1)
C(13)	22(1)	17(1)	23(1)	0(1)	2(1)	3(1)
C(14)	30(2)	19(1)	36(2)	4(1)	1(1)	7(1)
C(15)	41(2)	22(2)	53(2)	-5(1)	3(2)	12(1)
C(16)	44(2)	34(2)	37(2)	-15(1)	2(1)	8(2)
C(17)	33(2)	37(2)	25(1)	-3(1)	-2(1)	2(1)
C(18)	27(2)	23(1)	24(1)	2(1)	1(1)	6(1)
C(19)	20(1)	16(1)	26(1)	6(1)	2(1)	2(1)
C(20)	26(1)	20(1)	29(1)	1(1)	-3(1)	4(1)
C(21)	25(2)	29(2)	42(2)	4(1)	-5(1)	6(1)
C(22)	23(2)	35(2)	50(2)	9(1)	5(1)	10(1)
C(23)	31(2)	35(2)	34(2)	7(1)	9(1)	10(1)
C(24)	26(1)	26(1)	26(1)	8(1)	4(1)	6(1)
C(25)	27(1)	22(1)	24(1)	12(1)	2(1)	6(1)
C(26)	25(1)	24(1)	30(1)	13(1)	-1(1)	7(1)
C(27)	26(1)	27(1)	23(1)	9(1)	-3(1)	6(1)
C(28)	23(1)	17(1)	35(1)	3(1)	7(1)	7(1)
C(29)	24(2)	20(1)	50(2)	11(1)	13(1)	4(1)
C(30)	28(2)	25(1)	45(2)	19(1)	14(1)	7(1)
C(31)	22(1)	25(1)	22(1)	0(1)	2(1)	9(1)
C(32)	27(2)	41(2)	21(1)	-1(1)	6(1)	17(1)
C(33)	27(2)	45(2)	18(1)	6(1)	5(1)	14(1)
C(34)	22(1)	18(1)	20(1)	3(1)	4(1)	6(1)
C(35)	23(1)	22(1)	21(1)	4(1)	2(1)	8(1)
C(36)	26(1)	30(2)	23(1)	12(1)	3(1)	12(1)
C(37)	22(1)	19(1)	11(1)	0(1)	2(1)	3(1)
C(38)	26(1)	24(1)	17(1)	1(1)	1(1)	5(1)
C(39)	35(2)	23(1)	28(1)	6(1)	7(1)	0(1)
C(40)	27(2)	32(2)	32(2)	2(1)	7(1)	-4(1)
C(41)	23(1)	37(2)	28(1)	1(1)	3(1)	5(1)

C(42)	25(1)	24(1)	22(1)	2(1)	3(1)	6(1)
C(43)	28(1)	15(1)	16(1)	2(1)	3(1)	7(1)
C(44)	32(2)	19(1)	18(1)	2(1)	1(1)	4(1)
C(45)	46(2)	28(2)	18(1)	2(1)	-1(1)	7(1)
C(46)	52(2)	28(2)	17(1)	6(1)	7(1)	10(1)
C(47)	40(2)	24(1)	23(1)	5(1)	12(1)	11(1)
C(48)	30(1)	19(1)	20(1)	2(1)	5(1)	8(1)
C(49)	23(1)	22(1)	24(1)	4(1)	-6(1)	7(1)
C(50)	23(1)	28(2)	37(2)	5(1)	-5(1)	5(1)
C(51)	26(2)	32(2)	58(2)	7(2)	-7(1)	2(1)
C(52)	38(2)	30(2)	58(2)	1(2)	-19(2)	-1(1)
C(53)	49(2)	29(2)	37(2)	-6(1)	-17(1)	9(1)
C(54)	38(2)	25(1)	24(1)	1(1)	-9(1)	9(1)
C(55)	24(1)	22(1)	13(1)	2(1)	-1(1)	6(1)
C(56)	30(2)	29(2)	17(1)	2(1)	-1(1)	11(1)
C(57)	33(2)	43(2)	19(1)	2(1)	4(1)	15(1)
C(58)	40(2)	46(2)	21(1)	10(1)	8(1)	10(2)
C(59)	50(2)	34(2)	26(1)	15(1)	8(1)	14(2)
C(60)	31(2)	28(2)	21(1)	6(1)	3(1)	9(1)
C(61)	22(1)	24(1)	19(1)	1(1)	-2(1)	9(1)
C(62)	22(1)	20(1)	19(1)	2(1)	0(1)	10(1)
C(63)	19(1)	18(1)	18(1)	1(1)	1(1)	5(1)
C(64)	28(1)	19(1)	15(1)	2(1)	0(1)	7(1)
C(65)	37(2)	20(1)	16(1)	1(1)	0(1)	10(1)
C(66)	37(2)	23(1)	20(1)	1(1)	2(1)	15(1)
C(67)	30(2)	17(1)	19(1)	4(1)	-1(1)	5(1)
C(68)	34(2)	21(1)	20(1)	4(1)	-11(1)	4(1)
C(69)	30(2)	23(1)	30(1)	4(1)	-8(1)	9(1)
C(70)	25(1)	25(1)	16(1)	4(1)	4(1)	5(1)
C(71)	24(1)	36(2)	19(1)	3(1)	5(1)	1(1)
C(72)	21(1)	35(2)	22(1)	-1(1)	4(1)	6(1)
B(1)	27(2)	31(2)	24(1)	14(1)	9(1)	11(1)
B(2)	25(2)	27(2)	24(1)	2(1)	1(1)	13(1)

Table A2.35: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Tp^{Br}Ru(dppp)Cl 213c.

	x	y	z	U(eq)
H1A6	8405	8535	11266	81
H1B6	8917	8027	11707	81
H1C6	7801	7676	11511	81
H2A6	8720	6748	10935	56
H2B6	8092	7166	10502	56
H3A6	9445	8271	10377	50
H3B6	10073	7858	10814	50
H4A6	9842	6519	10075	53
H4B6	9196	6917	9641	53
H5A6	10521	7989	9467	129
H5B6	10709	6987	9279	129
H5C6	11175	7625	9920	129
H25	10037	8939	10703	50
H35	8955	9052	11476	60
H45	7943	7752	11667	61
H55	7903	6353	11037	67
H65	9045	6230	10310	67
H24	11543	8344	7244	72
H34	11016	8295	6224	61
H44	9495	8493	6006	68
H54	8548	8851	6811	61
H64	9060	8868	7829	58
H23	11453	8374	6887	73
H33	10564	8106	5939	74
H43	9012	8303	5902	67
H53	8291	8678	6810	57
H63	9178	8969	7771	50
H22	10092	5181	4501	94
H32	9639	3824	3792	95
H42	8026	3204	3496	64

H52	6931	4082	3805	75
H62	7364	5355	4591	94
H21	9927	5650	4108	79
H31	9465	4334	3356	93
H41	7926	3436	3289	68
H51	6926	3769	4077	51
H61	7334	5148	4776	50
H(2)	9624	839	7452	37
H(3)	10838	521	6819	49
H(4)	11445	1474	6141	50
H(5)	10816	2736	6073	43
H(6)	9556	3029	6667	32
H(8)	10322	3571	7702	35
H(9)	11023	4913	8383	50
H(10)	10221	5430	9242	57
H(11)	8757	4568	9427	48
H(12)	8053	3228	8754	35
H(14)	6605	-864	6752	34
H(15)	6682	-1830	5812	47
H(16)	6355	-1419	4871	49
H(17)	5914	-43	4867	40
H(18)	5860	944	5798	30
H(20)	4457	391	6331	31
H(21)	2864	352	6518	39
H(22)	2434	833	7524	43
H(23)	3614	1370	8335	39
H(24)	5212	1432	8149	31
H(25A)	6422	756	8103	28
H(25B)	6260	-190	7627	28
H(26A)	7913	307	7360	30
H(26B)	7774	12	8022	30
H(27A)	8900	1325	8249	30
H(27B)	7947	1638	8458	30
H(28)	8435	4549	7764	30
H(30)	8370	5197	6069	37

H(31)	8192	796	6192	27
H(33)	8176	2232	4828	35
H(34)	4815	2530	6932	23
H(36)	5439	3499	5366	29
H(38)	4989	4119	7839	27
H(39)	3520	3103	7841	36
H(40)	2103	3533	7638	39
H(41)	2148	4989	7440	36
H(42)	3603	6024	7473	29
H(44)	4346	5363	6499	28
H(45)	4562	5462	5457	37
H(46)	6050	6095	5149	38
H(47)	7347	6620	5882	34
H(48)	7140	6562	6930	27
H(50)	8394	8134	8686	36
H(51)	9464	9518	9053	48
H(52)	9213	10446	9975	53
H(53)	7988	9922	10576	48
H(54)	6919	8527	10222	35
H(56)	5203	7862	9803	30
H(57)	4516	7583	10719	37
H(58)	4858	6428	11194	42
H(59)	5908	5577	10754	42
H(60)	6620	5858	9844	31
H(61A)	7804	6585	8572	26
H(61B)	7627	6282	9228	26
H(62A)	6117	5277	8716	24
H(62B)	7083	4956	8548	24
H(63A)	6298	4779	7604	22
H(63B)	7090	5698	7646	22
H(64)	6993	9495	8990	25
H(66)	4492	10233	9246	31
H(67)	5234	7518	6693	26
H(69)	3140	8759	7290	33
H(70)	4377	5833	8974	27

H(72)	2392	7324	9065	32
H(1B)	7390(20)	3590(20)	5363(13)	31
H(2B)	3260(20)	8740(20)	8536(13)	30

Table A2.36: Crystal data and structure refinement for $Tp^{Br}Ru(dppb)Cl$ 213d.

Identification code: $Tp^{Br}Ru(dppb)Cl$ **213d**

Empirical formula: C37 H35 B Br3 Cl N6 P2 Ru

Formula weight: 1012.71

Temperature: 123(2) K

Wavelength: 0.71073 Å

Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.9759(8) Å	α= 90°.
	b = 20.4428(14) Å	β= 102.968(2)°.
	c = 16.1277(11) Å	γ = 90°.
Volume	3847.7(5) $Å^3$	
Z	4	
Density (calculated)	1.748 Mg/m^3	
Absorption coefficient	3.712 mm^{-1}	
F(000)	2000	
Crystal size	0.380 x 0.240 x 0.080 mm^3	
Theta range for data collection	1.634 to 28.347°.	
Index ranges	-15<=h<=16, -27<=k<=27, -21<=l<=21	
Reflections collected	51041	
Independent reflections	9586 [R(int) = 0.0180]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.5101	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9586 / 1 / 473	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0202, wR2 = 0.0474	
R indices (all data)	R1 = 0.0241, wR2 = 0.0495	
Largest diff. peak and hole	0.660 and -0.639 $e.Å^{-3}$	

Table A2.37: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppb)Cl 213d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3493(1)	3398(1)	7034(1)	10(1)
Br(1)	-858(1)	2558(1)	4466(1)	31(1)
Br(2)	5617(1)	3993(1)	4017(1)	23(1)
Br(3)	2728(1)	5977(1)	8603(1)	26(1)
Br(3A)	2192(18)	5897(4)	8594(8)	54(3)
Cl(1)	4094(1)	2344(1)	6620(1)	16(1)
P(1)	5379(1)	3542(1)	7833(1)	12(1)
P(2)	2706(1)	2911(1)	8072(1)	12(1)
N(1)	3379(1)	4297(1)	5506(1)	15(1)
N(2)	3996(1)	3794(1)	5943(1)	14(1)
N(3)	1512(1)	3846(1)	5636(1)	17(1)
N(4)	1902(1)	3309(1)	6121(1)	15(1)
N(5)	2451(1)	4721(1)	6648(1)	14(1)
N(6)	2938(1)	4316(1)	7304(1)	13(1)
C(1)	371(2)	3033(1)	5115(1)	21(1)
C(2)	591(2)	3686(1)	5024(1)	21(1)
C(3)	1210(2)	2813(1)	5806(1)	18(1)
C(4)	4675(2)	4022(1)	4802(1)	16(1)
C(5)	3783(2)	4440(1)	4809(1)	18(1)
C(6)	4776(1)	3620(1)	5514(1)	14(1)
C(7)	2624(2)	5290(1)	7828(1)	17(1)
C(8)	2260(2)	5317(1)	6957(1)	18(1)
C(9)	3030(1)	4658(1)	8021(1)	15(1)
C(10)	6005(2)	2928(1)	8646(1)	16(1)
C(11)	5734(2)	2956(1)	9531(1)	18(1)
C(12)	4490(2)	3100(1)	9533(1)	18(1)
C(13)	3666(2)	2590(1)	9030(1)	16(1)
C(14)	1708(1)	3425(1)	8498(1)	16(1)
C(15)	864(2)	3779(1)	7933(1)	20(1)

C(16)	75(2)	4159(1)	8233(1)	26(1)
C(17)	129(2)	4202(1)	9097(1)	31(1)
C(18)	957(2)	3856(1)	9664(1)	28(1)
C(19)	1738(2)	3465(1)	9368(1)	20(1)
C(20)	1822(2)	2171(1)	7777(1)	16(1)
C(21)	2347(2)	1581(1)	7638(1)	22(1)
C(22)	1708(2)	1010(1)	7460(1)	28(1)
C(23)	543(2)	1015(1)	7423(1)	32(1)
C(24)	19(2)	1595(1)	7565(2)	31(1)
C(25)	648(2)	2169(1)	7737(1)	22(1)
C(26)	6490(1)	3487(1)	7199(1)	14(1)
C(27)	6925(2)	4049(1)	6891(1)	18(1)
C(28)	7746(2)	4005(1)	6405(1)	23(1)
C(29)	8149(2)	3400(1)	6221(1)	26(1)
C(30)	7728(2)	2838(1)	6521(1)	24(1)
C(31)	6903(2)	2877(1)	7004(1)	19(1)
C(32)	5795(1)	4342(1)	8319(1)	14(1)
C(33)	6630(2)	4414(1)	9070(1)	21(1)
C(34)	6951(2)	5030(1)	9402(1)	27(1)
C(35)	6459(2)	5585(1)	8980(1)	24(1)
C(36)	5667(2)	5526(1)	8217(1)	20(1)
C(37)	5341(1)	4909(1)	7884(1)	16(1)
B(1)	2232(2)	4483(1)	5723(1)	16(1)

Table A2.38: Bond lengths [Å] and angles [°] for Tp^{Br}Ru(dppb)Cl 213d.

Ru(1)-N(6)	2.0696(13)	Br(2)-C(4)	1.8756(16)
Ru(1)-N(4)	2.1381(14)	Br(3)-C(7)	1.8662(16)
Ru(1)-N(2)	2.1428(13)	Br(3A)-C(7)	1.902(7)
Ru(1)-P(2)	2.3215(4)	P(1)-C(32)	1.8336(16)
Ru(1)-P(1)	2.3544(4)	P(1)-C(10)	1.8489(16)
Ru(1)-Cl(1)	2.4132(4)	P(1)-C(26)	1.8535(16)
Br(1)-C(1)	1.8746(17)	P(2)-C(13)	1.8275(17)

P(2)-C(14)	1.8381(17)	C(13)-H(13A)	0.9900
P(2)-C(20)	1.8469(16)	C(13)-H(13B)	0.9900
N(1)-C(5)	1.352(2)	C(14)-C(19)	1.397(2)
N(1)-N(2)	1.3658(18)	C(14)-C(15)	1.399(2)
N(1)-B(1)	1.539(2)	C(15)-C(16)	1.392(2)
N(2)-C(6)	1.330(2)	C(15)-H(15)	0.9500
N(3)-C(2)	1.345(2)	C(16)-C(17)	1.383(3)
N(3)-N(4)	1.3677(19)	C(16)-H(16)	0.9500
N(3)-B(1)	1.551(2)	C(17)-C(18)	1.383(3)
N(4)-C(3)	1.336(2)	C(17)-H(17)	0.9500
N(5)-C(8)	1.355(2)	C(18)-C(19)	1.394(3)
N(5)-N(6)	1.3667(18)	C(18)-H(18)	0.9500
N(5)-B(1)	1.535(2)	C(19)-H(19)	0.9500
N(6)-C(9)	1.335(2)	C(20)-C(25)	1.392(2)
C(1)-C(2)	1.373(3)	C(20)-C(21)	1.400(2)
C(1)-C(3)	1.398(2)	C(21)-C(22)	1.390(2)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-H(3)	0.9500	C(22)-C(23)	1.383(3)
C(4)-C(5)	1.371(2)	C(22)-H(22)	0.9500
C(4)-C(6)	1.394(2)	C(23)-C(24)	1.385(3)
C(5)-H(5)	0.9500	C(23)-H(23)	0.9500
C(6)-H(6)	0.9500	C(24)-C(25)	1.389(3)
C(7)-C(8)	1.375(2)	C(24)-H(24)	0.9500
C(7)-C(9)	1.391(2)	C(25)-H(25)	0.9500
C(8)-H(8)	0.9500	C(26)-C(27)	1.398(2)
C(9)-H(9)	0.9500	C(26)-C(31)	1.402(2)
C(10)-C(11)	1.534(2)	C(27)-C(28)	1.391(2)
C(10)-H(10A)	0.9900	C(27)-H(27)	0.9500
C(10)-H(10B)	0.9900	C(28)-C(29)	1.384(3)
C(11)-C(12)	1.519(2)	C(28)-H(28)	0.9500
C(11)-H(11A)	0.9900	C(29)-C(30)	1.384(3)
C(11)-H(11B)	0.9900	C(29)-H(29)	0.9500
C(12)-C(13)	1.536(2)	C(30)-C(31)	1.391(2)
C(12)-H(12A)	0.9900	C(30)-H(30)	0.9500
C(12)-H(12B)	0.9900	C(31)-H(31)	0.9500

C(32)-C(33)	1.395(2)	C(13)-P(2)-C(20)	98.02(7)
C(32)-C(37)	1.400(2)	C(14)-P(2)-C(20)	100.47(7)
C(33)-C(34)	1.390(2)	C(13)-P(2)-Ru(1)	118.93(6)
C(33)-H(33)	0.9500	C(14)-P(2)-Ru(1)	115.29(5)
C(34)-C(35)	1.384(3)	C(20)-P(2)-Ru(1)	117.86(5)
C(34)-H(34)	0.9500	C(5)-N(1)-N(2)	109.82(13)
C(35)-C(36)	1.380(3)	C(5)-N(1)-B(1)	129.74(14)
C(35)-H(35)	0.9500	N(2)-N(1)-B(1)	118.40(13)
C(36)-C(37)	1.392(2)	C(6)-N(2)-N(1)	107.15(13)
C(36)-H(36)	0.9500	C(6)-N(2)-Ru(1)	133.30(11)
C(37)-H(37)	0.9500	N(1)-N(2)-Ru(1)	119.29(10)
B(1)-H(1)	1.16(2)	C(2)-N(3)-N(4)	110.05(14)
		C(2)-N(3)-B(1)	128.22(15)
N(6)-Ru(1)-N(4)	86.75(5)	N(4)-N(3)-B(1)	120.70(13)
N(6)-Ru(1)-N(2)	89.58(5)	C(3)-N(4)-N(3)	106.81(14)
N(4)-Ru(1)-N(2)	80.64(5)	C(3)-N(4)-Ru(1)	134.98(12)
N(6)-Ru(1)-P(2)	92.04(4)	N(3)-N(4)-Ru(1)	117.59(10)
N(4)-Ru(1)-P(2)	91.00(4)	C(8)-N(5)-N(6)	109.82(13)
N(2)-Ru(1)-P(2)	171.39(4)	C(8)-N(5)-B(1)	129.46(14)
N(6)-Ru(1)-P(1)	94.90(4)	N(6)-N(5)-B(1)	120.69(13)
N(4)-Ru(1)-P(1)	169.92(4)	C(9)-N(6)-N(5)	106.85(12)
N(2)-Ru(1)-P(1)	89.42(4)	C(9)-N(6)-Ru(1)	133.64(11)
P(2)-Ru(1)-P(1)	98.865(15)	N(5)-N(6)-Ru(1)	119.23(10)
N(6)-Ru(1)-Cl(1)	176.18(4)	C(2)-C(1)-C(3)	106.15(15)
N(4)-Ru(1)-Cl(1)	90.49(4)	C(2)-C(1)-Br(1)	126.09(14)
N(2)-Ru(1)-Cl(1)	87.37(4)	C(3)-C(1)-Br(1)	127.70(14)
P(2)-Ru(1)-Cl(1)	90.640(14)	N(3)-C(2)-C(1)	107.65(16)
P(1)-Ru(1)-Cl(1)	87.369(14)	N(3)-C(2)-H(2)	126.2
C(32)-P(1)-C(10)	105.91(8)	C(1)-C(2)-H(2)	126.2
C(32)-P(1)-C(26)	97.52(7)	N(4)-C(3)-C(1)	109.35(15)
C(10)-P(1)-C(26)	97.09(7)	N(4)-C(3)-H(3)	125.3
C(32)-P(1)-Ru(1)	118.72(5)	C(1)-C(3)-H(3)	125.3
C(10)-P(1)-Ru(1)	119.31(6)	C(5)-C(4)-C(6)	106.55(14)
C(26)-P(1)-Ru(1)	114.19(5)	C(5)-C(4)-Br(2)	127.72(12)
C(13)-P(2)-C(14)	103.19(8)	C(6)-C(4)-Br(2)	125.71(13)

N(1)-C(5)-C(4)	107.22(14)	C(12)-C(13)-P(2)	114.20(11)
N(1)-C(5)-H(5)	126.4	C(12)-C(13)-H(13A)	108.7
C(4)-C(5)-H(5)	126.4	P(2)-C(13)-H(13A)	108.7
N(2)-C(6)-C(4)	109.25(14)	C(12)-C(13)-H(13B)	108.7
N(2)-C(6)-H(6)	125.4	P(2)-C(13)-H(13B)	108.7
C(4)-C(6)-H(6)	125.4	H(13A)-C(13)-H(13B)	107.6
C(8)-C(7)-C(9)	106.27(14)	C(19)-C(14)-C(15)	118.47(16)
C(8)-C(7)-Br(3)	127.77(13)	C(19)-C(14)-P(2)	122.37(13)
C(9)-C(7)-Br(3)	125.61(13)	C(15)-C(14)-P(2)	119.14(13)
C(8)-C(7)-Br(3A)	124.6(5)	C(16)-C(15)-C(14)	120.55(17)
C(9)-C(7)-Br(3A)	126.4(3)	C(16)-C(15)-H(15)	119.7
N(5)-C(8)-C(7)	107.34(14)	C(14)-C(15)-H(15)	119.7
N(5)-C(8)-H(8)	126.3	C(17)-C(16)-C(15)	120.30(18)
C(7)-C(8)-H(8)	126.3	C(17)-C(16)-H(16)	119.8
N(6)-C(9)-C(7)	109.71(14)	C(15)-C(16)-H(16)	119.8
N(6)-C(9)-H(9)	125.1	C(16)-C(17)-C(18)	119.84(17)
C(7)-C(9)-H(9)	125.1	C(16)-C(17)-H(17)	120.1
C(11)-C(10)-P(1)	119.86(12)	C(18)-C(17)-H(17)	120.1
C(11)-C(10)-H(10A)	107.4	C(17)-C(18)-C(19)	120.25(18)
P(1)-C(10)-H(10A)	107.4	C(17)-C(18)-H(18)	119.9
C(11)-C(10)-H(10B)	107.4	C(19)-C(18)-H(18)	119.9
P(1)-C(10)-H(10B)	107.4	C(18)-C(19)-C(14)	120.56(18)
H(10A)-C(10)-H(10B)	106.9	C(18)-C(19)-H(19)	119.7
C(12)-C(11)-C(10)	114.94(13)	C(14)-C(19)-H(19)	119.7
C(12)-C(11)-H(11A)	108.5	C(25)-C(20)-C(21)	118.41(15)
C(10)-C(11)-H(11A)	108.5	C(25)-C(20)-P(2)	121.89(13)
C(12)-C(11)-H(11B)	108.5	C(21)-C(20)-P(2)	119.59(13)
C(10)-C(11)-H(11B)	108.5	C(22)-C(21)-C(20)	120.61(17)
H(11A)-C(11)-H(11B)	107.5	C(22)-C(21)-H(21)	119.7
C(11)-C(12)-C(13)	112.46(14)	C(20)-C(21)-H(21)	119.7
C(11)-C(12)-H(12A)	109.1	C(23)-C(22)-C(21)	120.44(17)
C(13)-C(12)-H(12A)	109.1	C(23)-C(22)-H(22)	119.8
C(11)-C(12)-H(12B)	109.1	C(21)-C(22)-H(22)	119.8
C(13)-C(12)-H(12B)	109.1	C(22)-C(23)-C(24)	119.30(17)
H(12A)-C(12)-H(12B)	107.8	C(22)-C(23)-H(23)	120.4

C(24)-C(23)-H(23)	120.4	C(33)-C(32)-P(1)	122.53(12)
C(23)-C(24)-C(25)	120.69(19)	C(37)-C(32)-P(1)	119.16(12)
C(23)-C(24)-H(24)	119.7	C(34)-C(33)-C(32)	120.82(16)
C(25)-C(24)-H(24)	119.7	C(34)-C(33)-H(33)	119.6
C(24)-C(25)-C(20)	120.55(17)	C(32)-C(33)-H(33)	119.6
C(24)-C(25)-H(25)	119.7	C(35)-C(34)-C(33)	120.20(17)
C(20)-C(25)-H(25)	119.7	C(35)-C(34)-H(34)	119.9
C(27)-C(26)-C(31)	118.24(15)	C(33)-C(34)-H(34)	119.9
C(27)-C(26)-P(1)	121.07(12)	C(36)-C(35)-C(34)	119.92(16)
C(31)-C(26)-P(1)	120.68(12)	C(36)-C(35)-H(35)	120.0
C(28)-C(27)-C(26)	120.91(16)	C(34)-C(35)-H(35)	120.0
C(28)-C(27)-H(27)	119.5	C(35)-C(36)-C(37)	119.99(16)
C(26)-C(27)-H(27)	119.5	C(35)-C(36)-H(36)	120.0
C(29)-C(28)-C(27)	120.18(17)	C(37)-C(36)-H(36)	120.0
C(29)-C(28)-H(28)	119.9	C(36)-C(37)-C(32)	120.91(16)
C(27)-C(28)-H(28)	119.9	C(36)-C(37)-H(37)	119.5
C(28)-C(29)-C(30)	119.63(17)	C(32)-C(37)-H(37)	119.5
C(28)-C(29)-H(29)	120.2	N(5)-B(1)-N(1)	109.44(14)
C(30)-C(29)-H(29)	120.2	N(5)-B(1)-N(3)	108.91(13)
C(29)-C(30)-C(31)	120.60(17)	N(1)-B(1)-N(3)	106.16(13)
C(29)-C(30)-H(30)	119.7	N(5)-B(1)-H(1)	110.0(10)
C(31)-C(30)-H(30)	119.7	N(1)-B(1)-H(1)	112.9(10)
C(30)-C(31)-C(26)	120.42(16)	N(3)-B(1)-H(1)	109.4(10)
C(30)-C(31)-H(31)	119.8		
C(26)-C(31)-H(31)	119.8		
C(33)-C(32)-C(37)	118.04(15)		

Symmetry transformations used to generate equivalent atoms:

Table A2.39: Anisotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppb)Cl 213d. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	13(1)	9(1)	10(1)	0(1)	3(1)	0(1)
Br(1)	18(1)	41(1)	30(1)	-15(1)	0(1)	-8(1)
Br(2)	33(1)	21(1)	18(1)	0(1)	15(1)	-4(1)
Br(3)	40(1)	16(1)	20(1)	-6(1)	0(1)	10(1)
Br(3A)	58(7)	28(3)	94(7)	-10(3)	53(5)	-5(4)
Cl(1)	22(1)	11(1)	18(1)	-3(1)	8(1)	0(1)
P(1)	14(1)	10(1)	11(1)	1(1)	3(1)	0(1)
P(2)	15(1)	10(1)	13(1)	1(1)	5(1)	-1(1)
N(1)	19(1)	14(1)	12(1)	3(1)	2(1)	1(1)
N(2)	17(1)	12(1)	12(1)	1(1)	2(1)	-1(1)
N(3)	16(1)	20(1)	14(1)	0(1)	0(1)	1(1)
N(4)	16(1)	16(1)	13(1)	0(1)	3(1)	-1(1)
N(5)	15(1)	13(1)	14(1)	2(1)	2(1)	3(1)
N(6)	14(1)	11(1)	14(1)	2(1)	2(1)	1(1)
C(1)	13(1)	30(1)	19(1)	-8(1)	3(1)	-4(1)
C(2)	16(1)	29(1)	16(1)	-2(1)	0(1)	2(1)
C(3)	18(1)	21(1)	18(1)	-5(1)	6(1)	-4(1)
C(4)	22(1)	16(1)	12(1)	-1(1)	7(1)	-5(1)
C(5)	25(1)	16(1)	12(1)	2(1)	4(1)	-2(1)
C(6)	17(1)	14(1)	12(1)	-2(1)	3(1)	-2(1)
C(7)	20(1)	13(1)	19(1)	-3(1)	4(1)	3(1)
C(8)	20(1)	14(1)	20(1)	2(1)	4(1)	4(1)
C(9)	16(1)	13(1)	16(1)	-1(1)	4(1)	0(1)
C(10)	17(1)	14(1)	16(1)	4(1)	2(1)	2(1)
C(11)	21(1)	19(1)	13(1)	5(1)	1(1)	-2(1)
C(12)	23(1)	18(1)	12(1)	1(1)	4(1)	-1(1)
C(13)	19(1)	15(1)	16(1)	4(1)	4(1)	1(1)
C(14)	16(1)	13(1)	21(1)	-2(1)	7(1)	-3(1)
C(15)	18(1)	18(1)	24(1)	-1(1)	6(1)	-1(1)

C(16)	18(1)	19(1)	40(1)	-2(1)	6(1)	2(1)
C(17)	24(1)	26(1)	46(1)	-14(1)	16(1)	0(1)
C(18)	26(1)	33(1)	28(1)	-13(1)	14(1)	-6(1)
C(19)	20(1)	20(1)	22(1)	-3(1)	8(1)	-4(1)
C(20)	19(1)	13(1)	16(1)	0(1)	6(1)	-3(1)
C(21)	23(1)	16(1)	30(1)	-1(1)	13(1)	-2(1)
C(22)	32(1)	14(1)	41(1)	-5(1)	16(1)	-3(1)
C(23)	33(1)	18(1)	45(1)	-7(1)	12(1)	-10(1)
C(24)	20(1)	24(1)	47(1)	-6(1)	7(1)	-7(1)
C(25)	21(1)	17(1)	29(1)	-2(1)	6(1)	-1(1)
C(26)	13(1)	18(1)	13(1)	-1(1)	2(1)	1(1)
C(27)	19(1)	18(1)	19(1)	0(1)	6(1)	0(1)
C(28)	23(1)	25(1)	24(1)	2(1)	10(1)	-3(1)
C(29)	22(1)	33(1)	28(1)	-3(1)	14(1)	1(1)
C(30)	22(1)	24(1)	27(1)	-5(1)	9(1)	5(1)
C(31)	19(1)	18(1)	20(1)	0(1)	5(1)	2(1)
C(32)	15(1)	13(1)	15(1)	-2(1)	5(1)	-2(1)
C(33)	27(1)	17(1)	17(1)	2(1)	1(1)	-4(1)
C(34)	38(1)	22(1)	18(1)	-2(1)	-1(1)	-11(1)
C(35)	33(1)	16(1)	24(1)	-6(1)	9(1)	-7(1)
C(36)	21(1)	14(1)	26(1)	1(1)	8(1)	-1(1)
C(37)	16(1)	15(1)	18(1)	0(1)	5(1)	-1(1)
B(1)	17(1)	17(1)	14(1)	1(1)	2(1)	1(1)

Table A2.40: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Tp^{Br}Ru(dppb)Cl 213d.

	x	y	z	U(eq)
H(2)	168	3972	4605	25
H(3)	1278	2378	6019	22
H(5)	3500	4769	4399	22
H(6)	5316	3276	5667	17
H(8)	1935	5686	6632	22

H(9)	3328	4495	8578	18
H(10A)	5768	2491	8405	19
H(10B)	6848	2952	8727	19
H(11A)	5947	2532	9820	22
H(11B)	6219	3298	9869	22
H(12A)	4284	3538	9283	21
H(12B)	4398	3109	10128	21
H(13A)	3197	2404	9407	20
H(13B)	4122	2228	8865	20
H(15)	830	3758	7339	24
H(16)	-503	4390	7843	31
H(17)	-401	4470	9300	37
H(18)	993	3885	10257	33
H(19)	2296	3223	9760	24
H(21)	3148	1571	7666	27
H(22)	2074	614	7363	34
H(23)	107	624	7302	38
H(24)	-781	1601	7544	37
H(25)	275	2564	7828	27
H(27)	6656	4467	7016	22
H(28)	8031	4391	6198	28
H(29)	8712	3370	5891	32
H(30)	8004	2423	6396	29
H(31)	6617	2488	7204	22
H(33)	6984	4036	9358	25
H(34)	7510	5071	9920	32
H(35)	6665	6005	9216	29
H(36)	5344	5907	7919	24
H(37)	4802	4872	7355	20
H(1)	1735(17)	4878(10)	5272(13)	19

Table A2.41: Crystal data and structure refinement for Tp^{I}Ru(dppm)Cl 215a.

Identification code: Tp^{I}Ru(dppm)Cl **215a**

Empirical formula: C37H35BCl7I3N6P2Ru

Formula weight: 1366.38

Temperature/K: 123(2)

Crystal system: triclinic

Space group: P-1

a/Å: 10.3094(9) b/Å: 14.0030(13) c/Å: 17.2692(16)

α/°: 101.499(2) β/°: 97.677(2) γ/°: 100.169(2)

Volume/Å3: 2367.5(4) Z: 2 ρcalcg/cm3: 1.917

μ/mm 1 2.785: F(000): 1312.0

Crystal size/mm3: 0.380 × 0.050 × 0.020

Radiation: MoKα (λ = 0.71073)

2Θ range for data collection/° 3.036 to 56.848

Index ranges -13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23

Reflections collected 21151

Independent reflections 11448 [Rint = 0.0235, Rsigma = 0.0402]

Data/restraints/parameters 11448/232/608

Goodness-of-fit on F2 1.045

Final R indexes [I>=2σ (I)] R1 = 0.0336, wR2 = 0.0634

Final R indexes [all data] R1 = 0.0520, wR2 = 0.0680

Largest diff. peak/hole / e Å-31.06/-0.96

Table A2.42: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}Ru(dppm)Cl 215a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	110(30)	2160(20)	6676(13)	178(12)
Cl^{2_1}	-1900(20)	2076(16)	5323(10)	142(9)
C^{1_1}	-580(50)	1520(30)	5679(19)	68(3)
Cl^{1_2}	-3111(4)	2044(3)	5495(2)	49.7(9)
Cl^{2_2}	-319(5)	2100(5)	6073(4)	103(2)
C^{1_2}	-1632(8)	1763(11)	5229(6)	68(3)
Cl^{1_3}	150(6)	2122(5)	6568(5)	74.9(19)
Cl^{2_3}	-2340(7)	1986(5)	5527(5)	76.3(19)
C^{1_3}	-901(16)	1456(16)	5668(10)	68(3)
Cl^{1_4}	1390(30)	10180(17)	7096(11)	108(11)
Cl^{2_4}	380(20)	9543(18)	5386(10)	85(7)
C^{1_4}	620(50)	9150(17)	6298(12)	40(9)
Cl^{1_5}	2403.7(14)	10186.7(12)	6552.8(9)	61.0(5)
Cl^{2_5}	-400.8(12)	9205.7(9)	6336.0(8)	45.4(4)
C^{1_5}	1181(4)	9511(4)	6959(3)	35.7(10)
Cl^{1_6}	3193(2)	8930(2)	1764.0(13)	49.8(5)
Cl^{2_6}	293(2)	8636(2)	1526(2)	116.0(11)
C^{1_6}	1807(5)	9165(8)	2202(5)	83(2)
Cl^{1_7}	3109(17)	8910(20)	1868(14)	173(9)
Cl^{2_7}	455(11)	8401(12)	975(10)	142(5)
C^{1_7}	1429(19)	8950(40)	1942(14)	83(2)
I^1	7794.9(2)	5753.9(2)	10227.6(2)	22.14(6)
I^3	3479.4(2)	11138.5(2)	9325.1(2)	23.00(6)
I^2	-1817.6(2)	4292.0(2)	7830.8(2)	25.03(6)
Ru^1	3758.8(2)	6768.6(2)	7607.1(2)	11.21(6)
Cl^1	2327.8(8)	7252.4(6)	6603.6(4)	17.97(16)
P^1	5646.2(8)	7206.2(6)	7079.7(4)	13.89(16)
P^2	4019.1(8)	5394.6(6)	6746.5(4)	13.57(16)
N^2	2009(3)	6100(2)	7972.4(14)	14.8(5)
N^3	1849(3)	6354.4(19)	8753.1(14)	13.8(5)
N^1	4806(3)	6466.3(18)	8620.9(14)	12.5(5)
N^5	3617(3)	8121.2(19)	8409.6(14)	14.5(5)
N^4	3295(3)	8069.0(19)	9141.7(14)	13.3(5)
N^6	4279(2)	6606.5(18)	9312.2(14)	12.1(5)
C^{32}	3471(3)	9633(2)	9066.5(18)	17.2(7)
C^4	4187(3)	4254(2)	7059.2(18)	16.9(7)
C^{16}	5804(3)	7958(3)	6331.1(18)	19.6(7)
C^{31}	3724(3)	9065(2)	8356.3(18)	15.9(6)
C^{28}	668(3)	5851(2)	8848.5(18)	16.0(6)
C^{29}	41(3)	5250(2)	8109.4(18)	15.8(6)

C^{30}	914(3)	5432(2)	7581.6(18)	16.3(6)
C^{1}	6167(3)	6120(2)	9600.8(18)	16.1(6)
C^{22}	7275(3)	7696(2)	7724.7(18)	17.0(7)
C^{3}	5677(3)	5926(2)	6548.6(18)	17.7(7)
C^{23}	8442(3)	7429(3)	7511(2)	22.6(7)
C^{11}	1958(4)	4064(3)	5623(2)	30.9(9)
C^{14}	1995(4)	5220(3)	4497.6(19)	29.6(9)
C^{10}	2919(3)	4944(2)	5777.1(17)	18.3(7)
C^{15}	2928(3)	5525(3)	5207.3(18)	22.6(7)
C^{33}	3211(3)	8975(2)	9548.3(18)	15.4(6)
C^{5}	4909(3)	3607(3)	6666(2)	23.7(7)
C^{34}	5087(3)	6392(2)	9906.8(17)	14.8(6)
C^{2}	5947(3)	6170(2)	8796.7(18)	15.6(6)
C^{17}	6403(4)	7699(3)	5666(2)	28.1(8)
C^{9}	3565(4)	3995(3)	7678.0(19)	23.3(7)
C^{27}	7355(4)	8376(3)	8441(2)	27.4(8)
C^{24}	9669(4)	7838(3)	8008(2)	28.8(8)
C^{6}	5019(4)	2732(3)	6906(2)	33.5(9)
C^{18}	6650(4)	8348(3)	5166(2)	34.3(9)
C^{13}	1055(4)	4353(3)	4357(2)	34.2(10)
C^{21}	5447(5)	8873(3)	6470(3)	38.9(10)
C^{7}	4392(4)	2483(3)	7517(2)	35.4(10)
C^{8}	3655(4)	3103(3)	7897(2)	32.3(9)
C^{19}	6312(4)	9258(3)	5328(2)	38.9(10)
C^{25}	9734(4)	8526(3)	8710(2)	39.4(10)
C^{26}	8597(4)	8798(4)	8932(2)	42.6(11)
C^{12}	1041(5)	3776(3)	4907(3)	45.4(12)
C^{20}	5704(5)	9526(3)	5977(3)	46.9(12)
B^{1}	3016(4)	7049(3)	9371(2)	15.5(7)

Table A2.43: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{I}Ru(dppm)Cl$ 215a. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	250(20)	171(18)	98(9)	25(9)	-26(10)	53(15)
Cl^{2_1}	215(16)	161(16)	72(8)	6(8)	-13(10)	154(15)
C^{1_1}	80(6)	58(5)	73(5)	23(4)	16(4)	27(5)
Cl^{1_2}	35.8(18)	62(2)	56.8(19)	23.8(15)	17.8(16)	4.6(17)
Cl^{2_2}	61(3)	163(6)	98(4)	94(4)	-7(3)	4(3)
C^{1_2}	80(6)	58(5)	73(5)	23(4)	16(4)	27(5)
Cl^{1_3}	73(3)	58(3)	86(4)	34(3)	14(3)	-26(3)
Cl^{2_3}	93(4)	47(3)	93(5)	20(3)	20(4)	17(3)

C^{1_3}	80(6)	58(5)	73(5)	23(4)	16(4)	27(5)
Cl^{1_4}	170(30)	48(12)	77(11)	3(9)	-44(13)	22(14)
Cl^{2_4}	83(14)	112(16)	59(9)	31(9)	17(9)	3(12)
C^{1_4}	20(20)	49(15)	49(12)	4(10)	21(11)	5(14)
Cl^{1_5}	39.3(8)	68.8(10)	71.5(10)	28.9(8)	6.1(7)	-9.7(7)
Cl^{2_5}	30.5(7)	46.1(7)	55.6(7)	10.2(6)	-0.8(5)	5.0(5)
C^{1_5}	27(2)	36(3)	45(3)	11(2)	5.3(19)	6(2)
Cl^{1_6}	47.1(11)	65.8(13)	39.7(8)	5.6(8)	8.4(7)	26.4(9)
Cl^{2_6}	44.8(13)	100(2)	173(3)	-11(2)	-6.8(17)	2.6(13)
C^{1_6}	32(4)	90(7)	113(6)	-2(5)	22(4)	-1(4)
Cl^{1_7}	98(9)	220(20)	196(18)	17(15)	52(9)	45(10)
Cl^{2_7}	54(6)	137(11)	201(11)	-25(9)	4(7)	15(6)
C^{1_7}	32(4)	90(7)	113(6)	-2(5)	22(4)	-1(4)
I^{1}	15.88(11)	33.59(13)	21.3(1)	12.95(9)	2.03(8)	9.96(10)
I^{3}	27.83(13)	14.04(11)	26.08(11)	1.72(8)	1.84(9)	6.99(9)
I^{2}	14.80(11)	27.70(13)	27.92(11)	1.81(9)	4.03(9)	-2.92(9)
Ru^{1}	10.53(12)	12.90(12)	10.39(10)	2.34(9)	1.94(9)	3.27(9)
Cl^{1}	17.6(4)	21.9(4)	15.0(3)	4.8(3)	-0.1(3)	7.4(3)
P^{1}	11.8(4)	16.9(4)	13.4(3)	3.8(3)	2.6(3)	3.3(3)
P^{2}	13.5(4)	14.6(4)	12.1(3)	1.3(3)	2.3(3)	3.7(3)
N^{2}	16.0(14)	17.5(14)	11.0(11)	2.8(10)	2.2(10)	4.4(11)
N^{3}	12.6(13)	17.5(14)	11.8(11)	2.5(10)	3(1)	4.7(11)
N^{1}	15.5(14)	11.0(13)	11.9(11)	3.4(9)	3.2(10)	3.5(10)
N^{5}	15.9(14)	16.1(14)	11.8(11)	2.6(10)	2.1(10)	5.2(11)
N^{4}	10.4(13)	14.6(13)	14.5(12)	2.7(10)	1.8(10)	3(1)
N^{6}	12.3(13)	12.5(13)	11.7(11)	3.7(10)	2.5(10)	1.4(10)
C^{32}	16.1(17)	15.3(16)	18.1(14)	-0.6(12)	-0.7(12)	5.7(13)
C^{4}	18.0(17)	13.3(16)	17.0(14)	0.1(12)	-1.9(12)	4.6(13)
C^{16}	13.4(16)	28.0(19)	17.9(15)	9.7(13)	1.2(12)	1.6(14)
C^{31}	14.7(16)	15.2(16)	18.2(15)	4.4(12)	4.2(12)	2.3(13)
C^{28}	12.2(16)	19.3(17)	19.4(15)	7.3(13)	4.9(12)	5.9(13)
C^{29}	8.0(15)	16.0(16)	23.5(15)	6.3(13)	2.6(12)	0.7(12)
C^{30}	14.8(16)	15.0(16)	16.8(14)	1.4(12)	-1.4(12)	3.2(13)
C^{1}	14.5(16)	16.9(16)	16.7(14)	6.2(12)	0.0(12)	2.6(13)
C^{22}	14.7(16)	19.9(17)	17.1(14)	6.9(13)	2.2(12)	2.9(13)
C^{3}	16.7(17)	18.0(17)	19.1(15)	3.5(13)	5.3(13)	4.8(13)
C^{23}	19.9(18)	25.0(19)	24.1(16)	5.8(14)	5.0(14)	7.1(15)
C^{11}	33(2)	23(2)	31.1(19)	6.5(15)	-9.8(16)	3.0(16)
C^{14}	37(2)	43(2)	14.9(15)	6.4(15)	6.4(15)	23.2(19)
C^{10}	20.9(18)	20.6(17)	13.1(14)	-1.7(12)	2.1(12)	10.3(14)
C^{15}	21.8(19)	29(2)	18.1(15)	3.0(14)	5.3(13)	8.7(15)
C^{33}	10.6(15)	17.6(16)	15.9(14)	-1.0(12)	3.1(12)	2.6(12)
C^{5}	21.7(19)	19.3(18)	27.7(17)	1.2(14)	2.7(14)	4.2(14)
C^{34}	15.1(16)	13.6(15)	13.8(13)	2.7(11)	0.1(12)	0.4(12)

C^{2}	13.4(16)	17.5(16)	17.5(14)	5.9(12)	4.1(12)	4.1(13)
C^{17}	31(2)	32(2)	21.5(16)	7.2(15)	9.1(15)	4.0(17)
C^{9}	29(2)	19.0(18)	21.5(16)	2.6(13)	2.8(14)	7.8(15)
C^{27}	15.1(18)	36(2)	25.8(17)	-3.1(15)	4.0(14)	2.8(16)
C^{24}	12.9(18)	37(2)	40(2)	15.1(17)	3.7(15)	8.6(16)
C^{6}	34(2)	23(2)	40(2)	-3.6(16)	-4.2(17)	14.7(17)
C^{18}	32(2)	48(3)	21.2(17)	11.1(17)	8.3(16)	-1.0(19)
C^{13}	37(2)	37(2)	21.5(17)	-6.8(16)	-12.5(16)	19.2(19)
C^{21}	54(3)	37(2)	43(2)	23.3(19)	30(2)	22(2)
C^{7}	46(3)	22(2)	35(2)	7.6(16)	-9.1(18)	8.2(18)
C^{8}	43(2)	30(2)	23.6(18)	9.2(16)	1.5(17)	6.8(19)
C^{19}	40(3)	49(3)	35(2)	29(2)	8.7(18)	5(2)
C^{25}	15(2)	57(3)	39(2)	8(2)	-6.2(16)	-0.2(19)
C^{26}	22(2)	58(3)	32(2)	-13.3(19)	0.5(16)	-2(2)
C^{12}	47(3)	31(2)	43(2)	0.1(19)	-25(2)	0(2)
C^{20}	63(3)	41(3)	58(3)	33(2)	30(2)	28(2)
B^{1}	17.1(19)	17.2(18)	14.1(15)	4.9(13)	3.4(14)	6.6(15)

Table A2.44: Bond Lengths for Tp^{i}Ru(dppm)Cl 215a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.762(8)	N^{5}	C^{31}	1.329(4)
Cl^{2_1}	C^{1_1}	1.775(8)	N^{5}	N^{4}	1.362(3)
Cl^{1_2}	C^{1_2}	1.737(8)	N^{4}	C^{33}	1.346(4)
Cl^{2_2}	C^{1_2}	1.775(8)	N^{4}	B^{1}	1.546(4)
Cl^{1_3}	C^{1_3}	1.753(8)	N^{6}	C^{34}	1.350(4)
Cl^{2_3}	C^{1_3}	1.781(8)	N^{6}	B^{1}	1.545(4)
Cl^{1_4}	C^{1_4}	1.765(9)	C^{32}	C^{33}	1.375(5)
Cl^{2_4}	C^{1_4}	1.771(9)	C^{32}	C^{31}	1.406(4)
Cl^{1_5}	C^{1_5}	1.749(4)	C^{4}	C^{9}	1.393(5)
Cl^{2_5}	C^{1_5}	1.761(4)	C^{4}	C^{5}	1.402(4)
Cl^{1_6}	C^{1_6}	1.755(5)	C^{16}	C^{21}	1.380(5)
Cl^{2_6}	C^{1_6}	1.763(6)	C^{16}	C^{17}	1.391(5)
Cl^{1_7}	C^{1_7}	1.763(8)	C^{28}	C^{29}	1.384(4)
Cl^{2_7}	C^{1_7}	1.775(8)	C^{29}	C^{30}	1.392(4)
I^{1}	C^{1}	2.072(3)	C^{1}	C^{34}	1.375(4)
I^{3}	C^{32}	2.064(3)	C^{1}	C^{2}	1.395(4)
I^{2}	C^{29}	2.072(3)	C^{22}	C^{27}	1.385(4)
Ru^{1}	N^{1}	2.089(2)	C^{22}	C^{23}	1.395(5)
Ru^{1}	N^{2}	2.115(3)	C^{23}	C^{24}	1.386(5)
Ru^{1}	N^{5}	2.153(2)	C^{11}	C^{10}	1.392(5)
Ru^{1}	P^{2}	2.2651(8)	C^{11}	C^{12}	1.393(5)
Ru^{1}	P^{1}	2.2947(9)	C^{14}	C^{13}	1.370(6)

Ru[1]	Cl[1]	2.4035(8)	C[14]	C[15]	1.393(5)
P[1]	C[22]	1.822(3)	C[10]	C[15]	1.396(5)
P[1]	C[16]	1.829(3)	C[5]	C[6]	1.388(5)
P[1]	C[3]	1.851(3)	C[17]	C[18]	1.388(5)
P[1]	P[2]	2.6903(12)	C[9]	C[8]	1.390(5)
P[2]	C[4]	1.813(3)	C[27]	C[26]	1.397(5)
P[2]	C[10]	1.818(3)	C[24]	C[25]	1.376(6)
P[2]	C[3]	1.844(3)	C[6]	C[7]	1.379(6)
N[2]	C[30]	1.333(4)	C[18]	C[19]	1.365(6)
N[2]	N[3]	1.364(3)	C[13]	C[12]	1.365(6)
N[3]	C[28]	1.342(4)	C[21]	C[20]	1.384(6)
N[3]	B[1]	1.537(4)	C[7]	C[8]	1.379(6)
N[1]	C[2]	1.332(4)	C[19]	C[20]	1.377(6)
N[1]	N[6]	1.370(3)	C[25]	C[26]	1.373(6)

Table A2.45: Bond Angles for Tp^{I}Ru(dppm)Cl 215a.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl[1_1]	C[1_1]	Cl[2_1]	108.9(11)	N[5]	N[4]	B[1]	119.8(2)
Cl[1_2]	C[1_2]	Cl[2_2]	111.3(6)	C[34]	N[6]	N[1]	109.9(2)
Cl[1_3]	C[1_3]	Cl[2_3]	109.3(6)	C[34]	N[6]	B[1]	127.9(2)
Cl[1_4]	C[1_4]	Cl[2_4]	110.1(11)	N[1]	N[6]	B[1]	121.9(2)
Cl[1_5]	C[1_5]	Cl[2_5]	112.2(2)	C[33]	C[32]	C[31]	105.6(3)
Cl[1_6]	C[1_6]	Cl[2_6]	111.5(4)	C[33]	C[32]	I[3]	127.4(2)
Cl[1_7]	C[1_7]	Cl[2_7]	107.3(10)	C[31]	C[32]	I[3]	127.0(2)
N[1]	Ru[1]	N[2]	86.00(10)	C[9]	C[4]	C[5]	119.1(3)
N[1]	Ru[1]	N[5]	85.08(9)	C[9]	C[4]	P[2]	120.4(2)
N[2]	Ru[1]	N[5]	86.10(10)	C[5]	C[4]	P[2]	120.5(3)
N[1]	Ru[1]	P[2]	95.01(7)	C[21]	C[16]	C[17]	117.9(3)
N[2]	Ru[1]	P[2]	97.25(7)	C[21]	C[16]	P[1]	119.0(3)
N[5]	Ru[1]	P[2]	176.65(8)	C[17]	C[16]	P[1]	122.8(3)
N[1]	Ru[1]	P[1]	94.06(7)	N[5]	C[31]	C[32]	109.6(3)
N[2]	Ru[1]	P[1]	169.53(7)	N[3]	C[28]	C[29]	107.7(3)
N[5]	Ru[1]	P[1]	104.34(7)	C[28]	C[29]	C[30]	105.6(3)
P[2]	Ru[1]	P[1]	72.31(3)	C[28]	C[29]	I[2]	127.7(2)
N[1]	Ru[1]	Cl[1]	169.82(7)	C[30]	C[29]	I[2]	126.7(2)
N[2]	Ru[1]	Cl[1]	87.71(7)	N[2]	C[30]	C[29]	109.9(3)
N[5]	Ru[1]	Cl[1]	86.52(7)	C[34]	C[1]	C[2]	105.7(3)
P[2]	Ru[1]	Cl[1]	93.71(3)	C[34]	C[1]	I[1]	126.4(2)
P[1]	Ru[1]	Cl[1]	93.58(3)	C[2]	C[1]	I[1]	127.9(2)
C[22]	P[1]	C[16]	99.79(15)	C[27]	C[22]	C[23]	119.2(3)
C[22]	P[1]	C[3]	106.29(15)	C[27]	C[22]	P[1]	118.6(3)
C[16]	P[1]	C[3]	105.32(15)	C[23]	C[22]	P[1]	122.2(2)

C^{22}	P^{1}	Ru^{1}	121.09(10)	P^{2}	C^{3}	P^{1}	93.45(14)
C^{16}	P^{1}	Ru^{1}	125.98(11)	C^{24}	C^{23}	C^{22}	120.6(3)
C^{3}	P^{1}	Ru^{1}	95.94(11)	C^{10}	C^{11}	C^{12}	119.8(4)
C^{22}	P^{1}	P^{2}	131.10(11)	C^{13}	C^{14}	C^{15}	120.3(4)
C^{16}	P^{1}	P^{2}	122.26(11)	C^{11}	C^{10}	C^{15}	118.8(3)
C^{3}	P^{1}	P^{2}	43.17(10)	C^{11}	C^{10}	P^{2}	120.4(3)
Ru^{1}	P^{1}	P^{2}	53.34(2)	C^{15}	C^{10}	P^{2}	120.5(3)
C^{4}	P^{2}	C^{10}	102.94(15)	C^{14}	C^{15}	C^{10}	120.2(4)
C^{4}	P^{2}	C^{3}	106.02(15)	N^{4}	C^{33}	C^{32}	107.7(3)
C^{10}	P^{2}	C^{3}	106.65(15)	C^{6}	C^{5}	C^{4}	119.9(3)
C^{4}	P^{2}	Ru^{1}	122.38(10)	N^{6}	C^{34}	C^{1}	107.8(3)
C^{10}	P^{2}	Ru^{1}	119.80(10)	N^{1}	C^{2}	C^{1}	110.2(3)
C^{3}	P^{2}	Ru^{1}	97.16(10)	C^{18}	C^{17}	C^{16}	120.9(4)
C^{4}	P^{2}	P^{1}	132.24(11)	C^{8}	C^{9}	C^{4}	120.3(3)
C^{10}	P^{2}	P^{1}	119.24(12)	C^{22}	C^{27}	C^{26}	119.9(3)
C^{3}	P^{2}	P^{1}	43.39(10)	C^{25}	C^{24}	C^{23}	119.5(3)
Ru^{1}	P^{2}	P^{1}	54.35(2)	C^{7}	C^{6}	C^{5}	120.3(3)
C^{30}	N^{2}	N^{3}	106.8(2)	C^{19}	C^{18}	C^{17}	119.9(4)
C^{30}	N^{2}	Ru^{1}	133.1(2)	C^{12}	C^{13}	C^{14}	120.1(3)
N^{3}	N^{2}	Ru^{1}	120.08(19)	C^{16}	C^{21}	C^{20}	121.3(4)
C^{28}	N^{3}	N^{2}	110.1(2)	C^{6}	C^{7}	C^{8}	120.4(4)
C^{28}	N^{3}	B^{1}	130.9(3)	C^{7}	C^{8}	C^{9}	120.0(4)
N^{2}	N^{3}	B^{1}	118.8(2)	C^{18}	C^{19}	C^{20}	120.2(4)
C^{2}	N^{1}	N^{6}	106.5(2)	C^{26}	C^{25}	C^{24}	120.9(4)
C^{2}	N^{1}	Ru^{1}	135.8(2)	C^{25}	C^{26}	C^{27}	119.9(4)
N^{6}	N^{1}	Ru^{1}	117.70(18)	C^{13}	C^{12}	C^{11}	120.9(4)
C^{31}	N^{5}	N^{4}	107.0(2)	C^{19}	C^{20}	C^{21}	119.7(4)
C^{31}	N^{5}	Ru^{1}	134.5(2)	N^{3}	B^{1}	N^{6}	108.3(2)
N^{4}	N^{5}	Ru^{1}	118.53(19)	N^{3}	B^{1}	N^{4}	108.5(2)
C^{33}	N^{4}	N^{5}	110.2(2)	N^{6}	B^{1}	N^{4}	107.4(3)
C^{33}	N^{4}	B^{1}	129.9(3)				

Table A2.46: Torsion Angles for Tp^{I}Ru(dppm)Cl 215a.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C^{30}	N^{2}	N^{3}	C^{28}	0.1(3)	C^{3}	P^{2}	C^{10}	C^{11}	142.1(3)
Ru^{1}	N^{2}	N^{3}	C^{28}	179.3(2)	Ru^{1}	P^{2}	C^{10}	C^{11}	-109.2(3)
C^{30}	N^{2}	N^{3}	B^{1}	174.7(3)	P^{1}	P^{2}	C^{10}	C^{11}	-172.5(2)
Ru^{1}	N^{2}	N^{3}	B^{1}	-6.1(3)	C^{4}	P^{2}	C^{10}	C^{15}	-156.0(3)
C^{31}	N^{5}	N^{4}	C^{33}	-0.5(3)	C^{3}	P^{2}	C^{10}	C^{15}	-44.6(3)
Ru^{1}	N^{5}	N^{4}	C^{33}	-178.02(19)	Ru^{1}	P^{2}	C^{10}	C^{15}	64.1(3)
C^{31}	N^{5}	N^{4}	B^{1}	176.4(3)	P^{1}	P^{2}	C^{10}	C^{15}	0.8(3)
Ru^{1}	N^{5}	N^{4}	B^{1}	-1.1(3)	C^{13}	C^{14}	C^{15}	C^{10}	0.6(5)

C2	N1	N6	C34	-0.4(3)	C11	C10	C15	C14	-0.4(5)
Ru1	N1	N6	C34	-179.1(2)	P2	C10	C15	C14	-173.8(2)
C2	N1	N6	B1	174.1(3)	N5	N4	C33	C32	0.6(3)
Ru1	N1	N6	B1	-4.7(3)	B1	N4	C33	C32	-175.9(3)
C10	P2	C4	C9	-108.0(3)	C31	C32	C33	N4	-0.5(3)
C3	P2	C4	C9	140.1(3)	I3	C32	C33	N4	179.2(2)
Ru1	P2	C4	C9	30.5(3)	C9	C4	C5	C6	-1.3(5)
P1	P2	C4	C9	99.7(3)	P2	C4	C5	C6	-179.4(3)
C10	P2	C4	C5	70.0(3)	N1	N6	C34	C1	0.8(3)
C3	P2	C4	C5	-41.8(3)	B1	N6	C34	C1	-173.2(3)
Ru1	P2	C4	C5	-151.4(2)	C2	C1	C34	N6	-0.9(3)
P1	P2	C4	C5	-82.3(3)	I1	C1	C34	N6	177.6(2)
C22	P1	C16	C21	-87.8(3)	N6	N1	C2	C1	-0.2(3)
C3	P1	C16	C21	162.2(3)	Ru1	N1	C2	C1	178.2(2)
Ru1	P1	C16	C21	52.8(4)	C34	C1	C2	N1	0.7(4)
P2	P1	C16	C21	118.3(3)	I1	C1	C2	N1	-177.8(2)
C22	P1	C16	C17	85.2(3)	C21	C16	C17	C18	1.0(6)
C3	P1	C16	C17	-24.9(3)	P1	C16	C17	C18	-172.0(3)
Ru1	P1	C16	C17	-134.2(3)	C5	C4	C9	C8	-0.4(5)
P2	P1	C16	C17	-68.7(3)	P2	C4	C9	C8	177.7(3)
N4	N5	C31	C32	0.2(3)	C23	C22	C27	C26	1.1(6)
Ru1	N5	C31	C32	177.1(2)	P1	C22	C27	C26	-177.2(3)
C33	C32	C31	N5	0.2(4)	C22	C23	C24	C25	-1.1(6)
I3	C32	C31	N5	-179.5(2)	C4	C5	C6	C7	1.7(6)
N2	N3	C28	C29	0.1(3)	C16	C17	C18	C19	0.4(6)
B1	N3	C28	C29	-173.7(3)	C15	C14	C13	C12	-0.9(6)
N3	C28	C29	C30	-0.1(4)	C17	C16	C21	C20	-1.7(6)
N3	C28	C29	I2	-179.4(2)	P1	C16	C21	C20	171.7(4)
N3	N2	C30	C29	-0.2(3)	C5	C6	C7	C8	-0.3(6)
Ru1	N2	C30	C29	-179.3(2)	C6	C7	C8	C9	-1.4(6)
C28	C29	C30	N2	0.2(4)	C4	C9	C8	C7	1.8(6)
I2	C29	C30	N2	179.4(2)	C17	C18	C19	C20	-1.1(7)
C16	P1	C22	C27	101.7(3)	C23	C24	C25	C26	1.2(7)
C3	P1	C22	C27	-149.0(3)	C24	C25	C26	C27	-0.1(7)
Ru1	P1	C22	C27	-41.4(3)	C22	C27	C26	C25	-1.0(7)
P2	P1	C22	C27	-107.9(3)	C14	C13	C12	C11	1.2(7)
C16	P1	C22	C23	-76.6(3)	C10	C11	C12	C13	-1.0(7)
C3	P1	C22	C23	32.7(3)	C18	C19	C20	C21	0.5(7)
Ru1	P1	C22	C23	140.3(2)	C16	C21	C20	C19	1.0(8)
P2	P1	C22	C23	73.8(3)	C28	N3	B1	N6	120.3(3)
C4	P2	C3	P1	-135.58(14)	N2	N3	B1	N6	-53.0(3)
C10	P2	C3	P1	115.20(15)	C28	N3	B1	N4	-123.5(3)
Ru1	P2	C3	P1	-8.88(12)	N2	N3	B1	N4	63.2(3)
C22	P1	C3	P2	133.58(14)	C34	N6	B1	N3	-125.7(3)

C^{16}	P^{1}	C^{3}	P^{2}	-121.12(15)	N^{1}	N^{6}	B^{1}	N^{3}	60.9(4)
Ru^{1}	P^{1}	C^{3}	P^{2}	8.74(12)	C^{34}	N^{6}	B^{1}	N^{4}	117.3(3)
C^{27}	C^{22}	C^{23}	C^{24}	0.0(5)	N^{1}	N^{6}	B^{1}	N^{4}	-56.1(3)
P^{1}	C^{22}	C^{23}	C^{24}	178.2(3)	C^{33}	N^{4}	B^{1}	N^{3}	117.6(3)
C^{12}	C^{11}	C^{10}	C^{15}	0.6(5)	N^{5}	N^{4}	B^{1}	N^{3}	-58.6(3)
C^{12}	C^{11}	C^{10}	P^{2}	174.0(3)	C^{33}	N^{4}	B^{1}	N^{6}	-125.6(3)
C^{4}	P^{2}	C^{10}	C^{11}	30.7(3)	N^{5}	N^{4}	B^{1}	N^{6}	58.2(3)

Table A2.47: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Tp^{i}Ru(dppm)Cl 215a.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	-935	812	5656	81
H^{1AB_1}	113	1566	5337	81
H^{1A_2}	-1372	2124	4817	81
H^{1AB_2}	-1776	1040	4993	81
H^{1A_3}	-1177	749	5687	81
H^{1AB_3}	-415	1485	5213	81
H^{1A_4}	-248	8833	6407	47
H^{1AB_4}	1198	8652	6254	47
H^{1A_5}	1116	9909	7490	43
H^{1AB_5}	1453	8890	7042	43
H^{1A_6}	1883	9894	2373	100
H^{1AB_6}	1801	8885	2685	100
H^{1A_7}	1331	9642	2120	100
H^{1AB_7}	1131	8567	2336	100
H^{31}	3939	9317	7907	19
H^{28}	326	5899	9336	19
H^{30}	753	5127	7025	20
H^{3A}	5701	5864	5970	21
H^{3AB}	6407	5656	6803	21
H^{23}	8396	6963	7021	27
H^{11}	1929	3661	6006	37
H^{14}	2010	5615	4110	36
H^{15}	3572	6131	5304	27
H^{33}	3008	9133	10074	18
H^{5}	5322	3767	6235	28
H^{34}	4937	6423	10441	18
H^{2}	6526	6016	8428	19
H^{17}	6645	7068	5551	34
H^{9}	3078	4430	7951	28
H^{27}	6566	8556	8598	33
H^{24}	10458	7645	7864	35

H^{6}	5529	2303	6649	40
H^{18}	7055	8160	4712	41
H^{13}	412	4153	3875	41
H^{21}	5015	9059	6913	47
H^{7}	4468	1881	7677	42
H^{8}	3208	2921	8309	39
H^{19}	6496	9707	4991	47
H^{25}	10576	8816	9046	47
H^{26}	8655	9273	9419	51
H^{12}	396	3169	4801	55
H^{20}	5463	10158	6087	56
$H^{1'}$	2780(30)	7140(30)	10000(20)	19

Table A2.48: Atomic Occupancy for Tp^{i}Ru(dppm)Cl 215a.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl^{1_1}	0.2	Cl^{2_1}	0.2	C^{1_1}	0.2
H^{1A_1}	0.2	H^{1AB_1}	0.2	Cl^{1_2}	0.4
Cl^{2_2}	0.4	C^{1_2}	0.4	H^{1A_2}	0.4
H^{1AB_2}	0.4	Cl^{1_3}	0.4	Cl^{2_3}	0.4
C^{1_3}	0.4	H^{1A_3}	0.4	H^{1AB_3}	0.4
Cl^{1_4}	0.079(3)	Cl^{2_4}	0.079(3)	C^{1_4}	0.079(3)
H^{1A_4}	0.079(3)	H^{1AB_4}	0.079(3)	Cl^{1_5}	0.921(3)
Cl^{2_5}	0.921(3)	C^{1_5}	0.921(3)	H^{1A_5}	0.921(3)
H^{1AB_5}	0.921(3)	Cl^{1_6}	0.8	Cl^{2_6}	0.8
C^{1_6}	0.8	H^{1A_6}	0.8	H^{1AB_6}	0.8
Cl^{1_7}	0.2	Cl^{2_7}	0.2	C^{1_7}	0.2
H^{1A_7}	0.2	H^{1AB_7}	0.2		

Table A2.49: Crystal data and structure refinement for Tp^{I}Ru(dppe)Cl 215b.

Identification code: Tp^{I}Ru(dppe)Cl **215b**

Empirical formula: C35H31BClI3N6P2Ru

Formula weight: 1125.63

Temperature/K: 123(2)

Crystal system: monoclinic

Space group: P21/c

a/Å: 10.3780(4) b/Å: 23.3172(9) c/Å:15.8532(6)

α/°: 90 β/°: 95.644(2)γ/°: 90

Volume/Å3: 3817.7(3) Z:4 ρcalcg/cm3: 1.958

μ/mm 1 24.082 F(000) 2152.0

Crystal size/mm3 0.240 × 0.030 × 0.020

Radiation CuKα (λ = 1.54178)

2Θ range for data collection/° 6.764 to 133.24

Index ranges -12 ≤ h ≤ 9, -27 ≤ k ≤ 24, -18 ≤ l ≤ 18

Reflections collected 30433

Independent reflections 6706 [Rint = 0.0373, Rsigma = 0.0314]

Data/restraints/parameters 6706/0/449

Goodness-of-fit on F2 1.045

Final R indexes [I>=2σ (I)] R1 = 0.0231, wR2 = 0.0600

Final R indexes [all data] R1 = 0.0249, wR2 = 0.0610

Largest diff. peak/hole / e Å-30.61/-0.55

Table A2.50: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{I}Ru(dppe)Cl **215b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C^1	5448(3)	6465.8(13)	2861.0(18)	18.4(6)
C^2	6332(3)	6625.2(12)	2300.2(19)	19.2(6)
C^3	5880(3)	6388.9(13)	1534.7(18)	18.4(6)
C^4	4087(3)	4654.5(13)	913.0(18)	19.6(6)
C^5	3999(3)	4208.4(12)	1466.3(19)	18.2(6)
C^6	3599(3)	4453.2(13)	2203.9(18)	18.2(6)
C^7	1633(3)	6247.7(13)	443.8(17)	19.8(6)
C^8	482(3)	6366.3(13)	763.7(18)	19.7(6)
C^9	652(3)	6208.9(12)	1615.4(18)	17.7(6)
C^{10}	3425(3)	6624.2(13)	4663.1(18)	18.4(6)
C^{11}	3741(3)	6211.1(14)	5290.1(19)	24.1(7)
C^{12}	4570(3)	6337.4(15)	6001(2)	28.5(7)
C^{13}	5130(3)	6874.1(17)	6099(2)	31.9(8)
C^{14}	4850(4)	7281.7(17)	5481(2)	34.1(8)
C^{15}	3987(4)	7164.0(14)	4770(2)	27.1(7)
C^{16}	2004(3)	7130.5(13)	3215.1(18)	19.4(6)
C^{17}	2531(3)	7274.2(14)	2464.7(19)	22.0(6)
C^{18}	2336(3)	7813.6(14)	2107(2)	28.2(7)
C^{19}	1626(4)	8218.2(15)	2492(2)	30.0(8)
C^{20}	1057(4)	8081.6(14)	3223(2)	29.4(7)
C^{21}	1247(3)	7540.0(14)	3581(2)	25.0(7)
C^{22}	812(3)	6252.3(13)	4157.9(18)	19.3(6)
C^{23}	771(3)	5612.2(13)	4342.7(18)	19.1(6)
C^{24}	1586(3)	4494.8(13)	3922.6(18)	19.9(6)
C^{25}	2418(3)	4443.5(14)	4667.9(19)	22.2(7)
C^{26}	2599(3)	3919.7(15)	5075(2)	27.6(7)
C^{27}	1980(3)	3433.1(15)	4737(2)	29.2(8)
C^{28}	1189(4)	3471.7(14)	3982(2)	28.1(7)
C^{29}	992(3)	3999.7(14)	3579.1(19)	24.0(7)
C^{30}	-182(3)	5084.1(13)	2726.5(18)	20.3(6)
C^{31}	-37(3)	4901.4(14)	1896(2)	26.6(7)
C^{32}	-1113(4)	4797.2(16)	1333(2)	34.8(8)
C^{33}	-2344(4)	4866.6(17)	1583(3)	40.7(9)
C^{34}	-2512(4)	5049.1(18)	2394(3)	41.7(9)
C^{35}	-1425(3)	5156.1(15)	2971(2)	29.9(7)
B^1	3808(3)	5774.5(15)	1021(2)	18.3(7)
N^1	4779(2)	6101.0(11)	1639.5(14)	17.1(5)
N^2	4512(2)	6150.2(10)	2463.4(14)	17.2(5)
N^3	3772(2)	5142.4(11)	1301.4(14)	17.8(5)
N^4	3458(2)	5014.5(11)	2095.9(14)	17.7(5)

N^5	2452(2)	6029.7(10)	1075.1(14)	17.4(5)
N^6	1845(2)	6004.1(10)	1806.1(14)	16.5(5)
P^1	2347.1(7)	6430.7(3)	3715.9(4)	15.35(15)
P^2	1301.1(7)	5203.8(3)	3438.6(4)	15.72(15)
Cl^1	4554.8(7)	5295.0(3)	3915.9(4)	19.01(14)
Ru^1	2936.7(2)	5694.5(2)	2891.4(2)	13.70(6)
I^1	7974.2(2)	7123.8(2)	2595.9(2)	24.78(7)
I^2	4455.9(2)	3357.8(2)	1272.9(2)	26.29(7)
I^3	-1202.7(3)	6650.0(2)	72.8(2)	27.26(11)
$I^{3'}$	-969(18)	6883(13)	289(13)	27.26(11)

Table A2.51: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^lRu(dppe)Cl$ 215b. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C^1	19.4(15)	17.8(15)	17.6(14)	3.0(11)	-0.5(12)	0.8(12)
C^2	16.9(15)	15.4(15)	24.9(15)	3.3(11)	0.3(13)	0.3(12)
C^3	16.7(15)	18.7(16)	20.3(14)	5.5(11)	5.0(12)	2.1(12)
C^4	21.8(16)	22.1(16)	15.3(13)	-3.0(11)	3.0(12)	2.4(13)
C^5	18.1(15)	13.5(14)	22.7(14)	-2.8(11)	1.1(12)	4.4(12)
C^6	20.4(15)	16.7(15)	17.5(14)	-0.7(11)	1.7(12)	1.0(12)
C^7	25.8(17)	21.4(16)	11.7(13)	1.0(11)	-0.5(12)	-0.3(13)
C^8	20.2(16)	20.5(16)	17.5(14)	2.2(11)	-2.1(12)	3.1(13)
C^9	18.4(15)	17.8(15)	17.3(14)	-0.5(11)	4.1(12)	1.7(12)
C^{10}	19.5(16)	21.8(16)	14.3(13)	-2.7(11)	2.9(12)	0.7(12)
C^{11}	28.9(18)	21.9(17)	21.1(15)	-2.5(12)	0.2(13)	1.6(14)
C^{12}	29.5(18)	33.0(19)	21.7(16)	-0.9(13)	-3.9(14)	6.7(15)
C^{13}	28.7(19)	47(2)	18.8(15)	-8.5(14)	-3.7(14)	-4.3(16)
C^{14}	40(2)	35(2)	27.0(17)	-7.2(15)	1.7(16)	-20.2(17)
C^{15}	35.0(19)	27.6(18)	18.6(15)	0.3(12)	1.7(14)	-6.8(15)
C^{16}	21.7(16)	19.0(16)	16.9(14)	-1.1(11)	-1.0(12)	0.8(12)
C^{17}	23.0(17)	21.6(16)	21.4(15)	2.5(12)	2.2(13)	1.0(13)
C^{18}	29.8(19)	25.5(18)	29.6(17)	10.0(13)	5.1(15)	0.5(15)
C^{19}	35(2)	18.7(16)	34.5(18)	7.3(13)	-2.8(15)	4.3(15)
C^{20}	33.6(19)	19.7(17)	34.5(18)	-1.8(13)	1.7(15)	6.9(15)
C^{21}	29.3(18)	21.1(16)	24.8(15)	0.6(12)	4.1(14)	1.4(14)
C^{22}	20.0(16)	22.5(16)	15.9(13)	-0.3(11)	4.7(12)	0.3(13)
C^{23}	23.1(16)	19.5(15)	15.5(13)	-0.4(11)	5.8(12)	-3.0(13)
C^{24}	23.5(16)	19.9(16)	17.0(14)	2.1(11)	5.6(12)	-0.7(13)
C^{25}	21.4(16)	23.2(16)	22.0(15)	1.1(12)	1.8(13)	-4.1(13)
C^{26}	25.5(18)	28.8(18)	28.4(16)	9.6(14)	2.2(14)	2.2(14)
C^{27}	28.8(19)	27.8(18)	32.0(18)	8.8(14)	7.6(15)	4.4(15)

C^{28}	33.8(19)	15.7(16)	35.6(18)	-0.9(13)	7.0(15)	-2.5(14)
C^{29}	27.4(18)	23.1(17)	21.4(15)	0.0(12)	1.5(13)	-2.5(14)
C^{30}	22.0(16)	16.2(15)	21.8(14)	2.0(11)	-1.9(12)	-0.8(12)
C^{31}	30.4(18)	23.6(17)	24.9(16)	-0.5(13)	-1.5(14)	-4.0(14)
C^{32}	42(2)	30.8(19)	28.6(17)	-2.6(14)	-12.4(16)	-7.6(17)
C^{33}	33(2)	39(2)	45(2)	-0.5(17)	-18.5(18)	-6.8(17)
C^{34}	22.4(19)	46(2)	55(2)	1.4(19)	-4.1(17)	1.5(17)
C^{35}	25.5(18)	30.8(19)	32.3(17)	0.3(14)	-2.0(14)	0.6(15)
B^{1}	22.0(18)	20.3(18)	13.3(15)	0.7(12)	5.1(13)	3.1(14)
N^{1}	19.1(13)	17.8(13)	15.3(11)	3.2(9)	5.8(10)	5(1)
N^{2}	18.2(13)	18.6(13)	15.1(11)	0.8(9)	4.1(10)	1.1(10)
N^{3}	19.7(13)	20.1(13)	14.4(11)	-0.2(9)	5.7(10)	2.5(10)
N^{4}	21.5(13)	19.5(13)	12.4(11)	-0.2(9)	3(1)	2.4(10)
N^{5}	21.4(13)	18.1(13)	13.1(11)	0.4(9)	3.3(10)	1.7(10)
N^{6}	20.1(13)	17.5(13)	12.2(11)	-0.9(9)	3.5(10)	1.8(10)
P^{1}	19.4(4)	14.2(4)	12.4(3)	-0.7(3)	1.7(3)	0.7(3)
P^{2}	18.7(4)	15.7(4)	12.8(3)	0.2(3)	1.5(3)	-1.5(3)
Cl^{1}	20.6(4)	19.7(4)	16.2(3)	1.9(2)	-0.8(3)	1.1(3)
Ru^{1}	16.52(12)	14.22(12)	10.47(10)	-0.02(7)	1.94(8)	0.61(8)
I^{1}	20.33(11)	23.19(12)	31.08(12)	-0.15(8)	3.80(8)	-2.87(8)
I^{2}	35.75(13)	18.03(11)	24.89(11)	-2.11(7)	2.05(9)	7.12(8)
I^{3}	21.00(13)	40.6(2)	19.78(13)	7.85(13)	-0.06(10)	6.27(12)
$I^{3'}$	21.00(13)	40.6(2)	19.78(13)	7.85(13)	-0.06(10)	6.27(12)

Table A2.52: Bond Lengths for Tp^{i}Ru(dppe)Cl 215b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C^{1}	N^{2}	1.328(4)	C^{22}	C^{23}	1.522(4)
C^{1}	C^{2}	1.389(4)	C^{22}	P^{1}	1.849(3)
C^{2}	C^{3}	1.373(4)	C^{23}	P^{2}	1.849(3)
C^{2}	I^{1}	2.078(3)	C^{24}	C^{29}	1.394(5)
C^{3}	N^{1}	1.350(4)	C^{24}	C^{25}	1.398(4)
C^{4}	N^{3}	1.349(4)	C^{24}	P^{2}	1.834(3)
C^{4}	C^{5}	1.370(4)	C^{25}	C^{26}	1.385(5)
C^{5}	C^{6}	1.401(4)	C^{26}	C^{27}	1.386(5)
C^{5}	I^{2}	2.069(3)	C^{27}	C^{28}	1.385(5)
C^{6}	N^{4}	1.326(4)	C^{28}	C^{29}	1.393(5)
C^{7}	N^{5}	1.347(4)	C^{30}	C^{35}	1.394(5)
C^{7}	C^{8}	1.371(4)	C^{30}	C^{31}	1.406(4)
C^{8}	C^{9}	1.394(4)	C^{30}	P^{2}	1.838(3)
C^{8}	$I^{3'}$	2.015(16)	C^{31}	C^{32}	1.381(5)
C^{8}	I^{3}	2.078(3)	C^{32}	C^{33}	1.384(6)
C^{9}	N^{6}	1.333(4)	C^{33}	C^{34}	1.381(6)

C^{10}	C^{15}	1.390(4)	C^{34}	C^{35}	1.403(5)
C^{10}	C^{11}	1.400(4)	B^{1}	N^{1}	1.537(4)
C^{10}	P^{1}	1.839(3)	B^{1}	N^{5}	1.539(4)
C^{11}	C^{12}	1.380(5)	B^{1}	N^{3}	1.541(4)
C^{12}	C^{13}	1.382(5)	N^{1}	N^{2}	1.366(3)
C^{13}	C^{14}	1.376(5)	N^{2}	Ru^{1}	2.117(2)
C^{14}	C^{15}	1.396(5)	N^{3}	N^{4}	1.365(3)
C^{16}	C^{17}	1.398(4)	N^{4}	Ru^{1}	2.129(2)
C^{16}	C^{21}	1.398(4)	N^{5}	N^{6}	1.374(3)
C^{16}	P^{1}	1.834(3)	N^{6}	Ru^{1}	2.093(2)
C^{17}	C^{18}	1.386(5)	P^{1}	Ru^{1}	2.2776(7)
C^{18}	C^{19}	1.376(5)	P^{2}	Ru^{1}	2.2875(8)
C^{19}	C^{20}	1.388(5)	Cl^{1}	Ru^{1}	2.4060(7)
C^{20}	C^{21}	1.391(5)	I^{3}	$I^{3'}$	0.67(3)

Table A2.53: Bond Angles for Tp^{I}Ru(dppe)Cl 215b.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N^{2}	C^{1}	C^{2}	110.1(3)	C^{30}	C^{35}	C^{34}	120.3(3)
C^{3}	C^{2}	C^{1}	105.6(3)	N^{1}	B^{1}	N^{5}	108.6(2)
C^{3}	C^{2}	I^{1}	128.7(2)	N^{1}	B^{1}	N^{3}	108.8(2)
C^{1}	C^{2}	I^{1}	125.7(2)	N^{5}	B^{1}	N^{3}	107.8(3)
N^{1}	C^{3}	C^{2}	108.1(3)	C^{3}	N^{1}	N^{2}	109.2(2)
N^{3}	C^{4}	C^{5}	108.3(3)	C^{3}	N^{1}	B^{1}	132.6(2)
C^{4}	C^{5}	C^{6}	105.6(3)	N^{2}	N^{1}	B^{1}	118.0(2)
C^{4}	C^{5}	I^{2}	127.1(2)	C^{1}	N^{2}	N^{1}	107.0(2)
C^{6}	C^{5}	I^{2}	127.3(2)	C^{1}	N^{2}	Ru^{1}	132.72(19)
N^{4}	C^{6}	C^{5}	109.4(3)	N^{1}	N^{2}	Ru^{1}	119.98(18)
N^{5}	C^{7}	C^{8}	108.1(2)	C^{4}	N^{3}	N^{4}	109.1(2)
C^{7}	C^{8}	C^{9}	105.9(3)	C^{4}	N^{3}	B^{1}	131.4(2)
C^{7}	C^{8}	$I^{3'}$	128.9(5)	N^{4}	N^{3}	B^{1}	119.4(2)
C^{9}	C^{8}	$I^{3'}$	122.6(6)	C^{6}	N^{4}	N^{3}	107.5(2)
C^{7}	C^{8}	I^{3}	126.0(2)	C^{6}	N^{4}	Ru^{1}	133.62(19)
C^{9}	C^{8}	I^{3}	127.9(2)	N^{3}	N^{4}	Ru^{1}	118.79(18)
$I^{3'}$	C^{8}	I^{3}	18.9(10)	C^{7}	N^{5}	N^{6}	109.6(2)
N^{6}	C^{9}	C^{8}	109.9(3)	C^{7}	N^{5}	B^{1}	128.2(2)
C^{15}	C^{10}	C^{11}	118.1(3)	N^{6}	N^{5}	B^{1}	121.9(2)
C^{15}	C^{10}	P^{1}	122.4(2)	C^{9}	N^{6}	N^{5}	106.6(2)
C^{11}	C^{10}	P^{1}	119.5(2)	C^{9}	N^{6}	Ru^{1}	136.49(19)
C^{12}	C^{11}	C^{10}	121.1(3)	N^{5}	N^{6}	Ru^{1}	116.89(18)
C^{11}	C^{12}	C^{13}	120.5(3)	C^{16}	P^{1}	C^{10}	102.24(14)
C^{14}	C^{13}	C^{12}	119.2(3)	C^{16}	P^{1}	C^{22}	103.08(14)
C^{13}	C^{14}	C^{15}	120.9(3)	C^{10}	P^{1}	C^{22}	102.91(13)

C^{10}	C^{15}	C^{14}	120.3(3)	C^{16}	P^{1}	Ru^{1}	118.28(10)
C^{17}	C^{16}	C^{21}	118.2(3)	C^{10}	P^{1}	Ru^{1}	118.51(10)
C^{17}	C^{16}	P^{1}	120.4(2)	C^{22}	P^{1}	Ru^{1}	109.75(10)
C^{21}	C^{16}	P^{1}	121.4(2)	C^{24}	P^{2}	C^{30}	102.17(14)
C^{18}	C^{17}	C^{16}	120.8(3)	C^{24}	P^{2}	C^{23}	100.83(13)
C^{19}	C^{18}	C^{17}	120.3(3)	C^{30}	P^{2}	C^{23}	105.03(14)
C^{18}	C^{19}	C^{20}	120.2(3)	C^{24}	P^{2}	Ru^{1}	120.95(10)
C^{19}	C^{20}	C^{21}	119.6(3)	C^{30}	P^{2}	Ru^{1}	116.78(10)
C^{20}	C^{21}	C^{16}	120.9(3)	C^{23}	P^{2}	Ru^{1}	108.96(10)
C^{23}	C^{22}	P^{1}	109.6(2)	N^{6}	Ru^{1}	N^{2}	86.34(9)
C^{22}	C^{23}	P^{2}	109.85(19)	N^{6}	Ru^{1}	N^{4}	85.32(9)
C^{29}	C^{24}	C^{25}	118.1(3)	N^{2}	Ru^{1}	N^{4}	86.27(9)
C^{29}	C^{24}	P^{2}	122.4(2)	N^{6}	Ru^{1}	P^{1}	93.30(7)
C^{25}	C^{24}	P^{2}	119.4(2)	N^{2}	Ru^{1}	P^{1}	93.74(7)
C^{26}	C^{25}	C^{24}	120.9(3)	N^{4}	Ru^{1}	P^{1}	178.62(7)
C^{25}	C^{26}	C^{27}	120.3(3)	N^{6}	Ru^{1}	P^{2}	97.03(7)
C^{28}	C^{27}	C^{26}	119.6(3)	N^{2}	Ru^{1}	P^{2}	176.36(7)
C^{27}	C^{28}	C^{29}	120.1(3)	N^{4}	Ru^{1}	P^{2}	95.35(7)
C^{28}	C^{29}	C^{24}	120.9(3)	P^{1}	Ru^{1}	P^{2}	84.73(3)
C^{35}	C^{30}	C^{31}	118.9(3)	N^{6}	Ru^{1}	Cl^{1}	166.85(7)
C^{35}	C^{30}	P^{2}	123.6(2)	N^{2}	Ru^{1}	Cl^{1}	84.31(7)
C^{31}	C^{30}	P^{2}	117.5(2)	N^{4}	Ru^{1}	Cl^{1}	84.86(7)
C^{32}	C^{31}	C^{30}	120.3(3)	P^{1}	Ru^{1}	Cl^{1}	96.52(2)
C^{31}	C^{32}	C^{33}	120.4(3)	P^{2}	Ru^{1}	Cl^{1}	92.58(3)
C^{34}	C^{33}	C^{32}	120.5(3)	$I^{3'}$	I^{3}	C^{8}	75.3(13)
C^{33}	C^{34}	C^{35}	119.7(4)	I^{3}	$I^{3'}$	C^{8}	85.8(17)

Table A2.54: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Tp^{l}Ru(dppe)Cl 215b.

Atom	*x*	*y*	*z*	U(eq)
H^{1A}	5506	6568	3444	22
H^{3}	6274	6422	1021	22
H^{4}	4328	4625	352	24
H^{6}	3451	4249	2704	22
H^{7}	1820	6309	-124	24
H^{9}	13	6242	2003	21
H^{11}	3378	5838	5226	29
H^{12}	4758	6053	6425	34
H^{13}	5701	6961	6588	38
H^{14}	5250	7648	5538	41
H^{15}	3782	7454	4358	33
H^{17}	3028	6999	2197	26

H^{18}	2693	7904	1594	34
H^{19}	1525	8592	2257	36
H^{20}	541	8357	3477	35
H^{21}	857	7447	4082	30
H^{22A}	747	6472	4687	23
H^{22B}	70	6359	3748	23
H^{23A}	-122	5499	4440	23
H^{23B}	1346	5524	4862	23
H^{25}	2865	4772	4898	27
H^{26}	3150	3894	5589	33
H^{27}	2097	3075	5020	35
H^{28}	781	3138	3739	34
H^{29}	446	4023	3063	29
H^{31}	805	4850	1721	32
H^{32}	-1008	4677	771	42
H^{33}	-3079	4788	1194	49
H^{34}	-3358	5102	2560	50
H^{35}	-1538	5278	3530	36
H^{1}	4050(30)	5790(15)	390(20)	22

Table A2.55: Atomic Occupancy for $Tp^{I}Ru(dppe)Cl$ 215b.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
I^{3}	0.9844(15)	$I^{3'}$	0.0156(15)		

Table A2.56: Crystal data and structure refinement for Tp^{I}Ru(dppp)Cl 215c.

Identification code: Tp^{I}Ru(dppp)Cl **215c**

Empirical formula: C78H71B2Cl3I6N12P4Ru2

Formula weight: 2391.85

Temperature/K: 123(2)

Crystal system: monoclinic

Space group:P21/c

a/Å: 15.8009(11) b/Å: 21.0892(14) c/Å:26.054(2)

α/°: 90 β/°: 102.388(3) γ/°: 90

Volume/Å3: 8479.8(10) Z: 4 ρcalcg/cm3 1.874 μ/mm 1: 2.761 F(000): 4600.0

Crystal size/mm3 0.36 × 0.32 × 0.04

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 3.2 to 56.672

Index ranges -21 ≤ h ≤ 21, -28 ≤ k ≤ 27, -26 ≤ l ≤ 34

Reflections collected 81669

Independent reflections 21110 [Rint = 0.0263, Rsigma = 0.0247]

Data/restraints/parameters 21110/331/1028

Goodness-of-fit on F2 1.019

Final R indexes [I>=2σ (I)] R1 = 0.0246, wR2 = 0.0581

Final R indexes [all data] R1 = 0.0300, wR2 = 0.0608

Largest diff. peak/hole / e Å-31.49/-1.41

Table A2.57: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{l}Ru(dppp)Cl 215c. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	9005(5)	-7(3)	213(3)	64.8(3)
C^{1_1}	8323(11)	552(8)	402(7)	127(12)
C^{2_1}	8665(15)	1120(11)	619(15)	116(12)
C^{3_1}	8140(20)	1569(12)	763(16)	105(11)
C^{4_1}	7280(20)	1454(16)	726(17)	127(13)
C^{5_1}	6932(15)	897(18)	490(20)	164(14)
C^{6_1}	7458(12)	449(15)	340(19)	148(13)
Cl^{1_2}	7873.4(9)	-209.3(6)	-253.5(5)	64.8(3)
C^{1_2}	7784(3)	465.2(19)	126.8(16)	45.4(9)
C^{2_2}	6989(2)	736.8(19)	109.2(15)	40.3(8)
C^{3_2}	6930(3)	1279(2)	408.8(15)	41.9(9)
C^{4_2}	7655(4)	1517(2)	726.9(16)	56.9(13)
C^{5_2}	8440(4)	1241(3)	729(2)	68.4(14)
C^{6_2}	8524(3)	715(3)	426(2)	65.8(14)
C^{1}	4932.2(16)	4608.0(11)	3688.5(10)	20.5(5)
C^{2}	4627.0(15)	4044.4(11)	3431.8(9)	17.3(4)
C^{3}	3979.9(15)	2859.3(11)	3924.7(9)	18.8(5)
C^{4}	3106.9(17)	3010.5(13)	3895.0(11)	25.6(5)
C^{5}	2885(2)	3441.5(15)	4248.2(12)	37.3(7)
C^{6}	3515(2)	3718.1(15)	4631.3(13)	40.6(8)
C^{7}	4379(2)	3563.6(13)	4672.2(11)	32.2(6)
C^{8}	4613.5(17)	3135.6(12)	4322(1)	23.4(5)
C^{9}	4575.3(14)	1602.1(11)	3833.6(9)	17.4(4)
C^{10}	4780.3(16)	1056.1(11)	3580.1(10)	21.1(5)
C^{11}	4945.4(18)	486.0(12)	3847.4(11)	26.7(5)
C^{12}	4901(2)	448.5(13)	4372.0(12)	34.1(6)
C^{13}	4692(2)	982.6(14)	4624.7(11)	34.7(7)
C^{14}	4524.5(17)	1557.0(12)	4359.9(10)	24.8(5)
C^{15}	3337.3(14)	2071.7(11)	3013.0(9)	18.3(4)
C^{16}	2940.7(14)	2521.9(12)	2568.9(10)	20.2(5)
C^{17}	3456.9(14)	2532.8(11)	2133.2(9)	18.8(5)
C^{18}	4048.4(14)	3824.1(11)	2218.2(9)	16.3(4)
C^{19}	4638.7(15)	4325.3(11)	2335.0(9)	18.0(4)
C^{20}	4357.5(16)	4952.2(12)	2307.1(10)	22.8(5)
C^{21}	3480.4(19)	5086.2(13)	2170.3(12)	32.9(6)
C^{22}	2893.4(18)	4597.2(14)	2051.9(14)	38.2(7)
C^{23}	3168.9(15)	3971.0(12)	2071.1(11)	26.0(5)
C^{24}	4844.9(14)	2903.5(11)	1681.8(9)	17.6(4)
C^{25}	4902.3(16)	2297.3(12)	1477.7(10)	22.2(5)

C^{26}	5217.0(18)	2206.4(14)	1025.8(11)	30.0(6)
C^{27}	5505(2)	2718.2(15)	775.6(11)	34.4(6)
C^{28}	5472.4(19)	3320.8(15)	977.7(11)	32.6(6)
C^{29}	5130.8(17)	3416.3(12)	1422.5(10)	24.4(5)
C^{30}	7681.3(14)	3716.9(11)	2844.9(9)	18.3(4)
C^{31}	7535.0(14)	3400.9(11)	2369.0(9)	18.0(4)
C^{32}	6784.0(14)	3042.2(11)	2349.2(9)	16.7(4)
C^{33}	5818.3(16)	4559.1(11)	3800.6(10)	20.4(5)
C^{34}	6542.5(15)	2134.9(12)	4123.1(9)	19.3(5)
C^{35}	7213.9(16)	2312.3(12)	4539.2(10)	21.8(5)
C^{36}	7469.6(15)	2905.8(12)	4414.4(9)	21.4(5)
C^{37}	2249.9(16)	1703.5(14)	4750.5(10)	26.4(5)
C^{38}	1574.7(15)	1880.3(12)	4333.6(10)	21.8(5)
C^{39}	-1201.6(15)	1190.4(11)	3969.6(10)	20.1(5)
C^{40}	-686.0(18)	874.4(13)	4395.1(10)	27.6(6)
C^{41}	-1044(2)	431.8(15)	4677.1(12)	37.8(7)
C^{42}	-1919(2)	289.5(15)	4533.0(13)	43.6(8)
C^{43}	-2441(2)	601.6(15)	4118.7(13)	36.9(7)
C^{44}	-2086.7(16)	1053.8(12)	3837.8(11)	24.8(5)
C^{45}	-412.0(15)	2413.9(12)	3995.1(10)	21.7(5)
C^{46}	-385.0(16)	2398.3(14)	4535.3(11)	29.1(6)
C^{47}	-149(2)	2937.2(17)	4841.7(13)	41.5(8)
C^{48}	45(2)	3493.1(17)	4620.0(15)	48.5(9)
C^{49}	12(2)	3520.9(15)	4086.7(14)	42.6(8)
C^{50}	-216.0(18)	2985.8(13)	3773.5(12)	29.9(6)
C^{51}	-1577.7(15)	2032.3(11)	3080.8(10)	19.7(5)
C^{52}	-1924.2(14)	1590.4(12)	2618.6(10)	20.4(5)
C^{53}	-1318.2(15)	1559.9(11)	2231.2(9)	18.5(4)
C^{54}	-800.9(14)	240.6(11)	2300.3(9)	16.2(4)
C^{55}	-248.5(15)	-276.6(11)	2455.1(10)	20.1(5)
C^{56}	-512.2(17)	-892.0(12)	2315(1)	25.0(5)
C^{57}	-1335.1(18)	-1004.3(13)	2018.7(12)	32.3(6)
C^{58}	-1892.9(17)	-501.5(14)	1864.9(13)	34.8(7)
C^{59}	-1632.6(15)	115.5(12)	2003.4(11)	24.8(5)
C^{60}	156.6(14)	1156.0(12)	1886.0(9)	18.5(4)
C^{61}	366.3(16)	1768.0(13)	1748.5(10)	24.5(5)
C^{62}	828.2(19)	1858.3(15)	1353.1(12)	33.2(6)
C^{63}	1081.9(19)	1345.5(16)	1092.0(12)	35.5(7)
C^{64}	861.5(18)	740.5(15)	1218.0(11)	31.6(6)
C^{65}	401.8(16)	645.3(13)	1609.4(10)	23.3(5)
C^{66}	674.9(15)	-543.7(12)	4004.6(10)	20.4(5)
C^{67}	-212.5(16)	-575.0(11)	3842.7(10)	20.1(5)
C^{68}	-453.2(15)	-14.2(11)	3566.1(9)	16.7(4)
C^{69}	2443.3(16)	1088.9(13)	4651.9(10)	25.8(5)

C^{70}	1917.2(14)	920.8(11)	2633.3(9)	17.1(4)
C^{71}	2615.7(14)	504.7(11)	2664.5(10)	20.2(5)
C^{72}	2690.7(15)	187.0(12)	3132.6(11)	22.7(5)
B^{1}	6936.1(16)	3702.6(13)	3649.1(11)	18.1(5)
B^{2}	1869.1(17)	267.4(14)	3910.5(11)	20.8(5)
Cl^{1}	5735.4(4)	1771.5(3)	2716.4(2)	18.61(11)
Cl^{2}	881.2(4)	2258.1(3)	2990.7(2)	20.84(11)
I^{1}	4191.0(2)	5344.5(2)	3867.0(2)	38.25(5)
I^{2}	8279.4(2)	3446.2(2)	1808.0(2)	25.08(4)
I^{3}	7651.8(2)	1809.5(2)	5225.2(2)	34.19(5)
I^{4}	2835.5(2)	2235.3(2)	5398.0(2)	41.56(5)
I^{5}	-1012.8(2)	-1270.5(2)	4038.7(2)	30.21(4)
I^{6}	3339.5(2)	406.6(2)	2099.2(2)	28.03(4)
N^{1}	5294.6(12)	3671.9(9)	3389.9(7)	14.7(4)
N^{2}	6482.7(11)	3143.8(9)	2782.6(8)	15.0(4)
N^{3}	7040.2(12)	3555.9(9)	3089.0(8)	16.7(4)
N^{4}	6031.2(12)	3994.6(9)	3619.0(8)	16.5(4)
N^{5}	6966.9(12)	3072.3(10)	3951.2(8)	18.1(4)
N^{6}	6386.5(12)	2600.7(9)	3768.3(8)	16.7(4)
N^{7}	1360.3(12)	1389.6(10)	4007.1(8)	18.4(4)
N^{8}	247.6(12)	340.7(9)	3561.9(7)	14.9(4)
N^{9}	944.6(12)	5.6(9)	3834.8(8)	17.8(4)
N^{10}	1904.6(12)	903.3(10)	4205.7(8)	20.9(4)
N^{11}	2054.6(12)	400.2(10)	3364.2(8)	18.9(4)
N^{12}	1571.1(12)	846.0(9)	3052.0(8)	16.4(4)
P^{1}	4341.0(4)	2341.7(3)	3449.7(2)	14.22(11)
P^{2}	4450.2(3)	3007.6(3)	2292.6(2)	13.19(10)
P^{3}	-671.3(4)	1710.6(3)	3571.3(2)	15.47(11)
P^{4}	-377.7(3)	1045.4(3)	2446.7(2)	13.42(10)
Ru^{1}	5409.2(2)	2779.1(2)	3071.6(2)	11.60(4)
Ru^{2}	458.3(2)	1237.5(2)	3273.8(2)	12.58(4)

Table A2.58: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{I}Ru(dppp)Cl$ 215c. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	72.9(8)	63.0(7)	69.5(8)	5.6(6)	39.6(7)	12.2(6)
C^{1_1}	93(12)	119(15)	170(30)	-46(17)	33(14)	24(11)
C^{2_1}	78(14)	110(15)	150(30)	-33(16)	10(15)	35(11)
C^{3_1}	75(14)	115(16)	110(20)	-17(16)	-6(16)	45(13)
C^{4_1}	71(14)	140(20)	160(30)	-40(20)	2(17)	38(13)
C^{5_1}	96(14)	160(20)	230(30)	-80(20)	34(15)	20(13)

C^{6_1}	92(12)	145(19)	210(30)	-60(20)	41(14)	21(11)
Cl^{1_2}	72.9(8)	63.0(7)	69.5(8)	5.6(6)	39.6(7)	12.2(6)
C^{1_2}	52(2)	48(2)	41(2)	15.9(17)	20.5(17)	-3.1(17)
C^{2_2}	42.8(19)	49(2)	31.3(19)	1.3(16)	13.9(15)	-12.7(16)
C^{3_2}	53(2)	47(2)	30.3(19)	9.5(16)	18.8(16)	-2.5(17)
C^{4_2}	86(3)	52(3)	24(2)	11.8(17)	-7(2)	-27(2)
C^{5_2}	75(3)	83(4)	39(3)	20(2)	-8(2)	-17(3)
C^{6_2}	47(2)	89(4)	57(3)	34(2)	3(2)	-1(2)
C^{1}	28.2(12)	14.3(11)	21.1(12)	-1.3(9)	10.2(10)	2.1(9)
C^{2}	21.2(10)	14.2(11)	17.5(11)	3.0(8)	6.8(9)	2.3(8)
C^{3}	25.8(11)	15.5(11)	18.3(12)	4.4(9)	11.4(9)	2.1(9)
C^{4}	27.4(12)	28.7(14)	23.1(13)	7.6(10)	10.8(10)	8.1(10)
C^{5}	43.9(16)	39.0(17)	34.6(17)	9.1(13)	21.2(14)	19.4(13)
C^{6}	67(2)	30.5(16)	31.0(16)	0.0(12)	25.7(16)	14.7(14)
C^{7}	54.5(18)	23.6(14)	21.3(14)	0.2(10)	14.0(13)	-0.2(12)
C^{8}	32.9(13)	19.7(12)	19.8(12)	2.0(9)	10.2(10)	-0.8(10)
C^{9}	18.4(10)	15.2(11)	19.5(12)	4.1(9)	6.2(9)	-1.5(8)
C^{10}	28.4(12)	16.6(11)	20.2(12)	0.8(9)	9.4(10)	-2.7(9)
C^{11}	37.9(14)	16.4(12)	27.8(14)	1.5(10)	11.3(11)	2.8(10)
C^{12}	53.2(18)	22.3(14)	28.1(15)	11.3(11)	11.9(13)	7.3(12)
C^{13}	59.0(19)	27.9(15)	20.8(14)	9.3(11)	16.7(13)	7.6(13)
C^{14}	34.6(13)	20.5(13)	21.7(13)	3.2(10)	11.1(11)	3.4(10)
C^{15}	16.1(10)	18.5(11)	20.5(12)	1.3(9)	4.2(9)	-5.4(8)
C^{16}	15.7(10)	22.0(12)	22.4(12)	1.9(9)	3.4(9)	-3.0(8)
C^{17}	19.1(10)	17.9(11)	17.9(12)	1.0(9)	0.8(9)	-4.9(8)
C^{18}	19.8(10)	15.4(11)	13.3(11)	3.0(8)	2.7(8)	2.7(8)
C^{19}	19.6(10)	16.7(11)	16.6(11)	2.9(9)	1.7(9)	1.6(8)
C^{20}	30.1(12)	16.1(12)	21.0(13)	3.0(9)	3.1(10)	0.1(9)
C^{21}	36.0(14)	18.6(13)	43.1(17)	5.7(11)	6.2(13)	11.6(11)
C^{22}	23.1(12)	29.4(15)	58(2)	9.1(14)	-1.0(13)	12.5(11)
C^{23}	18.2(11)	21.7(13)	35.1(15)	5.6(11)	-1.3(10)	2.0(9)
C^{24}	17.3(10)	21.5(12)	12.9(11)	1.8(9)	1.0(8)	2.2(8)
C^{25}	25.1(11)	22.1(12)	19.3(12)	0.6(9)	4.9(10)	1.7(9)
C^{26}	38.6(14)	28.4(14)	24.6(14)	-5.3(11)	9.9(12)	6.1(11)
C^{27}	41.5(15)	43.7(18)	22.3(14)	2.1(12)	16.0(12)	8.4(13)
C^{28}	39.8(15)	36.1(16)	25.8(14)	10.8(12)	15.7(12)	3.7(12)
C^{29}	31.6(13)	22.3(13)	20.8(13)	4.3(10)	8.7(10)	2.2(10)
C^{30}	15.5(10)	18.8(11)	20.9(12)	3.5(9)	4.7(9)	-1.4(8)
C^{31}	16(1)	20.8(12)	17.9(11)	4.4(9)	5.6(9)	1.3(8)
C^{32}	16.5(10)	16.6(11)	17.2(11)	2.2(8)	4.1(8)	1.8(8)
C^{33}	26.9(11)	16.1(11)	19.5(12)	-3.2(9)	8.3(10)	-4.0(9)
C^{34}	19.3(10)	20.8(12)	18.4(12)	4.3(9)	5.1(9)	5.9(9)
C^{35}	24.0(11)	25.8(13)	15.6(12)	4.0(9)	4.2(9)	10.9(9)
C^{36}	19.1(10)	28.7(13)	14.5(11)	-3.4(9)	-0.6(9)	4.3(9)

C^{37}	23.8(12)	35.8(15)	18.4(12)	-1.4(10)	1.8(10)	-11.6(10)
C^{38}	19.4(10)	26.8(13)	19.7(12)	-4.2(10)	5.3(9)	-4.9(9)
C^{39}	24.8(11)	19.0(12)	19.3(12)	-1.8(9)	10.8(9)	3.2(9)
C^{40}	34.3(13)	30.5(14)	21.1(13)	0.1(10)	13.0(11)	11.0(11)
C^{41}	60(2)	35.4(16)	24.2(15)	6.7(12)	22.3(14)	16.3(14)
C^{42}	72(2)	31.6(17)	38.6(18)	2.0(13)	37.9(17)	-4.2(15)
C^{43}	41.6(16)	36.3(17)	40.6(18)	-8.2(13)	25.8(14)	-12.2(13)
C^{44}	27.0(12)	24.8(13)	25.7(13)	-7(1)	12.6(10)	-1.5(10)
C^{45}	18.3(10)	21.0(12)	25.5(13)	-8.1(10)	3.9(9)	2.8(9)
C^{46}	24.4(12)	39.3(16)	24.1(14)	-11.3(11)	6.4(10)	-0.7(11)
C^{47}	38.2(16)	56(2)	31.5(17)	-23.6(15)	9.1(13)	-2.6(14)
C^{48}	52.3(19)	43(2)	50(2)	-29.7(16)	10.6(16)	-6.7(15)
C^{49}	50.7(18)	25.9(16)	51(2)	-15.7(14)	10.2(16)	-5.3(13)
C^{50}	34.2(14)	23.3(14)	31.9(15)	-7.4(11)	6.3(12)	2.6(11)
C^{51}	18.9(10)	18.4(11)	21.0(12)	-1.0(9)	2.7(9)	7.4(8)
C^{52}	15.6(10)	22.1(12)	22.4(12)	-0.8(9)	1.6(9)	4.8(8)
C^{53}	20.5(10)	17.0(11)	16.6(11)	0.8(9)	0.6(9)	4.3(8)
C^{54}	19(1)	14.7(11)	15.5(11)	-1.8(8)	4.9(8)	-1.1(8)
C^{55}	22.2(11)	19.6(12)	16.8(12)	-1.3(9)	0.7(9)	2.1(9)
C^{56}	34.1(13)	15.4(12)	25.2(13)	-2.0(9)	5.8(11)	3.7(10)
C^{57}	35.3(14)	18.3(13)	42.7(17)	-9.4(11)	7.1(13)	-6.1(10)
C^{58}	23.4(12)	27.1(15)	49.7(19)	-12.8(13)	-1.6(12)	-5.5(10)
C^{59}	19.4(11)	19.2(12)	33.5(15)	-4.9(10)	0.8(10)	2.0(9)
C^{60}	18.5(10)	23.0(12)	13.9(11)	1.5(9)	3.4(8)	0.1(8)
C^{61}	28.2(12)	23.3(13)	22.0(13)	5.4(10)	5.5(10)	-1.8(10)
C^{62}	37.2(14)	35.0(16)	28.8(15)	11.1(12)	10.1(12)	-5.7(12)
C^{63}	35.7(15)	51.4(19)	22.3(14)	7.8(13)	13.0(12)	-0.7(13)
C^{64}	33.3(14)	40.7(17)	23.8(14)	-3.5(12)	13.1(11)	1.0(12)
C^{65}	25.5(11)	24.9(13)	20.5(12)	-2.5(10)	7(1)	-1.8(10)
C^{66}	25.3(11)	18.7(12)	17.7(12)	1.6(9)	5.6(9)	5.3(9)
C^{67}	26.5(11)	16.1(11)	18.7(12)	0.7(9)	7.1(9)	-1.0(9)
C^{68}	19.5(10)	14.9(11)	16.2(11)	-0.3(8)	4.7(9)	0.3(8)
C^{69}	19.2(11)	34.3(15)	21.4(13)	5.3(11)	-1.1(9)	-6.9(10)
C^{70}	14.9(9)	15.7(11)	21.0(12)	-2.2(9)	4.8(9)	-2.9(8)
C^{71}	16.9(10)	19.6(12)	25.8(13)	-6.7(9)	8.4(9)	-1.8(8)
C^{72}	16.1(10)	21.6(12)	31.2(14)	-0.3(10)	6.9(10)	3.9(9)
B^{1}	19.0(11)	20.1(13)	14.9(12)	-0.5(10)	2.6(10)	-2.4(9)
B^{2}	16.9(11)	24.9(14)	20.0(14)	3.6(11)	2.4(10)	3.1(10)
Cl^{1}	22.6(2)	12.9(2)	21.7(3)	0.6(2)	8.0(2)	2.79(19)
Cl^{2}	22.9(3)	14.9(3)	25.4(3)	-0.3(2)	6.8(2)	-3.4(2)
I^{1}	35.62(9)	24.43(10)	54.64(13)	-17.15(8)	9.53(9)	6.61(7)
I^{2}	23.07(7)	32.19(9)	23.39(8)	4.05(7)	12.57(6)	0.05(6)
I^{3}	44.88(10)	37.78(11)	17.58(9)	8.46(7)	1.54(7)	19.64(8)
I^{4}	49.39(11)	48.19(12)	21.41(9)	-4.77(8)	-5.04(8)	-24.62(9)

I^{5}	34.68(9)	20.41(9)	35.97(10)	7.96(7)	8.56(8)	-5.43(6)
I^{6}	24.83(8)	30.44(9)	33.3(1)	-7.84(7)	16.19(7)	0.89(6)
N^{1}	16.3(8)	13.7(9)	13.9(9)	0.7(7)	3.0(7)	-1.6(7)
N^{2}	14.8(8)	13.8(9)	16.0(9)	1.1(7)	2.7(7)	-0.5(7)
N^{3}	15.0(8)	17.5(10)	17.6(10)	0.3(7)	3.6(7)	-1.7(7)
N^{4}	19.3(9)	16.1(9)	14.4(9)	-2.1(7)	3.8(7)	-3.0(7)
N^{5}	16.5(8)	22.1(10)	15.1(10)	0.3(8)	1.9(7)	-0.1(7)
N^{6}	15.1(8)	18.9(10)	15.9(10)	2.0(7)	2.6(7)	1.1(7)
N^{7}	14.9(8)	22.6(10)	16.9(10)	-0.7(8)	1.3(7)	1.8(7)
N^{8}	15.0(8)	16.0(9)	13.3(9)	0.3(7)	1.8(7)	2.0(7)
N^{9}	18.4(9)	18.3(10)	16(1)	2.4(7)	2.0(7)	4.3(7)
N^{10}	16.7(9)	26.2(11)	17.9(10)	2.3(8)	-0.4(8)	0.1(8)
N^{11}	14.4(8)	20.4(10)	22.0(11)	2.7(8)	4.0(8)	4.3(7)
N^{12}	14.7(8)	15.3(9)	19.1(10)	0.0(7)	3.2(7)	2.0(7)
P^{1}	15.8(2)	12.3(3)	15.3(3)	2.1(2)	5.0(2)	-0.42(19)
P^{2}	13.9(2)	12.3(3)	13.0(3)	1.4(2)	2.1(2)	-0.10(19)
P^{3}	15.0(2)	16.0(3)	15.4(3)	-1.8(2)	3.1(2)	2.8(2)
P^{4}	14.2(2)	12.2(3)	13.6(3)	0.0(2)	2.4(2)	0.81(19)
Ru^{1}	12.35(7)	10.68(8)	11.81(8)	1.48(6)	2.69(6)	0.67(6)
Ru^{2}	11.64(7)	12.63(8)	13.24(8)	-0.88(6)	2.19(6)	0.52(6)

Table A2.59: Bond Lengths for Tp^{i}Ru(dppp)Cl 215c.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.740(11)	C^{39}	C^{44}	1.397(3)
C^{1_1}	C^{6_1}	1.360(12)	C^{39}	P^{3}	1.832(2)
C^{1_1}	C^{2_1}	1.382(12)	C^{40}	C^{41}	1.382(4)
C^{2_1}	C^{3_1}	1.364(12)	C^{41}	C^{42}	1.386(5)
C^{3_1}	C^{4_1}	1.372(12)	C^{42}	C^{43}	1.377(5)
C^{4_1}	C^{5_1}	1.380(12)	C^{43}	C^{44}	1.391(4)
C^{5_1}	C^{6_1}	1.373(12)	C^{45}	C^{46}	1.399(4)
Cl^{1_2}	C^{1_2}	1.756(4)	C^{45}	C^{50}	1.400(4)
C^{1_2}	C^{6_2}	1.364(6)	C^{45}	P^{3}	1.842(2)
C^{1_2}	C^{2_2}	1.372(5)	C^{46}	C^{47}	1.393(4)
C^{2_2}	C^{3_2}	1.399(5)	C^{47}	C^{48}	1.371(5)
C^{3_2}	C^{4_2}	1.357(6)	C^{48}	C^{49}	1.381(5)
C^{4_2}	C^{5_2}	1.368(7)	C^{49}	C^{50}	1.394(4)
C^{5_2}	C^{6_2}	1.385(7)	C^{51}	C^{52}	1.528(3)
C^{1}	C^{33}	1.371(3)	C^{51}	P^{3}	1.833(2)
C^{1}	C^{2}	1.398(3)	C^{52}	C^{53}	1.535(3)
C^{1}	I^{1}	2.058(2)	C^{53}	P^{4}	1.829(2)
C^{2}	N^{1}	1.338(3)	C^{54}	C^{59}	1.400(3)
C^{3}	C^{4}	1.402(3)	C^{54}	C^{55}	1.401(3)

C^{3}	C^{8}	1.403(4)	C^{54}	P^{4}	1.834(2)
C^{3}	P^{1}	1.831(2)	C^{55}	C^{56}	1.388(3)
C^{4}	C^{5}	1.391(4)	C^{56}	C^{57}	1.383(4)
C^{5}	C^{6}	1.379(5)	C^{57}	C^{58}	1.382(4)
C^{6}	C^{7}	1.385(5)	C^{58}	C^{59}	1.389(4)
C^{7}	C^{8}	1.389(4)	C^{60}	C^{65}	1.396(3)
C^{9}	C^{14}	1.394(3)	C^{60}	C^{61}	1.398(3)
C^{9}	C^{10}	1.399(3)	C^{60}	P^{4}	1.852(2)
C^{9}	P^{1}	1.847(2)	C^{61}	C^{62}	1.398(4)
C^{10}	C^{11}	1.386(3)	C^{62}	C^{63}	1.382(4)
C^{11}	C^{12}	1.386(4)	C^{63}	C^{64}	1.381(4)
C^{12}	C^{13}	1.380(4)	C^{64}	C^{65}	1.388(4)
C^{13}	C^{14}	1.391(4)	C^{66}	N^{9}	1.342(3)
C^{15}	C^{16}	1.524(3)	C^{66}	C^{67}	1.376(3)
C^{15}	P^{1}	1.833(2)	C^{67}	C^{68}	1.395(3)
C^{16}	C^{17}	1.534(3)	C^{67}	I^{5}	2.071(2)
C^{17}	P^{2}	1.833(2)	C^{68}	N^{8}	1.338(3)
C^{18}	C^{23}	1.395(3)	C^{69}	N^{10}	1.343(3)
C^{18}	C^{19}	1.399(3)	C^{70}	N^{12}	1.330(3)
C^{18}	P^{2}	1.831(2)	C^{70}	C^{71}	1.399(3)
C^{19}	C^{20}	1.392(3)	C^{71}	C^{72}	1.374(4)
C^{20}	C^{21}	1.384(4)	C^{71}	I^{6}	2.060(2)
C^{21}	C^{22}	1.377(4)	C^{72}	N^{11}	1.355(3)
C^{22}	C^{23}	1.388(4)	B^{1}	N^{3}	1.535(3)
C^{24}	C^{25}	1.395(3)	B^{1}	N^{5}	1.540(3)
C^{24}	C^{29}	1.400(3)	B^{1}	N^{4}	1.543(3)
C^{24}	P^{2}	1.843(2)	B^{2}	N^{9}	1.534(3)
C^{25}	C^{26}	1.386(4)	B^{2}	N^{11}	1.539(3)
C^{26}	C^{27}	1.387(4)	B^{2}	N^{10}	1.541(4)
C^{27}	C^{28}	1.381(4)	Cl^{1}	Ru^{1}	2.4171(6)
C^{28}	C^{29}	1.394(4)	Cl^{2}	Ru^{2}	2.4155(6)
C^{30}	N^{3}	1.350(3)	N^{1}	N^{4}	1.370(3)
C^{30}	C^{31}	1.383(3)	N^{1}	Ru^{1}	2.0809(19)
C^{31}	C^{32}	1.399(3)	N^{2}	N^{3}	1.366(3)
C^{31}	I^{2}	2.066(2)	N^{2}	Ru^{1}	2.1409(18)
C^{32}	N^{2}	1.334(3)	N^{5}	N^{6}	1.368(3)
C^{33}	N^{4}	1.350(3)	N^{6}	Ru^{1}	2.1491(19)
C^{34}	N^{6}	1.335(3)	N^{7}	N^{10}	1.367(3)
C^{34}	C^{35}	1.395(3)	N^{7}	Ru^{2}	2.149(2)
C^{35}	C^{36}	1.375(4)	N^{8}	N^{9}	1.372(3)
C^{35}	I^{3}	2.066(2)	N^{8}	Ru^{2}	2.0879(19)
C^{36}	N^{5}	1.342(3)	N^{11}	N^{12}	1.365(3)
C^{37}	C^{69}	1.369(4)	N^{12}	Ru^{2}	2.1315(18)
C^{37}	C^{38}	1.400(4)	P^{1}	Ru^{1}	2.3204(6)

C37	I4	2.071(3)	P2	Ru1	2.3083(6)
C38	N7	1.336(3)	P3	Ru2	2.3185(6)
C39	C40	1.396(4)	P4	Ru2	2.3089(6)

Table A2.60: Bond Angles for Tp^{I}Ru(dppp)Cl 215c.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C6_1	C1_1	C2_1	118.9(9)	C66	C67	C68	105.3(2)
C6_1	C1_1	Cl1_1	121.7(10)	C66	C67	I5	126.46(18)
C2_1	C1_1	Cl1_1	119.4(10)	C68	C67	I5	127.94(17)
C3_1	C2_1	C1_1	120.4(10)	N8	C68	C67	110.1(2)
C2_1	C3_1	C4_1	120.9(10)	N10	C69	C37	108.2(2)
C3_1	C4_1	C5_1	118.3(10)	N12	C70	C71	109.6(2)
C6_1	C5_1	C4_1	120.6(10)	C72	C71	C70	105.9(2)
C1_1	C6_1	C5_1	120.7(10)	C72	C71	I6	129.07(18)
C6_2	C1_2	C2_2	121.6(4)	C70	C71	I6	125.01(19)
C6_2	C1_2	Cl1_2	118.2(4)	N11	C72	C71	107.6(2)
C2_2	C1_2	Cl1_2	120.2(3)	N3	B1	N5	108.3(2)
C1_2	C2_2	C3_2	119.5(4)	N3	B1	N4	108.61(19)
C4_2	C3_2	C2_2	119.6(4)	N5	B1	N4	107.33(18)
C3_2	C4_2	C5_2	119.4(4)	N9	B2	N11	108.1(2)
C4_2	C5_2	C6_2	122.4(4)	N9	B2	N10	108.00(19)
C1_2	C6_2	C5_2	117.3(4)	N11	B2	N10	108.0(2)
C33	C1	C2	105.6(2)	C2	N1	N4	106.48(18)
C33	C1	I1	127.83(18)	C2	N1	Ru1	134.52(16)
C2	C1	I1	126.53(18)	N4	N1	Ru1	118.99(14)
N1	C2	C1	109.9(2)	C32	N2	N3	107.13(18)
C4	C3	C8	119.0(2)	C32	N2	Ru1	133.93(15)
C4	C3	P1	123.0(2)	N3	N2	Ru1	118.88(14)
C8	C3	P1	118.02(18)	C30	N3	N2	109.84(19)
C5	C4	C3	119.8(3)	C30	N3	B1	129.9(2)
C6	C5	C4	120.6(3)	N2	N3	B1	119.78(18)
C5	C6	C7	120.2(3)	C33	N4	N1	109.79(18)
C6	C7	C8	120.0(3)	C33	N4	B1	129.2(2)
C7	C8	C3	120.4(3)	N1	N4	B1	121.02(18)
C14	C9	C10	118.4(2)	C36	N5	N6	110.3(2)
C14	C9	P1	122.90(19)	C36	N5	B1	129.3(2)
C10	C9	P1	118.62(18)	N6	N5	B1	120.29(18)
C11	C10	C9	121.0(2)	C34	N6	N5	106.48(19)
C10	C11	C12	120.1(2)	C34	N6	Ru1	134.92(16)
C13	C12	C11	119.5(2)	N5	N6	Ru1	118.26(14)
C12	C13	C14	120.9(3)	C38	N7	N10	106.69(19)
C13	C14	C9	120.2(2)	C38	N7	Ru2	135.30(17)

C16	C15	P1	115.97(16)	N10	N7	Ru2	117.91(15)
C15	C16	C17	111.97(19)	C68	N8	N9	106.34(18)
C16	C17	P2	113.96(16)	C68	N8	Ru2	134.86(15)
C23	C18	C19	118.1(2)	N9	N8	Ru2	118.74(14)
C23	C18	P2	122.71(18)	C66	N9	N8	109.83(18)
C19	C18	P2	119.18(17)	C66	N9	B2	129.0(2)
C20	C19	C18	121.1(2)	N8	N9	B2	121.18(19)
C21	C20	C19	119.9(2)	C69	N10	N7	109.8(2)
C22	C21	C20	119.6(2)	C69	N10	B2	129.3(2)
C21	C22	C23	120.9(2)	N7	N10	B2	120.77(19)
C22	C23	C18	120.5(2)	C72	N11	N12	109.7(2)
C25	C24	C29	118.0(2)	C72	N11	B2	131.1(2)
C25	C24	P2	120.02(18)	N12	N11	B2	118.90(18)
C29	C24	P2	121.91(19)	C70	N12	N11	107.12(18)
C26	C25	C24	121.0(2)	C70	N12	Ru2	133.19(16)
C25	C26	C27	120.3(3)	N11	N12	Ru2	119.62(14)
C28	C27	C26	119.6(3)	C3	P1	C15	104.55(11)
C27	C28	C29	120.2(3)	C3	P1	C9	101.11(11)
C28	C29	C24	120.8(2)	C15	P1	C9	96.89(11)
N3	C30	C31	107.7(2)	C3	P1	Ru1	114.24(8)
C30	C31	C32	105.7(2)	C15	P1	Ru1	118.12(8)
C30	C31	I2	126.95(17)	C9	P1	Ru1	119.09(7)
C32	C31	I2	127.32(18)	C18	P2	C17	103.25(11)
N2	C32	C31	109.6(2)	C18	P2	C24	101.23(10)
N4	C33	C1	108.1(2)	C17	P2	C24	99.86(11)
N6	C34	C35	109.7(2)	C18	P2	Ru1	115.89(8)
C36	C35	C34	105.9(2)	C17	P2	Ru1	117.00(8)
C36	C35	I3	127.64(19)	C24	P2	Ru1	117.03(7)
C34	C35	I3	126.32(19)	C39	P3	C51	103.46(11)
N5	C36	C35	107.7(2)	C39	P3	C45	102.27(11)
C69	C37	C38	105.7(2)	C51	P3	C45	99.20(11)
C69	C37	I4	125.9(2)	C39	P3	Ru2	114.22(8)
C38	C37	I4	128.4(2)	C51	P3	Ru2	117.94(8)
N7	C38	C37	109.5(2)	C45	P3	Ru2	117.30(8)
C40	C39	C44	118.7(2)	C53	P4	C54	104.43(11)
C40	C39	P3	118.41(19)	C53	P4	C60	99.26(11)
C44	C39	P3	122.7(2)	C54	P4	C60	99.21(11)
C41	C40	C39	120.6(3)	C53	P4	Ru2	116.55(8)
C40	C41	C42	120.1(3)	C54	P4	Ru2	117.82(8)
C43	C42	C41	120.2(3)	C60	P4	Ru2	116.59(8)
C42	C43	C44	120.0(3)	N1	Ru1	N2	87.62(7)
C43	C44	C39	120.4(3)	N1	Ru1	N6	85.99(7)
C46	C45	C50	118.2(2)	N2	Ru1	N6	83.11(7)
C46	C45	P3	122.6(2)	N1	Ru1	P2	93.71(5)

C^{50}	C^{45}	P^{3}	119.1(2)	N^{2}	Ru^{1}	P^{2}	92.06(5)
C^{47}	C^{46}	C^{45}	120.3(3)	N^{6}	Ru^{1}	P^{2}	175.17(5)
C^{48}	C^{47}	C^{46}	120.8(3)	N^{1}	Ru^{1}	P^{1}	93.27(5)
C^{47}	C^{48}	C^{49}	119.8(3)	N^{2}	Ru^{1}	P^{1}	174.57(5)
C^{48}	C^{49}	C^{50}	120.3(3)	N^{6}	Ru^{1}	P^{1}	91.61(5)
C^{49}	C^{50}	C^{45}	120.5(3)	P^{2}	Ru^{1}	P^{1}	93.22(2)
C^{52}	C^{51}	P^{3}	114.70(16)	N^{1}	Ru^{1}	Cl^{1}	172.75(5)
C^{51}	C^{52}	C^{53}	112.04(19)	N^{2}	Ru^{1}	Cl^{1}	86.04(5)
C^{52}	C^{53}	P^{4}	113.80(16)	N^{6}	Ru^{1}	Cl^{1}	89.76(5)
C^{59}	C^{54}	C^{55}	117.7(2)	P^{2}	Ru^{1}	Cl^{1}	90.03(2)
C^{59}	C^{54}	P^{4}	123.14(18)	P^{1}	Ru^{1}	Cl^{1}	92.71(2)
C^{55}	C^{54}	P^{4}	118.92(17)	N^{8}	Ru^{2}	N^{12}	87.19(7)
C^{56}	C^{55}	C^{54}	121.3(2)	N^{8}	Ru^{2}	N^{7}	86.67(8)
C^{57}	C^{56}	C^{55}	120.0(2)	N^{12}	Ru^{2}	N^{7}	82.55(7)
C^{58}	C^{57}	C^{56}	119.7(2)	N^{8}	Ru^{2}	P^{4}	94.19(5)
C^{57}	C^{58}	C^{59}	120.6(2)	N^{12}	Ru^{2}	P^{4}	91.10(6)
C^{58}	C^{59}	C^{54}	120.7(2)	N^{7}	Ru^{2}	P^{4}	173.55(5)
C^{65}	C^{60}	C^{61}	118.2(2)	N^{8}	Ru^{2}	P^{3}	94.36(5)
C^{65}	C^{60}	P^{4}	122.27(19)	N^{12}	Ru^{2}	P^{3}	175.07(6)
C^{61}	C^{60}	P^{4}	119.45(19)	N^{7}	Ru^{2}	P^{3}	92.86(5)
C^{62}	C^{61}	C^{60}	120.3(3)	P^{4}	Ru^{2}	P^{3}	93.45(2)
C^{63}	C^{62}	C^{61}	120.6(3)	N^{8}	Ru^{2}	Cl^{2}	173.17(5)
C^{64}	C^{63}	C^{62}	119.4(3)	N^{12}	Ru^{2}	Cl^{2}	87.94(5)
C^{63}	C^{64}	C^{65}	120.5(3)	N^{7}	Ru^{2}	Cl^{2}	87.95(6)
C^{64}	C^{65}	C^{60}	121.0(2)	P^{4}	Ru^{2}	Cl^{2}	90.68(2)
N^{9}	C^{66}	C^{67}	108.4(2)	P^{3}	Ru^{2}	Cl^{2}	90.11(2)

Table A2.61: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}Ru(dppp)Cl 215c.

Atom	*x*	*y*	*z*	U(eq)
H^{2_1}	9270	1197	667	139
H^{3_1}	8378	1967	891	126
H^{4_1}	6922	1751	857	152
H^{5_1}	6326	822	439	197
H^{6_1}	7215	62	190	178
H^{2_2}	6482	558	-105	48
H^{3_2}	6386	1480	390	50
H^{4_2}	7618	1871	946	68
H^{5_2}	8945	1417	946	82
H^{6_2}	9076	536	426	79
H^{2}	4034	3941	3306	21
H^{4}	2668	2819	3634	31

H^{5}	2293	3546	4225	45
H^{6}	3356	4015	4868	49
H^{7}	4811	3750	4940	39
H^{8}	5206	3029	4352	28
H^{10}	4807	1077	3220	25
H^{11}	5089	121	3671	32
H^{12}	5013	58	4556	41
H^{13}	4661	958	4984	42
H^{14}	4375	1919	4538	30
H^{15A}	3454	1662	2856	22
H^{15B}	2903	1992	3228	22
H^{16A}	2922	2955	2712	24
H^{16B}	2338	2389	2418	24
H^{17A}	3082	2703	1809	23
H^{17B}	3612	2092	2060	23
H^{19}	5241	4236	2435	22
H^{20}	4767	5288	2382	27
H^{21}	3285	5513	2158	40
H^{22}	2292	4690	1956	46
H^{23}	2755	3640	1983	31
H^{25}	4723	1941	1651	27
H^{26}	5235	1791	887	36
H^{27}	5723	2654	467	41
H^{28}	5683	3671	813	39
H^{29}	5091	3834	1551	29
H^{30}	8149	3997	2976	22
H^{32}	6528	2768	2070	20
H^{33}	6214	4869	3976	24
H^{34}	6242	1742	4096	23
H^{36}	7921	3153	4619	26
H^{38}	1310	2287	4290	26
H^{40}	-84	964	4492	33
H^{41}	-690	225	4970	45
H^{42}	-2160	-24	4721	52
H^{43}	-3042	508	4025	44
H^{44}	-2449	1271	3554	30
H^{46}	-528	2019	4694	35
H^{47}	-123	2919	5209	50
H^{48}	202	3858	4833	58
H^{49}	145	3906	3933	51
H^{50}	-239	3009	3407	36
H^{51A}	-2057	2135	3257	24
H^{51B}	-1389	2433	2942	24
H^{52A}	-2502	1741	2432	24

H^{52B}	-1995	1159	2754	24
H^{53A}	-1113	1994	2178	22
H^{53B}	-1651	1406	1888	22
H^{55}	317	-205	2660	24
H^{56}	-127	-1236	2423	30
H^{57}	-1516	-1425	1921	39
H^{58}	-2459	-579	1663	42
H^{59}	-2023	456	1895	30
H^{61}	194	2124	1925	29
H^{62}	969	2276	1263	40
H^{63}	1405	1409	828	43
H^{64}	1026	387	1035	38
H^{65}	252	226	1690	28
H^{66}	1035	-857	4203	24
H^{68}	-1031	99	3404	20
H^{69}	2883	837	4863	31
H^{70}	1720	1212	2355	20
H^{72}	3112	-125	3269	27
$H^{1'}$	7514(18)	4041(13)	3862(11)	22
$H^{2'}$	2375(18)	-92(14)	4150(12)	25

Table A2.62: Atomic Occupancy for Tp^{I}Ru(dppp)Cl 215c.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Cl^{1_1}	0.150(2)	C^{1_1}	0.150(2)	C^{2_1}	0.150(2)
H^{2_1}	0.150(2)	C^{3_1}	0.150(2)	H^{3_1}	0.150(2)
C^{4_1}	0.150(2)	H^{4_1}	0.150(2)	C^{5_1}	0.150(2)
H^{5_1}	0.150(2)	C^{6_1}	0.150(2)	H^{6_1}	0.150(2)
Cl^{1_2}	0.850(2)	C^{1_2}	0.850(2)	C^{2_2}	0.850(2)
H^{2_2}	0.850(2)	C^{3_2}	0.850(2)	H^{3_2}	0.850(2)
C^{4_2}	0.850(2)	H^{4_2}	0.850(2)	C^{5_2}	0.850(2)
H^{5_2}	0.850(2)	C^{6_2}	0.850(2)	H^{6_2}	0.850(2)

Table A2.63: Crystal data and structure refinement for Tp^{I}Ru(dppb)Cl 215d.

Identification code	Tp^{I}Ru(dppb)Cl **215d**
Empirical formula	C38H37BCl3I3N6P2Ru
Formula weight	1238.60
Temperature/K	123(2)
Crystal system	monoclinic
Space group	P21/n
a/Å: 15.2176(11) b/Å: 14.3246(11) c/Å: 20.7011(15)	
α/°: 90 β/°: 110.580(2) γ/°: 90	
Volume/Å3: 4224.6(5) Z: 4 ρcalcg/cm3 1.947 μ/mm-1	2.866 F(000) 2384.0
Crystal size/mm3	0.200 × 0.180 × 0.150
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.536 to 56.754
Index ranges	-20 ≤ h ≤ 19, 0 ≤ k ≤ 19, 0 ≤ l ≤ 27
Reflections collected	101971
Independent reflections	10536 [Rint = 0.0180, Rsigma = 0.0082]
Data/restraints/parameters	10536/51/518
Goodness-of-fit on F2	1.038
Final R indexes [I>=2σ (I)]	R1 = 0.0163, wR2 = 0.0415
Final R indexes [all data]	R1 = 0.0178, wR2 = 0.0420
Largest diff. peak/hole / e Å-3	0.53/-0.51

Table A2.64: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}Ru(dppb)Cl 215d. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	3697(5)	1940(4)	5472(2)	36.2(7)
Cl^{2_1}	4609(4)	1661(3)	6965(3)	31.2(8)
C^{1_1}	4572(6)	2328(8)	6244(4)	33.5(18)
Cl^{1_2}	3527(12)	1993(9)	5419(6)	50.7(19)
Cl^{2_2}	4566(9)	1743(9)	6894(7)	54(2)
C^{1_2}	4583(11)	2212(14)	6111(10)	42(3)
C^{1}	7004.0(11)	6005.7(11)	8578.2(8)	13.0(3)
C^{2}	7873.6(11)	5914.0(11)	8495.9(8)	14.3(3)
C^{3}	7852.3(11)	6528.7(11)	7974.7(8)	14.1(3)
C^{4}	7010.2(11)	9395.9(11)	7882.0(8)	14.2(3)
C^{5}	6773.7(11)	9810.0(11)	8401.0(8)	14.2(3)
C^{6}	6113.1(10)	9215.9(11)	8516.7(8)	12.9(3)
C^{7}	5403.3(11)	7474.3(11)	6024.0(8)	13.7(3)
C^{8}	4469.3(11)	7215.7(11)	5772.9(8)	13.8(3)
C^{9}	4212.9(11)	7112.9(10)	6352.0(8)	12.5(3)
C^{10}	3876.9(12)	9053.7(13)	9054.0(8)	18.1(3)
C^{11}	3910.6(13)	9833.5(14)	9462.7(9)	24.1(4)
C^{12}	4006.6(13)	10723.5(14)	9227.1(10)	26.1(4)
C^{13}	4074.6(13)	10823.7(13)	8579.6(10)	23.8(4)
C^{14}	4027.3(12)	10043.8(12)	8164.5(9)	18.0(3)
C^{15}	3920.2(10)	9146.5(11)	8390.7(8)	13.6(3)
C^{16}	3807.5(11)	9060.8(11)	6679.9(8)	15.6(3)
C^{17}	3458.4(13)	9329.7(13)	5990.6(9)	20.8(3)
C^{18}	2553.0(14)	9080.2(13)	5578.2(9)	24.2(4)
C^{19}	1984.3(13)	8599.4(13)	5857.9(9)	22.4(4)
C^{20}	2323.1(11)	8354.3(12)	6556.2(8)	16.9(3)
C^{21}	3246.4(11)	8564.7(11)	6972.3(8)	12.9(3)
C^{22}	2824.3(11)	7525.6(12)	8035.6(8)	15.0(3)
C^{23}	3170.5(11)	6802.8(11)	8622.8(8)	15.4(3)
C^{24}	2993.4(11)	5798.6(12)	8358.3(8)	16.0(3)
C^{25}	3252.0(11)	5575.7(11)	7725.3(8)	14.6(3)
C^{26}	3657.4(12)	4974.0(12)	6466.4(8)	17.1(3)
C^{27}	3677.1(13)	4661.3(13)	5832.7(9)	20.7(3)
C^{28}	4520.5(13)	4596.1(13)	5722.9(9)	21.0(3)
C^{29}	5353.5(13)	4830.3(12)	6251.9(9)	19.4(3)
C^{30}	5333.6(11)	5150.1(11)	6881.4(8)	15.9(3)
C^{31}	4482.9(11)	5236.9(11)	6996.8(8)	13.0(3)
C^{32}	5077.6(13)	3898.2(12)	8183.6(9)	20.4(3)
C^{33}	5433.1(15)	3168.9(13)	8644.7(10)	26.1(4)
C^{34}	5736.1(14)	3330.7(14)	9350.9(10)	26.5(4)

C^{35}	5678.1(13)	4226.7(13)	9590.7(9)	22.9(4)
C^{36}	5325.0(12)	4959.1(12)	9130.7(8)	17.9(3)
C^{37}	5024.3(11)	4802.5(11)	8418.4(8)	13.7(3)
B^{1}	6636.8(12)	7781.0(12)	7254.1(9)	12.2(3)
N^{1}	7005.1(9)	6951.9(9)	7758.9(7)	12.2(2)
N^{2}	6484.6(9)	6633.2(9)	8129.9(6)	11.6(2)
N^{3}	6506.0(9)	8604.6(9)	7696.2(6)	12.3(2)
N^{4}	5950.0(9)	8494.9(9)	8085.2(6)	11.7(2)
N^{5}	5679.4(9)	7515.9(9)	6721.6(7)	12.1(2)
N^{6}	4944.2(9)	7290.9(9)	6926.4(6)	11.1(2)
P^{1}	4482.3(3)	5758.6(3)	7810.8(2)	10.55(7)
P^{2}	3797.0(3)	8093.7(3)	7845.2(2)	10.40(7)
Cl^{1}	5596.6(3)	7331.4(3)	9218.2(2)	13.68(7)
Ru^{1}	5153.1(2)	7246.7(2)	7973.8(2)	8.68(3)
I^{1}	7254.9(2)	11060.2(2)	8899.0(2)	19.22(3)
I^{2}	3581.2(2)	7040.4(2)	4762.7(2)	20.64(3)
I^{3}	8966.8(2)	5070.9(2)	9080.2(2)	22.12(3)

Table A2.65: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{I}Ru(dppb)Cl$ 215d. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	32.5(15)	48.8(11)	30.8(10)	1.9(6)	15.7(9)	-0.4(9)
Cl^{2_1}	38.1(10)	31.0(13)	30.5(9)	2.6(6)	19.7(7)	-6.2(7)
C^{1_1}	36(3)	29(3)	36(2)	5(2)	13(2)	-8(2)
Cl^{1_2}	45(4)	65(3)	56(3)	8(2)	36(3)	2(2)
Cl^{2_2}	50(3)	72(4)	50(3)	-6(2)	28(2)	-19(3)
C^{1_2}	52(5)	26(5)	62(6)	10(5)	37(5)	2(4)
C^{1}	13.8(7)	12.5(7)	11.6(6)	-0.6(5)	2.9(5)	0.4(5)
C^{2}	12.7(7)	14.4(7)	13.4(7)	-1.3(6)	1.5(5)	3.0(6)
C^{3}	11.1(7)	15.9(8)	15.3(7)	-2.3(6)	4.4(5)	0.7(6)
C^{4}	15.2(7)	12.5(7)	14.7(7)	2.3(5)	5.0(6)	-2.1(6)
C^{5}	14.3(7)	11.6(7)	14.7(7)	-1.1(5)	2.7(6)	-2.5(6)
C^{6}	12.0(6)	13.3(7)	12.5(6)	-0.3(5)	3.2(5)	-0.3(6)
C^{7}	17.8(7)	12.8(7)	11.9(7)	0.9(5)	6.9(6)	1.7(6)
C^{8}	16.9(7)	12.9(7)	10.0(6)	-0.3(5)	2.8(6)	3.8(6)
C^{9}	13.4(7)	10.4(7)	13.0(7)	-0.4(5)	3.6(6)	1.5(5)
C^{10}	17.3(7)	20.5(8)	16.1(7)	-2.1(6)	5.3(6)	0.2(6)
C^{11}	22.2(8)	30.9(10)	18.2(8)	-8.3(7)	5.9(7)	1.4(7)
C^{12}	21.0(8)	24.4(9)	27.2(9)	-12.7(7)	1.6(7)	2.6(7)
C^{13}	20.1(8)	16.1(8)	29.1(9)	-3.2(7)	1.2(7)	1.4(7)
C^{14}	16.6(7)	15.7(8)	18.7(7)	0.3(6)	2.5(6)	1.3(6)
C^{15}	9.5(6)	15.6(7)	14.4(7)	-2.5(6)	2.5(5)	1.5(5)

C^{16}	17.0(7)	14.4(7)	15.3(7)	0.8(6)	5.8(6)	4.7(6)
C^{17}	28.5(9)	20.0(8)	17.6(8)	5.4(6)	12.8(7)	10.5(7)
C^{18}	33.5(10)	26.0(9)	11.1(7)	2.2(6)	5.5(7)	14.6(8)
C^{19}	20.4(8)	23.9(9)	15.6(7)	-5.0(6)	-2.8(6)	6.8(7)
C^{20}	16.7(7)	15.5(8)	16.6(7)	-2.5(6)	3.4(6)	3.3(6)
C^{21}	15.6(7)	11.1(7)	11.2(6)	0.3(5)	3.7(5)	4.9(6)
C^{22}	10.5(6)	16.3(8)	19.0(7)	0.9(6)	6.0(6)	-0.7(6)
C^{23}	16.1(7)	16.3(8)	16.2(7)	0.1(6)	8.6(6)	-2.3(6)
C^{24}	16.4(7)	15.7(8)	17.9(7)	1.0(6)	8.5(6)	-2.5(6)
C^{25}	12.0(7)	15.5(7)	16.6(7)	-0.6(6)	5.2(6)	-2.2(6)
C^{26}	16.8(7)	16.0(8)	17.5(7)	-1.9(6)	4.7(6)	-0.3(6)
C^{27}	21.6(8)	21.1(8)	15.5(7)	-4.0(6)	1.8(6)	-1.0(7)
C^{28}	30.1(9)	19.1(8)	14.7(7)	-3.2(6)	9.1(7)	0.3(7)
C^{29}	22.7(8)	18.0(8)	20.5(8)	-3.2(6)	11.2(7)	-0.3(6)
C^{30}	15.9(7)	15.2(7)	17.2(7)	-1.8(6)	6.4(6)	-0.8(6)
C^{31}	15.9(7)	9.7(7)	12.4(7)	-0.3(5)	3.8(6)	0.0(5)
C^{32}	27.0(9)	15.2(8)	17.3(7)	0.6(6)	5.7(7)	1.9(7)
C^{33}	37.5(10)	13.8(8)	25.9(9)	3.2(7)	9.6(8)	6.0(7)
C^{34}	31.2(10)	20.8(9)	24.9(9)	9.9(7)	6.7(7)	5.1(7)
C^{35}	27.5(9)	23.1(9)	14.9(7)	4.4(6)	3.7(7)	0.0(7)
C^{36}	20.3(8)	16.9(8)	17.0(7)	1.2(6)	7.1(6)	-0.6(6)
C^{37}	11.9(7)	13.2(7)	15.7(7)	2.9(6)	4.6(5)	-0.4(5)
B^{1}	11.6(7)	13.1(8)	12.0(7)	0.3(6)	4.1(6)	0.1(6)
N^{1}	11.3(6)	13.4(6)	12.6(6)	0.3(5)	5.0(5)	0.8(5)
N^{2}	11.0(6)	12.6(6)	11.0(5)	0.1(5)	3.6(5)	-0.2(5)
N^{3}	12.5(6)	12.2(6)	12.8(6)	0.4(5)	5.2(5)	-1.3(5)
N^{4}	10.5(6)	12.7(6)	12.8(6)	0.2(5)	5.0(5)	-1.1(5)
N^{5}	12.6(6)	13.1(6)	11.9(6)	1.0(5)	5.9(5)	0.2(5)
N^{6}	11.5(6)	11.2(6)	11.6(6)	1.0(5)	5.4(5)	1.1(5)
P^{1}	10.33(16)	10.54(17)	10.37(16)	0.23(13)	3.12(13)	-0.58(13)
P^{2}	9.47(16)	10.96(17)	10.72(16)	0.56(13)	3.48(13)	0.72(13)
Cl^{1}	14.80(16)	15.92(17)	9.38(14)	0.39(12)	3.09(12)	-0.36(13)
Ru^{1}	8.14(5)	9.44(6)	8.20(5)	0.52(4)	2.55(4)	0.02(4)
I^{1}	25.43(6)	13.42(5)	17.81(5)	-2.98(4)	6.36(4)	-5.91(4)
I^{2}	22.66(6)	26.11(6)	9.74(5)	-1.12(4)	1.43(4)	3.76(4)
I^{3}	16.81(5)	23.79(6)	22.27(6)	4.63(4)	2.53(4)	9.43(4)

Table A2.66: Bond Lengths for Tp^{i}Ru(dppb)Cl 215d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.772(5)	C^{21}	P^{2}	1.8325(15)
Cl^{2_1}	C^{1_1}	1.757(5)	C^{22}	C^{23}	1.542(2)
Cl^{1_2}	C^{1_2}	1.765(8)	C^{22}	P^{2}	1.8491(16)

Cl2_2	C1_2	1.763(8)	C23	C24	1.529(2)
C1	N2	1.334(2)	C24	C25	1.528(2)
C1	C2	1.399(2)	C25	P1	1.8364(16)
C2	C3	1.384(2)	C26	C27	1.396(2)
C2	I3	2.0676(15)	C26	C31	1.399(2)
C3	N1	1.3507(19)	C27	C28	1.383(3)
C4	N3	1.347(2)	C28	C29	1.394(2)
C4	C5	1.381(2)	C29	C30	1.392(2)
C5	C6	1.401(2)	C30	C31	1.402(2)
C5	I1	2.0678(16)	C31	P1	1.8436(16)
C6	N4	1.330(2)	C32	C33	1.390(2)
C7	N5	1.3560(19)	C32	C37	1.396(2)
C7	C8	1.381(2)	C33	C34	1.389(3)
C8	C9	1.393(2)	C34	C35	1.390(3)
C8	I2	2.0679(15)	C35	C36	1.391(2)
C9	N6	1.3368(19)	C36	C37	1.400(2)
C10	C11	1.391(2)	C37	P1	1.8464(16)
C10	C15	1.404(2)	B1	N5	1.534(2)
C11	C12	1.391(3)	B1	N3	1.548(2)
C12	C13	1.388(3)	B1	N1	1.551(2)
C13	C14	1.396(2)	N1	N2	1.3612(18)
C14	C15	1.397(2)	N2	Ru1	2.1264(13)
C15	P2	1.8536(16)	N3	N4	1.3669(17)
C16	C17	1.391(2)	N4	Ru1	2.1270(13)
C16	C21	1.401(2)	N5	N6	1.3670(18)
C17	C18	1.389(3)	N6	Ru1	2.0788(13)
C18	C19	1.382(3)	P1	Ru1	2.3362(4)
C19	C20	1.398(2)	P2	Ru1	2.3272(4)
C20	C21	1.399(2)	Cl1	Ru1	2.4258(4)

Table A2.67: Bond Angles for Tp^{i}Ru(dppb)Cl 215d.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl2_1	C1_1	Cl1_1	112.6(4)	C32	C37	P1	121.19(12)
Cl2_2	C1_2	Cl1_2	112.0(8)	C36	C37	P1	120.07(12)
N2	C1	C2	109.46(14)	N5	B1	N3	109.05(12)
C3	C2	C1	105.75(13)	N5	B1	N1	108.76(13)
C3	C2	I3	128.40(12)	N3	B1	N1	106.04(12)
C1	C2	I3	125.79(12)	C3	N1	N2	109.87(13)
N1	C3	C2	107.54(14)	C3	N1	B1	130.05(13)
N3	C4	C5	107.79(14)	N2	N1	B1	119.52(12)
C4	C5	C6	105.72(14)	C1	N2	N1	107.37(12)
C4	C5	I1	128.05(12)	C1	N2	Ru1	133.18(11)

C^{6}	C^{5}	I^{1}	126.21(12)	N^{1}	N^{2}	Ru^{1}	119.21(9)
N^{4}	C^{6}	C^{5}	109.43(14)	C^{4}	N^{3}	N^{4}	109.69(13)
N^{5}	C^{7}	C^{8}	107.77(13)	C^{4}	N^{3}	B^{1}	129.15(13)
C^{7}	C^{8}	C^{9}	105.48(13)	N^{4}	N^{3}	B^{1}	119.71(12)
C^{7}	C^{8}	I^{2}	129.29(12)	C^{6}	N^{4}	N^{3}	107.36(12)
C^{9}	C^{8}	I^{2}	125.20(12)	C^{6}	N^{4}	Ru^{1}	133.64(11)
N^{6}	C^{9}	C^{8}	110.37(14)	N^{3}	N^{4}	Ru^{1}	118.69(10)
C^{11}	C^{10}	C^{15}	120.95(17)	C^{7}	N^{5}	N^{6}	109.81(12)
C^{12}	C^{11}	C^{10}	120.57(17)	C^{7}	N^{5}	B^{1}	129.54(13)
C^{13}	C^{12}	C^{11}	119.10(17)	N^{6}	N^{5}	B^{1}	120.64(12)
C^{12}	C^{13}	C^{14}	120.44(18)	C^{9}	N^{6}	N^{5}	106.57(12)
C^{13}	C^{14}	C^{15}	121.13(16)	C^{9}	N^{6}	Ru^{1}	134.13(11)
C^{14}	C^{15}	C^{10}	117.78(15)	N^{5}	N^{6}	Ru^{1}	119.27(9)
C^{14}	C^{15}	P^{2}	122.89(12)	C^{25}	P^{1}	C^{31}	100.50(7)
C^{10}	C^{15}	P^{2}	119.30(13)	C^{25}	P^{1}	C^{37}	98.97(7)
C^{17}	C^{16}	C^{21}	120.85(16)	C^{31}	P^{1}	C^{37}	100.28(7)
C^{18}	C^{17}	C^{16}	119.88(17)	C^{25}	P^{1}	Ru^{1}	121.54(6)
C^{19}	C^{18}	C^{17}	120.18(15)	C^{31}	P^{1}	Ru^{1}	111.18(5)
C^{18}	C^{19}	C^{20}	120.03(16)	C^{37}	P^{1}	Ru^{1}	120.70(5)
C^{19}	C^{20}	C^{21}	120.55(16)	C^{21}	P^{2}	C^{22}	104.44(7)
C^{20}	C^{21}	C^{16}	118.42(14)	C^{21}	P^{2}	C^{15}	102.38(7)
C^{20}	C^{21}	P^{2}	122.70(12)	C^{22}	P^{2}	C^{15}	98.36(7)
C^{16}	C^{21}	P^{2}	118.41(12)	C^{21}	P^{2}	Ru^{1}	112.61(5)
C^{23}	C^{22}	P^{2}	112.73(11)	C^{22}	P^{2}	Ru^{1}	119.36(5)
C^{24}	C^{23}	C^{22}	112.40(13)	C^{15}	P^{2}	Ru^{1}	117.31(5)
C^{25}	C^{24}	C^{23}	115.94(13)	N^{6}	Ru^{1}	N^{2}	87.67(5)
C^{24}	C^{25}	P^{1}	116.65(11)	N^{6}	Ru^{1}	N^{4}	87.70(5)
C^{27}	C^{26}	C^{31}	120.93(16)	N^{2}	Ru^{1}	N^{4}	81.63(5)
C^{28}	C^{27}	C^{26}	120.24(16)	N^{6}	Ru^{1}	P^{2}	93.47(4)
C^{27}	C^{28}	C^{29}	119.65(15)	N^{2}	Ru^{1}	P^{2}	172.81(4)
C^{30}	C^{29}	C^{28}	120.13(16)	N^{4}	Ru^{1}	P^{2}	91.31(4)
C^{29}	C^{30}	C^{31}	120.93(15)	N^{6}	Ru^{1}	P^{1}	88.76(4)
C^{26}	C^{31}	C^{30}	118.08(14)	N^{2}	Ru^{1}	P^{1}	89.40(4)
C^{26}	C^{31}	P^{1}	122.54(12)	N^{4}	Ru^{1}	P^{1}	170.48(4)
C^{30}	C^{31}	P^{1}	119.26(12)	P^{2}	Ru^{1}	P^{1}	97.718(15)
C^{33}	C^{32}	C^{37}	120.97(16)	N^{6}	Ru^{1}	Cl^{1}	171.72(4)
C^{34}	C^{33}	C^{32}	120.16(17)	N^{2}	Ru^{1}	Cl^{1}	87.98(3)
C^{33}	C^{34}	C^{35}	119.37(17)	N^{4}	Ru^{1}	Cl^{1}	84.69(4)
C^{34}	C^{35}	C^{36}	120.64(16)	P^{2}	Ru^{1}	Cl^{1}	89.990(13)
C^{35}	C^{36}	C^{37}	120.30(16)	P^{1}	Ru^{1}	Cl^{1}	98.243(13)
C^{32}	C^{37}	C^{36}	118.56(15)				

Table A2.68: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}Ru(dppb)Cl 215d.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	5192	2298	6189	40
H^{1AB_1}	4450	2988	6326	40
H^{1A_2}	5113	1936	6004	51
H^{1AB_2}	4687	2894	6163	51
H^{1}	6813	5672	8903	16
H^{3}	8344	6634	7801	17
H^{4}	7450	9628	7690	17
H^{6}	5826	9313	8851	15
H^{7}	5784	7600	5756	16
H^{9}	3605	6941	6340	15
H^{10}	3824	8450	9226	22
H^{11}	3868	9757	9907	29
H^{12}	4025	11255	9506	31
H^{13}	4154	11427	8418	29
H^{14}	4069	10124	7721	22
H^{16}	4434	9215	6956	19
H^{17}	3839	9683	5802	25
H^{18}	2324	9240	5103	29
H^{19}	1363	8435	5575	27
H^{20}	1923	8042	6750	20
H^{22A}	2452	8010	8165	18
H^{22B}	2406	7212	7613	18
H^{23A}	3852	6892	8871	19
H^{23B}	2846	6911	8955	19
H^{24A}	3353	5375	8737	19
H^{24B}	2319	5657	8246	19
H^{25A}	2853	5963	7336	18
H^{25B}	3091	4914	7599	18
H^{26}	3075	5009	6538	20
H^{27}	3109	4493	5476	25
H^{28}	4532	4393	5289	25
H^{29}	5936	4772	6183	23
H^{30}	5905	5312	7238	19
H^{32}	4868	3779	7702	25
H^{33}	5469	2558	8476	31
H^{34}	5981	2834	9667	32
H^{35}	5881	4340	10073	27
H^{36}	5288	5568	9301	21
H^{1B}	7143(14)	7971(14)	7012(10)	15

Table A2.69: Atomic Occupancy for Tp^{I}Ru(dppb)Cl 215d.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl^{1_1}	0.63(3)	Cl^{2_1}	0.63(3)	C^{1_1}	0.63(3)
H^{1A_1}	0.63(3)	H^{1AB_1}	0.63(3)	Cl^{1_2}	0.37(3)
Cl^{2_2}	0.37(3)	C^{1_2}	0.37(3)	H^{1A_2}	0.37(3)
H^{1AB_2}	0.37(3)				

Table A2.70: Crystal data and structure refinement for $Tp^{Cl}RuPPh_3Cl_2$ 216c.

Identification code: $Tp^{Cl}RuPPh_3Cl_2$ **216c**		
Empirical formula: C28 H24 B Cl7 N6 P Ru		
Formula weight: 835.53		
Temperature: 123(2) K		
Wavelength: 0.71073 Å		
Crystal system: Orthorhombic		
Space group: P b c a		
Unit cell dimensions	a = 13.6836(10) Å	α= 90°.
	b = 16.0488(12) Å	β= 90°.
	c = 29.928(2) Å	γ = 90°.
Volume	6572.4(8) $Å^3$	
Z	8	
Density (calculated)	1.689 Mg/m^3	
Absorption coefficient	1.127 mm^{-1}	
F(000)	3336	
Crystal size	0.28 x 0.26 x 0.10 mm^3	
Theta range for data collection	2.017 to 28.448°.	
Index ranges	-18<=h<=18, -20<=k<=21, -40<=l<=40	
Reflections collected	67586	
Independent reflections	8258 [R(int) = 0.0168]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.6827	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8258 / 0 / 400	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0785	
R indices (all data)	R1 = 0.0363, wR2 = 0.0828	
Largest diff. peak and hole	1.085 and -0.711 $e.Å^{-3}$	

Table A2.71: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Cl}RuPPh_3Cl_2$ 216c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2763(1)	5393(1)	3665(1)	13(1)
Cl(1)	3364(1)	6481(1)	4109(1)	19(1)
Cl(2)	2018(1)	6340(1)	3187(1)	21(1)
Cl(3)	4877(1)	3458(1)	5034(1)	32(1)
Cl(4)	-821(1)	6287(1)	4646(1)	31(1)
Cl(5)	1327(1)	2887(1)	2396(1)	21(1)
Cl(6)	6999(1)	5062(1)	4465(1)	40(1)
Cl(7)	8053(1)	3513(1)	4667(1)	38(1)
P(1)	4189(1)	5278(1)	3205(1)	14(1)
N(1)	3268(2)	4541(1)	4136(1)	16(1)
N(2)	2643(2)	3936(1)	4282(1)	17(1)
N(3)	1073(2)	4705(1)	4190(1)	17(1)
N(4)	1492(2)	5431(1)	4059(1)	16(1)
N(5)	1688(2)	3784(1)	3581(1)	16(1)
N(6)	2103(1)	4410(1)	3335(1)	15(1)
C(1)	4098(2)	4459(2)	4366(1)	19(1)
C(2)	4012(2)	3791(2)	4657(1)	21(1)
C(3)	3088(2)	3467(2)	4595(1)	20(1)
C(4)	231(2)	4873(2)	4407(1)	20(1)
C(5)	120(2)	5727(2)	4414(1)	20(1)
C(6)	929(2)	6054(2)	4195(1)	19(1)
C(7)	1385(2)	3172(2)	3312(1)	17(1)
C(8)	1584(2)	3416(1)	2879(1)	16(1)
C(9)	2022(2)	4191(2)	2902(1)	16(1)
C(10)	4003(2)	5156(1)	2602(1)	15(1)
C(11)	3445(2)	5740(2)	2368(1)	20(1)
C(12)	3318(2)	5672(2)	1909(1)	24(1)
C(13)	3748(2)	5021(2)	1675(1)	26(1)
C(14)	4306(2)	4441(2)	1904(1)	27(1)

C(15)	4434(2)	4505(2)	2363(1)	22(1)
C(16)	5459(2)	6496(2)	2853(1)	21(1)
C(17)	6151(2)	7131(2)	2888(1)	26(1)
C(18)	6489(2)	7379(2)	3301(1)	27(1)
C(19)	6151(2)	6990(2)	3683(1)	25(1)
C(20)	5457(2)	6358(2)	3653(1)	20(1)
C(21)	5098(2)	6112(1)	3235(1)	17(1)
C(22)	4861(2)	4336(2)	3362(1)	16(1)
C(23)	5828(2)	4359(2)	3509(1)	20(1)
C(24)	6276(2)	3643(2)	3673(1)	24(1)
C(25)	5782(2)	2890(2)	3676(1)	24(1)
C(26)	4831(2)	2852(2)	3511(1)	23(1)
C(27)	4372(2)	3572(2)	3362(1)	19(1)
C(28)	7500(3)	4437(2)	4882(1)	37(1)
B(1)	1593(2)	3873(2)	4093(1)	17(1)

Table A2.72: Bond lengths [Å] and angles [°] for $Tp^{Cl}RuPPh_3Cl_2$ 216c.

Ru(1)-N(6)	2.069(2)	N(2)-C(3)	1.347(3)
Ru(1)-N(1)	2.0832(19)	N(2)-B(1)	1.546(3)
Ru(1)-N(4)	2.102(2)	N(3)-C(4)	1.349(3)
Ru(1)-Cl(2)	2.3220(6)	N(3)-N(4)	1.358(3)
Ru(1)-Cl(1)	2.3424(6)	N(3)-B(1)	1.540(3)
Ru(1)-P(1)	2.3948(6)	N(4)-C(6)	1.326(3)
Cl(3)-C(2)	1.720(3)	N(5)-C(7)	1.337(3)
Cl(4)-C(5)	1.718(3)	N(5)-N(6)	1.369(3)
Cl(5)-C(8)	1.711(2)	N(5)-B(1)	1.544(3)
Cl(6)-C(28)	1.742(3)	N(6)-C(9)	1.346(3)
Cl(7)-C(28)	1.786(3)	C(1)-C(2)	1.387(3)
P(1)-C(21)	1.830(2)	C(1)-H(1)	0.9500
P(1)-C(22)	1.832(2)	C(2)-C(3)	1.380(4)
P(1)-C(10)	1.834(2)	C(3)-H(3)	0.9500
N(1)-C(1)	1.333(3)	C(4)-C(5)	1.380(4)
N(1)-N(2)	1.366(3)	C(4)-H(4)	0.9500

C(5)-C(6)	1.390(3)	C(25)-H(25)	0.9500
C(6)-H(6)	0.9500	C(26)-C(27)	1.388(3)
C(7)-C(8)	1.381(3)	C(26)-H(26)	0.9500
C(7)-H(7)	0.9500	C(27)-H(27)	0.9500
C(8)-C(9)	1.383(3)	C(28)-H(28A)	0.9900
C(9)-H(9)	0.9500	C(28)-H(28B)	0.9900
C(10)-C(15)	1.396(3)	B(1)-H(1B)	1.06(3)
C(10)-C(11)	1.397(3)		
C(11)-C(12)	1.388(3)	N(6)-Ru(1)-N(1)	88.11(8)
C(11)-H(11)	0.9500	N(6)-Ru(1)-N(4)	85.93(8)
C(12)-C(13)	1.388(4)	N(1)-Ru(1)-N(4)	85.04(8)
C(12)-H(12)	0.9500	N(6)-Ru(1)-Cl(2)	90.82(6)
C(13)-C(14)	1.384(4)	N(1)-Ru(1)-Cl(2)	172.92(6)
C(13)-H(13)	0.9500	N(4)-Ru(1)-Cl(2)	87.90(6)
C(14)-C(15)	1.390(4)	N(6)-Ru(1)-Cl(1)	172.80(6)
C(14)-H(14)	0.9500	N(1)-Ru(1)-Cl(1)	89.32(6)
C(15)-H(15)	0.9500	N(4)-Ru(1)-Cl(1)	87.15(6)
C(16)-C(21)	1.389(3)	Cl(2)-Ru(1)-Cl(1)	90.92(2)
C(16)-C(17)	1.395(3)	N(6)-Ru(1)-P(1)	91.30(6)
C(16)-H(16)	0.9500	N(1)-Ru(1)-P(1)	93.89(6)
C(17)-C(18)	1.377(4)	N(4)-Ru(1)-P(1)	177.05(6)
C(17)-H(17)	0.9500	Cl(2)-Ru(1)-P(1)	93.13(2)
C(18)-C(19)	1.384(4)	Cl(1)-Ru(1)-P(1)	95.59(2)
C(18)-H(18)	0.9500	C(21)-P(1)-C(22)	104.48(11)
C(19)-C(20)	1.392(4)	C(21)-P(1)-C(10)	102.79(11)
C(19)-H(19)	0.9500	C(22)-P(1)-C(10)	103.57(10)
C(20)-C(21)	1.401(3)	C(21)-P(1)-Ru(1)	117.97(8)
C(20)-H(20)	0.9500	C(22)-P(1)-Ru(1)	108.99(8)
C(22)-C(23)	1.394(3)	C(10)-P(1)-Ru(1)	117.41(8)
C(22)-C(27)	1.397(3)	C(1)-N(1)-N(2)	107.38(19)
C(23)-C(24)	1.392(4)	C(1)-N(1)-Ru(1)	134.14(17)
C(23)-H(23)	0.9500	N(2)-N(1)-Ru(1)	118.36(15)
C(24)-C(25)	1.385(4)	C(3)-N(2)-N(1)	109.7(2)
C(24)-H(24)	0.9500	C(3)-N(2)-B(1)	129.5(2)
C(25)-C(26)	1.392(4)	N(1)-N(2)-B(1)	120.80(19)

C(4)-N(3)-N(4)	109.2(2)	C(9)-C(8)-Cl(5)	125.35(18)
C(4)-N(3)-B(1)	131.2(2)	N(6)-C(9)-C(8)	108.6(2)
N(4)-N(3)-B(1)	119.58(19)	N(6)-C(9)-H(9)	125.7
C(6)-N(4)-N(3)	108.22(19)	C(8)-C(9)-H(9)	125.7
C(6)-N(4)-Ru(1)	132.43(17)	C(15)-C(10)-C(11)	118.4(2)
N(3)-N(4)-Ru(1)	119.17(15)	C(15)-C(10)-P(1)	121.65(18)
C(7)-N(5)-N(6)	110.00(19)	C(11)-C(10)-P(1)	119.89(18)
C(7)-N(5)-B(1)	129.8(2)	C(12)-C(11)-C(10)	120.8(2)
N(6)-N(5)-B(1)	120.14(19)	C(12)-C(11)-H(11)	119.6
C(9)-N(6)-N(5)	107.06(19)	C(10)-C(11)-H(11)	119.6
C(9)-N(6)-Ru(1)	133.91(16)	C(11)-C(12)-C(13)	120.3(2)
N(5)-N(6)-Ru(1)	118.90(14)	C(11)-C(12)-H(12)	119.9
N(1)-C(1)-C(2)	109.2(2)	C(13)-C(12)-H(12)	119.9
N(1)-C(1)-H(1)	125.4	C(14)-C(13)-C(12)	119.4(2)
C(2)-C(1)-H(1)	125.4	C(14)-C(13)-H(13)	120.3
C(3)-C(2)-C(1)	106.5(2)	C(12)-C(13)-H(13)	120.3
C(3)-C(2)-Cl(3)	127.0(2)	C(13)-C(14)-C(15)	120.6(2)
C(1)-C(2)-Cl(3)	126.5(2)	C(13)-C(14)-H(14)	119.7
N(2)-C(3)-C(2)	107.3(2)	C(15)-C(14)-H(14)	119.7
N(2)-C(3)-H(3)	126.4	C(14)-C(15)-C(10)	120.5(2)
C(2)-C(3)-H(3)	126.4	C(14)-C(15)-H(15)	119.7
N(3)-C(4)-C(5)	107.4(2)	C(10)-C(15)-H(15)	119.7
N(3)-C(4)-H(4)	126.3	C(21)-C(16)-C(17)	120.2(2)
C(5)-C(4)-H(4)	126.3	C(21)-C(16)-H(16)	119.9
C(4)-C(5)-C(6)	106.3(2)	C(17)-C(16)-H(16)	119.9
C(4)-C(5)-Cl(4)	127.5(2)	C(18)-C(17)-C(16)	120.4(3)
C(6)-C(5)-Cl(4)	126.1(2)	C(18)-C(17)-H(17)	119.8
N(4)-C(6)-C(5)	108.8(2)	C(16)-C(17)-H(17)	119.8
N(4)-C(6)-H(6)	125.6	C(17)-C(18)-C(19)	119.9(2)
C(5)-C(6)-H(6)	125.6	C(17)-C(18)-H(18)	120.0
N(5)-C(7)-C(8)	107.3(2)	C(19)-C(18)-H(18)	120.0
N(5)-C(7)-H(7)	126.3	C(18)-C(19)-C(20)	120.2(2)
C(8)-C(7)-H(7)	126.3	C(18)-C(19)-H(19)	119.9
C(7)-C(8)-C(9)	107.0(2)	C(20)-C(19)-H(19)	119.9
C(7)-C(8)-Cl(5)	127.69(19)	C(19)-C(20)-C(21)	120.1(2)

C(19)-C(20)-H(20)	119.9	C(25)-C(26)-H(26)	120.0
C(21)-C(20)-H(20)	119.9	C(26)-C(27)-C(22)	120.9(2)
C(16)-C(21)-C(20)	119.1(2)	C(26)-C(27)-H(27)	119.6
C(16)-C(21)-P(1)	121.69(18)	C(22)-C(27)-H(27)	119.6
C(20)-C(21)-P(1)	119.23(18)	Cl(6)-C(28)-Cl(7)	112.67(17)
C(23)-C(22)-C(27)	118.6(2)	Cl(6)-C(28)-H(28A)	109.1
C(23)-C(22)-P(1)	122.37(19)	Cl(7)-C(28)-H(28A)	109.1
C(27)-C(22)-P(1)	118.93(18)	Cl(6)-C(28)-H(28B)	109.1
C(24)-C(23)-C(22)	120.4(2)	Cl(7)-C(28)-H(28B)	109.1
C(24)-C(23)-H(23)	119.8	H(28A)-C(28)-H(28B)	107.8
C(22)-C(23)-H(23)	119.8	N(3)-B(1)-N(5)	107.76(19)
C(25)-C(24)-C(23)	120.5(2)	N(3)-B(1)-N(2)	107.71(19)
C(25)-C(24)-H(24)	119.8	N(5)-B(1)-N(2)	106.88(19)
C(23)-C(24)-H(24)	119.8	N(3)-B(1)-H(1B)	113.2(17)
C(24)-C(25)-C(26)	119.5(2)	N(5)-B(1)-H(1B)	110.8(17)
C(24)-C(25)-H(25)	120.2	N(2)-B(1)-H(1B)	110.2(17)
C(26)-C(25)-H(25)	120.2		
C(27)-C(26)-C(25)	120.0(2)		
C(27)-C(26)-H(26)	120.0		

Table A2.73: Anisotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Cl}RuPPh_3Cl_2$ 216c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	13(1)	11(1)	0(1)	0(1)	0(1)
Cl(1)	23(1)	17(1)	17(1)	-3(1)	0(1)	-3(1)
Cl(2)	22(1)	22(1)	18(1)	5(1)	1(1)	5(1)
Cl(3)	32(1)	38(1)	27(1)	8(1)	-11(1)	7(1)
Cl(4)	27(1)	35(1)	31(1)	6(1)	12(1)	13(1)
Cl(5)	26(1)	20(1)	16(1)	-4(1)	-2(1)	0(1)
Cl(6)	54(1)	37(1)	30(1)	-7(1)	-8(1)	5(1)
Cl(7)	42(1)	37(1)	34(1)	-1(1)	1(1)	1(1)
P(1)	13(1)	14(1)	13(1)	0(1)	0(1)	-1(1)

N(1)	18(1)	16(1)	13(1)	1(1)	-1(1)	0(1)
N(2)	21(1)	16(1)	14(1)	1(1)	1(1)	1(1)
N(3)	18(1)	18(1)	14(1)	1(1)	3(1)	-3(1)
N(4)	17(1)	16(1)	14(1)	1(1)	0(1)	0(1)
N(5)	16(1)	17(1)	14(1)	1(1)	-1(1)	-1(1)
N(6)	14(1)	16(1)	15(1)	0(1)	0(1)	-2(1)
C(1)	20(1)	23(1)	15(1)	-1(1)	-1(1)	1(1)
C(2)	25(1)	23(1)	16(1)	1(1)	-4(1)	6(1)
C(3)	28(1)	19(1)	13(1)	2(1)	0(1)	2(1)
C(4)	16(1)	28(1)	17(1)	2(1)	3(1)	1(1)
C(5)	18(1)	27(1)	16(1)	1(1)	2(1)	4(1)
C(6)	21(1)	20(1)	16(1)	1(1)	0(1)	2(1)
C(7)	16(1)	16(1)	19(1)	-1(1)	-1(1)	0(1)
C(8)	16(1)	17(1)	15(1)	-3(1)	-2(1)	2(1)
C(9)	15(1)	19(1)	14(1)	1(1)	-1(1)	1(1)
C(10)	12(1)	18(1)	16(1)	1(1)	1(1)	-2(1)
C(11)	22(1)	18(1)	19(1)	2(1)	2(1)	2(1)
C(12)	26(1)	26(1)	19(1)	4(1)	1(1)	5(1)
C(13)	28(1)	34(1)	16(1)	-2(1)	-2(1)	4(1)
C(14)	30(1)	31(1)	20(1)	-6(1)	1(1)	10(1)
C(15)	22(1)	24(1)	19(1)	-1(1)	0(1)	6(1)
C(16)	19(1)	21(1)	22(1)	-1(1)	0(1)	-3(1)
C(17)	20(1)	26(1)	31(1)	2(1)	2(1)	-6(1)
C(18)	20(1)	22(1)	40(2)	-4(1)	0(1)	-7(1)
C(19)	23(1)	25(1)	27(1)	-8(1)	-3(1)	-4(1)
C(20)	19(1)	22(1)	20(1)	-3(1)	0(1)	-1(1)
C(21)	14(1)	16(1)	21(1)	-1(1)	1(1)	-1(1)
C(22)	18(1)	18(1)	13(1)	0(1)	1(1)	2(1)
C(23)	20(1)	22(1)	20(1)	-4(1)	-1(1)	2(1)
C(24)	23(1)	28(1)	21(1)	-4(1)	-5(1)	7(1)
C(25)	33(1)	24(1)	17(1)	4(1)	0(1)	9(1)
C(26)	27(1)	19(1)	23(1)	3(1)	6(1)	2(1)
C(27)	18(1)	21(1)	19(1)	3(1)	3(1)	0(1)
C(28)	46(2)	40(2)	25(1)	-2(1)	2(1)	4(1)
B(1)	18(1)	18(1)	15(1)	0(1)	1(1)	-2(1)

Table A2.74: Crystal data and structure refinement for $Tp^{Br}RuPPh_3Cl_2$ 216d.

Identification code	$Tp^{Br}RuPPh_3Cl_2$ **216d**	
Empirical formula	C27 H22 B Br3 Cl2 N6 P Ru	
Formula weight	883.98	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 11.6113(7) Å	α= 90°.
	b = 18.4508(11) Å	β= 90.4680(10)°.
	c = 14.3478(8) Å	γ = 90°.
Volume	3073.7(3) $Å^3$	
Z	4	
Density (calculated)	1.910 Mg/m^3	
Absorption coefficient	4.666 mm^{-1}	
F(000)	1716	
Crystal size	0.320 x 0.140 x 0.050 mm^3	
Theta range for data collection	2.820 to 28.393°.	
Index ranges	-15<=h<=15, -24<=k<=24, -18<=l<=19	
Reflections collected	23343	
Independent reflections	7370 [R(int) = 0.0180]	
Completeness to theta = 25.242°	97.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.5052	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7370 / 0 / 373	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0204, wR2 = 0.0532	
R indices (all data)	R1 = 0.0233, wR2 = 0.0548	
Largest diff. peak and hole	0.856 and -0.749 $e.Å^{-3}$	

Table A2.75: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Br}RuPPh_3Cl_2$ 216d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7813(1)	3857(1)	2647(1)	10(1)
Br(1)	8483(1)	5467(1)	-1000(1)	18(1)
Br(2)	2848(1)	2880(1)	2326(1)	27(1)
Br(3)	7847(1)	6454(1)	5257(1)	29(1)
Cl(1)	9772(1)	4113(1)	2802(1)	15(1)
Cl(2)	8021(1)	2885(1)	1624(1)	16(1)
P(1)	7991(1)	3069(1)	3944(1)	12(1)
N(1)	6815(1)	5028(1)	1385(1)	14(1)
N(2)	7693(1)	4542(1)	1467(1)	13(1)
N(3)	5389(1)	4360(1)	2336(1)	15(1)
N(4)	6025(1)	3757(1)	2534(1)	13(1)
N(5)	6667(1)	5276(1)	3086(1)	15(1)
N(6)	7516(1)	4819(1)	3391(1)	14(1)
C(1)	11134(2)	1540(1)	4246(2)	24(1)
C(2)	10443(2)	1688(1)	5007(1)	23(1)
C(3)	9501(2)	2152(1)	4913(1)	19(1)
C(4)	9280(2)	2501(1)	4058(1)	15(1)
C(5)	9983(2)	2352(1)	3299(1)	18(1)
C(6)	10894(2)	1862(1)	3390(2)	22(1)
C(7)	8899(2)	3731(1)	5563(1)	20(1)
C(8)	8838(2)	4214(1)	6312(1)	27(1)
C(9)	7817(2)	4553(1)	6528(2)	32(1)
C(10)	6830(2)	4421(1)	5996(2)	27(1)
C(11)	6889(2)	3951(1)	5236(1)	19(1)
C(12)	7907(2)	3590(1)	5023(1)	15(1)
C(13)	6872(2)	2368(1)	4003(1)	15(1)
C(14)	5912(2)	2394(1)	4581(1)	22(1)
C(15)	5017(2)	1898(1)	4470(2)	27(1)
C(16)	5081(2)	1364(1)	3790(2)	25(1)

C(17)	6056(2)	1309(1)	3242(1)	20(1)
C(18)	6945(2)	1808(1)	3344(1)	16(1)
C(19)	8334(2)	4598(1)	702(1)	14(1)
C(20)	7863(2)	5130(1)	120(1)	15(1)
C(21)	6901(2)	5390(1)	570(1)	15(1)
C(22)	4274(2)	4180(1)	2231(1)	18(1)
C(23)	4186(2)	3439(1)	2358(1)	18(1)
C(24)	5294(2)	3192(1)	2540(1)	16(1)
C(25)	8039(2)	5145(1)	4118(1)	17(1)
C(26)	7511(2)	5810(1)	4286(1)	19(1)
C(27)	6648(2)	5877(1)	3623(1)	18(1)
B(1)	5959(2)	5104(1)	2198(1)	15(1)

Table A2.76: Bond lengths [Å] and angles [°] for $Tp^{Br}RuPPh_3Cl_2$ 216d.

Ru(1)-N(4)	2.0890(15)	N(4)-C(24)	1.343(2)
Ru(1)-N(6)	2.1005(15)	N(5)-C(27)	1.351(2)
Ru(1)-N(2)	2.1166(14)	N(5)-N(6)	1.366(2)
Ru(1)-Cl(1)	2.3323(5)	N(5)-B(1)	1.544(2)
Ru(1)-Cl(2)	2.3327(4)	N(6)-C(25)	1.344(2)
Ru(1)-P(1)	2.3699(4)	C(1)-C(2)	1.388(3)
Br(1)-C(20)	1.8713(18)	C(1)-C(6)	1.389(3)
Br(2)-C(23)	1.8654(19)	C(1)-H(1)	0.9500
Br(3)-C(26)	1.8716(18)	C(2)-C(3)	1.394(3)
P(1)-C(12)	1.8257(18)	C(2)-H(2)	0.9500
P(1)-C(4)	1.8328(19)	C(3)-C(4)	1.407(2)
P(1)-C(13)	1.8353(18)	C(3)-H(3)	0.9500
N(1)-C(21)	1.351(2)	C(4)-C(5)	1.394(3)
N(1)-N(2)	1.362(2)	C(5)-C(6)	1.398(3)
N(1)-B(1)	1.546(3)	C(5)-H(5)	0.9500
N(2)-C(19)	1.335(2)	C(6)-H(6)	0.9500
N(3)-C(22)	1.344(2)	C(7)-C(8)	1.398(3)
N(3)-N(4)	1.365(2)	C(7)-C(12)	1.407(3)
N(3)-B(1)	1.537(2)	C(7)-H(7)	0.9500

C(8)-C(9)	1.378(3)	N(6)-Ru(1)-N(2)	83.82(6)
C(8)-H(8)	0.9500	N(4)-Ru(1)-Cl(1)	173.35(4)
C(9)-C(10)	1.393(3)	N(6)-Ru(1)-Cl(1)	86.84(4)
C(9)-H(9)	0.9500	N(2)-Ru(1)-Cl(1)	90.77(4)
C(10)-C(11)	1.396(3)	N(4)-Ru(1)-Cl(2)	89.50(4)
C(10)-H(10)	0.9500	N(6)-Ru(1)-Cl(2)	171.12(4)
C(11)-C(12)	1.392(3)	N(2)-Ru(1)-Cl(2)	87.81(4)
C(11)-H(11)	0.9500	Cl(1)-Ru(1)-Cl(2)	96.261(16)
C(13)-C(14)	1.396(3)	N(4)-Ru(1)-P(1)	94.97(4)
C(13)-C(18)	1.403(2)	N(6)-Ru(1)-P(1)	97.66(4)
C(14)-C(15)	1.394(3)	N(2)-Ru(1)-P(1)	178.20(4)
C(14)-H(14)	0.9500	Cl(1)-Ru(1)-P(1)	88.287(16)
C(15)-C(16)	1.389(3)	Cl(2)-Ru(1)-P(1)	90.764(16)
C(15)-H(15)	0.9500	C(12)-P(1)-C(4)	105.94(8)
C(16)-C(17)	1.387(3)	C(12)-P(1)-C(13)	106.81(8)
C(16)-H(16)	0.9500	C(4)-P(1)-C(13)	99.87(8)
C(17)-C(18)	1.391(3)	C(12)-P(1)-Ru(1)	109.73(6)
C(17)-H(17)	0.9500	C(4)-P(1)-Ru(1)	119.16(6)
C(18)-H(18)	0.9500	C(13)-P(1)-Ru(1)	114.25(5)
C(19)-C(20)	1.397(2)	C(21)-N(1)-N(2)	109.83(15)
C(19)-H(19)	0.9500	C(21)-N(1)-B(1)	131.42(15)
C(20)-C(21)	1.381(3)	N(2)-N(1)-B(1)	118.69(14)
C(21)-H(21)	0.9500	C(19)-N(2)-N(1)	107.43(14)
C(22)-C(23)	1.382(3)	C(19)-N(2)-Ru(1)	132.14(12)
C(22)-H(22)	0.9500	N(1)-N(2)-Ru(1)	120.41(11)
C(23)-C(24)	1.388(3)	C(22)-N(3)-N(4)	109.88(15)
C(24)-H(24)	0.9500	C(22)-N(3)-B(1)	128.48(15)
C(25)-C(26)	1.393(3)	N(4)-N(3)-B(1)	121.50(15)
C(25)-H(25)	0.9500	C(24)-N(4)-N(3)	107.04(15)
C(26)-C(27)	1.381(3)	C(24)-N(4)-Ru(1)	134.09(12)
C(27)-H(27)	0.9500	N(3)-N(4)-Ru(1)	118.64(11)
B(1)-H(1B)	1.06(2)	C(27)-N(5)-N(6)	109.87(15)
		C(27)-N(5)-B(1)	128.93(16)
N(4)-Ru(1)-N(6)	86.98(6)	N(6)-N(5)-B(1)	120.99(14)
N(4)-Ru(1)-N(2)	86.12(6)	C(25)-N(6)-N(5)	106.98(14)

C(25)-N(6)-Ru(1)	134.18(13)	C(11)-C(12)-C(7)	118.90(17)
N(5)-N(6)-Ru(1)	118.69(11)	C(11)-C(12)-P(1)	119.28(13)
C(2)-C(1)-C(6)	119.91(19)	C(7)-C(12)-P(1)	120.99(15)
C(2)-C(1)-H(1)	120.0	C(14)-C(13)-C(18)	118.62(17)
C(6)-C(1)-H(1)	120.0	C(14)-C(13)-P(1)	124.90(14)
C(1)-C(2)-C(3)	120.17(18)	C(18)-C(13)-P(1)	116.15(14)
C(1)-C(2)-H(2)	119.9	C(15)-C(14)-C(13)	120.49(19)
C(3)-C(2)-H(2)	119.9	C(15)-C(14)-H(14)	119.8
C(2)-C(3)-C(4)	120.20(19)	C(13)-C(14)-H(14)	119.8
C(2)-C(3)-H(3)	119.9	C(16)-C(15)-C(14)	120.2(2)
C(4)-C(3)-H(3)	119.9	C(16)-C(15)-H(15)	119.9
C(5)-C(4)-C(3)	119.12(17)	C(14)-C(15)-H(15)	119.9
C(5)-C(4)-P(1)	121.71(13)	C(17)-C(16)-C(15)	119.86(19)
C(3)-C(4)-P(1)	118.89(15)	C(17)-C(16)-H(16)	120.1
C(4)-C(5)-C(6)	120.15(17)	C(15)-C(16)-H(16)	120.1
C(4)-C(5)-H(5)	119.9	C(16)-C(17)-C(18)	120.05(18)
C(6)-C(5)-H(5)	119.9	C(16)-C(17)-H(17)	120.0
C(1)-C(6)-C(5)	120.3(2)	C(18)-C(17)-H(17)	120.0
C(1)-C(6)-H(6)	119.8	C(17)-C(18)-C(13)	120.64(19)
C(5)-C(6)-H(6)	119.8	C(17)-C(18)-H(18)	119.7
C(8)-C(7)-C(12)	119.7(2)	C(13)-C(18)-H(18)	119.7
C(8)-C(7)-H(7)	120.2	N(2)-C(19)-C(20)	109.18(16)
C(12)-C(7)-H(7)	120.2	N(2)-C(19)-H(19)	125.4
C(9)-C(8)-C(7)	120.73(19)	C(20)-C(19)-H(19)	125.4
C(9)-C(8)-H(8)	119.6	C(21)-C(20)-C(19)	106.15(16)
C(7)-C(8)-H(8)	119.6	C(21)-C(20)-Br(1)	127.19(13)
C(8)-C(9)-C(10)	120.20(19)	C(19)-C(20)-Br(1)	126.52(15)
C(8)-C(9)-H(9)	119.9	N(1)-C(21)-C(20)	107.41(15)
C(10)-C(9)-H(9)	119.9	N(1)-C(21)-H(21)	126.3
C(9)-C(10)-C(11)	119.4(2)	C(20)-C(21)-H(21)	126.3
C(9)-C(10)-H(10)	120.3	N(3)-C(22)-C(23)	107.60(16)
C(11)-C(10)-H(10)	120.3	N(3)-C(22)-H(22)	126.2
C(12)-C(11)-C(10)	121.02(19)	C(23)-C(22)-H(22)	126.2
C(12)-C(11)-H(11)	119.5	C(22)-C(23)-C(24)	106.28(16)
C(10)-C(11)-H(11)	119.5	C(22)-C(23)-Br(2)	127.30(15)

C(24)-C(23)-Br(2)	126.40(14)	N(5)-C(27)-H(27)	126.2
N(4)-C(24)-C(23)	109.20(16)	C(26)-C(27)-H(27)	126.2
N(4)-C(24)-H(24)	125.4	N(3)-B(1)-N(5)	107.73(14)
C(23)-C(24)-H(24)	125.4	N(3)-B(1)-N(1)	107.27(14)
N(6)-C(25)-C(26)	109.36(16)	N(5)-B(1)-N(1)	107.45(15)
N(6)-C(25)-H(25)	125.3	N(3)-B(1)-H(1B)	111.8(13)
C(26)-C(25)-H(25)	125.3	N(5)-B(1)-H(1B)	110.2(12)
C(27)-C(26)-C(25)	106.15(16)	N(1)-B(1)-H(1B)	112.1(13)
C(27)-C(26)-Br(3)	126.93(15)		
C(25)-C(26)-Br(3)	126.82(14)		
N(5)-C(27)-C(26)	107.63(16)		

Symmetry transformations used to generate equivalent atoms:

Table A2.77: Anisotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Br}RuPPh_3Cl_2$ 216d. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	11(1)	9(1)	10(1)	0(1)	0(1)	0(
Br(1)	19(1)	21(1)	13(1)	5(1)	-1(1)	-2(1)
Br(2)	16(1)	27(1)	38(1)	3(1)	0(1)	-8(1)
Br(3)	41(1)	20(1)	25(1)	-11(1)	-4(1)	-1(1)
Cl(1)	13(1)	15(1)	18(1)	2(1)	0(1)	-2(1)
Cl(2)	20(1)	13(1)	14(1)	-2(1)	0(1)	2(1)
P(1)	13(1)	11(1)	11(1)	1(1)	-1(1)	-1(1)
N(1)	16(1)	12(1)	15(1)	1(1)	-2(1)	2(1)
N(2)	14(1)	12(1)	14(1)	1(1)	-1(1)	2(1)
N(3)	13(1)	14(1)	17(1)	0(1)	0(1)	3(1)
N(4)	12(1)	13(1)	15(1)	1(1)	-1(1)	1(1)
N(5)	16(1)	11(1)	16(1)	0(1)	2(1)	1(1)
N(6)	15(1)	12(1)	15(1)	0(1)	1(1)	1(1)
C(1)	18(1)	14(1)	41(1)	4(1)	-6(1)	1(1)
C(2)	25(1)	16(1)	27(1)	5(1)	-11(1)	-1(1)

C(3)	22(1)	15(1)	19(1)	2(1)	-3(1)	-2(1)
C(4)	14(1)	11(1)	20(1)	2(1)	-4(1)	-1(1)
C(5)	18(1)	14(1)	23(1)	2(1)	0(1)	-2(1)
C(6)	15(1)	15(1)	34(1)	0(1)	4(1)	-1(1)
C(7)	24(1)	17(1)	18(1)	-1(1)	-4(1)	-1(1)
C(8)	34(1)	27(1)	21(1)	-5(1)	-9(1)	-4(1)
C(9)	41(1)	34(1)	20(1)	-13(1)	3(1)	-4(1)
C(10)	29(1)	27(1)	25(1)	-7(1)	9(1)	-2(1)
C(11)	20(1)	20(1)	18(1)	-1(1)	3(1)	-3(1)
C(12)	19(1)	14(1)	13(1)	1(1)	0(1)	-2(1)
C(13)	17(1)	13(1)	14(1)	3(1)	-2(1)	-2(1)
C(14)	26(1)	19(1)	19(1)	1(1)	4(1)	-5(1)
C(15)	24(1)	28(1)	28(1)	3(1)	8(1)	-9(1)
C(16)	24(1)	20(1)	30(1)	4(1)	-2(1)	-9(1)
C(17)	24(1)	13(1)	24(1)	1(1)	-7(1)	-1(1)
C(18)	18(1)	13(1)	18(1)	2(1)	-2(1)	1(1)
C(19)	14(1)	14(1)	13(1)	1(1)	0(1)	-1(1)
C(20)	16(1)	15(1)	13(1)	1(1)	-2(1)	-2(1)
C(21)	19(1)	12(1)	15(1)	3(1)	-3(1)	0(1)
C(22)	12(1)	21(1)	20(1)	0(1)	0(1)	2(1)
C(23)	14(1)	20(1)	19(1)	1(1)	1(1)	-4(1)
C(24)	15(1)	16(1)	16(1)	2(1)	0(1)	-3(1)
C(25)	20(1)	15(1)	16(1)	0(1)	0(1)	-3(1)
C(26)	26(1)	14(1)	17(1)	-4(1)	2(1)	-2(1)
C(27)	21(1)	13(1)	20(1)	-2(1)	4(1)	1(1)
B(1)	16(1)	13(1)	16(1)	1(1)	0(1)	2(1)

Table A2.78: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $Tp^{Br}RuPPh_3Cl_2$ 216d.

	x	y	z	U(eq)
H(1)	11770	1220	4309	29
H(2)	10613	1473	5594	27
H(3)	9007	2232	5427	22

H(5)	9843	2585	2719	22
H(6)	11351	1747	2864	26
H(7)	9606	3500	5419	24
H(8)	9508	4309	6677	33
H(9)	7787	4878	7040	38
H(10)	6123	4649	6150	32
H(11)	6224	3876	4858	23
H(14)	5869	2753	5055	26
H(15)	4361	1925	4860	32
H(16)	4457	1037	3700	30
H(17)	6117	929	2797	24
H(18)	7609	1770	2964	20
H(19)	9003	4321	574	16
H(21)	6393	5756	347	18
H(22)	3658	4502	2094	21
H(24)	5502	2702	2651	19
H(25)	8669	4951	4463	20
H(27)	6134	6275	3557	21
H(1B)	5340(20)	5516(12)	2074(16)	18

Table A2.79: Crystal data and structure refinement for $Tp^{I}RuPPh_3Cl_2$ 216e.

Identification code	$Tp^{I}RuPPh_3Cl_2$ **216e**
Empirical formula	C55H46B2Cl6I6N12P2Ru2
Formula weight	2134.84
Temperature/K	123(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	21.069(3) b/Å 16.634(2) c/Å 22.052(3)
α/°	90 β/° 118.515(3) γ/° 90
Volume/Å3	6790.7(15)
Z	4
ρcalcg/cm3	2.088μ/mm 1 3.502 F(000) 4032.0
Crystal size/mm3	0.34 × 0.28 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.226 to 56.986
Index ranges	-28 ≤ h ≤ 24, 0 ≤ k ≤ 22, 0 ≤ l ≤ 29
Reflections collected	104747
Independent reflections	17023 [Rint = 0.0245, Rsigma = 0.0134]
Data/restraints/parameters	17023/4/790
Goodness-of-fit on F2	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0214, wR2 = 0.0541
Final R indexes [all data]	R1 = 0.0249, wR2 = 0.0572
Largest diff. peak/hole / e Å	-31.34/-1.03

Table A2.80: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}RuPPh$_3$Cl$_2$ 216e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C^1	5504.0(12)	4442.3(13)	4589.0(11)	16.7(4)
C^2	5756.9(12)	3797.3(13)	5042.2(11)	16.4(4)
C^3	5775.6(11)	3145.8(13)	4651.9(11)	15.4(4)
C^4	5634.2(13)	5078.0(13)	2588.6(12)	19.9(4)
C^5	5985.7(13)	4695.2(13)	2275.1(13)	20.6(4)
C^6	5934.3(12)	3876.0(13)	2369.9(11)	17.5(4)
C^7	3629.2(11)	3002.1(13)	2439.5(11)	16.4(4)
C^8	3137.7(12)	3619.9(14)	2333.5(12)	18.9(4)
C^9	3548.2(12)	4308.4(13)	2600.7(11)	17.6(4)
C^{10}	7065.6(11)	2650.2(13)	4403.1(11)	16.2(4)
C^{11}	7165.1(13)	3489.1(14)	4455.8(12)	21.4(4)
C^{12}	7571.8(14)	3853.5(16)	5092.6(14)	28.6(5)
C^{13}	7875.9(15)	3391.7(18)	5690.5(14)	31.7(6)
C^{14}	7752.4(14)	2566.5(17)	5648.3(13)	28.0(5)
C^{15}	7349.0(13)	2200.7(14)	5010.6(12)	21.0(4)
C^{16}	6622.2(12)	1126.6(12)	3645.6(11)	16.0(4)
C^{17}	7324.8(12)	818.2(13)	4026.8(11)	18.2(4)
C^{18}	7451.9(13)	1.2(14)	4029.0(12)	20.9(4)
C^{19}	6886.0(13)	-512.7(13)	3626.0(12)	22.1(5)
C^{20}	6191.8(13)	-215.6(13)	3240.6(13)	21.6(4)
C^{21}	6058.2(12)	605.4(13)	3254.1(11)	18.0(4)
C^{22}	6964.5(11)	2413.0(13)	3053.4(11)	15.2(4)
C^{23}	7481.7(12)	3018.1(14)	3207.2(12)	21.6(4)
C^{24}	7794.1(13)	3144.6(16)	2782.5(14)	27.3(5)
C^{25}	7606.8(13)	2664.8(16)	2209.1(13)	26.3(5)
C^{26}	7098.5(13)	2063.5(15)	2051.6(13)	24.0(5)
C^{27}	6777.6(12)	1937.3(13)	2468.6(12)	19.3(4)
C^{28}	4843.8(12)	8166.2(13)	3412.7(11)	16.7(4)
C^{29}	4798.2(12)	8808.5(13)	3801.3(11)	18.2(4)
C^{30}	4536.5(12)	9453.1(13)	3344.9(11)	17.0(4)
C^{31}	2730.9(11)	7994.2(13)	1177.9(11)	15.3(4)
C^{32}	2240.9(11)	8611.1(13)	1061.6(11)	16.5(4)
C^{33}	2650.4(11)	9299.0(13)	1316.3(11)	16.5(4)
C^{34}	4855.7(12)	10082.1(12)	1472.3(11)	17.6(4)
C^{35}	5299.8(12)	9705.4(13)	1255.3(12)	19.0(4)
C^{36}	5222.2(12)	8885.4(13)	1323.5(11)	17.0(4)
C^{37}	4707.7(12)	7210.0(12)	429.5(12)	16.7(4)
C^{38}	5449.9(13)	7079.1(14)	822.8(13)	22.9(5)
C^{39}	5904.2(15)	7201.6(15)	536.0(16)	31.3(6)
C^{40}	5629.4(18)	7455.1(16)	-146.0(18)	37.5(7)

C^{41}	4893.4(19)	7546.8(18)	-545.7(17)	40.3(7)
C^{42}	4433.1(15)	7427.9(16)	-265.3(13)	28.4(5)
C^{43}	3258.8(12)	7477.8(14)	147.9(11)	18.2(4)
C^{44}	3244.0(13)	8305.9(14)	10.6(12)	22.1(4)
C^{45}	2602.0(15)	8677.7(17)	-455.2(13)	30.9(6)
C^{46}	1967.6(16)	8234.3(19)	-772.2(14)	38.4(7)
C^{47}	1974.3(15)	7418.6(19)	-634.9(15)	35.7(6)
C^{48}	2619.9(13)	7038.9(16)	-181.2(13)	26.0(5)
C^{49}	4017.1(12)	5970.4(13)	787.6(11)	17.2(4)
C^{50}	3538.8(14)	5608.7(14)	976.5(13)	24.6(5)
C^{51}	3491.0(16)	4774.8(15)	996.8(14)	29.9(6)
C^{52}	3928.3(16)	4292.4(15)	841.8(15)	32.3(6)
C^{53}	4394.3(15)	4637.7(15)	640.4(16)	32.5(6)
C^{54}	4437.9(13)	5471.7(14)	608.8(14)	24.2(5)
C^{55}	2005.8(18)	6512.7(18)	1810.7(17)	39.0(7)
B^{1}	4044.6(13)	9593.9(13)	2001.6(12)	14.1(4)
B^{2}	4947.6(13)	4592.2(14)	3246.1(12)	15.1(4)
N^{1}	5546.2(10)	3385.8(10)	4000.6(9)	13.6(3)
N^{2}	5374.7(10)	4181.4(10)	3962.7(9)	14.6(3)
N^{3}	5583.6(10)	3762.7(10)	2736.6(9)	14.0(3)
N^{4}	5393.6(10)	4508.1(10)	2862.7(10)	16.3(3)
N^{5}	4296.7(9)	3299(1)	2747.5(9)	13.8(3)
N^{6}	4247.6(10)	4100.1(10)	2845.9(9)	14.2(3)
N^{7}	4621.1(9)	8403.9(10)	2767.3(9)	13.9(3)
N^{8}	4431.3(9)	9194.9(10)	2723.0(9)	13.5(3)
N^{9}	3400.3(9)	8291.7(10)	1480.4(9)	13.0(3)
N^{10}	3348.3(9)	9098(1)	1568.5(9)	14.2(3)
N^{11}	4534.7(10)	9509.4(10)	1660.5(9)	14.5(3)
N^{12}	4754.5(9)	8766.1(10)	1566.8(9)	13.8(3)
P^{1}	6489.4(3)	2212.9(3)	3556.3(3)	12.34(9)
P^{2}	4111.7(3)	7063.2(3)	811.8(3)	13.08(9)
Cl^{1}	4930.3(3)	1699.4(3)	3569.2(3)	17.42(9)
Cl^{2}	4918.8(3)	2121.8(3)	2043.5(3)	16.62(9)
Cl^{3}	3983.9(3)	6707.3(3)	2301.5(3)	17.86(10)
Cl^{4}	5578.4(3)	7254.2(3)	2425.7(3)	17.93(10)
Cl^{5}	2035.9(4)	5936.1(4)	2492.7(4)	39.83(16)
Cl^{6}	1958.9(4)	5900.8(5)	1141.5(5)	45.84(18)
Ru^{1}	5312.7(2)	2756.9(2)	3110.6(2)	10.54(3)
Ru^{2}	4403.4(2)	7753.5(2)	1869.1(2)	10.95(3)
I^{1}	6090(3)	3819(3)	6068.4(17)	20.71(19)
I^{2}	2031.2(2)	3512.1(2)	1885.4(4)	26.92(10)
I^{3}	6543.9(2)	5192.1(2)	1810.6(2)	36.23(5)
I^{4}	5968.0(2)	10218.4(2)	915.9(2)	31.39(4)
I^{5}	4972.0(3)	8738.4(2)	4808.8(2)	23.75(9)

I^{6}	1132.6(2)	8480.5(2)	624.4(3)	21.04(8)
$I^{1'}$	5985.3(13)	3727.9(12)	6068.9(4)	20.71(19)
$I^{2'}$	2046(3)	3558(5)	1673(8)	26.92(10)
$I^{5'}$	5190(7)	8836(4)	4803(3)	23.75(9)
$I^{6'}$	1155(7)	8453(9)	412(17)	21.04(8)

Table A2.81: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{I}RuPPh_3Cl_2$ 216e. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C^{1}	16.4(10)	17.5(9)	16.7(10)	-5.1(8)	8.3(8)	-0.2(8)
C^{2}	14.8(10)	19.8(10)	13.9(9)	-3.1(8)	6.3(8)	1.0(8)
C^{3}	14.6(9)	18.3(9)	13.9(9)	-0.1(7)	7.3(8)	2.3(7)
C^{4}	21.6(11)	14.9(9)	23.7(11)	4.2(8)	11.1(9)	0.4(8)
C^{5}	20.1(11)	20(1)	25.2(11)	6.8(8)	13.6(9)	1.5(8)
C^{6}	17.6(10)	18(1)	19.5(10)	5.3(8)	10.9(9)	3.4(8)
C^{7}	15(1)	18.6(9)	15.3(10)	-2.4(7)	7.1(8)	-1.2(8)
C^{8}	10.5(9)	25.7(11)	18(1)	-2.8(8)	4.9(8)	2.4(8)
C^{9}	15.9(10)	19.2(10)	16.5(10)	-1.0(8)	6.8(8)	4.6(8)
C^{10}	14.2(9)	18.3(9)	16.1(10)	-2.4(8)	7.2(8)	-0.5(7)
C^{11}	22.3(11)	20.1(10)	21.4(11)	-2.1(8)	10.2(9)	-2.1(8)
C^{12}	29.6(13)	26.0(12)	30.3(13)	-9.9(10)	14.2(11)	-7.9(10)
C^{13}	26.7(13)	42.6(15)	20.7(12)	-13.2(11)	7.1(10)	-5.0(11)
C^{14}	26.0(12)	36.3(13)	17.7(11)	-2.2(10)	7.1(10)	3.9(10)
C^{15}	20.8(11)	24.8(11)	16.1(10)	0.4(8)	7.9(9)	2.7(9)
C^{16}	16.8(10)	14.6(9)	17.3(10)	3.2(7)	8.7(8)	3.3(7)
C^{17}	15.3(10)	20.4(10)	19.2(10)	1.5(8)	8.4(8)	1.3(8)
C^{18}	19.2(11)	22(1)	22.2(11)	6.0(8)	10.5(9)	6.4(8)
C^{19}	27.5(12)	15.4(9)	24.8(11)	3.6(8)	13.7(10)	4.3(9)
C^{20}	22.7(11)	17.5(10)	24.0(11)	-1.9(8)	10.6(10)	-1.0(8)
C^{21}	16.1(10)	17.4(10)	19.3(10)	1.5(8)	7.5(8)	2.5(8)
C^{22}	11.9(9)	17.8(9)	15.7(10)	3.0(7)	6.4(8)	2.8(7)
C^{23}	16.1(10)	26.5(11)	18.6(11)	-0.8(9)	5.5(9)	-3.8(9)
C^{24}	17.9(11)	33.9(13)	29.0(13)	5.1(10)	10.2(10)	-5.7(9)
C^{25}	21.2(11)	35.4(13)	27.0(12)	7.5(10)	15.2(10)	3.2(10)
C^{26}	25.5(12)	28.6(12)	21.8(11)	1.5(9)	14.5(10)	3.6(9)
C^{27}	19.9(10)	18.5(10)	21.5(11)	0.1(8)	11.7(9)	1.0(8)
C^{28}	15.3(10)	16.2(9)	16.4(10)	-0.5(8)	5.7(8)	0.5(8)
C^{29}	16.8(10)	19.3(10)	15.6(10)	-2.6(8)	5.3(8)	-0.7(8)
C^{30}	15.1(10)	17.1(9)	17.4(10)	-4.2(8)	6.7(8)	-1.0(8)
C^{31}	13.9(9)	16.1(9)	16.7(10)	-0.8(7)	7.9(8)	-0.6(7)
C^{32}	10.5(9)	19.9(10)	17.6(10)	0.4(8)	5.4(8)	0.4(8)

C^{33}	14.6(10)	16.3(9)	17.9(10)	1.0(8)	7.1(8)	3.3(8)
C^{34}	20.3(10)	11.9(9)	19.7(10)	0.4(7)	8.7(9)	-2.3(8)
C^{35}	19.8(10)	17.1(10)	22.0(11)	0.3(8)	11.6(9)	-4.7(8)
C^{36}	16.7(10)	15.5(9)	21(1)	-2.0(8)	10.9(9)	-2.0(8)
C^{37}	20.7(10)	12.9(9)	20.8(10)	-1.4(7)	13.4(9)	0.2(8)
C^{38}	21.5(11)	22.4(10)	27.2(12)	-6.6(9)	13.6(10)	-0.5(9)
C^{39}	24.6(12)	25.8(12)	52.9(17)	-16.6(11)	26.2(13)	-6.5(10)
C^{40}	54.4(18)	24.2(12)	62(2)	-1.4(12)	50.4(17)	-0.1(12)
C^{41}	59(2)	37.9(15)	44.4(17)	15.1(13)	41.2(16)	19.3(14)
C^{42}	35.2(14)	32.2(13)	24.9(12)	9(1)	20.1(11)	12.1(11)
C^{43}	16.5(10)	23.5(10)	12.7(9)	-1.8(8)	5.4(8)	4.2(8)
C^{44}	22.5(11)	25.6(11)	16.8(10)	2.1(8)	8.3(9)	6.0(9)
C^{45}	35.2(14)	33.8(13)	20.3(12)	4.9(10)	10.5(11)	16.5(11)
C^{46}	28.7(14)	50.0(17)	21.2(12)	-5.1(12)	-0.6(11)	19.4(13)
C^{47}	18.7(12)	45.2(16)	29.2(14)	-14.6(12)	0.2(11)	4.5(11)
C^{48}	18.6(11)	30.7(12)	23.3(12)	-9.1(10)	5.7(10)	1.7(9)
C^{49}	19.1(10)	15.0(9)	14.5(9)	-2.5(7)	5.8(8)	-1.7(8)
C^{50}	32.9(13)	21.3(11)	24.9(12)	-7.3(9)	18.0(11)	-8.3(9)
C^{51}	40.8(15)	23.6(12)	27.7(13)	-3.9(10)	18.4(12)	-13.5(11)
C^{52}	39.5(15)	16.9(11)	36.3(14)	-2(1)	14.9(12)	-6.9(10)
C^{53}	30.2(14)	18.7(11)	45.8(16)	-6.1(11)	16.0(12)	-1.7(10)
C^{54}	20.4(11)	16.5(10)	36.3(13)	-2.5(9)	14.2(10)	-1.2(8)
C^{55}	46.9(18)	29.3(14)	57(2)	7.3(13)	37.8(17)	1.6(12)
B^{1}	14.6(10)	11.4(9)	16.7(11)	-0.4(8)	7.6(9)	0.9(8)
B^{2}	15.5(11)	12.9(10)	16.3(11)	0.7(8)	7.2(9)	1.5(8)
N^{1}	14.5(8)	11.6(7)	14.9(8)	0.3(6)	7.2(7)	1.2(6)
N^{2}	14.7(8)	12.6(8)	16.2(8)	-1.3(6)	7.2(7)	0.7(6)
N^{3}	14.9(8)	12.4(8)	15.4(8)	0.8(6)	7.7(7)	1.3(6)
N^{4}	18.1(9)	10.8(7)	20.2(9)	0.5(6)	9.4(8)	1.0(6)
N^{5}	13.7(8)	13.4(8)	13.8(8)	0.3(6)	6.1(7)	2.1(6)
N^{6}	13.5(8)	13.4(8)	14.5(8)	-0.6(6)	5.7(7)	2.2(6)
N^{7}	12.8(8)	12.4(8)	15.5(8)	-0.3(6)	5.8(7)	0.1(6)
N^{8}	12.4(8)	10.9(7)	16.5(8)	-1.7(6)	6.3(7)	-0.9(6)
N^{9}	12.3(8)	11.2(7)	14.5(8)	-0.5(6)	5.5(7)	0.4(6)
N^{10}	13.3(8)	11.4(7)	17.3(8)	-0.8(6)	6.8(7)	1.2(6)
N^{11}	15.8(8)	11.0(7)	16.0(8)	0.3(6)	7.2(7)	0.4(6)
N^{12}	13.7(8)	10.1(7)	17.5(8)	0.0(6)	7.5(7)	0.7(6)
P^{1}	11.4(2)	11.8(2)	12.9(2)	0.36(17)	5.01(19)	0.81(17)
P^{2}	12.7(2)	12.8(2)	13.2(2)	-0.29(18)	5.8(2)	-0.05(18)
Cl^{1}	21.3(2)	14.1(2)	20.2(2)	0.75(17)	12.6(2)	-1.39(18)
Cl^{2}	18.9(2)	16.7(2)	13.1(2)	-2.38(17)	6.76(19)	0.47(18)
Cl^{3}	21.8(2)	14.2(2)	18.6(2)	0.83(17)	10.5(2)	-3.07(18)
Cl^{4}	13.1(2)	17.3(2)	20.2(2)	1.49(18)	5.39(19)	3.12(17)
Cl^{5}	36.1(4)	36.2(3)	42.4(4)	13.3(3)	14.9(3)	1.6(3)

Cl^{6}	33.5(4)	54.8(5)	48.7(4)	-6.6(4)	19.2(3)	-3.6(3)
Ru^{1}	11.02(7)	10.01(7)	10.68(7)	0.14(5)	5.26(6)	0.59(5)
Ru^{2}	10.26(7)	9.54(7)	12.53(7)	0.49(5)	5.02(6)	0.04(5)
I^{1}	23.1(4)	25.4(3)	12.24(7)	-1.37(11)	7.29(14)	4.8(3)
I^{2}	11.16(7)	35.63(9)	29.9(2)	-9.54(9)	6.46(8)	0.64(6)
I^{3}	35.72(10)	33.94(9)	54.31(12)	20.51(8)	33.85(9)	6.63(7)
I^{4}	37.11(10)	26.52(8)	43.79(10)	-1.18(7)	30.01(8)	-10.76(7)
I^{5}	29.78(19)	24.76(9)	13.64(7)	-1.93(6)	7.88(8)	-0.7(1)
I^{6}	10.53(7)	23.49(7)	24.91(19)	1.26(7)	5.05(7)	0.93(5)
$I^{1'}$	23.1(4)	25.4(3)	12.24(7)	-1.37(11)	7.29(14)	4.8(3)
$I^{2'}$	11.16(7)	35.63(9)	29.9(2)	-9.54(9)	6.46(8)	0.64(6)
$I^{5'}$	29.78(19)	24.76(9)	13.64(7)	-1.93(6)	7.88(8)	-0.7(1)
$I^{6'}$	10.53(7)	23.49(7)	24.91(19)	1.26(7)	5.05(7)	0.93(5)

Table A2.82: Bond Lengths for $Tp^{I}RuPPh_3Cl_2$ 216e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C^{1}	N^{2}	1.346(3)	C^{34}	C^{35}	1.387(3)
C^{1}	C^{2}	1.388(3)	C^{35}	C^{36}	1.390(3)
C^{2}	C^{3}	1.396(3)	C^{35}	I^{4}	2.068(2)
C^{2}	I^{1}	2.024(4)	C^{36}	N^{12}	1.343(3)
C^{2}	$I^{1'}$	2.081(2)	C^{37}	C^{38}	1.396(3)
C^{3}	N^{1}	1.339(3)	C^{37}	C^{42}	1.403(3)
C^{4}	N^{4}	1.347(3)	C^{37}	P^{2}	1.833(2)
C^{4}	C^{5}	1.386(3)	C^{38}	C^{39}	1.391(3)
C^{5}	C^{6}	1.391(3)	C^{39}	C^{40}	1.394(4)
C^{5}	I^{3}	2.065(2)	C^{40}	C^{41}	1.378(5)
C^{6}	N^{3}	1.344(3)	C^{41}	C^{42}	1.391(4)
C^{7}	N^{5}	1.331(3)	C^{43}	C^{48}	1.392(3)
C^{7}	C^{8}	1.397(3)	C^{43}	C^{44}	1.407(3)
C^{8}	C^{9}	1.386(3)	C^{43}	P^{2}	1.827(2)
C^{8}	$I^{2'}$	2.056(7)	C^{44}	C^{45}	1.393(3)
C^{8}	I^{2}	2.060(2)	C^{45}	C^{46}	1.388(4)
C^{9}	N^{6}	1.350(3)	C^{46}	C^{47}	1.389(5)
C^{10}	C^{15}	1.395(3)	C^{47}	C^{48}	1.397(4)
C^{10}	C^{11}	1.408(3)	C^{49}	C^{50}	1.397(3)
C^{10}	P^{1}	1.824(2)	C^{49}	C^{54}	1.401(3)
C^{11}	C^{12}	1.387(3)	C^{49}	P^{2}	1.827(2)
C^{12}	C^{13}	1.390(4)	C^{50}	C^{51}	1.393(3)
C^{13}	C^{14}	1.392(4)	C^{51}	C^{52}	1.382(4)
C^{14}	C^{15}	1.389(3)	C^{52}	C^{53}	1.381(4)
C^{16}	C^{21}	1.389(3)	C^{53}	C^{54}	1.394(3)
C^{16}	C^{17}	1.405(3)	C^{55}	Cl^{6}	1.756(3)

C^{16}	P^{1}	1.825(2)	C^{55}	Cl^{5}	1.759(3)
C^{17}	C^{18}	1.385(3)	B^{1}	N^{11}	1.547(3)
C^{18}	C^{19}	1.389(3)	B^{1}	N^{8}	1.548(3)
C^{19}	C^{20}	1.385(3)	B^{1}	N^{10}	1.551(3)
C^{20}	C^{21}	1.398(3)	B^{2}	N^{4}	1.541(3)
C^{22}	C^{27}	1.400(3)	B^{2}	N^{6}	1.543(3)
C^{22}	C^{23}	1.401(3)	B^{2}	N^{2}	1.554(3)
C^{22}	P^{1}	1.845(2)	N^{1}	N^{2}	1.364(2)
C^{23}	C^{24}	1.394(3)	N^{1}	Ru^{1}	2.0655(18)
C^{24}	C^{25}	1.384(4)	N^{3}	N^{4}	1.372(2)
C^{25}	C^{26}	1.383(4)	N^{3}	Ru^{1}	2.0625(17)
C^{26}	C^{27}	1.393(3)	N^{5}	N^{6}	1.362(2)
C^{28}	N^{7}	1.328(3)	N^{5}	Ru^{1}	2.0976(17)
C^{28}	C^{29}	1.401(3)	N^{7}	N^{8}	1.365(2)
C^{29}	C^{30}	1.392(3)	N^{7}	Ru^{2}	2.1063(18)
C^{29}	$I^{5'}$	1.956(6)	N^{9}	N^{10}	1.367(2)
C^{29}	I^{5}	2.075(2)	N^{9}	Ru^{2}	2.0670(17)
C^{30}	N^{8}	1.351(3)	N^{11}	N^{12}	1.370(2)
C^{31}	N^{9}	1.334(3)	N^{12}	Ru^{2}	2.0736(17)
C^{31}	C^{32}	1.390(3)	P^{1}	Ru^{1}	2.3673(6)
C^{32}	C^{33}	1.381(3)	P^{2}	Ru^{2}	2.4009(6)
C^{32}	$I^{6'}$	2.056(14)	Cl^{1}	Ru^{1}	2.3547(5)
C^{32}	I^{6}	2.069(2)	Cl^{2}	Ru^{1}	2.3403(6)
C^{33}	N^{10}	1.343(3)	Cl^{3}	Ru^{2}	2.3502(5)
C^{34}	N^{11}	1.343(3)	Cl^{4}	Ru^{2}	2.3289(6)

Table A2.83: Bond Angles for $Tp^{I}RuPPh_3Cl_2$ 216e.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N^{2}	C^{1}	C^{2}	108.05(18)	Cl^{6}	C^{55}	Cl^{5}	111.52(17)
C^{1}	C^{2}	C^{3}	105.68(18)	N^{11}	B^{1}	N^{8}	108.33(17)
C^{1}	C^{2}	I^{1}	126.91(19)	N^{11}	B^{1}	N^{10}	107.86(17)
C^{3}	C^{2}	I^{1}	127.3(2)	N^{8}	B^{1}	N^{10}	106.48(16)
C^{1}	C^{2}	$I^{1'}$	129.52(16)	N^{4}	B^{2}	N^{6}	107.74(17)
C^{3}	C^{2}	$I^{1'}$	124.59(16)	N^{4}	B^{2}	N^{2}	108.00(17)
N^{1}	C^{3}	C^{2}	109.14(19)	N^{6}	B^{2}	N^{2}	106.24(17)
N^{4}	C^{4}	C^{5}	107.81(19)	C^{3}	N^{1}	N^{2}	107.72(17)
C^{4}	C^{5}	C^{6}	106.07(19)	C^{3}	N^{1}	Ru^{1}	131.95(14)
C^{4}	C^{5}	I^{3}	129.04(17)	N^{2}	N^{1}	Ru^{1}	119.82(13)
C^{6}	C^{5}	I^{3}	124.77(17)	C^{1}	N^{2}	N^{1}	109.40(17)
N^{3}	C^{6}	C^{5}	109.42(19)	C^{1}	N^{2}	B^{2}	129.57(18)
N^{5}	C^{7}	C^{8}	109.31(19)	N^{1}	N^{2}	B^{2}	119.78(17)
C^{9}	C^{8}	C^{7}	105.93(19)	C^{6}	N^{3}	N^{4}	107.03(17)

C9	C8	I2'	127.1(3)	C6	N3	Ru1	133.70(14)
C7	C8	I2'	124.8(3)	N4	N3	Ru1	119.27(13)
C9	C8	I2	127.56(16)	C4	N4	N3	109.66(18)
C7	C8	I2	126.51(17)	C4	N4	B2	129.87(18)
N6	C9	C8	107.38(18)	N3	N4	B2	120.44(17)
C15	C10	C11	118.3(2)	C7	N5	N6	107.59(17)
C15	C10	P1	122.68(17)	C7	N5	Ru1	132.26(14)
C11	C10	P1	118.69(17)	N6	N5	Ru1	120.07(13)
C12	C11	C10	120.8(2)	C9	N6	N5	109.79(17)
C11	C12	C13	120.1(2)	C9	N6	B2	130.95(18)
C12	C13	C14	119.7(2)	N5	N6	B2	119.05(16)
C15	C14	C13	120.3(2)	C28	N7	N8	107.78(17)
C14	C15	C10	120.8(2)	C28	N7	Ru2	131.42(14)
C21	C16	C17	119.24(19)	N8	N7	Ru2	120.19(13)
C21	C16	P1	120.62(16)	C30	N8	N7	109.47(17)
C17	C16	P1	119.32(17)	C30	N8	B1	131.12(18)
C18	C17	C16	120.5(2)	N7	N8	B1	118.64(16)
C17	C18	C19	119.7(2)	C31	N9	N10	107.32(16)
C20	C19	C18	120.3(2)	C31	N9	Ru2	132.38(14)
C19	C20	C21	120.0(2)	N10	N9	Ru2	120.09(13)
C16	C21	C20	120.1(2)	C33	N10	N9	109.37(17)
C27	C22	C23	118.2(2)	C33	N10	B1	130.49(17)
C27	C22	P1	117.21(16)	N9	N10	B1	119.53(16)
C23	C22	P1	124.53(17)	C34	N11	N12	109.70(17)
C24	C23	C22	120.5(2)	C34	N11	B1	129.57(18)
C25	C24	C23	120.4(2)	N12	N11	B1	120.49(16)
C26	C25	C24	119.7(2)	C36	N12	N11	107.00(16)
C25	C26	C27	120.3(2)	C36	N12	Ru2	133.71(14)
C26	C27	C22	120.8(2)	N11	N12	Ru2	119.11(13)
N7	C28	C29	109.63(19)	C10	P1	C16	106.96(10)
C30	C29	C28	105.32(19)	C10	P1	C22	104.86(10)
C30	C29	I5'	127.4(2)	C16	P1	C22	98.30(10)
C28	C29	I5'	126.4(2)	C10	P1	Ru1	109.02(7)
C30	C29	I5	128.61(16)	C16	P1	Ru1	119.97(7)
C28	C29	I5	125.68(16)	C22	P1	Ru1	116.28(7)
N8	C30	C29	107.80(18)	C43	P2	C49	107.49(10)
N9	C31	C32	109.46(18)	C43	P2	C37	102.06(10)
C33	C32	C31	105.78(18)	C49	P2	C37	102.02(10)
C33	C32	I6'	131.4(4)	C43	P2	Ru2	107.19(7)
C31	C32	I6'	121.0(6)	C49	P2	Ru2	118.56(7)
C33	C32	I6	128.58(16)	C37	P2	Ru2	117.98(7)
C31	C32	I6	125.61(16)	N3	Ru1	N1	89.04(7)
N10	C33	C32	108.07(18)	N3	Ru1	N5	85.72(7)
N11	C34	C35	107.95(18)	N1	Ru1	N5	83.21(7)

C34	C35	C36	105.80(19)	N3	Ru1	Cl2	89.84(5)
C34	C35	I4	128.78(16)	N1	Ru1	Cl2	173.34(5)
C36	C35	I4	125.41(17)	N5	Ru1	Cl2	90.16(5)
N12	C36	C35	109.56(19)	N3	Ru1	Cl1	173.95(5)
C38	C37	C42	118.3(2)	N1	Ru1	Cl1	86.87(5)
C38	C37	P2	120.24(18)	N5	Ru1	Cl1	89.37(5)
C42	C37	P2	121.41(18)	Cl2	Ru1	Cl1	93.71(2)
C39	C38	C37	120.3(2)	N3	Ru1	P1	92.37(5)
C38	C39	C40	120.9(3)	N1	Ru1	P1	94.12(5)
C41	C40	C39	119.0(2)	N5	Ru1	P1	176.74(5)
C40	C41	C42	120.7(3)	Cl2	Ru1	P1	92.484(19)
C41	C42	C37	120.7(3)	Cl1	Ru1	P1	92.37(2)
C48	C43	C44	119.0(2)	N9	Ru2	N12	88.04(7)
C48	C43	P2	123.79(18)	N9	Ru2	N7	83.57(7)
C44	C43	P2	117.01(17)	N12	Ru2	N7	86.22(7)
C45	C44	C43	120.5(2)	N9	Ru2	Cl4	172.80(5)
C46	C45	C44	119.9(3)	N12	Ru2	Cl4	90.37(5)
C45	C46	C47	120.1(2)	N7	Ru2	Cl4	89.32(5)
C46	C47	C48	120.2(3)	N9	Ru2	Cl3	88.91(5)
C43	C48	C47	120.3(3)	N12	Ru2	Cl3	173.17(5)
C50	C49	C54	118.2(2)	N7	Ru2	Cl3	87.37(5)
C50	C49	P2	120.27(17)	Cl4	Ru2	Cl3	91.90(2)
C54	C49	P2	121.50(17)	N9	Ru2	P2	93.86(5)
C51	C50	C49	120.8(2)	N12	Ru2	P2	92.38(5)
C52	C51	C50	120.2(2)	N7	Ru2	P2	177.11(5)
C53	C52	C51	119.9(2)	Cl4	Ru2	P2	93.21(2)
C52	C53	C54	120.2(3)	Cl3	Ru2	P2	93.92(2)
C53	C54	C49	120.6(2)				

Table A2.84: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Tp^{i}RuPPh$_3$Cl$_2$ 216e.

Atom	*x*	*y*	*z*	U(eq)
H1	5434	4975	4701	20
H1B	3927(15)	10206(16)	2034(14)	18(7)
H2B	4836(14)	5205(15)	3295(13)	13(6)
H3	5927	2617	4821	18
H4	5574	5642	2607	24
H6	6119	3461	2202	21
H7	3506	2456	2312	20
H9	3370	4831	2610	21
H11	6951	3810	4050	26
H12	7643	4419	5120	34

H^{13}	8166	3638	6126	38
H^{14}	7945	2252	6057	34
H^{15}	7265	1638	4988	25
H^{17}	7716	1173	4285	22
H^{18}	7924	-207	4305	25
H^{19}	6976	-1071	3615	26
H^{20}	5807	-570	2967	26
H^{21}	5581	807	2995	22
H^{23}	7621	3345	3604	26
H^{24}	8138	3563	2887	33
H^{25}	7826	2748	1925	32
H^{26}	6968	1735	1657	29
H^{27}	6428	1524	2355	23
H^{28}	5009	7641	3585	20
H^{30}	4448	9981	3452	20
H^{31}	2608	7446	1060	18
H^{33}	2470	9823	1314	20
H^{34}	4790	10646	1486	21
H^{36}	5463	8473	1215	20
H^{38}	5645	6906	1288	27
H^{39}	6408	7111	809	38
H^{40}	5945	7563	-332	45
H^{41}	4698	7693	-1018	48
H^{42}	3927	7495	-547	34
H^{44}	3675	8613	237	27
H^{45}	2598	9234	-556	37
H^{46}	1528	8489	-1084	46
H^{47}	1538	7118	-850	43
H^{48}	2623	6479	-97	31
H^{50}	3243	5935	1092	30
H^{51}	3157	4537	1118	36
H^{52}	3908	3724	874	39
H^{53}	4686	4306	523	39
H^{54}	4756	5704	465	29
H^{55A}	1579	6871	1628	47
H^{55B}	2443	6855	1987	47

Table A2.85: Atomic Occupancy for $Tp^{I}RuPPh_3Cl_2$ 216e.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
I^{1}	0.208(13)	I^{2}	0.963(3)	I^{5}	0.959(3)
I^{6}	0.985(3)	$I^{1'}$	0.792(13)	$I^{2'}$	0.037(3)
$I^{5'}$	0.041(3)	$I^{6'}$	0.015(3)		

Table A2.86: Crystal data and structure refinement for $Tp^{Br}RuPPh_3Br_2$ 218.

Identification code: $Tp^{Br}RuPPh_3Br_2$ **218**

Empirical formula: C27 H22 B Br5 N6 P Ru

Formula weight:	972.90	
Temperature: 123(2) K		
Wavelength: 0.71073 Å		
Crystal system: Monoclinic		
Space group: P 21/n		
Unit cell dimensions		
	a = 11.552(2) Å	α= 90°.
	b = 18.582(3) Å	β= 90.239(4)°.
	c = 14.514(3) Å	γ = 90°.
Volume	3115.5(10) $Å^3$	
Z	4	
Density (calculated)	2.074 Mg/m^3	
Absorption coefficient	6.997 mm^{-1}	
F(000)	1860	
Crystal size	0.300 x 0.180 x 0.120 mm^3	
Theta range for data collection	2.076 to 28.300°.	
Index ranges	-15<=h<=14, -24<=k<=24, -19<=l<=19	
Reflections collected	39639	
Independent reflections	7739 [R(int) = 0.0188]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7457 and 0.5074	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7739 / 0 / 373	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0175, wR2 = 0.0437	
R indices (all data)	R1 = 0.0197, wR2 = 0.0449	
Largest diff. peak and hole	0.987 and -1.027 $e.Å^{-3}$	

Table A2.87: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Br}RuPPh_3Br_2$ 218. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1688(2)	5406(1)	9245(1)	13(1)
C(2)	2184(2)	4879(1)	9811(1)	14(1)
C(3)	3152(2)	4635(1)	9358(1)	15(1)
C(4)	4728(2)	6841(1)	7459(1)	14(1)
C(5)	5847(2)	6596(1)	7623(1)	17(1)
C(6)	5766(2)	5857(1)	7721(1)	17(1)
C(7)	1991(2)	4897(1)	5853(1)	16(1)
C(8)	2530(2)	4241(1)	5682(1)	18(1)
C(9)	3395(2)	4172(1)	6340(1)	17(1)
C(10)	2108(2)	6456(1)	4988(1)	14(1)
C(11)	3135(2)	6100(1)	4754(1)	19(1)
C(12)	3177(2)	5650(1)	3988(2)	27(1)
C(13)	2187(2)	5529(1)	3465(2)	30(1)
C(14)	1156(2)	5858(1)	3705(1)	26(1)
C(15)	1109(2)	6322(1)	4462(1)	19(1)
C(16)	742(2)	7539(1)	5929(1)	15(1)
C(17)	553(2)	7884(1)	5079(1)	18(1)
C(18)	-386(2)	8346(1)	4963(1)	23(1)
C(19)	-1108(2)	8496(1)	5696(2)	24(1)
C(20)	-897(2)	8180(1)	6552(2)	22(1)
C(21)	8(2)	7690(1)	6663(1)	18(1)
C(22)	3158(2)	7661(1)	6016(1)	14(1)
C(23)	4147(2)	7632(1)	5471(1)	21(1)
C(24)	5040(2)	8131(1)	5597(2)	27(1)
C(25)	4943(2)	8666(1)	6254(1)	24(1)
C(26)	3938(2)	8724(1)	6774(1)	20(1)
C(27)	3052(2)	8226(1)	6656(1)	16(1)
B(1)	4077(2)	4936(1)	7750(1)	14(1)
N(1)	2326(1)	5473(1)	8487(1)	12(1)

N(2)	3223(1)	5000(1)	8556(1)	13(1)
N(3)	4648(1)	5676(1)	7617(1)	14(1)
N(4)	3999(1)	6278(1)	7448(1)	13(1)
N(5)	2513(1)	5220(1)	6573(1)	14(1)
N(6)	3370(1)	4766(1)	6873(1)	14(1)
P(1)	2028(1)	6966(1)	6061(1)	11(1)
Br(1)	1972(1)	7169(1)	8432(1)	17(1)
Br(2)	123(1)	5892(1)	7168(1)	16(1)
Br(3)	1581(1)	4531(1)	10922(1)	18(1)
Br(4)	7192(1)	7149(1)	7673(1)	28(1)
Br(5)	2200(1)	3599(1)	4720(1)	27(1)
Ru(1)	2199(1)	6169(1)	7332(1)	9(1)

Table A2.88: Bond lengths [Å] and angles [°] for $Tp^{Br}RuPPh_3Br_2$ 218.

C(1)-N(1)	1.334(2)	C(8)-Br(5)	1.8744(18)
C(1)-C(2)	1.399(2)	C(9)-N(6)	1.348(2)
C(1)-H(1)	0.9500	C(9)-H(9)	0.9500
C(2)-C(3)	1.377(3)	C(10)-C(11)	1.401(3)
C(2)-Br(3)	1.8746(17)	C(10)-C(15)	1.403(3)
C(3)-N(2)	1.351(2)	C(10)-P(1)	1.8254(18)
C(3)-H(3)	0.9500	C(11)-C(12)	1.393(3)
C(4)-N(4)	1.344(2)	C(11)-H(11)	0.9500
C(4)-C(5)	1.390(3)	C(12)-C(13)	1.389(3)
C(4)-H(4)	0.9500	C(12)-H(12)	0.9500
C(5)-C(6)	1.383(3)	C(13)-C(14)	1.384(3)
C(5)-Br(4)	1.8634(18)	C(13)-H(13)	0.9500
C(6)-N(3)	1.343(2)	C(14)-C(15)	1.398(3)
C(6)-H(6)	0.9500	C(14)-H(14)	0.9500
C(7)-N(5)	1.346(2)	C(15)-H(15)	0.9500
C(7)-C(8)	1.392(3)	C(16)-C(21)	1.394(3)
C(7)-H(7)	0.9500	C(16)-C(17)	1.407(2)
C(8)-C(9)	1.385(3)	C(16)-P(1)	1.8372(19)

C(17)-C(18)	1.393(3)	N(1)-C(1)-C(2)	108.90(16)
C(17)-H(17)	0.9500	N(1)-C(1)-H(1)	125.5
C(18)-C(19)	1.383(3)	C(2)-C(1)-H(1)	125.5
C(18)-H(18)	0.9500	C(3)-C(2)-C(1)	106.37(15)
C(19)-C(20)	1.394(3)	C(3)-C(2)-Br(3)	127.05(13)
C(19)-H(19)	0.9500	C(1)-C(2)-Br(3)	126.44(14)
C(20)-C(21)	1.395(3)	N(2)-C(3)-C(2)	107.34(15)
C(20)-H(20)	0.9500	N(2)-C(3)-H(3)	126.3
C(21)-H(21)	0.9500	C(2)-C(3)-H(3)	126.3
C(22)-C(23)	1.394(3)	N(4)-C(4)-C(5)	109.24(16)
C(22)-C(27)	1.408(3)	N(4)-C(4)-H(4)	125.4
C(22)-P(1)	1.8375(18)	C(5)-C(4)-H(4)	125.4
C(23)-C(24)	1.399(3)	C(6)-C(5)-C(4)	106.23(16)
C(23)-H(23)	0.9500	C(6)-C(5)-Br(4)	126.85(14)
C(24)-C(25)	1.383(3)	C(4)-C(5)-Br(4)	126.90(14)
C(24)-H(24)	0.9500	N(3)-C(6)-C(5)	107.63(16)
C(25)-C(26)	1.391(3)	N(3)-C(6)-H(6)	126.2
C(25)-H(25)	0.9500	C(5)-C(6)-H(6)	126.2
C(26)-C(27)	1.389(3)	N(5)-C(7)-C(8)	109.27(16)
C(26)-H(26)	0.9500	N(5)-C(7)-H(7)	125.4
C(27)-H(27)	0.9500	C(8)-C(7)-H(7)	125.4
B(1)-N(2)	1.538(2)	C(9)-C(8)-C(7)	106.25(16)
B(1)-N(3)	1.538(2)	C(9)-C(8)-Br(5)	126.79(14)
B(1)-N(6)	1.543(2)	C(7)-C(8)-Br(5)	126.89(14)
B(1)-H(1")	1.08(2)	N(6)-C(9)-C(8)	107.61(16)
N(1)-N(2)	1.362(2)	N(6)-C(9)-H(9)	126.2
N(1)-Ru(1)	2.1218(14)	C(8)-C(9)-H(9)	126.2
N(3)-N(4)	1.368(2)	C(11)-C(10)-C(15)	118.73(17)
N(4)-Ru(1)	2.0952(15)	C(11)-C(10)-P(1)	119.78(14)
N(5)-N(6)	1.370(2)	C(15)-C(10)-P(1)	120.78(14)
N(5)-Ru(1)	2.1114(15)	C(12)-C(11)-C(10)	120.58(19)
P(1)-Ru(1)	2.3725(5)	C(12)-C(11)-H(11)	119.7
Br(1)-Ru(1)	2.4641(4)	C(10)-C(11)-H(11)	119.7
Br(2)-Ru(1)	2.4629(5)	C(13)-C(12)-C(11)	120.2(2)
		C(13)-C(12)-H(12)	119.9

C(11)-C(12)-H(12)	119.9	C(25)-C(24)-H(24)	119.8
C(14)-C(13)-C(12)	119.87(19)	C(23)-C(24)-H(24)	119.8
C(14)-C(13)-H(13)	120.1	C(24)-C(25)-C(26)	120.04(18)
C(12)-C(13)-H(13)	120.1	C(24)-C(25)-H(25)	120.0
C(13)-C(14)-C(15)	120.4(2)	C(26)-C(25)-H(25)	120.0
C(13)-C(14)-H(14)	119.8	C(27)-C(26)-C(25)	119.80(18)
C(15)-C(14)-H(14)	119.8	C(27)-C(26)-H(26)	120.1
C(14)-C(15)-C(10)	120.15(19)	C(25)-C(26)-H(26)	120.1
C(14)-C(15)-H(15)	119.9	C(26)-C(27)-C(22)	120.80(18)
C(10)-C(15)-H(15)	119.9	C(26)-C(27)-H(27)	119.6
C(21)-C(16)-C(17)	119.06(17)	C(22)-C(27)-H(27)	119.6
C(21)-C(16)-P(1)	122.15(14)	N(2)-B(1)-N(3)	107.62(14)
C(17)-C(16)-P(1)	118.56(14)	N(2)-B(1)-N(6)	107.70(14)
C(18)-C(17)-C(16)	120.30(18)	N(3)-B(1)-N(6)	107.77(14)
C(18)-C(17)-H(17)	119.8	N(2)-B(1)-H(1")	112.5(12)
C(16)-C(17)-H(17)	119.8	N(3)-B(1)-H(1")	109.9(12)
C(19)-C(18)-C(17)	120.18(18)	N(6)-B(1)-H(1")	111.2(12)
C(19)-C(18)-H(18)	119.9	C(1)-N(1)-N(2)	107.56(14)
C(17)-C(18)-H(18)	119.9	C(1)-N(1)-Ru(1)	132.29(12)
C(18)-C(19)-C(20)	119.85(18)	N(2)-N(1)-Ru(1)	120.11(11)
C(18)-C(19)-H(19)	120.1	C(3)-N(2)-N(1)	109.83(14)
C(20)-C(19)-H(19)	120.1	C(3)-N(2)-B(1)	131.10(15)
C(19)-C(20)-C(21)	120.36(19)	N(1)-N(2)-B(1)	119.00(14)
C(19)-C(20)-H(20)	119.8	C(6)-N(3)-N(4)	109.97(15)
C(21)-C(20)-H(20)	119.8	C(6)-N(3)-B(1)	128.55(15)
C(16)-C(21)-C(20)	120.10(18)	N(4)-N(3)-B(1)	121.22(14)
C(16)-C(21)-H(21)	119.9	C(4)-N(4)-N(3)	106.93(14)
C(20)-C(21)-H(21)	119.9	C(4)-N(4)-Ru(1)	134.26(12)
C(23)-C(22)-C(27)	118.50(17)	N(3)-N(4)-Ru(1)	118.63(11)
C(23)-C(22)-P(1)	125.22(14)	C(7)-N(5)-N(6)	106.99(14)
C(27)-C(22)-P(1)	115.97(13)	C(7)-N(5)-Ru(1)	134.44(13)
C(22)-C(23)-C(24)	120.39(19)	N(6)-N(5)-Ru(1)	118.33(11)
C(22)-C(23)-H(23)	119.8	C(9)-N(6)-N(5)	109.86(15)
C(24)-C(23)-H(23)	119.8	C(9)-N(6)-B(1)	128.94(15)
C(25)-C(24)-C(23)	120.33(19)	N(5)-N(6)-B(1)	121.01(14)

C(10)-P(1)-C(16)	104.81(8)	N(1)-Ru(1)-P(1)	178.65(4)
C(10)-P(1)-C(22)	107.25(8)	N(4)-Ru(1)-Br(2)	173.37(4)
C(16)-P(1)-C(22)	99.38(8)	N(5)-Ru(1)-Br(2)	86.82(4)
C(10)-P(1)-Ru(1)	109.59(6)	N(1)-Ru(1)-Br(2)	90.77(4)
C(16)-P(1)-Ru(1)	120.46(6)	P(1)-Ru(1)-Br(2)	88.716(13)
C(22)-P(1)-Ru(1)	114.15(6)	N(4)-Ru(1)-Br(1)	89.05(4)
N(4)-Ru(1)-N(5)	87.10(6)	N(5)-Ru(1)-Br(1)	170.61(4)
N(4)-Ru(1)-N(1)	85.93(6)	N(1)-Ru(1)-Br(1)	87.40(4)
N(5)-Ru(1)-N(1)	83.79(6)	P(1)-Ru(1)-Br(1)	91.423(19)
N(4)-Ru(1)-P(1)	94.70(4)	Br(2)-Ru(1)-Br(1)	96.552(9)
N(5)-Ru(1)-P(1)	97.43(4)		

Symmetry transformations used to generate equivalent atoms:

Table A2.89: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Br}RuPPh_3Br_2$ 218. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	13(1)	12(1)	1(1)	-2(1)	-1(1)
C(2)	18(1)	14(1)	11(1)	2(1)	-2(1)	-3(1)
C(3)	19(1)	12(1)	13(1)	3(1)	-5(1)	0(1)
C(4)	17(1)	13(1)	13(1)	2(1)	0(1)	-2(1)
C(5)	13(1)	20(1)	19(1)	0(1)	1(1)	-3(1)
C(6)	12(1)	20(1)	18(1)	-1(1)	0(1)	1(1)
C(7)	20(1)	14(1)	13(1)	0(1)	-2(1)	-2(1)
C(8)	25(1)	13(1)	14(1)	-3(1)	0(1)	-1(1)
C(9)	21(1)	12(1)	16(1)	-1(1)	3(1)	2(1)
C(10)	20(1)	14(1)	10(1)	1(1)	0(1)	-2(1)
C(11)	20(1)	20(1)	18(1)	-2(1)	3(1)	-3(1)
C(12)	31(1)	26(1)	24(1)	-8(1)	10(1)	-1(1)
C(13)	43(1)	29(1)	18(1)	-10(1)	3(1)	-4(1)
C(14)	36(1)	24(1)	18(1)	-4(1)	-9(1)	-4(1)
C(15)	25(1)	16(1)	16(1)	0(1)	-4(1)	-1(1)

C(16)	16(1)	10(1)	17(1)	1(1)	-4(1)	-1(1)
C(17)	24(1)	14(1)	16(1)	2(1)	-4(1)	-1(1)
C(18)	27(1)	16(1)	26(1)	6(1)	-12(1)	-1(1)
C(19)	17(1)	16(1)	40(1)	5(1)	-8(1)	1(1)
C(20)	16(1)	16(1)	33(1)	3(1)	4(1)	0(1)
C(21)	18(1)	14(1)	21(1)	4(1)	0(1)	0(1)
C(22)	18(1)	13(1)	11(1)	4(1)	-2(1)	-2(1)
C(23)	26(1)	21(1)	15(1)	1(1)	4(1)	-7(1)
C(24)	26(1)	30(1)	25(1)	3(1)	7(1)	-10(1)
C(25)	24(1)	21(1)	27(1)	6(1)	-4(1)	-10(1)
C(26)	25(1)	13(1)	21(1)	2(1)	-7(1)	-1(1)
C(27)	18(1)	13(1)	17(1)	3(1)	-3(1)	1(1)
B(1)	14(1)	12(1)	15(1)	0(1)	-1(1)	1(1)
N(1)	14(1)	11(1)	12(1)	1(1)	-2(1)	1(1)
N(2)	15(1)	11(1)	14(1)	2(1)	-2(1)	1(1)
N(3)	13(1)	14(1)	15(1)	0(1)	0(1)	2(1)
N(4)	13(1)	12(1)	12(1)	1(1)	-1(1)	1(1)
N(5)	17(1)	11(1)	12(1)	1(1)	-1(1)	1(1)
N(6)	16(1)	11(1)	14(1)	0(1)	0(1)	2(1)
P(1)	14(1)	10(1)	9(1)	1(1)	-1(1)	0(1)
Br(1)	23(1)	14(1)	13(1)	-2(1)	0(1)	2(1)
Br(2)	14(1)	17(1)	17(1)	2(1)	-1(1)	-1(1)
Br(3)	21(1)	22(1)	12(1)	6(1)	-2(1)	-3(1)
Br(4)	15(1)	26(1)	42(1)	2(1)	1(1)	-8(1)
Br(5)	41(1)	19(1)	20(1)	-9(1)	-7(1)	2(1)
Ru(1)	11(1)	9(1)	8(1)	1(1)	0(1)	0(1)

Table A2.90: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $Tp^{Br}RuPPh_3Br_2$ 218.

	x	y	z	U(eq)
H(1)	1007	5672	9379	16
H(1'')	4733(19)	4532(12)	7871(15)	16

H(3)	3674	4276	9570	18
H(4)	4513	7329	7368	17
H(6)	6389	5536	7840	20
H(7)	1356	5087	5514	19
H(9)	3913	3778	6403	20
H(11)	3809	6167	5122	23
H(12)	3885	5424	3823	33
H(13)	2217	5221	2943	36
H(14)	476	5767	3354	31
H(15)	400	6548	4620	23
H(17)	1068	7802	4581	22
H(18)	-531	8559	4379	27
H(19)	-1745	8813	5617	29
H(20)	-1372	8300	7063	26
H(21)	123	7459	7240	21
H(23)	4215	7271	5010	25
H(24)	5717	8102	5229	32
H(25)	5562	8993	6351	29
H(26)	3857	9104	7208	24
H(27)	2367	8268	7012	19

Table A2.91: Crystal data and structure refinement for $Tp^{Cl}RuAsPh_3Cl_2$ 223.

Identification code: $Tp^{Cl}RuAsPh_3Cl_2$ **223**	
Empirical formula: C28 H24 As B Cl7 N6 Ru	
Formula weight: 879.48	
Temperature: 123(2) K	
Wavelength:	0.71073 Å
Crystal system: Orthorhombic	
Space group: P b c a	
Unit cell dimensions	a = 13.9096(10) Å α= 90°. b = 15.9523(11) Å β= 90°. c = 30.044(2) Å γ = 90°.
Volume	6666.4(8) $Å^3$
Z	8
Density (calculated)	1.753 Mg/m^3
Absorption coefficient	2.048 mm^{-1}
F(000)	3480
Crystal size	0.320 x 0.060 x 0.040 mm^3
Theta range for data collection	2.369 to 27.878°.
Index ranges	-15<=h<=18, -20<=k<=20, -37<=l<=39
Reflections collected	47617
Independent reflections	7949 [R(int) = 0.0203]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.7457 and 0.6259
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7949 / 0 / 400
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0496
R indices (all data)	R1 = 0.0265, wR2 = 0.0518
Largest diff. peak and hole	0.724 and -0.435 $e.Å^{-3}$

Table A2.92: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Cl}RuAsPh_3Cl_2$ 223. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7272(1)	5390(1)	3687(1)	12(1)
As(1)	5828(1)	5286(1)	3201(1)	13(1)
Cl(1)	6635(1)	6470(1)	4125(1)	19(1)
Cl(2)	7985(1)	6345(1)	3205(1)	20(1)
Cl(3)	10825(1)	6277(1)	4635(1)	30(1)
Cl(4)	5140(1)	3427(1)	5026(1)	34(1)
Cl(5)	8663(1)	2865(1)	2420(1)	20(1)
Cl(6)	1954(1)	3547(1)	4657(1)	37(1)
Cl(7)	3026(1)	5086(1)	4453(1)	40(1)
N(1)	8507(1)	5427(1)	4077(1)	16(1)
N(2)	8921(1)	4695(1)	4210(1)	16(1)
N(3)	6758(1)	4525(1)	4147(1)	15(1)
N(4)	7371(1)	3916(1)	4298(1)	17(1)
N(5)	7904(1)	4395(1)	3358(1)	15(1)
N(6)	8317(1)	3767(1)	3603(1)	15(1)
C(1)	9076(1)	6054(1)	4205(1)	18(1)
C(2)	9876(1)	5721(1)	4418(1)	19(1)
C(3)	9759(1)	4860(1)	4418(1)	19(1)
C(4)	5928(1)	4436(1)	4367(1)	19(1)
C(5)	6005(1)	3762(1)	4658(1)	22(1)
C(6)	6918(1)	3445(1)	4606(1)	21(1)
C(7)	7973(1)	4173(1)	2929(1)	15(1)
C(8)	8411(1)	3395(1)	2901(1)	16(1)
C(9)	8616(1)	3152(1)	3333(1)	16(1)
C(10)	6013(1)	5167(1)	2560(1)	15(1)
C(11)	6627(1)	5711(1)	2334(1)	19(1)
C(12)	6741(1)	5641(1)	1876(1)	23(1)
C(13)	6244(2)	5036(1)	1640(1)	25(1)
C(14)	5633(2)	4495(1)	1864(1)	29(1)

C(15)	5514(1)	4558(1)	2324(1)	23(1)
C(16)	4860(1)	6164(1)	3226(1)	17(1)
C(17)	4512(1)	6428(1)	3640(1)	20(1)
C(18)	3827(1)	7062(1)	3660(1)	25(1)
C(19)	3496(1)	7435(1)	3274(1)	28(1)
C(20)	3831(1)	7170(1)	2864(1)	25(1)
C(21)	4511(1)	6528(1)	2839(1)	20(1)
C(22)	5105(1)	4280(1)	3355(1)	16(1)
C(23)	5579(1)	3508(1)	3349(1)	19(1)
C(24)	5106(1)	2790(1)	3493(1)	23(1)
C(25)	4175(2)	2842(1)	3658(1)	24(1)
C(26)	3705(2)	3606(1)	3664(1)	24(1)
C(27)	4162(1)	4325(1)	3505(1)	20(1)
C(28)	2533(2)	4457(2)	4871(1)	39(1)
B(1)	8403(2)	3855(1)	4113(1)	16(1)

Table A2.93: Bond lengths [Å] and angles [°] for $Tp^{Cl}RuAsPh_3Cl_2$ 223.

Ru(1)-N(5)	2.0654(14)	N(2)-C(3)	1.348(2)
Ru(1)-N(3)	2.0792(14)	N(2)-B(1)	1.548(2)
Ru(1)-N(1)	2.0810(15)	N(3)-C(4)	1.337(2)
Ru(1)-Cl(2)	2.3239(4)	N(3)-N(4)	1.370(2)
Ru(1)-Cl(1)	2.3422(4)	N(4)-C(6)	1.347(2)
Ru(1)-As(1)	2.4883(3)	N(4)-B(1)	1.543(3)
As(1)-C(16)	1.9438(17)	N(5)-C(7)	1.341(2)
As(1)-C(22)	1.9494(17)	N(5)-N(6)	1.3700(19)
As(1)-C(10)	1.9528(17)	N(6)-C(9)	1.341(2)
Cl(3)-C(2)	1.7184(18)	N(6)-B(1)	1.543(2)
Cl(4)-C(5)	1.7195(19)	C(1)-C(2)	1.389(3)
Cl(5)-C(8)	1.7104(17)	C(1)-H(1)	0.9500
Cl(6)-C(28)	1.780(2)	C(2)-C(3)	1.384(3)
Cl(7)-C(28)	1.746(2)	C(3)-H(3)	0.9500
N(1)-C(1)	1.331(2)	C(4)-C(5)	1.390(3)
N(1)-N(2)	1.3610(19)	C(4)-H(4)	0.9500

C(5)-C(6)	1.376(3)	C(25)-H(25)	0.9500
C(6)-H(6)	0.9500	C(26)-C(27)	1.395(3)
C(7)-C(8)	1.386(2)	C(26)-H(26)	0.9500
C(7)-H(7)	0.9500	C(27)-H(27)	0.9500
C(8)-C(9)	1.382(2)	C(28)-H(28A)	0.9900
C(9)-H(9)	0.9500	C(28)-H(28B)	0.9900
C(10)-C(15)	1.389(2)	B(1)-H(1B)	1.05(2)
C(10)-C(11)	1.394(2)		
C(11)-C(12)	1.392(2)	N(5)-Ru(1)-N(3)	87.37(6)
C(11)-H(11)	0.9500	N(5)-Ru(1)-N(1)	86.56(6)
C(12)-C(13)	1.382(3)	N(3)-Ru(1)-N(1)	85.91(6)
C(12)-H(12)	0.9500	N(5)-Ru(1)-Cl(2)	91.37(4)
C(13)-C(14)	1.384(3)	N(3)-Ru(1)-Cl(2)	174.73(4)
C(13)-H(13)	0.9500	N(1)-Ru(1)-Cl(2)	88.90(4)
C(14)-C(15)	1.396(3)	N(5)-Ru(1)-Cl(1)	174.21(4)
C(14)-H(14)	0.9500	N(3)-Ru(1)-Cl(1)	89.15(4)
C(15)-H(15)	0.9500	N(1)-Ru(1)-Cl(1)	88.57(4)
C(16)-C(21)	1.389(2)	Cl(2)-Ru(1)-Cl(1)	91.668(16)
C(16)-C(17)	1.398(2)	N(5)-Ru(1)-As(1)	90.67(4)
C(17)-C(18)	1.391(3)	N(3)-Ru(1)-As(1)	93.85(4)
C(17)-H(17)	0.9500	N(1)-Ru(1)-As(1)	177.23(4)
C(18)-C(19)	1.383(3)	Cl(2)-Ru(1)-As(1)	91.284(13)
C(18)-H(18)	0.9500	Cl(1)-Ru(1)-As(1)	94.185(13)
C(19)-C(20)	1.383(3)	C(16)-As(1)-C(22)	103.12(7)
C(19)-H(19)	0.9500	C(16)-As(1)-C(10)	101.50(7)
C(20)-C(21)	1.395(3)	C(22)-As(1)-C(10)	102.79(7)
C(20)-H(20)	0.9500	C(16)-As(1)-Ru(1)	119.23(5)
C(21)-H(21)	0.9500	C(22)-As(1)-Ru(1)	109.42(5)
C(22)-C(27)	1.388(3)	C(10)-As(1)-Ru(1)	118.59(5)
C(22)-C(23)	1.396(2)	C(1)-N(1)-N(2)	108.01(14)
C(23)-C(24)	1.391(3)	C(1)-N(1)-Ru(1)	132.34(12)
C(23)-H(23)	0.9500	N(2)-N(1)-Ru(1)	119.32(11)
C(24)-C(25)	1.388(3)	C(3)-N(2)-N(1)	109.48(14)
C(24)-H(24)	0.9500	C(3)-N(2)-B(1)	131.14(15)
C(25)-C(26)	1.384(3)	N(1)-N(2)-B(1)	119.39(14)

C(4)-N(3)-N(4)	107.32(14)	C(7)-C(8)-Cl(5)	125.66(13)
C(4)-N(3)-Ru(1)	134.08(12)	N(6)-C(9)-C(8)	107.44(15)
N(4)-N(3)-Ru(1)	118.47(11)	N(6)-C(9)-H(9)	126.3
C(6)-N(4)-N(3)	109.44(15)	C(8)-C(9)-H(9)	126.3
C(6)-N(4)-B(1)	130.24(15)	C(15)-C(10)-C(11)	119.54(16)
N(3)-N(4)-B(1)	120.33(14)	C(15)-C(10)-As(1)	120.41(13)
C(7)-N(5)-N(6)	107.11(13)	C(11)-C(10)-As(1)	120.02(13)
C(7)-N(5)-Ru(1)	133.89(12)	C(12)-C(11)-C(10)	120.11(17)
N(6)-N(5)-Ru(1)	118.89(10)	C(12)-C(11)-H(11)	119.9
C(9)-N(6)-N(5)	109.82(13)	C(10)-C(11)-H(11)	119.9
C(9)-N(6)-B(1)	130.15(14)	C(13)-C(12)-C(11)	120.36(17)
N(5)-N(6)-B(1)	120.00(13)	C(13)-C(12)-H(12)	119.8
N(1)-C(1)-C(2)	108.78(15)	C(11)-C(12)-H(12)	119.8
N(1)-C(1)-H(1)	125.6	C(12)-C(13)-C(14)	119.64(17)
C(2)-C(1)-H(1)	125.6	C(12)-C(13)-H(13)	120.2
C(3)-C(2)-C(1)	106.48(16)	C(14)-C(13)-H(13)	120.2
C(3)-C(2)-Cl(3)	127.13(15)	C(13)-C(14)-C(15)	120.57(18)
C(1)-C(2)-Cl(3)	126.39(14)	C(13)-C(14)-H(14)	119.7
N(2)-C(3)-C(2)	107.24(16)	C(15)-C(14)-H(14)	119.7
N(2)-C(3)-H(3)	126.4	C(10)-C(15)-C(14)	119.78(17)
C(2)-C(3)-H(3)	126.4	C(10)-C(15)-H(15)	120.1
N(3)-C(4)-C(5)	109.07(17)	C(14)-C(15)-H(15)	120.1
N(3)-C(4)-H(4)	125.5	C(21)-C(16)-C(17)	119.77(16)
C(5)-C(4)-H(4)	125.5	C(21)-C(16)-As(1)	120.77(13)
C(6)-C(5)-C(4)	106.50(16)	C(17)-C(16)-As(1)	119.46(13)
C(6)-C(5)-Cl(4)	127.20(15)	C(18)-C(17)-C(16)	119.76(17)
C(4)-C(5)-Cl(4)	126.26(16)	C(18)-C(17)-H(17)	120.1
N(4)-C(6)-C(5)	107.67(16)	C(16)-C(17)-H(17)	120.1
N(4)-C(6)-H(6)	126.2	C(19)-C(18)-C(17)	120.23(18)
C(5)-C(6)-H(6)	126.2	C(19)-C(18)-H(18)	119.9
N(5)-C(7)-C(8)	108.97(15)	C(17)-C(18)-H(18)	119.9
N(5)-C(7)-H(7)	125.5	C(20)-C(19)-C(18)	120.20(18)
C(8)-C(7)-H(7)	125.5	C(20)-C(19)-H(19)	119.9
C(9)-C(8)-C(7)	106.63(15)	C(18)-C(19)-H(19)	119.9
C(9)-C(8)-Cl(5)	127.69(13)	C(19)-C(20)-C(21)	120.11(18)

C(19)-C(20)-H(20)	119.9	C(27)-C(26)-H(26)	119.9
C(21)-C(20)-H(20)	119.9	C(22)-C(27)-C(26)	119.95(17)
C(16)-C(21)-C(20)	119.92(17)	C(22)-C(27)-H(27)	120.0
C(16)-C(21)-H(21)	120.0	C(26)-C(27)-H(27)	120.0
C(20)-C(21)-H(21)	120.0	Cl(7)-C(28)-Cl(6)	112.84(12)
C(27)-C(22)-C(23)	119.72(16)	Cl(7)-C(28)-H(28A)	109.0
C(27)-C(22)-As(1)	121.42(13)	Cl(6)-C(28)-H(28A)	109.0
C(23)-C(22)-As(1)	118.63(13)	Cl(7)-C(28)-H(28B)	109.0
C(24)-C(23)-C(22)	119.94(17)	Cl(6)-C(28)-H(28B)	109.0
C(24)-C(23)-H(23)	120.0	H(28A)-C(28)-H(28B)	107.8
C(22)-C(23)-H(23)	120.0	N(4)-B(1)-N(6)	106.91(14)
C(25)-C(24)-C(23)	120.17(17)	N(4)-B(1)-N(2)	108.07(14)
C(25)-C(24)-H(24)	119.9	N(6)-B(1)-N(2)	107.52(14)
C(23)-C(24)-H(24)	119.9	N(4)-B(1)-H(1B)	111.5(11)
C(26)-C(25)-C(24)	119.88(17)	N(6)-B(1)-H(1B)	112.2(11)
C(26)-C(25)-H(25)	120.1	N(2)-B(1)-H(1B)	110.4(11)
C(24)-C(25)-H(25)	120.1		
C(25)-C(26)-C(27)	120.26(18)		
C(25)-C(26)-H(26)	119.9		

Symmetry transformations used to generate equivalent atoms:

Table A2.94: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tp^{Cl}RuAsPh_3Cl_2$ 223. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	12(1)	11(1)	0(1)	0(1)	0(1)
As(1)	13(1)	13(1)	13(1)	0(1)	0(1)	1(1)
Cl(1)	23(1)	16(1)	17(1)	-3(1)	0(1)	3(1)
Cl(2)	22(1)	20(1)	18(1)	5(1)	-1(1)	-5(1)
Cl(3)	27(1)	33(1)	30(1)	6(1)	-12(1)	-13(1)
Cl(4)	34(1)	41(1)	28(1)	9(1)	12(1)	-10(1)

Cl(5)	26(1)	19(1)	16(1)	-5(1)	2(1)	1(1)
Cl(6)	42(1)	36(1)	33(1)	-2(1)	-1(1)	-1(1)
Cl(7)	54(1)	37(1)	30(1)	-8(1)	7(1)	-5(1)
N(1)	19(1)	14(1)	14(1)	2(1)	-1(1)	0(1)
N(2)	18(1)	16(1)	14(1)	1(1)	-2(1)	2(1)
N(3)	19(1)	16(1)	12(1)	0(1)	0(1)	0(1)
N(4)	22(1)	15(1)	13(1)	1(1)	-1(1)	0(1)
N(5)	15(1)	15(1)	14(1)	1(1)	-1(1)	1(1)
N(6)	16(1)	13(1)	15(1)	1(1)	-1(1)	1(1)
C(1)	21(1)	18(1)	14(1)	1(1)	0(1)	-3(1)
C(2)	18(1)	24(1)	14(1)	1(1)	-3(1)	-4(1)
C(3)	18(1)	24(1)	15(1)	2(1)	-2(1)	1(1)
C(4)	20(1)	21(1)	16(1)	-1(1)	1(1)	-3(1)
C(5)	26(1)	23(1)	17(1)	1(1)	4(1)	-7(1)
C(6)	31(1)	16(1)	15(1)	3(1)	1(1)	-3(1)
C(7)	16(1)	17(1)	13(1)	0(1)	0(1)	-1(1)
C(8)	15(1)	15(1)	16(1)	-2(1)	2(1)	-2(1)
C(9)	17(1)	13(1)	18(1)	-1(1)	1(1)	0(1)
C(10)	14(1)	16(1)	14(1)	1(1)	-1(1)	3(1)
C(11)	23(1)	15(1)	18(1)	0(1)	-2(1)	-1(1)
C(12)	25(1)	23(1)	19(1)	4(1)	2(1)	-3(1)
C(13)	27(1)	34(1)	15(1)	0(1)	0(1)	-4(1)
C(14)	33(1)	35(1)	19(1)	-7(1)	-2(1)	-14(1)
C(15)	23(1)	28(1)	17(1)	0(1)	-1(1)	-9(1)
C(16)	14(1)	14(1)	22(1)	-1(1)	1(1)	-1(1)
C(17)	19(1)	21(1)	21(1)	-2(1)	1(1)	-1(1)
C(18)	20(1)	27(1)	28(1)	-10(1)	5(1)	2(1)
C(19)	20(1)	21(1)	41(1)	-4(1)	1(1)	6(1)
C(20)	21(1)	24(1)	30(1)	4(1)	-3(1)	6(1)
C(21)	18(1)	21(1)	21(1)	0(1)	0(1)	2(1)
C(22)	18(1)	16(1)	13(1)	0(1)	-2(1)	-3(1)
C(23)	18(1)	22(1)	19(1)	2(1)	-3(1)	0(1)
C(24)	29(1)	18(1)	22(1)	4(1)	-7(1)	0(1)
C(25)	33(1)	23(1)	18(1)	3(1)	-1(1)	-9(1)
C(26)	23(1)	29(1)	19(1)	-4(1)	6(1)	-8(1)

C(27)	20(1)	20(1)	19(1)	-5(1)	2(1)	-1(1)
C(28)	53(2)	41(1)	24(1)	-2(1)	-4(1)	-6(1)
B(1)	20(1)	14(1)	14(1)	1(1)	-3(1)	1(1)

Table A2.95: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $Tp^{Cl}RuAsPh_3Cl_2$ 223.

	x	y	z	U(eq)
H(1)	8955	6633	4157	21
H(3)	10189	4459	4540	23
H(4)	5375	4778	4330	23
H(6)	7182	2977	4759	25
H(7)	7756	4498	2683	18
H(9)	8914	2643	3421	19
H(11)	6968	6131	2494	22
H(12)	7163	6011	1723	27
H(13)	6320	4991	1327	30
H(14)	5293	4078	1703	35
H(15)	5094	4185	2475	27
H(17)	4742	6176	3906	24
H(18)	3585	7240	3941	30
H(19)	3037	7875	3290	33
H(20)	3598	7424	2599	30
H(21)	4734	6341	2557	24
H(23)	6224	3474	3246	23
H(24)	5420	2262	3478	28
H(25)	3862	2354	3767	29
H(26)	3068	3642	3776	29
H(27)	3829	4844	3499	24
H(28A)	2062	4790	5042	47
H(28B)	3051	4283	5077	47
H(1B)	8780(15)	3355(13)	4257(7)	19

Table A2.96: Crystal data and structure refinement for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c.

Identification code: $Tp^{Cl}RuPPh_3(MeCN)Cl$ **224c**

Empirical formula: C32.02H31.7BCl6.71N7PRu

Formula weight: 895.20

Temperature/K: 123(2)

Crystal system: triclinic

Space group P-1

a/Å: 10.6018(8) b/Å: 11.0650(8) c/Å: 18.1294(13)

α/°: 74.3180(10)

β/°: 81.5240(10)

γ/°: 66.4960(10)

Volume/Å3: 1875.8(2) Z: 2 ρ calcg/cm3: 1.585

μ/mm ^{1}: 0.973

F(000) 902.0 Crystal size/mm^3 0.440 × 0.380 × 0.200

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 4.128 to 55.07

Index ranges -13 ≤ h ≤ 10, -14 ≤ k ≤ 13, -23 ≤ l ≤ 21

Reflections collected 11648

Independent reflections 8360 [Rint = 0.0134, Rsigma = 0.0202]

Data/restraints/parameters 8360/78/495

Goodness-of-fit on F2 1.063

Final R indexes [I>=2σ (I)] R1 = 0.0224, wR2 = 0.0578

Final R indexes [all data] R1 = 0.0230, wR2 = 0.0582

Largest diff. peak/hole / e Å-30.66/-0.68

Table A2.97: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{Cl}RuPPh$_3$(MeCN)Cl 224c. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C^{1_1}	-993(9)	12228(10)	-1054(5)	59(2)
C^{2_1}	-456(12)	11381(10)	-269(6)	54(2)
C^{3_1}	-41(7)	9870(7)	-203(4)	46.8(17)
C^{4_1}	438(8)	8983(10)	581(5)	57(2)
C^{5_1}	857(10)	7457(12)	661(7)	64(3)
Cl^{1_2}	1228.7(18)	8900.5(16)	914.0(9)	42.6(5)
Cl^{2_2}	938(2)	6429.7(18)	877.6(11)	52.5(6)
C^{1_2}	608(12)	8124(7)	401(6)	39(2)
C^{1}	6330.3(16)	3598.2(15)	1601.6(8)	14.5(3)
C^{2}	5048.0(16)	4538.6(16)	1333.1(9)	17.0(3)
C^{3}	4955.4(18)	5707.6(17)	771.4(9)	21.7(3)
C^{4}	6133(2)	5954.5(18)	469.1(10)	26.0(4)
C^{5}	7410(2)	5028(2)	725.6(11)	30.2(4)
C^{6}	7508.0(17)	3858.2(17)	1288.6(10)	23.0(3)
N^{6}	1723.8(13)	3591.3(13)	3875.0(7)	13.6(2)
C^{7}	8176.0(15)	1498.7(15)	2657.9(8)	14.1(3)
N^{7}	5837.0(13)	1934.6(12)	4108.3(7)	13.7(2)
C^{8}	9316.1(16)	520.0(16)	2383.2(9)	18.3(3)
C^{9}	10636.3(17)	227.7(17)	2594.1(10)	23.3(3)
C^{10}	10842.1(17)	882.3(18)	3089.6(10)	25.2(4)
C^{11}	9713.1(18)	1860.1(19)	3366.8(10)	23.9(3)
C^{12}	8398.0(17)	2174.1(16)	3146.1(9)	18.3(3)
C^{13}	6634.5(15)	866.7(15)	1740.8(9)	14.8(3)
C^{14}	7007.7(17)	-521.4(16)	2079.8(9)	19.7(3)
C^{15}	7064.0(19)	-1407.3(18)	1648.5(11)	26.5(4)
C^{16}	6738(2)	-933(2)	883.9(11)	29.7(4)
C^{17}	6381.7(19)	432(2)	540.1(10)	26.4(4)
C^{18}	6337.7(17)	1328.4(17)	964.7(9)	19.3(3)
C^{19}	2527.3(16)	6485.1(15)	2860.3(9)	18.2(3)
C^{20}	3813.8(16)	6528.4(15)	2843.0(9)	17.5(3)
C^{21}	4747.2(15)	5185.0(15)	2961.4(8)	14.1(3)
C^{22}	3200.1(16)	2036.6(17)	1921.2(9)	17.5(3)
C^{23}	1952.2(17)	2731.6(19)	1559.7(9)	21.4(3)
C^{24}	1190.3(17)	3760.6(18)	1920.6(9)	21.2(3)
C^{25}	7447.9(19)	1316.7(19)	5215.8(10)	25.3(4)
C^{26}	2780.1(16)	1852.0(16)	4771.1(9)	16.1(3)
C^{27}	1433.8(17)	2480.6(17)	5046.6(9)	18.7(3)
C^{28}	791.7(16)	3577.1(16)	4469.3(9)	17.0(3)
C^{29}	6517.7(16)	1670.6(15)	4604.5(9)	16.7(3)
C^{30}	3726.2(18)	3818.7(18)	5733.1(10)	24.6(3)

B^{1}	1607.8(17)	4548.4(17)	3070.6(10)	15.1(3)
Cl^{1}	4995.3(4)	-85.4(4)	3600.1(2)	17.24(7)
Cl^{2}	4206.0(4)	7939.9(4)	2712.8(3)	27.62(10)
Cl^{3}	1446.7(5)	2350.8(5)	820.0(2)	31.07(10)
Cl^{4}	709.3(5)	1931.7(5)	5921.9(2)	32.38(10)
Cl^{7}	3194.8(5)	5004.6(5)	4857.4(3)	31.81(10)
Cl^{8}	2438.5(5)	4188.5(5)	6471.3(3)	33.08(10)
N^{1}	4063.7(13)	4365.5(12)	3045.3(7)	12.6(2)
N^{2}	2703.3(13)	5170.4(13)	2980.7(7)	14.4(2)
N^{3}	1967.6(13)	3689.7(14)	2468.9(7)	16.2(3)
N^{4}	3207.8(13)	2636.6(13)	2468.4(7)	14.2(2)
N^{5}	2943.0(13)	2537.7(13)	4060.2(7)	13.6(2)
P^{1}	6429.0(4)	2045.2(4)	2335.8(2)	11.14(7)
Ru^{1}	4625.7(2)	2289.5(2)	3252.6(2)	10.03(4)

Table A2.98: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C^{1_1}	47(4)	76(5)	66(5)	-46(4)	9(4)	-19(4)
C^{2_1}	42(5)	92(7)	55(6)	-50(5)	19(4)	-39(5)
C^{3_1}	30(3)	90(5)	40(4)	-47(3)	11(3)	-27(3)
C^{4_1}	46(4)	110(7)	35(4)	-31(4)	5(3)	-44(4)
C^{5_1}	43(5)	98(7)	55(6)	-21(5)	-2(4)	-28(5)
Cl^{1_2}	52.8(10)	43.5(9)	37.6(8)	-17.2(6)	9.5(7)	-23.3(7)
Cl^{2_2}	62.0(12)	33.9(9)	58.4(11)	1.1(7)	-11.2(8)	-19.6(8)
C^{1_2}	49(5)	29(4)	37(4)	-5(3)	-4(3)	-13(4)
C^{1}	17.3(7)	14.0(6)	12.1(6)	-3.1(5)	-0.7(5)	-5.9(6)
C^{2}	17.1(7)	18.8(7)	14.0(7)	-2.9(6)	-0.9(5)	-6.1(6)
C^{3}	24.0(8)	19.6(7)	16.8(7)	-0.7(6)	-5.6(6)	-4.1(6)
C^{4}	33.9(10)	20.6(8)	21.9(8)	4.8(6)	-5.4(7)	-13.4(7)
C^{5}	26.2(9)	32.1(9)	30.3(9)	6.8(8)	-1.8(7)	-18.0(8)
C^{6}	18.2(8)	22.3(8)	24.1(8)	3.2(7)	-2.7(6)	-8.2(6)
N^{6}	12.1(6)	15.9(6)	14.3(6)	-5.4(5)	-0.3(4)	-5.7(5)
C^{7}	13.4(7)	14.3(6)	13.3(7)	0.6(5)	-2.4(5)	-5.7(5)
N^{7}	14.9(6)	12.4(5)	13.7(6)	-3.7(5)	0.2(5)	-5.0(5)
C^{8}	16.6(7)	16.4(7)	20.0(7)	-2.2(6)	-1.0(6)	-5.4(6)
C^{9}	14.0(7)	18.5(7)	30.1(9)	1.8(6)	-1.8(6)	-3.2(6)
C^{10}	17.0(8)	30.1(9)	25.5(8)	7.9(7)	-8.0(6)	-12.5(7)
C^{11}	26.1(9)	32.3(9)	19.3(8)	-1.7(7)	-3.9(6)	-18.9(7)
C^{12}	19.5(8)	21.0(7)	16.4(7)	-3.3(6)	-0.4(6)	-10.4(6)
C^{13}	12.9(7)	17.6(7)	15.6(7)	-7.9(6)	2.0(5)	-6.0(6)

C^{14}	20.9(8)	19.4(7)	19.7(7)	-7.6(6)	5.0(6)	-8.6(6)
C^{15}	32.3(9)	22.3(8)	30.3(9)	-13.9(7)	10.8(7)	-14.9(7)
C^{16}	35.4(10)	35.5(10)	31.0(9)	-23.7(8)	10.7(8)	-20.5(8)
C^{17}	27.9(9)	38.7(10)	18.7(8)	-14.6(7)	1.8(6)	-14.7(8)
C^{18}	18.6(7)	24.4(8)	16.3(7)	-7.3(6)	0.4(6)	-8.2(6)
C^{19}	16.7(7)	13.2(7)	21.7(8)	-2.2(6)	-2.0(6)	-3.4(6)
C^{20}	18.6(7)	12.8(7)	21.0(7)	-3.2(6)	-1.8(6)	-6.2(6)
C^{21}	13.8(7)	14.2(7)	14.8(7)	-3.8(5)	-1.5(5)	-5.2(5)
C^{22}	18.9(7)	25.8(8)	13.8(7)	-7.9(6)	2.4(5)	-13.4(6)
C^{23}	22.9(8)	37.1(9)	12.6(7)	-8.5(6)	0.2(6)	-18.7(7)
C^{24}	16.8(7)	32.7(9)	16.3(7)	-4.7(6)	-4.3(6)	-10.9(7)
C^{25}	27.6(9)	31.2(9)	19.0(8)	-0.5(7)	-9.8(7)	-13.7(7)
C^{26}	18.9(7)	17.3(7)	14.0(7)	-4.4(6)	0.4(5)	-8.8(6)
C^{27}	21.7(8)	24.8(8)	13.4(7)	-6.8(6)	4.3(6)	-13.0(6)
C^{28}	14.3(7)	23.3(7)	17.2(7)	-9.3(6)	2.2(5)	-8.9(6)
C^{29}	18.3(7)	16.2(7)	16.2(7)	-3.8(6)	-0.6(6)	-7.2(6)
C^{30}	21.9(8)	24.5(8)	25.4(8)	-7.3(7)	-2.6(6)	-5.0(7)
B^{1}	13.1(8)	17.5(8)	14.8(8)	-3.7(6)	-1.0(6)	-5.8(6)
Cl^{1}	22.81(18)	12.86(15)	17.52(17)	-4.50(13)	1.53(13)	-8.45(14)
Cl^{2}	19.38(19)	12.17(16)	50.5(3)	-3.31(17)	-6.26(17)	-6.15(14)
Cl^{3}	30.5(2)	58.4(3)	18.54(19)	-17.24(19)	-0.30(16)	-26.2(2)
Cl^{4}	31.2(2)	43.9(3)	17.65(19)	-2.40(18)	9.63(16)	-16.5(2)
Cl^{7}	38.8(3)	36.7(2)	22.4(2)	-4.90(18)	-3.43(17)	-17.3(2)
Cl^{8}	20.4(2)	46.5(3)	25.3(2)	-2.48(19)	-1.55(16)	-9.01(19)
N^{1}	11.2(6)	13.6(6)	13.0(6)	-3.8(5)	-1.1(4)	-4.1(5)
N^{2}	11.9(6)	13.6(6)	16.2(6)	-2.9(5)	-2.1(4)	-3.1(5)
N^{3}	13.5(6)	21.9(6)	14.4(6)	-4.8(5)	-2.5(5)	-6.9(5)
N^{4}	13.7(6)	18.6(6)	12.6(6)	-4.8(5)	0.1(4)	-8.1(5)
N^{5}	14.4(6)	14.3(6)	13.7(6)	-5.0(5)	-0.4(5)	-6.0(5)
P^{1}	11.27(17)	11.60(16)	10.61(16)	-2.97(13)	-0.84(12)	-4.01(13)
Ru^{1}	11.09(6)	10.70(6)	9.39(6)	-3.20(4)	-0.66(4)	-4.59(4)

Table A2.99: Bond Lengths for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C^{1_1}	C^{2_1}	1.523(11)	C^{15}	C^{16}	1.385(3)
C^{2_1}	C^{3_1}	1.524(11)	C^{16}	C^{17}	1.385(3)
C^{3_1}	C^{4_1}	1.518(10)	C^{17}	C^{18}	1.394(2)
C^{4_1}	C^{5_1}	1.535(11)	C^{19}	N^{2}	1.3501(19)
Cl^{1_2}	C^{1_2}	1.761(8)	C^{19}	C^{20}	1.379(2)
Cl^{2_2}	C^{1_2}	1.753(7)	C^{20}	C^{21}	1.397(2)
C^{1}	C^{6}	1.398(2)	C^{20}	Cl^{2}	1.7198(16)
C^{1}	C^{2}	1.400(2)	C^{21}	N^{1}	1.3370(19)

C1	P1	1.8431(15)	C22	N4	1.337(2)
C2	C3	1.391(2)	C22	C23	1.394(2)
C3	C4	1.387(3)	C23	C24	1.375(2)
C4	C5	1.386(3)	C23	Cl3	1.7206(16)
C5	C6	1.392(2)	C24	N3	1.3495(19)
N6	C28	1.3516(19)	C25	C29	1.461(2)
N6	N5	1.3626(17)	C26	N5	1.3331(19)
N6	B1	1.542(2)	C26	C27	1.399(2)
C7	C8	1.397(2)	C27	C28	1.377(2)
C7	C12	1.399(2)	C27	Cl4	1.7229(16)
C7	P1	1.8363(15)	C30	Cl7	1.7628(18)
N7	C29	1.139(2)	C30	Cl8	1.7704(18)
N7	Ru1	2.0163(13)	B1	N2	1.540(2)
C8	C9	1.393(2)	B1	N3	1.545(2)
C9	C10	1.384(3)	Cl1	Ru1	2.4109(4)
C10	C11	1.393(3)	N1	N2	1.3623(17)
C11	C12	1.388(2)	N1	Ru1	2.0690(12)
C13	C18	1.398(2)	N3	N4	1.3655(18)
C13	C14	1.404(2)	N4	Ru1	2.0743(13)
C13	P1	1.8374(15)	N5	Ru1	2.1114(13)
C14	C15	1.389(2)	P1	Ru1	2.3205(4)

Table A2.100: Bond Angles for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1_1	C2_1	C3_1	112.1(9)	C28	C27	Cl4	127.08(13)
C4_1	C3_1	C2_1	114.3(6)	C26	C27	Cl4	126.25(13)
C3_1	C4_1	C5_1	115.2(8)	N6	C28	C27	107.05(14)
Cl2_2	C1_2	Cl1_2	110.6(4)	N7	C29	C25	177.27(17)
C6	C1	C2	118.47(14)	Cl7	C30	Cl8	110.98(9)
C6	C1	P1	121.86(12)	N2	B1	N6	107.55(12)
C2	C1	P1	119.65(11)	N2	B1	N3	107.76(12)
C3	C2	C1	120.45(15)	N6	B1	N3	108.23(12)
C4	C3	C2	120.39(15)	C21	N1	N2	106.90(12)
C5	C4	C3	119.80(15)	C21	N1	Ru1	134.64(10)
C4	C5	C6	120.04(16)	N2	N1	Ru1	118.46(9)
C5	C6	C1	120.85(16)	C19	N2	N1	110.30(12)
C28	N6	N5	110.02(12)	C19	N2	B1	128.90(13)
C28	N6	B1	131.29(13)	N1	N2	B1	120.77(12)
N5	N6	B1	118.68(12)	C24	N3	N4	109.97(13)
C8	C7	C12	118.30(14)	C24	N3	B1	129.58(14)
C8	C7	P1	122.81(12)	N4	N3	B1	120.37(12)
C12	C7	P1	118.64(12)	C22	N4	N3	107.20(12)

C^{29}	N^{7}	Ru^{1}	176.51(12)	C^{22}	N^{4}	Ru^{1}	134.33(11)
C^{9}	C^{8}	C^{7}	120.52(15)	N^{3}	N^{4}	Ru^{1}	118.47(9)
C^{10}	C^{9}	C^{8}	120.73(16)	C^{26}	N^{5}	N^{6}	107.46(12)
C^{9}	C^{10}	C^{11}	119.23(15)	C^{26}	N^{5}	Ru^{1}	133.20(11)
C^{12}	C^{11}	C^{10}	120.24(16)	N^{6}	N^{5}	Ru^{1}	119.33(9)
C^{11}	C^{12}	C^{7}	120.96(15)	C^{7}	P^{1}	C^{13}	103.00(7)
C^{18}	C^{13}	C^{14}	118.70(14)	C^{7}	P^{1}	C^{1}	100.20(7)
C^{18}	C^{13}	P^{1}	121.53(12)	C^{13}	P^{1}	C^{1}	101.62(7)
C^{14}	C^{13}	P^{1}	119.63(12)	C^{7}	P^{1}	Ru^{1}	118.19(5)
C^{15}	C^{14}	C^{13}	120.15(16)	C^{13}	P^{1}	Ru^{1}	115.74(5)
C^{16}	C^{15}	C^{14}	120.63(17)	C^{1}	P^{1}	Ru^{1}	115.56(5)
C^{17}	C^{16}	C^{15}	119.82(16)	N^{7}	Ru^{1}	N^{1}	92.54(5)
C^{16}	C^{17}	C^{18}	120.06(16)	N^{7}	Ru^{1}	N^{4}	173.49(5)
C^{17}	C^{18}	C^{13}	120.62(16)	N^{1}	Ru^{1}	N^{4}	88.26(5)
N^{2}	C^{19}	C^{20}	107.23(13)	N^{7}	Ru^{1}	N^{5}	88.37(5)
C^{19}	C^{20}	C^{21}	106.16(13)	N^{1}	Ru^{1}	N^{5}	86.12(5)
C^{19}	C^{20}	Cl^{2}	127.41(12)	N^{4}	Ru^{1}	N^{5}	85.24(5)
C^{21}	C^{20}	Cl^{2}	126.43(12)	N^{7}	Ru^{1}	P^{1}	93.30(4)
N^{1}	C^{21}	C^{20}	109.41(13)	N^{1}	Ru^{1}	P^{1}	93.39(4)
N^{4}	C^{22}	C^{23}	108.90(14)	N^{4}	Ru^{1}	P^{1}	93.11(4)
C^{24}	C^{23}	C^{22}	106.73(14)	N^{5}	Ru^{1}	P^{1}	178.28(3)
C^{24}	C^{23}	Cl^{3}	126.62(13)	N^{7}	Ru^{1}	Cl^{1}	88.29(4)
C^{22}	C^{23}	Cl^{3}	126.63(14)	N^{1}	Ru^{1}	Cl^{1}	172.23(4)
N^{3}	C^{24}	C^{23}	107.18(14)	N^{4}	Ru^{1}	Cl^{1}	90.06(4)
N^{5}	C^{26}	C^{27}	108.85(14)	N^{5}	Ru^{1}	Cl^{1}	86.17(3)
C^{28}	C^{27}	C^{26}	106.61(14)	P^{1}	Ru^{1}	Cl^{1}	94.277(13)

Table A2.101: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	-243	12033	-1445	89
H^{1B_1}	-1342	13192	-1054	89
H^{1C_1}	-1737	12003	-1168	89
H^{2A_1}	-1179	11667	131	65
H^{2AB_1}	350	11550	-176	65
H^{3A_1}	-837	9717	-326	56
H^{3AB_1}	709	9585	-590	56
H^{4A_1}	-312	9274	968	68
H^{4AB_1}	1234	9138	702	68
H^{5A_1}	42	7270	625	96
H^{5B_1}	1261	6958	1160	96
H^{5C_1}	1534	7170	250	96

H^{1A_2}	-396	8621	345	47
H^{1AB_2}	1060	8162	-119	47
H^{2}	4236	4377	1536	20
H^{3}	4080	6340	594	26
H^{4}	6065	6756	87	31
H^{5}	8219	5192	517	36
H^{6}	8387	3229	1462	28
H^{8}	9190	50	2050	22
H^{9}	11404	-428	2396	28
H^{10}	11743	667	3239	30
H^{11}	9843	2314	3708	29
H^{12}	7638	2858	3329	22
H^{14}	7222	-856	2605	24
H^{15}	7328	-2347	1880	32
H^{16}	6759	-1543	596	36
H^{17}	6167	758	15	32
H^{18}	6104	2262	724	23
H^{19}	1676	7240	2799	22
H^{21}	5717	4898	2979	17
H^{22}	3927	1262	1799	21
H^{24}	286	4402	1805	25
H^{25A}	8240	483	5178	38
H^{25B}	6960	1176	5715	38
H^{25C}	7768	2054	5165	38
H^{26}	3466	1065	5046	19
H^{28}	-132	4205	4486	20
H^{30A}	4584	3835	5877	30
H^{30B}	3925	2897	5671	30
H^{1}	580(20)	5340(20)	2983(11)	18

Table A2.102: Atomic Occupancy for $Tp^{Cl}RuPPh_3(MeCN)Cl$ 224c.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C^{1_1}	0.333(3)	H^{1A_1}	0.333(3)	H^{1B_1}	0.333(3)
H^{1C_1}	0.333(3)	C^{2_1}	0.333(3)	H^{2A_1}	0.333(3)
H^{2AB_1}	0.333(3)	C^{3_1}	0.333(3)	H^{3A_1}	0.333(3)
H^{3AB_1}	0.333(3)	C^{4_1}	0.333(3)	H^{4A_1}	0.333(3)
H^{4AB_1}	0.333(3)	C^{5_1}	0.333(3)	H^{5A_1}	0.333(3)
H^{5B_1}	0.333(3)	H^{5C_1}	0.333(3)	Cl^{1_2}	0.354(2)
Cl^{2_2}	0.354(2)	C^{1_2}	0.354(2)	H^{1A_2}	0.354(2)
H^{1AB_2}	0.354(2)				

Table A2.103: Crystal data and structure refinement for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d.

Identification code: $Tp^{Br}RuPPh_3(MeCN)Cl$ **224d**

Empirical formula: $C_{31.88}H_{31.33}BBr_3Cl_{3.87}N_7PRu$

Formula weight: 1032.28

Temperature/K: 123(2)

Crystal system: triclinic

Space group P-1

a/Å: 10.7372(11) b/Å: 11.1263(12) c/Å: 18.2930(19)

α/°: 74.076(2) β/°: 81.554(2) γ/°: 65.998(2)

Volume/Å3 1918.3(3) Z: 2 r_{calc}g/cm^3: 1.787 m/mm^{-1}: 3.879

F(000) 1013.0

Crystal size/mm3 0.42 × 0.36 × 0.22

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/°4.126 to 56.6

Index ranges -14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24

Reflections collected 34567

Independent reflections 9486 [Rint = 0.0162, Rsigma = 0.0124]

Data/restraints/parameters9486/499/500

Goodness-of-fit on F2 1.002

Final R indexes [I>=2σ (I)] R1 = 0.0190, wR2 = 0.0462

Final R indexes [all data] R1 = 0.0202, wR2 = 0.0469

Largest diff. peak/hole / e Å-31.20/-0.69

Table A2.104: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{Br}RuPPh$_3$(MeCN)Cl 224d. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C^{1_1}	913(11)	7373(14)	668(8)	85(4)
C^{2_1}	512(10)	8949(12)	589(5)	61(3)
C^{3_1}	-32(7)	9852(8)	-196(4)	46.0(19)
C^{4_1}	-426(15)	11386(12)	-295(7)	54(3)
C^{5_1}	-1005(10)	12199(11)	-1088(5)	60(3)
Cl^{1_2}	980.9(17)	6483.8(16)	879.6(10)	55.1(5)
Cl^{2_2}	1270.6(15)	8922.7(14)	934.6(8)	43.6(4)
C^{1_2}	672(11)	8142(6)	428(5)	42.7(17)
C^{1}	8147.8(14)	1561.4(15)	2664.5(8)	14.0(3)
C^{2}	9292.4(15)	597.1(16)	2392.9(9)	17.8(3)
C^{3}	10590.2(16)	311.1(17)	2611.1(10)	22.1(3)
C^{4}	10768.6(17)	971.6(18)	3102.1(10)	23.8(3)
C^{5}	9642.2(17)	1935.5(18)	3371.5(10)	22.5(3)
C^{6}	8344.5(16)	2235.2(16)	3151.8(9)	17.6(3)
C^{7}	6302.4(15)	3630.7(15)	1606.2(8)	15.1(3)
C^{8}	5031.0(16)	4561.0(16)	1336.0(9)	17.7(3)
C^{9}	4922.6(17)	5727.1(17)	774.2(9)	22.6(3)
C^{10}	6078.9(19)	5977.4(18)	473.5(10)	27.5(4)
C^{11}	7344.8(19)	5059(2)	732.9(11)	32.4(4)
C^{12}	7460.0(17)	3894.0(18)	1294.4(10)	24.9(3)
C^{13}	6666.4(15)	890.7(15)	1762.5(8)	15.1(3)
C^{14}	6361.4(16)	1334.8(17)	994.7(9)	20.3(3)
C^{15}	6424.1(19)	420(2)	586.1(10)	27.4(4)
C^{16}	6812(2)	-939(2)	936.0(11)	30.6(4)
C^{17}	7149.0(19)	-1397.5(18)	1694.4(11)	26.8(4)
C^{18}	7070.4(16)	-490.5(16)	2109.1(9)	19.5(3)
C^{19}	1244.1(16)	3762.7(17)	1931.7(9)	19.5(3)
C^{20}	2005.2(17)	2731.6(18)	1580.3(9)	19.8(3)
C^{21}	3249.5(16)	2051.1(16)	1934.2(8)	16.8(3)
C^{22}	2820.3(15)	1866.2(15)	4745.6(8)	14.7(3)
C^{23}	1481.8(16)	2484.6(16)	5010.7(8)	16.9(3)
C^{24}	847.6(15)	3589.7(16)	4440.0(8)	15.6(3)
C^{25}	4736.7(15)	5204.3(15)	2959.3(8)	14.0(3)
C^{26}	3807.2(15)	6546.6(15)	2832.6(9)	16.4(3)
C^{27}	2542.5(15)	6503.4(15)	2842.3(9)	16.7(3)
C^{28}	6505.6(16)	1661.6(15)	4601.5(9)	16.7(3)
C^{29}	7412.6(18)	1273.7(19)	5219.2(10)	26.0(4)
C^{30}	3686.3(18)	3856.7(19)	5712.0(11)	27.1(4)
B^{1}	1651.0(16)	4571.5(17)	3059.3(9)	13.9(3)
Br^{1}	1461.2(2)	2301.4(2)	793.6(2)	28.86(5)

Br^{2}	693.9(2)	1844.1(2)	5938.2(2)	28.34(4)
Br^{3}	4221.1(3)	8068.0(2)	2724.4(7)	23.92(13)
Br^{4}	4271(4)	8042(3)	2472(5)	23.92(13)
Cl^{1}	5041.3(4)	-53.9(3)	3595.7(2)	16.71(7)
Cl^{2}	2422.0(4)	4258.3(5)	6441.1(3)	34.45(10)
Cl^{3}	3170.7(6)	5048.2(5)	4840.6(3)	35.63(10)
N^{1}	3253.0(12)	2661.3(13)	2469.0(7)	13.5(2)
N^{2}	2013.7(13)	3706.2(13)	2469.4(7)	15.0(2)
N^{3}	1773.2(12)	3616.9(12)	3857.2(7)	13.0(2)
N^{4}	2983.6(12)	2564.9(12)	4043.8(7)	12.8(2)
N^{5}	2723.6(12)	5193.5(12)	2966.2(7)	13.5(2)
N^{6}	4073.3(12)	4387.3(12)	3040.7(7)	12.1(2)
N^{7}	5841.1(12)	1947.5(12)	4102.9(7)	13.7(2)
P^{1}	6427.5(4)	2084.3(4)	2342.0(2)	11.37(7)
Ru^{1}	4648.2(2)	2317.3(2)	3248.2(2)	9.77(3)

Table A2.105: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C^{1_1}	50(6)	95(8)	85(9)	56(6)	-30(5)	-45(6)
C^{2_1}	50(5)	119(8)	26(4)	-13(4)	-2(4)	-49(5)
C^{3_1}	27(3)	90(5)	36(4)	-41(3)	6(3)	-25(4)
C^{4_1}	36(6)	106(7)	44(6)	-47(5)	8(4)	-36(6)
C^{5_1}	52(5)	85(6)	54(5)	-48(5)	-1(4)	-18(5)
Cl^{1_2}	61.7(10)	38.5(8)	66.1(10)	-1.1(7)	-13.7(7)	-23.8(7)
Cl^{2_2}	54.5(8)	45.6(7)	42.2(7)	-22.0(6)	13.4(6)	-28.4(6)
C^{1_2}	48(5)	41(3)	45(4)	-11(3)	-4(3)	-22(3)
C^{1}	12.8(6)	13.8(6)	13.8(6)	0.4(5)	-1.5(5)	-5.7(5)
C^{2}	15.5(7)	16.4(7)	18.9(7)	-1.9(6)	0.2(5)	-5.2(6)
C^{3}	13.4(7)	18.9(7)	26.8(8)	1.6(6)	0.2(6)	-4.0(6)
C^{4}	15.7(7)	27.9(8)	24.2(8)	6.4(6)	-6.1(6)	-11.2(6)
C^{5}	22.4(8)	28.0(8)	22.1(8)	-2.0(6)	-4.5(6)	-16.1(7)
C^{6}	16.4(7)	18.9(7)	18.8(7)	-3.4(6)	-0.1(5)	-8.8(6)
C^{7}	16.3(7)	14.6(7)	13.4(6)	-1.2(5)	-0.6(5)	-6.4(5)
C^{8}	16.3(7)	19.8(7)	15.5(7)	-1.8(6)	-0.8(5)	-7.0(6)
C^{9}	22.5(8)	20.0(8)	19.7(8)	1.0(6)	-5.5(6)	-4.7(6)
C^{10}	31.5(9)	22.3(8)	24.6(8)	6.9(7)	-6.0(7)	-12.6(7)
C^{11}	24.9(9)	33.7(10)	33.8(10)	10.4(8)	-3.1(7)	-17.6(8)
C^{12}	17.0(7)	24.4(8)	26.9(8)	5.3(7)	-2.1(6)	-8.5(6)
C^{13}	13.2(6)	17.8(7)	15.9(7)	-7.3(5)	2.7(5)	-6.8(5)
C^{14}	19.8(7)	25.3(8)	16.7(7)	-7.5(6)	1.5(6)	-8.7(6)

C^{15}	30.6(9)	39.8(10)	19.1(8)	-15.4(7)	3.0(7)	-16.8(8)
C^{16}	36.7(10)	37.4(10)	31.0(9)	-23.5(8)	11.8(8)	-22.1(8)
C^{17}	31.7(9)	22.0(8)	31.2(9)	-14.0(7)	11.4(7)	-14.0(7)
C^{18}	20.3(7)	19.2(7)	19.2(7)	-6.7(6)	4.6(6)	-8.4(6)
C^{19}	16.2(7)	29.3(8)	15.7(7)	-4.1(6)	-3.8(5)	-11.1(6)
C^{20}	20.9(7)	32.8(9)	13.4(7)	-7.3(6)	-0.2(6)	-16.9(7)
C^{21}	18.5(7)	23.4(7)	14.5(7)	-6.5(6)	2.1(5)	-13.8(6)
C^{22}	17.0(7)	14.9(6)	13.8(6)	-3.2(5)	-0.1(5)	-7.9(5)
C^{23}	17.8(7)	21.9(7)	13.2(6)	-4.9(5)	3.3(5)	-10.8(6)
C^{24}	12.9(6)	20.6(7)	16.2(7)	-7.3(5)	1.6(5)	-8.3(5)
C^{25}	12.6(6)	14.2(6)	15.8(7)	-3.5(5)	-1.3(5)	-5.5(5)
C^{26}	15.5(7)	12.4(6)	21.7(7)	-3.4(5)	-2.0(5)	-5.7(5)
C^{27}	13.9(7)	13.0(7)	20.2(7)	-1.7(5)	-1.9(5)	-3.2(5)
C^{28}	17.2(7)	16.9(7)	16.8(7)	-3.6(5)	-0.8(6)	-7.6(6)
C^{29}	26.4(8)	31.7(9)	21.7(8)	-1.2(7)	-11.0(7)	-12.9(7)
C^{30}	24.3(8)	26.9(9)	28.6(9)	-8.4(7)	-2.7(7)	-6.6(7)
B^{1}	11.6(7)	16.2(7)	14.2(7)	-3.5(6)	-1.1(5)	-5.5(6)
Br^{1}	31.43(9)	52.81(12)	17.42(8)	-14.64(7)	0.28(6)	-27.61(8)
Br^{2}	26.22(9)	37.12(10)	17.18(8)	-1.29(7)	7.81(6)	-13.93(7)
Br^{3}	16.31(8)	11.28(7)	44.0(4)	-3.69(11)	-5.38(11)	-5.61(6)
Br^{4}	16.31(8)	11.28(7)	44.0(4)	-3.69(11)	-5.38(11)	-5.61(6)
Cl^{1}	20.93(17)	12.39(15)	18.08(16)	-4.13(12)	1.31(13)	-8.05(13)
Cl^{2}	19.99(19)	46.5(3)	28.4(2)	-3.28(19)	-2.72(16)	-7.37(18)
Cl^{3}	46.0(3)	39.9(3)	24.8(2)	-5.29(18)	-5.20(19)	-20.7(2)
N^{1}	12.5(5)	16.3(6)	13.8(6)	-4.2(5)	0.4(4)	-7.5(5)
N^{2}	12.4(5)	19.0(6)	13.9(6)	-3.0(5)	-2.6(4)	-6.4(5)
N^{3}	10.9(5)	14.9(6)	14.4(6)	-4.4(4)	-0.5(4)	-5.6(4)
N^{4}	12.2(5)	13.3(5)	13.3(6)	-3.8(4)	-0.7(4)	-4.8(4)
N^{5}	10.5(5)	13.2(6)	15.4(6)	-2.2(4)	-1.7(4)	-3.5(4)
N^{6}	10.3(5)	12.6(5)	13.0(5)	-3.2(4)	-1.7(4)	-3.6(4)
N^{7}	13.7(6)	12.4(5)	15.0(6)	-3.4(4)	0.4(4)	-5.5(4)
P^{1}	10.90(15)	11.56(16)	11.42(16)	-2.61(12)	-0.49(12)	-4.16(13)
Ru^{1}	10.04(5)	10.15(5)	10.04(5)	-2.71(4)	-0.72(4)	-4.49(4)

Table A2.106: Bond Lengths for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C^{1_1}	C^{2_1}	1.596(13)	C^{20}	Br^{1}	1.8690(15)
C^{2_1}	C^{3_1}	1.546(10)	C^{21}	N^{1}	1.3363(18)
C^{3_1}	C^{4_1}	1.546(12)	C^{22}	N^{4}	1.3342(19)
C^{4_1}	C^{5_1}	1.547(11)	C^{22}	C^{23}	1.396(2)
Cl^{1_2}	C^{1_2}	1.716(6)	C^{23}	C^{24}	1.374(2)
Cl^{2_2}	C^{1_2}	1.760(7)	C^{23}	Br^{2}	1.8729(15)

C^{1}	C^{2}	1.396(2)	C^{24}	N^{3}	1.3494(19)
C^{1}	C^{6}	1.397(2)	C^{25}	N^{6}	1.3331(18)
C^{1}	P^{1}	1.8319(15)	C^{25}	C^{26}	1.395(2)
C^{2}	C^{3}	1.391(2)	C^{26}	C^{27}	1.376(2)
C^{3}	C^{4}	1.382(3)	C^{26}	Br^{4}	1.851(4)
C^{4}	C^{5}	1.384(3)	C^{26}	Br^{3}	1.8720(15)
C^{5}	C^{6}	1.388(2)	C^{27}	N^{5}	1.3469(19)
C^{7}	C^{8}	1.395(2)	C^{28}	N^{7}	1.136(2)
C^{7}	C^{12}	1.397(2)	C^{28}	C^{29}	1.458(2)
C^{7}	P^{1}	1.8396(15)	C^{30}	Cl^{3}	1.7629(19)
C^{8}	C^{9}	1.391(2)	C^{30}	Cl^{2}	1.7671(19)
C^{9}	C^{10}	1.385(3)	B^{1}	N^{5}	1.536(2)
C^{10}	C^{11}	1.382(3)	B^{1}	N^{3}	1.539(2)
C^{11}	C^{12}	1.388(2)	B^{1}	N^{2}	1.544(2)
C^{13}	C^{14}	1.395(2)	Cl^{1}	Ru^{1}	2.4074(5)
C^{13}	C^{18}	1.398(2)	N^{1}	N^{2}	1.3653(17)
C^{13}	P^{1}	1.8355(15)	N^{1}	Ru^{1}	2.0697(12)
C^{14}	C^{15}	1.395(2)	N^{3}	N^{4}	1.3598(17)
C^{15}	C^{16}	1.381(3)	N^{4}	Ru^{1}	2.1080(12)
C^{16}	C^{17}	1.387(3)	N^{5}	N^{6}	1.3626(16)
C^{17}	C^{18}	1.390(2)	N^{6}	Ru^{1}	2.0644(12)
C^{19}	N^{2}	1.3478(19)	N^{7}	Ru^{1}	2.0151(13)
C^{19}	C^{20}	1.373(2)	P^{1}	Ru^{1}	2.3169(4)
C^{20}	C^{21}	1.393(2)			

Table A2.107: Bond Angles for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C^{3_1}	C^{2_1}	C^{1_1}	113.9(9)	N^{7}	C^{28}	C^{29}	177.43(17)
C^{2_1}	C^{3_1}	C^{4_1}	115.4(7)	Cl^{3}	C^{30}	Cl^{2}	110.99(10)
C^{3_1}	C^{4_1}	C^{5_1}	111.2(9)	N^{5}	B^{1}	N^{3}	107.80(12)
Cl^{1_2}	C^{1_2}	Cl^{2_2}	112.1(4)	N^{5}	B^{1}	N^{2}	107.86(12)
C^{2}	C^{1}	C^{6}	118.29(14)	N^{3}	B^{1}	N^{2}	107.88(12)
C^{2}	C^{1}	P^{1}	122.70(12)	C^{21}	N^{1}	N^{2}	107.22(12)
C^{6}	C^{1}	P^{1}	118.78(11)	C^{21}	N^{1}	Ru^{1}	134.32(11)
C^{3}	C^{2}	C^{1}	120.46(15)	N^{2}	N^{1}	Ru^{1}	118.44(9)
C^{4}	C^{3}	C^{2}	120.65(15)	C^{19}	N^{2}	N^{1}	109.88(12)
C^{3}	C^{4}	C^{5}	119.40(15)	C^{19}	N^{2}	B^{1}	129.67(13)
C^{4}	C^{5}	C^{6}	120.33(16)	N^{1}	N^{2}	B^{1}	120.38(12)
C^{5}	C^{6}	C^{1}	120.86(15)	C^{24}	N^{3}	N^{4}	109.97(12)
C^{8}	C^{7}	C^{12}	118.44(14)	C^{24}	N^{3}	B^{1}	131.30(13)
C^{8}	C^{7}	P^{1}	119.95(11)	N^{4}	N^{3}	B^{1}	118.71(11)
C^{12}	C^{7}	P^{1}	121.60(12)	C^{22}	N^{4}	N^{3}	107.45(12)

C^{9}	C^{8}	C^{7}	120.57(15)	C^{22}	N^{4}	Ru^{1}	133.20(10)
C^{10}	C^{9}	C^{8}	120.31(15)	N^{3}	N^{4}	Ru^{1}	119.35(9)
C^{11}	C^{10}	C^{9}	119.66(16)	C^{27}	N^{5}	N^{6}	110.14(12)
C^{10}	C^{11}	C^{12}	120.33(17)	C^{27}	N^{5}	B^{1}	129.15(12)
C^{11}	C^{12}	C^{7}	120.69(16)	N^{6}	N^{5}	B^{1}	120.65(12)
C^{14}	C^{13}	C^{18}	118.86(14)	C^{25}	N^{6}	N^{5}	106.82(11)
C^{14}	C^{13}	P^{1}	121.64(12)	C^{25}	N^{6}	Ru^{1}	134.66(10)
C^{18}	C^{13}	P^{1}	119.34(12)	N^{5}	N^{6}	Ru^{1}	118.52(9)
C^{15}	C^{14}	C^{13}	120.48(16)	C^{28}	N^{7}	Ru^{1}	175.63(12)
C^{16}	C^{15}	C^{14}	120.15(17)	C^{1}	P^{1}	C^{13}	102.87(7)
C^{15}	C^{16}	C^{17}	119.87(16)	C^{1}	P^{1}	C^{7}	100.29(7)
C^{16}	C^{17}	C^{18}	120.36(17)	C^{13}	P^{1}	C^{7}	101.62(7)
C^{17}	C^{18}	C^{13}	120.25(16)	C^{1}	P^{1}	Ru^{1}	118.01(5)
N^{2}	C^{19}	C^{20}	107.29(14)	C^{13}	P^{1}	Ru^{1}	115.82(5)
C^{19}	C^{20}	C^{21}	106.73(13)	C^{7}	P^{1}	Ru^{1}	115.70(5)
C^{19}	C^{20}	Br^{1}	126.61(12)	N^{7}	Ru^{1}	N^{6}	92.91(5)
C^{21}	C^{20}	Br^{1}	126.65(13)	N^{7}	Ru^{1}	N^{1}	173.23(5)
N^{1}	C^{21}	C^{20}	108.87(14)	N^{6}	Ru^{1}	N^{1}	88.39(5)
N^{4}	C^{22}	C^{23}	108.81(13)	N^{7}	Ru^{1}	N^{4}	88.21(5)
C^{24}	C^{23}	C^{22}	106.58(13)	N^{6}	Ru^{1}	N^{4}	86.04(5)
C^{24}	C^{23}	Br^{2}	127.32(12)	N^{1}	Ru^{1}	N^{4}	85.25(5)
C^{22}	C^{23}	Br^{2}	125.97(12)	N^{7}	Ru^{1}	P^{1}	93.56(4)
N^{3}	C^{24}	C^{23}	107.19(13)	N^{6}	Ru^{1}	P^{1}	93.22(3)
N^{6}	C^{25}	C^{26}	109.59(13)	N^{1}	Ru^{1}	P^{1}	93.00(4)
C^{27}	C^{26}	C^{25}	105.97(13)	N^{4}	Ru^{1}	P^{1}	178.12(3)
C^{27}	C^{26}	Br^{4}	127.41(16)	N^{7}	Ru^{1}	Cl^{1}	87.78(4)
C^{25}	C^{26}	Br^{4}	124.74(16)	N^{6}	Ru^{1}	Cl^{1}	172.29(3)
C^{27}	C^{26}	Br^{3}	127.87(11)	N^{1}	Ru^{1}	Cl^{1}	90.05(4)
C^{25}	C^{26}	Br^{3}	126.09(11)	N^{4}	Ru^{1}	Cl^{1}	86.30(3)
Br^{4}	C^{26}	Br^{3}	14.3(3)	P^{1}	Ru^{1}	Cl^{1}	94.400(13)
N^{5}	C^{27}	C^{26}	107.47(13)				

Table A2.108: Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	82	7194	707	127
H^{1B_1}	1435	6849	1126	127
H^{1C_1}	1469	7108	220	127
H^{2A_1}	-194	9246	987	73
H^{2AB_1}	1325	9086	682	73
H^{3A_1}	-844	9711	-286	55
H^{3AB_1}	674	9545	-592	55

H^{4A_1}	389	11548	-233	65
H^{4AB_1}	-1117	11704	104	65
H^{5A_1}	-1400	13168	-1102	90
H^{5B_1}	-1712	11923	-1184	90
H^{5C_1}	-268	12019	-1479	90
H^{1A_2}	-322	8647	366	51
H^{1AB_2}	1123	8183	-86	51
H^{2}	9184	133	2057	21
H^{3}	11362	-345	2421	27
H^{4}	11656	766	3253	29
H^{5}	9758	2394	3708	27
H^{6}	7580	2907	3335	21
H^{8}	4233	4396	1538	21
H^{9}	4051	6355	596	27
H^{10}	6002	6776	91	33
H^{11}	8140	5226	526	39
H^{12}	8335	3269	1468	30
H^{14}	6109	2267	748	24
H^{15}	6199	734	66	33
H^{16}	6848	-1560	658	37
H^{17}	7435	-2336	1932	32
H^{18}	7292	-810	2630	23
H^{19}	342	4398	1817	23
H^{21}	3977	1279	1815	20
H^{22}	3503	1077	5020	18
H^{24}	-71	4217	4453	19
H^{25}	5696	4916	2984	17
H^{27}	1696	7259	2774	20
H^{29A}	8245	498	5149	39
H^{29B}	6953	1025	5706	39
H^{29C}	7650	2037	5218	39
H^{30A}	4547	3844	5854	33
H^{30B}	3860	2943	5654	33
H^{1B}	650(20)	5344(19)	2977(11)	16(5)

Table A2.109: Atomic Occupancy for $Tp^{Br}RuPPh_3(MeCN)Cl$ 224d.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C^{1_1}	0.288(3)	H^{1A_1}	0.288(3)	H^{1B_1}	0.288(3)
H^{1C_1}	0.288(3)	C^{2_1}	0.288(3)	H^{2A_1}	0.288(3)
H^{2AB_1}	0.288(3)	C^{3_1}	0.288(3)	H^{3A_1}	0.288(3)
H^{3AB_1}	0.288(3)	C^{4_1}	0.288(3)	H^{4A_1}	0.288(3)
H^{4AB_1}	0.288(3)	C^{5_1}	0.288(3)	H^{5A_1}	0.288(3)

H^{5B_1}	0.288(3)	H^{5C_1}	0.288(3)	Cl^{1_2}	0.436(2)		
Cl^{2_2}	0.436(2)	C^{1_2}	0.436(2)	H^{1A_2}	0.436(2)		
H^{1AB_2}	0.436(2)	Br^{3}	0.915(4)	Br^{4}	0.085(4)		

Table A2.110: Crystal data and structure refinement for $Tp^{I}RuPPh_3(MeCN)Cl$ 224e.

Identification code: $Tp^{I}RuPPh_3(MeCN)Cl$ **224e**

Empirical formula : C30H27BCl3I3N7PRu

Formula weight: 1115.48

Temperature/K: 123(2)

Crystal system: monoclinic

Space group: P21/c

a/Å: 15.6006(4) b/Å: 13.8713(4) c/Å:17.2388(5)

α/°: 90 β/°: 93.4110(10) γ/°: 90

Volume/Å3: 3723.88(18) Z: 4 ρcalcg/cm3 1.990

μ/mm 1: 25.583 F(000): 2120.0

Crystal size/mm3 0.08 × 0.06 × 0.01

Radiation: CuKα (λ = 1.54178)

2Θ range for data collection/° 5.674 to 133.178

Index ranges -18 ≤ h ≤ 18, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20

Reflections collected 24083

Independent reflections 6514 [Rint = 0.0418, Rsigma = 0.0438]

Data/restraints/parameters 6514/51/443

Goodness-of-fit on F2 1.115

Final R indexes [I>=2σ (I)] R1 = 0.0416, wR2 = 0.1083

Final R indexes [all data] R1 = 0.0431, wR2 = 0.1091

Largest diff. peak/hole / e Å-31.31/-0.84

Table A2.111: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Tp^{i}RuPPh$_3$(MeCN)Cl 224e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl^{1_1}	1677(4)	175(7)	2624(8)	81(4)
Cl^{2_1}	1427(8)	1095(13)	1096(7)	127(6)
C^{1_1}	1385(19)	1241(12)	2111(8)	73(6)
Cl^{1_2}	1640(3)	345(3)	1966(6)	73(3)
Cl^{2_2}	1482(3)	1811(4)	750(3)	56.0(17)
C^{1_2}	1393(13)	1563(8)	1748(6)	51(4)
I^1	7190.1(14)	3153(2)	3930(4)	41.4(6)
I$^{1'}$	7202(4)	3095(6)	3708(5)	41.4(6)
I^3	3585.7(16)	8569.2(16)	4116.8(17)	35.4(4)
I$^{3'}$	3767(14)	8390(14)	4316(14)	35.4(4)
I^2	3494.3(3)	3655.7(3)	-510.3(2)	19.79(12)
Ru^1	3356.9(3)	4265.0(3)	3055.8(3)	12.90(12)
Cl^1	3325.7(10)	2535.7(11)	2808.7(9)	20.7(3)
P^1	1892.7(10)	4514.7(12)	2901.8(9)	14.9(3)
N^7	3361(3)	4106(4)	4214(3)	14.4(11)
N^2	3536(3)	4374(4)	1888(3)	11.4(10)
N^1	4719(3)	4126(4)	3162(3)	18.8(12)
N^3	4136(3)	5024(4)	1642(3)	15.9(11)
N^4	4219(3)	6141(4)	2796(3)	17.5(11)
N^6	5191(3)	4738(4)	2746(3)	18.7(12)
N^5	3600(3)	5725(4)	3221(3)	16.6(11)
C^{24}	3346(4)	6395(5)	3708(4)	18.3(13)
C^1	6086(5)	3786(7)	3407(5)	41.4(6)
C^{21}	4216(4)	4922(5)	872(4)	17.0(13)
C^2	5245(4)	3548(5)	3563(4)	19.6(14)
C^{22}	3653(4)	4212(5)	620(4)	21.5(14)
C^3	1148(4)	3582(5)	3197(4)	19.3(14)
C^{25}	3791(6)	7246(6)	3594(5)	35.4(4)
C^9	1558(4)	4779(5)	1883(4)	19.2(14)
C^{23}	3255(4)	3884(5)	1261(4)	17.2(13)
C^4	262(5)	3707(5)	3083(4)	25.2(15)
C^{15}	1453(4)	5522(5)	3456(4)	21.5(14)
C^{11}	1822(5)	5689(5)	723(4)	25.5(16)
C^{10}	1969(4)	5530(5)	1517(4)	19.8(14)
C^{26}	4343(4)	7065(5)	3021(4)	20.5(14)
C^{27}	6032(4)	4539(5)	2891(4)	22.9(15)
C^{28}	3507(5)	3977(6)	4865(5)	32.6(18)
C^{17}	1023(5)	6098(6)	4693(5)	33.7(18)
C^{16}	1318(4)	5351(6)	4237(4)	26.7(16)
C^{20}	1299(5)	6437(6)	3153(5)	29.5(17)

C^{5}	-292(4)	2998(6)	3341(5)	32.1(18)
C^{8}	1463(5)	2764(5)	3587(5)	28.2(16)
C^{6}	34(5)	2170(6)	3694(5)	36.2(19)
C^{18}	880(5)	7003(6)	4395(5)	35.5(19)
C^{12}	1263(5)	5122(6)	290(4)	32.1(18)
C^{14}	997(4)	4201(6)	1435(4)	26.4(16)
C^{19}	1017(6)	7173(6)	3623(5)	39(2)
C^{13}	851(5)	4358(7)	657(5)	35.0(19)
C^{29}	3766(7)	3787(8)	5675(5)	48(2)
C^{7}	893(6)	2074(7)	3831(5)	40(2)
B^{1}	4745(5)	5533(6)	2247(5)	19.8(16)

Table A2.112: Anisotropic Displacement Parameters ($Å^2×10^3$) for $Tp^{i}RuPPh_3(MeCN)Cl$ 224e. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl^{1_1}	35(3)	72(5)	134(9)	-48(6)	-4(4)	-1(3)
Cl^{2_1}	120(8)	171(14)	88(7)	-69(8)	-18(6)	31(8)
C^{1_1}	46(14)	73(11)	96(11)	-57(9)	-13(9)	1(9)
Cl^{1_2}	39(2)	41(2)	138(7)	3(3)	-5(3)	-0.4(18)
Cl^{2_2}	47(2)	63(3)	58(3)	-23(2)	1.9(19)	4(2)
C^{1_2}	42(9)	46(7)	64(8)	-14(6)	3(7)	11(6)
I^{1}	17.1(3)	62.0(5)	44.7(18)	21.8(10)	-0.5(7)	11.0(3)
$I^{1'}$	17.1(3)	62.0(5)	44.7(18)	21.8(10)	-0.5(7)	11.0(3)
I^{3}	47.7(6)	22.5(5)	37.9(7)	-12.3(5)	18.4(6)	-9.4(5)
$I^{3'}$	47.7(6)	22.5(5)	37.9(7)	-12.3(5)	18.4(6)	-9.4(5)
I^{2}	23.2(2)	22.0(2)	14.4(2)	-2.88(16)	2.71(16)	-4.10(16)
Ru^{1}	10.4(2)	15.7(2)	12.7(2)	0.11(18)	1.17(17)	-0.27(17)
Cl^{1}	22.8(7)	17.5(7)	21.8(7)	1.6(6)	2.8(6)	1.0(6)
P^{1}	10.7(7)	19.3(8)	14.7(7)	-0.8(6)	1.9(6)	1.7(6)
N^{7}	13(2)	18(3)	12(3)	-1(2)	-2(2)	0(2)
N^{2}	10(2)	13(3)	11(2)	-1(2)	1.5(19)	1.8(19)
N^{1}	15(3)	24(3)	18(3)	-3(2)	2(2)	4(2)
N^{3}	13(2)	18(3)	17(3)	-1(2)	3(2)	-2(2)
N^{4}	14(3)	21(3)	17(3)	0(2)	3(2)	-4(2)
N^{6}	13(3)	30(3)	14(3)	-4(2)	5(2)	0(2)
N^{5}	15(3)	20(3)	15(3)	2(2)	4(2)	-2(2)
C^{24}	16(3)	22(3)	17(3)	-4(3)	1(3)	0(3)
C^{1}	17.1(3)	62.0(5)	44.7(18)	21.8(10)	-0.5(7)	11.0(3)
C^{21}	15(3)	20(3)	17(3)	-2(3)	3(2)	0(3)
C^{2}	19(3)	23(4)	17(3)	1(3)	-2(3)	0(3)
C^{22}	21(3)	31(4)	12(3)	-8(3)	-4(3)	0(3)

C^{3}	19(3)	24(4)	15(3)	-5(3)	5(3)	-6(3)
C^{25}	47.7(6)	22.5(5)	37.9(7)	-12.3(5)	18.4(6)	-9.4(5)
C^{9}	15(3)	26(4)	16(3)	1(3)	-1(2)	5(3)
C^{23}	14(3)	19(3)	18(3)	-8(3)	0(2)	-2(3)
C^{4}	20(3)	29(4)	27(4)	-2(3)	5(3)	1(3)
C^{15}	12(3)	29(4)	23(3)	-4(3)	1(3)	-2(3)
C^{11}	26(4)	26(4)	25(4)	8(3)	11(3)	11(3)
C^{10}	19(3)	17(3)	23(3)	0(3)	1(3)	5(3)
C^{26}	23(3)	21(3)	18(3)	-1(3)	2(3)	-11(3)
C^{27}	9(3)	32(4)	28(4)	-9(3)	-1(3)	-3(3)
C^{28}	37(4)	23(4)	37(5)	0(3)	1(4)	-8(3)
C^{17}	31(4)	45(5)	26(4)	-4(4)	6(3)	-2(4)
C^{16}	21(3)	35(4)	25(4)	-2(3)	4(3)	-5(3)
C^{20}	32(4)	30(4)	26(4)	-4(3)	3(3)	11(3)
C^{5}	12(3)	48(5)	37(4)	-9(4)	8(3)	-10(3)
C^{8}	22(4)	27(4)	36(4)	3(3)	8(3)	-2(3)
C^{6}	33(4)	43(5)	34(4)	-5(4)	14(3)	-20(4)
C^{18}	31(4)	42(5)	33(4)	-19(4)	0(3)	12(4)
C^{12}	32(4)	45(5)	19(4)	4(3)	-1(3)	10(4)
C^{14}	19(3)	34(4)	27(4)	-1(3)	2(3)	-4(3)
C^{19}	43(5)	34(5)	40(5)	-2(4)	-5(4)	17(4)
C^{13}	27(4)	50(5)	27(4)	-16(4)	-5(3)	-5(4)
C^{29}	68(7)	53(6)	25(4)	0(4)	1(4)	-2(5)
C^{7}	40(5)	36(5)	44(5)	6(4)	11(4)	-11(4)
B^{1}	14(3)	24(4)	22(4)	-3(3)	3(3)	-6(3)

Table A2.113: Bond Lengths for $Tp^{I}RuPPh_3(MeCN)Cl$ 224e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl^{1_1}	C^{1_1}	1.768(9)	N^{6}	C^{27}	1.348(8)
Cl^{2_1}	C^{1_1}	1.768(9)	N^{6}	B^{1}	1.539(10)
Cl^{1_2}	C^{1_2}	1.768(8)	N^{5}	C^{24}	1.327(9)
Cl^{2_2}	C^{1_2}	1.767(8)	C^{24}	C^{25}	1.390(10)
I^{1}	C^{1}	2.090(8)	C^{1}	C^{27}	1.372(12)
$I^{1'}$	C^{1}	2.028(10)	C^{1}	C^{2}	1.395(11)
I^{3}	C^{25}	2.078(8)	C^{21}	C^{22}	1.373(10)
$I^{3'}$	C^{25}	2.017(13)	C^{22}	C^{23}	1.377(10)
I^{2}	C^{22}	2.096(6)	C^{3}	C^{8}	1.393(10)
Ru^{1}	N^{7}	2.009(5)	C^{3}	C^{4}	1.395(10)
Ru^{1}	N^{2}	2.055(5)	C^{25}	C^{26}	1.373(10)
Ru^{1}	N^{5}	2.077(6)	C^{9}	C^{14}	1.387(10)
Ru^{1}	N^{1}	2.130(5)	C^{9}	C^{10}	1.393(10)
Ru^{1}	P^{1}	2.3100(16)	C^{4}	C^{5}	1.399(11)

Ru^{1}	Cl^{1}	2.4364(16)	C^{15}	C^{20}	1.389(11)
P^{1}	C^{3}	1.831(7)	C^{15}	C^{16}	1.395(10)
P^{1}	C^{9}	1.840(7)	C^{11}	C^{12}	1.364(12)
P^{1}	C^{15}	1.847(7)	C^{11}	C^{10}	1.393(10)
N^{7}	C^{28}	1.146(10)	C^{28}	C^{29}	1.455(12)
N^{2}	C^{23}	1.328(8)	C^{17}	C^{18}	1.370(13)
N^{2}	N^{3}	1.385(7)	C^{17}	C^{16}	1.395(11)
N^{1}	C^{2}	1.314(9)	C^{20}	C^{19}	1.391(11)
N^{1}	N^{6}	1.357(8)	C^{5}	C^{6}	1.383(13)
N^{3}	C^{21}	1.349(8)	C^{8}	C^{7}	1.388(11)
N^{3}	B^{1}	1.540(9)	C^{6}	C^{7}	1.354(13)
N^{4}	C^{26}	1.351(9)	C^{18}	C^{19}	1.381(12)
N^{4}	N^{5}	1.374(7)	C^{12}	C^{13}	1.407(12)
N^{4}	B^{1}	1.540(9)	C^{14}	C^{13}	1.364(11)

Table A2.114: Bond Angles for $Tp^{I}RuPPh_{3}(MeCN)Cl$ 224e.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl^{2_1}	C^{1_1}	Cl^{1_1}	112.1(10)	C^{27}	C^{1}	I^{1}	128.1(6)
Cl^{2_2}	C^{1_2}	Cl^{1_2}	111.4(6)	C^{2}	C^{1}	I^{1}	125.3(6)
N^{7}	Ru^{1}	N^{2}	171.8(2)	$I^{1'}$	C^{1}	I^{1}	10.82(17)
N^{7}	Ru^{1}	N^{5}	88.9(2)	N^{3}	C^{21}	C^{22}	107.0(6)
N^{2}	Ru^{1}	N^{5}	91.6(2)	N^{1}	C^{2}	C^{1}	108.6(6)
N^{7}	Ru^{1}	N^{1}	87.8(2)	C^{21}	C^{22}	C^{23}	107.0(6)
N^{2}	Ru^{1}	N^{1}	84.1(2)	C^{21}	C^{22}	I^{2}	126.6(5)
N^{5}	Ru^{1}	N^{1}	84.5(2)	C^{23}	C^{22}	I^{2}	126.2(5)
N^{7}	Ru^{1}	P^{1}	94.30(15)	C^{8}	C^{3}	C^{4}	119.1(6)
N^{2}	Ru^{1}	P^{1}	93.86(14)	C^{8}	C^{3}	P^{1}	119.9(5)
N^{5}	Ru^{1}	P^{1}	92.33(15)	C^{4}	C^{3}	P^{1}	120.9(6)
N^{1}	Ru^{1}	P^{1}	176.17(16)	C^{26}	C^{25}	C^{24}	106.6(6)
N^{7}	Ru^{1}	Cl^{1}	93.69(16)	C^{26}	C^{25}	$I^{3'}$	128.5(7)
N^{2}	Ru^{1}	Cl^{1}	84.47(15)	C^{24}	C^{25}	$I^{3'}$	123.6(7)
N^{5}	Ru^{1}	Cl^{1}	170.30(15)	C^{26}	C^{25}	I^{3}	126.4(6)
N^{1}	Ru^{1}	Cl^{1}	86.29(16)	C^{24}	C^{25}	I^{3}	126.8(6)
P^{1}	Ru^{1}	Cl^{1}	96.78(6)	$I^{3'}$	C^{25}	I^{3}	13.9(8)
C^{3}	P^{1}	C^{9}	104.9(3)	C^{14}	C^{9}	C^{10}	118.2(6)
C^{3}	P^{1}	C^{15}	97.4(3)	C^{14}	C^{9}	P^{1}	123.4(6)
C^{9}	P^{1}	C^{15}	104.5(3)	C^{10}	C^{9}	P^{1}	117.9(5)
C^{3}	P^{1}	Ru^{1}	120.1(2)	N^{2}	C^{23}	C^{22}	110.0(6)
C^{9}	P^{1}	Ru^{1}	111.3(2)	C^{3}	C^{4}	C^{5}	119.7(7)
C^{15}	P^{1}	Ru^{1}	116.7(2)	C^{20}	C^{15}	C^{16}	119.0(7)
C^{28}	N^{7}	Ru^{1}	168.3(6)	C^{20}	C^{15}	P^{1}	123.9(5)
C^{23}	N^{2}	N^{3}	106.3(5)	C^{16}	C^{15}	P^{1}	117.0(6)

C^{23}	N^{2}	Ru^{1}	134.6(4)	C^{12}	C^{11}	C^{10}	120.6(7)
N^{3}	N^{2}	Ru^{1}	118.7(4)	C^{11}	C^{10}	C^{9}	120.7(7)
C^{2}	N^{1}	N^{6}	108.5(5)	N^{4}	C^{26}	C^{25}	107.2(6)
C^{2}	N^{1}	Ru^{1}	133.5(5)	N^{6}	C^{27}	C^{1}	107.3(6)
N^{6}	N^{1}	Ru^{1}	117.9(4)	N^{7}	C^{28}	C^{29}	175.1(9)
C^{21}	N^{3}	N^{2}	109.6(5)	C^{18}	C^{17}	C^{16}	121.4(7)
C^{21}	N^{3}	B^{1}	128.7(5)	C^{15}	C^{16}	C^{17}	119.5(7)
N^{2}	N^{3}	B^{1}	119.6(5)	C^{15}	C^{20}	C^{19}	120.4(7)
C^{26}	N^{4}	N^{5}	109.8(5)	C^{6}	C^{5}	C^{4}	120.3(7)
C^{26}	N^{4}	B^{1}	128.6(6)	C^{7}	C^{8}	C^{3}	119.6(7)
N^{5}	N^{4}	B^{1}	121.1(5)	C^{7}	C^{6}	C^{5}	119.5(7)
C^{27}	N^{6}	N^{1}	109.1(6)	C^{17}	C^{18}	C^{19}	119.1(7)
C^{27}	N^{6}	B^{1}	130.7(6)	C^{11}	C^{12}	C^{13}	118.9(7)
N^{1}	N^{6}	B^{1}	120.1(5)	C^{13}	C^{14}	C^{9}	121.2(7)
C^{24}	N^{5}	N^{4}	106.8(5)	C^{18}	C^{19}	C^{20}	120.6(8)
C^{24}	N^{5}	Ru^{1}	135.3(4)	C^{14}	C^{13}	C^{12}	120.5(7)
N^{4}	N^{5}	Ru^{1}	117.6(4)	C^{6}	C^{7}	C^{8}	121.7(9)
N^{5}	C^{24}	C^{25}	109.6(6)	N^{6}	B^{1}	N^{4}	106.8(5)
C^{27}	C^{1}	C^{2}	106.5(6)	N^{6}	B^{1}	N^{3}	106.9(6)
C^{27}	C^{1}	$I^{1'}$	123.0(6)	N^{4}	B^{1}	N^{3}	109.6(5)
C^{2}	C^{1}	$I^{1'}$	130.0(7)				

Table A2.115: Hydrogen Atom Coordinates (Å×10^{4}) and Isotropic Displacement Parameters (Å^{2}×10^{3}) for Tp^{i}RuPPh$_{3}$(MeCN)Cl 224e.

Atom	*x*	*y*	*z*	U(eq)
H^{1A_1}	796	1428	2233	87
H^{1AB_1}	1778	1768	2287	87
H^{1A_2}	801	1705	1890	61
H^{1AB_2}	1790	1988	2060	61
H^{24}	2925	6305	4077	22
H^{21}	4591	5275	563	20
H^{2}	5079	3051	3903	23
H^{23}	2841	3382	1256	21
H^{4}	37	4269	2832	30
H^{11}	2114	6198	480	31
H^{10}	2354	5937	1813	24
H^{26}	4738	7508	2820	25
H^{27}	6500	4861	2675	27
H^{17}	920	5976	5222	40
H^{16}	1425	4731	4456	32
H^{20}	1388	6562	2622	35
H^{5}	-896	3087	3274	39

H^{8}	2064	2679	3686	34
H^{6}	-343	1672	3839	43
H^{18}	688	7507	4715	43
H^{12}	1152	5240	-250	39
H^{14}	708	3687	1674	32
H^{19}	917	7798	3411	47
H^{13}	470	3949	360	42
H^{29A}	3818	3090	5757	73
H^{29B}	3333	4047	6008	73
H^{29C}	4321	4096	5807	73
H^{7}	1111	1521	4100	48
H^{1B}	5250(50)	5950(60)	2000(40)	24

Table A2.116: Atomic Occupancy for $Tp^{I}RuPPh_3(MeCN)Cl$ 224e.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Cl^{1_1}	0.420(12)	Cl^{2_1}	0.420(12)	C^{1_1}	0.420(12)
H^{1A_1}	0.420(12)	H^{1AB_1}	0.420(12)	Cl^{1_2}	0.580(12)
Cl^{2_2}	0.580(12)	C^{1_2}	0.580(12)	H^{1A_2}	0.580(12)
H^{1AB_2}	0.580(12)	I^{1}	0.723(16)	$I^{1'}$	0.277(16)
I^{3}	0.920(12)	$I^{3'}$	0.080(12)		

APPENDEX SEVEN: Cyclic Voltammetry

Ligand exchange reactions of $Tp^{X}Ru(diene)Cl$ to mono- and di-phosphine complexes and their oxidation potentials.

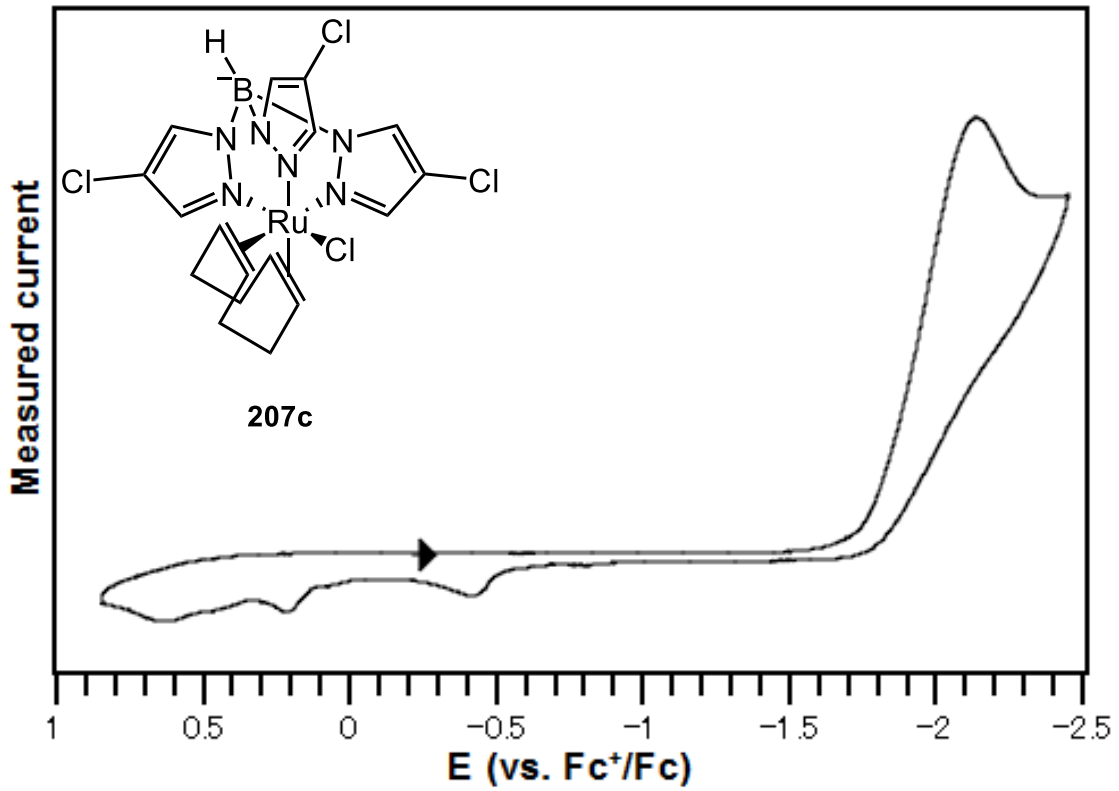


Figure A2.67: Cyclic voltammogram of 207c[42]

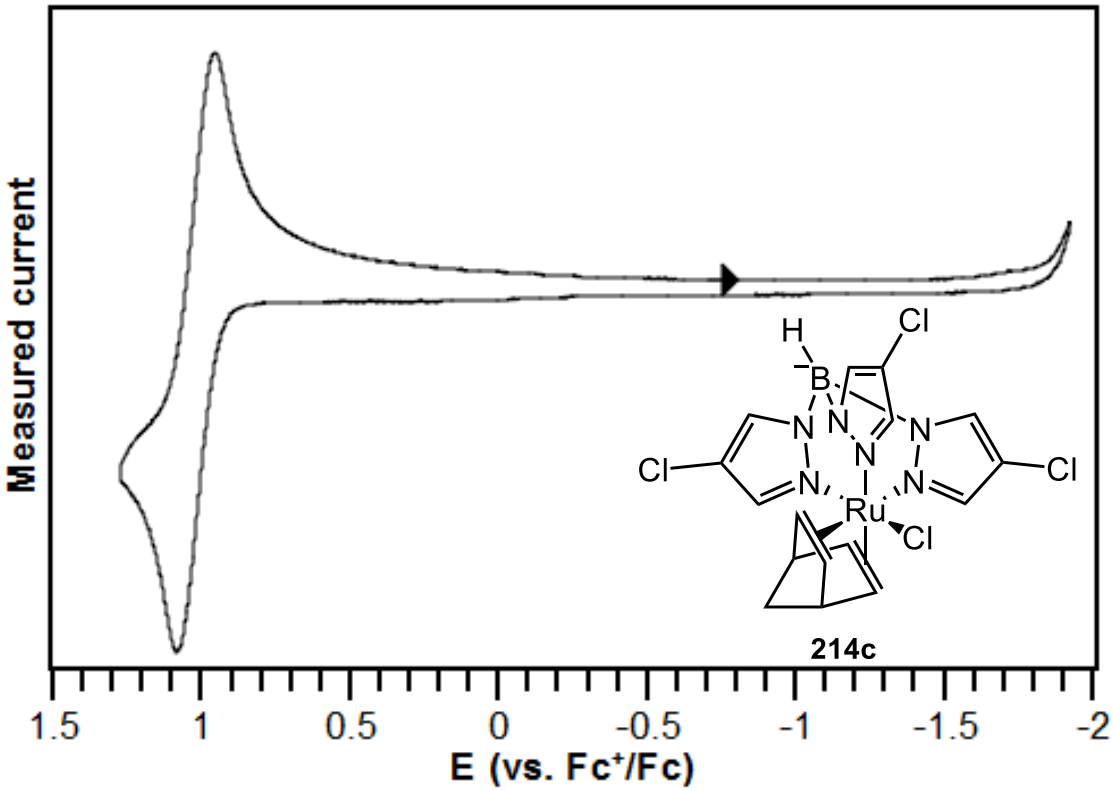


Figure A2.68: Cyclic voltammogram of 214c[42]

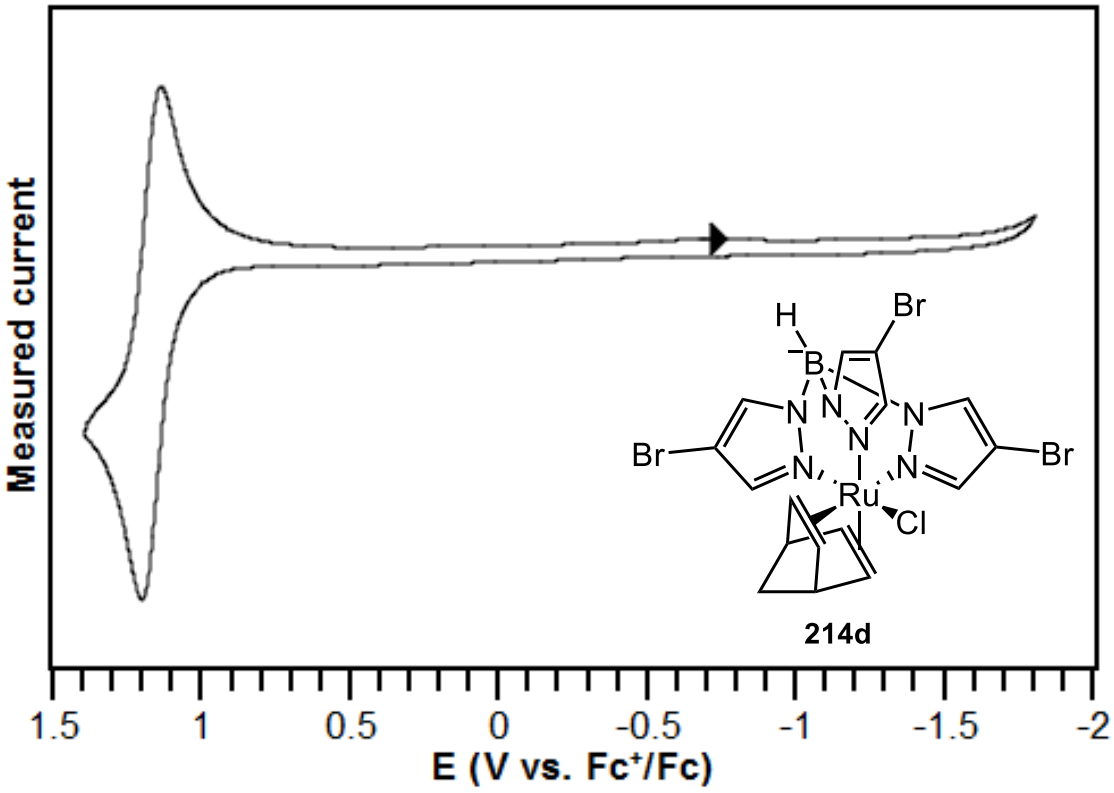


Figure A2.69: Cyclic voltammogram of 214d[42]

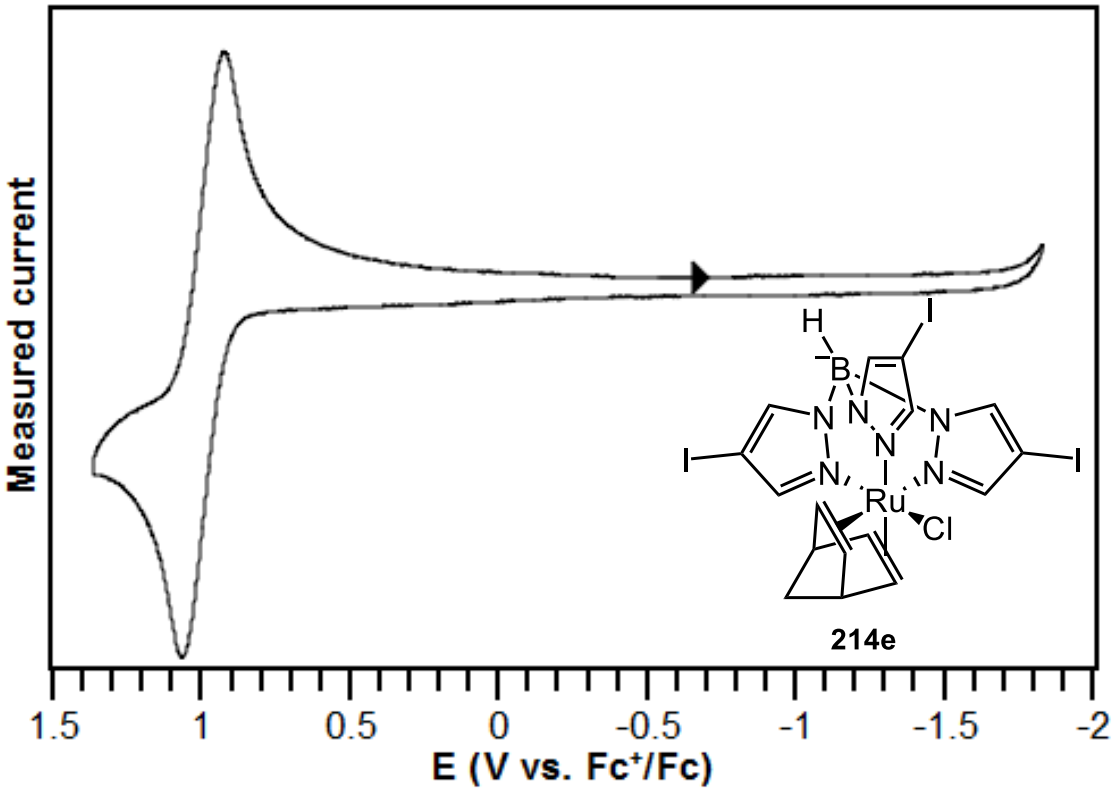
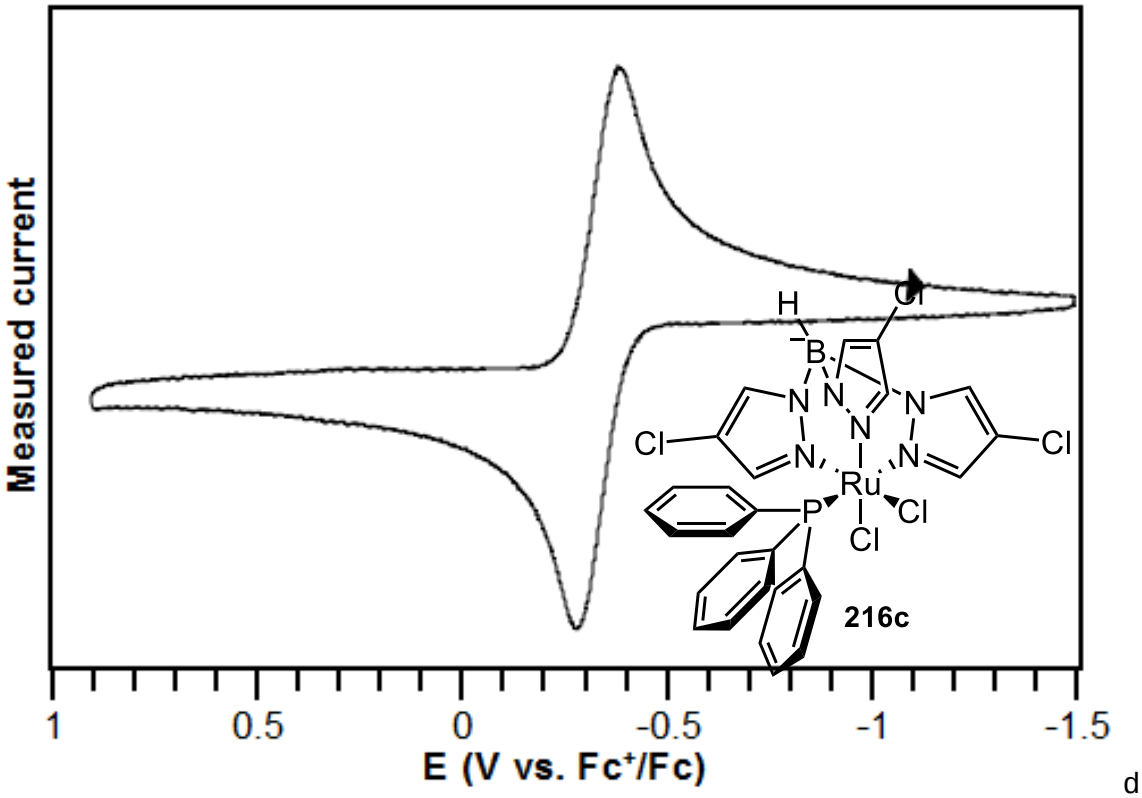


Figure A2.70: Cyclic voltammogram of 214e[42]



d

Figure A2.71: Cyclic voltammogram of 216c. [42]

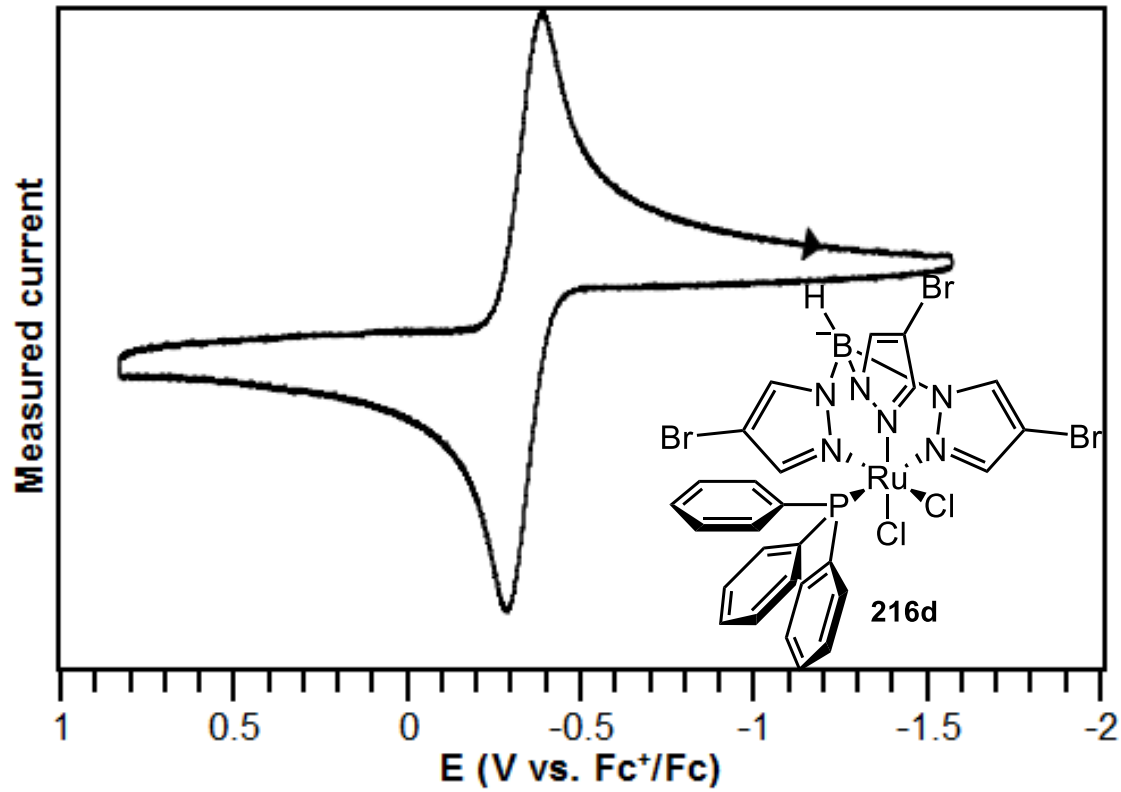


Figure A2.72: Cyclic voltammogram of 216d. [42]

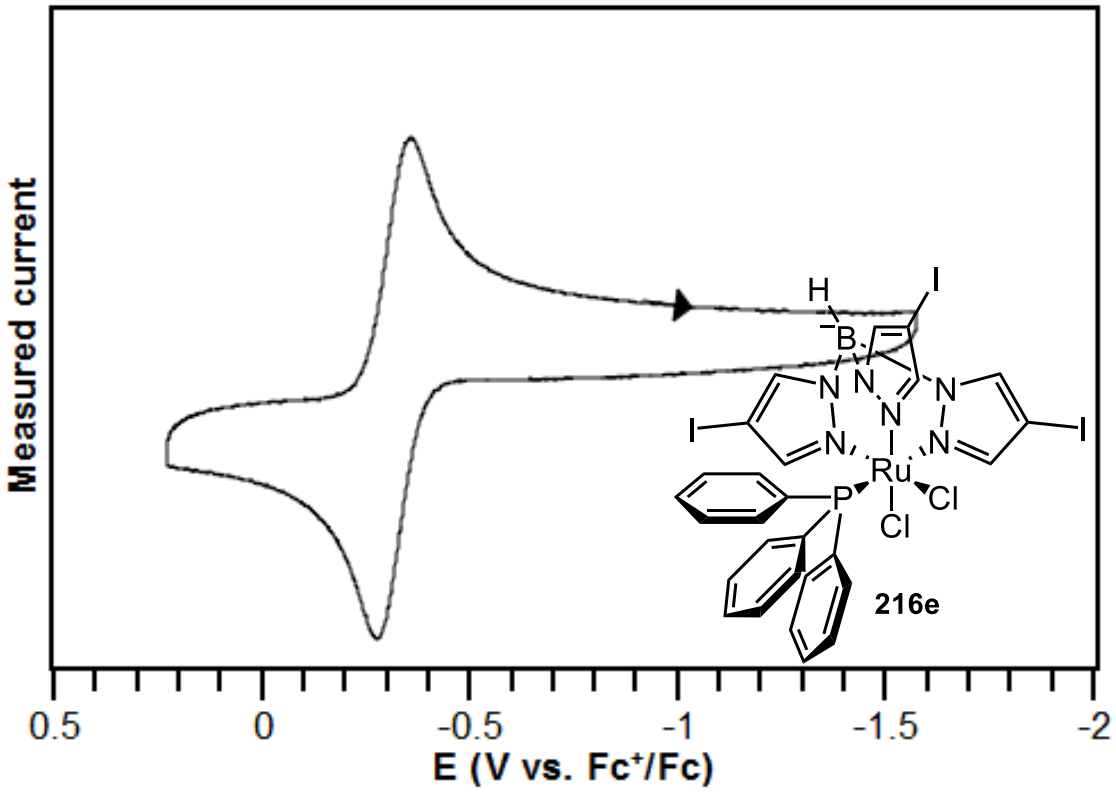


Figure A2.73: Cyclic voltammogram of 216e[42]

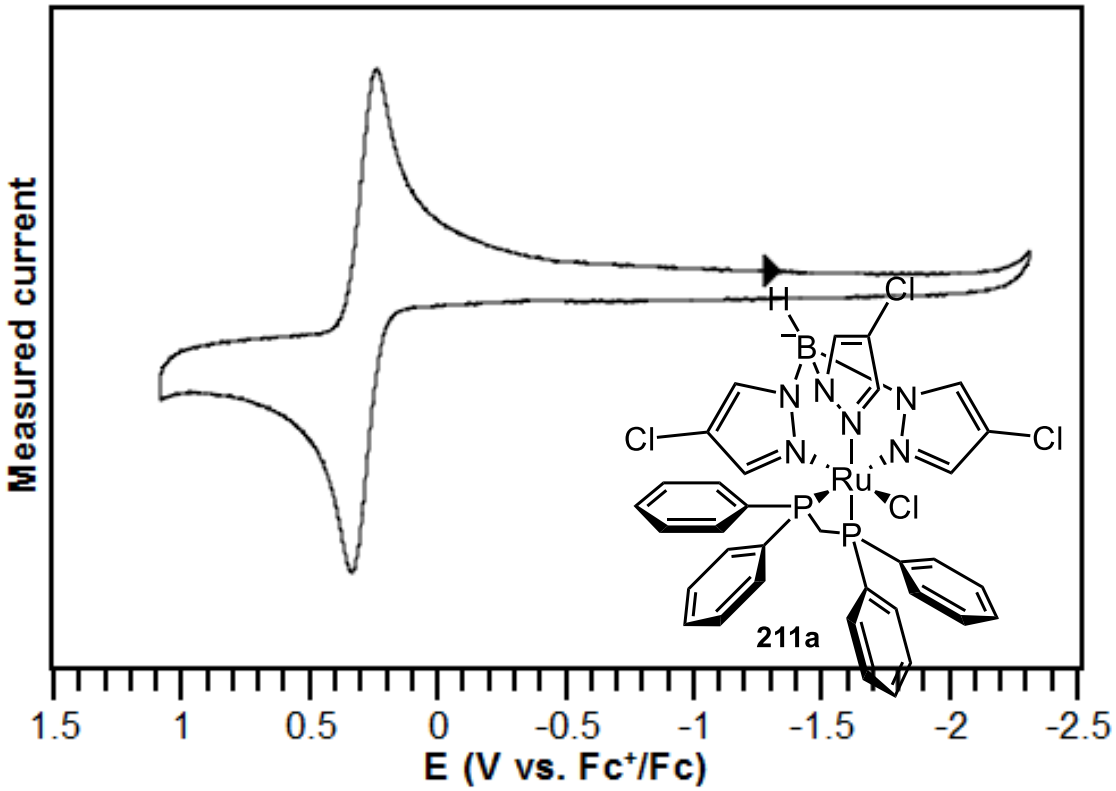


Figure A2.74: Cyclic voltammogram of 211a[42]

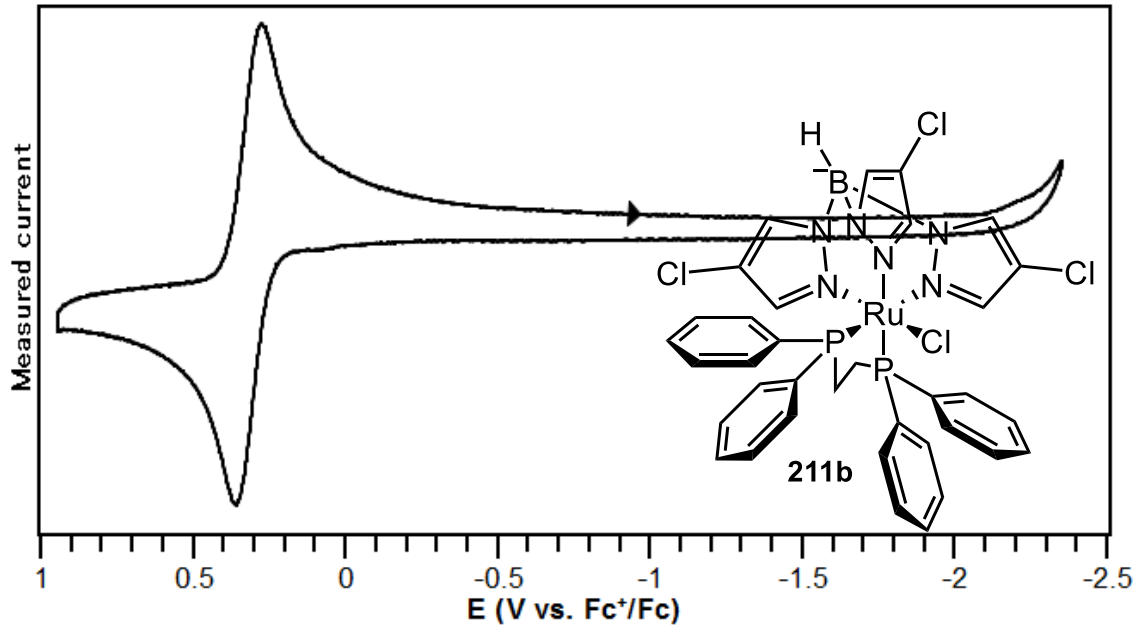


Figure A2.75: Cyclic voltammogram of 211b[42]

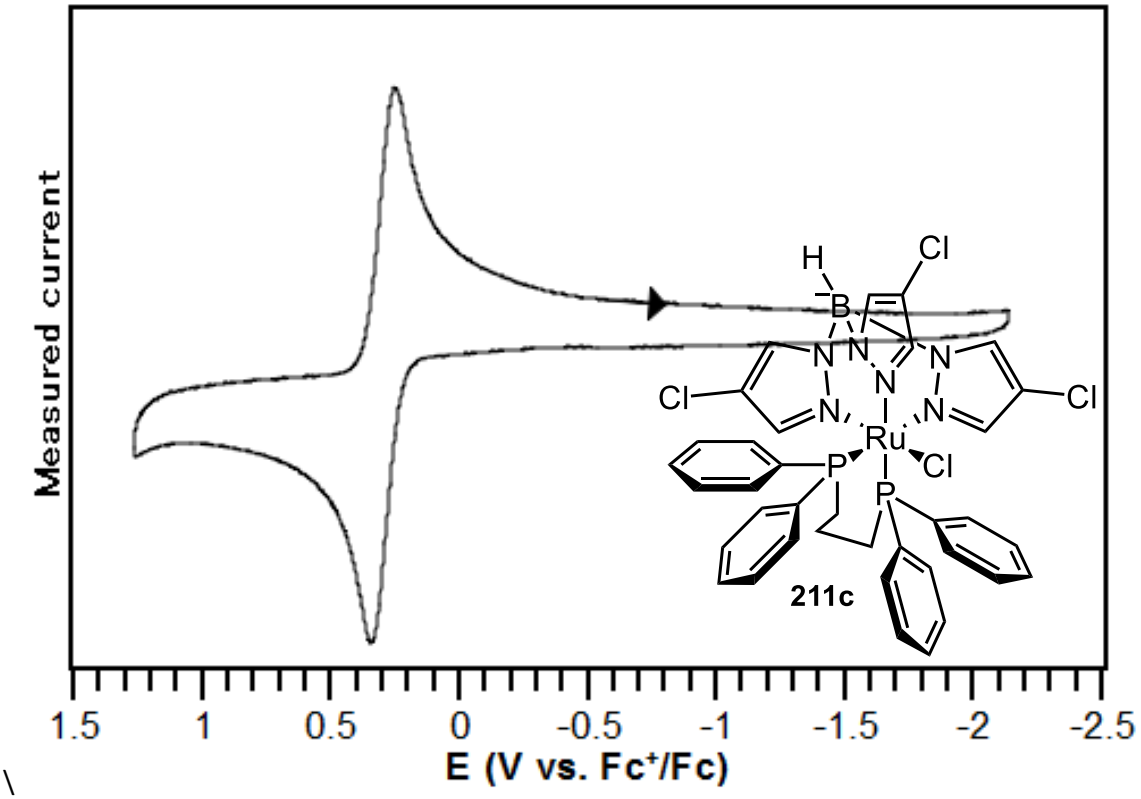


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Figure A2.76: Cyclic voltammogram of 211c[42]

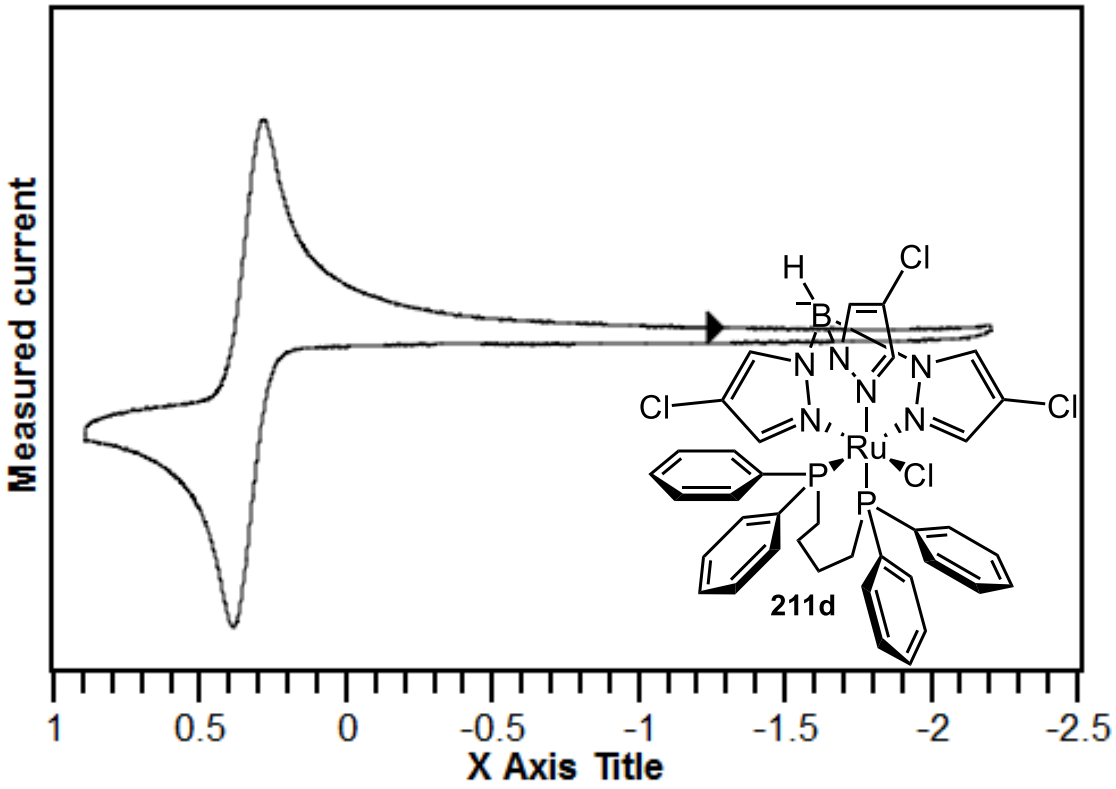


Figure A2.77: Cyclic voltammogram of 211d[42]

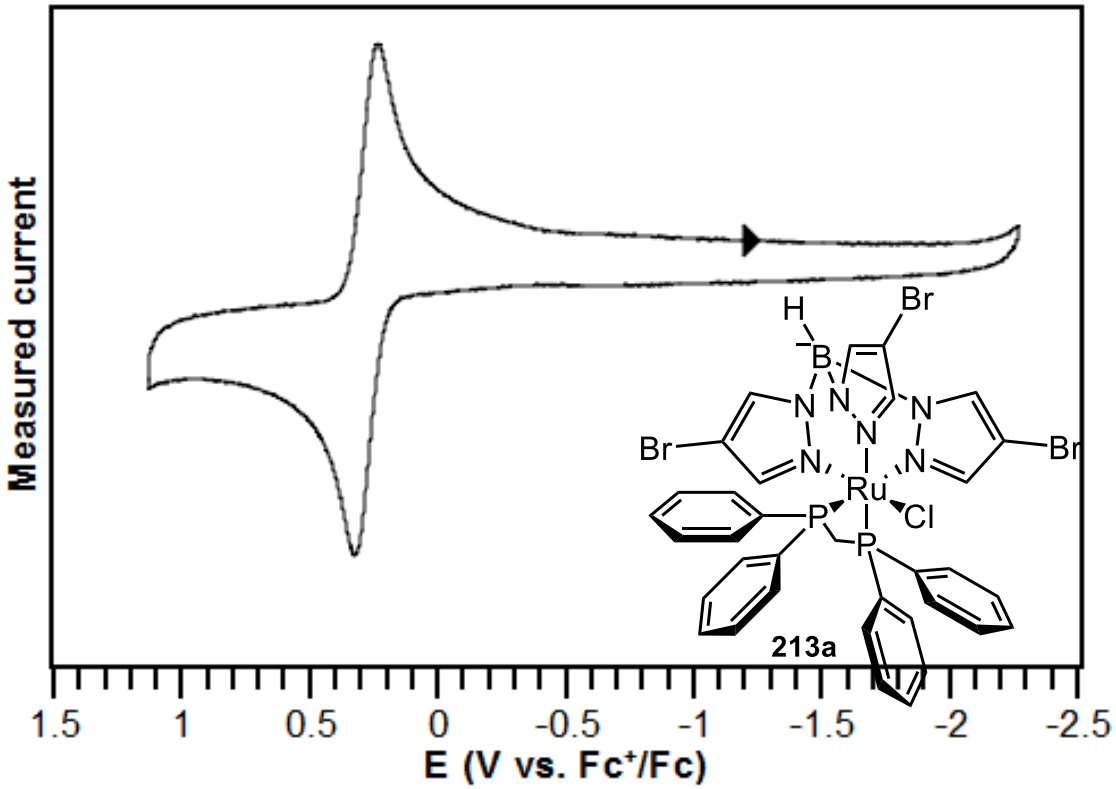


Figure A2.78: Cyclic voltammogram of 213a[42]

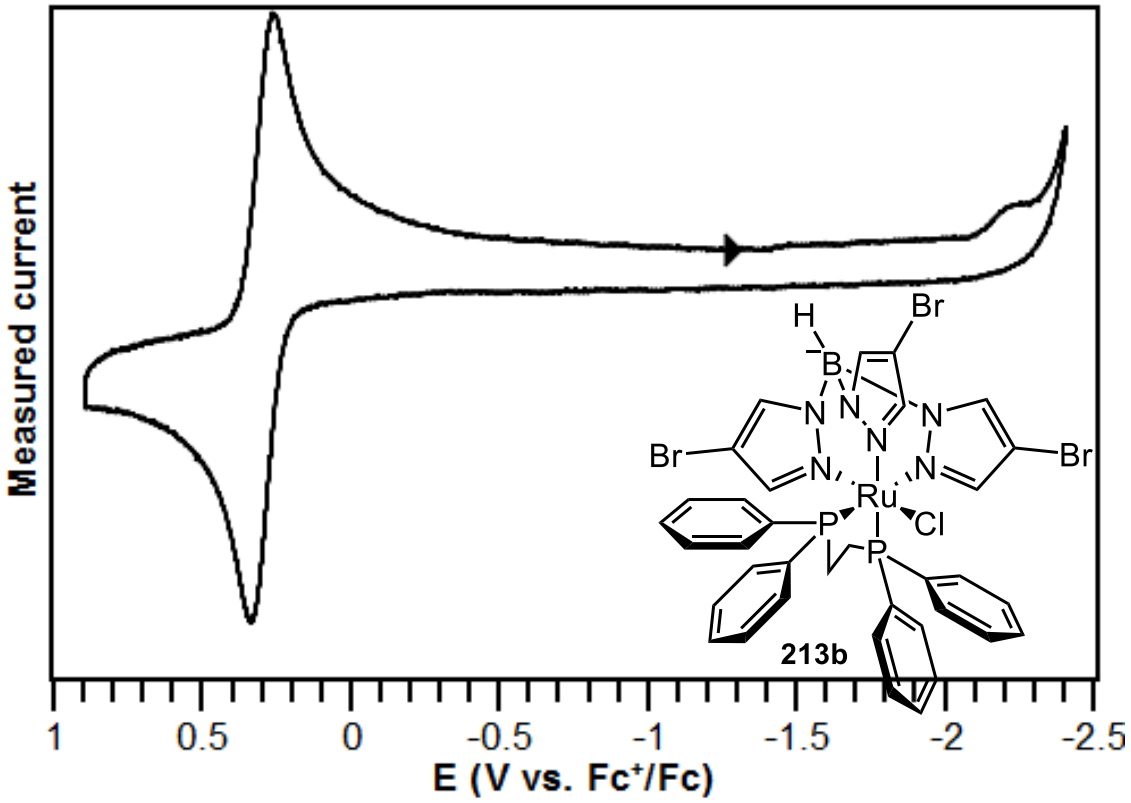


Figure A2.79: Cyclic voltammogram of 213b[42]

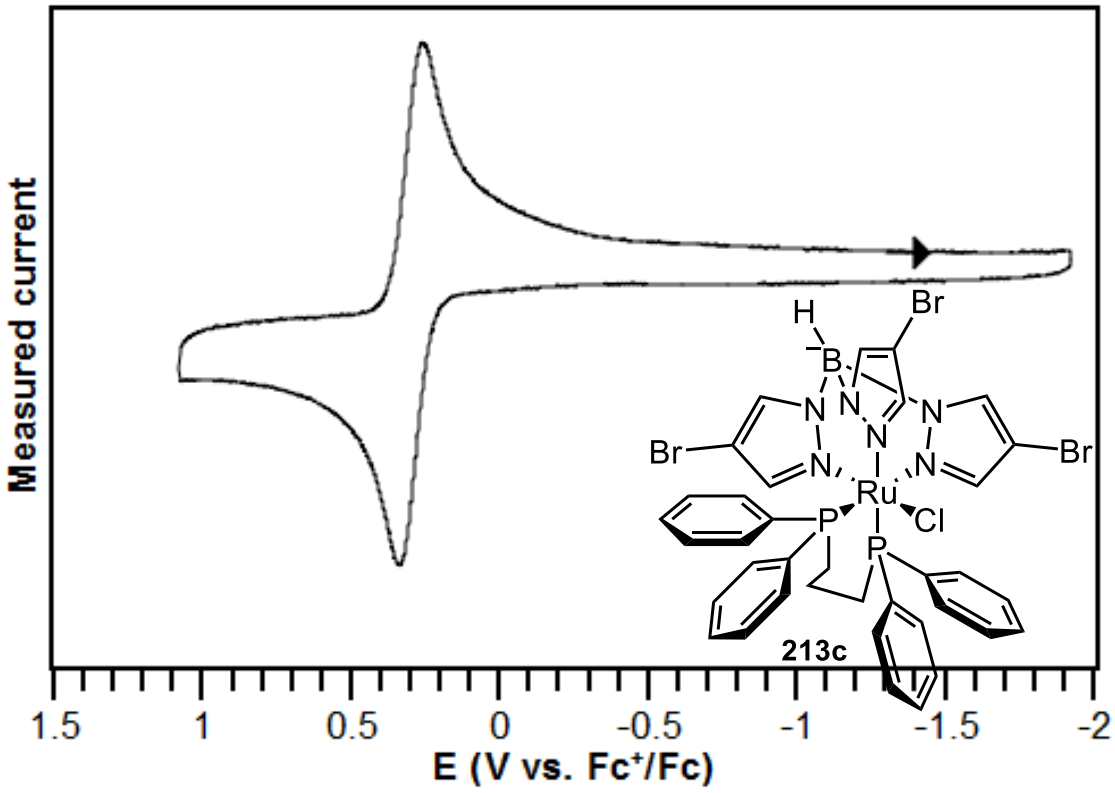


Figure A2.80: Cyclic voltammogram of 213c[42]

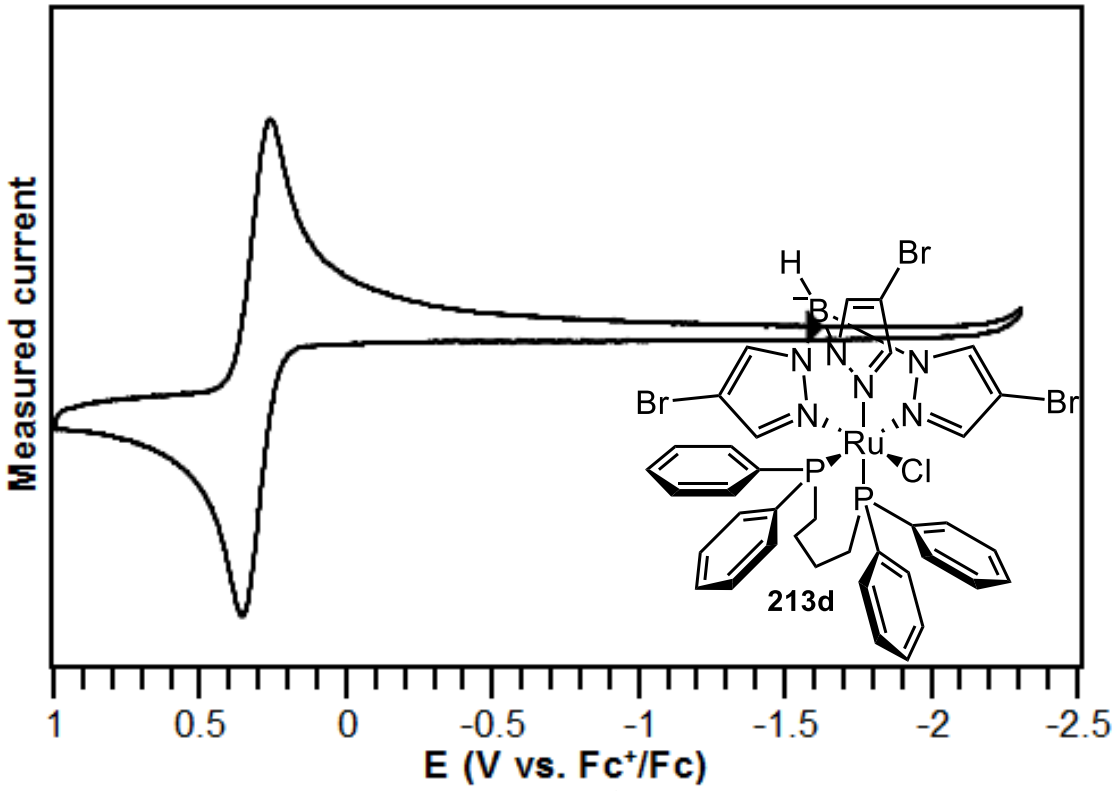


Figure A2.81: Cyclic voltammogram of 213d[42]

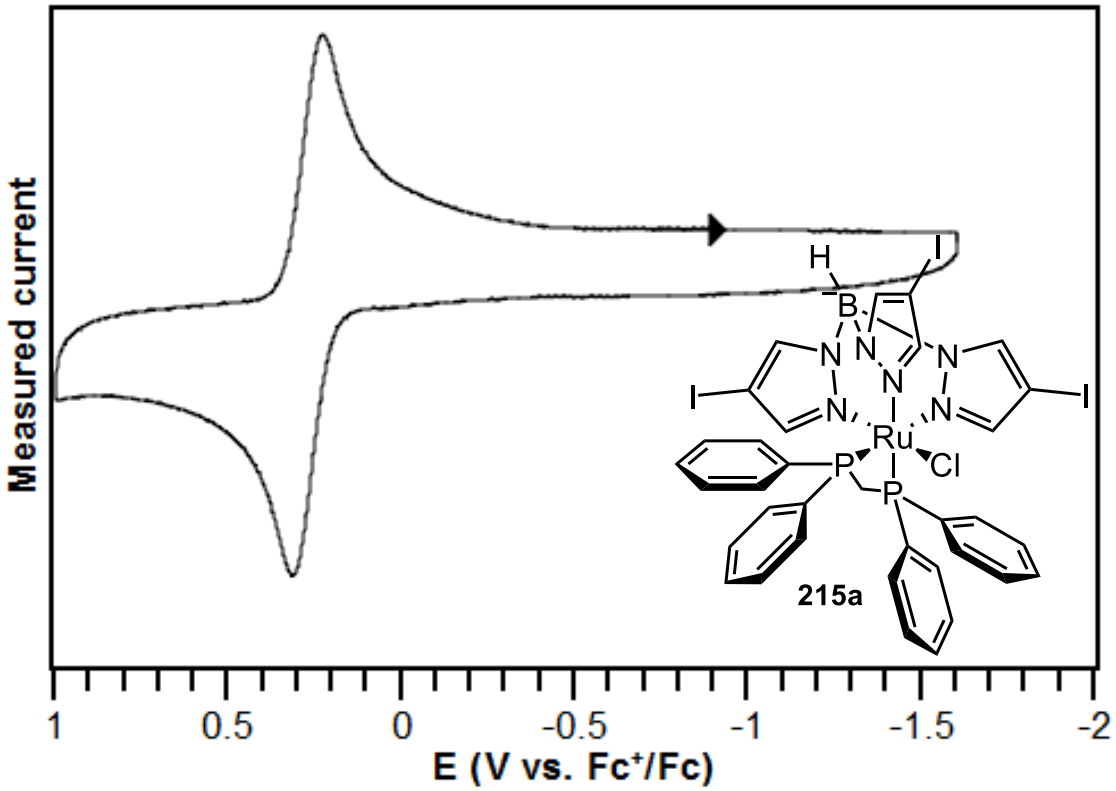


Figure A2.82: Cyclic voltammogram of 215a[42]

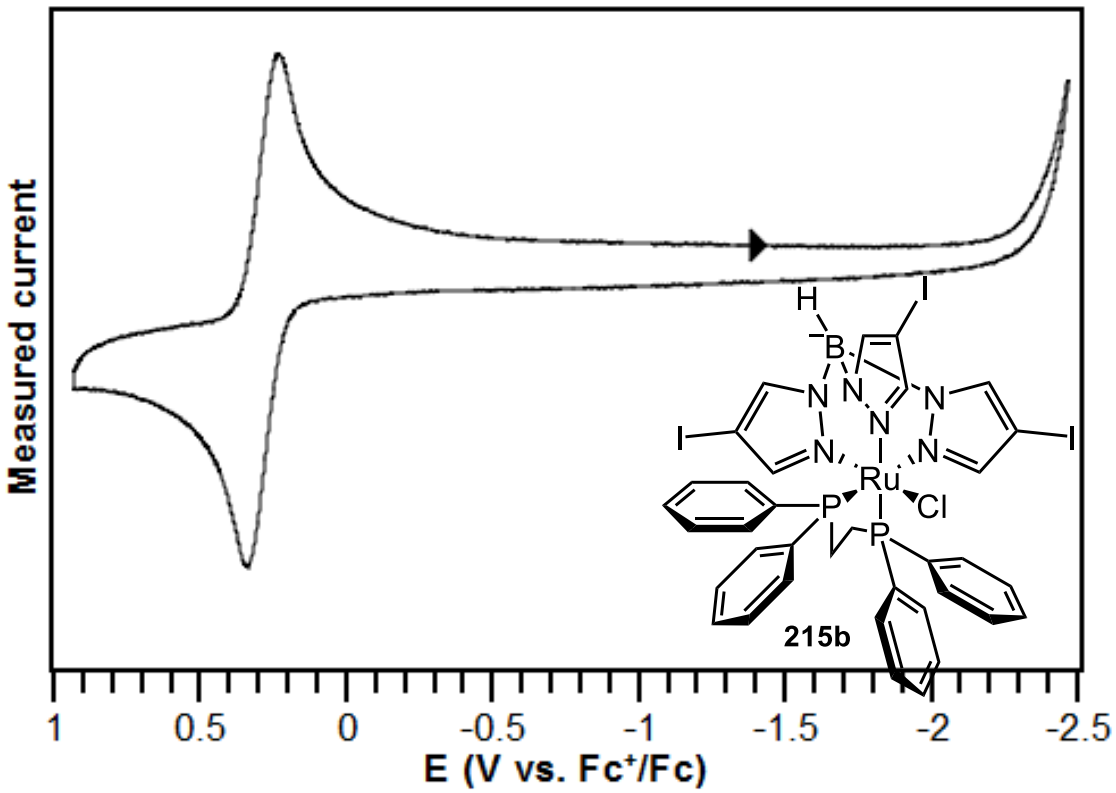


Figure A2.83: Cyclic voltammogram of 215b[42]

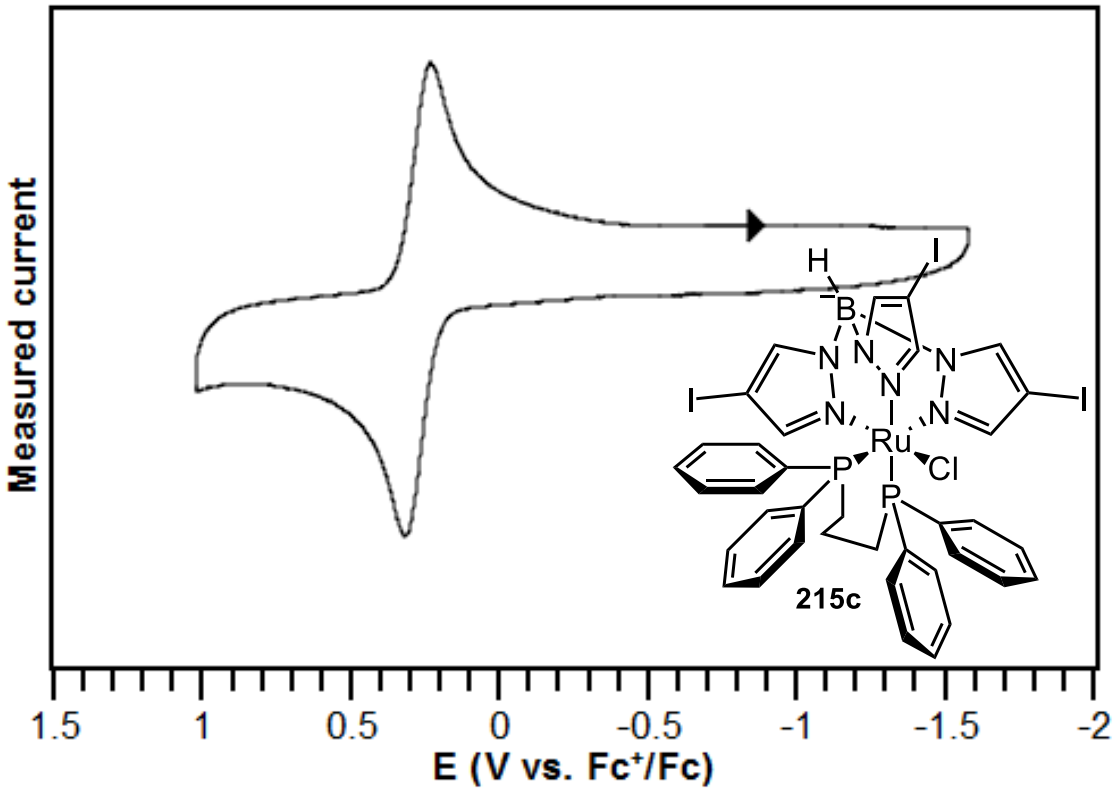


Figure A2.84: Cyclic voltammogram of 215c[42]

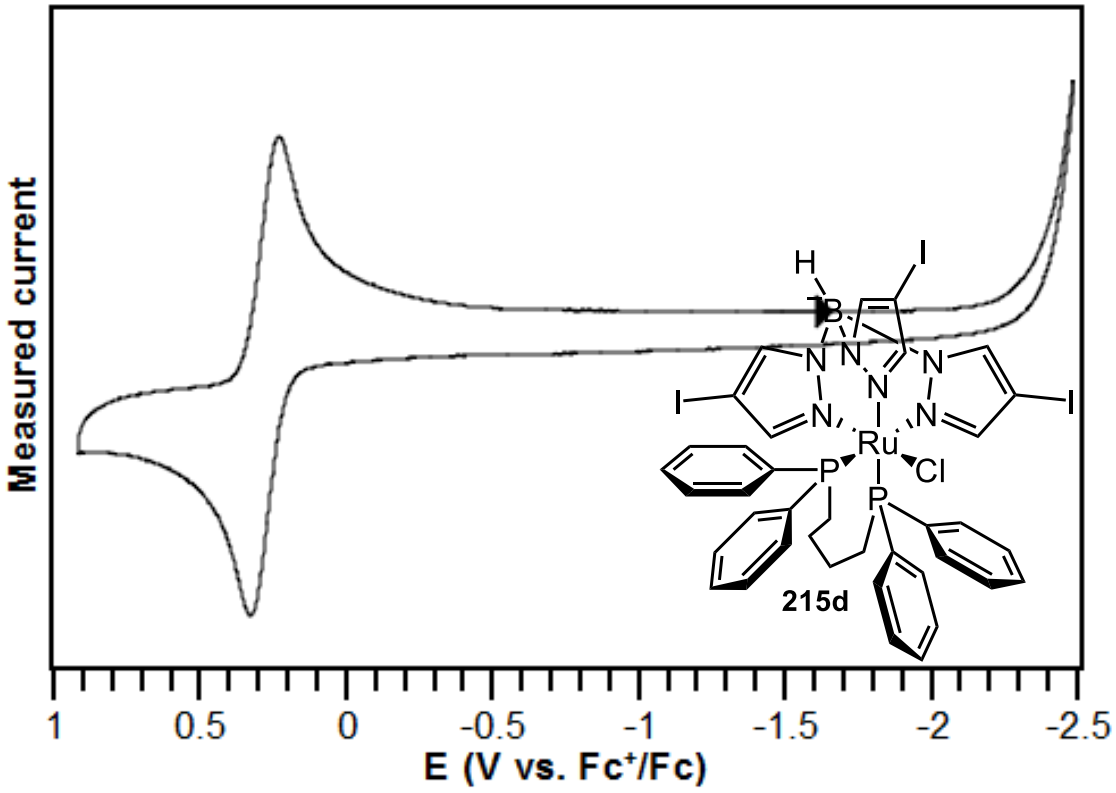


Figure A2.85: Cyclic voltammogram of 215d[42]

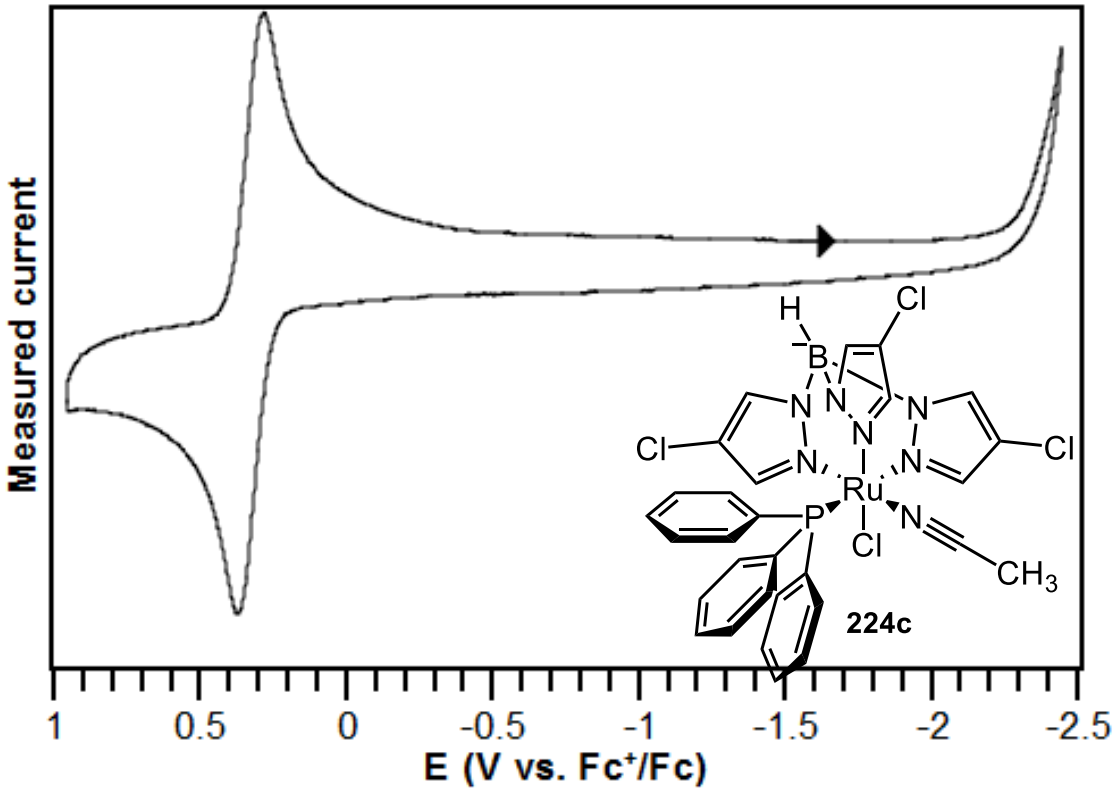


Figure A2.86: Cyclic voltammogram of 224c[42]

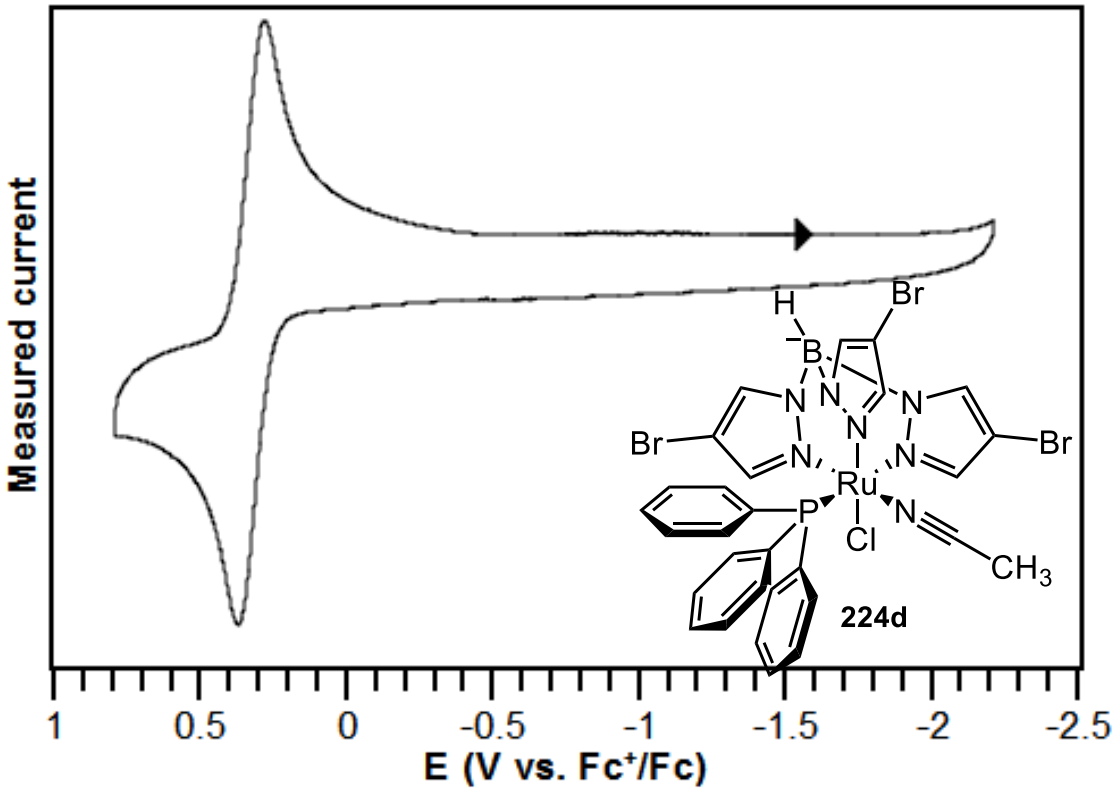


Figure A2.87: Cyclic voltammogram of 224d[42]

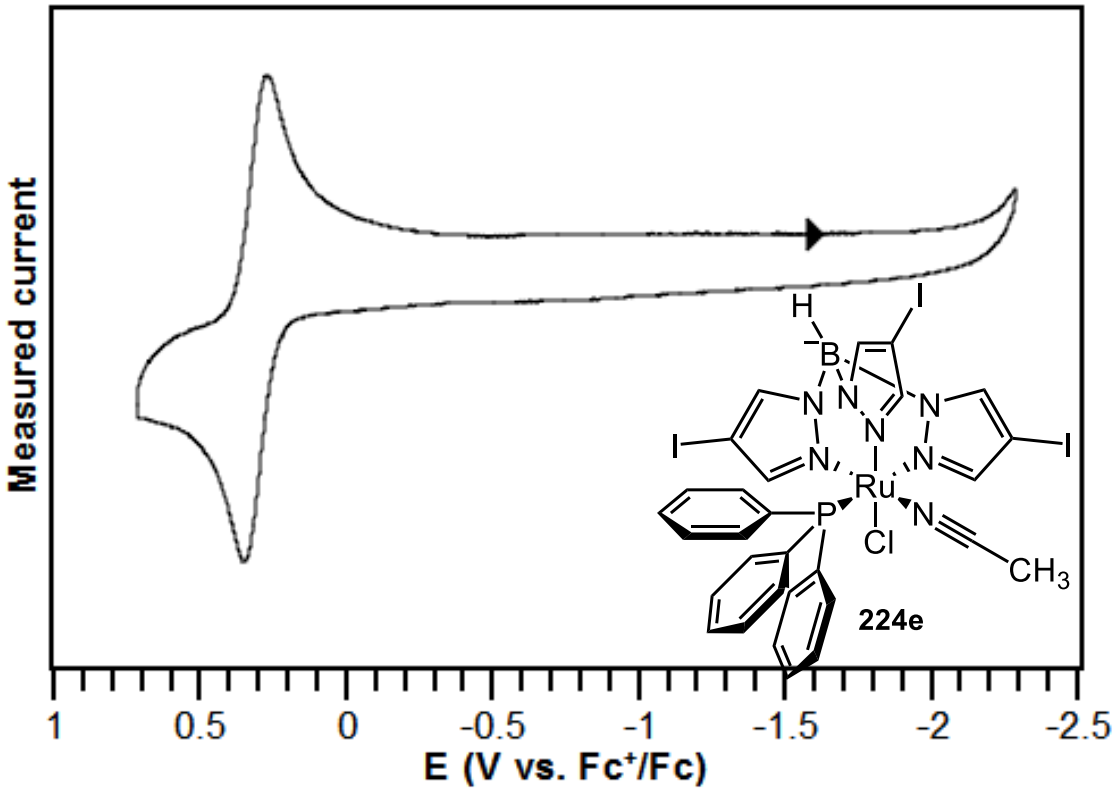


Figure A2.88: Cyclic voltammogram of 224e[42]

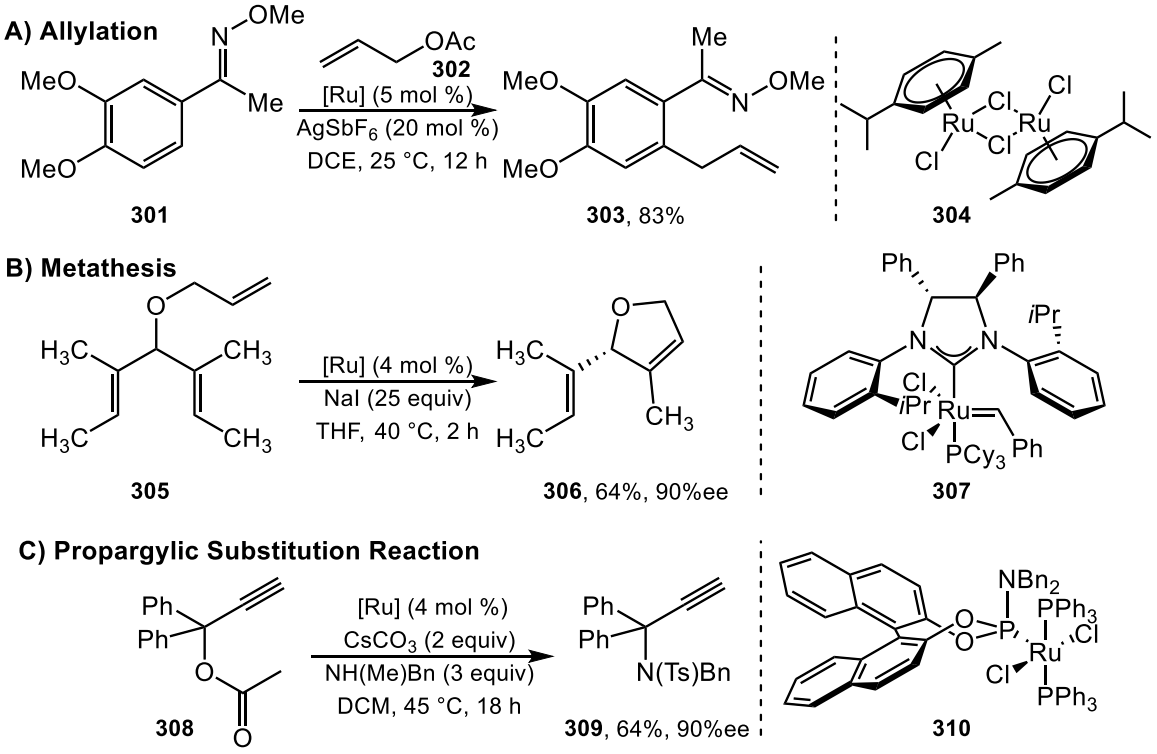
CHAPTER 3: Evaluation of $Tp^{X}Ru$ Complexes in Catalysis

3.1 Background

Ruthenium mediates or catalyzes many reactions.[43] One famous class of reactions is the hydrogenation of C=O[44] and C=C[45] bonds. Even enantiomeric versions are available for this reaction.[46] In hydrogen transfer reactions, ruthenium carries hydrogen from one compound to another.[47] These catalysts originate from the ability of ruthenium to form Ru-H bonds.

Current interest in ruthenium catalysis is shifting to C-C bond formation. These reactions encompass allylation,[48] metathesis,[49] and propargylations (Scheme 3.1).[31,50] Among these categories of reactions, metathesis and propargylic substitution reactions are relevant to the project because these reactions involve carbene and allenylidene formations.

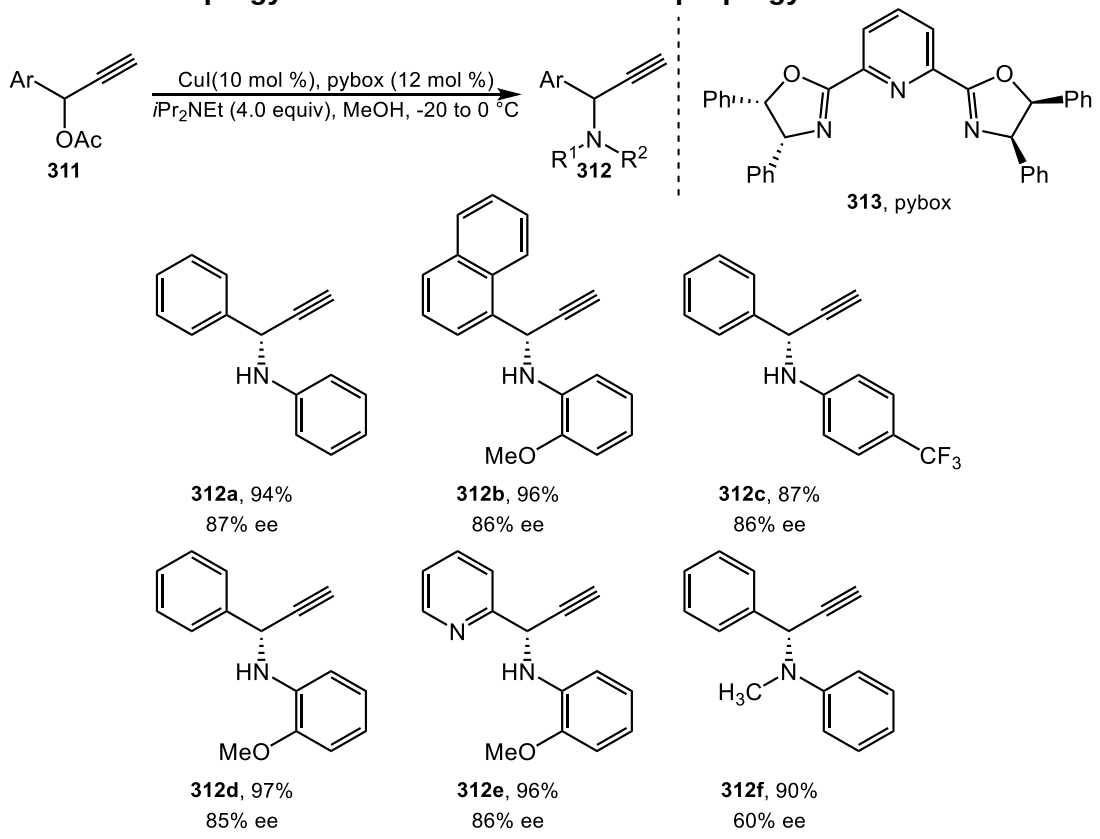
Scheme 3.1: A) Allylation, B) metathesis and C) propargylic substitution reactions.



Catalysts in metathesis reactions are prepared as carbene complexes. In contrast, catalysts in propargylic substitution reactions do not have Ru=C bonds initially, but they are believed to form allenylidenes *in situ*. The metals that have shown promising results are copper,[51] rhenium,[52] gold,[53] rhodium,[54] and ruthenium.[40]

A mixture of copper iodide and pybox enantioselectively converts propargylic acetates into propargylic amines (Scheme 3.2).[51] Despite high yields and enantiomeric excesses, copper catalysis needs an acetoxy group as an leaving group, and the products were generally limited to amine adducts. These limitations attenuate the practicality of the methodology.

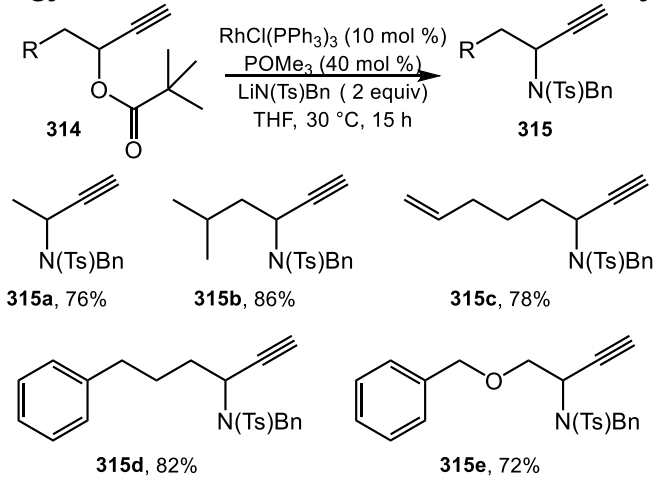
Scheme 3.2: Propargylic substitution reactions of propargyl acetates.



A rhodium catalyzed propargylic reaction was reported by the Evans group (Scheme 3.3).[54] Normally, the propargylic substitution reactions are limited to aryl

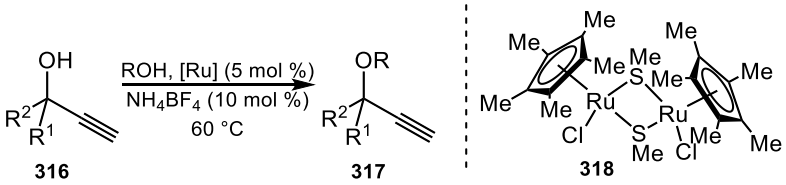
substituted propargylic substrates. However, Evan's Rh complex was compatible with aliphatic substrates. Still, no active enantioselective Rh catalyst has been reported.

Scheme 3.3: Propargylic substitution reaction with Evan's catalyst.



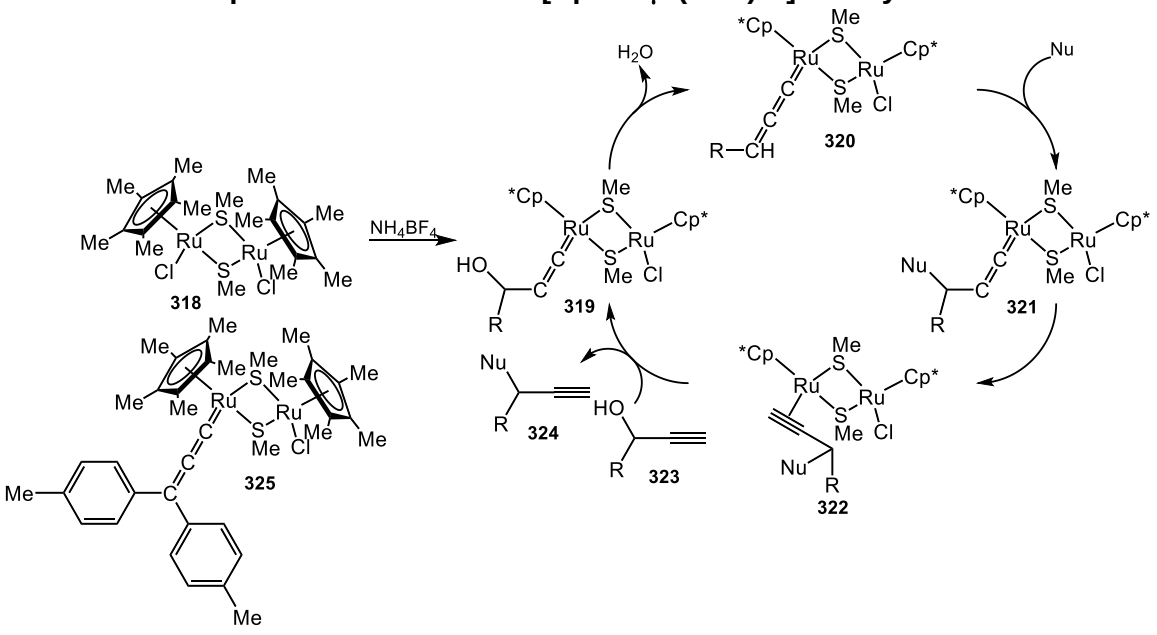
In 2000, a major advancement in ruthenium catalyzed propargylic substitution reactions was reported by Hidai's group (Scheme 3.4).[40] According to their detailed reaction mechanism, NH_4BF_4 abstracts one of the chloro ligand from the ruthenium thiolate bridged complex to make an open coordination site. Then, ruthenium reacts at the terminal alkyne carbon to form a vinylidene, **319**, which is changed into allenylidene, **320** as a molecule of water is lost. This allenylidene formation was corroborated by a single crystal of **325**, which was isolated from the stoichiometric reaction of ruthenium and a propargylic alcohol. The incoming nucleophile (sodium ethoxide) attacks at the Cγ in **320** to give the substituted product.

Table 3.1: The first propargylic substitution reaction catalyzed by [Cp*Ru-μ-(SMe)Cl]$_2$.



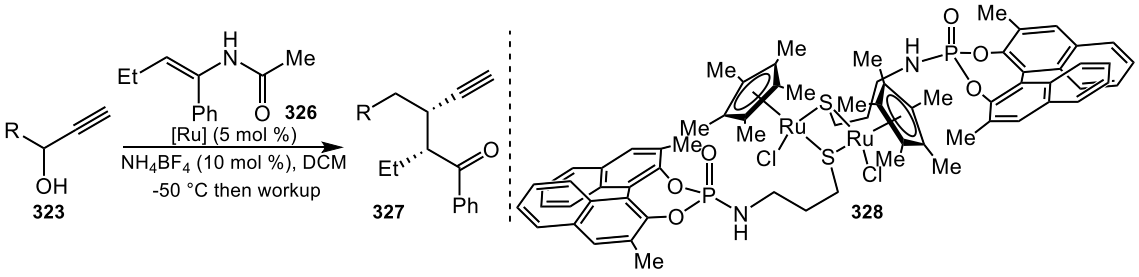
Entry	Alcohol	R^1	R^2	Time	Yield
1	ethanol	Ph	H	15 min	**317a**, 88%
2	methanol	Ph	H	15 min	**317b**, 84%
3	isopropanol	Ph	H	15 min	**317c**, 91%
4	ethanol	Ph	Ph	20 h	**317d**, 88%
5	Phenol	Ph	H	60 min	**317e**, 65%
6	isopropanol	nC_5H_{11}	H	15 min	**317f**, 75%

Scheme 3.4: Proposed mechanism for [Cp*Ru-μ-(SMe)Cl]$_2$ catalysis



Since then, this project has been developed by their group to use chiral complexes that can carry out enantioselective propargylic substitution reactions new C-C bond (Scheme 3.5).[31e, 31g]

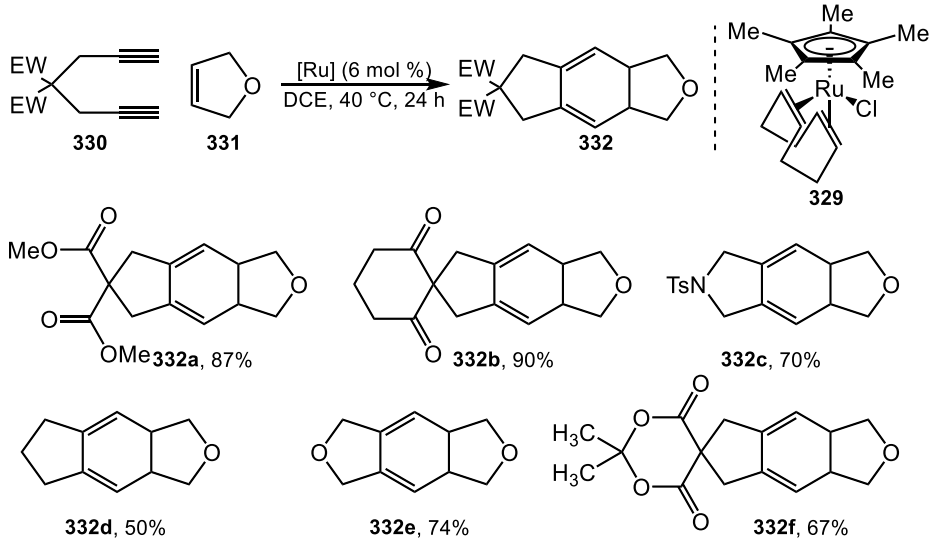
Scheme 3.5: Enantioselective propargylic substitution reaction



Inspired by the great successes of ruthenium catalyzed propargylic substitution reaction, our group proceed to utilize the TpRu complexes prepared in the last two chapters to some known ruthenium catalyzed reactions. Especially, the purpose was to compare catalysis performance between the $Tp^{X}Ru$ complexes. In addition to the reactions mentioned above, two more reactions were tested.

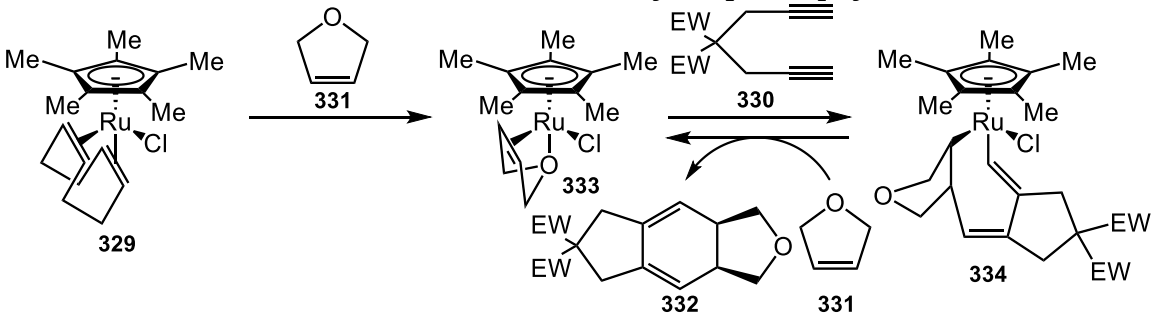
One additional reaction is the [2+2+2] cycloaddition reaction of 1,6-heptadiene with 2,5-dihydro furan catalyzed by Cp*Ru(cod)Cl, **329** (Scheme 3.6).[55] This reaction affords tricyclic products in high yields. Because the reactions with reactants that were derived from malonates gave higher yields, a malonate derived substrate was used in our exploratory studies.

Scheme 3.6: [2+2+2] Cycloaddition reaction catalyzed by 329



The Itoh group hypothesized that catalysis begins with the dissociation of the cod ligand from **329**. As a result, two coordination sites would be open. Dihydrofuran **331** has a double bond and lone pair on the oxygen that can coordinate the Ru at these sites. For this reason, $Tp^{Cl}RuPPh_3Cl_2$ **335c** was chosen as a test in this catalysis system because two coordination sites could be open if the chloro ligands dissociate.

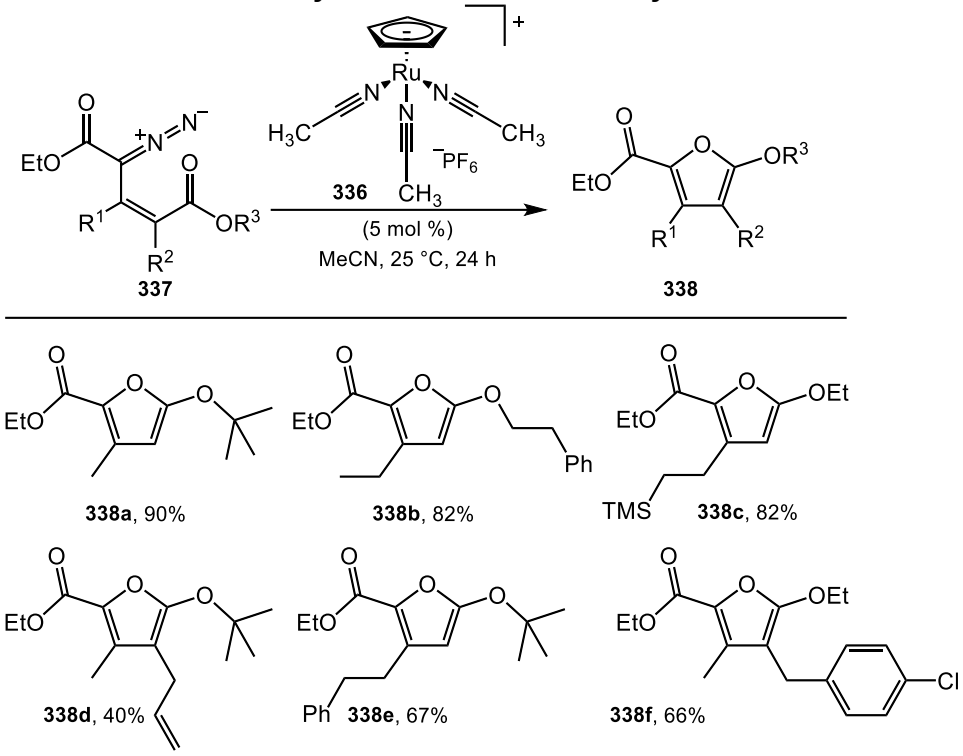
Scheme 3.7: Mechanism of the ruthenium catalyzed [2+2+2] cycloaddition reaction.



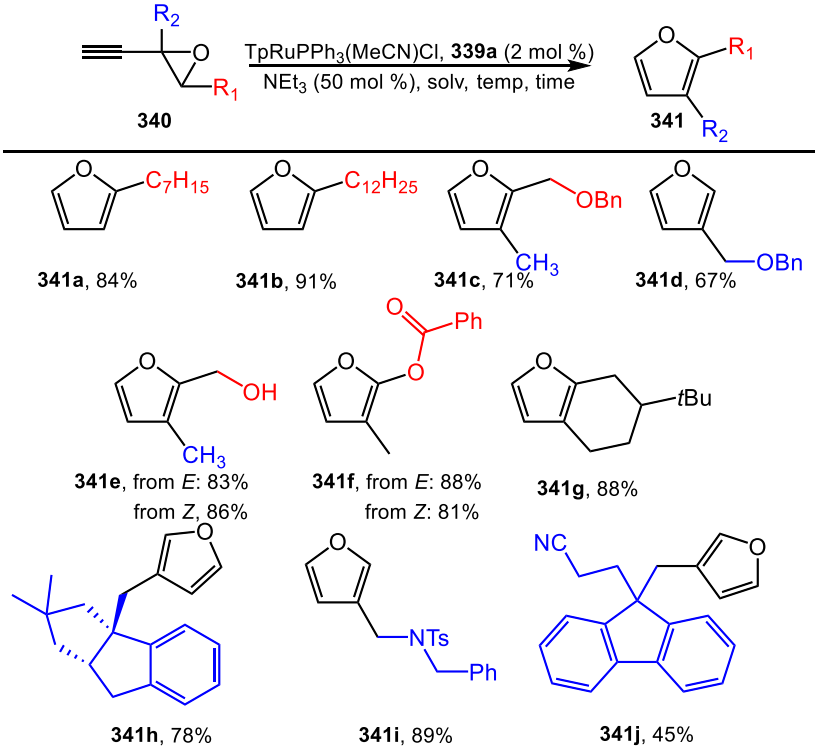
Another reaction that could be tested is furan synthesis through diazo cyclization. Rhodium complexes are known to form carbenes when they react with diazo compounds.[56] Ruthenium is also a good candidate to catalyze this reaction, as it can form Ru carbenes under appropriate reaction conditions. Indeed, $CpRu(MeCN)_3PF_6$, **336** was found to cyclize a series of diazo compounds (Scheme 3.8).[57] The author believes that this reaction occurs through Ru carbene formation. The ruthenium complexes we have synthesized might be applicable in this reaction.

Another furan synthesis from epoxy alkynes was catalyzed by another ruthenium complex,[39] which had a Tp ligand (Scheme 3.9). The data shows that most of the substrates used here give the corresponding furan in high yields with a minute amount of **339a** in the presence of NEt_3. To discuss whether halogenation of the Tp ligands has positive or negative effect on this catalysis system, substrate **340d** was chosen. If the $Tp^{X}Ru$ complex is superior, the yield should be higher than 67% and vice versa.

Scheme 3.8: Ruthenium catalyzed substituted furan synthesis.



Scheme 3.9: Furan synthesis from epoxyalkyne catalyzed by 339a.



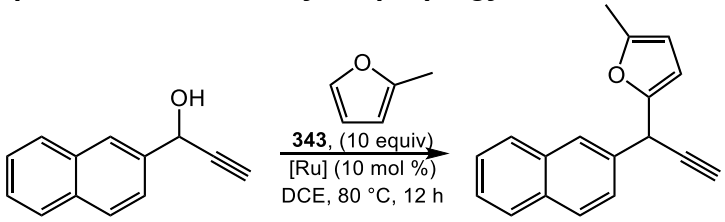
3.2 Evaluation of the $Tp^{X}Ru$ Complexes Relative to the Known Catalysis Systems

Using the ruthenium complexes from Chapters 1 and 2 and substrates from Chapter 3, the behavior of the ruthenium complexes was investigated. Since the propargylic substitution reaction was the top interest, it is given first.

All examples of the ruthenium complexes were used in the propargylic substitution reaction of 2-methylfuran **343** with 1-(naphthalen-2-yl)prop-2-yn-1-ol **342** (Table 3.2). The nucleophile **343** was chosen to be compared to Nishibayashi's substrate scope.[4] The methyl group on the furan blocks one of the nucleophilic sites, preventing polymerization. Previously, our group used $NaPF_6$ to abstract a chloro ligand from ruthenium complexes. However, a negative control reaction showed that impure $NaPF_6$ alone can produce the substituted product. KPF_6, therefore, was used for Cl ligand abstraction instead. Diene complex **345a** gave a brown mixture (entry 1), and TLC analysis showed that there was no desired product. When **346a** or **346b** was used, the mixture remained yellow, and new spots were not observed (entries 2 and 3). The reactant spot also remained big, and it was concluded that no reaction occurred. When **346c** was used, the mixture became purple several hours after heating, whereas **346d** did the same after the complex was added at room temperature (entries 4 and 5). Because some allenylidene complexes are known to be purple, the color might originate to allenylidene.[58] Although the mixture was not analyzed further because no organic compound was found on TLC, ^{13}C NMR of the crude mixture would have given a Cα peak of the allenylidene if this is the case. When **335c**, **347**, or **348** was used, a complex mixture of compounds was always obtained. The mixture was purified three times, but even the big spot at the similar Rf value as the desired product was found to be the aggregate of different compounds. The reactions with **347** and **348** were run at lower temperature to reduce the byproducts, but it invariably gave a

complex mixture of compounds (entries 7 and 8). The usage of **339c** in the propargylic substitution reaction resulted in a brown mixture. However, there was no product spot (entry 9).

Table 3.2: Attempted ruthenium catalyzed propargylic substitution reaction



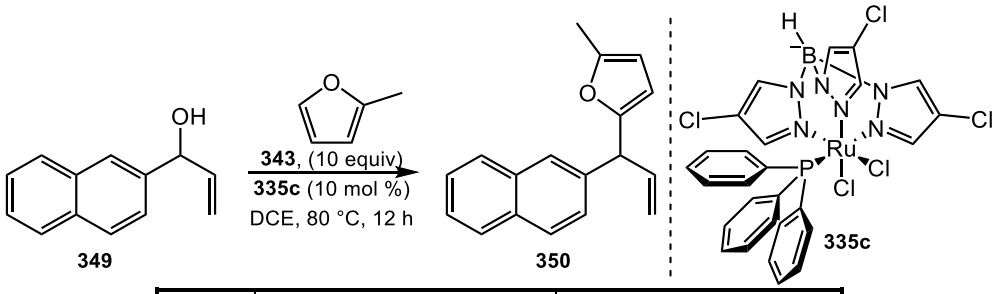
342 344

Entry	[Ru]	Yield
1	$Tp^{Cl}Ru(cod)Cl$, **345c**	No product
2	$Tp^{Cl}Ru(dppm)Cl$, **346a**	No Rxn
3	$Tp^{Cl}Ru(dppe)Cl$, **346b**	No Rxn
4	$Tp^{Cl}Ru(dppp)Cl$, **346c**	No product
5	$Tp^{Cl}Ru(dppb)Cl$, **346d**	No product
6	$Tp^{Cl}RuPPh_3Cl_2$, **335c**	Complex mixture
7[a]	$Tp^{Br}RuPPh_3ClBr$, **347**	Complex mixture
8[a]	$Tp^{Br}RuPPh_3Br_2$, **348**	Complex mixture
9[b]	$Tp^{Cl}RuPPh_3(MeCN)Cl$, **339c**	No product

a, run at 60 ^oC, b, TEA instead of KPF_6

Allylation reactions were attempted with **335c** in different solvents (Table 3.3). The relatively non-polar solvent did not facilitate any reaction (entries 1-4) while polar ones created a complex mixture of compounds (entries 5 and 6).

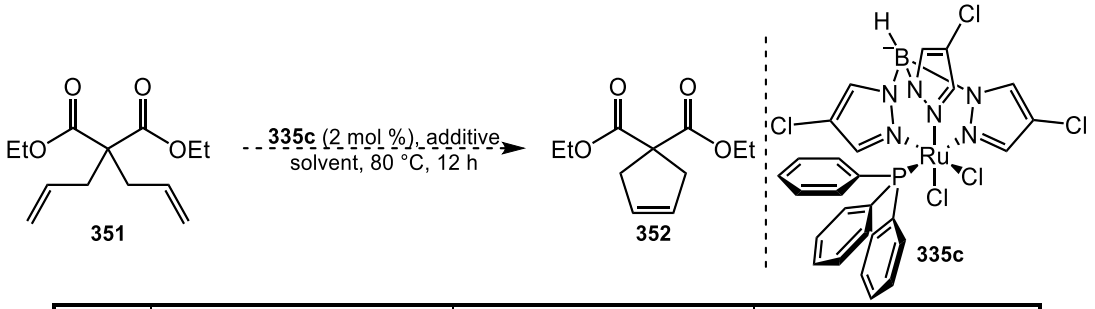
Table: 3.3: Attempted allylation reaction of 349



Entry	Solvent	Yield
1	DCE	No reaction
2	1,4-dioxane	No reaction
3	toluene	No reaction
4	chlorobenzene	No reaction
5	EtOH	Complex mixture
6	MeCN	Complex mixture

The ability of **335c** as catalyst was assessed in a ring closing metathesis system (Scheme 3.4). When the reaction was run with 0.5 molar equivalents of TEA, the mixture became brown, but the TLC analysis did not show new organic compound spots. Roughly mixing **335c** and TEA alone changed the color into brown. Chance is high that the color change would originate from the reaction between the ruthenium complex and TEA. NMR spectrum of the mixture will be analyzed to see what was made. The addition of potassium hexafluorophosphate did not give any change to the mixture.

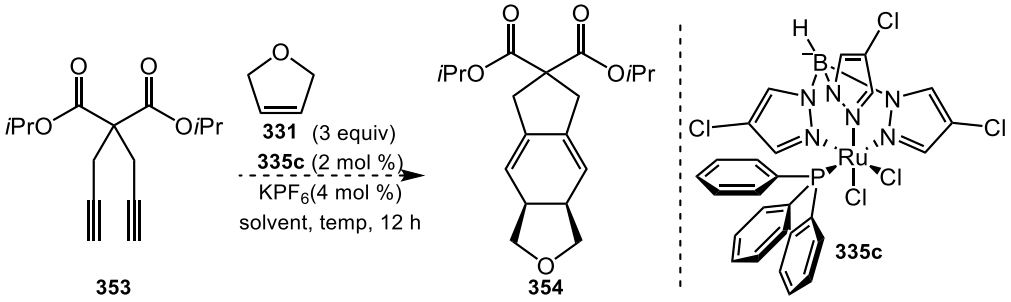
Table 3.4: Attempted metathesis reaction with 335c



Entry	Solvent	Additive	Yield
1	Benzene	TEA (0.5 equiv)	No product
2	Benzene	KPF_6 (1.0 equiv)	No reaction
3	DCE	TEA (0.5 equiv)	No product
4	DCE	KPF_6 (1.0 equiv)	No reaction

The [2+2+2] cycloaddition reaction was screened in a variety of solvents (Table 3.5). In DCM, DCE and MeCN, the color of the solvent remained red, and new spots were not observed on TLC (entries 1 and 2). The color of the mixture changed to yellow in 2,5-hydrofuran **331**, THF, EtOH, and benzene, but no product spot was observed (entries 3-6). Because TpRu(II) typically shows a yellow color, the ruthenium might be reduced. It could be demonstrated by analyzing the crude mixture by ^{1}H NMR because The broadened peaks from paramagnetic Ru(III) should be sharpened. No reaction occurred in DCE even the temperature was raised to 80 °C (entry 7).

Table:3.5 Attempted [2+2+2] cycloaddition reaction with 335c.

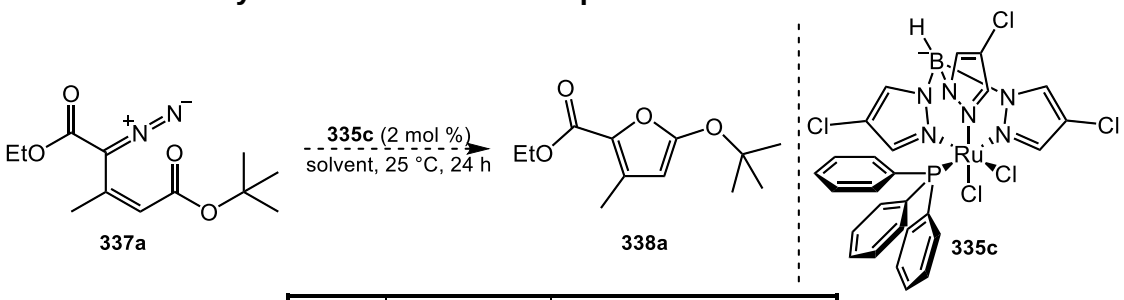


Entry	Solvent	Temp	Yield
1	DCM	40 °C	No reaction
2	MeCN	80 °C	No reaction
3	neat	40 °C	No product
4	THF	60 °C	No product
5	EtOH	80 °C	No product
6	Benzene	80 °C	No product
7	DCE	80 °C	No reaction

Furan synthesis from diazo compounds was screened with **335c** in several solvents (Scheme 3.6). The reaction was run at room temperature since that is where $CpRu(MeCN)_3PF_6$ **336** catalysis worked well. Unfortunately, the diazo compound did not react to form **338a**, nor did it react with the ruthenium to form a different complex. The reactant spot was distinct and large on TLC. There could be three reasons that this reaction did not work. One reason is that the geometry of the Tp ligated complexes

(octahedral) and Cp ligated complexed (tetrahedral) are different. Second, **336** is a cationic complex that might trigger the nucleophilic attack of the diazo compound. Lastly, the paper[57] shows that bulkier $Cp^*Ru(MeCN)_3PF_6$ **355** leaves most of the reactant intact (66% recovery) giving the furan product in a much lower yield (18%) than **336** (90% yield). A bulkier ligand might hinder the effective coordination to the ruthenium; thus, it slows down the reaction. Since Tp is even bulkier than Cp*,[3] no reaction would be an understandable outcome.

Table 3.6: Furan synthesis from diazo compound.

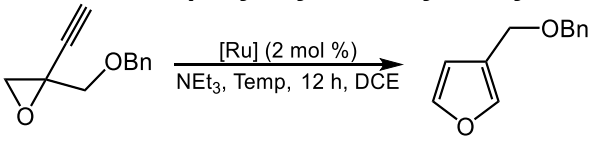


Entry	Solvent	Yield
1	DCM	No reaction
2	benzene	No reaction
3	MeCN	No reaction

The only catalysis system where one can compare $Tp^XRuPPh_3(MeCN)Cl$ complexes is the syntheses of furans from epokyalkynes. According to the Liu group,[39] 2 mol % catalyst loading of **339a** in the presence of NEt_3 (a half equivalent to epoxyalkyne) can give the corresponding furans in 45−91% yield (Scheme 3.9). To begin with, an epoxyalkane **340d** was allowed to cyclize in the presence of $TpRuPPh_3(MeCN)Cl$ **339a** under the identical conditions. This reaction is supposed to give furan **341d** in 67% yield. However, only 4% of the epoxyalkyne **340d** was successfully turned into the **341d** while 67% of the epoxyallyne was recovered unreacted (entry 10). Although the reaction was run repeatedly, the yield did not improve at all. Next, the diene complex **356e** and the di-

phosphine complexes **357a-d** were added as catalysts (entries 1-5). The product spot was not detected on TLC at all, and the complexes remained unreacted. One considerable rationale was that bidentate either sterically blocked Ru-Cl or strengthened the Ru-Cl bonds through the ligation to the ruthenium. With 2 mol % catalyst loading, all mono-phosphine complexes gave about 4% furan **341d** and 63 to 72% recovery of epoxyalkyne **340d** (entries 6-13).

Table 3.7: Furan synthesis from epoxyalkyne catalyzed by ruthenium complexes.



340d **341d**

Entry	Catalyst	Temp	Yield	Recovery	[a]E (V)
1	**356e**, Tp^{I}Ru(nbd)Cl	80 °C	No Rxn	-	0.99
2	**357a**, Tp^{I}Ru(dppm)Cl	80 °C	No Rxn	-	0.27
3	**357b**, Tp^{I}Ru(dppe)Cl	80 °C	No Rxn	-	0.28
4	**357c**, Tp^{I}Ru(dppp)Cl	80 °C	No Rxn	-	0.27
5	**357d**, Tp^{I}Ru(dppb)Cl	80 °C	No Rxn	-	0.28
6	**335a**, TpRuPPh$_3$Cl$_2$	60 °C	3%	67%	-0.53
7	**335b**, Tp^{Cl}RuPPh$_3$Cl$_2$	60 °C	4%	72%	-0.33
8	**335c**, Tp^{Br}RuPPh$_3$Cl$_2$	60 °C	4%	67%	-0.34
9	**335d**, Tp^{I}RuPPh$_3$Cl$_2$	60 °C	5%	66%	-0.32
10	**339a**, TpRuPPh$_3$(MeCN)Cl	80 °C	4%	63%	0.13
11	**339b**, Tp^{Cl}RuPPh$_3$(MeCN)Cl	80 °C	5%	68%	0.32
12	**339c**, Tp^{Br}RuPPh$_3$(MeCN)Cl	80 °C	4%	71%	0.32
13	**339d**, Tp^{I}RuPPh$_3$(MeCN)Cl	80 °C	6%	66%	0.31

[a]Oxidation potential is against ferrocene

To figure out how fast the ruthenium complexes catalyze the reaction and how they lose their catalytic activity, the progress of the reaction was monitored by isolating the product at different reaction times. The graph in Figure 3.1 shows the product yield of the reaction catalyzed by **339a** or **335c** versus reaction time. The catalyst loading was increased to 10 mol %. The volume of DCE was tripled to make sure that the ruthenium

complex completely dissolves. The amount of TEA was also was increased three times so that the concentration of TEA was the same as the original conditions.

The plot shows that $Tp^{Cl}RuPPh_3Cl_2$ **335c** catalyzed reaction was complete within 15 minutes, while when $TpRuPPh_3(MeCN)Cl$ **339a** catalyzed the reaction process was slower and took 5 hours. These selected reaction times were used to benchmark the $Tp^{X}Ru$ catalysts.

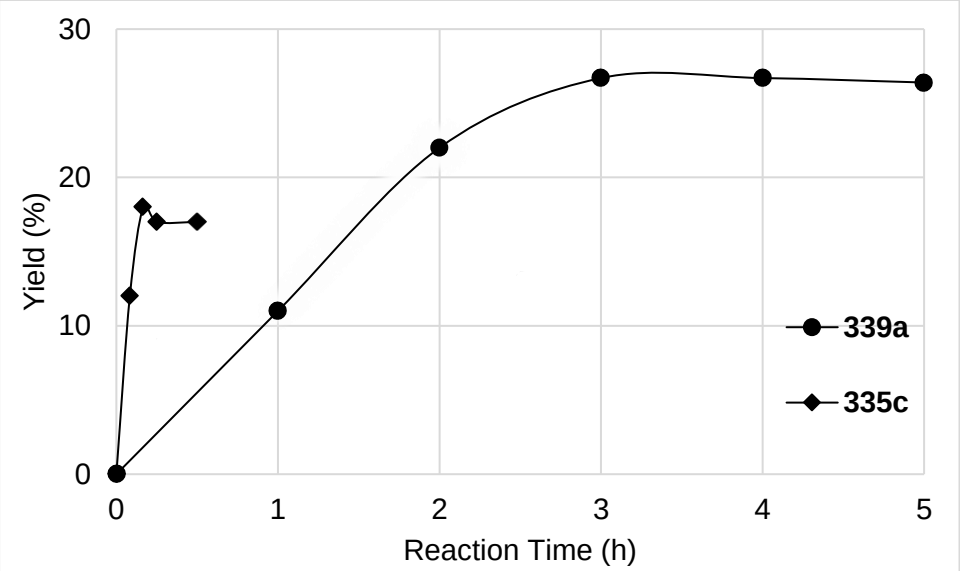


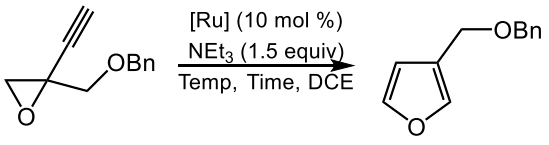
Figure 3.1: The Plot of the yield of 341d or vs reaction time

Except **335c**, which gave the slightly higher yield of 17%, **335** generally gives yields of 14% (Table 3.8, entries 1-4). As shown in the NMR analysis in Chapter 1, only the chlorine substituent was a strong enough substituent to overwhelm the resonance effect to take away the electron density out of Tp ligand. Therefore, in the Ru(III) system, reducing the electron density in the Tp ligand seemed beneficial in catalysis.

Catalysts **339a** and **339e** gave higher yields of 26 and 28% (entries 5 and 8). The electronegativity of H and I are 2.2 and 2.7 (Pauling) and therefore do not withdraw electron density out of the Tp ligand as strongly as Cl and Br (3.2 and 3.0). On the other hand, **339c** and **339d** gave 23% and 22% yields (entries 6 and 7). A common feature of these complexes is that their elecronegativity is relatively higher than carbon (2.6). Thus, in a Ru(II) system, $Tp^{X}Ru$ complexes whose Tp ligands have electronegative halogens seemed to perform better.

The oxidation potentials of the complexes made a clear demarcation between non-halogenated complexes and halogenated complexes. However, catalytic activity was not as simple. For instance, the oxidation potentials of the di-phosphine complexes are about the same as the acetonitrile mono-phosphine complexes (Table 3.7), yet, di-phosphine complexes did not show any activity in Liu's system while the acetonitrile mono-phosphine complexes showed some activity. In this case, steric pressure exerted by the di-phosphine ligands could prevent access by the substrate to the ruthenium, or the di-phosphine ligands could inhibit a geometrical change in the complex. Also, the observation that the halogenated mono-phosphine ruthenium complexes **335** and **339** showed slight difference was curious. Some recent papers found that oxidation potentials of the reagents influence the mechanism of the reactions.[59] In their cases, the oxidation potentials fit because these reactions involve simple electron transfer, which is the same process as in CV. In contrast, furan synthesis includes more than simple electron transfer. Therefore, oxidation potentials were not a good indicator of catalysis performance.

Table 3.8: Furan synthesis from epoxyalkyne catalyzed by ruthenium complexes in increased catalyst loading (10 mol %)



340d 341d

Entry	Catalyst	Temp (°C)	Time (h)	Yield
1[a]	**335a**, $TpRuPPh_3Cl_2$	60	0.5	14%
2[a]	**335b**, $Tp^{Cl}RuPPh_3Cl_2$	60	0.5	17%
3[a]	**335c**, $Tp^{Br}RuPPh_3Cl_2$	60	0.5	14%
4[a]	**335d**, $Tp^{I}RuPPh_3Cl_2$	60	0.5	14%
5[a]	**339a**, $TpRuPPh_3(MeCN)Cl$	80	5	26%
6[a]	**339b**, $Tp^{Cl}RuPPh_3(MeCN)Cl$	80	5	23%
7[a]	**339c**, $Tp^{Br}RuPPh_3(MeCN)Cl$	80	5	22%
8[a]	**339d**, $Tp^{I}RuPPh3(MeCN)Cl$	80	5	28%

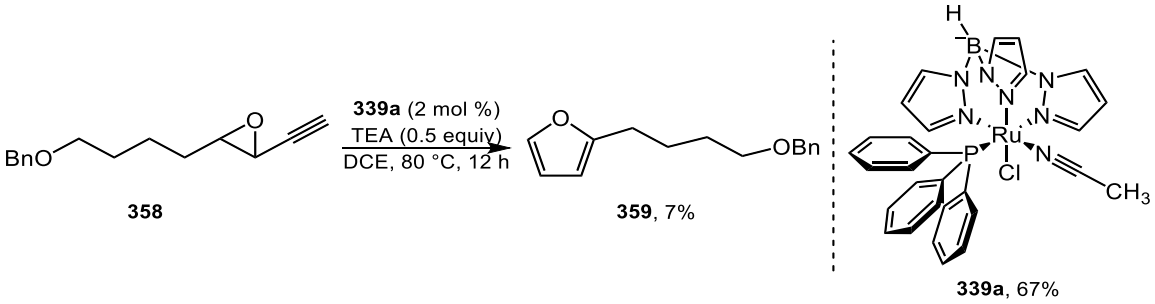
[a]DCE and NEt_3 was increased 3x to dissolve Ru

[b]Oxidation potential is against ferrocene

Because Ru(III) complexes **335** catalyzes the reaction very fast and loses the activity very quickly, the kinetics data of the catalyst at lower temperatures will be obtained within next couple of months. Once the reaction time needed to complete the catalysis is found, catalyst loading will be increased to 25 mol% to stress the difference.

Furan synthesis from internal epoxides was also examined to see if there was any difference in the yield. Because the yield of the epoxidation step at the last step of the preparation of **358** was very low, the catalysis was tried only a couple of times. Nonetheless, slightly improved yield (7% from **359** vs 4% from **341d**) of the furan product was obtained (Scheme 3.9 and Table 3.7, entry 10). The trend was consistent with the Liu group's data. Still, the yield was much less than any of the furan products on their paper.

Scheme 3.9: Furan synthesis from internal epoxyalkane.



3.3 Conclusion

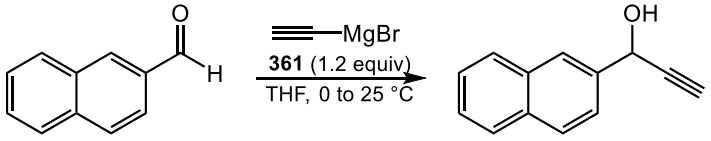
$Tp^{X}Ru$ complexes including diene complexes, mono-phosphine complexes, and di-phosphine complexes were tested for catalytic activity. Only furan synthesis from epoxyalkynes worked, but with much lower yields than found in the literature. Utilizing this system, it was concluded that oxidation potentials of the complex do not predict the performance of the catalysts, and that $Tp^{X}Ru(II)$ complexes that have non-electronegative substituents such as H and I on the Tp ligands gave higher yields. In the $Tp^{X}Ru(III)$ complexes with strongly enough electronegative substituent (Cl) on the Tp ligand seemed slightly superior.

3.4 Experimental Section
Materials and Methods

All reactions were carried out in a flame-dried Shlenk flask under an Ar atmosphere. 2,3-bromopropene (80% technical grade) was purchased from Sigma Aldrich and distilled before use. THF and toluene were purged with argon and dried over activated alumina columns and used after degassing by repetitive vacuum and Ar purges. 2-methyl furan was distilled before use. DCE was distilled over CaH_2. TEA was distilled before use. Flash column chromatography was performed on 60 Å silica gel (Sorbent technologies Inc.) unless otherwise stated. Analytical thin layer chromatography was performed on 250mm

EMD silicagel/TLC plates with fluorescent detector (254 nm). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 500 spectrometer using the residual solvent peak as an internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.6 ppm for ^{13}C NMR).

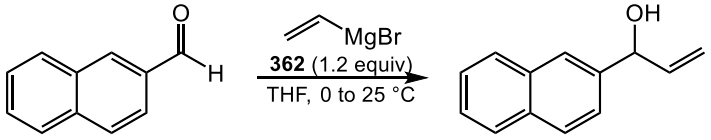
1-(Naphthalen-2-yl)prop-2-yn-1-ol, **342**



360 **342**, 74%

To 2-napthalde **360** (2.00 g, 12.8 mmol) in a flame dried 50 mL Shlenk flask was added ethynyl magnesium bromide solution in THF **361** (30 mL, 0.5 M, 1.2 equiv) dropwise. The mixture was stirred at 0 °C, then at 25 °C as the addition finishes. After 2 hours, the reaction was quenched by adding saturated ammonium chloride solution. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated and purified via column chromatography, and the product was eluted with Hex:EtOAc=10:1. The product was recrystallized from DCM/pentane to give white solid **342** (1.73 g, 74%). ^{1}H-NMR (500 MHz, Chloroform-d) δ 8.00 (*s*, 1H), 7.92-7.79 (*m*, 3H), 7.65 (*dd*, J = 8.6, 1.7 Hz, 1H), 7.55-7.47 (*m*, 2H), 5.63 (*dd*, J = 6.3, 1.7 Hz, 1H), 2.73 (*d*, J = 2.3 Hz, 1H), 2.43 (*d*, J = 6.9 Hz, 1H), 1.62 (*t*, J = 4.9 Hz, 1H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 64.68, 75.25, 83.52, 124.54, 125.59, 126.49, 126.54, 127.81, 128.32, 128.76, 133.22, 133.4, 137.4,

1-(Naphthalen-2-yl)prop-2-en-1-ol, **349**

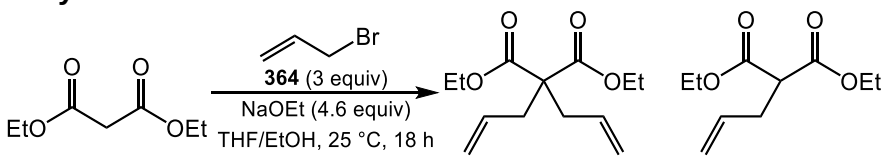


360 **349**, 36%

To a THF (40 mL) solution of 2-napthalde **360** (2.00 g, 12.8 mmol) in a flame dried 100 mL Shlenk flask was added vinyl magnesium bromide (**362**) solution in THF (38 mL,

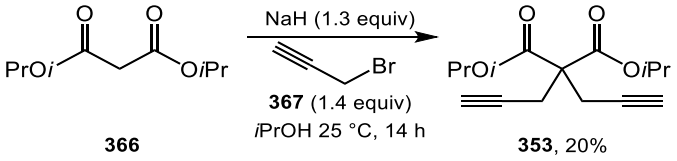
1.0 M, 1.2 equiv) dropwise. The mixture was stirred at 0 °C, then at 25 °C as the addition finishes. 5 hours later, the reaction was quenched by adding saturated ammonium chloride solution. The organic layer was washed with brine and dried over $MgSO_4$. The filtrate was concentrated and s purified via column chromatography, and the product was eluted with Hex:EtOAc=4:1. The product was collected and concentrated under vacuum to give yellow oil **349** (2.13 g, 26%). ^{1}H-NMR (500 MHz, Chloroform-d) δ 8.00-7.75 (*m*, 4H), 7.62-7.41 (*m*, 3H), 6.25-6.09 (*m*, 1H), 5.43 (*d*, J = 17.2 Hz, 1H), 5.37-5.19 (*m*, 2H), 2.07 (*s*, 1H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 75.5, 115.5, 125, 125.3, 126.2, 126.4, 128, 128.3, 128.5, 133.2, 133.6, 140.4, 140.5

Diethyl-2,2-allylmalonate 351



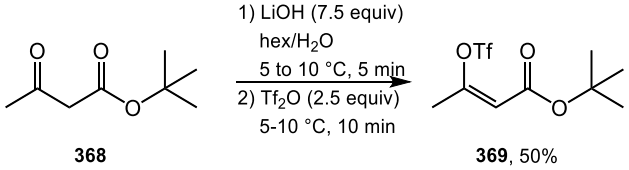
A flame dried 100 mL Shlenk flask was charged with diethyl malonate **363** (5 mL, 32.9 mmol), allyl bromide **364** (7 mL, 100 mmol, 3 equiv), and EtOH (40 mL). The mixture was cooled in an icy water bath, and NaOEt (10.4 g, 152.8 mmol 4.6 equiv) was added to the flask. The mixture was stirred overnight (17 h). The mixture was diluted with ethyl acetate and was washed with brine. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The mixture was purified via column chromatography, and the product was eluted with Hex/EtOAc=30:1. The product was collected and concentrated under vacuum to give yellow oil **351** (1.45 g, 22%).^{1}H-NMR (500 MHz, Chloroform-d) δ 5.71-5.57 (*m*, 2H), 5.15-5.05 (*m*, 4H), 4.18 (*q*, J = 7.1 Hz, 4H), 2.63 (*d*, J = 7.4 Hz, 4H), 1.24 (*t*, J = 7.2 Hz, 6H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 14.7, 37.2, 57.7, 61.8, 119.7, 132.8, 171.3

Diisopropyl propargyl malonate 353



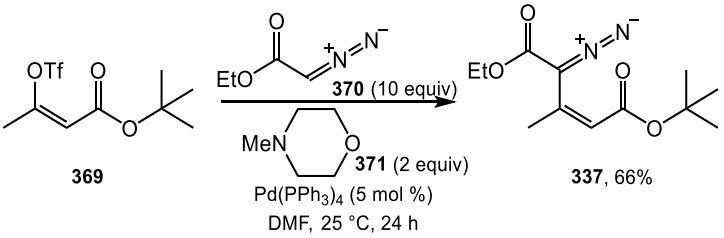
A flame dried 100 mL Shlenk flask in an icy water bath was charged with NaH (1.99g, 56 mmol, 1.3 equiv) and *i*PrOH (89 mL). Diisopropyl malonate **366** (7.05 g, 37.5 mmol) was added to the flask dropwise, and the mixture was stirred for 2 hours. Propargyl bromide **367** (10.4 g, 70 mmol, 1.4 equiv) was added to the mixture dropwise, and the mixture was stirred overnight. The solvent was removed under reduced pressure and vacuum, and the residue was diluted in water. The product was extracted into ether, and ether solution was dried over $MgSO_4$. The product was recrystallized from hexane to give colorless needle **353** (2.00 g, 20 %).

(*Z*)-tert-Butyl 3-(trifluoromethylsulfonyloxy)but-2-enoate 369



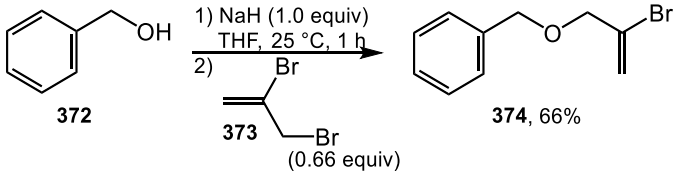
A 250 mL round-bottom flask was charged with *tert*-butyl acetoacetate **368** (4.0 mL 24 mmol) and 120 mL of hexane. The flask was bathed in icy water, and LiOH (4.29 g, 179.5 mmol) in water (36 mL) was added to the hexane solution. The mixture was stirred for 10 minutes, and TfO_2 (10 mL, 60 mmol) was added to the mixture. After another 10 minutes, water (30 mL) and EtOAc (60 mL) were added to the mixture, and the organic layer was washed. The organic layer was further washed with water (30 mL) and brine (30 mL). The organic layer was dried over $MgSO_4$, and the filtrate was purified via column chromatography. The product was eluted with Hex:EtOAc=30:1 to give white solid **369** (50%).

1-(*tert*-Butyl) 5-ethyl (*Z*)-4-diazo-3-methylpent-2-enedioate 337



A flame dried 250 mL round-bottom flask was charged with (*Z*)-tert-butyl 3-(trifluoromethylsulfonyloxy)but-2-enoate **369** (3.5 g ,12 mmol), DMF (60 mL), 4-methylmorpholine **371** (2.7 mL, 240 mmol, 2 equiv), and ethyl diazoacetate **370** (12.5 mL, 119 mmol, 10 equiv). $Pd(PPh_3)_4$ (701.7 mg, 0.6 mmol, 0.05 equiv) was added to the mixture, and the mixture was stirred for 16 hours. The mixture was washed with brine three times, and the organic layer was purified via column chromatography. The product was eluted with Hex:EtOAc=30:1. The product was collected and concentrated in a round-bottom flask under vacuum to give orange liquid **337** (2.03 g, 66.4%).

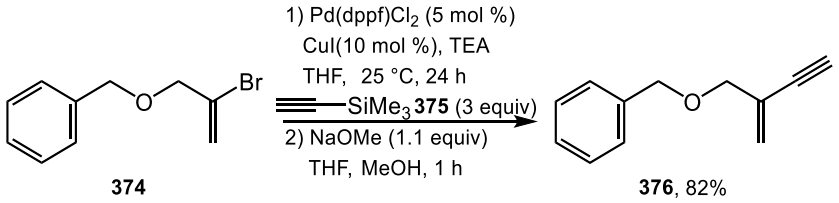
1-Bromoethenoxymethylbenzene 374



A flame dried 100 mL Shlenk flask was charged with NaH (7.01 g, 175 mmol) in 20 mL of THF. BnOH **372** (10 mL, 175 mmol, 1 equiv) in THF (20 mL) was added to the NaH suspension dropwise, and the mixture was stirred for an hour. 2,3-Bromopropene **373** (11.4 mL, 116.6 mmol, 1 equiv) in THF (20 mL) was added to the mixture dropwise, and the mixture was stirred overnight. The solvent was removed under vacuum, and the residue was diluted with EtOAc. The mixture was washed with brine 3 times, and the organic layer was dried over $MgSO_4$. The mixture was purified via column chromatography, and the product was eluted with hex/toluene=10:1. The product was dried under vacuum

to give slightly greenish liquid **374** (9.72 g, 66%).[1]H-NMR (500 MHz, Chloroform) δ 7.48-7.30 (*m*, 5H), 6.00 (*q*, J = 1.5 Hz, 1H), 5.69 (*d*, J = 1.4 Hz, 1H), 4.59 (*s*, 2H), 4.17 (*d*, J = 1.1 Hz, 2H)

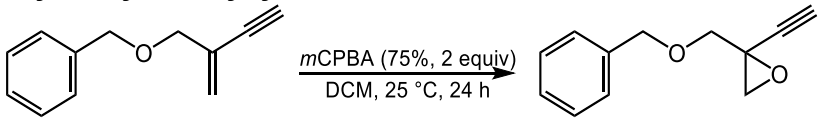
2-[(Benzyloxy)methyl]-2-(1-ethynyl)oxirane 376



374 **376**, 82%

A flame dried 100 mL Shlenk flask was charged with 1-bromoethenoxymethylbenzene **374** (9.05 g, 39.8 mmol), TEA (50 mL), CuI (754.6 mg, 3.96 mmol 10 mol %), and Pd(dppf)Cl (1450.3 mg, 1.98 mmol, 5 mol %). Ethynyltrimethylsilane **375** (16.5 mL, 119mmol, 3.0 equiv) was slowly added to the mixture, and the mixture was stirred overnight (12 hs). The solvent was removed under vacuum, and the residue was purified with column chromatography. The product was eluted with Hex/EtOAc=60:1 and collected and concentrated in a flask under reduced pressure. The product was dissolved in THF (20 mL) and transferred to 1 50 mL Shlenk flask. MeOH (5 mL) was added to the THF solution. The mixture was stirred for a while after NaOMe (2567.4 mg, 47.5 mmol, 1.1 equiv) was added to the solution. The mixture was purified via column chromatography, and the product was eluted with Hex/EtOAc=60:1 to give yellow liquid **376** (5.65 g, 82%).[1]H-NMR (500 MHz, Chloroform-d) δ 7.47-7.26 (*m*, 5H), 5.65 (*s*, 2H), 4.57 (*d*, J = 5.2 Hz, 2H), 4.14-3.98 (*m*, 2H), 2.95 (*d*, J = 5.2 Hz, 1H)

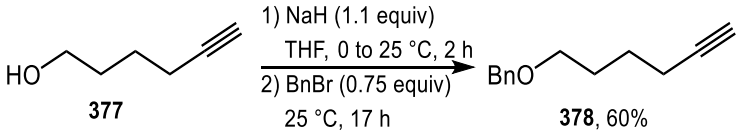
(±)-2-Benzyloxymethyl-2-ethynyloxirane 340d



376 **340d**, 65%

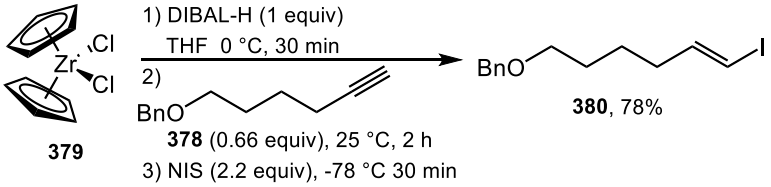
A 250 mL round-bottom flask was charged with 2-[(benzyloxy)methyl]-2-(1-ethynyl)oxirane **376** (5.10 g, 30 mmol) and DCM. *m*CPBA (13.34 g, 58 mmol, 2 equiv) was added to the solution, and the mixture was stired overnight (24 hs). The mixture was purified via basic alumina column chromatography, and the product was eluted with Hex/EtOAc=12:1. Partially purified product was purified via silica gel column chromatography, and the product was eluted with Hex:EtOAc=15:1 to give colorless liquid **340d** (3.61 g, 65%). ^{1}H-NMR (500 MHz, Chloroform-d) δ 7.54-7.15 (*m*, 5H), 4.63 (*dd*, J = 14.9, 12.0 Hz, 2H), 3.77 (*d*, J = 11.5 Hz, 1H), 3.64 (*d*, J = 12.0 Hz, 1H), 3.04 (*d*, J = 5.7 Hz, 1H), 2.96 (*d*, J = 5.7 Hz, 1H), 2.41 (*s*, 1H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 49.9, 51.8, 71.4, 72.9, 73.7, 80.7, 128.1, 128.2, 128.8, 138.

1-Benzyloxy-5-hexyne 378



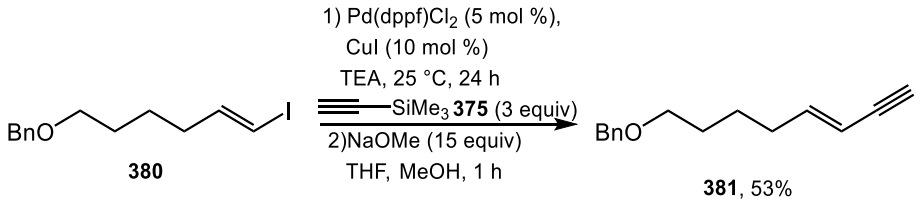
To a flame-dried 100 mL Shlenk flask was charged with NaH (1297.2 mg, 32.4 mmol, 1.1 equiv). The NaH was suspended in THF (58 mL), and the mixture was bathed in icy water. 5-Hexyn-1-ol **377** (2889.6 mg, 29.4 mmol) in THF (10 mL) was added to the mixture dropwise, and the mixture was stirred for an hour. Benzyl bromide (3.6 mL, 22 mmol, 0.75 equiv) in THF was added to the mixture dropwise, and the mixture was stirred overnight (17 hs). The mixture was filtered through a glass frit, and the filtrate was concentrated under reduced pressure. The mixture was purified via column chromatography, and the product was eluted with Hex:EtOAc=100:1 to give slightly greenish liquid **378** (3.3 g, 60%).

(*E*)-(6-Iodohex-5-en-1-yloxy)methylbenzene 380



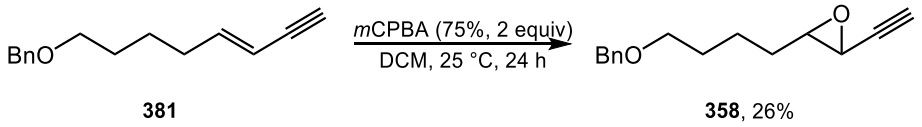
A flame dried 250 mL round-bottom flask was charged with Cp_2ZrCl_2 **379** (8132.8 mg, 27.8 mmol) and THF (100 mL). The flask was bathed in icy water bath. DIBAL-H (28 mL, 1 M) was added to the mixture dropwise, and the mixture was stirred for 30 minutes. 1-Benzyloxy-5-hexyne **378** (18.5 mmol, 1.5 equiv) in THF (44 mL) was added to the mixture. The mixture was stirred for 2 hours, and NIS (13.5 g, 60 mmol, 2.2 equiv) in THF (61 mL) was added to the mixture dropwise. The mixture was stirred for 30 minutes, and 25 mL of 1 M HCl was added to the mixture to quench the reaction. The mixture was extracted into ether, and the ether layer was washed with Na_2CO_3 aq, $Na_2S_2O_7$ aq, and brine. organic layer was dried over $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified with column chromatography, and the product was eluted with Hex/EtOAc=100:1 to give yellow oil **380** (4.5 g, 77.5 %). ^{1}H-NMR (500 MHz, Chloroform-d) δ 7.61-7.19 (*m*, 5H), 6.53 (*q*, J = 7.3 Hz, 1H), 6.02 (*d*, J = 14.3 Hz, 1H), 4.54 (*s*, 2H), 3.50 (*t*, J = 6.3 Hz, 2H), 2.10 (*q*, J = 7.3 Hz, 2H), 1.59 (*dq*, J = 57.9, 7.1 Hz, 4H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 25.3, 29.3, 36.1, 70.2, 73.2, 75.2, 127.8, 127.9, 128.7, 138.8, 146.6

8-[(Benzyloxy)methyl]-1-yl-3-octene 381



A flame-dried 100 mL Shlenk flask was charged with (*E*)-(6-Iodohex-5-en-1-yloxy)methylbenzene **380** (3.82 g, 12 mmol), TEA (57 mL), CuI (233.3 mg, 1.22 mmo 10 mol %), and Pd(dppf)Cl_2 (442.9 mg, 0.6 mmol, 5 mol %). Ethynyltromethyl silane **375** (3.4 mL, 24 mmol 2 equiv) was added to the mixture, and the mixture was stirred overnight (16 hs). The solvent was removed under vacuum, and the residue was purified via column chromatography. The product was eluted with Hex/EtOAc=100:1 and was concentrated in a flask. The product was rinsed with THF (20 mL) and transferred to a 50 mL Shlenk flask. MeOH (10 mL) and NaOMe (785.4 mg, 14.5 mmol 1.2 equiv) were added to the solution, and the mixture was stirred for a while. The product was purified via column chromatography, and the product was eluted with Hex:EtOAc=100:1. The product was concentrated to give yellow liquid **381** (2.15 g, 53%).^{1}H-NMR (500 MHz, Chloroform-d) δ 7.47-7.27 (5H), 6.31-6.20 (1H), 5.53-5.41 (1H), 4.56-4.47 (2H), 3.58-3.44 (3H), 2.85-2.77 (1H), 2.28-2.04 (2H), 1.74-1.58 (2H), 1.58-1.44 (2H), 1.26-1.18 (1H) ^{13}C-NMR (500 MHz, Chloroform-d) δ15.8, 25.7, 29.7, 33.3, 66.4, 70.5, 73.4, 76.2, 83.0, 109.3, 128.0, 128.1, 128.9, 139.0, 147.

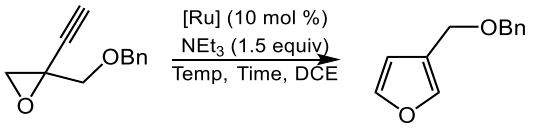
(±)-8-Benzyloxy-3,4-epoxyoct-1-yne 358



A 250 mL round-bottom flask was charged with 8-[(benzyloxy)methyl]-1-yl-3-octene **381** (2.0 g, 9.3 mmol) and DCM. *m*CPBA (4.18 g, 18 mmol, 2 equiv) was added to the solution, and the mixture was stirred overnight (24 hs). The mixture was purified via

basic alumina column chromatography, and the product was eluted with Hex/EtOAc=10:1. Partially purified product was purified via silica gel column chromatography, and the product was eluted with Hex:EtOAc=20:1 to give colorless liquid **358** (556.5 mg, 26%).

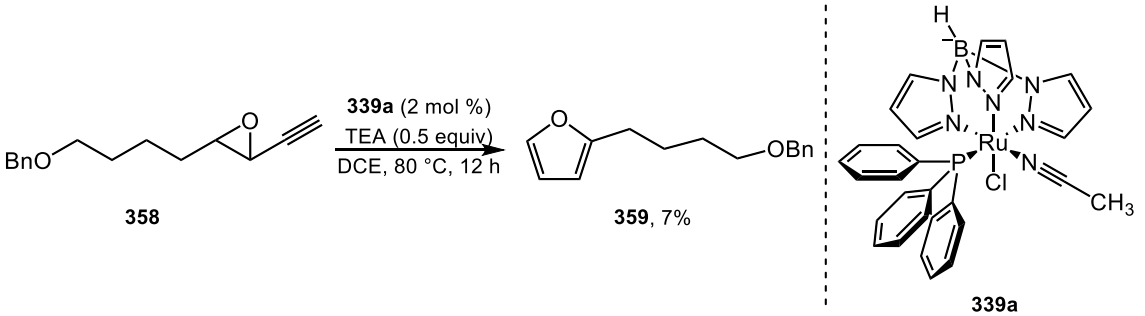
General procedures for ruthenium catalyzed furan synthesis from epoxyalkyne 341d



340d **341d**

To a flame-dried 10 mL Shlenk flask was charged with (±)-2-benzyloxymethyl-2-ethynyloxirane **340d** (92.3, mg, 0.49 mmol), TEA (100 μL), and DCE (1 mL). The mixture was stirred under argon for a while. A ruthenium catalyst (0.05 mmol, 10 mol%) was added to the mixture, and the mixture was heated for hours. The mixture was purified with column chromatography, and the product was eluted with Hex:EtOAc=30:1. The product was concentrated under reduced pressure and weighed to give yellow oil **341d**. ^{1}H-NMR (500 MHz, Chloroform-d) δ 7.42 (*d*, J = 5.7 Hz, 2H), 7.36 (*dd*, J = 12.6, 8.6 Hz, 4H), 7.30 (*td*, J = 8.6, 4.0 Hz, 1H), 6.45 (*s*, 1H), 4.54 (*s*, 2H), 4.43 (*s*, 2H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 63.8, 72.3, 110.9, 122.7, 128.2, 128.4, 129.0, 138.6, 141.3, 143.9

Ruthenium catalyzed furan synthesis from internal epoxyalkyne 359



358 **359**, 7% **339a**

To a flame-dried 10 mL Shlenk flask was charged with (+/-)-2-benzyloxymethyl-2-ethynyloxirane **358** (169.5, mg, 0.73 mmol), TEA (50 μL, 0.5 equiv), and DCE (0.3 mL). The mixture was stirred under argon for a while. A ruthenium catalyst (0.015 mmol, 2 mol %) was added to the mixture, and the mixture was heated 12 hours. The mixture was purified with column chromatography, and the product was eluted with Hex:EtOAc=15:1. The product was concentrated under reduced pressure and weighed to give yellow oil **359** (12.5 mg, 7%). ^{1}H-NMR (500 MHz, Chloroform-d) δ 7.47-7.24 (*m*, 6H), 6.27 (*t*, J = 2.6 Hz, 1H), 5.98 (*d*, J = 2.9 Hz, 1H), 4.50 (*s*, 2H), 3.49 (*t*, J = 6.3 Hz, 2H), 2.65 (*t*, J = 7.4 Hz, 2H), 1.84-1.63 (*m*, 4H) ^{13}C-NMR (500 MHz, Chloroform-d) δ 25.3, 28.3, 29.7, 70.5, 73.4, 105.3, 110.6, 128, 128.2, 128.9, 139.1, 141.3, 156.7

APPENDEX EIGHT: NMR Spectra

Evaluation of $Tp^{X}Ru$ Complexes in Catalysis

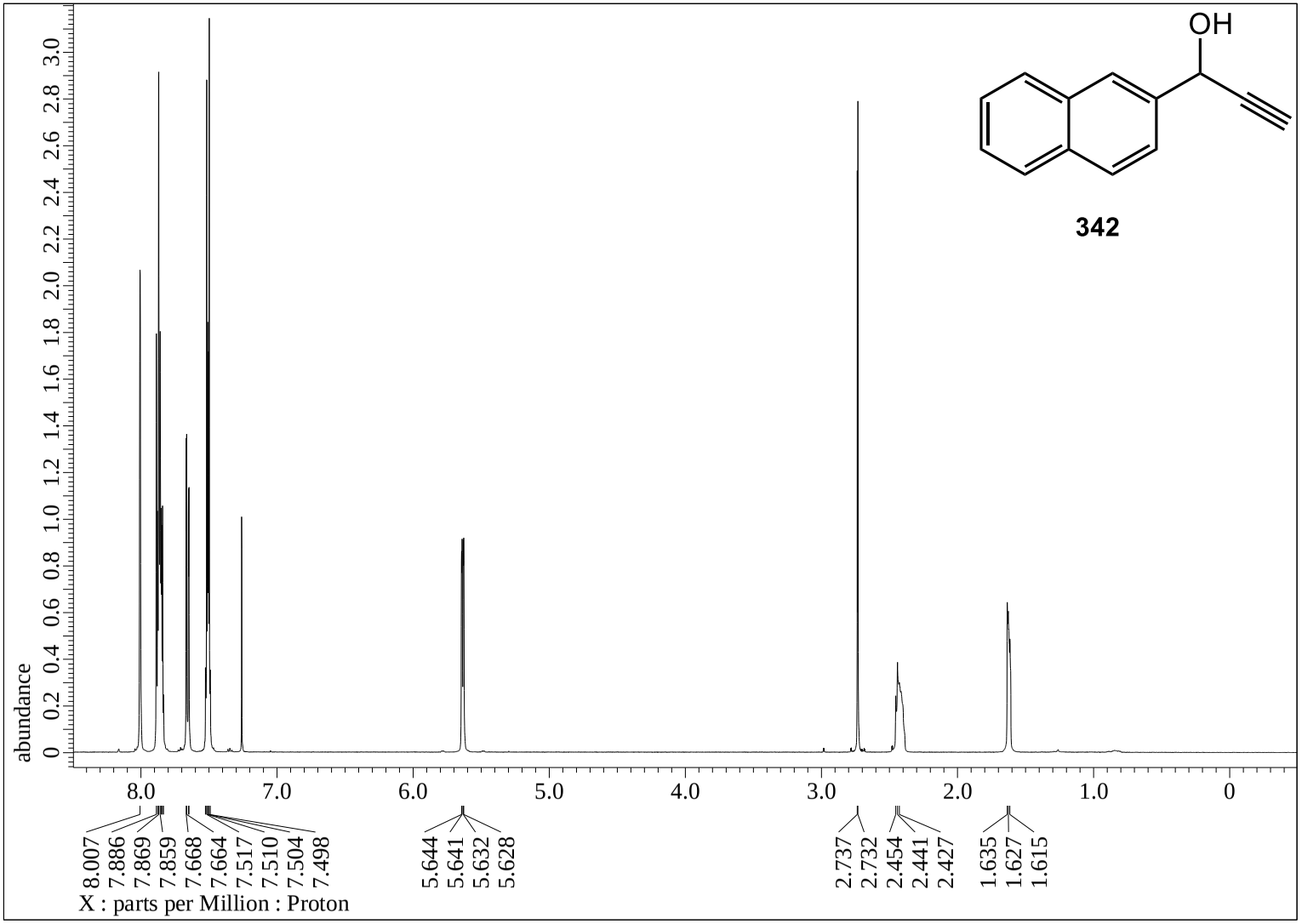


Figure A3.1: ^{1}H-NMR spectrum of 342 (500 MHz, $CDCl_3$)

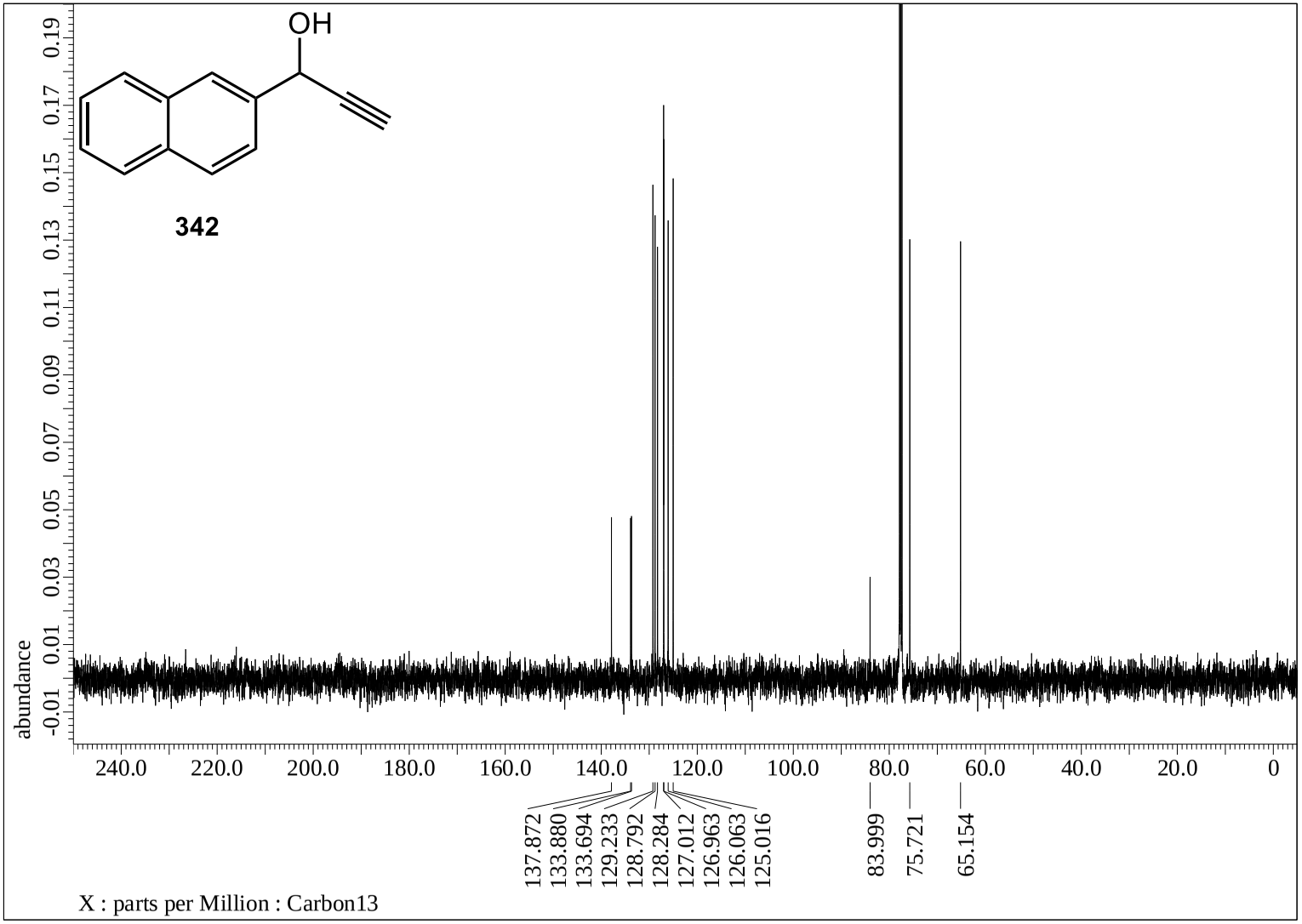


Figure A3.2: ^{13}C-NMR spectrum of 342 (500 MHz, $CDCl_3$)

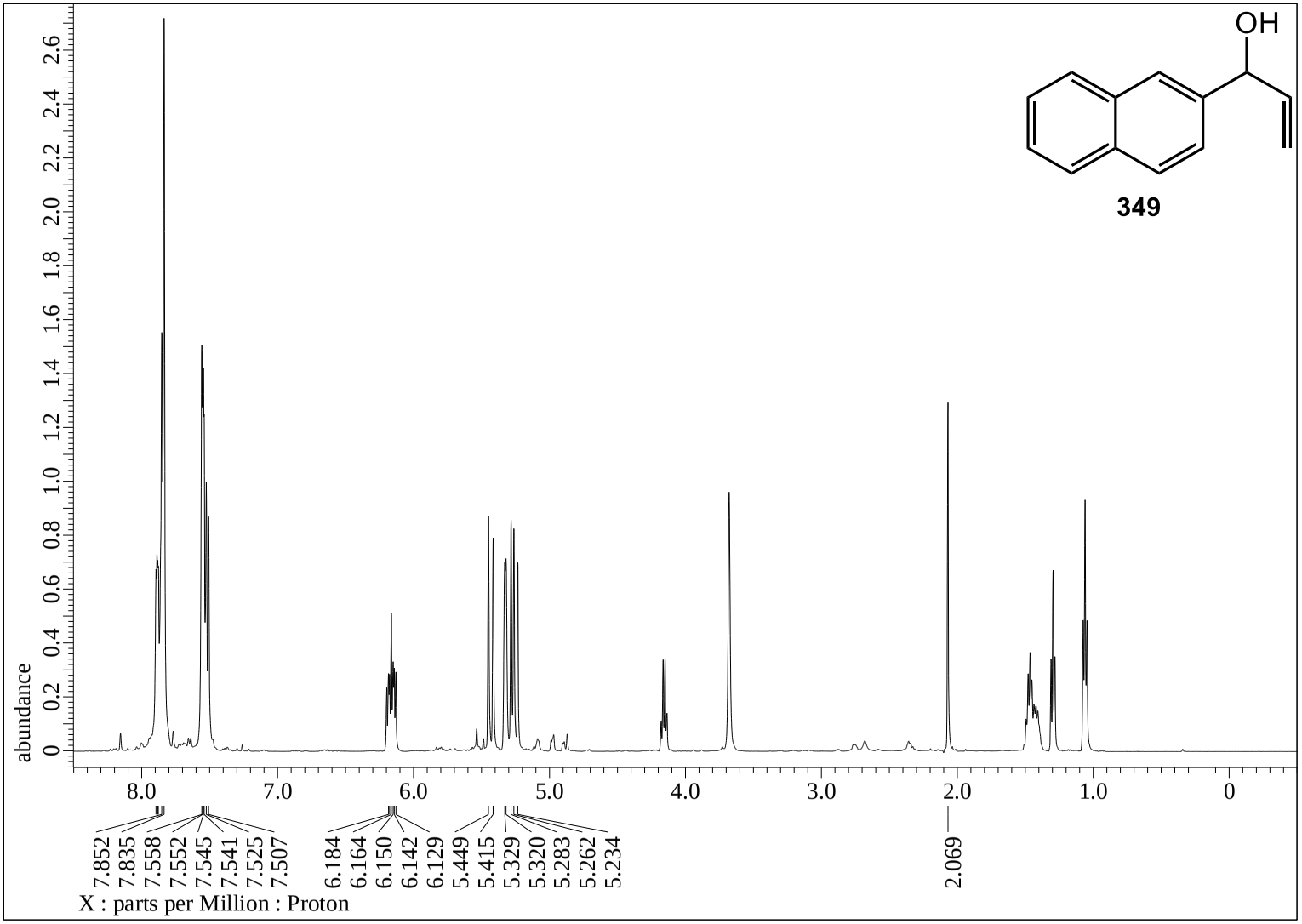


Figure A3.3: ^{1}H-NMR spectrum of 349 (500 MHz, $CDCl_3$)

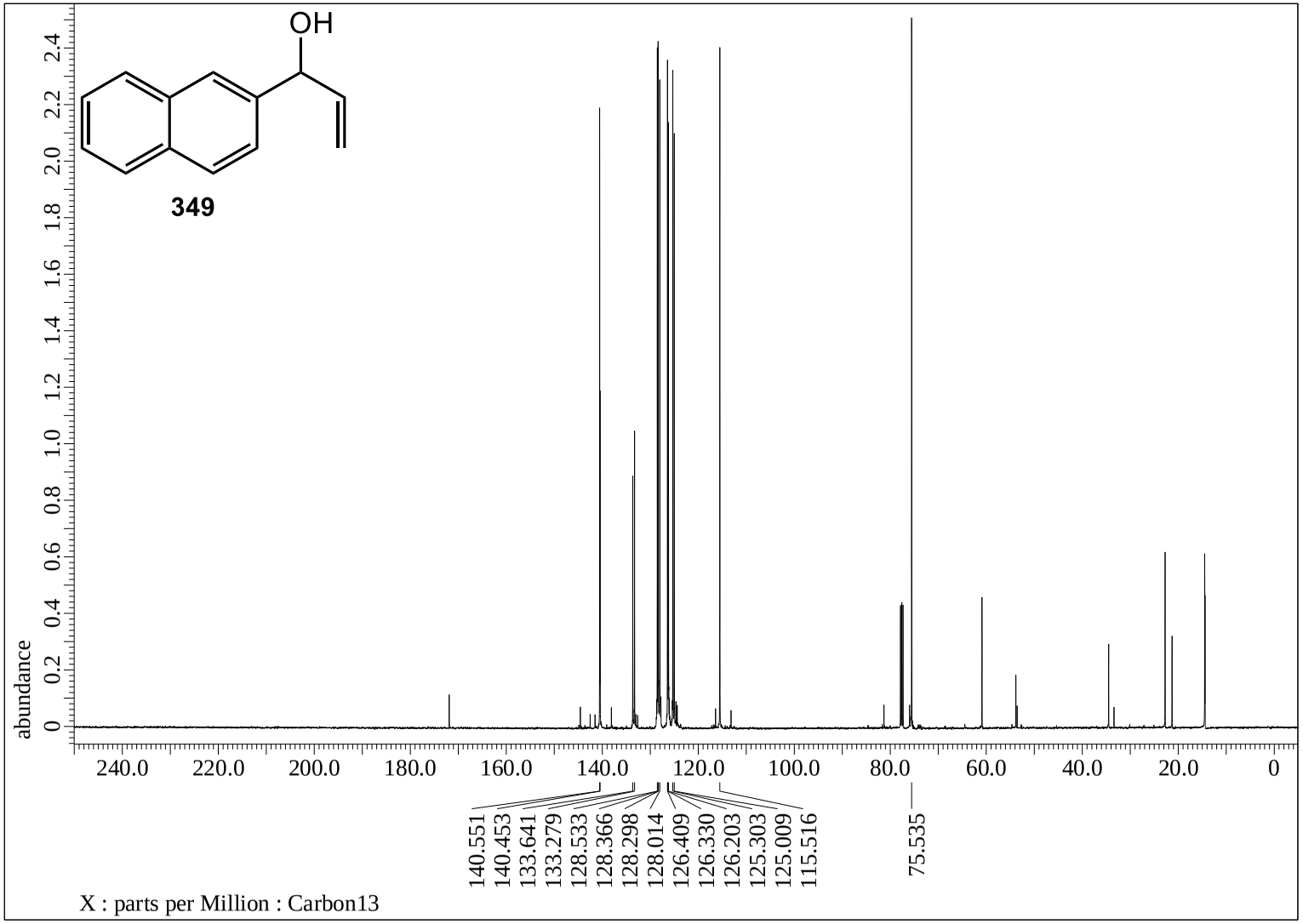


Figure A3.4: ^{13}C-NMR spectrum of 349 (500 MHz, $CDCl_3$)

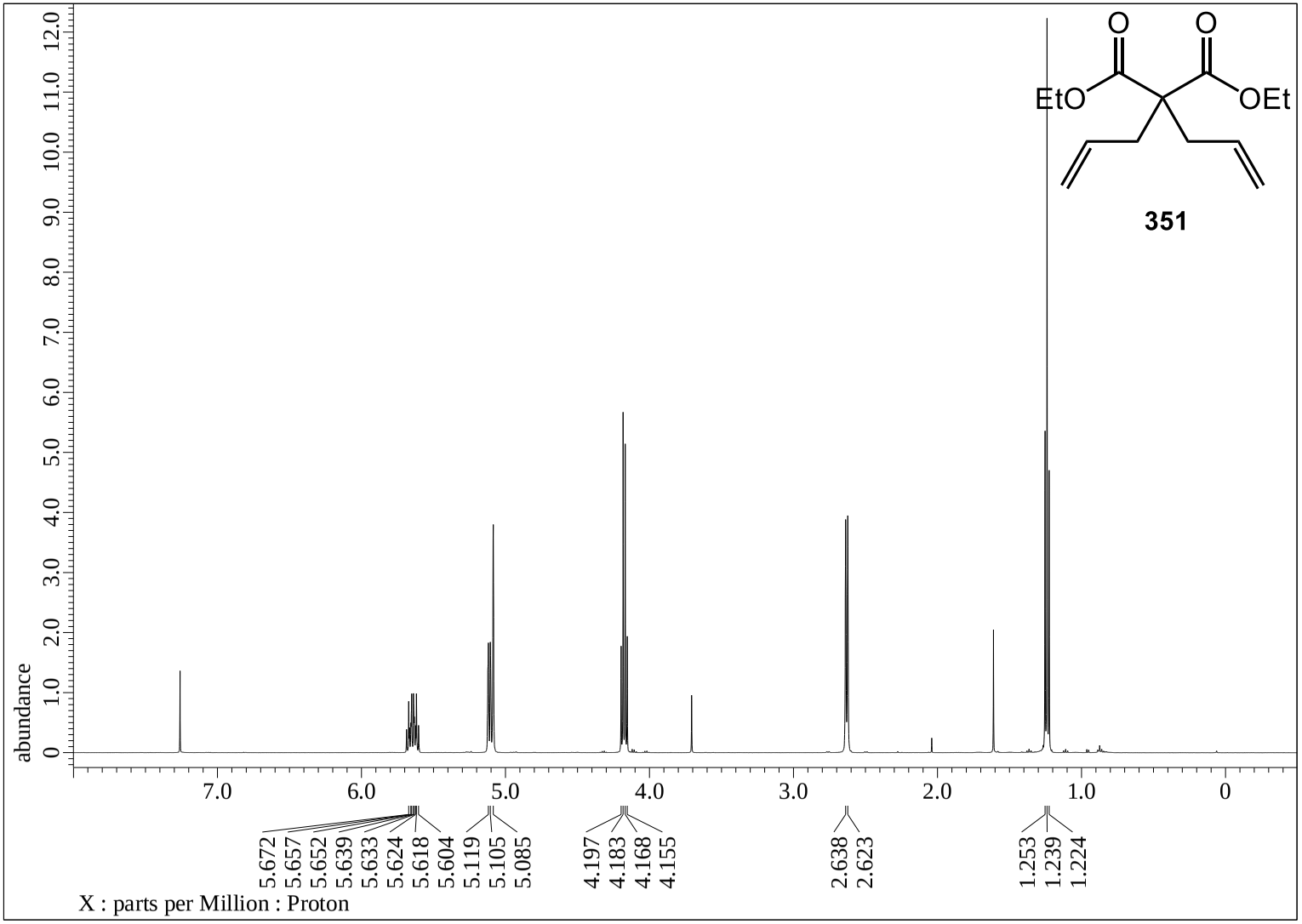


Figure A3.5: ^{1}H-NMR spectrum of 351 (500 MHz, $CDCl_3$)

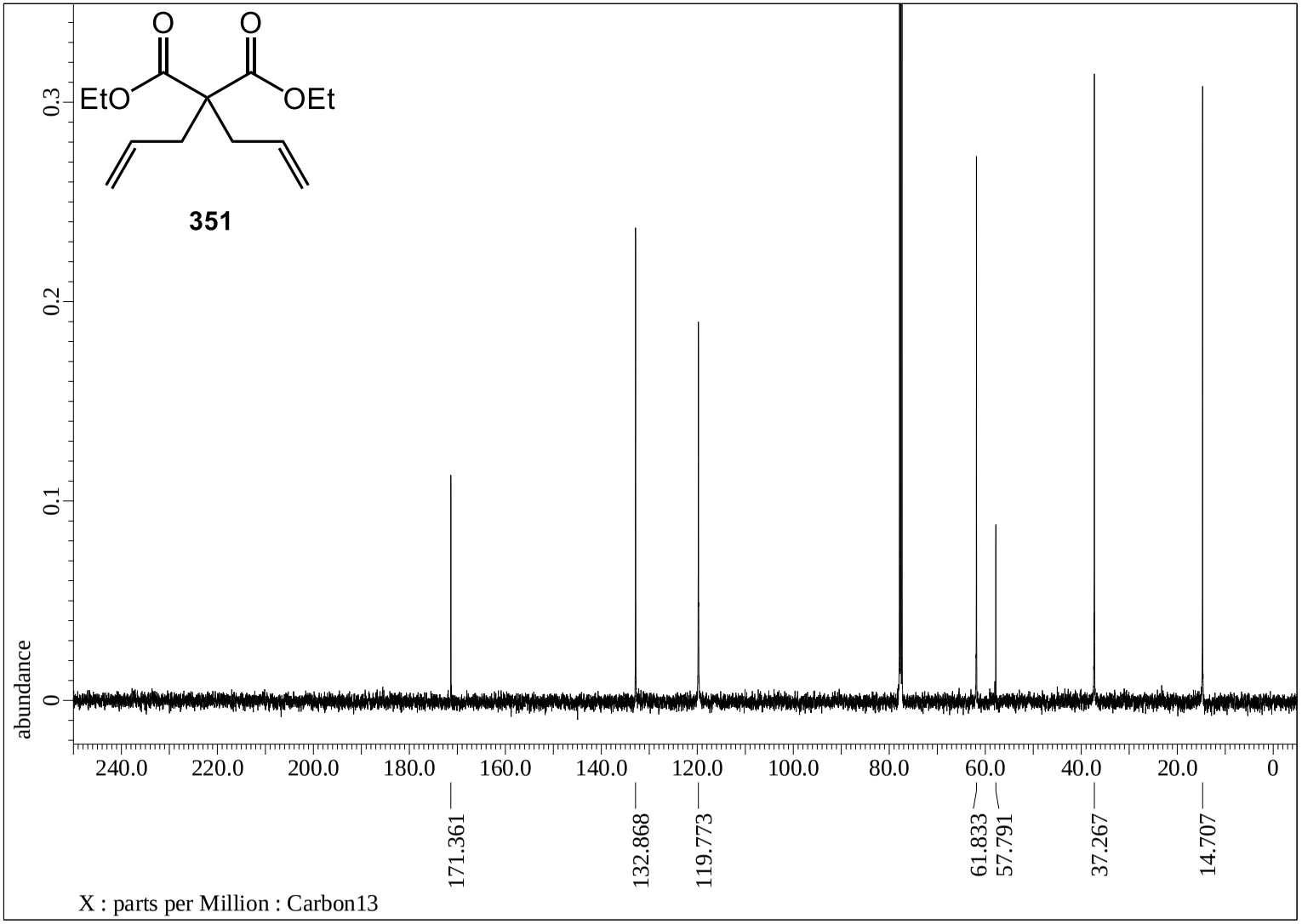


Figure A3.6: ^{13}C-NMR spectrum of 351 (500 MHz, $CDCl_3$)

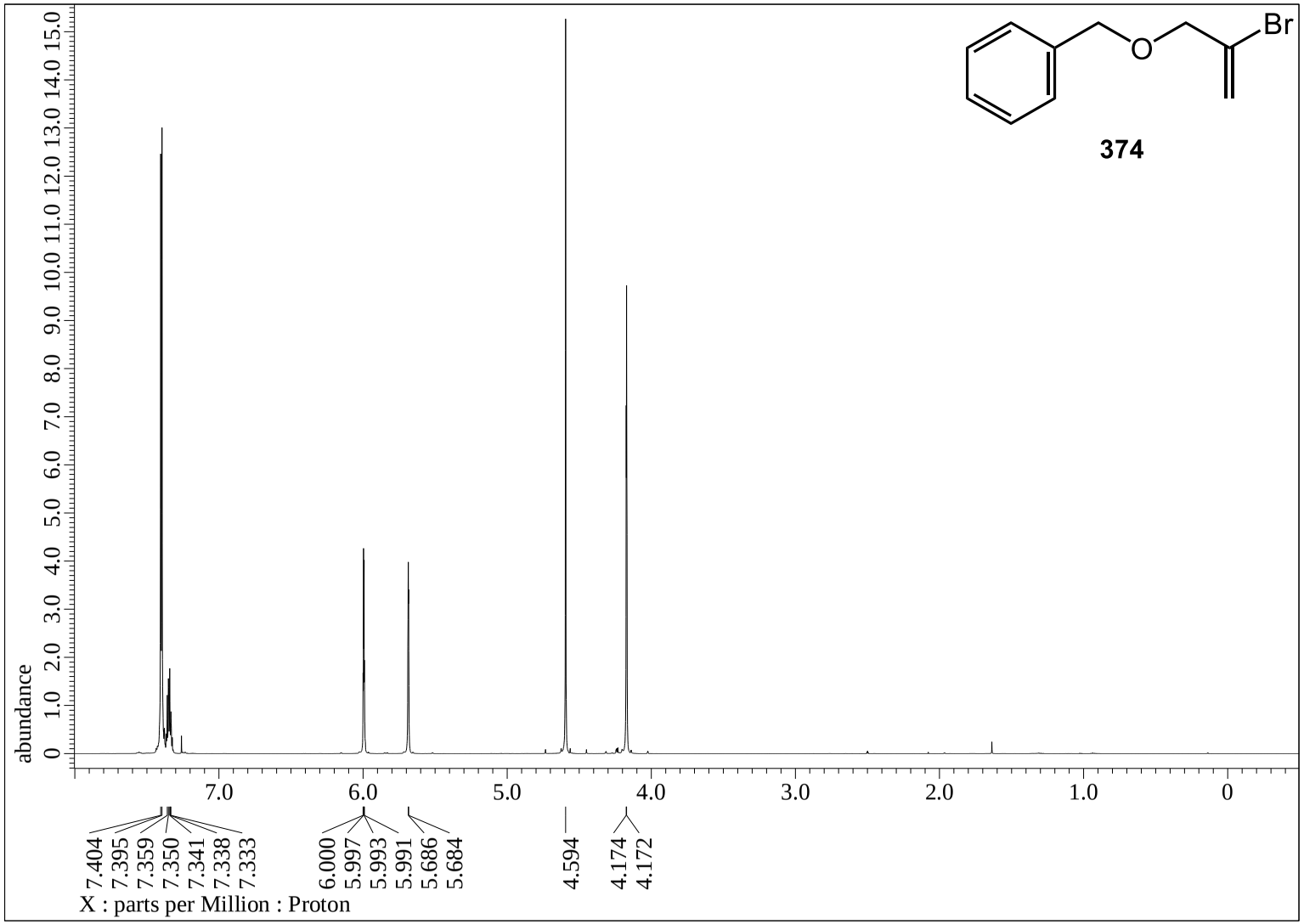


Figure A3.7: ^{1}H-NMR spectrum of 374 (500 MHz, $CDCl_3$)

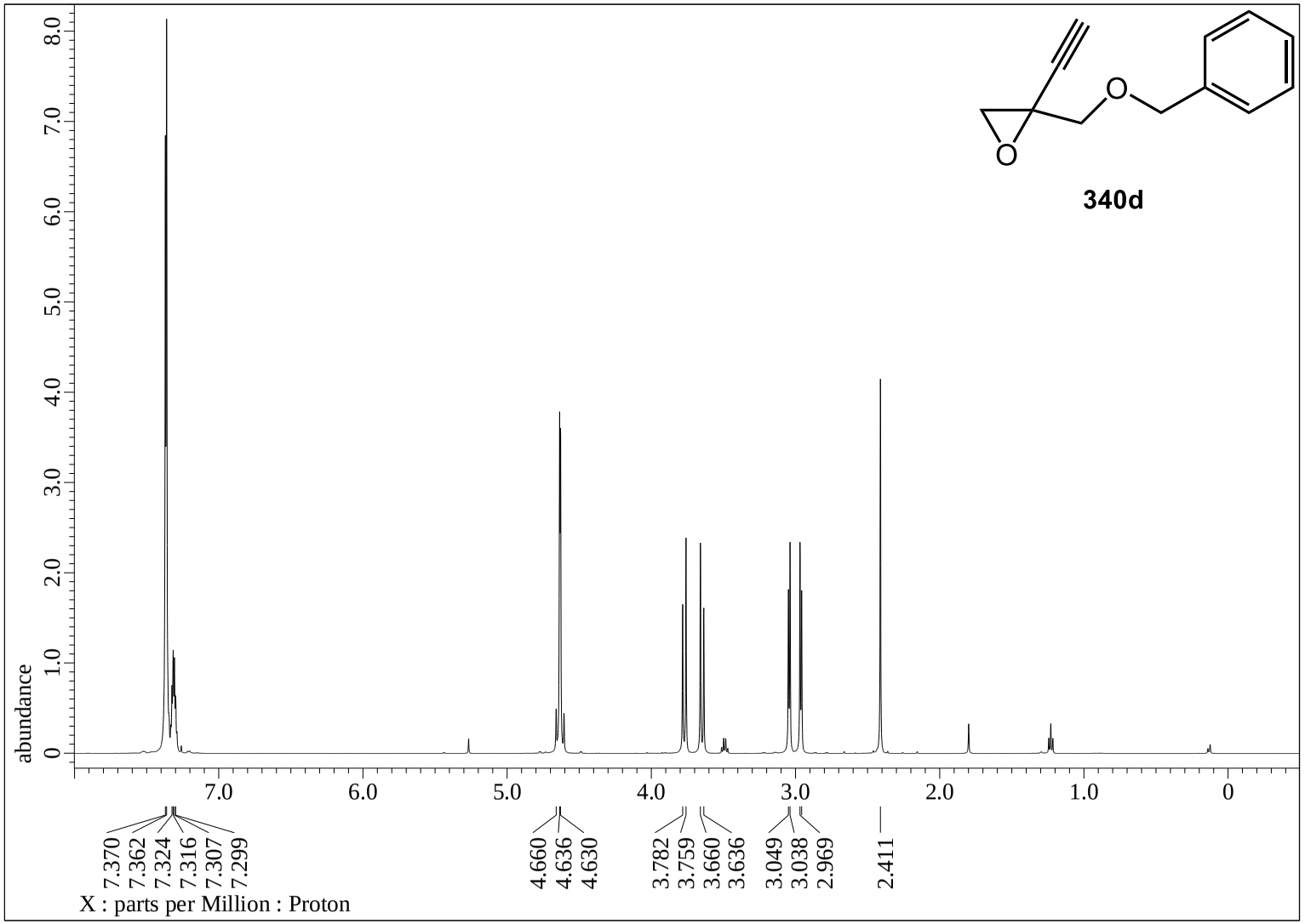


Figure A3.8: ^{1}H-NMR spectrum of 340b (500 MHz, $CDCl_3$)

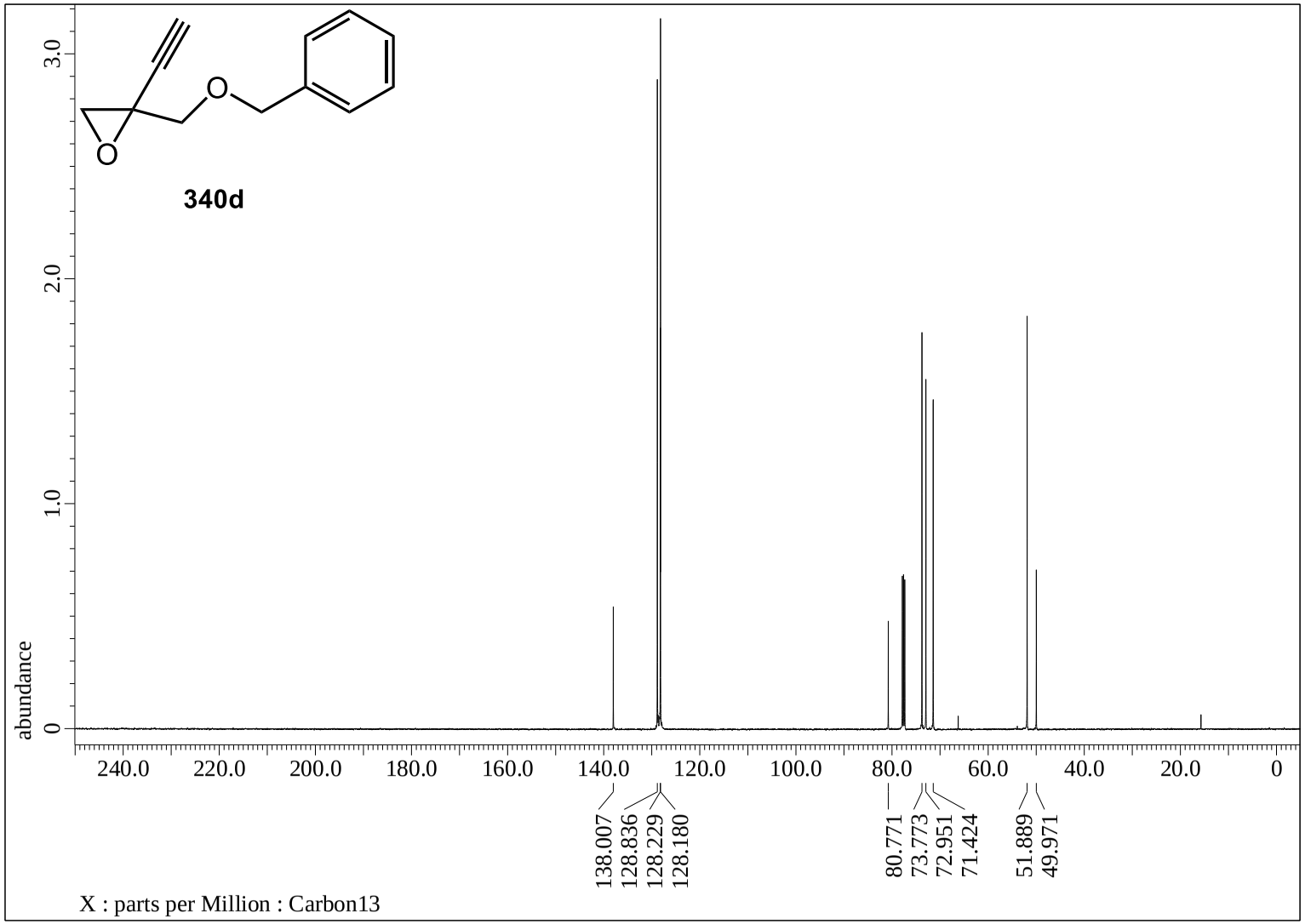


Figure A3.9: ^{13}C-NMR spectrum of 340b (500 MHz, $CDCl_3$)

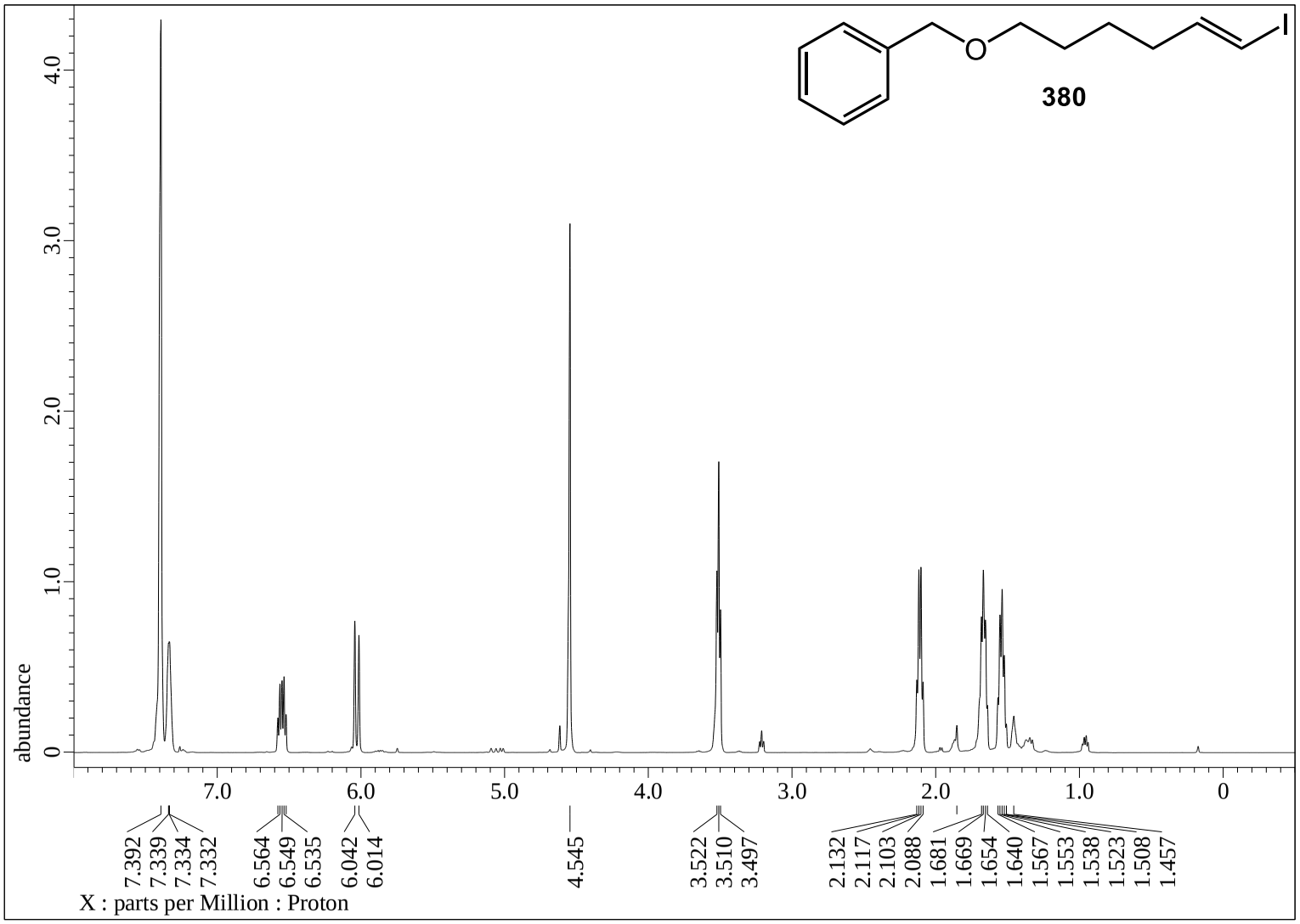


Figure A3.10: ^{1}H-NMR spectrum of 380 (500 MHz, $CDCl_3$)

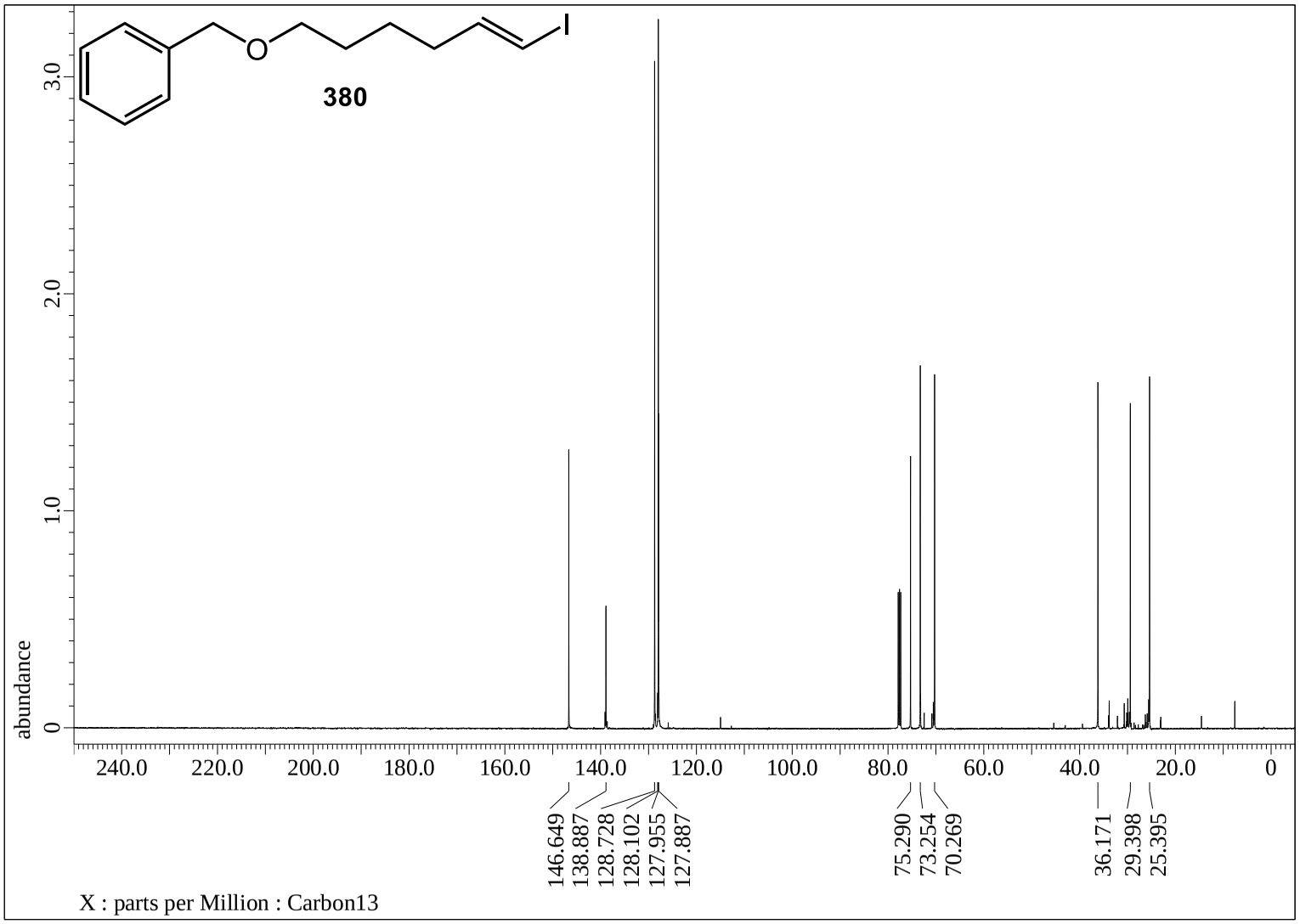


Figure A3.11: ^{13}C-NMR spectrum of 380 (500 MHz, $CDCl_3$)

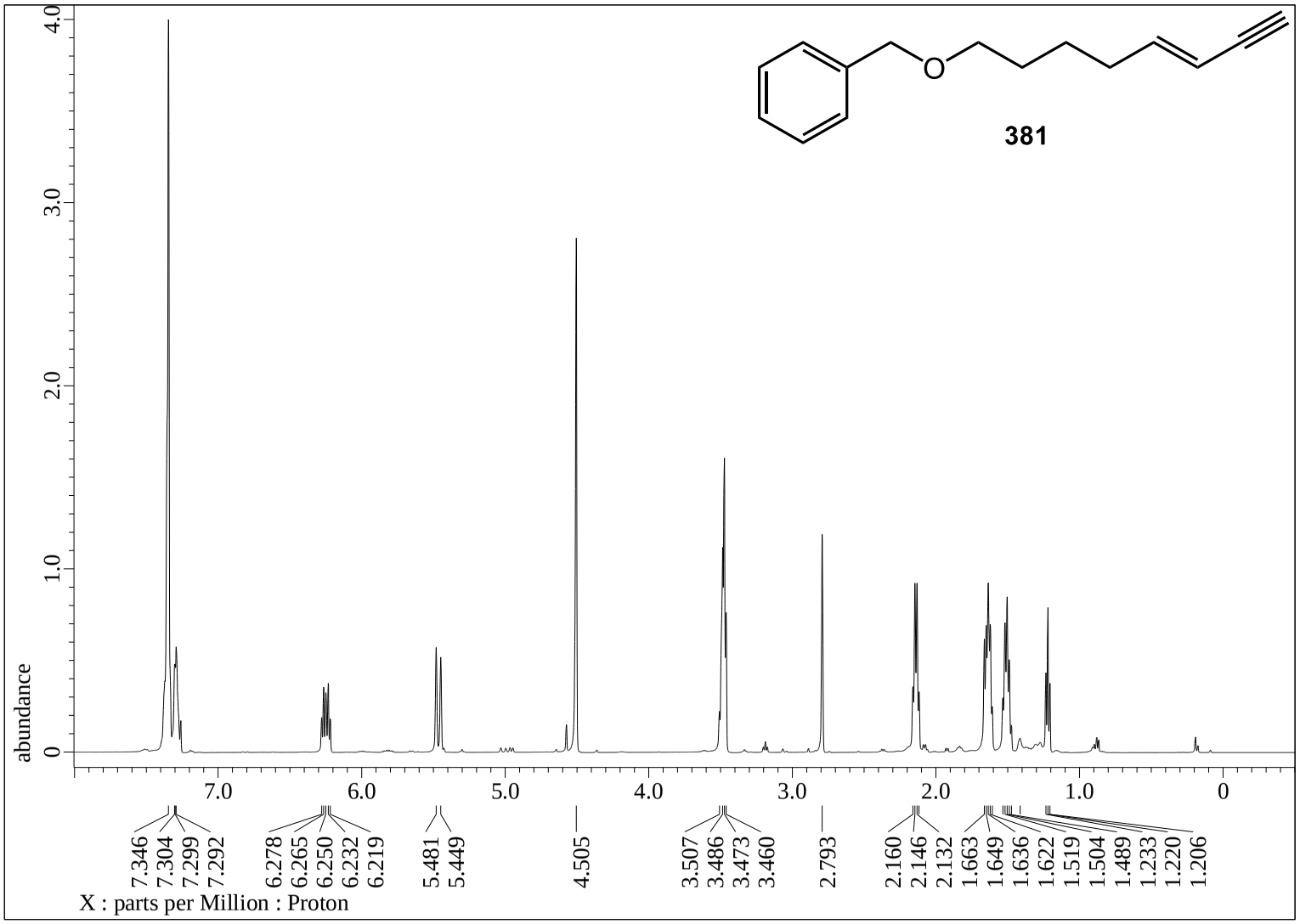


Figure A3.12: ^{1}H-NMR spectrum of 381 (500 MHz, $CDCl_3$)

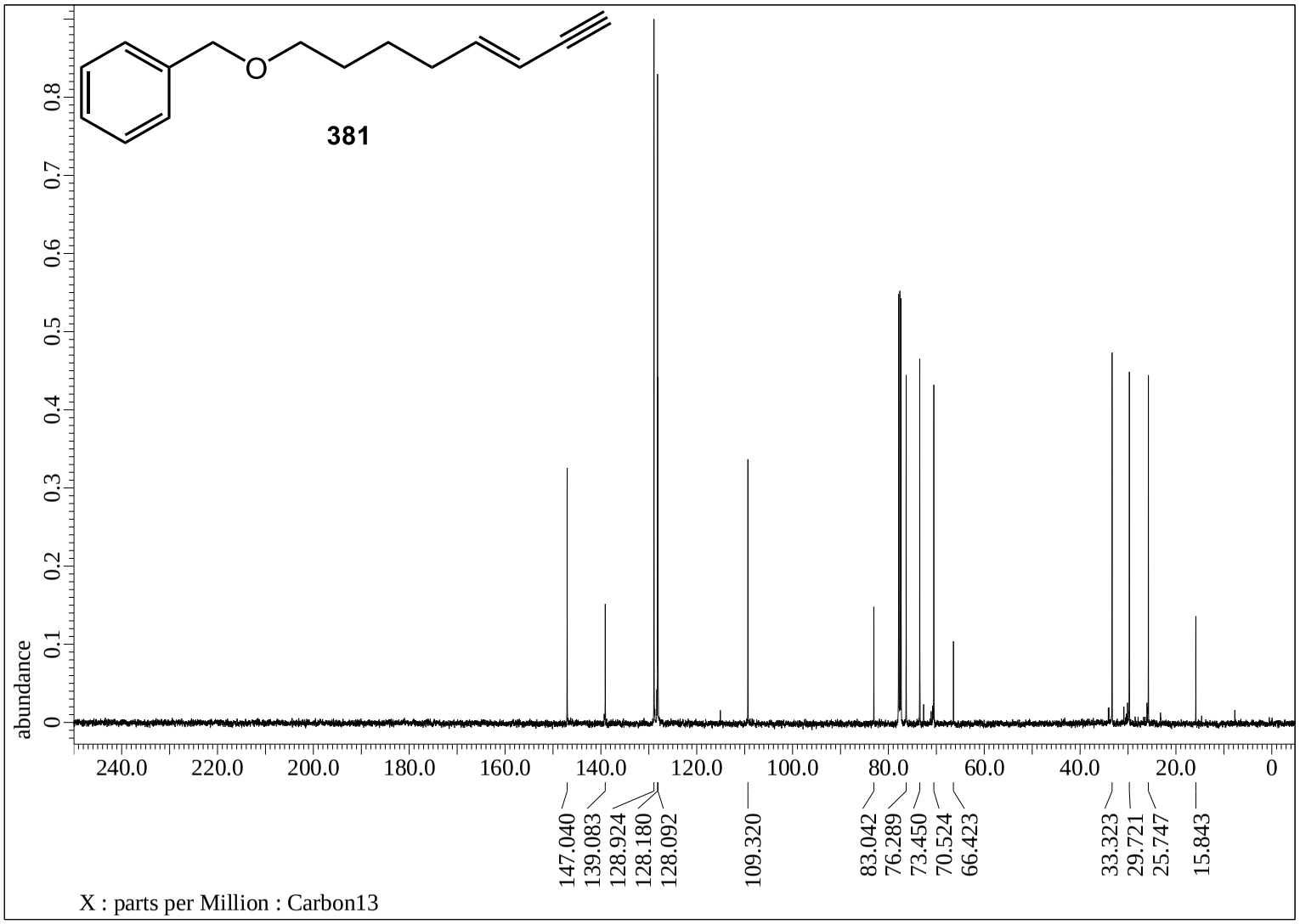


Figure A3.13: ^{13}C-NMR spectrum of 381 (500 MHz, $CDCl_3$)

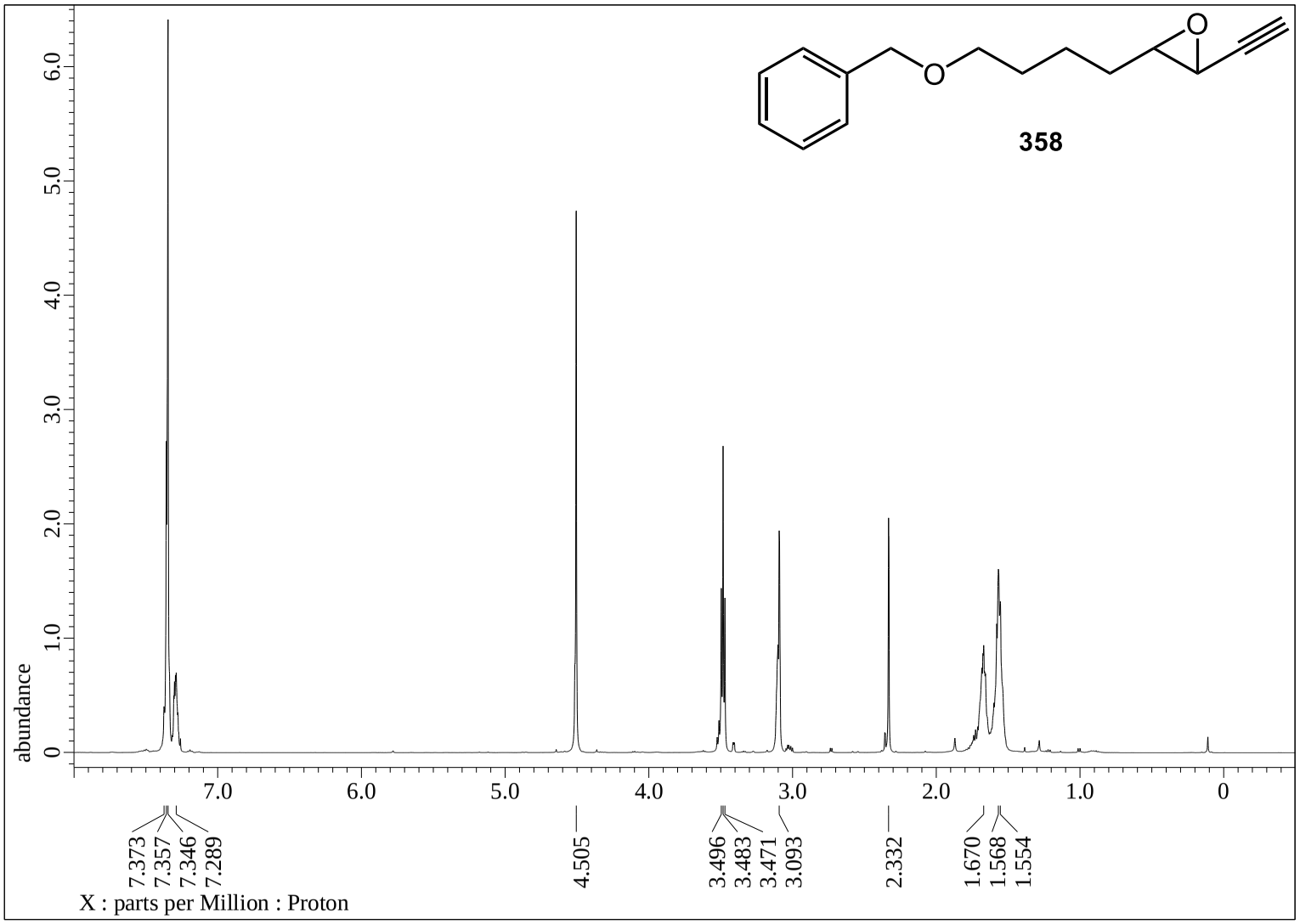


Figure A3.14: ^{1}H-NMR spectrum of 358 (500 MHz, $CDCl_3$)

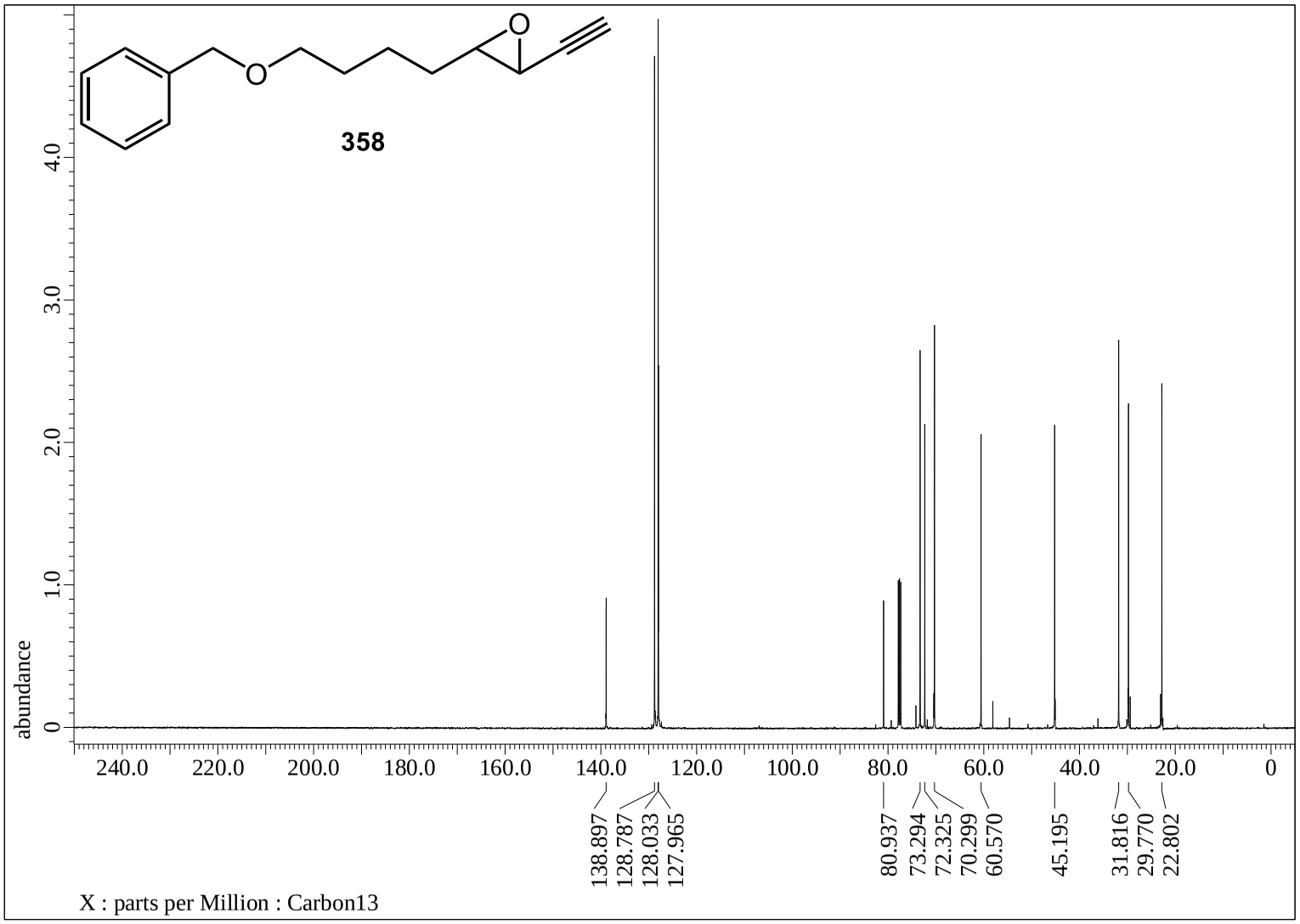


Figure A3.15: ^{13}C-NMR spectrum of 358 (500 MHz, $CDCl_3$)

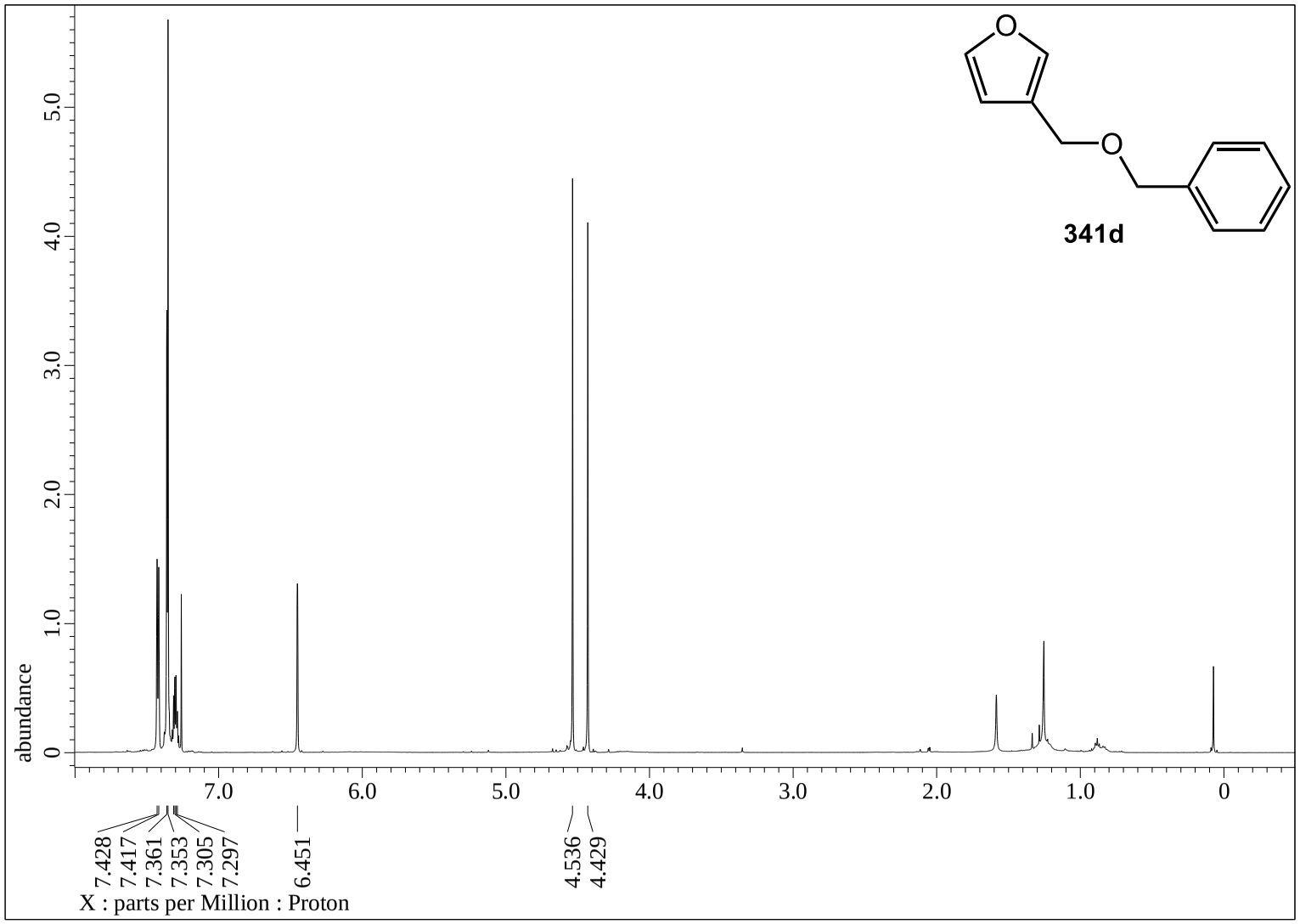


Figure S3.16: ^{1}H-NMR spectrum of 341d (500 MHz, $CDCl_3$)

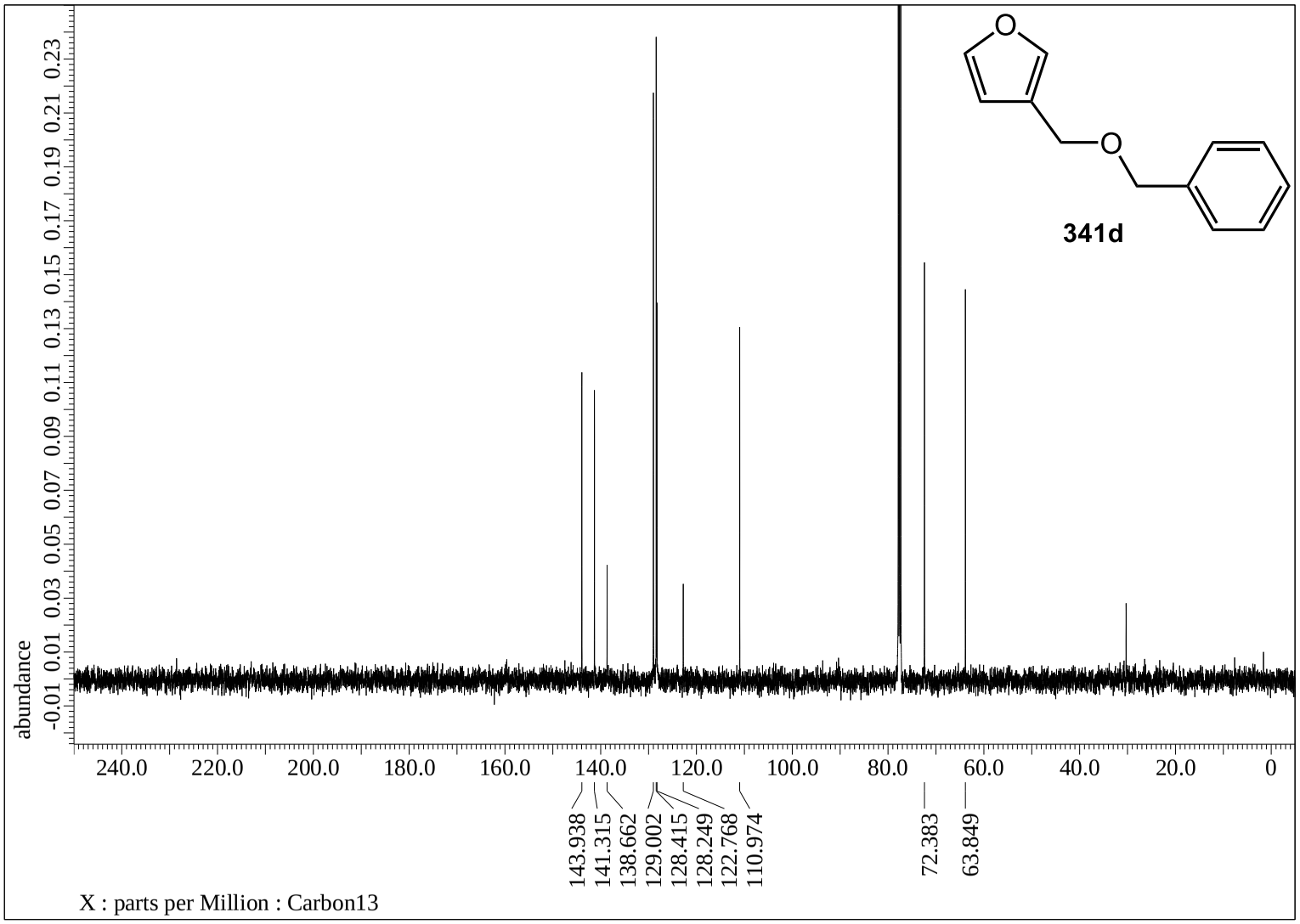


Figure A3.17: ^{13}C-NMR spectrum of 341d (500 MHz, $CDCl_3$)

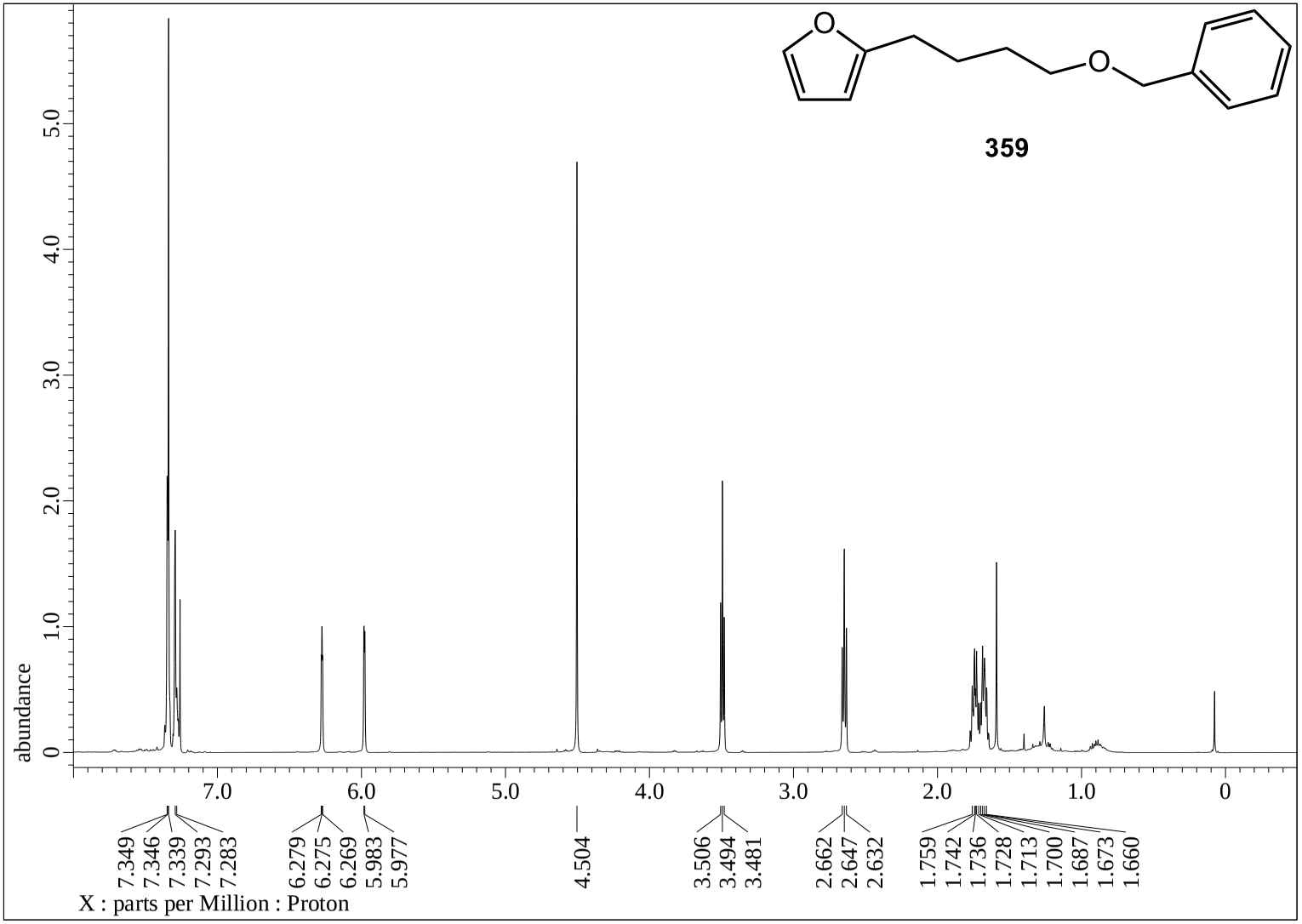


Figure A3. 18 ^{1}H-NMR spectrum of 359 (500 MHz, $CDCl_3$)

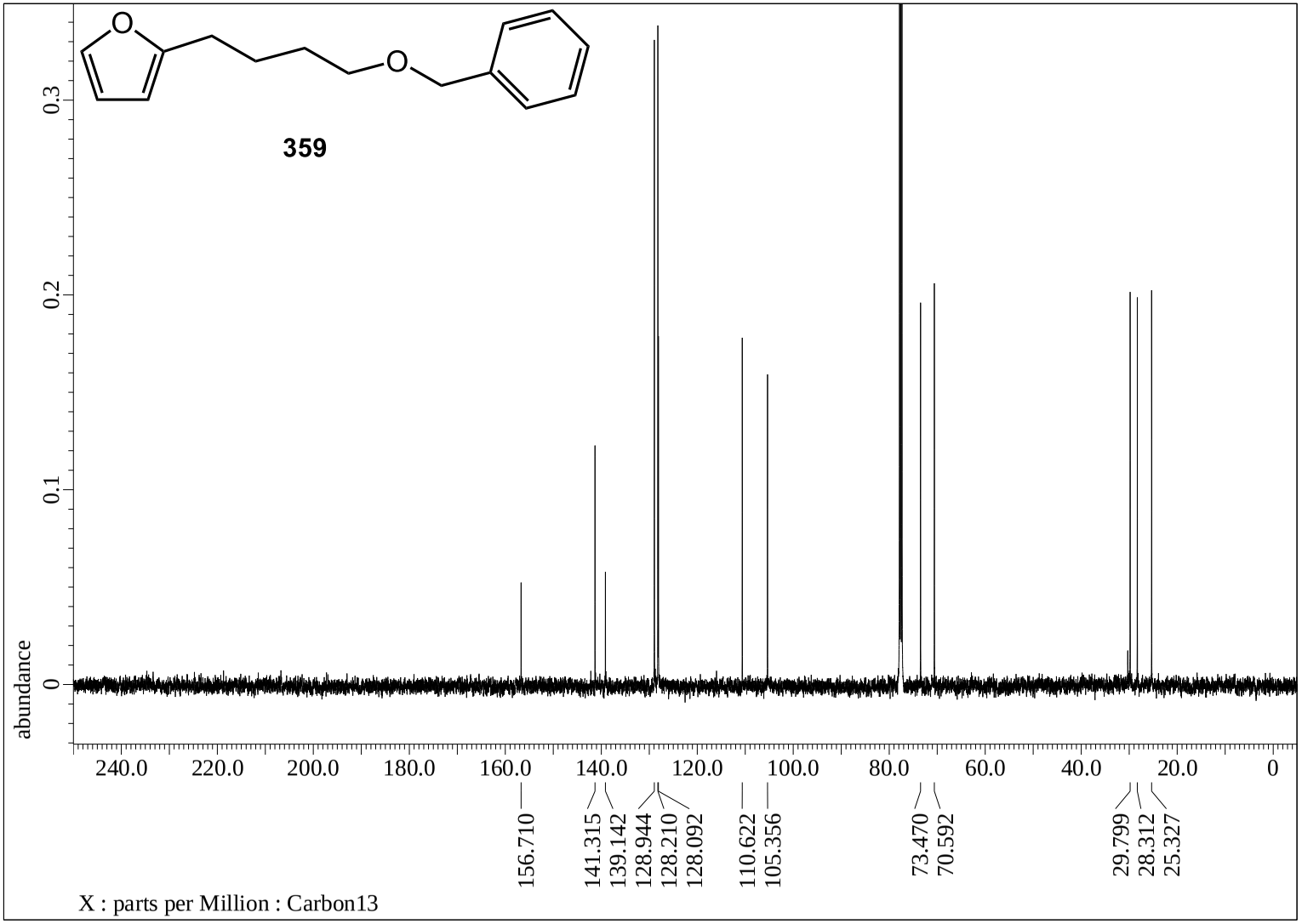


Figure A3.19: ^{13}C-NMR spectrum of 359 (500 MHz, $CDCl_3$)

Notes and References

(1) (a) Jutzi, P.; Burford, N. Structurally Diverse π-Cp Complexes of the Main Group Elements. *Chem. Rev.* **1999**, *99*, 969−990. (b) Poli, R. Monocyclopentadieny Halide Complexes of the d- and f-Block Elements *Chem. Rev.* **1991**, *91*, 509−551. (c) Coville, N. J.; Plooy, K. E.; Pickl, W. Monosubstituted Cyclopentadienyl Half-Sandwich Transition Metal Complexes *Coord. Chem. Rev.* **1992**, *116*, 1−267.

(2) Kondo, T.; Uenoyama, S.-Y.; Fujita, K.-I.; Mitsudo, T.-A. "First Transition-Metal Complex Catalyzed Addition of Organic Disulfides to Alkenes Enables the Rapid Synthesis of *Vicinal*-Dithioethers" *J. Am. Chem. Soc.* **1999**, *121*, 482−483.

(3) Curtis, M. D.; Shiu, K.-B.; Butler, W. M.; Huffman, J. C. Syntheses, Structures, and Molecular Orbital Anals of Hydridotris(pyrazolyl)borate (Tp) Molybdenum Carbonyls: Paramagnetic $TpMo(CO)_3$ and Triply Bonded $Tp_2Mo_2(CO)_4$ (Mo≡Mo) *J. Am. Chem. Soc.* **1986**, *108*, 3335−3343.

(4) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols *Eur. J. Org. Chem.* **2006**, *2006*, 881−890.

(5) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols. *J. Am. Chem. Soc.* **2002**, *124*, 11846−11847.

(6) Nishibayashi Y.; Wakiji, I.; Hidai, M. "Novel Propargylic Substitution Reactions Catalyzed by Thiolate-Bridged Diruthenium Complexes via Allenylidene Intermediates" *J. Am. Chem. Soc.* **2000**, *122*, 11019−11020.

(7) Berke, H.; Huttner, G.; von Seyerl, Struktur und Reaktivität von Carbonyl (cyclopentadienyl) (allenyliden) -Komplexen J. *Z. Naturforsch.* **1981**, *36b*, 1277−1288.

(8) Trofimenko, S. Boron-Pyrazole Chemistry. II. Poly(1-pyrazolyl)borates *J. Am. Chem. Soc.* **1967**, *89*, 3170-3177.

(9)(a) Santini, C.; Pellei, M.; Gioia Lobbia, G.; Alidori, S.; Berrettini, M.; Fedeli, D. New (Diphenylphosphane)benzoic Acid Copper(I) Derivatives of ''Scorpionate'' Ligands with Superoxide Scavenging Activity *Inorg Chim Acta* **2004**, *357*, 3349−3555 (b) Millar J. A.; Doonan, J.C.; Laughlin, J. L.; Tiekink, T. R. R.; Young, G. C. Atom Transfer Chemistry and Electrochemical Behavior of Mo(VI) and Mo(V) Trispyrazolylborate Complexes: New Mononuclear and Dinuclear Species *Inorg. Chim. Acta* **2002**, *337*, 393−406. (c) Doonan, C. J.; Nielsen, D. J.; Smith, P. D.; White, J. W.; George, G. N.; Young, C. G. Models for the Molybdenum Hydroxylases: Synthesis, Characterization and Reactivity of *cis*-Oxosulfido-Mo(VI) Complexes *J. Am. Chem. Soc.* **2006**, *128*, 305−316. (d) Sun, -J. Y.; Zhang, Z. L.; Cheng, P.; Lin,.-K. H.; Yan, -P. S., Liao, -Z. D.; Jiang, -H. Z.; Shen -W. P. Spectroscopic Properties, Catalytic Activities and Mechanism Studies of $(Tp^{Ph})Co(X)(CH_3OH)nCH_3OH$: Bicarbonate Dehydration in the Presence of Inhibitors *Biophys. Chem.* **2004**, *109*, 281−293; (e) Dias, H. V. R.; Lu, H.-L.; Kim, H.-J.; Polach, S. A.; Goh, T. K. H. H.; Browning, R. G.; Lovely, C. J. Copper(I) Ethylene Adducts and Aziridination Catalysts Based on Fluorinated Tris(pyrazolyl)borates $[HB(3\text{-}(CF_3),5\text{-}(R)Pz)_3]^-$ (where R = CF_3, C_6H_5, H; Pz = pyrazolyl) *Organometallics* **2002**, *21*, 1466−1473

(f) Trofimenko, S. Transition Metal Polypyrazolylborates Containing Other Ligands *J. Am. Chem. Soc.* **1969**, *91*, 588−595. (g) Santini, C.; Lobbia, G. G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. Syntheses and Spectroscopic and Structural Characterization of Silver(I) Complexes Containing Tertiary Phosphines and Hydrotris(pyrazol-1-yl)-Hydrotris(4-bromopyrazol-1-yl)-, Hydrotris(3,5-dimethypyrazol-1-yl)-, and Hydrotris(3-methyl-2-thioxo-1-imidazolyl)borates *Inorg. Chem.* **1998***, 37,* 890−900. (h) Liu, X.; Xing, N.; Song, J.; Wu, Q.; Yan, Z.; Zhang, Y.; Xing, Y. Two Novel Oxomolybdenum(V)-Trispyrazolylborate Complexes: Synthesis, Structure, and Catalytic Performance in the Cyclohexane Oxidation *Polyhedron* **2015**, *102*, 386−393.

(10) (a) Wilson, D. C.; Nelson, J. H. Reactions of Ruthenium(II) Tris(pyrazolyl)borate and tris(pyrazolyl)methane Complexes with Diphenylvinylphosphine and 3,4-dimethyl-1-Phenylphosphole *J. Organomet. Chem.* **2003**, *682*, 272−289. (b) Ashworth, V. T.; Singleton, E. Hough, J. J. Cationic Ruthenium(II) Systems. Part 1. The Preparation and Reactivity of Diene(hydrazine)ruthenium(II) Cations, and the Formation of Aminobonded Hydrazone Complexes *J. Chem. Soc., Dalton Trans.* **1977**, *19*, 1809−1815. (c)Tenorio, M. J.; Puerta, M. C.; Valerga, P. Atom-Economical Synthesis of the Versatile Ruthenium Precursor [TpRuCl(COD)] (Tp=Hydrotris(pyrazol-1-yl)borate) Discloses a Diamine Ligand Dealkylation Process *Organometallics* **2015**, *34*, 1001−1004.

(11)Standfest-Hauser, C.; Mereiter, C.; Schmid, R.; Kirchner, K. Reaction of Diaryl Disulfides with RuTp(COD)Cl in *N*,*N*‘-Dimethylformamide: Formation of 2 (Arylmercapto)aryl Mercaptan Complexes *Organometallics* **2004**, *23*, 2194−2196.

(12) Pavlik, S.; Puchberger, M.; Mereiter, K.; Kirchner, K. Synthesis and Reactivity of the RuIII Complexes [RuTp(PR_3)Cl_2] − Precursors for RuTp Dihydrogen Complexes *Eur. J. Inorg. Chem.* **2006**, 4137-4142.

(13) (a) Kharasch, M. S.; Brown, H. C. Chlorinations with Sulfuryl Chloride, I. The Peroxide-Catalyzed Chlorination of Hydrocarbons *J. Am. Chem. Soc.* **1939**, *61*, 2142−2150. (b) Harvey, L.; Gleicher, T. G.; Totherow, D. W.; Radical Chlorination of Substituted *t*-Butylbenzenes *Tetrahedron*, **1969**, *25*, 5019−5026

(14) Young, C. G.; Thomas, S.; Gable, R. W. Halocarbonyltungsten(II) Complexes Containing Tripodal Tris(pyrazolyl)borate Ligands *Inorg. Chem.* **1998**, *37*, 1299−1306.

(15) Morales-Ceron, P. J.; Salazar-Pereda, V.; Mendoza-Espinosa, D. Alvarado-Rodríguez, G. J.; Cruz-Borbolla, J.; Andrade-Lopez, N.; and Vazquez-Perez, M. J. “Synthesis of Ir(III) Complexes with $Tp^{Me}{}_2$ and acac Ligands and their Reactivity with Electrophiles “ *Dalton Trans.*, **2015**, *44*, 13881−13889.

(16) Rodrıǵuez-Franco, M. I.; Dorronsoro, I.; Hernańdez-Higueras, A. I.; Antequera, G. A Mild and Efficient Mthod for the Regioselective Iodination of Pyrazoles *Tetrahedron Lett.* **2001**, *42*, 863−865.

(17) Olsen, L. K.; Jensen, R. M.; MackKay, A. J., A Mild Halogenation of Pyrazoles Using Sodium Halide Salts and Oxone *Tetrahedron Lett.* **2017**, *58*, 4111−4114.

(18) (a) Minisci, F.; Bernardi, R.; Bertini, F.; Galli, R.; Perchinummo, M. Nucleophilic Character of Alkyl radicals—VI: A New Convenient Selective Alkylation of Heteroaromatic Bases. Tetrahedron **1971**, *27*, 3575−3579 (b) Begg, C.; Grimmett, M.; Yu-Man, L. The

Synthesis of 2-Alkyl- and 2-Acyl-Imidazoles by Substitution Methods. *Aust. J. Chem.* **1973**, *26*, 415−420.

(19) (a) Patrick, T. B.; Johri, K. K.; White, D. H. "FIuoro-decarboxylation with Xenon Difluoride" *J. Org. Chem.* **1983**, *48*, 4158−4159. (b) Eisenberg, M.; DesMarteau, D. D. The Reaction of Xenon Difluoride with Some Strong Oxy-acid *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29−34.

(20) *Modern Nucleophilic Aromatic Substitution.*; Terrier, F.: Wiley: **2013**, pp 1−94.

(21) Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. Innate C-H Trifluoromethylation of Heterocycles. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 14411−14415.

(22) Fujiwara, Y.; Dixon, J.A.; O'Hara, F.; Daa Funder, E.; Dixon, D.D.; Rodriguez, R.A.; Baxter, R.D.; Herlé, B.; Sach, N.; Collins, M.R.; Ishihara, Y.; Baran, P.S. Practical and Innate Carbon-Hydrogen Functionalization of Heterocycles, *Nature* **2012**, *492*, 95−100.

(23) Matlachowski, C.; Schwalbe, M. Synthesis and Characterization of Mono- and Dinuclear Phenanthroline-extended Tetramesitylporphyrin Complexes as well as UV-Vis and EPR Studies on their One-electron Reduced Species *Dalton Trans.* **2013**, *42*, 3490−3503.

(24) Kang, Y.; Zyryanov, V. G.; Rudkevich, M. D.; Disproportionation Reaction of NO_2/N_2O_4 with a Ru(II) Porphyrin *Chem. Commun.* **2003**, *19*, 2470−2471

(25) Ravi, P.; Gore, M. G.; Sikder, K. A.; Tewari, P. S. Silica–sulfuric Acid Catalyzed Nitrodeiodination of Iodopyrazoles *Synthetic Communications* **2012**, *142*, 3463–3471.

(26) Tschaen, D. M.; Desmond, R.; King, A. O.; Fortin, M. C.; Pipik, B.; King, S.; Verhoeven, T. R. An Improved Procedure for Aromatic Cyanation *Synth. Commun.* **1994**, *24*, 887−890.

(27) (a) Parlier, A.; Rudler, H. J. Direct Formation of Fischer-type Carbene Complexes from $W(CO)_6$ and Alkynes *Chem. Soc, Chem. Commun.* **1986**, 514−515. (b) Mutoh, Y.; Ikeda, Y.; Kimura, Y.; Ishii, Y. Internal Alkyne-to-vinylidene Isomerization at Cationic Ruthenium and Iron Complexes *Chem.Lett.* **2009**, *38*, 534−535. (c) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. Some Neutral Ruthenium Vinylidene Complexes and a Novel 1,3-Elimination Reaction: Preparation of Chiral Ruthenium Acetylides *J. Organomet. Chem.* **1996**, *522*, 307−310. (d) Ilg, K.; Werner, H. The First Structurally Characterized Metal Complex with the Molecular Unit M=C=C=C=CR *Angew. Chem. Int. Ed.* **2000**, *39*, 1632−1634. (e) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. First Isolable Pentatetraenylidene Metal Complex Containing the $Ru=C=C=C=CPh_2$ Assembly. A Key Intermediate to Provide Functional Allenylidene Complexes *J. Am. Chem. Soc.* **1994**, *116*, 11157−11158. (f) Dede, M; Drexler, M.; Fischer, H. Heptahexaenylidene Complexes: Synthesis and Characterization of the First Complexes with an $M=C=C=C=C=C=CR_2$ Moiety (M = Cr, W) *Organometallics* **2007**, *26*, 4294−4299.

(28) Cadierno, V.; Gimeno, J. "Allenylidene and Higher Cumulenylidene Complexes." *Chem. Rev.* **2009**, *109*, 3512−3560.

(29) Dykstra, C. E.; Parsons, C. A.; Oates, C. L. Structures and Energies of Cumulene Carbenes *J. Am. Chem. Soc.* **1979**, *101*, 1962−1965.

(30)(a) Novak, B. M.; Grubbs, R. H. Catalytic Organometallic Chemistry in Water: The Aqueous Ring-opening Metathesis Polymerization of 7-Oxanorbornene Derivatives. *J. Am. Chem. Soc.* **1988**, *110*, 7542−7543. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. Ring-opening Metathesis Polymerization (ROMP) of Norbornene by a Group VIII Carbene Complex in Protic Media. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (c) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. Increased Ring Closing Metathesis Activity of Ruthenium-based Olefin Metathesis Catalysts Coordinated with Imidazolin-2-ylidene Ligands. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (d) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. A Recyclable Ru-based Metathesis Catalyst. *J. Am. Chem. Soc.* **1999**, *121*, 791−799. (e) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. Efficient and Recyclable Monomeric and Dendritic Ru-based Metathesis Catalysts. *J. Am. Chem. Soc.* **2000**, *122*, 8168−8179. (f) Grela, K.; Harutyunyan, S.; Michrowska, A. A Highly Efficient Ruthenium Catalyst for Metathesis Reactions. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038−4040. (g) Dinger, M. B.; Mol, J. C. High Turnover Numbers with Ruthenium-based Metathesis Catalysts. *Adv. Synth. Catal.* **2002**, *344*, 671−677. (h) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. Latent Ruthenium Olefin Metathesis Catalysts that Contain an *N*-Heterocyclic Carbene Ligand. *Organometallics* **2004**, *23*, 5399−5401. (i) Ritter, T.; Day, M. W.; Grubbs, R. H. Rate Acceleration in Olefin Metathesis through a Fluorine-ruthenium Interaction. *J. Am. Chem. Soc.* **2006**, *128*, 11768−11769. (j) Funk, T. W.; Berlin, J. M.; Grubbs, R. H. Highly Active Chiral Ruthenium Catalysts for Asymmetric Ring-closing Olefin Metathesis. *J. Am. Chem. Soc.* **2006**, *128*, 1840−1846.

(31) (a) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Rodríguez, M. A. Activation of Propargylic Alcohols Derived from Hormonal Steroids by the Indenyl-Ruthenium(II) Complex [RuCl(η^5-C_9H_7)(PPh_3)$_2$]. *Organometallics* **2002**, *21*, 203−209. (b) Cadierno, V.; Diez, J.; Garcia-Garrido, E. S.; Gimeno J., [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] a Mononuclear 16e$^-$ Ruthenium(II) Catalyst for Propargylic Substitution and Isomerization of HC≡CCPh_2(OH). *J. Chem. Commun.* **2004**, 2716−2717. (c) Fischmeister, C.; Toupet, L.; Dixneuf, P. H. Direct Propargylation of Furan and Arene by Propargylic Alcohols Promoted by Bisoxazoline-ruthenium Catalysts. *New J. Chem.* **2005**, *29*, 765−768. (d) Bustelo, E.; Dixneuf, P. H. Mononuclear Ruthenium Catalysts for the Direct Propargylation of Heterocycles with Propargyl Alcohols. *Adv. Synth. Catal.* **2005**, *347*, 393−397. (e) Inada, Y.; Nishibayashi, Y.; Uemura, S. Ruthenium-catalyzed Asymmetric Propargylic Substitution Reactions of Propargylic Alcohols with Acetone. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715−7717. (f) Widaman, A. K.; Rath, N. P.; Bauer, E. B. New Five-coordinate Ru(II) Phosphoramidite Complexes and Their Catalytic Activity in Propargylic Amination Reactions. *New J. Chem.* **2011**, *35*, 2427−2434. (g) Senda, Y.; Nakajima, K.; Nishibayashi, Y. Cooperative Catalysis Enantioselective Propargylic Alkylation of Propargylic Alcohols with Enecarbamates Using Ruthenium Phosphoramide Hybrid Catalysts. *Angew. Chem., Int. Ed.* **2015**, *54*, 4060−4064.

(32) Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. Reaction of the RuTp(PR_3)Cl Fragment with Alkynols: Formation of Carbene, Vinylidene, Allenylidene, and Carbyne Complexes *J. Organomet. Chem.* **2005**, *690*, 5497−5507.

(33) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. Ruthenium Tris(pyrazolyl)borate Complexes. 1. Synthesis and Reactivity of

Ru(HB(pz)3)(COD)X (X = Cl, Br) and Ru(HB(pz)3)(L2)Cl (L = Nitrogen and Phosphorus Donor Ligands). *Organometallics* **1996**, *15*, 3998−4004.

(34) Slugovc, C.; Sapunov, N. V.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. Ruthenium(II) Tris(pyrazolyl)borate Complexes. Reversible Vinylidene Complex Formation *J. Chem. Soc., Dalton Trans.* **1997**, *22*, 4209−4216

(35) Zhang, T.; Brumboiu, I. E.; Grazioli, C.; Guarnaccio, A.; Coreno, M.; de Simone, M.; Santagata, A.; Rensmo, H.; Brena, B.; Lanzilotto, V.; Puglia, C. Lone-pair Delocalization Effects within Electron Donor Molecules: The Case of Triphenylamine and Its Thiophene-Analog. *J. Phys. Chem. C* **2018**, *122*, 17706−17717.

(36) (a) Stephenson, T. A.; Wilkinson, G. New Complexes of Ruthenium (II) and (III) with Triphenylphosphine, Triphenylarsine, Trichlorostannate, Pyridine and Other Ligands *J. Inorg. Nucl. Chem.* **1966**, *28*, 945−956. (b) Prater, B. E. New Isocyanide Complexes of Ruthenium(II) Containing Triphenylphosphine, Triphenylarsine Triphenylstibine *J. Organomet. Chem*. **1972**, *34*, 379−386.

(37) Wuyts, L. F.; Van De Vondel, D. F.; Van Der Kelen, G. P. A Fourier Transform ^{13}C NMR Study of Phenyl-phosphorus, -arsenic, -antimony and -bismuth Derivatives *J. Organomet. Chem.* **1977**, *129*, 163−168.

(38) Chan, W. C.; Lau, C. P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. Syntheses and Characterization of Hydrotris(1-pyrazolyl)borate Dihydrogen Complexes of Ruthenium and Their Roles in Catalytic Hydrogenation Reactions *Organometallics* 1997, *16*, 34−44.

(39) Lo, C.-Y.; Guo, H.; Lian, J.-J.; Shen, F.-M.; Liu, R.-S. Efficient Synthesis of Functionalized Furans via Ruthenium-Catalyzed Cyclization of Epoxyalkyne Derivatives. *J. Org. Chem.* 2002, 67, 3930−3932.

(40) Nishibayashi Y.; Wakiji, I.; Hidai, M. “Novel Propargylic Substitution Reactions Catalyzed by Thiolate-bridged Diruthenium Complexes via Allenylidene Intermediates” *J. Am. Chem. Soc.* **2000**, *122*, 11019−11020.

(41) Touchard, D.; Dixneuf, P. H. A New Class of Carbon-rich Organometallics: The C3, C4 and C5 Metallacumulenes Ru=(C=)$_n$CR$_2$. *Coord. Chem. Rev.* **1998**, *178−180* (Part 1), 409−429.

(42) The vertical axes in the cyclic voltammograms represent the degree of current and direction. All the cyclic voltammograms were measured in clockwise direction. The upper peaks in each cyclic voltammogram show that the complexes are reduced because, the current flows out of the complexes as the applied voltage is reduced. The electron moves opposite to the current and is added to the complex in this case. Conversely, the downside peaks show that the complexes are oxidized because the electron leaves the complexes as the voltage is intensified.

(43) Naota, T.; Takaya, H.; Murahashi, S.-I. Ruthenium-Catalyzed Reactions for Organic Synthesis. *Chem. Rev.* **1998**, *98*, 2599−2660.

(44) (a) Tsuji, J.; Suzuki, H. Homogeneous Hydrogenation of Aldehyde to Alcohols Catalyzed by $RuCl_2(PPh_3)_3$ *Chem. Lett.* **1977**, *6*, 1085−1086.

(45) Evans, D. Osborn, A. J.; Jardine, H. F.; Wilkinson, G. Homogeneous Hydrogenation and Hydroformylation Using Ruthenium Complexes *Nature,* **1965**, *208*, 1203−1204

(46) (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. Synthesis of 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), an Atropisomeric Chiral Bis(triaryl)phosphine, and its Use in the Rhodium(I)-Catalyzed Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids. *J. Am. Chem. Soc.* **1980**, *102*, 7932−7934.

(b) Ikariya, T.; Ishii, Y.; Kawano, H.; Arai, T.; Saburi, M.; Yoshikawa, S.; Akutagawa, S. Synthesis of Novel Chiral Ruthenium Complexes of 2,2′-bis(Diphenylphosphino)-1,1′-Binaphthyl and their Use as Asymmetric Catalysts *J. Chem. Soc. Chem. Commun.* **1985**, *13*, 922−924. (c) Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. Asymmetric Synthesis of Isoquinoline Alkaloids by Homogeneous Catalysis *J. Am. Chem. Soc.* **1986**, *108*, 7117−7119.

(47) Sasson, Y,; Blum, J.; Dichlorotris(triphenylphosphine)ruthenium-catalyzed Hydrogen Transfer from Alcohols to Saturated and ,3-Unsaturated Ketones *J. Org. Chem.*, **1975**, *40* 1887−1896

(48) Tsuji, Y.; Mukai, T.; Kondo, T.; Watanabe, Y. Ruthenium Complex Catalyzed Allylation of Aldehydes with Allylic Acetates *J. Organomet. Chem.* **1989**, *369*, C51−C53. (b) Morisaki, Y.; Kondo, T.; Mitsudo, T. Ruthenium-Catalyzed Allylic Substitution of Cyclic Allyl Carbonates with Nucleophiles. Stereoselectivity and Scope of the Reaction *Organometallics* **1999**, *18*, 4742−4746. (c) Kondo, T.; Morisaki, Y.; Uenoyama, S.; Wada, K.; Mitsudo, T. First Ruthenium-Catalyzed Allylation of Thiols Enables the General Synthesis of Allylic Sulfides *J. Am. Chem. Soc.* **1999**, *121*, 8657−8658. (d) Onodera, G.; Imajima, H.; Yamanashi, M.; Nishibayashi, Y.; Hidai, M.; Uemura, S. Ruthenium-Catalyzed Allylation of Aromatic Compounds and Allylic Ether Formation *Organometallics* **2004**, *23*, 5841−5848. (e) Oi, S.; Tanaka, Y.; Inoue, Y. Ortho-Selective Allylation of 2-Pyridylarenes with Allyl Acetates Catalyzed by Ruthenium Complexes *Organometallics* **2006**, *25*, 4773−4778. (f) Zhang, H.-J.; Demerseman, B.; Toupet, L.; Xi, Z.; Bruneau, C. Ruthenium-Catalyzed Nucleophilic Allylic Substitution Reactions from β-Silylated Allylic Carbonates *Organometallics* **2009**, *28*, 5173−5182. (g) van Rijn, J. A.; Siegler, M. A.; Spek, A. L.; Bouwman, E.; Drent, E. Ruthenium-Diphosphine-Catalyzed Allylation of Phenols: A *gem*-Dialkyl-Type Effect Induces High Selectivity toward *O*-Allylation *Organometallics* **2009**, *28*, 7006−7014. (h) Manikandan, R.; Madasamy, P.; Jeganmohan, M. Ruthenium-Catalyzed Oxidant-Free Allylation of Aromatic Ketoximes with Allylic Acetates at Room Temperature *Chem. - Eur. J.* **2015**, *21*, 13934−13938. (i) Kumar, G. S.; Kapur, M. Ruthenium-Catalyzed, Site-selective C–H Allylation of Indoles with Allyl Alcohols as Coupling Partners *Org. Lett.* **2016**, *18*, 1112−1115. (j) Mizuno, S.; Terasaki, S.; Shinozawa T.; and Kawatsura M. Regioselective Construction of α,α-Disubstituted Allylic Amines by the Ruthenium-catalyzed Allylic Amination of Tertiary Allylic Acetates, *Org. Lett.*, **2017**, *29*, 504−507.

(49) (a) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. Highly Selective Skeletal Reorganization of 1,6- and 1,7-Enynes to 1-Vinylcycloalkenes Catalyzed by $[RuCl_2(CO)_3]$. *J. Am. Chem. Soc.* **1994**, *116*, 6049−6050. (b) Kinoshita, A.; Mori, M. Ruthenium Catalyzed Enyne Metathesis. *Synlett* **1994**, *12*, 1020−1022. (c) Stragies, R.; Schuster, M.; Blechert, S. A Crossed Yne-ene Metathesis Showing Atom Economy. *Angew. Chem., Int. Ed. Engl.*

1997, *36*, 2518−2520. (d) Mori, M.; Sakakibara, N.; Kinoshita, A. Remarkable Effect of Ethylene Gas in the Intramolecular Enyne Metathesis of Terminal Alkynes. *J. Org. Chem.* **1998**, *63*, 6082−6083. (e) Stragies, R.; Voigtmann, U.; Blechert, S. Improved Yne-ene-cross Metathesis Utilizing a Dihydroimidazole Carbene Ruthenium Complex. *Tetrahedron Lett.* **2000**, *41*, 5465−5468. (f) Smulik, J. A.; Diver, S. T. Expanded Scope in Ethylene-Alkyne Cross-metathesis Coordinating Heteroatom Functionality at the Propargylic Position. *Org. Lett.* **2000**, *2*, 2271−2274.

(50) (a) Patman, R. L.; Williams, V. M.; Bower, J. F.; Krische, M. Carbonyl Propargylation from the Alcohol or Aldehyde Oxidation Level Employing 1,3-Enynes as Surrogates to Preformed Allenylmetal Reagents. *Angew. Chem., Int. Ed.* **2008**, *47*, 5220−5223. (b) Geary, L. M.; Leung, J. C.; Krische, M. Ruthenium-Catalyzed Reductive Coupling of 1,3-Enynes and Aldehydes by Transfer Hydrogenation *anti*-Diastereoselective Carbonyl Propargylation. *J. Chem. - Eur. J.* **2012**, *18*, 16823−16827. (c) Nguyen, K. D.; Herkommer, D.; Krische, M. J. Ruthenium-BINAP Catalyzed Alcohol C−H *tert*-Prenylation via 1,3-Enyne Transfer Hydrogenation. *J. Am. Chem. Soc.* **2016**, *138*, 5238−5241.

(51) Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. Enantioselective Copper-Catalyzed Propargylic Amination *Angew. Chem. Int. Ed.* **2008**, *47*, 3777−3780.

(52)Sherry, D. B.; Radosevich, T. A.; Toste, D. F.; A Mild C-O Bond Formation Catalyzed by a Rhenium-oxo Complex *J. Am. Chem. Soc.* **2003**, *125*, 6076−6077.

(53)Georgy, M.; Boucard, V.; Campagne, J. Gold(III)-Catalyzed Nucleophilic Substitution of Propargylic Alcohols *J. Am. Chem. Soc.* **2005**, *127*, 14180−14181

(54) Evans, P. A.; Lawler, M. J., Rhodium-Catalyzed Propargylic Substitution: A Divergent Approach to Propargylic and Allenyl Sulfonamides *Angew. Chem., Int. Ed*., **2006**, *45*, 4970−4972.

(55) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. Cp*Ru(cod)Cl-Catalyzed [2 + 2 + 2] Cycloaddition of 1,6-Heptadiynes with Allylic Ethers. A Decisive Role of Coordination to the Ether Oxygen Atom *J. Org. Chem.* **1998**, *63*, 9610−9611.

(56) Taber, D. F.; Meagley, R. P.; Louey, J. P.; Rheingold, A. L. Molecular Complex Design: Bridging the *tetrakis*Carboxykatidirhodium Core *Inorg. Chim. Acta* **1995**, *239*, 25−28.

(57) El Arba, M.; Dibrell, S. E.; Meece, F.; Frantz, D. E. Ru(II)-catalyzed Synthesis of Substituted Furans and Their Conversion to Butenolides. *Org. Lett.* **2018**, *20*, 5886−5888.

(58)Bruce, M. I. Transition Metal Complexes Containing Allenylidene, Cumulenylidene, and Related Ligands. *Chem. Rev.* **1998**, *98*, 2797−2858.

(59) (a) Zhang, L.; Zhang, G.; Wang, P.; Li, Y.; Lei, A. Electrochemical Oxidation with Lewis-acid Catalysis Leads to Trifluoromethylative Difunctionalization of Alkenes Using CF_3SO_2Na. *Org. Lett.* **2018**, *20*, 7396−7399. (b) Wang, M.; Huan, L.; Zhu, C. Cyanohydrin-Mediated Cyanation of Remote Unactivated C(sp_3)-H bonds *Org. Lett.* **2019**, *21*, 821−825.