

University of Nevada, Reno

Synthesis and Characterization of Ruthenium (II) Complexes and their Applications to Atom Transfer Radical Addition Reactions

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requirements

for the degree of

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By

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University of Nevada, Reno
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THE GRADUATE SCHOOL

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prepared under our supervision by

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Abstract

A series of mixed-phosphine ruthenium complexes of the type $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$, where $\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}, \text{Tp}$; $\text{PR}_3 = \text{PTA}$ or PMe_3 have been synthesized by ligand exchange reactions with $\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl}$, and characterized by multinuclear NMR spectroscopy and X-ray crystallography. We have explored the efficiency of these complexes as catalysts for the atom transfer radical addition (ATRA) of various chloro-substrates (CCl_4 , CHCl_3 , $p\text{-TsCl}$, $\text{CCl}_3\text{CO}_2\text{Et}$, and $\text{CH}_2\text{ClCO}_2\text{Et}$) to styrene in the presence of AIBN as a radical source. For comparison purposes, we also investigated the activity of $\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and $\text{Cp}'\text{Ru}(\text{PTA})_2\text{Cl}$ complexes towards ATRA. In general, these complexes efficiently catalyzed the radical addition reactions affording the 1:1 adduct in almost quantitative yields. Catalyst performance was found to depend mainly on the electron-donating ability of the Cp' ancillary ligands and on the nature of the phosphines. Among the ruthenium (II) complexes studied $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ and $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ were very active at 60°C with TOFs of 1060 h^{-1} and 933 h^{-1} , respectively; $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ was the most active for the addition of CCl_4 to styrene with a TOF $>960\text{ h}^{-1}$ at room temperature. The reactivity decreased significantly upon substitution of the labile PPh_3 with stronger binding phosphines such as PTA or PMe_3 ($\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl} > \text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl} > \text{Cp}'\text{Ru}(\text{PTA})_2\text{Cl}$). Based on the Cp' ancillary ligand, the order of reactivity was found to be: $\text{Cp}^*\text{Ru} \gg \text{DpRu} > \text{IndRu} > \text{CpRu} > \text{TpRu}$.

The activity of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$, $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$, and $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ was further explored for the addition of CCl_4 to more challenging

olefins. Both terminal and internal olefins were utilized for the addition reactions. All the three complexes exhibited high reactivity towards CCl_4 addition to terminal olefins. Total turnovers (TTO) in excess of 80,000 were obtained for the addition of CCl_4 to hexene, making the Cp^* complexes the most active and robust catalysts for ATRA reported to date. Contrary to this, the internal olefins were less prone to CCl_4 addition whatever the catalytic system may be. These results indicate that the rate of the reaction depends not only on the type of catalyst, but also on the nature of substrate employed.

The synthesis and characterization of the air-sensitive hydride, $\text{IndRu(PTA)(PPh}_3\text{)H}$, is also described. The rate of H/D exchange of the hydride complex was found to be very low ($t_{1/2} \sim 5.5$ d). We explored the activity of $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ for the selective transfer hydrogenation of α,β -unsaturated carbonyl compounds in aqueous-biphasic media. Electrochemical studies on some of the $\text{Cp}'\text{Ru(PR}_3\text{)(PPh}_3\text{)Cl}$ complexes in dichloromethane are also reported.

Dedicated to
My parents and husband

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Table of Contents

	Page
Abstract	i
Dedication	iii
Acknowledgements	iv
Table of Contents	vi
List of Tables	x
List of Figures	xii
Abbreviations	xviii
Compound Numbers	xiv
Chapter 1 Introduction and Background	
1.1 Ruthenium in Catalysis	1
1.2 Hydrogenation and Transfer Hydrogenation	2
1.3 Kharasch Addition (Atom Transfer Radical Addition)	6
1.3.1 Overview	6
1.3.2 Mechanistic Insights	8
1.3.3 ATRA in Organic Synthesis	10
1.3.4 Ruthenium-based catalysts in ATRA	12
1.4 Organization and Scope	16

1.5	References	17
Chapter 2	Synthesis and characterization of half-sandwich ruthenium (II) complexes of general formula $\text{Cp}'\text{RuCl}(\text{PPh}_3)(\text{PR}_3)$ [$\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}, \text{Tp}$; $\text{PR}_3 = \text{PTA}, \text{PMe}_3$]	
2.1	Introduction	25
2.2	Experimental Section	27
2.2.1	Materials and Methods	27
2.2.2	Synthesis	28
2.2.3	Transfer Hydrogenation Procedure	33
2.2.4	X-Ray Crystallography	34
2.3	Results and Discussion	36
2.3.1	Synthesis and Characterization of $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ Complexes	36
2.3.2	Structures of Ruthenium Complexes 1, 3, 6, 8, and 10	44
2.3.3	Structure of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$	48
2.3.4	$\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$: Synthesis, Characterization and Structure	49
2.3.5	$\text{CpRu}(\text{PTA})_2\text{SnCl}_3$: Synthesis, Characterization and Structure	51
2.3.6	Electrochemical Studies	53
2.3.7	Reactivity of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$	57
2.3.8	Reactivity of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$	58

2.4	Conclusion	60
2.5	References	61

Chapter 3 Atom transfer radical addition reactions of various organic halides (CCl_4 , *p*-TsCl, $\text{CCl}_3\text{CO}_2\text{Et}$, $\text{CH}_2\text{ClCO}_2\text{Et}$, and CHCl_3) to styrene catalyzed by $\text{Cp}^*\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes

3.1	Introduction	65
3.2	Experimental Section	68
3.2.1	Materials and Methods	68
3.2.2	Atom Transfer Radical Addition Procedure	69
3.3	Results and Discussion	71
3.3.1	ATRA of CCl_4 to styrene	71
3.3.2	Role of AIBN	79
3.3.3	ATRA of <i>p</i> -toluenesulfonyl chloride to styrene	81
3.3.4	ATRA of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene	85
3.3.5	ATRA of CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene	89
3.3.6	Variations in TOF values	92
3.3.7	Significance of phosphine dissociation in ATRA	93
3.4	Conclusion	94
3.5	References	95

Chapter 4	Atom transfer radical addition of CCl₄ to more challenging substrates catalyzed by Cp*Ru(PPh₃)(PR₃)Cl [PR₃ = PTA, PMe₃, PPh₃] complexes	
4.1	Introduction	99
4.2	Experimental Section	101
4.2.1	Materials and Methods	101
4.2.2	X-Ray Crystallography	102
4.2.3	Catalytic Experiments	102
4.3	Results and Discussion	105
4.3.1	Catalytic activity	105
4.3.2	Characterization and structures of the compounds (33) and (34)	114
4.4	Conclusion	117
4.5	References	117
Chapter 5	Conclusion	119
Appendix		123

List of Tables

Table #	Title	Page #
2.1	Crystallographic data for complexes 1, 3, 6, and 8.	35
2.2	Crystallographic data for complexes 10, and 19-21.	36
2.3	$^{31}\text{P}\{^1\text{H}\}$ chemical shifts and coupling constants for the series of $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes; $\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Cp}, \text{Ind}, \text{or Tp}$, and $\text{PR}_3 = \text{PTA}$ or PMe_3 .	39
2.4	Selected Bond Lengths [\AA] and Angles [deg] for a series of $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes; $\text{Cp}' = \text{Cp}^*, \text{Ind}, \text{or Tp}$, and $\text{PR}_3 = \text{PTA}$ or PMe_3 .	48
2.5	Cyclic voltammetry data ^a of $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes ($\text{Cp}' = \text{Dp}, \text{Ind}, \text{Cp}, \text{Tp}$; $\text{PR}_3 = \text{PTA}, \text{PPh}_3$).	54
2.6	Selective transfer hydrogenation of cinnamaldehyde, benzylidene acetone, and chalcone by $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$.	60
3.1	Atom transfer radical addition of CCl_4 to styrene catalyzed by $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes 1 – 10 ($\text{PR}_3 = \text{PMe}_3, \text{PTA}$).	73
3.2	Atom transfer radical addition of CCl_4 to styrene catalyzed by $\text{Cp}'\text{Ru}(\text{PR}_3)_2\text{Cl}$ complexes 11 – 18 ($\text{PR}_3 = \text{PPh}_3, \text{PTA}$).	75
3.3	TTOs obtained at 0.005 mol% catalyst loading for the addition of CCl_4 to styrene catalyzed by $\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes ($\text{PR}_3 = \text{PTA}, \text{PMe}_3, \text{PPh}_3$).	77
3.4	Atom transfer radical addition of <i>p</i> -toluenesulfonyl chloride to styrene catalyzed by complexes 1-11.	82
3.5	Atom transfer radical addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene catalyzed by complexes 1-11.	87
3.6	Atom transfer radical additions of CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene catalyzed by complexes 1, 6 and 11.	90

3.7	TOFs calculated at different times for the addition of CCl ₄ to styrene.	92
3.8	TOFs calculated at different times for the addition of <i>p</i> -TsCl to styrene.	92
4.1	Crystallographic data for compounds 33 and 34.	104
4.2	Atom transfer radical addition of CCl ₄ to terminal olefins catalyzed by Cp*Ru(PTA)(PPh ₃)Cl (1), Cp*Ru(PMe ₃)(PPh ₃)Cl (6), and Cp*Ru(PPh ₃) ₂ Cl (11).	107
4.3	Atom transfer radical addition of CCl ₄ to internal olefins catalyzed by Cp*Ru(PTA)(PPh ₃)Cl (1), Cp*Ru(PMe ₃)(PPh ₃)Cl (6), and Cp*Ru(PPh ₃) ₂ Cl (11).	110

List of Figures

Figure #	Title	Page #
1.1	Ruthenium-catalyzed hydrogenation reactions.	3
1.2	Ruthenium-catalyzed asymmetric hydrogenation.	4
1.3	ATRA and related reactions.	11
1.4	Ruthenium half-sandwich complexes as ATRA catalysts.	13
1.5	Ruthenium-carbene complexes as ATRA catalysts.	14
1.6	Polynuclear complexes as ATRA catalysts.	15
2.1	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) in CD_2Cl_2 .	40
2.2	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (6) in CD_2Cl_2 .	40
2.3	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19) in CD_2Cl_2 .	40
2.4	^1H NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) in CDCl_3 ; Solvent (S).	41
2.5	^1H NMR spectrum of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (3) in CD_2Cl_2 ; Solvent (S).	42
2.6	^1H NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (6) in CD_2Cl_2 ; Solvent (S).	42
2.7	^1H NMR spectrum of $\text{DpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (7) in CD_2Cl_2 ; Solvent (S).	43
2.8	^1H NMR spectrum of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (10) in CD_2Cl_2 ; Solvent (S).	43
2.9	Thermal ellipsoid (50% probability) representation of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.	45

- 2.10 Thermal ellipsoid (50% probability) representation of IndRu(PTA)(PPh₃)Cl (3) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. 46
- 2.11 Thermal ellipsoid (50% probability) representation of Cp*Ru(PMe₃)(PPh₃)Cl (6) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. 46
- 2.12 Thermal ellipsoid (50% probability) representation of IndRu(PMe₃)(PPh₃)Cl (8) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. 47
- 2.13 Thermal ellipsoid (50% probability) representation of TpRu(PMe₃)(PPh₃)Cl (10) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. 47
- 2.14 Thermal ellipsoid (50% probability) representation of the cationic complex [IndRu(PTA)₂(PPh₃)](SnCl₃) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.3076(19); Ru1-P2 = 2.2576(18); Ru1-P3 = 2.3456(19); Ru1-Ind_{cent} = 1.936; P1-Ru1-P2 = 92.99(7); P1-Ru1-P3 = 97.47(7); P2-Ru1-P3 = 95.56(7). 49
- 2.15 ¹H NMR spectrum of IndRu(PTA)(PPh₃)H (20) in CD₃OD. 50
- 2.16 Thermal ellipsoid (50% probability) representation of IndRu(PTA)(PPh₃)H (20) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.2564(8); Ru1-P2 = 2.2539(8); Ru1-H1 = 1.52(4); Ru1-Ind_{cent} = 1.929; P1-Ru1-P2 = 97.59(3); P1-Ru1-H = 83.1(15); P2-Ru1-H = 82.7(15). 51
- 2.17 ³¹P NMR spectrum of CpRu(PTA)₂SnCl₃ (21) in CD₂Cl₂. 52
- 2.18 ¹H NMR spectrum of CpRu(PTA)₂SnCl₃ (21) in D₂O; Solvent (S). 52
- 2.19 Thermal ellipsoid (50% probability) representation of CpRu(PTA)₂SnCl₃ (21) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.2747(5); Ru1-P2 = 2.2805(5); Ru1-Sn1 = 2.5319(2); P1-Ru1-P2 = 93.474(17); P1-

Ru1-Sn1 = 93.964(13); P2-Ru1-Sn1 = 91.336(13).

- 2.20 Cyclic voltammograms of Ru-complexes in dichloromethane (supporting electrolyte, 100 mM *n*Bu₄NBF₄), obtained at scan rates of 50 mV/s; (A) Cp^{*}Ru(PTA)(PPh₃)Cl complexes, (B) Cp^{*}Ru(PR₃)₂Cl complexes (PR₃ = PTA, PPh₃). 55-56
- 2.21 Plot of ln([A]/[A]₀) versus time for the H/D exchange reaction of IndRu(PTA)(PPh₃)H; peak height of the hydride at a given time (A), peak height of the hydride at zero time (A₀). 58
- 3.1 Cp^{*}Ru(PR₃)(PPh₃)Cl complexes used as catalyst precursors for ATRA. 66
- 3.2 ¹H NMR spectrum in toluene-*d*₈ of the reaction mixture, showing the 1:1 adduct **23** (1,3,3,3-tetrachloropropyl benzene) formed by the addition of CCl₄ to styrene; Internal standard (*), AIBN (▲), Solvent (S). 74
- 3.3 Comparison of the rates (TOF's in h⁻¹) of CCl₄ addition to styrene catalyzed by PTA complexes (1-4), PMe₃ complexes (6-9), and and bis-PPh₃ complexes (11-14). 74
- 3.4 Kinetics plot for the addition of CCl₄ to styrene (▲) yielding the Kharasch product (◆), (1,3,3,3-tetrachloropropyl)benzene, catalyzed by Cp^{*}Ru(PTA)(PPh₃)Cl and followed by ¹H NMR spectroscopy. Conditions: 60 °C, 1 mol% catalyst, 5 mol% AIBN. 77
- 3.5 Kinetics plot for the addition of CCl₄ to styrene yielding the Kharasch product (◆), (1,3,3,3-tetrachloropropyl)benzene, catalyzed by (A) DpRu(PTA)(PPh₃)Cl and (B) IndRu(PTA)(PPh₃)Cl followed by ¹H NMR spectroscopy in toluene-*d*₈. 78
- 3.6 Array of ¹H NMR spectra in toluene-*d*₈ for the IndRu(PTA)(PPh₃)Cl catalyzed CCl₄ addition to styrene. The spectra were recorded every half hour, at 60 °C, beginning at 1.25 h after the reaction started, and displayed from 1.2 ppm through 7.0 ppm. 79

- 3.7 Plot of [AIBN] versus time for the addition of CCl_4 to styrene catalyzed by $\text{DpRu(PTA)(PPh}_3\text{)Cl}$. 80
- 3.8 ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **24** (2-chloro-2-phenylethyl *p*-tolyl sulfone) formed by the addition of *p*-TsCl to styrene; Internal standard (*), AIBN (\blacktriangle), excess *p*-TsCl (\bullet). 83
- 3.9 Kinetics plot for the addition of *p*-TsCl to styrene yielding the Kharasch product (\blacklozenge) catalyzed by (A) $\text{Cp}^*\text{Ru(PTA)(PPh}_3\text{)Cl}$, (B) $\text{DpRu(PTA)(PPh}_3\text{)Cl}$, (C) $\text{IndRu(PTA)(PPh}_3\text{)Cl}$, and (D) $\text{CpRu(PTA)(PPh}_3\text{)Cl}$ followed by ^1H NMR spectroscopy. 84
- 3.10 Comparison of the rates (TOF's in h^{-1}) of *p*-TsCl addition to styrene catalyzed by PTA complexes (1-4) and PMe_3 complexes (6-9). 85
- 3.11 ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **25** (2,2,4-trichloro-4-phenyl-butyric acid ethyl ester) formed by $\text{CCl}_3\text{CO}_2\text{Et}$ addition to styrene; Internal standard (*), AIBN (\blacktriangle), excess $\text{CCl}_3\text{CO}_2\text{Et}$ (\bullet). 87
- 3.12 Kinetics plot for the addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene yielding the Kharasch product (\blacklozenge) catalyzed by (A) $\text{Cp}^*\text{Ru(PTA)(PPh}_3\text{)Cl}$, (B) $\text{DpRu(PTA)(PPh}_3\text{)Cl}$, (C) $\text{IndRu(PTA)(PPh}_3\text{)Cl}$, and (D) $\text{CpRu(PTA)(PPh}_3\text{)Cl}$ followed by ^1H NMR spectroscopy. 88
- 3.13 Comparison of the rates (TOF's in h^{-1}) of $\text{CCl}_3\text{CO}_2\text{Et}$ addition to styrene catalyzed by PTA complexes (1-4) and PMe_3 complexes (6-9). 89
- 3.14 ^1H NMR spectrum in CDCl_3 of the reaction mixture, showing the 1:1 adduct **26** (1,3,3-trichloropropyl-benzene) formed by the addition of CHCl_3 to styrene. Internal standard (*), AIBN (\blacktriangle), Solvent (S). 91
- 3.15 ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **27** (4-chloro-4-phenyl-butyric acid ethyl ester) formed by the addition of $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene; Internal standard (*). 91

4.1	Ruthenium complexes used as catalyst precursors for ATRA.	100
4.2	^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 28 (1,1,1,3-tetrachloro-heptane) formed by the addition of CCl_4 to hexene; internal standard (*).	106
4.3	^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 29 (1,1,1,3-tetrachloro-undecane) formed by the addition of CCl_4 to decene; internal standard (*).	108
4.4	^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 30 (2,4,4,4-tetrachloro-butyric acid butyl ester) formed by the addition of CCl_4 to <i>n</i> -butyl acrylate; internal standard (*), AIBN (\blacktriangle).	109
4.5	^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 31 (1,3,3,3-tetrachloro-2-methyl-propyl-benzene) formed by the addition of CCl_4 to <i>trans</i> - β -methyl styrene; internal standard (*), AIBN (\blacktriangle), minor isomer (\bullet).	112
4.6	^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 32 (4-chloro-4-phenyl-3-(trichloromethyl)-butan-2-one) formed by the addition of CCl_4 to benzylidene acetone; internal standard (*), AIBN (\blacktriangle), minor isomer (\bullet), benzylidene acetone (\blacklozenge).	112
4.7	^1H NMR spectrum in CDCl_3 of 3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one (33) formed by the addition of CCl_4 to chalcone; residual toluene (*), minor isomer (\bullet).	113
4.8	^1H NMR spectrum in CDCl_3 of 1,3,3,3-tetrachloro-1,2-diphenylpropane (34) formed by the addition of CCl_4 to <i>cis</i> -stilbene; residual toluene (*), minor isomer (\bullet).	113
4.9	Mass spectrum (bottom) along with computer simulation (top) of 33 (chalcone- CCl_4 adduct).	114
4.10	Mass spectrum (bottom) along with computer simulation (top) of 34 (<i>cis</i> -stilbene- CCl_4 adduct).	115

4.11	Thermal ellipsoid (50% probability) representation of chalcone- CCl ₄ adduct (33) with the atomic numbering scheme.	116
4.12	Thermal ellipsoid (50% probability) representation of <i>cis</i> -stilbene- CCl ₄ adduct (34) with the atomic numbering scheme.	116

Abbreviations

Cyclopentadienyl; (η^5 -C ₅ H ₅ ⁻)	Cp
Pentamethylcyclopentadienyl; (η^5 -C ₅ Me ₅ ⁻)	Cp*
1,2-dihydropentalenyl; (η^5 -C ₈ H ₉ ⁻)	Dp
Indenyl; (η^5 -C ₉ H ₇ ⁻)	Ind
Hydrotris(pyrazolyl)borate; (η^3 -HB(pz) ₃)	Tp
1,3,5-Triaza-7-phosphaadamantane; PN ₃ C ₆ H ₁₂	PTA
Trimethylphosphine; PC ₃ H ₉	PMe ₃
Triphenylphosphine; PC ₁₈ H ₁₅	PPh ₃
2,2'-azobis(isobutyronitrile)	AIBN
Atom transfer radical addition	ATRA
Turnover frequency	TOF
Total turnovers	TTO

Compound Numbers

Compound	Number
Cp*Ru(PTA)(PPh ₃)Cl	1
DpRu(PTA)(PPh ₃)Cl	2
IndRu(PTA)(PPh ₃)Cl	3
CpRu(PTA)(PPh ₃)Cl	4
TpRu(PTA)(PPh ₃)Cl	5
Cp*Ru(PMe ₃)(PPh ₃)Cl	6
DpRu(PMe ₃)(PPh ₃)Cl	7
IndRu(PMe ₃)(PPh ₃)Cl	8
CpRu(PMe ₃)(PPh ₃)Cl	9
TpRu(PMe ₃)(PPh ₃)Cl	10
Cp*Ru(PPh ₃) ₂ Cl	11
DpRu(PPh ₃) ₂ Cl	12
IndRu(PPh ₃) ₂ Cl	13
CpRu(PPh ₃) ₂ Cl	14
TpRu(PPh ₃) ₂ Cl	15
Cp*Ru(PTA) ₂ Cl	16
DpRu(PTA) ₂ Cl	17
CpRu(PTA) ₂ Cl	18
[IndRu(PTA) ₂ (PPh ₃)]Cl	19

IndRu(PTA)(PPh ₃)H	20
CpRu(PTA) ₂ SnCl ₃	21
TpRu(PTA) ₂ Cl	22
1,3,3,3-tetrachloropropyl benzene	23
2-chloro-2-phenylethyl <i>p</i> -tolyl sulfone	24
2,2,4-trichloro-4-phenyl-butyric acid ethyl ester	25
1,3,3-trichloropropyl-benzene	26
4-chloro-4-phenyl-butyric acid ethyl ester	27
1,1,1,3-tetrachloro-heptane	28
1,1,1,3-tetrachloro-undecane	29
2,4,4,4-tetrachloro-butyric acid butyl ester	30
1,3,3,3-tetrachloro-2-methyl-propyl-benzene	31
4-chloro-4-phenyl-3-(trichloromethyl)-butan-2-one	32
3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one	33
1,3,3,3-tetrachloro-1,2-diphenylpropane	34

Chapter 1

Introduction and Background

1.1 Ruthenium in Catalysis

During the past two decades, ruthenium complexes have promoted tremendous developments in organic synthesis and polymer chemistry, leading to the selective preparation of fine chemicals.¹⁻⁴ Ruthenium-catalyzed reactions have gained considerable attention in both industry and academia, much of which is due to the interesting properties exhibited by the metal complexes. The advantages of ruthenium catalysts include low redox potential, high Lewis acidity, high electron transfer ability, high tolerance toward a variety of functional groups, and stabilities of reactive metallic intermediates such as oxometals, metallacycles, and metal-carbenes.^{1,2} The Ru, Rh, and Pd metals are among the most used in catalysis, of which ruthenium is relatively less expensive.⁴ Moreover, ruthenium offers a wide range of oxidation states (from -2 in $\text{Ru}(\text{CO})_4^{2-}$ to +8 in RuO_4), which are stabilized by various coordination geometries. A great variety of ruthenium complexes have been synthesized,² and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ is frequently used as the starting material. Based on their supporting ligands, the ruthenium complexes are broadly classified into five groups: carbonyls, tertiary phosphines,

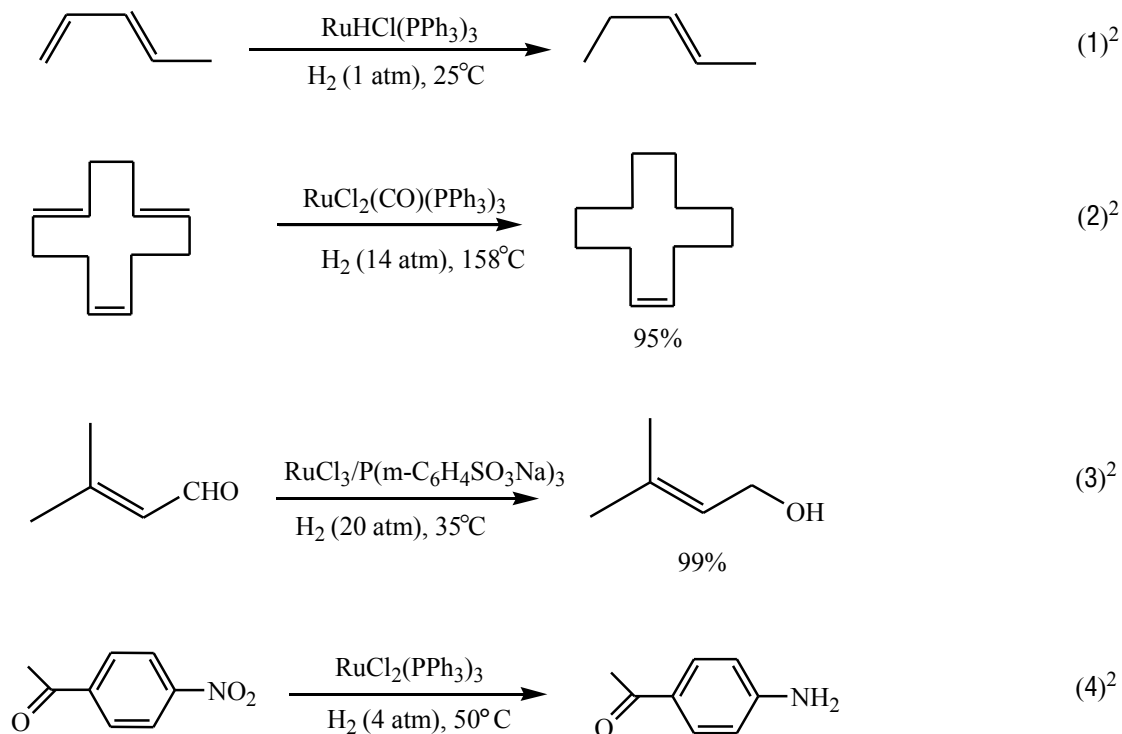
cyclopentadienyls, arenes/dienes, and carbenes.^{1,2} These ligands enable the fine tuning of the electronic and steric properties of the metal, and hence the reactivity of the metal complexes. Ruthenium complexes have served as efficient catalysts in numerous organic transformations such as hydrogenation,^{2,5} oxidation,^{2,6} epoxidation,⁷ isomerization,^{2,8} cyclopropanation,⁹ olefin metathesis,¹⁰ Kharasch addition,¹¹ and other related processes. In fact, two Nobel Prizes have been awarded to R. Noyori (2001), for asymmetric hydrogenation using chiral ruthenium catalysts,¹² and to R. H. Grubbs (2005), for olefin metathesis using ruthenium-carbene complexes.¹³ Of the aforementioned organic transformations, hydrogenation/transfer hydrogenation and Kharasch addition reactions are of particular interest to our group and hence the main focus of this dissertation.

1.2 Hydrogenation and Transfer Hydrogenation

The transition-metal catalyzed hydrogenation of unsaturated compounds using molecular hydrogen (H_2) is a key reaction in the synthesis of fine chemicals and pharmaceuticals.^{2,5} The discovery of RuO_2 ¹⁴ and $RuCl_2(PCy_3)_3$ ¹⁵ as efficient catalysts for selective hydrogenation provided an impetus to the development of ruthenium-based hydrogenation catalysts. A number of homogeneous and heterogeneous ruthenium catalysts are known to reduce various substrates including functionalized and unfunctionalized olefins, aldehydes and ketones, carboxylic acids, nitriles, imines, and nitro compounds.^{2,5} High chemo- and regioselective reduction of the double bonds can be achieved using ruthenium complexes. Typical examples of these are shown in Figure 1.1, eqs 1-4. In the case of conjugated dienes, terminal C=C bond is selectively reduced (eq

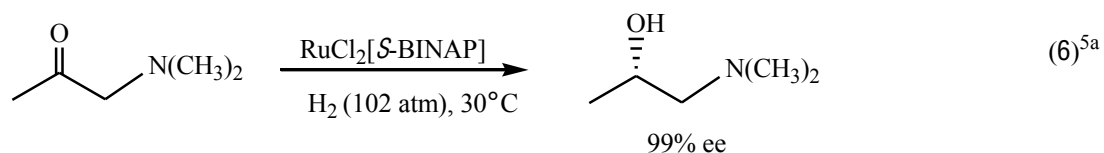
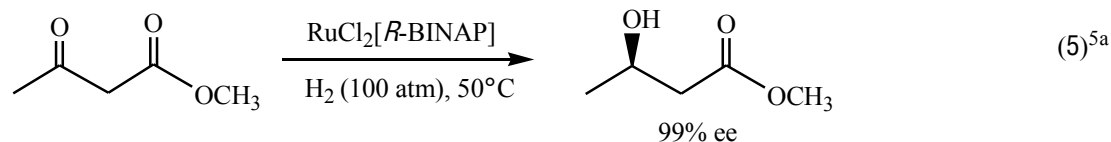
1). Partial hydrogenation of cyclic trienes to the corresponding monoolefins has also been achieved (eq 2). Ru complexes are known to catalyze chemoselective hydrogenation of α,β -unsaturated aldehydes to the corresponding alcohols (eq 3). As exemplified in eq 4, nitro groups may be selectively reduced over the carbonyl functionalities.

Figure 1.1: Ruthenium-catalyzed hydrogenation reactions



Catalytic asymmetric hydrogenation is one of the most practical and efficient methods for the synthesis of optically active compounds.¹⁶ Since the pioneering work of Noyori,¹⁷ great progress has been made in asymmetric hydrogenation using chiral Ru-BINAP catalysts (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl). Today, a wide variety of prochiral olefins and ketones are hydrogenated with excellent enantioselectivity using Ru-BINAP and related catalytic systems (Figure 1.2).^{5a,18,19}

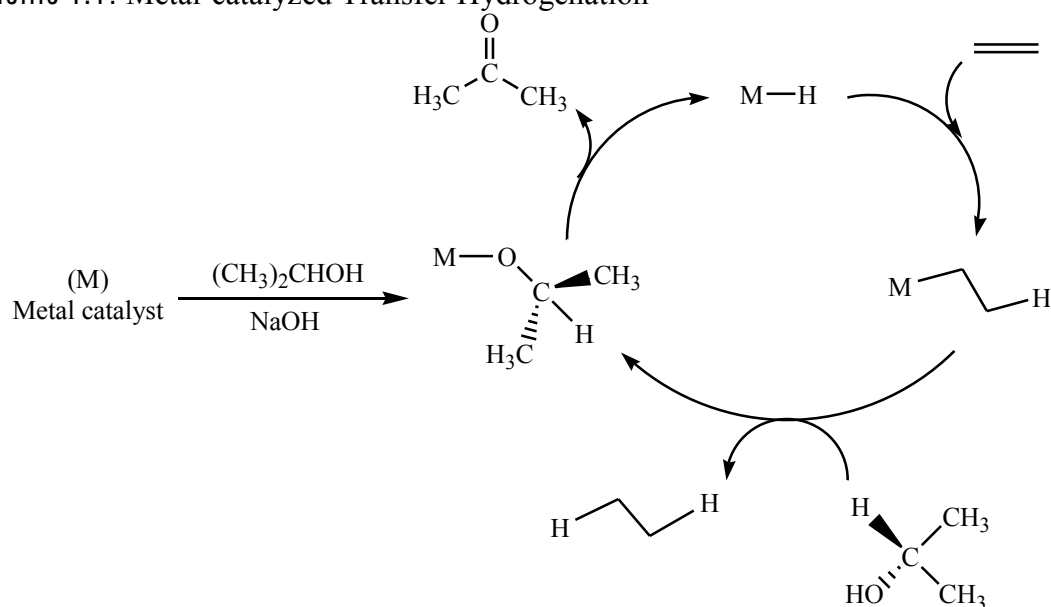
Figure 1.2: Ruthenium-catalyzed asymmetric hydrogenation



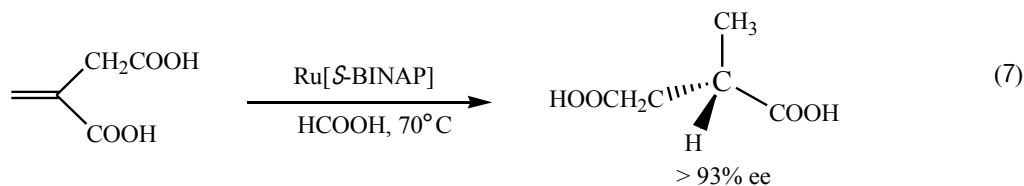
The reduction of multiple bonds in the presence of a hydrogen donor (other than dihydrogen) and a metal catalyst is known as transfer hydrogenation or hydrogen-transfer reaction (Scheme 1.1).^{2,5,20} The first step involves H⁺ abstraction from the hydrogen donor and formation of a metal alkoxide. The metal alkoxide undergoes β-hydride elimination to form a metal-hydride. Olefin insertion into the metal-hydride followed by protonation of the olefin yields the hydrogenated product. Hydrogen donors successfully employed include cyclohexene, cyclohexadiene, primary or secondary alcohols (such as benzyl alcohol, isopropyl alcohol), formic acid, etc.²⁰ Of these, formic acid and 2-propanol are most commonly used as hydrogen donors.^{5a,20a} The addition of strong bases like NaOH, KOH, or sodium alkoxides promotes the transfer hydrogenation.^{20a} The use of hydrogen donors is advantageous over the use of molecular hydrogen since it avoids the risks associated with handling the latter. A number of olefins (hydrogen acceptors) have been reduced by catalytic transfer hydrogenation, examples of which include aldehydes and ketones, α,β-unsaturated carbonyls, nitro compounds, azo compounds,

nitriles, imines, and quinolines.^{5a,20b} Low valent ruthenium complexes are exceptional catalysts for transfer hydrogenation due to their low redox potential and high affinity for hetero atom compounds.²

Scheme 1.1: Metal-catalyzed Transfer Hydrogenation



Asymmetric hydrogen transfer reactions have been explored to the same level as asymmetric hydrogenation. High enantioselectivity has been achieved using ruthenium complexes bearing chiral ligands such as phosphines, diamines, aminophosphines, and aminoalcohols.^{2,5a,21} For instance, Ru-BINAP complexes are efficient catalysts for the asymmetric transfer hydrogenation of α,β -unsaturated carboxylic acids with formic acid, eq 7.^{21a}

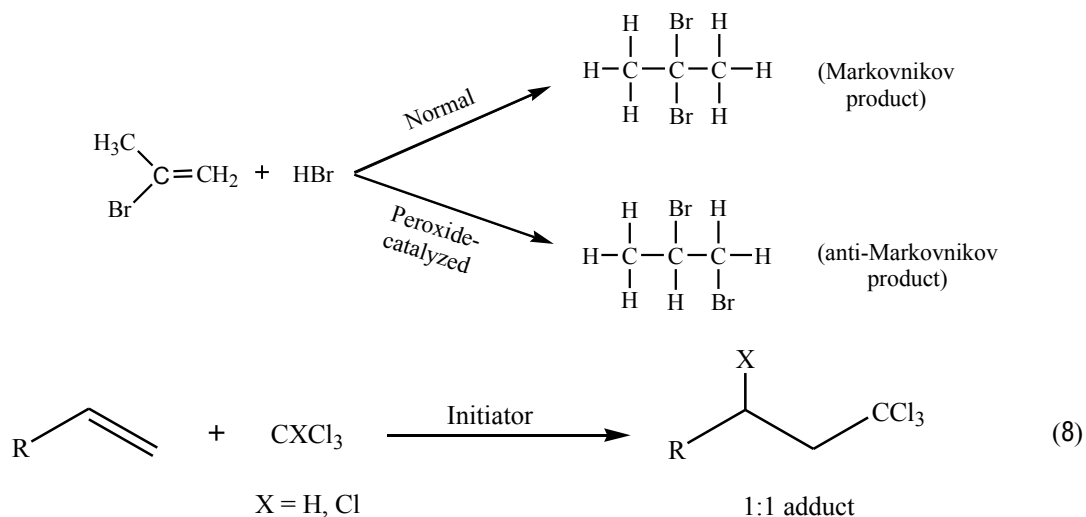


1.3 Kharasch Addition (Atom Transfer Radical Addition)*

1.3.1 Overview

In 1937, Kharasch and coworkers investigated the addition of hydrobromic and hydrochloric acid to olefins.²² They observed that in the presence of small amount of peroxide, anti-Markovnikov addition product was formed (Scheme 2.2). This is known as the “peroxide effect”. Later in the mid-1940s, they reported a similar addition of CCl_4 and CHCl_3 to olefinic double bonds catalyzed by peroxides or UV-light as radical initiators.²³ This simple addition of polyhalogenated compounds to olefins is referred to as the Kharasch addition or atom transfer radical addition (ATRA, eq 8), and it is accepted to occur via a free-radical mechanism.

Scheme 2.2: Addition of hydrobromic acid to 2-bromopropene



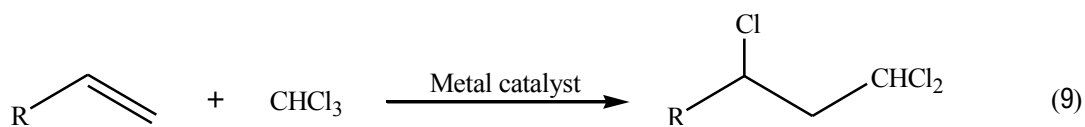
The application of the Kharasch addition suffered from a major drawback that narrowed its synthetic viability. The peroxide- or photo-induced addition of CCl_4 to non-

* This dissertation largely focuses on Kharasch addition catalyzed by ruthenium complexes. Hence a detailed introduction for the same is provided in this chapter.

polymerizable olefins exclusively gave the 1:1 adduct. However, in the case of easily polymerizable olefins (styrene, acrylates, etc.), the yield of the desired product was significantly lower due to competing telomerization and polymerization reactions. In the 1950s, researchers began to explore the use of transition metal complexes to initiate these reactions. The first successful examples of transition-metal-promoted ATRA were the additions of CCl_4 and CHCl_3 to a variety of olefins in the presence of iron and copper salts.^{24,25} Since then, a wide variety of transition metal complexes have been shown to catalyze these addition reactions.²⁶ Amongst them, nickel-,²⁷ copper-,²⁸ and particularly ruthenium-based²⁹ systems have displayed remarkable catalytic performance. $\text{RuCl}_2(\text{PPh}_3)_3$ was the first ruthenium complex reported as a highly efficient and versatile catalyst for Kharasch addition.³⁰ $\text{RuCl}_2(\text{PPh}_3)_3$ and other ruthenium-based catalysts for ATRA are discussed in detail in this chapter.

Transition-metal-catalyzed ATRA offers several advantages over the conventional methods using peroxide or UV-light as radical initiators. First, a high yield of the monoadduct is obtained due to the minimization/elimination of telomer or polymer formation even with highly polymerizable olefins.²⁵ Second, the redox system provides high stereoselectivity and regioselectivity.³¹ High enantioselectivity, however, has not yet been achieved. Attempts to perform asymmetric radical addition reactions using chiral ruthenium complexes afforded only 10-30% enantioselectivity.³² High stereoselectivity is exemplified by the $\text{RuCl}_2(\text{PPh}_3)_3$ catalyzed addition of CCl_4 to cyclohexene, which gave a 96:4 mixture of *trans*- and *cis*-adducts whilst the peroxide initiated reaction gave a nearly equimolar mixture (53:47) of the *trans*- and *cis*-adducts.^{31a} Moreover, the nature of the 1:1 adduct is different in the two processes, as observed in the case of CHCl_3 addition

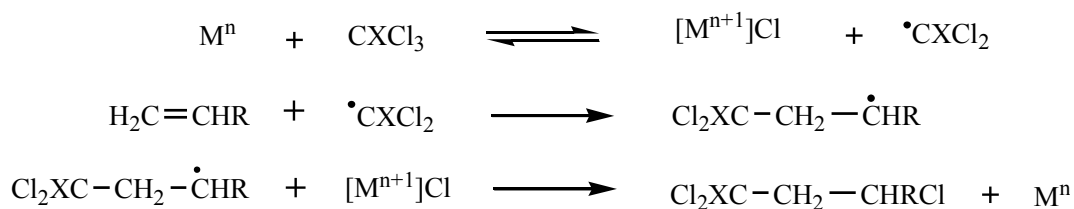
to terminal olefins; the peroxide-catalyzed addition gave 1,1,1-trichloroalkanes (eq 8) whereas with metal catalyst, 1,1,3-trichloroalkanes were obtained (eq 9).^{24b,25}



1.3.2 Mechanistic Insights

For metal-catalyzed reactions, two distinct (but related) mechanisms have been proposed.^{27a,27d,33} The first mechanism involves a free-radical chain process as depicted in Scheme 1.3.^{25,34} The metal complex abstracts a halogen atom from the polyhalogenated alkane and undergoes one-electron oxidation, generating a radical species that further adds to the olefin. Transfer of a halogen atom from the metal-halide leads to the 1:1 adduct and regeneration of the reduced metal catalyst.

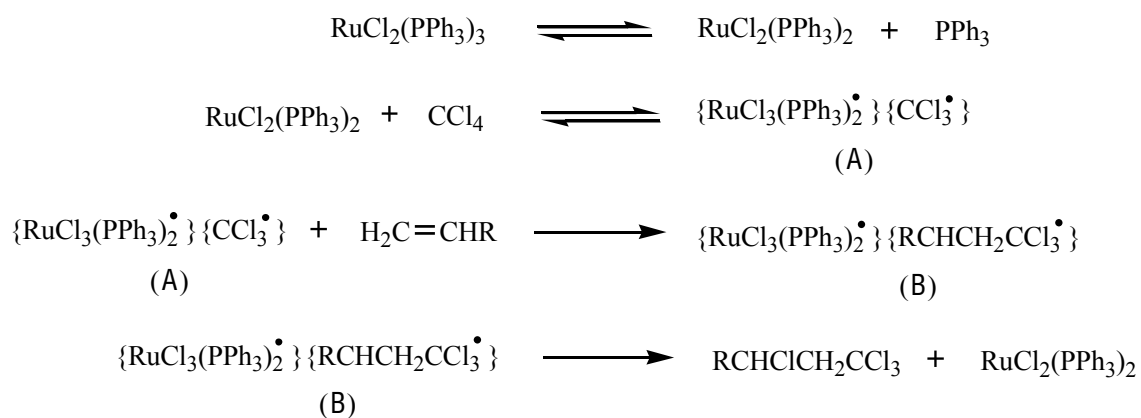
Scheme 1.3



The second type of mechanism proceeds via a non-chain pathway. The organic radicals resulting from a single electron transfer (SET) remain within the coordination

sphere of the metal center (i.e., “caged” radicals).^{31a,35} A detailed mechanistic study of the ruthenium system by Davis and coworkers suggests a non-chain pathway as represented in Scheme 1.4.^{35c,35d} A key step is the dissociation of a phosphine ligand generating a coordinatively unsaturated Ru^{II} complex, which in turn reacts with CCl₄ to form the radical pair A. The phosphine dissociation step is in accord with the inhibition of the reaction in the presence of excess phosphine. The reaction of A with the olefin generates a second radical pair B. Final step involves the transfer of a chlorine atom from the Ru^{III} species to the carbon radical, yielding the desired product and regenerating the four-coordinate catalyst precursor.

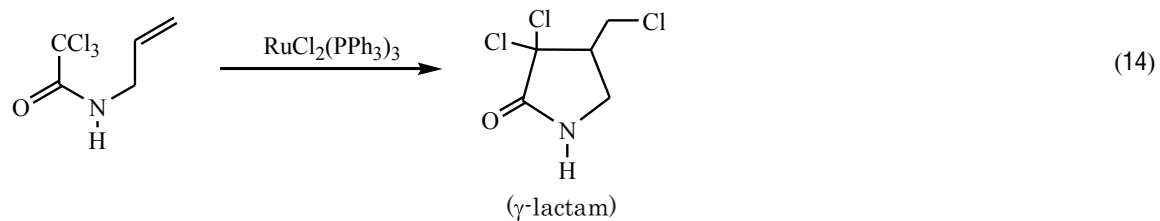
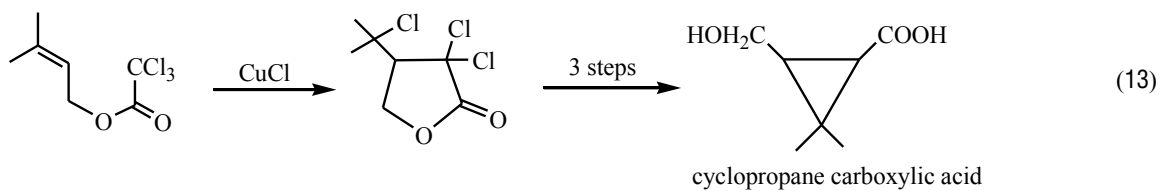
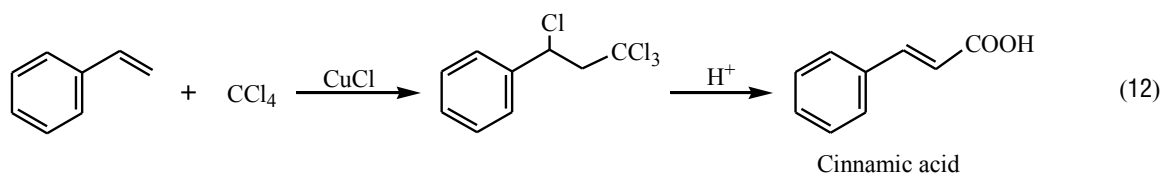
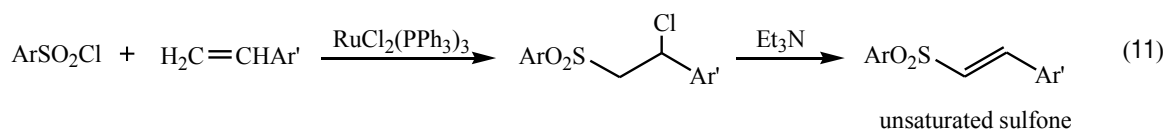
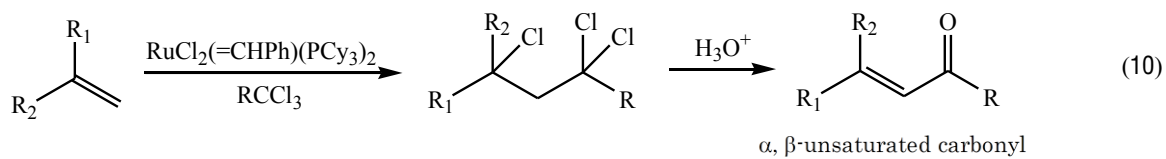
Scheme 1.4 (adapted from Ref. 13d)



1.3.3 ATRA in Organic Synthesis

Transition-metal-mediated ATRA has found widespread application in synthetic organic chemistry; it is an effective method for carbon-carbon bond formation, and the resulting 1:1 adducts serve as starting materials for further organic transformations.^{26,28f,36} Classic examples of these are shown in Figure 1.3 (eq 10-12). The metal-catalyzed polymerization of acrylates and vinyl monomers was discovered independently by the groups of Sawamoto³⁷ and Matyjaszewski.³⁸ This process is an extension of ATRA at high olefin/halide ratio, and hence the name atom transfer radical polymerization (ATRP) or “controlled living polymerization” (Figure 1.3, eq 15).³⁹ ATRP has opened an efficient pathway for the synthesis of polymers with well-defined compositions and functionalities. ATRA and ATRP are mechanistically similar, and several metal complexes are known to catalyze both reactions.^{40-42,43b} However, not all complexes that catalyze ATRP display the same activity in ATRA. For instance, $\text{RuCl}_2(\text{p-cymene})(\text{PCy}_3)$ is an outstanding catalyst for ATRP,^{43a} but is not active towards ATRA.^{43b} Besides intermolecular Kharasch addition, intramolecular versions are also known, which may be referred to as atom transfer radical cyclization (ATRC). It provides a very effective tool for the synthesis of 5- or 6-membered carbocycles, macrocyclic compounds, lactams and lactones, alkaloids, and other functionalized ring systems (Figure 1.3; eq 13, 14).^{28e,28f,36,44,45}

Figure 1.3: ATRA and related reactions



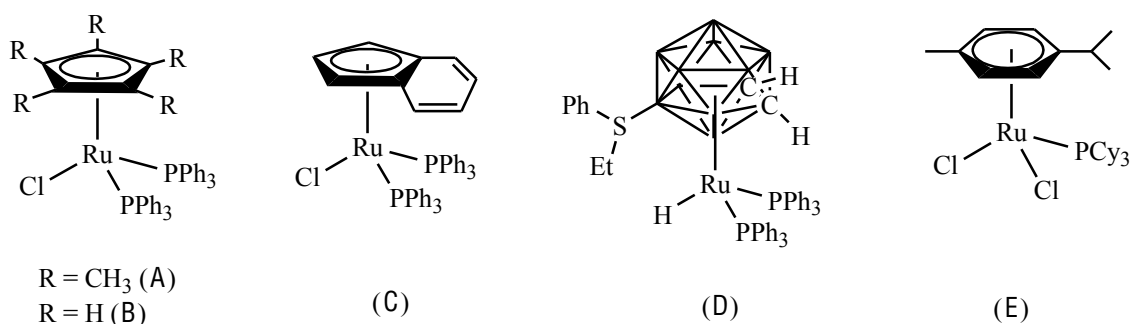
1.3.4 Ruthenium-based catalysts in ATRA

In 1973, $\text{RuCl}_2(\text{PPh}_3)_3$ was reported as an efficient catalyst for ATRA.³⁰ Subsequently, it has been extensively used to catalyze ATRA and the related reactions, ATRP and ATRC, which lead to the successful preparation of fine organic compounds and well-defined polymers. Mechanistic studies revealed that the coordination sphere of the metal center play a vital role in tuning the activity of the catalyst.^{35c,35d} The electronic properties of the ligands alter the redox potential of the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple. Strong electron-donating ligands are likely to facilitate the oxidation step, whilst electron-withdrawing ligands would stabilize the metal in the lower oxidation state. Surprisingly, it was not until the late 1990s that new catalytic systems with ligand variation were investigated. The “rebirth” of ruthenium-catalyzed Kharasch addition is the result of the discovery of $\text{RuCl}_2(\text{PPh}_3)_3$ as an efficient catalyst for controlled polymerization.^{37,38} Since 1999, several new ruthenium complexes with superior catalytic performances have been reported. Severin has recently published a review on ‘*Ruthenium catalysts for ATRA*’.²⁹ These new complexes are broadly classified into the following four classes.^{29,33}

(i) *Half-sandwich complexes*: Half-sandwich ruthenium complexes bearing η^6 -arene or η^5 -cyclopentadienyl type ligands have been reported to efficiently catalyze ATRA and/or ATRP, Figure 1.4.^{41,42,46-48} $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (A) showed exceptional performance for the addition of CCl_4 and CHCl_3 to olefins.^{41b,48} With total turnovers (TTO) of 1600-1700 and turnover frequencies (TOF) of 400 h^{-1} , $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ is among the superior catalysts for ATRA described so far. The activity of the Ind analog (C) was comparable to that of the Cp^* -complex, whereas the CpRu complex (B) exhibited the least reactivity.^{41b} Likewise, the ruthenium carborane complex (D), an analogue of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$,

showed outstanding activity for the addition of CCl_4 to styrene and methyl methacrylate (MMA) under very mild conditions.⁴⁹ A TTO of 9000 (styrene)/4200 (MMA) and TOF of 1500 h^{-1} (styrene)/ 1900 h^{-1} (MMA) was observed at 40°C . These are the highest values reported to date for ruthenium catalyzed ATRA. However, complex D showed rather poor activity for CHCl_3 addition to olefins. The ruthenium-arene complex (E) is known for its high activity towards ATRP.^{43a}

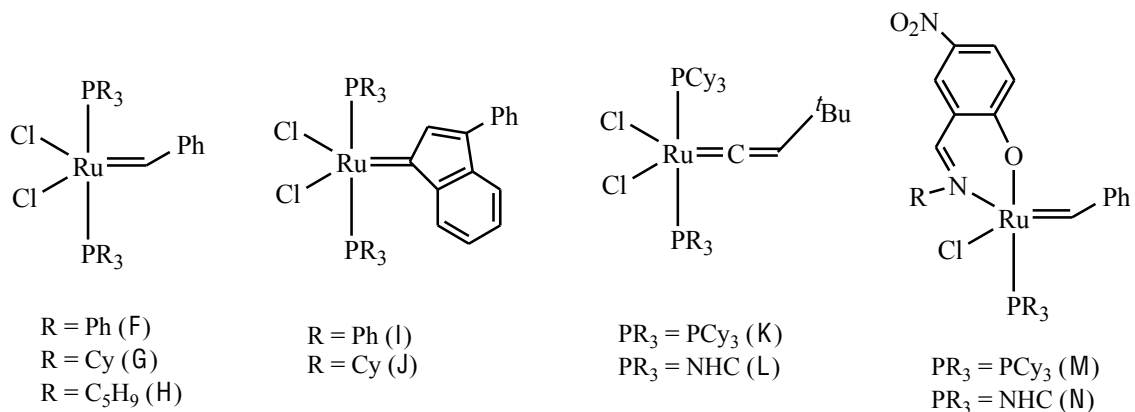
Figure 1.4: Ruthenium half-sandwich complexes as ATRA catalysts.



(ii) *Grubbs and related complexes*: The Grubbs' ruthenium-carbene complexes have been reported as efficient promoters for the addition of CCl_4 and CHCl_3 to olefins, Figure 1.5.^{40,43b,50-53} These complexes also catalyze the controlled polymerization of various monomers. Among the series of $\text{RuCl}_2(=\text{CHPh})(\text{PR}_3)_2$ complexes investigated (F-H), the PPh_3 derivative $\text{RuCl}_2(=\text{CHPh})(\text{PPh}_3)_2$ exhibited the highest activity for both ATRA and ATRP.^{43b} Similar results were observed for the indenylidene complexes (I, J), where the PPh_3 complex is more active than the PCy_3 analog.⁴⁰ The utility of ruthenium alkylidene complexes in ATRA was further expanded to the vinylidene complexes⁵² (K, L) and

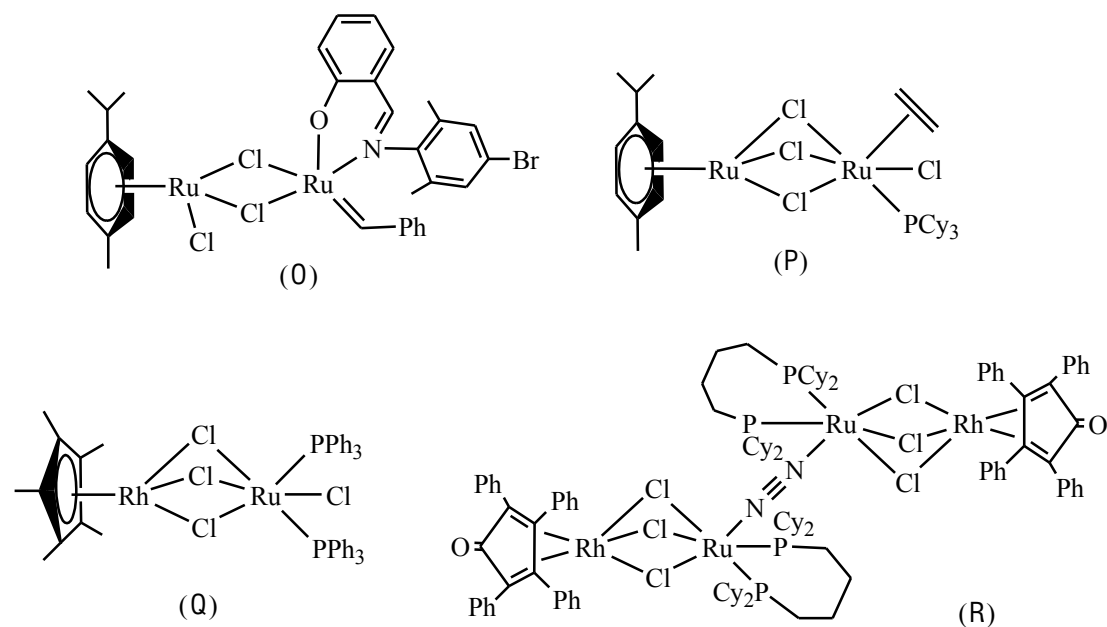
Schiff base complexes⁵³ (M, N). In both cases, the NHC complexes were more reactive than their PCy₃ counterparts.

Figure 1.5: Ruthenium-carbene complexes as ATRA catalysts.



(iii) *Polynuclear complexes:* A range of homo- and heteropolynuclear ruthenium complexes has been reported to catalyze the radical reactions, Figure 1.6.⁵⁴⁻⁵⁶ The first results along these lines were reported for the CCl₄ addition to olefins promoted by homobimetallic complex O.⁵⁴ This complex exhibited higher catalytic activity as compared to the ruthenium-carbene complexes in Figure 5. The complex P showed exceptional catalytic performance for the addition of CCl₄ to styrene while displaying TOF of 1550 h⁻¹ at 40°C,⁵⁶ which is comparable to that of the Ru-carborane complex D. The heterometallic complexes (Q, R) are highly active Kharasch catalysts. For CCl₄ addition to styrene, a TOF of 1200 h⁻¹ and TTO of 4500 was achieved with the complex in Figure (6d).⁵⁵

Figure 1.6: Polynuclear complexes as ATRA catalysts.



(iv) *Polymer-supported complexes*: A few polymer-bound ruthenium complexes are known to catalyze ATRA.⁵⁷⁻⁶⁰ The first of its kind was the polyethylene-bound Ru(II) catalyst $\text{RuCl}_2[\text{PE-PPh}_2]_3$, reported to promote inter- and intramolecular Kharasch additions.⁵⁷ Recently, a polystyrene-polyethylene glycol resin-supported Ru complex $[\text{PS-PEG-PPh}_2\text{-Cp}^*\text{RuCl}_2]$ was found to catalyze the addition of halogenated compounds to olefins in aqueous media. A TOF of 1450 h^{-1} was determined, which is comparable to the highest TOF value reported for complex D.⁶⁰

1.4 Organization and Scope

This dissertation is divided into the following five chapters:

Chapter 1 provides general introduction on ruthenium complexes used as catalysts in various organic transformations. In particular, the ruthenium catalyzed hydrogenation/transfer hydrogenation and atom transfer radical addition (ATRA) reactions are discussed in detail.

Chapter 2 outlines the synthesis and characterization (both spectroscopic and crystallographic) of half-sandwich ruthenium complexes of the type $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{X}$, where $\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}$ or Tp ; $\text{PR}_3 = \text{PTA}$ or PMe_3 ; $\text{X} = \text{Cl}$ or H . H/D exchange of the hydride complex $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$, and reactivity towards transfer hydrogenation of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ are also discussed.

Chapter 3 describes the catalytic activity of the ruthenium complexes $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$, ($\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}$ or Tp ; $\text{PR}_3 = \text{PTA}, \text{PMe}_3$, or PPh_3) for the addition of such halogenated alkanes as CCl_4 , CHCl_3 , *p*- TsCl , $\text{CCl}_3\text{CO}_2\text{Et}$, and $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene. The role of the ancillary ligands (Cp'), and the phosphines (PR_3) is discussed in detail.

Chapter 4 contains the reactivity of $\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes, ($\text{PR}_3 = \text{PTA}, \text{PMe}_3$, or PPh_3) towards the addition of CCl_4 to more challenging olefinic substrates. The reactivity is observed to depend mainly on the nature of the substrate. The synthesis and characterization of two new organic compounds are also discussed.

Chapter 5 provides some general conclusions. This is followed by an Appendix which contains NMR spectra, and tables of bond lengths and angles for the crystal structures discussed elsewhere in the dissertation.

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Chapter 2

Synthesis and characterization of half-sandwich ruthenium (II) complexes of general formula **Cp'RuCl(PPh₃)(PR₃)** [**Cp' = Cp*, Dp, Ind, Cp, Tp; PR₃ = PTA, PMe₃**]*

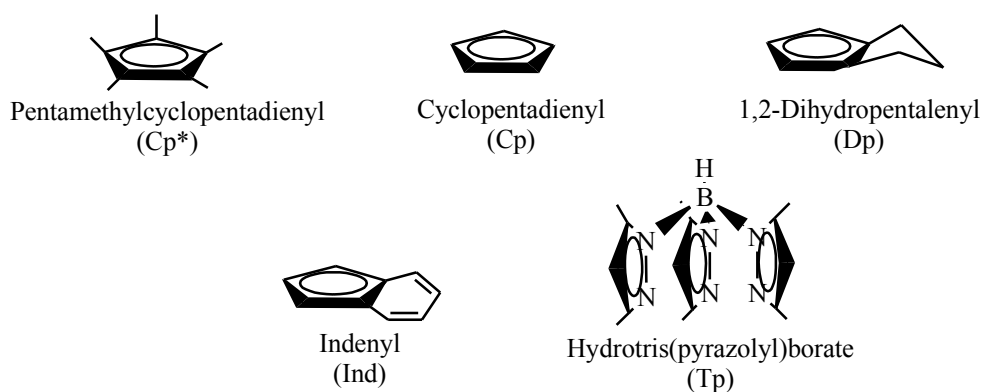
2.1 Introduction

The discovery of ferrocene in 1952¹ was a milestone in the development of the cyclopentadienyl ligand ($\eta^5\text{-C}_5\text{H}_5^-$, Cp) in organometallic chemistry. A number of reviews on Cp-transition metal complexes² and Cp-lanthanide complexes³ have been reported. A wide variety of substituted cyclopentadienyls are also known, above all these is the pentamethylcyclopentadienyl ligand ($\eta^5\text{-C}_5\text{Me}_5^-$, Cp*).⁴ However, less attention has been devoted to the η^5 -ring derivatives such as indenyl ($\eta^5\text{-C}_9\text{H}_7^-$, Ind) and 1,2-dihydropentalenyl ($\eta^5\text{-C}_8\text{H}_9^-$, Dp), and the analogous tripodal ligand hydrotris(pyrazolyl)borate ($\kappa^3\text{-HB(pz)}_3$, Tp), of which Ind and Tp metal complexes have gained preferential interest in recent years.^{5,6} The monoanionic Cp' ligands (Cp*, Cp, Dp, Ind, and Tp, Scheme 2.1) provide three pairs of electrons for σ -bonding to the metal,

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thereby occupying three coordination sites in the metal complex. They form a wide range of stable metal complexes in both high and low oxidation states. The Cp' fragments serve as “ancillary ligands” providing additional stability to the metal-complex through multiple bonding as compared to the co-ligands. The differences in steric and electronic properties of the cyclopentadienyl-based ligands can be used as a tool in fine tuning the reactivity of metal complexes. Ruthenium is among the highly catalytically active metals. Half-sandwich ruthenium complexes are among the most active catalysts for organic transformations such as olefination of carbonyl compounds⁷, cycloadditions⁸, isomerizations⁹, hydrogenations¹⁰, and atom transfer radical reactions¹¹. Our goal was to explore the effect of various Cp' ligands and phosphines on the catalytic behaviour of ruthenium (II) complexes. In this regard, we synthesized and characterized a series of half-sandwich ruthenium (II) chloride complexes containing the ancillary ligands Cp*, Cp, Dp, Ind, or Tp, and the phosphines trimethylphosphine (PMe₃), 1,3,5-triaza-7-phosphaadamantane (PTA), and triphenylphosphine (PPh₃).

Scheme 2.1: Cyclopentadienyl-type ligands.



2.2 Experimental Section

2.2.1 *Materials and methods*

All reactions were performed under a dry nitrogen atmosphere, using conventional Schlenk vacuum-line techniques or nitrogen filled glovebox. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, dicyclopentadiene, cyclooctadiene (COD), $[\text{Cp}^*\text{RuCl}_2]_n$, indene, triphenylphosphine (PPh_3), and trimethylphosphine (PMe_3) were purchased from commercial suppliers, and used as received. Solvents were dried on molecular sieves and degassed with N_2 prior to use. Methanol was freshly distilled from standard drying reagents (Mg/I_2). 1,3,5-triaza-7-phosphaadamantane (PTA),¹² $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ ¹³, $\text{DpRu}(\text{PPh}_3)_2\text{Cl}$,¹⁴ $\text{IndRu}(\text{PPh}_3)_2\text{Cl}$,¹⁵ $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$,¹⁶ and $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ ¹⁷ were synthesized according to literature procedure. ^1H NMR spectra were recorded on a Varian 400 spectrometer (400 MHz). All chemical shifts are reported in ppm and referenced to residual solvent relative to TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian 400 spectrometer (162 MHz) or 500 spectrometer (202 MHz), and all chemical shifts are referenced to a solution of 85% H_3PO_4 in D_2O with positive values downfield of the reference. IR spectra were recorded on Perkin-Elmer 2000 FT-IR spectrometer, in a 0.1 mm CaF_2 cell for solutions or as a KBr pellet for solid samples. GC/MS analyses were obtained using a Varian CP 3800 GC (DB5 column) equipped with a Saturn 2200 MS and a CP 8400 auto-injector. Column chromatography was performed using Silicycle silica gel (230-400 mesh). Elemental analysis was performed by Midwest Microlab, LLC. Cyclic voltammetry experiments were performed at room temperature with Princeton Applied Research PARSTAT 2273 potentiostat, using a three-electrode cell equipped with a Ag/AgCl /saturated KCl reference electrode, a platinum auxiliary electrode, and a glassy carbon working

electrode. Tetrabutylammonium tetrafluoroborate was used as the supporting electrolyte and all the potentials were referenced to ferrocene, $E^\circ(\text{Fc}/\text{Fc}^+) = 0.65 \text{ V}$.

2.2.2 Synthesis

*Synthesis of Cp*Ru(PTA)(PPh₃)Cl (1)*

Cp*Ru(PPh₃)₂Cl (0.30 g, 0.37 mmol) and PTA (0.06 g, 0.37 mmol) were dissolved in 70 mL CH₂Cl₂ and refluxed under nitrogen for 2h. The solution was cooled to room temperature, filtered, and pulled dry under vacuum. The resulting solid was washed with water followed by diethyl ether (3 x 10 mL), affording 169 mg 1 as an orange powder (65% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.33 (m, 15H, Ph); 4.39, 4.27 (AB quartet, ²J_{(HAHB)} = 13 Hz, 6H, NC H₂N); 3.95, 3.36 (AB quartet, ²J_{(HAHB)} = 15 Hz, 6H, PC H₂N); 1.34 (s, 15H, CH₃); ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 47.6 ppm (d, PPh₃, ²J_{PP} = 40.4 Hz), -38.9 ppm (d, PTA, ²J_{PP} = 40.4 Hz). Anal. calcd for C₃₄H₄₂N₃P₂RuCl: C, 59.08; H, 6.12; N, 6.08. Found: C, 59.28; H, 6.17; N, 5.94. Orange crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a toluene solution of 1.}}}}

Synthesis of IndRu(PTA)(PPh₃)Cl (3)

A mixture of IndRu(PPh₃)₂Cl (1.00 g, 1.30 mmol) and PTA (204 mg, 1.3 mmol) in 105 mL toluene was refluxed for 5 h under nitrogen. The solvent was removed under vacuum and the residue washed several times with diethyl ether and air-dried affording 3 as an orange-red solid (312 mg, 72% yield). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.49-7.23 (m, 19H, PPh₃ and indenyl); 7.01 (t, 1H, indenyl); 6.77 (d, 2H, indenyl) 4.35, 4.18 (AB

quartet, $^2J_{(\text{HAHB})} = 12.9$ Hz, PTA, 6H, $\text{NC}H_2N$), 3.91, 3.54 (AB quartet, $^2J_{(\text{HAHB})} = 15.0$ Hz, PTA, 6H, $\text{PC}H_2N$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 50.8 ppm (d, PPh_3 , $^2J_{\text{PP}} = 42.8$ Hz), -22.6 ppm (d, PTA, $^2J_{\text{PP}} = 42.8$ Hz). Anal. calc. for $\text{C}_{33}\text{H}_{34}\text{N}_3\text{P}_2\text{ClRu}$: C, 59.06; H, 5.11; N, 6.26. Found: C, 58.17; H, 5.04; N, 6.35. Anal. calc. for $\text{C}_{33}\text{H}_{34}\text{N}_3\text{P}_2\text{ClRu}$: C, 59.06; H, 5.11; N, 6.26. Found: C, 58.17; H, 5.04; N, 6.35. X-ray quality crystals of **3** were grown by slow diffusion of diethyl ether into a dichloromethane solution of $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$.

Synthesis of $\text{Cp}^\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**6**)*

$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (0.50 g, 0.63 mmol) and excess PMe_3 (200 μL , 1.93 mmol) were dissolved in 30 mL toluene and heated in an oil-bath at 35°C for 10 minutes under nitrogen. The toluene was then evaporated under vacuum, and the solid washed with methanol (3 x 10 mL) affording 220 mg **6** as yellow powder (57 % yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.61-7.28 (m, 15H, Ph); 1.28 (s, 15H, $\text{Cp}(\text{C}H_3)_5$); 1.06 (d, 9H, $\text{P}(\text{C}H_3)_3$, $^2J_{\text{PH}} = 8.4$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 47.5 ppm (d, PPh_3 , $^2J_{\text{PP}} = 44.1$ Hz), 1.1 ppm (d, PMe_3 , $^2J_{\text{PP}} = 44.1$ Hz). Anal. calcd for $\text{C}_{31}\text{H}_{39}\text{P}_2\text{RuCl}$: C, 61.03; H, 6.44; N, 0.00. Found: C, 60.96; H, 6.49; N, 0.04. Orange crystals suitable for X-ray diffraction were obtained by refrigerating the solution of **6** in hot methanol.

Synthesis of DpRu(PMe₃)(PPh₃)Cl (7)

A solution of DpRu(PPh₃)₂Cl (0.60 g, 0.78 mmol) and excess PMe₃ (200 μL, 1.93 mmol) in toluene (50 mL) was heated in an oil-bath at 35°C for 2 hours under nitrogen. The solvent was evaporated under vacuum and the resulting solid was purified by column chromatography on silica. The band eluted with dichloromethane was collected and dried under vacuum yielding 270 mg **7** as orange crystalline solid (60 % yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.56-7.32 (m, 15H, Ph); 4.03, 3.63, 3.15 (s, 3H, Cp), 2.50-2.10 (m, 6H, Cp(CH₂)₃); 1.17 (d, 9H, P(CH₃)₃, ²J_{PH} = 8.8 Hz); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 49.1 ppm (d, PPh₃, ²J_{PP} = 46.8 Hz), 0.5 ppm (d, PMe₃, ²J_{PP} = 46.8 Hz). Anal. calcd for C₂₉H₃₃P₂RuCl: C, 60.05; H, 5.73; N, 0.00. Found: C, 60.08; H, 5.69; N, 0.06.

Solid-state structure of IndRu(PMe₃)(PPh₃)Cl (8)

Solid-state structure of the previously synthesized complex IndRu(PMe₃)(PPh₃)Cl¹⁸ is reported here. X-ray quality crystals were obtained by layering a dichloromethane solution of **8** with acetone.

Synthesis of CpRu(PMe₃)(PPh₃)Cl (9)

CpRu(PMe₃)(PPh₃)Cl was synthesized by an alternative method from that reported.¹⁹ A mixture of CpRu(PPh₃)₂Cl (1.00 g, 1.38 mmol) and excess PMe₃ (300 μL, 2.90 mmol) in 80 mL toluene was heated in an oil-bath at 35°C for 30 hours under nitrogen. The reaction mixture was pulled dry under vacuum and the solid residue was purified by column chromatography on silica. The fraction eluted with dichloromethane was collected and dried under vacuum affording **9** as yellow crystalline solid (370 mg, 50 % yield). ¹H NMR data for CpRu(PMe₃)(PPh₃)Cl obtained by this method are identical to

those reported in the literature. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 48.6 ppm (d, PPh_3 , $^2J_{\text{PP}} = 38.2$ Hz), 2.1 ppm (d, PMe_3 , $^2J_{\text{PP}} = 38.2$ Hz).

Synthesis of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (10)

A mixture of $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ (1.15 g, 1.31 mmol) and excess PMe_3 (300 μL , 2.90 mmol) in 80 mL toluene was heated in an oil-bath at 35°C for 4 hours under nitrogen. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica. The band eluted with dichloromethane was collected and dried under vacuum yielding 400 mg 10 as greenish-yellow crystalline solid (45 % yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.98 (1H, pyrazolyl); 7.65-7.21 (m, 18H, PPh_3 and pyrazolyl); 6.60 (1H, pyrazolyl); 6.18 (1H, pyrazolyl); 5.78 (1H, pyrazolyl); 5.70 (1H, pyrazolyl); 5.57 (1H, pyrazolyl); 1.10 (d, 9H, $\text{P}(\text{CH}_3)_3$, $^2J_{\text{PH}} = 8.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 50.4 ppm (d, PPh_3 , $^2J_{\text{PP}} = 35.1$ Hz), 10.4 ppm (d, PMe_3 , $^2J_{\text{PP}} = 35.1$ Hz). Anal. calcd for $\text{C}_{31}\text{H}_{39}\text{P}_2\text{RuCl}$: C, 52.38; H, 4.98; N, 12.22. Found: C, 52.47; H, 4.89; N, 12.00. Green crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of 10.

Synthesis of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19)

A mixture of $\text{IndRuCl}(\text{PPh}_3)_2$ (0.30 g, 0.39 mmol) and PTA (0.12 g, 0.78 mmol) was refluxed under nitrogen in 40 ml toluene for 4 hours. The resulting yellow precipitate was filtered and dried under vacuum yielding 197 mg of 19 (62 % yield). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.4-7.07 (m, 19H, PPh_3 and indenyl), 7.02 (t, 1H, indenyl); 6.75 (d, 2H, indenyl), 4.1, 3.8 (AB quartet, $^2J_{(\text{HAHB})} = 14$ Hz, PTA, 12H, NCCH_2N), 4.40

(s, 12H, PCH_2N); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 48.9 ppm (t, PPh_3), -34.1 ppm (d, PTA), $^2J_{PP} = 30.1$ Hz. Anal. calc. for $C_{39}H_{46}N_6P_3ClRu$: C, 56.55; H, 5.60; N, 10.15. Found: C, 56.62; H, 5.60; N, 10.87. $[IndRu(PTA)_2(PPh_3)](SnCl_3)$ was synthesized by stirring a mixture of 19 (58 mg, 0.07 mmol) and $SnCl_2 \cdot 2H_2O$ (316 mg, 0.14 mmol) in 40 ml dichloromethane for 14 hours under nitrogen. The solution was filtered to remove excess $SnCl_2 \cdot 2H_2O$ and the solvent evaporated under vacuum leaving a light brown solid. X-ray quality crystals of $[IndRu(PTA)_2(PPh_3)](SnCl_3)$ were grown by slow diffusion of diethyl ether into a dichloromethane solution of the ruthenium complex.

Synthesis of $(\eta^5-C_9H_7)Ru(PTA)(PPh_3)H$ (20)

A mixture of $IndRu(PTA)(PPh_3)Cl$ (0.134 g, 0.20 mmol) and CH_3ONa (0.20 mmol) were refluxed under nitrogen for 5 h in 40 ml MeOH. The resulting yellow solution was cooled to room temperature, filtered, and the solvent removed under vacuum resulting in 118 mg of 20 as a pale yellow solid (92% yield). 1H NMR (400 MHz, CD_3OD): δ -16.3 (dd, $^2J_{PTA-H} = 32.0$ Hz, $^2J_{PPh_3-H} = 29.2$ Hz, 1H, RuH); 4.30, 4.06 (AB quartet, $^2J_{(H_A)H_B} = 12.5$ Hz, 6H, NCH_2N); 4.66 (s, 6H, PCH_2N); δ 7.58-7.13 (m, PPh_3 indenyl, 19H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD): δ 62.7 ppm (d, PPh_3 , $^2J_{PP} = 29.0$ Hz), -23.3 ppm (d, PTA, $^2J_{PP} = 29.0$ Hz). IR (KBr): $\nu(Ru-H)$ 1977 cm^{-1} . X-ray quality crystals of $(\eta^5-C_9H_7)Ru(PTA)(PPh_3)H$ were grown by slow diffusion of diethyl ether into a methanol solution of 20.

Synthesis of (η^5 -C₅H₅)Ru(PTA)₂SnCl₃ (21)

A mixture of CpRu(PTA)₂Cl (0.13 g, 0.25 mmol) and SnCl₂•2H₂O (0.113 g, 0.50 mmol) in dichloromethane was stirred for 14 h under nitrogen. The reaction mixture was filtered to remove unreacted SnCl₂•2H₂O, and the solvent removed under vacuum resulting in 125 mg of 21 as a yellow solid (67 % yield). ¹H NMR (400 MHz, D₂O): δ 5.13 (s, 5H, C₅H₅); 4.8, 4.7 (AB quartet, ²J_{(HAHB)} = 12.6 Hz, 12H, NC₂H₂N); 4.1 (s, 12H, PC₂H₂N). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -27.9 ppm (s, PTA). Yellow crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of 21.}

2.2.3 Transfer Hydrogenation Procedure

The transfer hydrogenation reactions were carried out in a 20 mL Schlenk tube with a Teflon valve. The reactions were conducted under acidic conditions using HCOOH (formic acid) as the hydrogen source. Each catalytic run was repeated at least twice to ensure reproducibility. In a typical catalytic run, 5 mol % catalyst and the unsaturated carbonyl compound were treated with 150 μ L of 88% HCOOH in a water/methanol mixture (2/1 mL). The resultant solution was stirred at 80°C in an oil bath. The solution was cooled to room temperature and the product(s) extracted with hexane (2 x 3 mL). The hexane layer was analyzed by GC-MS and ¹H NMR spectroscopy and the peaks identified by comparison with authentic samples.

2.2.4 X-Ray Crystallography

X-ray quality crystals of 1, 3, 6, 8, 10, and 19-21 were obtained as described above. Due to air-sensitivity, crystals of the hydride complex 20 were placed in paratone oil on a glass-slide in the glove-box and carried to the microscope. X-ray crystallographic data was collected at 100(\pm 1) K on a Bruker APEX CCD diffractometer with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a detector-to-crystal distance of 4.94 cm. Data collection was optimized utilizing the APEX2 software with a 0.5 $^{\circ}$ rotation about ω between frames, and an exposure time of 10s per frame. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS, and corrected for absorption using SADABS. The structures were solved using direct methods followed by successive least squares refinement on F 2 using the SHELXTL 5.12 software package.²⁰ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. Crystallographic data and data collection parameters are listed in Tables 2.1 and 2.2. A complete list of bond lengths and angles may be found in the Appendix.

Table 2.1: Crystallographic data for complexes 1, 3, 6 and 8.

	Cp*Ru(PTA)(PPh ₃)Cl (1)	IndRu(PTA)(PPh ₃)Cl (3)	Cp*Ru(PMe ₃)(PPh ₃)Cl (6)	IndRu(PMe ₃)(PPh ₃)Cl (8)
Empirical formula	C ₃₄ H ₄₂ ClN ₃ P ₂ Ru	C ₃₃ H ₃₄ N ₃ P ₂ ClRu	C ₃₁ H ₃₉ ClP ₂ Ru	C ₃₀ H ₃₁ ClP ₂ Ru
Formula weight	691.17	671.09	610.08	590.01
Color	orange	yellow	orange	Red
T (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/n	P-1
a (Å)	11.6045(2)	16.9997(9)	11.3789(2)	12.3176(2)
b (Å)	14.8894(3)	9.6556(5)	14.3410(2)	13.1046(2)
c (Å)	18.4456(4)	18.9784(10)	18.3738(2)	17.1601(3)
α (deg)	90	90	90	80.5320(10)
β (deg)	102.0290(10)	115.7220(10)	107.3420(10)	82.1640(10)
γ (deg)	90	90	90	89.4570(10)
Volume (Å ³)	3117.12(11)	2806.5(3)	2862.03(7)	2706.45(8)
Z	4	4	4	4
D _{calcd} (Mg/m ³)	1.473	1.588	1.416	1.448
Abs coeff (mm ⁻¹)	0.720	0.798	0.771	0.813
F(000)	1432	1376	1264	1208
Crystal size (mm ³)	0.27 x 0.13 x 0.04	0.34 × 0.09 × 0.03	0.16 x 0.07 x 0.06	0.16 x 0.12 x 0.10
θ range (deg)	1.77 - 27.50	2.17 - 25.99	1.83 - 28.28	1.58 - 27.64
Index ranges	-12 ≤ h ≤ 15 -19 ≤ k ≤ 15 -23 ≤ l ≤ 13	-20 ≤ h ≤ 20 -11 ≤ k ≤ 11 -23 ≤ l ≤ 13	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -19 ≤ l ≤ 24	-15 ≤ h ≤ 16, -17 ≤ k ≤ 15, -22 ≤ l ≤ 22
no. of reflns collected	34336	31312	31805	51558
no. of indep reflns	7153	5505	6867	12486
no. of data/restraints/params	7153 / 0 / 360	5505/0/395	6867 / 0 / 324	12486 / 0 / 619
GOF on F ²	1.026	0.983	1.094	1.087
final R indices	R ₁ = 0.0364 wR ₂ = 0.0749	R ₁ = 0.0403 wR ₂ = 0.0866	R ₁ = 0.0301, wR ₂ = 0.0631	R ₁ = 0.0289, wR ₂ = 0.0675
R indices (all data)	R ₁ = 0.0518 wR ₂ = 0.0797	R ₁ = 0.0692 wR ₂ = 0.0934	R ₁ = 0.0434, wR ₂ = 0.0808	R ₁ = 0.0448, wR ₂ = 0.0827
CCDC no.	699360	616217	713868	713866

Table 2.2: Crystallographic data for complexes 10, and 19-21.

	TpRu(PMe ₃)(PPh ₃)Cl (10)	[IndRu(PTA) ₂ (PPh ₃)](SnCl ₃) (19)	IndRu(PTA)(PPh ₃)H (20)	CpRu(PTA) ₂ SnCl ₃ (21)
Empirical formula	C ₃₀ H ₃₄ B Cl N ₆ P ₂ Ru	C ₃₉ H ₄₆ N ₆ P ₃ Cl ₃ SnRu	C ₃₃ H ₃₅ N ₃ P ₂ Ru	C _{17.5} H ₃₀ Cl ₄ N ₆ P ₂ Ru Sn
Formula weight	687.90	1102.76	636.65	746.97
Color	Green	orange	colorless	yellow
T(K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	P $\bar{1}$	C2/c
a (Å)	12.3342(2)	14.0277(10)	9.9727(7)	29.2196(11)
b (Å)	20.1362(3)	11.7222(8)	10.4488(7)	12.6120(4)
c (Å)	13.1231(2)	26.5468(19)	15.4665(13)	17.9178(8)
α (deg)	90	90	95.4810(10)	90
β (deg)	105.6100(10)	95.6880(10)	90.6990(10)	126.7800(10)
γ (deg)	90	90	117.4650(10)	90
Volume (Å ³)	3139.09(8)	4343.7(5)	1420.58(18)	5288.6(4)
Z	4	4	2	8
D _{calcd} (Mg/m ³)	1.456	1.6	1.488	1.876
Abs coeff (mm ⁻¹)	0.717	1.379	0.693	2.060
F(000)	1408	2216	656	2944
Crystal size (mm ³)	0.19 x 0.07 x 0.02	0.14 x 0.02 x 0.03	0.16 x 0.12 x 0.03	0.38 x 0.23 x 0.06
θ range (deg)	1.90 - 26.00	1.90 - 27.50	2.21 - 32.35	1.74 - 32.30
Index ranges	-15 \leq h \leq 12, -24 \leq k \leq 24, -14 \leq l \leq 16	-18 \leq h \leq 18 -15 \leq k \leq 15 -34 \leq l \leq 34	-14 \leq h \leq 14, -15 \leq k \leq 15, -23 \leq l \leq 23	-43 \leq h \leq 43, -18 \leq k \leq 18, -26 \leq l \leq 26
no. of reflns collected	27640	41651	25339	46431
no. of indep reflns	5785	9982	9979	9384
no. of data/restraints/params	R _{int} = 0.0662 5785 / 0 / 373	R _{int} = 0.2002 9982/0/505	R _{int} = 0.0622 9979 / 36 / 375	R(int) = 0.0259 9384 / 0 / 289
GOF on F ²	1.038	0.904	1.004	1.036
final R indices [I > 2 σ (I)]	R ₁ = 0.0420, wR ₂ = 0.0781	R ₁ = 0.0641 wR ₂ = 0.1045	R ₁ = 0.0548, wR ₂ = 0.1228	R ₁ = 0.0265, wR ₂ = 0.0677
R indices (all data)	R ₁ = 0.0704, wR ₂ = 0.0844	R ₁ = 0.1542 wR ₂ = 0.1221	R ₁ = 0.0886, wR ₂ = 0.1378	R ₁ = 0.0293, wR ₂ = 0.0690
CCDC no.	713867	616216	616219	---

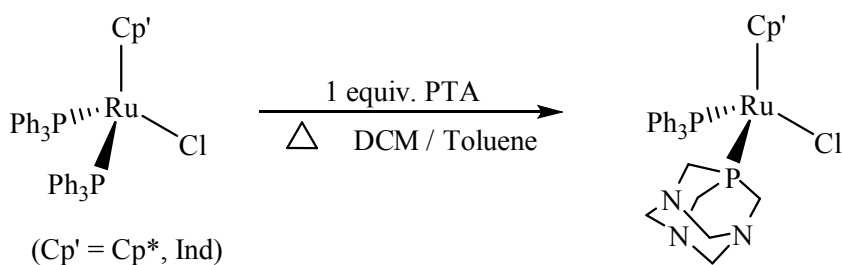
2.3 Results and discussion

2.3.1 Synthesis and characterization of Cp'Ru(PR₃)(PPh₃)Cl complexes

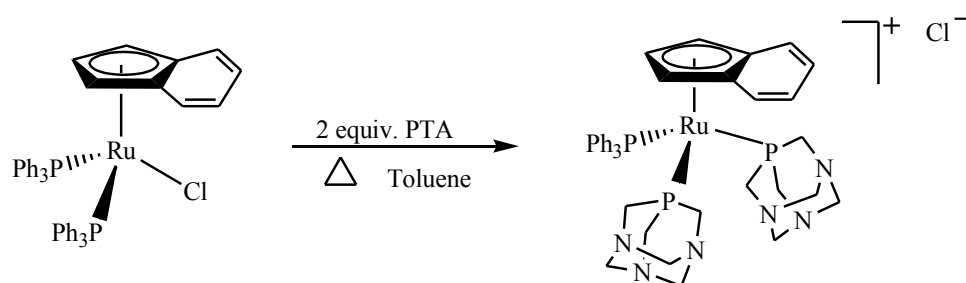
The synthesis of a series of half-sandwich ruthenium(II) complexes of the type Cp'Ru(PR₃)(PPh₃)Cl (Cp' = Cp*, Cp, Dp, Ind or Tp; PR₃ = PTA or PMe₃) was accomplished in good yields by ligand exchange reaction of Cp'Ru(PPh₃)₂Cl with the appropriate phosphine. The monosubstituted complexes Cp*Ru(PTA)(PPh₃)Cl (1) and

IndRu(PTA)(PPh₃)Cl (**3**) were prepared by refluxing equimolar amounts of PTA and Cp'Ru(PPh₃)₂Cl in a suitable solvent affording **1** in 65% yield and **3** in 72% yield, Scheme 2.2. The disubstituted complexes Cp*Ru(PTA)₂Cl,²¹ CpRu(PTA)₂Cl,^{21,22} DpRu(PTA)₂Cl,²³ and TpRu(PTA)₂Cl²⁴ were synthesized by the addition of two equivalents of PTA to Cp'Ru(PPh₃)₂Cl. Our attempts to synthesize IndRu(PTA)₂Cl in an analogous manner resulted in the formation of the cationic species [IndRu(PTA)₂(PPh₃)]Cl (**19**) in 89% yield, Scheme 2.3.

Scheme 2.2: Synthesis of Cp'Ru(PTA)(PPh₃)Cl complexes



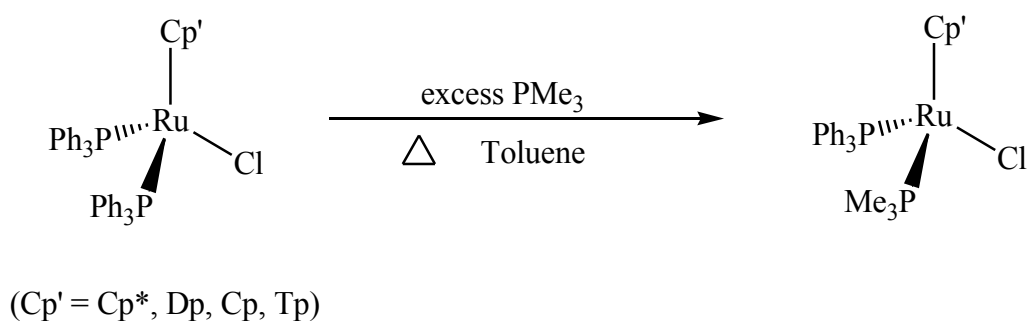
Scheme 2.3: Synthesis of [IndRu(PTA)₂(PPh₃)]Cl



The synthesis of IndRu(PMe₃)(PPh₃)Cl (**8**) and CpRu(PMe₃)(PPh₃)Cl (**9**) have been reported in the literature.^{18,19} Complex **8** was obtained by simple ligand substitution reaction of IndRu(PPh₃)₂Cl with PMe₃,¹⁸ whereas complex **9** was prepared by condensing PMe₃ onto CpRu(PPh₃)₂Cl in light petroleum in a Carius tube followed by heating the

sealed tube at 200 °C for 14 h.¹⁹ Alternatively, we obtained complex 9 as a yellow crystalline solid in 50% yield by heating CpRu(PPh₃)₂Cl with excess PMe₃ at 35 °C in toluene. The monosubstituted complexes Cp*Ru(PMe₃)(PPh₃)Cl (6), DpRu(PMe₃)(PPh₃)Cl (7), and TpRu(PMe₃)(PPh₃)Cl (10) were also synthesized in an analogous manner affording 6, 7, and 10 in 57%, 60%, and 45% yield, respectively, Scheme 2.4.

Scheme 2.4: Synthesis of Cp'Ru(PMe₃)(PPh₃)Cl complexes



All the complexes were characterized by elemental analysis and NMR spectroscopic techniques (¹H and ³¹P NMR). The ³¹P{¹H} NMR spectra of the series of Cp'Ru(PR₃)(PPh₃)Cl complexes each consist of two doublets due to coupling of the inequivalent phosphorus nuclei: ²J_{pp} = 40.4 Hz, 1; 42.8 Hz, 3; 44.1 Hz, 6; 46.8 Hz, 7; 38.2 Hz, 9; 35.1 Hz, 10; Table 2.3. The PTA and PMe₃ ligands are more sensitive to the metal environment than PPh₃ as evidenced by the range of ³¹P chemical shifts for PTA Δ_{ppm} ~16 (-22.6 – -38.9 ppm) and PMe₃ Δ_{ppm} ~16 (0.5 – 16.3 ppm) versus PPh₃ Δ_{ppm} ~8 (43.2 – 50.8 ppm). ³¹P{¹H} NMR spectra of the monosubstituted complexes 1 and 6 are shown in Figures 2.1 and 2.2, respectively (*the spectra of 3, 7, 9, and 10, are available in*

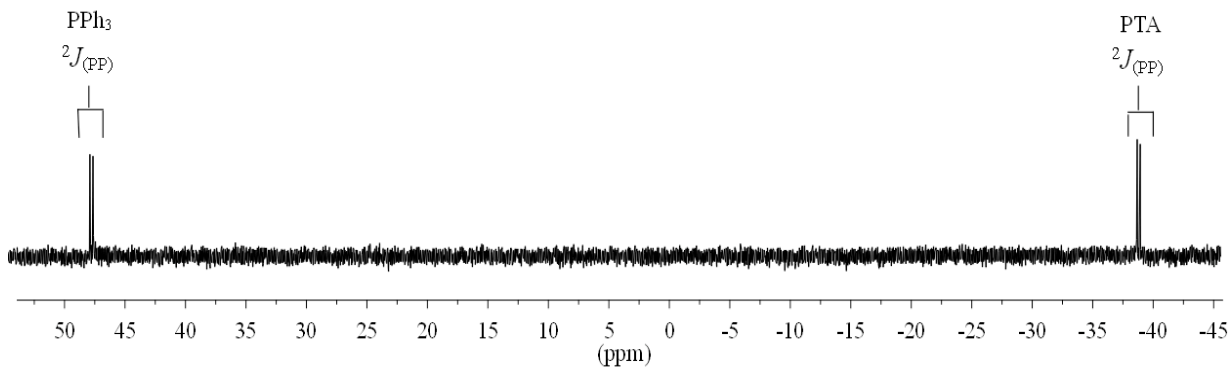
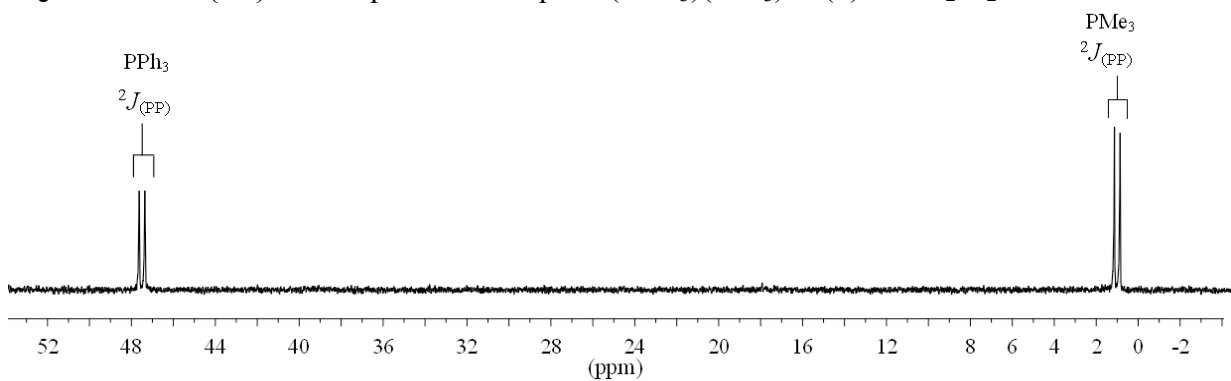
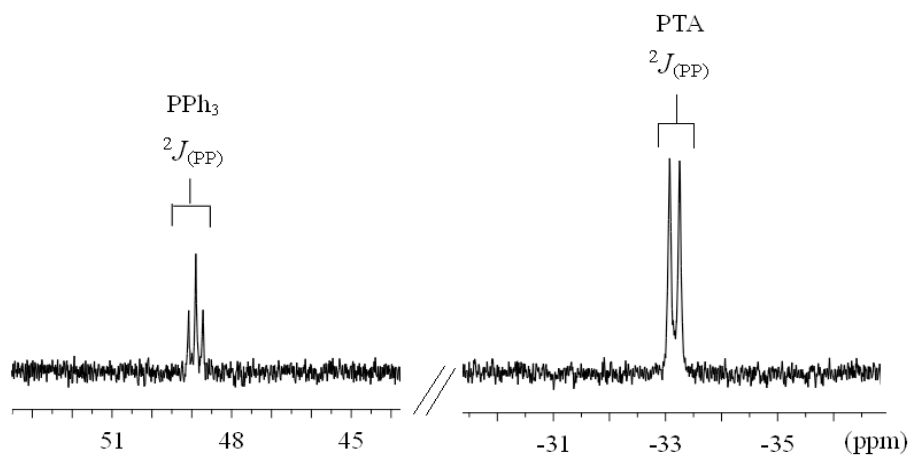
the Appendix). The indenyl complex [IndRu(PTA)₂(PPh₃)]Cl (**19**) also exhibits two sets of resonances in the ³¹P{¹H} NMR spectrum; 48.9 (t, PPh₃, ²J_{PP} = 30.1 Hz) and -34.1 ppm (d, PTA, ²J_{PP} = 30.1 Hz), Figure 2.3.*

Table 2.3: ³¹P{¹H} chemical shifts and coupling constants for the series of Cp'Ru(PR₃)(PPh₃)Cl complexes; Cp' = Cp*, Dp, Cp, Ind, or Tp, and PR₃ = PTA or PMe₃

Entry	Complex	³¹ P{ ¹ H} NMR	² J _{PP} , Hz
1	Cp*Ru(PTA)(PPh ₃)Cl (1)	47.6 (PPh ₃), -38.9 (PTA)	40.4
2	DpRu(PTA)(PPh ₃)Cl ²³	43.2 (PPh ₃), -39.6 (PTA)	45.2
3	IndRu(PTA)(PPh ₃)Cl (3)	50.8 (PPh ₃), -22.6 (PTA)	42.8
4	CpRu(PTA)(PPh ₃)Cl ²³	48.4 (PPh ₃), -32.5 (PTA)	45.0
5	TpRu(PTA)(PPh ₃)Cl ²⁴	46.9 (PPh ₃), -34.2 (PTA)	33.1
6	Cp*Ru(PMe ₃)(PPh ₃)Cl (6)	47.5 (PPh ₃), 1.1 (PMe ₃)	44.1
7	DpRu(PMe ₃)(PPh ₃)Cl (7)	49.1 (PPh ₃), 0.5 (PMe ₃)	46.8
8	IndRu(PMe ₃)(PPh ₃)Cl (8) ¹⁸	50.1 (PPh ₃), 16.3 (PMe ₃)	44.8
9	CpRu(PMe ₃)(PPh ₃)Cl (9)	48.6 (PPh ₃), 2.1 (PMe ₃)	38.2
10	TpRu(PMe ₃)(PPh ₃)Cl (10)	50.4 (PPh ₃), 10.4 (PMe ₃)	35.1
11	[IndRu(PTA) ₂ (PPh ₃)]Cl (19)	48.9 (PPh ₃), -34.1 (PTA)	30.1
12	IndRu(PTA)(PPh ₃)H (20)	62.7 (PPh ₃), -23.3 (PTA)	29.0
13 ^a	CpRu(PTA) ₂ SnCl ₃ (21)	-27.97	---

^a ²J_{P-Sn(119)}} = 434.4 Hz, ²J_{P-Sn(117)}} = 416.3 Hz.

* *The synthesis and characterization of 20 and 21 are discussed later in this chapter.*

Figure 2.1: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) in CD_2Cl_2 .Figure 2.2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (6) in CD_2Cl_2 .Figure 2.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19) in CD_2Cl_2 .

The ^1H NMR spectrum of **1**, in CDCl_3 , contains a single resonance at 1.34 ppm for the $\text{Cp}(\text{CH}_3)_5$ protons. The NCCH_2N and PCH_2N protons of PTA appear as AB quartets centered at 4.33 ppm ($^2J_{\text{HAHB}} = 13$ Hz) and 3.65 ppm ($^2J_{\text{HAHB}} = 15$ Hz), respectively. The PPh_3 signals appear as a multiplet in the range δ 7.62-7.33 ppm, Figure 2.4. The ^1H NMR spectrum of **3**, in CD_2Cl_2 , exhibit two AB quartets attributed to the PTA ligand centered at 4.26 ppm for NCCH_2N protons ($^2J_{\text{HAHB}} = 12.9$ Hz) and 3.72 ppm for PCH_2N protons ($^2J_{\text{HAHB}} = 15$ Hz). The C_5H_3 protons appear at 7.01 ppm (t, 1H) and 6.77 ppm (d, 2H). The resonance of the $\text{Cp}(\text{CH})_4$ protons overlap with that of PPh_3 ligand at 7.49-7.23 ppm, Figure 2.5. The ^1H NMR spectrum of **19** (*see appendix*) is similar to that of **3** except for minor differences in the chemical shift values.

Figure 2.4: ^1H NMR spectrum of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (**1**) in CDCl_3 ; solvent (S), residual water (*).

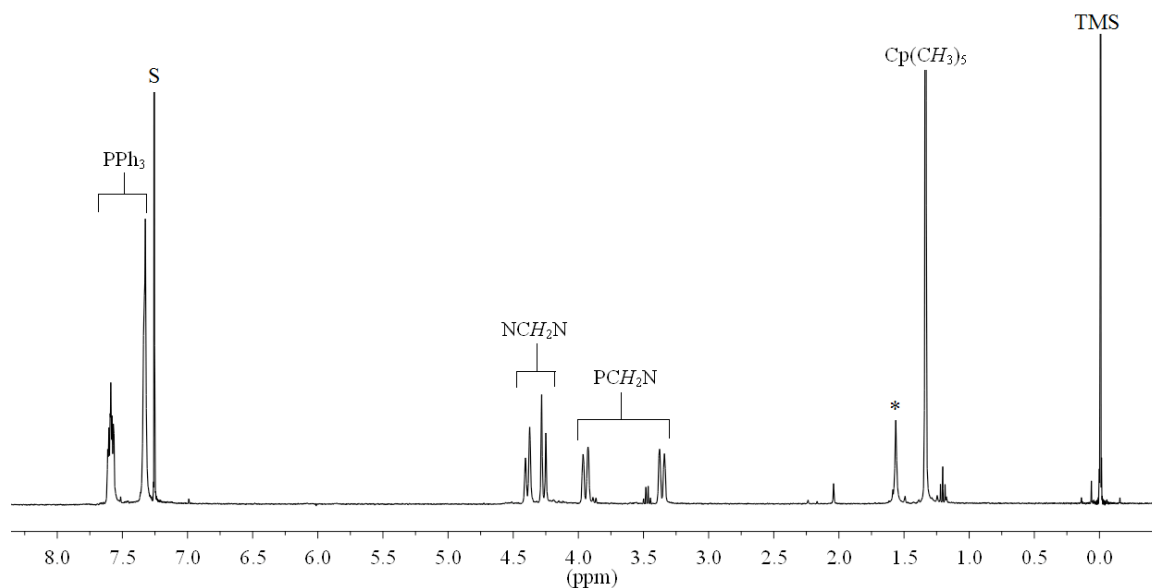
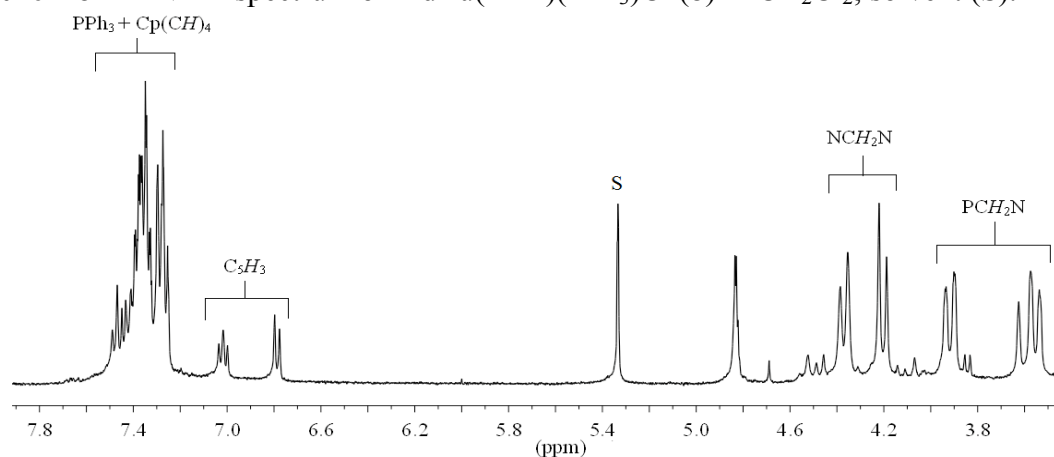


Figure 2.5: ^1H NMR spectrum of $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ (**3**) in CD_2Cl_2 ; solvent (S).



The ^1H NMR spectra of complexes **8** and **9** have been reported in the literature.^{18,19} The ^1H NMR spectra of **6**, **7**, and **10**, in CD_2Cl_2 , exhibit doublets corresponding to the PMe_3 ligand at 1.06 ppm ($^2J_{\text{PH}} = 8.4$ Hz), 1.17 ppm ($^2J_{\text{PH}} = 8.8$ Hz), and 1.1 ppm ($^2J_{\text{PH}} = 8.0$ Hz), respectively. The PPh_3 resonances of **6**, **7**, and **10** appear in the range δ 7.65-7.21 ppm. The characteristic signals of the Cp^* , Dp , and Tp ligands appear as follows: singlet at 1.28 ppm for the $\text{Cp}(\text{CH}_3)_5$ protons, **6**; three singlet's at 4.03, 3.63, and 3.15 ppm for the Cp protons, and multiplet at 2.50-2.10 ppm for the $\text{Cp}(\text{CH}_2)_3$ protons, **7**; and the pyrazolyl protons in the range δ 7.98-5.57 ppm, **10**, Figures 2.6-2.8.

Figure 2.6: ^1H NMR spectrum of $\text{Cp}^*\text{Ru(PMe}_3\text{)(PPh}_3\text{)Cl}$ (**6**) in CD_2Cl_2 ; solvent (S).

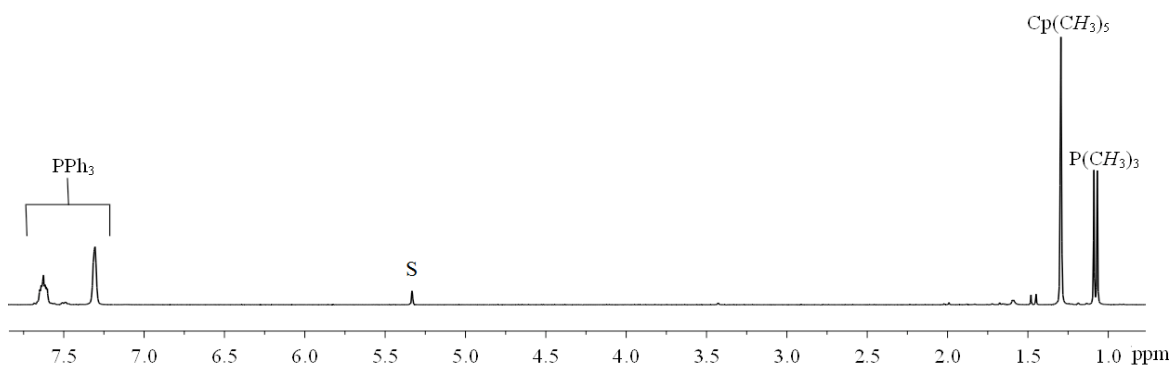


Figure 2.7: ^1H NMR spectrum of $\text{DpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**7**) in CD_2Cl_2 ; solvent (S), residual water (*).

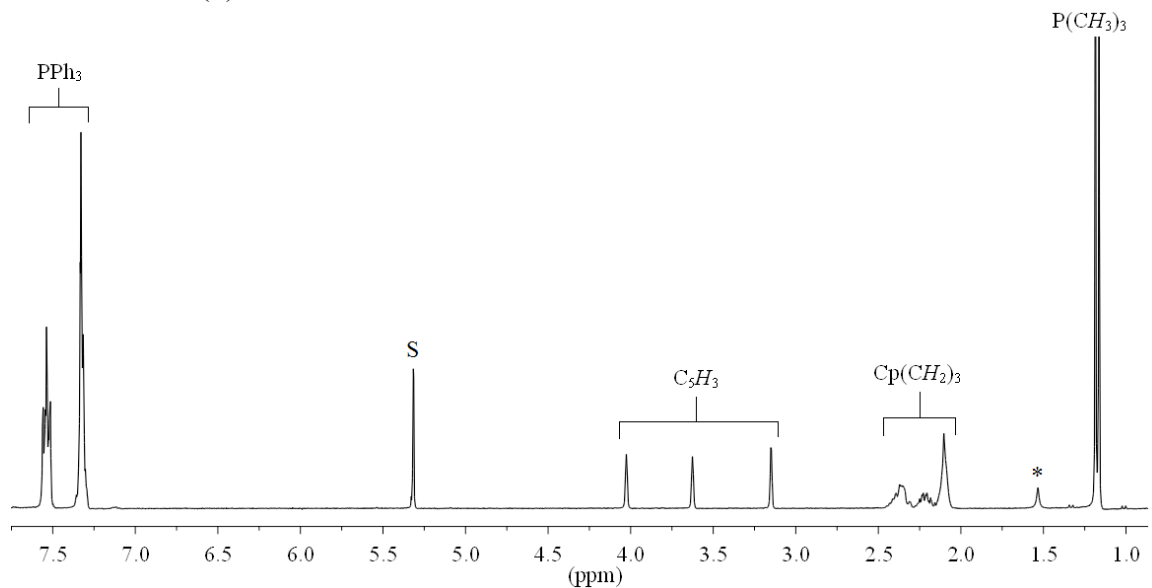
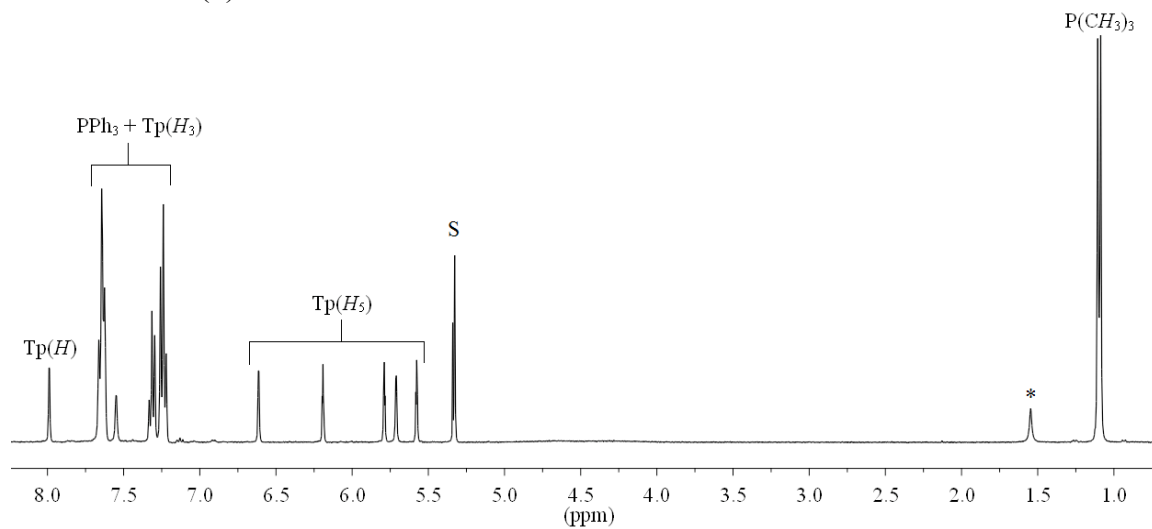


Figure 2.8: ^1H NMR spectrum of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**10**) in CD_2Cl_2 ; solvent (S), residual water (*).



2.3.2 Structures of ruthenium complexes 1, 3, 6, 8, and 10

The solid-state structures of 1, 3, 6, 8, and 10 were determined by X-ray crystallography (*vide infra*). Orange plates of Cp*Ru(PTA)(PPh₃)Cl (1) suitable for X-ray diffraction, were obtained by slow diffusion of diethyl ether into a toluene solution of 1. X-ray quality crystals of IndRu(PTA)(PPh₃)Cl (3) were obtained as orange-red rods by slow diffusion of diethyl ether into a dichloromethane solution of the complex. Orange crystals of 6 suitable for X-ray diffraction were obtained by dissolving 6 in hot methanol followed by slow cooling in the refrigerator. Crystals of 8 and 10 were obtained by layering dichloromethane solution of 8 with acetone, and slow evaporation of dichloromethane solution of 10, respectively. Thermal ellipsoid representations of 1, 3, 6, 8, and 10 are depicted in Figures 2.9-2.13, along with the atomic numbering schemes. Selected bond distances and angles are summarized in Table 2.4. All five Cp'Ru(PR₃)(PPh₃)Cl complexes exhibit classic three-legged piano-stool geometry with one PPh₃, one PTA (or PMe₃), a chloride, and a Cp' ancillary ligand (η^5 -Cp*, η^5 -Ind; κ^3 -Tp) occupying the six coordination sites around the ruthenium atom. The Ru-Cl distances are in the range 2.404 – 2.458 Å. PTA and PMe₃ are stronger binding phosphines as compared to PPh₃. Hence, the Ru-PTA and Ru-PMe₃ bond distances should be shorter than that of Ru-PPh₃. As expected, the Ru-PMe₃ (Ru-P1) distances in 6, 8, and 10 are slightly shorter than that of Ru-PPh₃ (Ru-P2), Table 2.4. However, in complexes 1 and 3, the Ru-PTA (Ru-P1) bond lengths are longer by ~ 0.02 Å than that of Ru-PPh₃, Table 2.4. For complexes 6 and 8, the P1-Ru-P2 angles are slightly larger in comparison to their PTA counterparts. This is in accord with the fact that the Tolman cone angle of PMe₃

(118°)²⁵ is larger than that of PTA (102°).²⁶ However, this does not hold true for 10, which has a smaller P1-Ru-P2 angle than TpRu(PTA)(PPh₃)Cl.²⁴ For the Cp* complexes 1 and 6, the distance from Ru to the Cp centroid (Cp'_{cent}) is shorter compared to the indenyl analogues 3 and 8. The variation in Ru-Cp'_{cent} may be attributed to the steric properties of the Cp' ligand. The Cp-ML₂ angle between the plane defined by the Cp' ligand and the plane defined by Ru1, P1, and P2 is observed to be in the range 51.4° - 62.7° , and are similar to those found for other ruthenium complexes bearing Cp' ligand.²³

Figure 2.9: Thermal ellipsoid (50% probability) representation of Cp*Ru(PTA)(PPh₃)Cl (1) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.

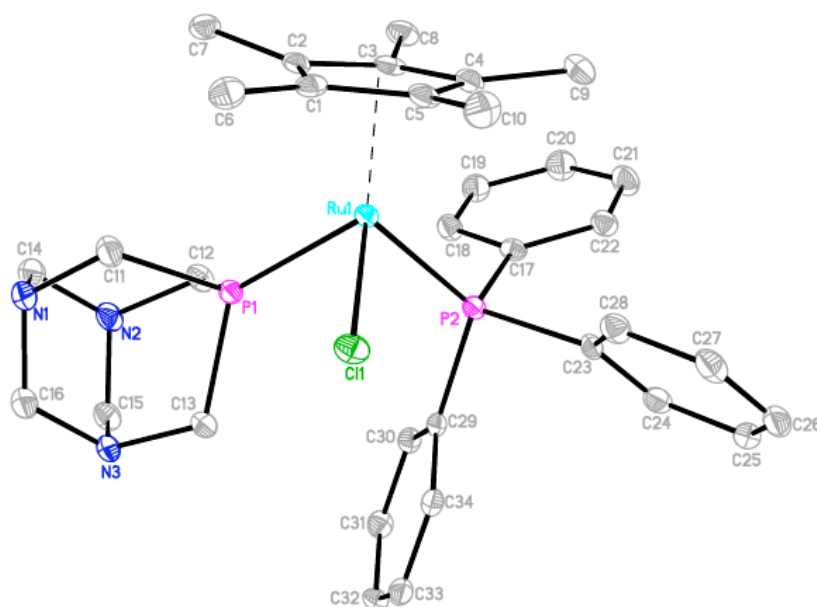


Figure 2.10: Thermal ellipsoid (50% probability) representation of $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ (**3**) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.

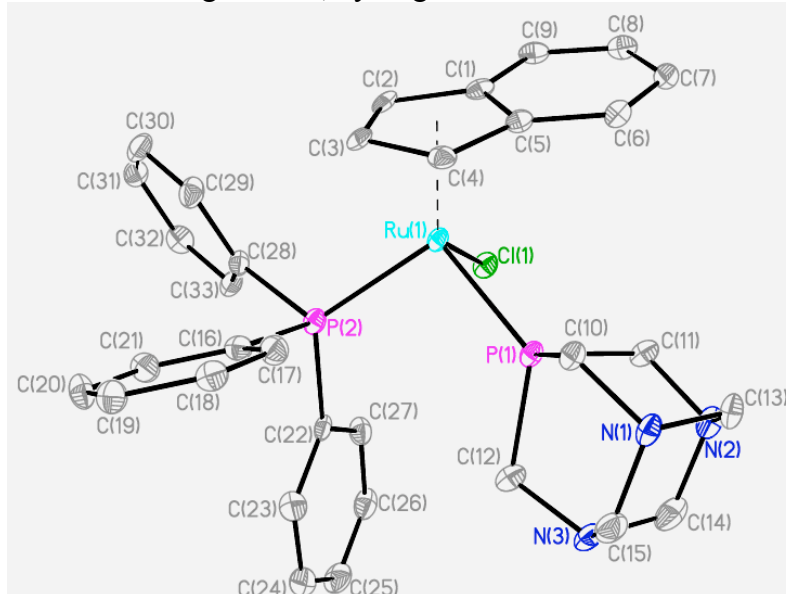


Figure 2.11: Thermal ellipsoid (50% probability) representation of $\text{Cp}^*\text{Ru(PMe}_3\text{)(PPh}_3\text{)Cl}$ (**6**) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.

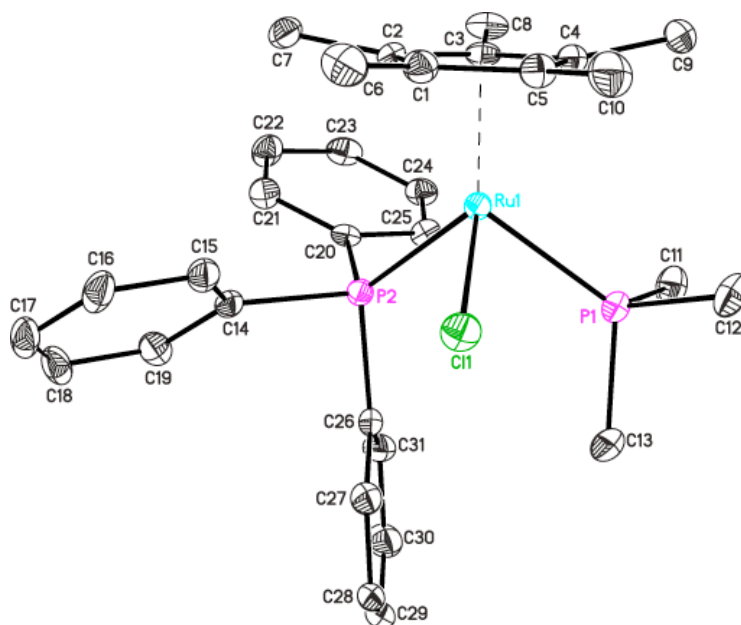


Figure 2.12: Thermal ellipsoid (50% probability) representation of $\text{IndRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (8) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.

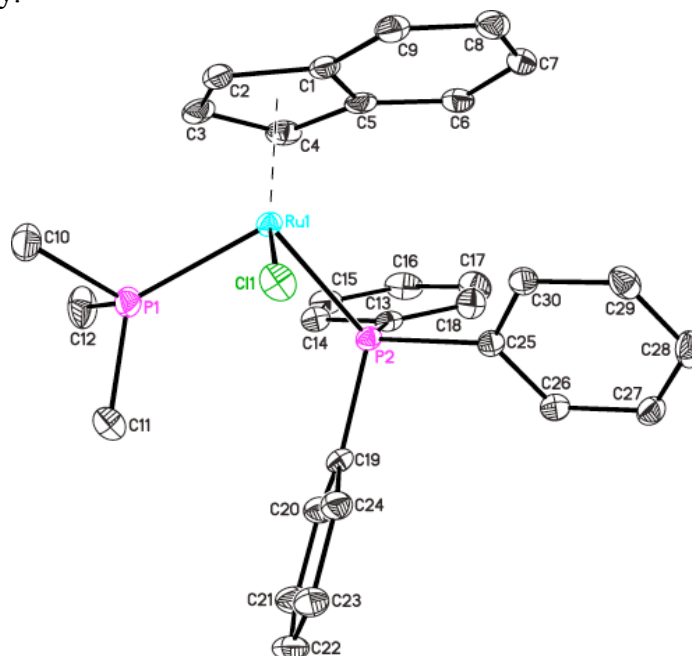


Figure 2.13: Thermal ellipsoid (50% probability) representation of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (10) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity.

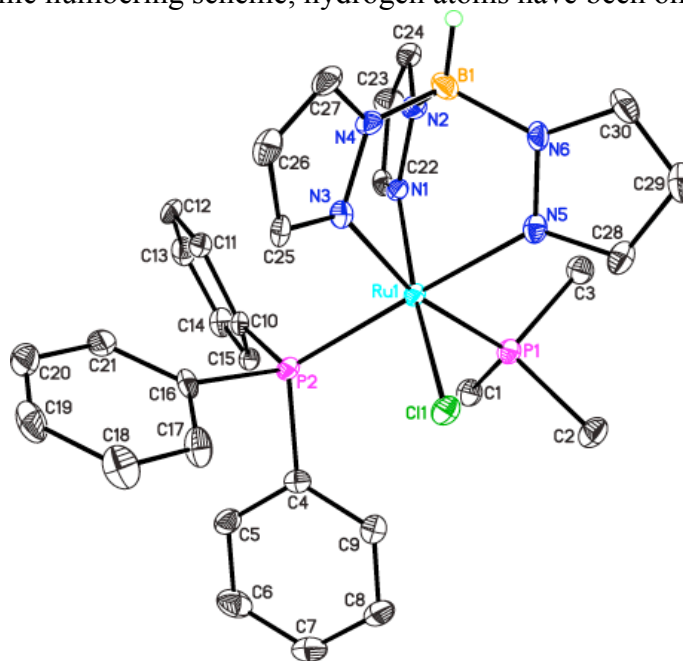


Table 2.4: Selected Bond Lengths [\AA] and Angles [deg] for a series of $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes; $\text{Cp}' = \text{Cp}^*, \text{Ind}, \text{ or } \text{Tp}$, and $\text{PR}_3 = \text{PTA or PMe}_3$.

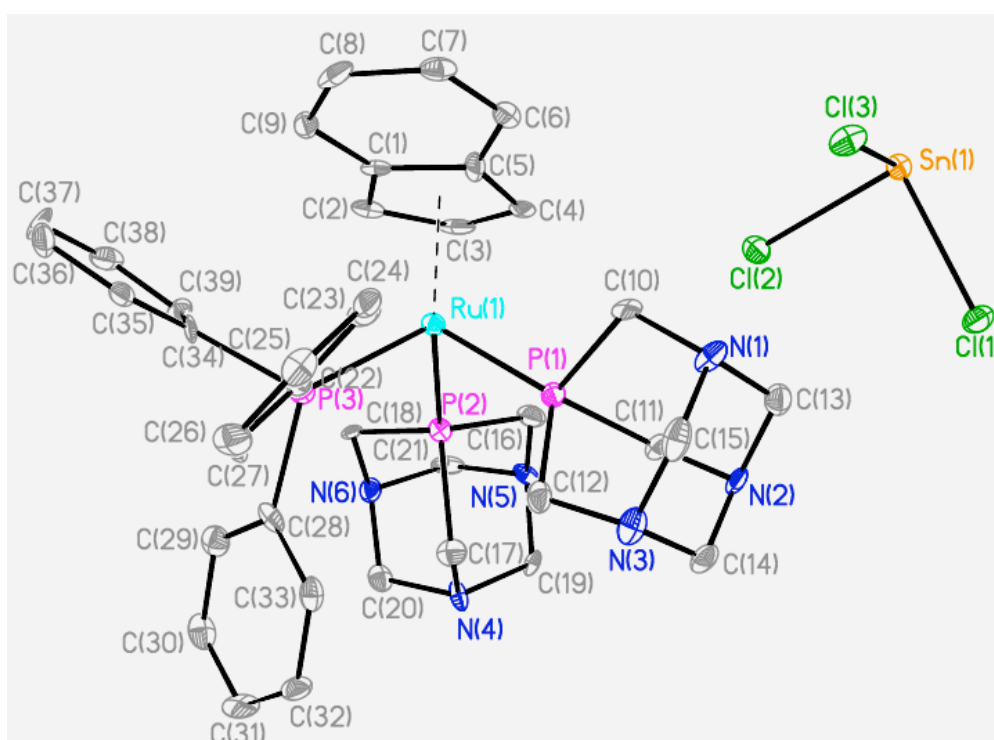
	1	3	6	8	10
Ru-Cl	2.4494(6)	2.4465(9)	2.4583(6)	2.4399(6)	2.4046(8)
Ru-P1	2.3008(7)	2.2931(10)	2.3006(7)	2.2608(7)	2.2993(11)
Ru-P2	2.2853(7)	2.2697(10)	2.3049(7)	2.3077(6)	2.3125(9)
Ru-Cp' _{cent}	1.868	1.890	1.870	1.895	-----
P1-Ru-P2	94.81(2)	98.19(4)	96.78(2)	98.72(2)	96.31(3)
P1-Ru-Cl	84.22(2)	90.03(3)	83.82(2)	87.03(2)	94.98(3)
P2-Ru-Cl	92.14(2)	91.99(3)	92.75(2)	92.54(2)	90.66(3)
Cp'-ML ₂	51.9	51.4	62.7	51.6	-----

2.3.3 Structure of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$

Due to difficulties related to crystal growth of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19), $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$ was synthesized by stirring a mixture of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ and excess $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in dichloromethane. Spectroscopically, both 19 and $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$ are identical, with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of both compounds displaying a triplet at 48.9 ppm ($^2J_{\text{PP}} = 30.1$ Hz) for the PPh_3 ligand and a doublet at -34.1 ppm ($^2J_{\text{PP}} = 30.1$ Hz) for the two PTA ligands. X-ray quality crystals of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$ was obtained by layering a dichloromethane solution of the ruthenium complex with diethyl ether. A thermal ellipsoid representation of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)](\text{SnCl}_3)$ is depicted in Figure 2.14, along with the atomic numbering scheme, and selected bond lengths and angles. The structure is not atypical with the indenyl ligand bound to ruthenium in an η^5 mode, and the two PTA ligands and one PPh_3 bound in a classic piano-stool fashion about the metal. It is interesting that the two PTA

ligands are inequivalent with one Ru-P_{PTA} distance significantly shorter than the other (Ru-P_{PTA} = 2.3076(19) and 2.2576(18) Å). The triphenylphosphine ligand exhibits the longest Ru-P bond length at 2.3456(19) Å, Ru-P3.

Figure 2.14: Thermal ellipsoid (50% probability) representation of the cationic complex [IndRu(PTA)₂(PPh₃)](SnCl₃) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.3076(19); Ru1-P2 = 2.2576(18); Ru1-P3 = 2.3456(19); Ru1-Ind_{cent} = 1.936; P1-Ru1-P2 = 92.99(7); P1-Ru1-P3 = 97.47(7); P2-Ru1-P3 = 95.56(7).



2.3.4 IndRu(PTA)(PPh₃)H: Synthesis, characterization and structure

The air-sensitive ruthenium-hydride, IndRu(PTA)(PPh₃)H (20), was obtained in 92% yield by the reaction of IndRu(PTA)(PPh₃)Cl (3) with sodium methoxide in refluxing methanol. The ³¹P{¹H} NMR spectrum (*see Appendix*) consists of two doublets due to coupling of the inequivalent phosphorus nuclei: ²J_{pp} = 29.0 Hz, Table 2.3. The ¹H

NMR spectrum is similar to that of the parent compound **3**, except for the characteristic Ru-H resonance at -16.3 ppm (dd, $^2J_{\text{PTA-H}} = 32.0$ Hz, $^2J_{\text{PPh}_3\text{-H}} = 29.2$ Hz), Figure 2.15. In the IR spectrum, $\nu(\text{Ru-H})$ of $\text{IndRu(PTA)(PPh}_3\text{)H}$ was observed at 1977 cm^{-1} . Crystals suitable for X-ray diffraction was grown by slow evaporation of a concentrated methanol solution of **20**. Thermal ellipsoid plot of $\text{IndRu(PTA)(PPh}_3\text{)H}$ is depicted in Figure 2.16, along with the atomic numbering scheme, and selected bond lengths and angles. The structure of $\text{IndRu(PTA)(PPh}_3\text{)H}$ is similar to that of the parent Ru-Cl complex **3**, except for a difference in the Ind- ML_2 angle by $\sim 18^\circ$ (51.4° , **3**; 69.9° , **20**). The increase in Ind- ML_2 angle from the Ru-Cl to the Ru-H complex can be attributed to both steric and electronic properties of H^- versus Cl^- .

Figure 2.15: ^1H NMR spectrum of $\text{IndRu(PTA)(PPh}_3\text{)H}$ (**20**) in CD_3OD .

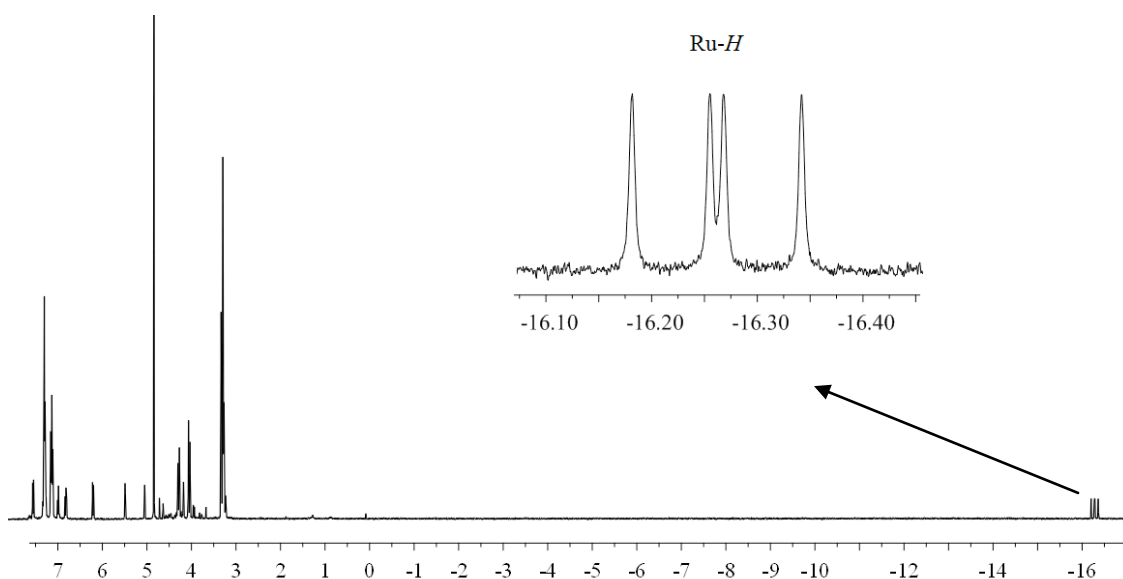
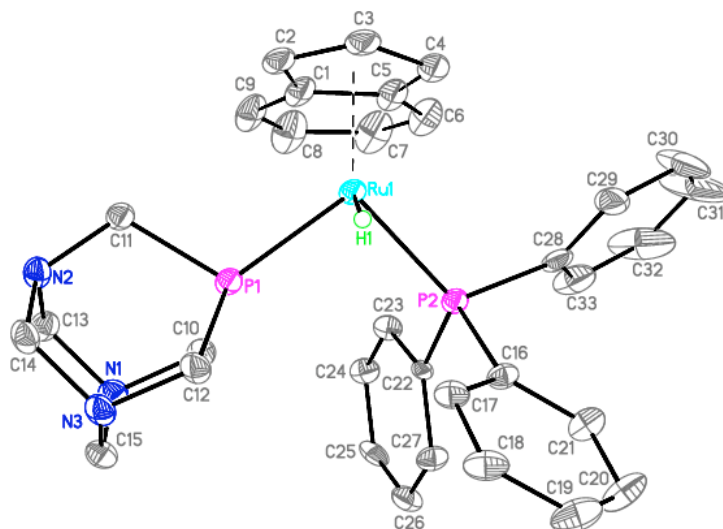


Figure 2.16: Thermal ellipsoid (50% probability) representation of IndRu(PTA)(PPh₃)H (20) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.2564(8); Ru1-P2 = 2.2539(8); Ru1-H1 = 1.52(4); Ru1-Ind_{cent} = 1.929; P1-Ru1-P2 = 97.59(3); P1-Ru1-H = 83.1(15); P2-Ru1-H = 82.7(15).



2.3.5 CpRu(PTA)₂SnCl₃: Synthesis, characterization and structure

CpRu(PTA)₂SnCl₃ (21) was obtained in 67% yield by stirring CpRu(PTA)₂Cl with SnCl₂•2H₂O in dichloromethane. The ³¹P{¹H} NMR spectrum in CD₂Cl₂ contains a single resonance at -27.9 ppm due to PTA ligands, and satellites due to ¹¹⁷Sn and ¹¹⁹Sn (²J_{P-Sn(119)} = 434.4 Hz, ²J_{P-Sn(117)} = 416.3 Hz), Figure 2.17. The ¹H NMR spectrum in D₂O displays a singlet at 5.83 ppm for the C₅H₅ protons. The PC₂H₂N and NC₂H₂N protons of the PTA ligands appear as a singlet at 4.1 ppm and an AB quartet centered at 4.75 ppm, respectively, Figure 2.18. X-ray quality crystals of (21) were obtained as yellow plates by slow diffusion of diethyl ether into a dichloromethane solution of the complex. Thermal ellipsoid plot of CpRu(PTA)₂SnCl₃ is depicted in Figure 2.19, along with the atomic numbering scheme, and selected bond lengths and angles.

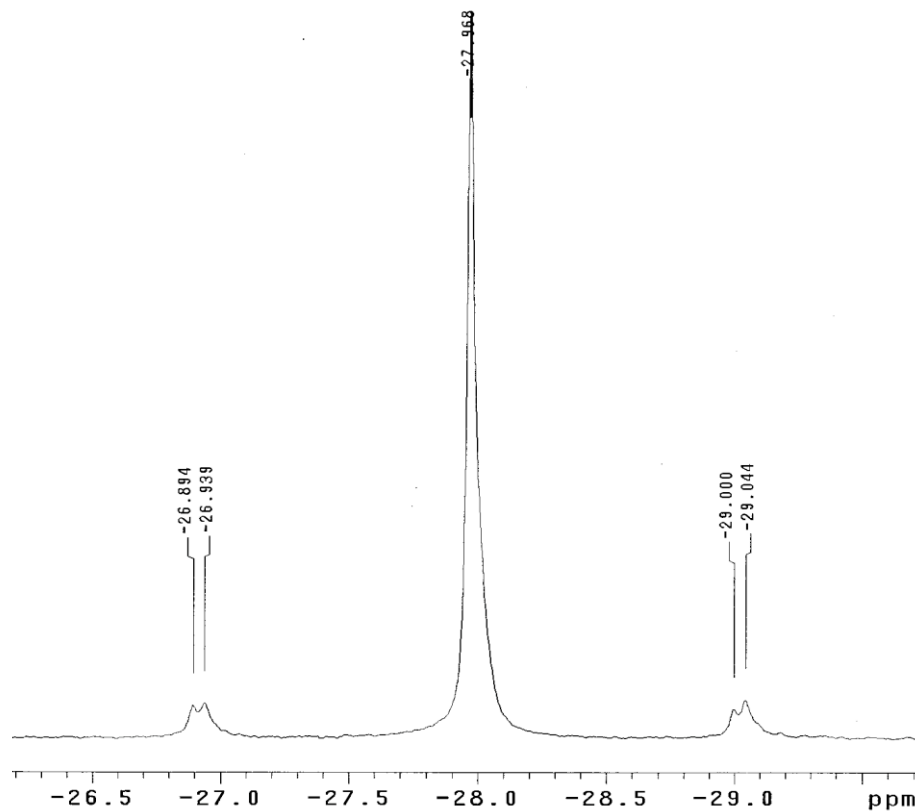
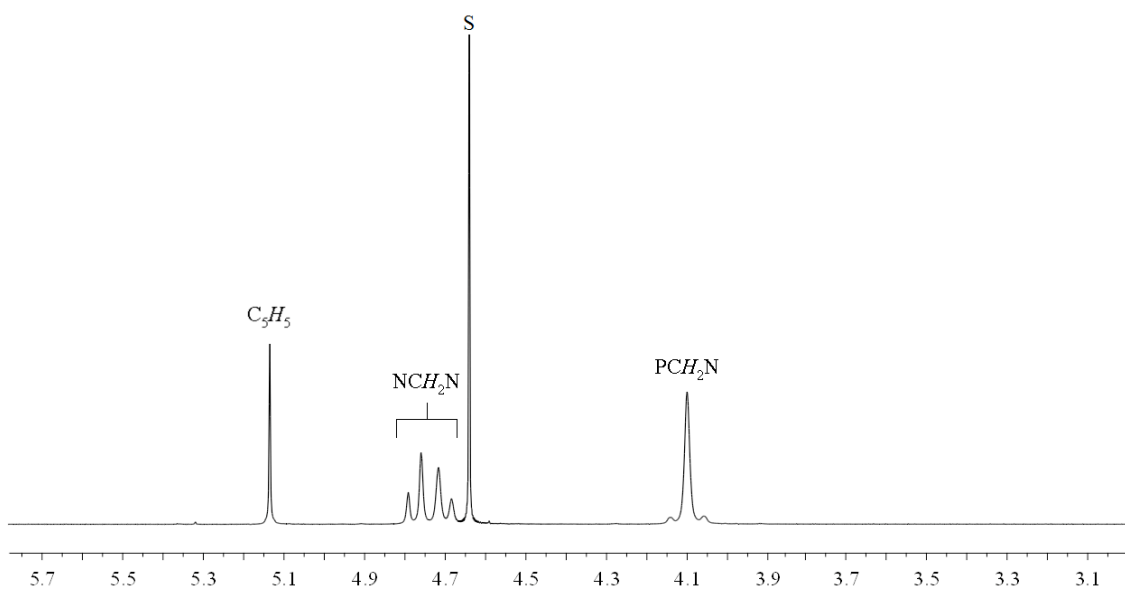
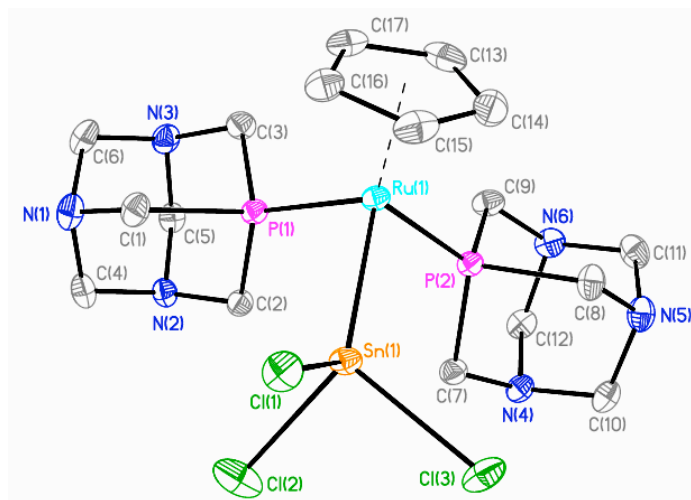
Figure 2.17: ^{31}P NMR spectrum of $\text{CpRu}(\text{PTA})_2\text{SnCl}_3$ (21) in CD_2Cl_2 .Figure 2.18: ^1H NMR spectrum of $\text{CpRu}(\text{PTA})_2\text{SnCl}_3$ (21) in D_2O ; Solvent (S).

Figure 2.19: Thermal ellipsoid (50% probability) representation of $\text{CpRu(PTA)}_2\text{SnCl}_3$ (21) with the atomic numbering scheme, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-P1 = 2.2747(5); Ru1-P2 = 2.2805(5); Ru1-Sn1 = 2.5319(2); P1-Ru1-P2 = 93.474(17); P1-Ru1-Sn1 = 93.964(13); P2-Ru1-Sn1 = 91.336(13).



2.3.6 Electrochemical studies

Cyclic voltammograms obtained using 1 mM solutions of $\text{Cp}'\text{Ru(PR}_3\text{)(PPh}_3\text{)Cl}$ complexes ($\text{Cp}' = \text{Dp, Ind, Cp, Tp}$; $\text{PR}_3 = \text{PTA, PPh}_3$) in dichloromethane are shown in Figure 2.20. Electrochemical data of these complexes, along with some literature values are summarized in Table 2.5. Among the series of complexes investigated, $\text{CpRu(PTA)(PPh}_3\text{)Cl}$ (4) displayed two chemically irreversible oxidation processes at 0.95 V and 0.77 V (Figure 2.20-A), whereas $\text{CpRu(PTA)}_2\text{Cl}$ (18) displayed an irreversible oxidation at 0.75 V (Figure 2.20-B). These results are different from the literature data where complexes 4 and 18 are reported to undergo reversible one-electron oxidation in DMF (Table 2.5, entries 4 and 10).²⁷ All other complexes investigated

exhibits a reversible Ru(II)/Ru(III) couple in the potential range of 0.55-0.85 V. The $E_{1/2}$ and ΔE values of CpRu(PPh₃)₂Cl (14) in DCM are greater than that of 14 in DMF (Table 2.5, entries 6 and 7).²⁷ The $E_{1/2}$ values indicated ease of oxidation of the complexes in the following order: 2 > 3 > 14 > (13, 15, and 22). These results are in good agreement with the electron donating ability of the Cp' ligands (Dp > Ind > Cp > Tp). Similar trends have been reported previously.²⁸

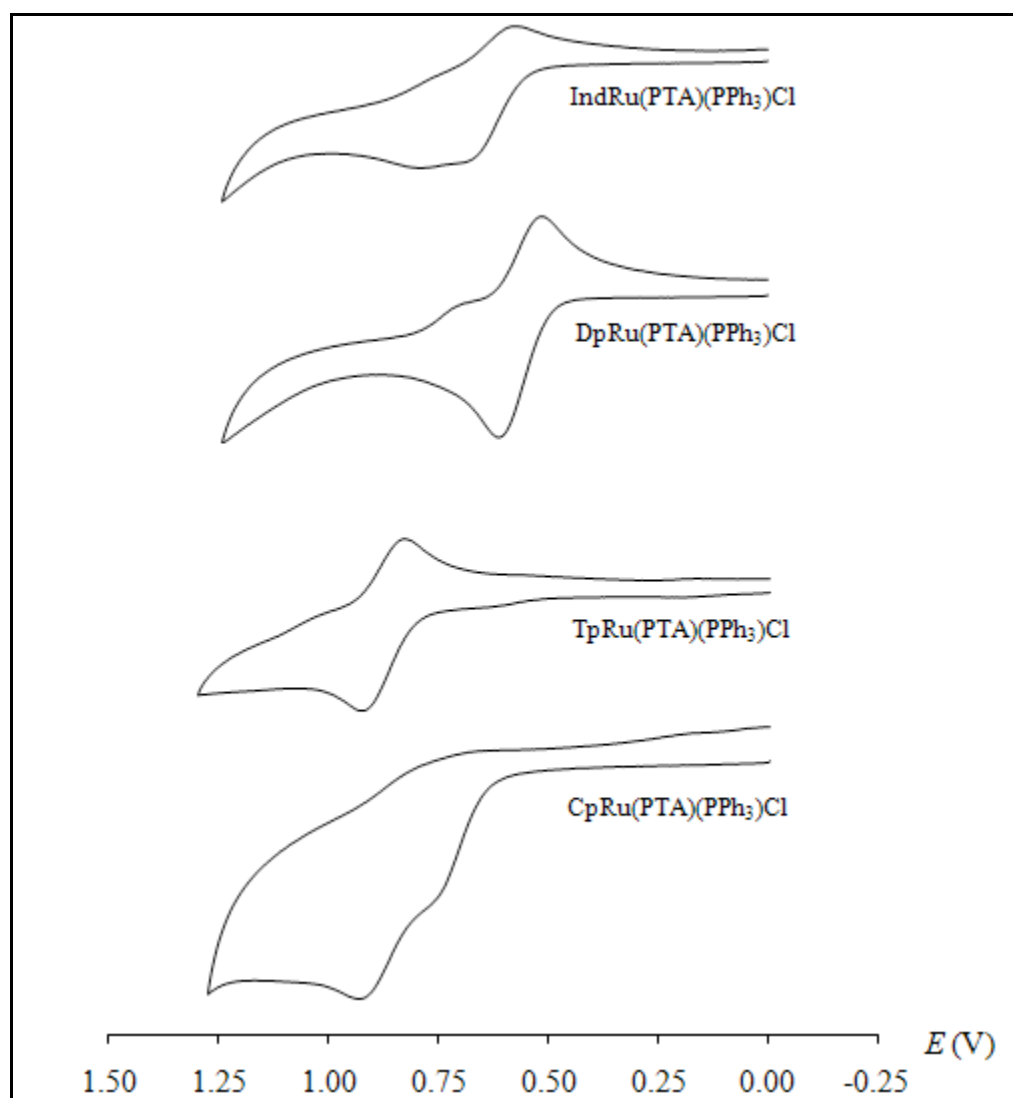
Table 2.5: Cyclic voltammetry data^a of Cp'Ru(PR₃)(PPh₃)Cl complexes (Cp' = Dp, Ind, Cp, Tp; PR₃ = PTA, PPh₃), together with some literature data.

Entry	Complex	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV) ^b	ΔE (mV) ^c
1	DpRu(PTA)(PPh ₃)Cl (2)	650	533	591.5	117
2	IndRu(PTA)(PPh ₃)Cl (3)	725	603	664	122
3	CpRu(PTA)(PPh ₃)Cl (4)	949/775	--	--	--
4 ^d	CpRu(PTA)(PPh ₃)Cl (4)	--	--	525	82
5	TpRu(PTA)(PPh ₃)Cl (13)	928	827	877.5	101
6	CpRu(PPh ₃) ₂ Cl (14)	863	736	799.5	127
7 ^d	CpRu(PPh ₃) ₂ Cl (14)	--	--	601	86
8	TpRu(PPh ₃) ₂ Cl (15)	905	783	844	122
9	CpRu(PTA) ₂ Cl (18)	747	--	--	--
10 ^d	CpRu(PTA) ₂ Cl (18)	--	--	451	84
11	TpRu(PTA) ₂ Cl (22)	944	811	877.5	133

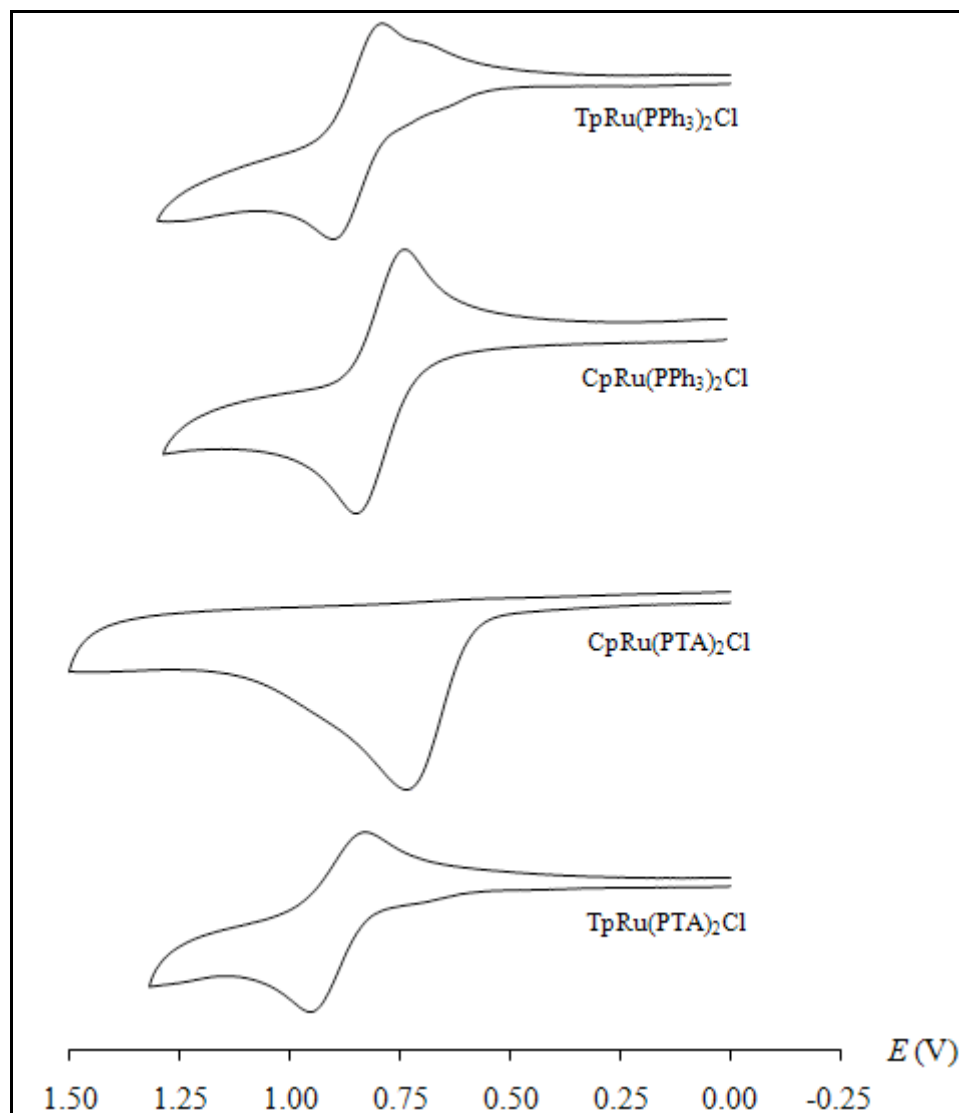
^a Sample, 1 mM; *n*Bu₄NBF₄ (100 mM) in dry and degassed CH₂Cl₂, under nitrogen at room temperature; scan rate, 50 mV/s; potentials are reported in mV versus ferrocene as an internal standard. ^b $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. ^c $\Delta E = E_{pa} - E_{pc}$. ^d Literature data: Sample, 1 mM; LiClO₄ (50 mM) in DMF.²⁷

Figure 2.20: Cyclic voltammograms of 1mM of ruthenium complexes in dichloromethane (supporting electrolyte, 100 mM *n*Bu₄NBF₄), obtained at scan rates of 50 mV/s; (A) Cp'Ru(PTA)(PPh₃)Cl complexes, (B) Cp'Ru(PR₃)₂Cl complexes (PR₃ = PTA, PPh₃).

(A) Cp'Ru(PTA)(PPh₃)Cl complexes



(B) $\text{Cp}^*\text{Ru}(\text{PR}_3)_2\text{Cl}$ complexes ($\text{PR}_3 = \text{PTA}, \text{PPh}_3$)



2.3.7 Reactivity of $\text{IndRu(PTA)(PPh}_3\text{)H}$ (20)

The Ru-hydride complexes undergo H/D exchange in some deuterated solvents. The H/D exchange occurs via protonation of the metal hydride, in which case one would expect the rate of H/D exchange to be faster with electron-rich metal centers. The results of the electrochemical studies (discussed above, and in Ref. 28) reveal that the Ind-Ru complexes are more electron rich than the Cp analogs. Despite high electron density, the H/D exchange of $\text{IndRu(PTA)(PPh}_3\text{)H}$ in CD_3OD at 25 °C ($t_{1/2} \sim 5.5$ d, $k_{\text{obs}} \sim 0.12$ d⁻¹) was found to be much slower than that of $\text{CpRu(PTA)(PPh}_3\text{)H}$ ($t_{1/2} \ll 10$ min), Scheme 2.5.²³ Hence, we believe that electronic difference alone between $\text{IndRu(PTA)(PPh}_3\text{)H}$ and $\text{CpRu(PTA)(PPh}_3\text{)H}$ is not likely responsible for this difference. The exact causes, however, remain unknown. The formation of $\text{IndRu(PTA)(PPh}_3\text{)D}$ was confirmed by the disappearance of the hydride resonance at -16.3 ppm in the ¹H NMR spectrum. The rate of the reaction (k_{obs} , pseudo-first-order kinetics) was measured from the plot of $\ln([A]/[A]_0)$ versus time (days) at room temperature, Figure 2.21.

Scheme 2.5: H/D exchange between $\text{IndRu(PTA)(PPh}_3\text{)H}$ and CD_3OD .

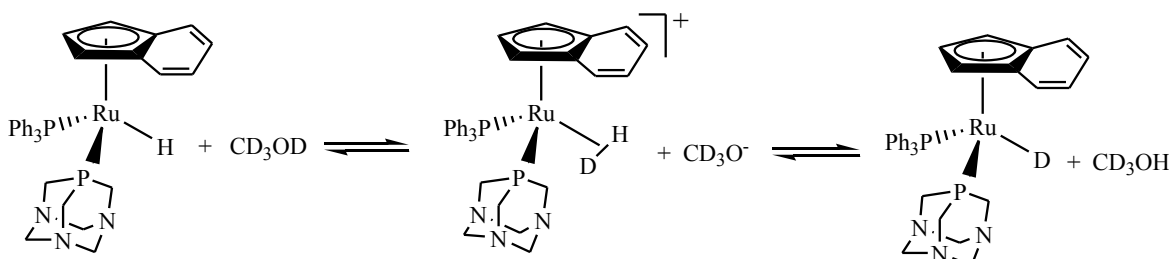
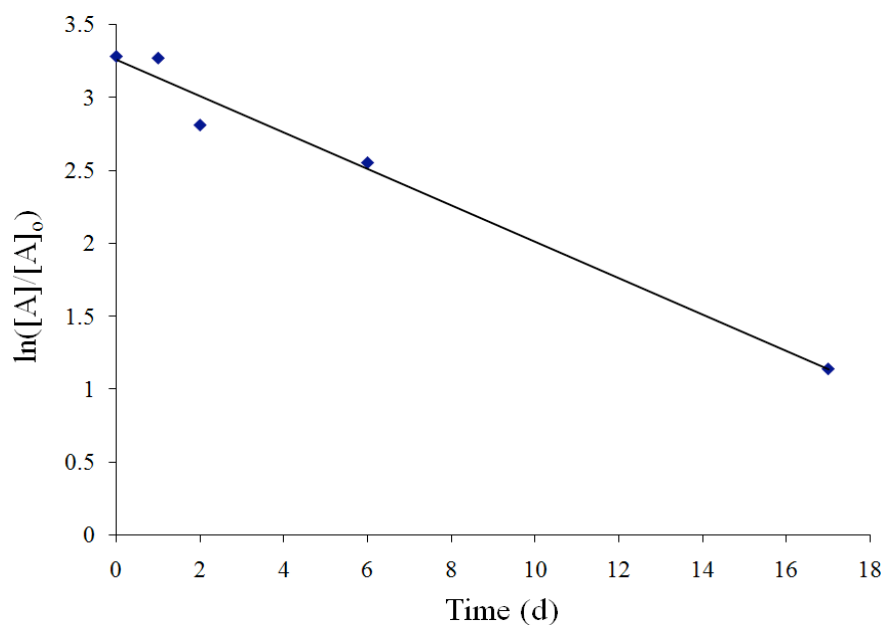


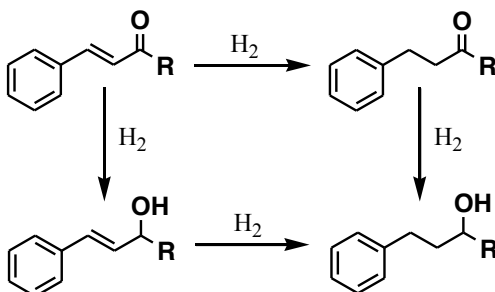
Figure 2.21: Plot of $\ln([A]/[A]_0)$ versus time for the H/D exchange reaction of $\text{IndRu(PTA)(PPh}_3\text{)H}$; peak height of the hydride at a given time (A), peak height of the hydride at zero time (A_0).



2.3.8 Reactivity of $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ (3)

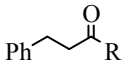
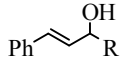
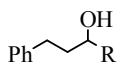
Transfer hydrogenation is the reduction of multiple bonds in the presence of a hydrogen donor (other than dihydrogen) and a metal catalyst.²⁹ A variety of substrates including ketones, imines, nitro compounds and α,β -unsaturated carbonyl compounds have been successfully reduced by transfer hydrogenation.^{29,30} We investigated the catalytic activity of $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ for the selective transfer hydrogenation of α,β -unsaturated carbonyls (cinnamaldehyde, benzylidene acetone, and chalcone) in aqueous media using formic acid as hydrogen donor. After the reaction, the products were extracted from the biphasic system with hexane and analyzed by ^1H NMR spectroscopy and GC-MS. The hydrogenation products of the aforementioned substrates are shown in Scheme 2.6.

Scheme 2.6: Hydrogenation pathway for the unsaturated substrates (R = H, cinnamaldehyde; Me, benzylidene acetone; Ph, chalcone).



The results of transfer hydrogenation reactions catalyzed by $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ (**3**) are summarized in Table 2.6. Complex **3** selectively reduced the C=O bond of cinnamaldehyde prior to reduction of the C=C bond affording a mixture of products; 54.8% cinnamyl alcohol and 45.2% dihydrocinnamyl alcohol (Table 2.6, entry 1). On the contrary, $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ catalyzed transfer hydrogenation of benzylidene acetone and chalcone resulted in exclusive formation of the C=C bond reduction products, 4-phenyl-butan-2-one (48.9%) and 1,3-diphenyl-propan-1-one (43.5%), respectively, (Table 2.6, entries 2 and 3). $\text{IndRu(PTA)(PPh}_3\text{)Cl}$ was found to be somewhat less active in comparison with its Cp and Dp counterparts.²³ For instance, the TOFs obtained for the transfer hydrogenation of cinnamaldehyde catalyzed by Cp and Dp analogs were 3.3 h^{-1} and 3.5 h^{-1} , respectively, as compared to TOF of 0.83 h^{-1} observed for $\text{IndRu(PTA)(PPh}_3\text{)Cl}$.²³ Similar results were obtained for the hydrogenation of benzylidene acetone and chalcone.

Table 2.6: Selective transfer hydrogenation of cinnamaldehyde, benzylidene acetone, and chalcone by IndRu(PTA)(PPh₃)Cl.

Entry	Substrate	Conv. (%)	TOF (h ⁻¹)	% Selectivity		
						
1	Cinnamaldehyde	>99.0	0.83	0.0	54.8	45.2
2	Benzylidene acetone	48.9	0.41	100.0	0.0	0.0
3	Chalcone	43.5	0.36	100.0	0.0	0.0

General conditions: 5 mol% IndRu(PTA)(PPh₃)Cl, 150 μ L 88% HCOOH, 2 mL H₂O, 1 mL MeOH, 24 h, 80 °C.

2.4 Conclusion

We have synthesized a series of air stable half-sandwich ruthenium(II) complexes of the type Cp'Ru(PR₃)(PPh₃)Cl (Cp' = Cp*, Cp, Dp, Ind or Tp; PR₃ = PTA or PMe₃), CpRu(PTA)₂SnCl₃, and air-sensitive hydride IndRu(PTA)(PPh₃)H by ligand substitution reaction of PPh₃ for PTA or PMe₃. They were characterized by NMR spectroscopy and X-ray crystallography. All these complexes exhibited classic three-legged piano stool geometry. Our attempts to synthesize IndRu(PTA)₂Cl resulted in the cationic complex [IndRu(PTA)₂PPh₃]Cl. Electrochemical studies performed on Cp'Ru(PR₃)(PPh₃)Cl complexes revealed that the ease of oxidation of the metal is proportional to the electron donating ability of Cp' ligands. IndRu(PTA)(PPh₃)H underwent H/D exchange in CD₃OD; the rate of exchange, however was unexpectedly slow. IndRu(PTA)(PPh₃)Cl was found to be moderately active for the transfer hydrogenation of α,β -unsaturated carbonyls. In the next chapter, we will discuss the atom transfer radical addition reactions catalyzed by a series of Cp'Ru(PR₃)(PPh₃)Cl complexes.

2.5 References:

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Chapter 3

Atom transfer radical addition reactions of various organic halides (CCl_4 , *p*-TsCl, $\text{CCl}_3\text{CO}_2\text{Et}$, $\text{CH}_2\text{ClCO}_2\text{Et}$, and CHCl_3) to styrene catalyzed by $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes*

3.1 Introduction

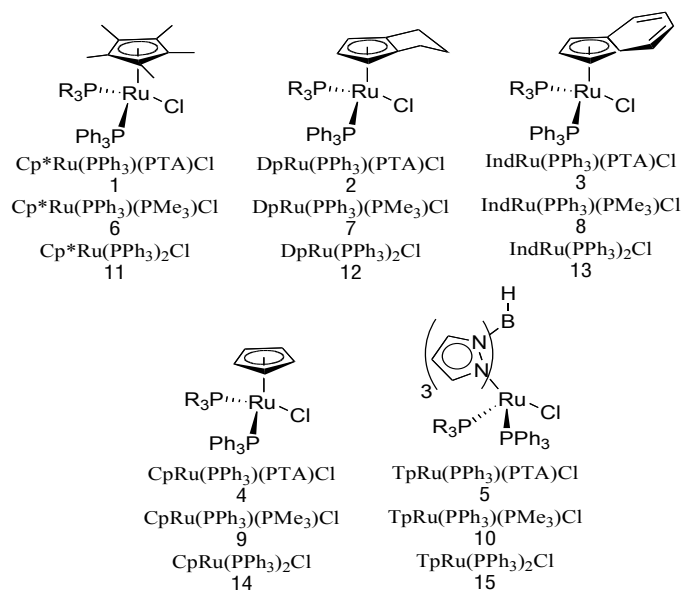
The addition of polyhalogenated compounds to olefins via radical intermediates was first reported by Kharasch and coworkers in the late 1930s, and is commonly referred to as the Kharasch addition or atom transfer radical addition (ATRA).¹ The transition-metal-promoted ATRA emerged in the early 1960s with the discovery of iron and copper salts as catalysts for the addition of CCl_4 and CHCl_3 to various olefins.^{2,3} The mechanistic details and applications of metal-catalyzed-ATRA have been discussed in Chapter 1. A wide variety of metal complexes are known to catalyze the radical reactions.^{4,5,6} Ruthenium complexes, in particular, have displayed remarkable catalytic performance, with $\text{RuCl}_2(\text{PPh}_3)_3$ being the first ruthenium complex reported as a highly efficient and versatile ATRA catalyst.^{7,8,9} Besides promoting ATRA, $\text{RuCl}_2(\text{PPh}_3)_3$ also

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initiates the mechanistically related reactions, namely controlled polymerization (ATRP) and cyclization (ATRC).^{5,8,10} Recent developments in ATRA chemistry have focused on half-sandwich Ru(II) and Ru(III) phosphine complexes bearing η^6 -arene or η^5 -cyclopentadienyl type ligands.^{8,11-13} Among the various ruthenium catalysts discussed in Chapter 1, $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ ^{12a,12b} and $[(\eta^5\text{-CB})\text{Ru}(\text{PPh}_3)_2\text{H}]$ ¹³ (where CB is a monoanionic carborane ligand) are the superior ATRA catalysts known to date.

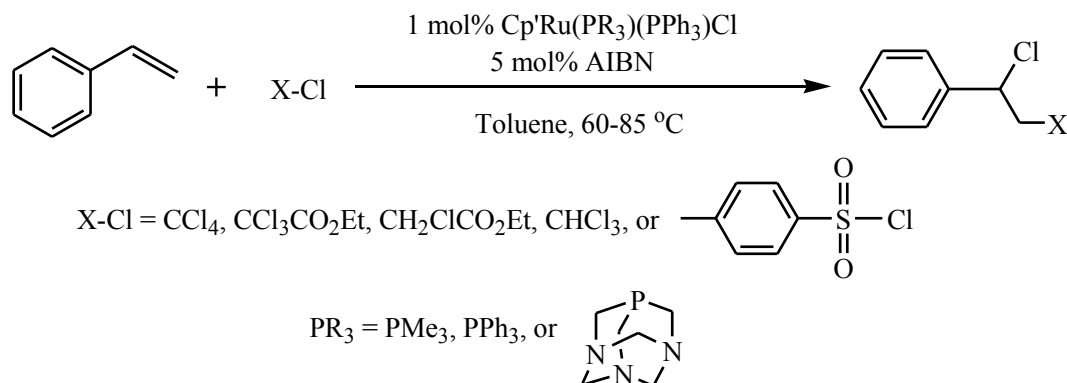
Azobis-isobutyronitrile (AIBN) has recently been employed in ruthenium-catalyzed ATRA reactions by Severin and coworkers who have suggested that AIBN allows for the reduction of $\text{Cp}^*\text{Ru}^{\text{III}}(\text{PPh}_3)\text{Cl}_2$ back to the catalytically active $\text{Cp}^*\text{Ru}^{\text{II}}(\text{PPh}_3)\text{Cl}$.^{11a} Recently, this methodology has been applied with great success to copper-catalyzed ATRA reactions.¹⁴

Figure 3.1: $\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes with various PR_3 ligands used as catalyst precursors for ATRA.



In chapter 2, we described the synthesis and characterization of a series of ruthenium mixed-phosphine complexes of the type $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{X}$, where $\text{Cp}' = (\eta^5\text{-C}_5\text{Me}_5^-, \text{Cp}^*), (\eta^5\text{-C}_8\text{H}_9^-, \text{Dp}), (\eta^5\text{-C}_9\text{H}_7^-, \text{Ind}), (\eta^5\text{-C}_5\text{H}_5^-, \text{Cp}),$ or $(\eta^3\text{-HB}(\text{pz})_3, \text{Tp})$; $\text{PR}_3 = 1, 3, 5\text{-triaza-7-phosphadamantane (PTA) or } \text{PMe}_3$; and $\text{X} = \text{Cl}$ or H . In this chapter, we report on the efficiency of a series of $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ ($\text{PR}_3 = \text{PTA}, \text{PMe}_3, \text{PPh}_3$) complexes, Figure 3.1, as catalysts for the additions of $\text{CCl}_4, \text{CHCl}_3, p\text{-toluenesulfonylchloride (TsCl)}, \text{CCl}_3\text{COOEt},$ and $\text{CH}_2\text{ClCOOEt}$ to styrene in the presence of AIBN (Scheme 3.1).

Scheme 3.1: Atom transfer radical addition of various organic halides to styrene catalyzed by $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ ($\text{PR}_3 = \text{PTA}, \text{PMe}_3, \text{PPh}_3$) complexes.



3.2 Experimental Section

3.2.1 *Materials and methods*

All reactions were performed under a dry nitrogen atmosphere, using conventional Schlenk vacuum-line techniques. Reagents were purchased from commercial suppliers, and used as received. Solvents were dried with molecular sieves and degassed with N₂, prior to use. Cp'Ru(PPh₃)₂Cl (Cp' = Cp*,¹⁵ Dp,¹⁶ Ind,¹⁷ Cp,¹⁸ Tp¹⁹), Cp'Ru(PTA)₂Cl (Cp = Cp*,²⁰ Dp,²¹ Cp^{20,22}), DpRu(PTA)(PPh₃)Cl,²¹ CpRu(PTA)(PPh₃)Cl,^{21,23} TpRu(PTA)(PPh₃)Cl,²⁴ and IndRu(PPh₃)(PMe₃)Cl²⁵ were prepared as described in the literature. The synthetic procedures for Cp*Ru(PTA)(PPh₃)Cl, IndRu(PTA)(PPh₃)Cl, and Cp'Ru(PPh₃)(PMe₃)Cl (Cp' = Cp*, Dp, Cp, Tp) may be found in Chapter 2. Kharasch addition reactions were carried out under nitrogen atmosphere in standard NMR tubes or in 1.5 mL vials. The following Kharasch adducts were identified by comparison of their spectral data with those reported in the literature: 1,3,3,3-tetrachloropropyl benzene (23),²⁶ 2-chloro-2-phenylethyl *p*-tolyl sulfone (24),²⁷ 2,2,4-trichloro-4-phenyl-butyric acid ethyl ester (25),²⁷ 1,3,3-trichloropropyl-benzene (26),²⁶ and 4-chloro-4-phenyl-butyric acid ethyl ester (27)²⁸. Each catalytic run was repeated at least twice to ensure reproducibility. NMR spectra were recorded with a Varian NMR System 400 spectrometer. ¹H NMR spectra were referenced to a residual solvent relative to tetramethylsilane (TMS).

3.2.2 Atom transfer radical addition procedure

ATRA of CCl₄ to styrene

To a 1.5 mL vial was added 1 mol % catalyst (0.0138 mmol), 5 mol % AIBN (11.3 mg, 0.069 mmol), styrene (158 μ L, 1.38 mmol), CCl₄ (533 μ L, 5.52 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene-*d*₈ was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated at 60°C in an oil-bath. The formation of product was monitored by ¹H NMR spectroscopy at predetermined intervals.

1,3,3,3-tetrachloropropyl benzene (23): ¹H NMR (400 MHz, toluene-*d*₈; Figure 3.2): δ 3.4-3.6 (m, 2H, CH₂CCl₃); 5.24 (t, 1H, CHCl), 7.2-7.4 (m, 5H, C₆H₅).

ATRA of p-TsCl to styrene

To a 1.5 mL vial was added 1 mol % catalyst (0.0044 mmol), 5 mol % AIBN (4 mg, 0.022 mmol), styrene (50 μ L, 0.44 mmol), *p*-TsCl (99 mg, 0.52 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene-*d*₈ was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated at 60°C in an oil-bath. The formation of product was monitored by ¹H NMR spectroscopy at predetermined intervals.

2-chloro-2-phenylethyl *p*-tolyl sulfone (24): ¹H NMR (400 MHz, toluene-*d*₈; Figure 3.8): δ 2.1 (s, 3H, CH₃); 3.6-3.9 (m, 2H, CH₂SO₂); 5.4 (t, 1H, CHCl); 6.9 (d, 2H, (CH)₂); 7.0-7.2 (m, 5H, C₆H₅); 7.6 (d, 2H, (CH)₂).

ATRA of CCl₃CO₂Et to styrene

To a 1.5 mL vial was added 1 mol % catalyst (0.0138 mmol), 5 mol % AIBN (11.3 mg, 0.069 mmol), styrene (158 μ L, 1.38 mmol), CCl₃CO₂Et (230 μ L, 1.66 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene-*d*₈ was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated at 60°C in an oil-bath. The formation of product was monitored by ¹H NMR spectroscopy at predetermined intervals.

Ethyl-2,2,4-trichloro-4-phenyl-butyric acid ethyl ester (25): ¹H NMR (400 MHz, toluene-*d*₈; Figure 3.11): δ 1.04 (t, 3H, OCH₂CH₃); 3.1-3.5 (m, 2H, CH₂); 3.8-4.0 (m, 2H, OCH₂CH₃); 5.25 (t, 1H, CHCl); 7.0-7.3 (m, 5H, C₆H₅).

ATRA of CHCl₃ to styrene

To a 1.5 mL vial was added 1 mol % catalyst (0.0138 mmol), 5 mol % AIBN (11.3 g, 0.069 mmol), styrene (158 μ L, 1.38 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). The reaction mixture was brought to 1 mL with the addition of CHCl₃, and heated at 60°C in an oil-bath. Aliquots of the reaction mixture (~30 μ L) were diluted with CDCl₃ and analyzed by ¹H NMR spectroscopy.

1,3,3-trichloropropyl benzene (26): ¹H NMR (400 MHz, CDCl₃; Figure 3.14): δ 2.7-3.0 (m, 2H, CH₂); 5.0 (m, 1H, CHCl); 5.74 (m, 1H, CHCl₂); 7.2-7.3 (m, 5H, C₆H₅).

ATRA of CH₂ClCO₂Et to styrene

To a 1.5 mL vial was added 1 mol % catalyst (0.0138 mmol), 5 mol % AIBN (11.3 mg, 0.069 mmol), styrene (158 μ L, 1.38 mmol), CH₂ClCO₂Et (177 μ L, 1.66 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene-*d*₈ was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and

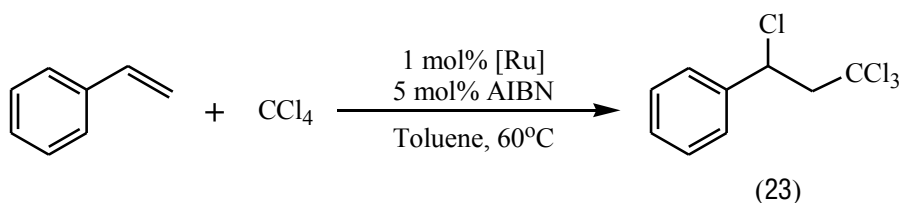
heated at 85°C in an oil-bath. The formation of product was monitored by ^1H NMR spectroscopy at predetermined intervals.

Ethyl-4-chloro-4-phenylbutanoate (27): ^1H NMR (400 MHz, toluene- d_8 ; Figure 3.15): δ 1.03 (t, 3H, OCH_2CH_3); 2.25-2.4 (m, 4H, $(\text{CH}_2)_2$); 4.02 (m, 2H, OCH_2CH_3); 4.86 (t, 1H, CHCl); 7.0-7.4 (m, 5H, C_6H_5).

3.3 Results and Discussion

3.3.1 ATRA of CCl_4 to styrene

Scheme 3.2: Addition of CCl_4 to styrene



Current ruthenium catalysts for ATRA, such as $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$, are active but have exhibited limited Total Turnovers (TTO). For example, $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ and $\text{Cp}^*\text{RuCl}_2(\text{PPh}_3)$ catalyzed addition of CCl_4 to styrene with TTO of 1600-1700^{12a} and 13,200,^{11a} respectively. We hypothesized that replacement of one labile PPh_3 ligand with a more strongly bound ligand, such as PTA or PMe_3 , would increase stability and therefore longevity of the catalyst. Complexes 1-10 were examined as catalysts for the addition of CCl_4 to styrene (Scheme 3.2). The results of these experiments are summarized in Table 3.1. Complex 1, with the electron rich Cp^* ligand, exhibited the highest activity with >99% conversion in 22 min at 60 °C (Table 3.1, entry 2). A turn over frequency (TOF) of 1060 h^{-1} and TTO of 11,600 was achieved with

Cp*Ru(PTA)(PPh₃)Cl **1** at 60°C which are comparable to the highest reported for a Ru ATRA catalyst (TOF = 1500 h⁻¹, TTO = 9000). Even at room temperature catalyst **1** provided >99% conversion in 4 h (TOF 33 h⁻¹; Table 3.1, entry 1).¹³ The next most active catalyst among the series 1-10 was the PMe₃ analogue **6**; a TOF of 933 h⁻¹ and TTO of 6000 was obtained. Trends in catalytic activity for compounds 1-10 towards addition of CCl₄ to styrene correlate with the electron donating ability of the Cp' ligand, Cp* >> Dp > Ind > Cp > Tp. These results indicate that Cp' ligands play a significant role in the catalyst performance. The high activity of complexes **1** and **6** may be attributed to the steric bulk and higher electron donating ability of the Cp* ligands, which would allow the stabilization of the coordinatively unsaturated 16-electron ruthenium center (*Refer to the mechanism discussed in Chapter 1*). A bar graph comparing the rates of the reactions (TOFs) catalyzed by complexes 1-4 and 6-9 is depicted in Figure 3.3. The initial rates were determined by calculating the TOFs at 50-65% conversion, as the reaction rates slow at high conversion. The TOFs of Cp* complexes **1** and **6** were significantly high in comparison with those of Dp, Ind, and Cp complexes, Figure 3.3. The Tp complexes **5** and **10** exhibited the least reactivity with only 27% yield (after 75 h) and 46% yield (after 31 h), respectively. For slow reactions (> 10 h), although complete conversion of styrene was observed, the yield of the monoadduct was considerably lower (Table 3.1, entries 7, 8, 12 and 13). This difference may be attributed to the formation of side-products such as oligomers/polymers. A control experiment was performed in order to assess the role of the catalyst in the radical reactions. As expected, in the absence of catalyst, no Kharasch product was detected by ¹H NMR spectroscopy (Table 3.1, entry 14). However, only

13% styrene was left in the reaction mixture after 3 days, indicating the formation of polymers/oligomers.

It has been reported previously that the reactivity of the catalyst is dependent on the Ru-P bond strength and largely independent of the electronics of the phosphine.^{12a} In our case, Cp*Ru(PMe₃)(PPh₃)Cl complexes 7-10 showed enhanced reactivity towards ATRA reactions as compared to their PTA counterparts, which corresponds to the electron donating ability of the phosphines (PMe₃ > PTA).²⁹ An exception was the most electron rich Cp* complexes 1 and 6; the addition of CCl₄ to styrene catalyzed by 6 was slightly slower than that for 1 (TOF 933 h⁻¹ vs. TOF 1060 h⁻¹; Table 3.1, entries 2 and 9).

Table 3.1: Atom transfer radical addition of CCl₄ to styrene catalyzed by Cp*Ru(PR₃)(PPh₃)Cl complexes 1 – 10 (PR₃ = PMe₃, PTA).^a

Entry	Catalyst	Substrate	TOF ^b (h ⁻¹)	Time (h)	Yield ^c (%)	Conv. ^d (%)
1 ^e	Cp*Ru(PTA)(PPh ₃)Cl (1)	CCl ₄	33	4	>99	>99
2	Cp*Ru(PTA)(PPh ₃)Cl (1)	CCl ₄	1060	0.37	>99	>99
3 ^f	Cp*Ru(PTA)(PPh ₃)Cl (1)	CCl ₄	415	0.63	>99	>99
4 ^g	Cp*Ru(PTA)(PPh ₃)Cl (1)	CCl ₄	444	1.25	>99	>99
5	DpRu(PTA)(PPh ₃)Cl (2)	CCl ₄	24	3.5	>99	>99
6	IndRu(PTA)(PPh ₃)Cl (3)	CCl ₄	12	8	>99	>99
7	CpRu(PTA)(PPh ₃)Cl (4)	CCl ₄	2	28	61	>99
8	TpRu(PTA)(PPh ₃)Cl (5)	CCl ₄	--	75	27	>99
9	Cp*RuCl(PMe ₃)(PPh ₃) (6)	CCl ₄	933	1.25	>99	>99
10	DpRuCl(PMe ₃)(PPh ₃) (7)	CCl ₄	51	2	>99	>99
11	IndRuCl(PMe ₃)(PPh ₃) (8)	CCl ₄	20	6	>99	>99
12	CpRuCl(PMe ₃)(PPh ₃) (9)	CCl ₄	8	11	95	>99
13	TpRuCl(PMe ₃)(PPh ₃) (10)	CCl ₄	--	31	46	>99
14 ^h	---	CCl ₄	0.0	72	0.0	87

^a All reactions were performed in toluene-*d*₈ at 60°C using 1 mol% catalyst and 5 mol% AIBN; CCl₄/styrene is 4:1; ^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene; ^c Yield is determined by ¹H NMR spectroscopy of product versus internal standard; ^d Conversion is based on the consumption of styrene; ^e 25 °C; ^f without AIBN; ^g 10 mol% PPh₃; ^h No catalyst.

Figure 3.2: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **23** (1,3,3,3-tetrachloropropyl benzene) formed by the addition of CCl_4 to styrene; Internal standard (*), AIBN (\blacktriangle), Solvent (S).

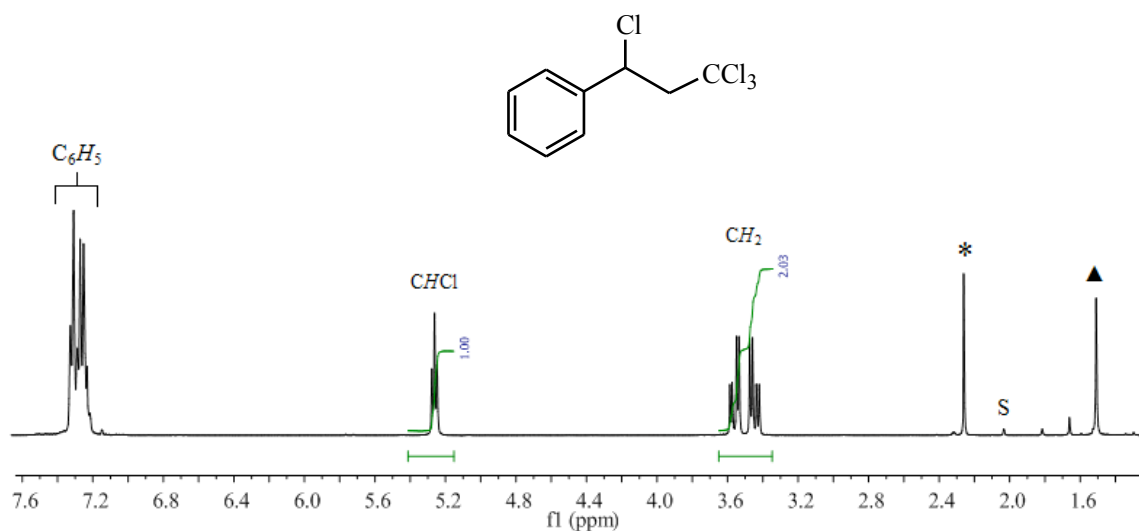
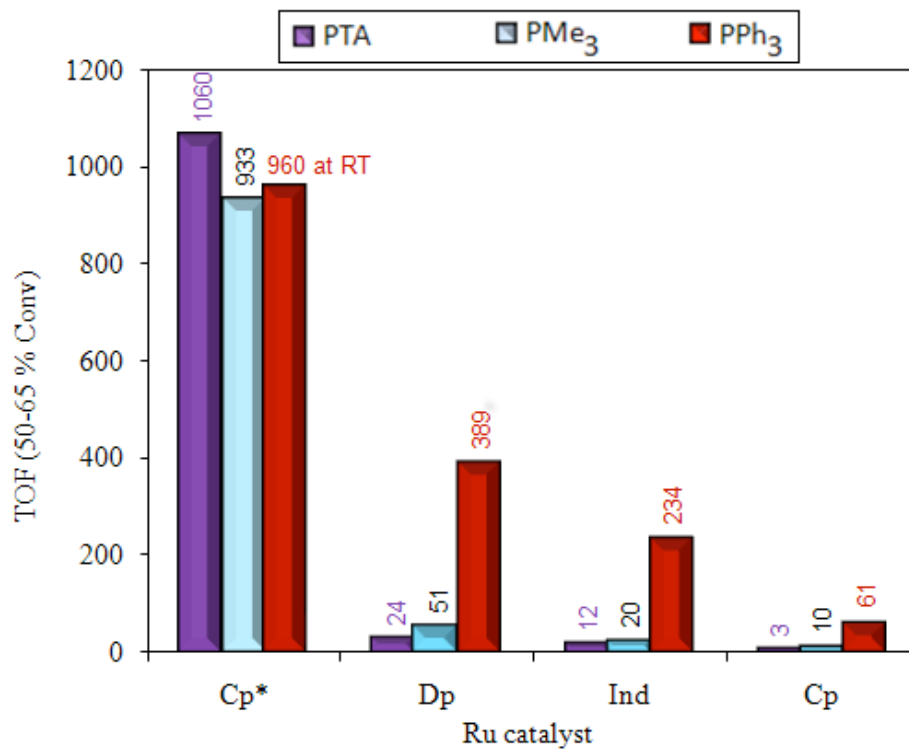


Figure 3.3: Comparison of the rates (TOF's in h^{-1}) of CCl_4 addition to styrene catalyzed by PTA complexes (1-4), PMe_3 complexes (6-9), and bis- PPh_3 complexes (11-14).



For comparison purposes, we investigated the activity of Cp'Ru(PPh₃)₂Cl complexes (11-15) towards the addition of CCl₄ to styrene under the same conditions as complexes 1 – 10, Table 3.2, entries 1-5 (compounds 11, 13 and 14 have been previously reported as ATRA catalysts^{12a,12b}).

Table 3.2: Atom transfer radical addition of CCl₄ to styrene catalyzed by Cp'Ru(PR₃)₂Cl complexes 11 – 18 (PR₃ = PPh₃, PTA)^a

Entry	Catalyst	Substrate	TOF ^b (h ⁻¹)	Time (h)	Yield ^c (%)
1 ^d	Cp*Ru(PPh ₃) ₂ Cl (11)	CCl ₄	>960	0.1	96
2	DpRu(PPh ₃) ₂ Cl (12)	CCl ₄	389	1.25	>99
3	IndRu(PPh ₃) ₂ Cl (13)	CCl ₄	234	1.75	>99
4	CpRu(PPh ₃) ₂ Cl (14)	CCl ₄	61	2.75	>99
5	TpRu(PPh ₃) ₂ Cl (15)	CCl ₄	---	55	38
6 ^e	Cp*Ru(PTA) ₂ Cl (16)	CCl ₄	44	2.5	>99
7 ^e	DpRu(PTA) ₂ Cl (17)	CCl ₄	---	24	31
8 ^e	CpRu(PTA) ₂ Cl (18)	CCl ₄	---	24	5

^a All reactions were performed in toluene-*d*₈ at 60 °C using 1 mol% catalyst and 5 mol% AIBN, CCl₄/styrene is 4:1; ^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene; ^c Yield is determined by ¹H NMR spectroscopy of product versus internal standard. ^d Room temperature, TOF calculated at 96 % yield; ^e For solubility reasons, the reactions were performed in CD₂Cl₂.

The Cp'Ru(PPh₃)₂Cl complexes 11-15 all exhibited superior performance relative to their mixed-phosphine counterparts. We also tested the catalytic activity of the substitutionally inert Cp'Ru(PTA)₂Cl complexes 16-18 of which only the Cp* complex exhibited any significant reactivity (Table 3.2, entries 6-8). The reactivity order was Cp'Ru(PPh₃)₂Cl > Cp'Ru(PR₃)(PPh₃)Cl > Cp'Ru(PTA)₂Cl. These results suggest that the dissociation of the phosphine is crucial in the reaction, which was confirmed by the retardation of the reaction rate in presence of excess PPh₃ (Table 3.1, entry 4). Substitution of one of the two labile PPh₃ ligands in Cp'Ru(PPh₃)₂Cl with a strongly

bound phosphine, such as PTA or PMe_3 , lead to reduced activity of the mixed-phosphine complexes 1-10. We also tested the activity of $\text{CpRu}(\text{dppe})\text{Cl}$, where 'dppe' is a chelating phosphine (dppe = diphenylphosphinoethane). Only $\sim 20\%$ yield was obtained after 4 days at $80\text{ }^\circ\text{C}$. These results also indicate the significance of having labile phosphines on the catalyst.

The $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11) catalyzed reaction was remarkably fast; a 96% yield was obtained after only 6 minutes at room temperature ($\text{TOF} > 960\text{ h}^{-1}$) as compared to 99% yield after 4 h for (1) ($\text{TOF} 33\text{ h}^{-1}$). The Dp (12), Ind (13), and Cp (14) complexes also exhibited high reactivity with $>99\%$ yield in 1-3 h. The TOFs of (12), (13), and (14) were an order of magnitude greater than that of the PTA and PMe_3 analogs. The reactivity of $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ (15) was low (38% yield after 55 h) and comparable to that of (5) and (10).

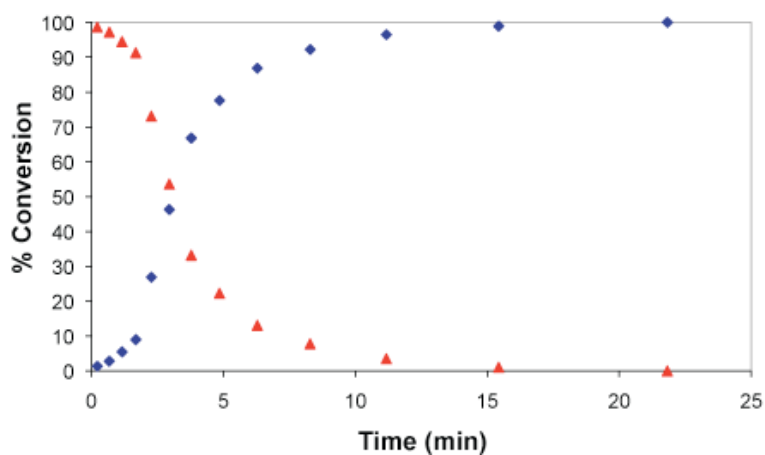
We also calculated total turnover (TTO) for Cp^*Ru catalysts. Total turnovers indicate the longevity of the catalyst; for an ideal catalyst, total turnover is infinite. Using 0.005 mol% of (11), a TTO of 16,400 was obtained after 24 h at $60\text{ }^\circ\text{C}$ (Table 3.3, entry 3). Reducing the catalyst loading of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) from 1 mol% to 0.005 mol%, we obtained a TTO of 11,600 in 24 h which is slightly lower than that reported for $\text{Cp}^*\text{Ru}(\text{PPh}_3)\text{Cl}_2$ ^{11a} (Table 3.3, entry 1). The PMe_3 analogue (6), at 0.005 mol% catalyst loading, provided a TTO of 6,000 after 24 h (Table 3.3, entry 2). In all three cases, the conversion of styrene was higher than the yield of the 1:1 adduct, which is indicative of the formation of side-products (polymers).

Table 3.3: TTOs obtained at 0.005 mol% catalyst loading for the addition of CCl₄ to styrene catalyzed by Cp*Ru(PR₃)(PPh₃)Cl complexes (PR₃ = PTA, PMe₃, PPh₃).^a

Entry	Catalyst	TTO ^b	Time (h)	Conv. (%)	Yield ^c (%)
1	Cp*Ru(PTA)(PPh ₃)Cl (1)	11600	24	95	58
2	Cp*Ru(PMe ₃)(PPh ₃)Cl (6)	6000	24	88	30
3	Cp*Ru(PPh ₃) ₂ Cl (11)	16400	24	99	82

^a All reactions were performed in toluene-*d*₈ at 60 °C with 0.005 mol% catalyst and 5 mol% AIBN, CCl₄/styrene is 4:1; ^b TTO is defined as mol-product/mol-catalyst; ^c NMR yield determined by ¹H NMR spectroscopy of product versus internal standard.

Figure 3.4: Kinetics plot for the addition of CCl₄ to styrene (▲) yielding the Kharasch product (◆), (1,3,3,3-tetrachloropropyl)benzene, catalyzed by Cp*Ru(PTA)(PPh₃)Cl and followed by ¹H NMR spectroscopy. Conditions: 60 °C, 1 mol% catalyst, 5 mol% AIBN.



The plot of [styrene] and Kharasch product formation versus time for the reaction of CCl₄ with styrene catalyzed by 1 (Figure 3.4) contains a sigmoidal curve suggesting an initiation step. Similar plots for the addition of CCl₄ to styrene catalyzed by DpRu(PTA)(PPh₃)Cl and IndRu(PTA)(PPh₃)Cl also show various degrees of induction (Figure 3.5). The induction is presumably due to a combination of phosphine dissociation and activation of the C-Cl bond. The potential importance of phosphine dissociation was

examined by addition of excess PPh_3 (10 mol%) to the catalytic mixture. As expected, PPh_3 inhibits the reaction rate, although the reaction still proceeds to >99% conversion (Table 3.1, entry 4). This is in contrast to other catalysts where the reaction is almost completely inhibited upon addition of excess phosphine.^{12b,30} An array of ^1H NMR spectra showing the formation of the Kharasch product and the disappearance of styrene is depicted in Figure 3.6.

Figure 3.5: Kinetics plot for the addition of CCl_4 to styrene yielding the Kharasch product (\blacklozenge), (1,3,3,3-tetrachloropropyl)benzene, catalyzed by (A) $\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ and (B) $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ followed by ^1H NMR spectroscopy in toluene- d_8 .

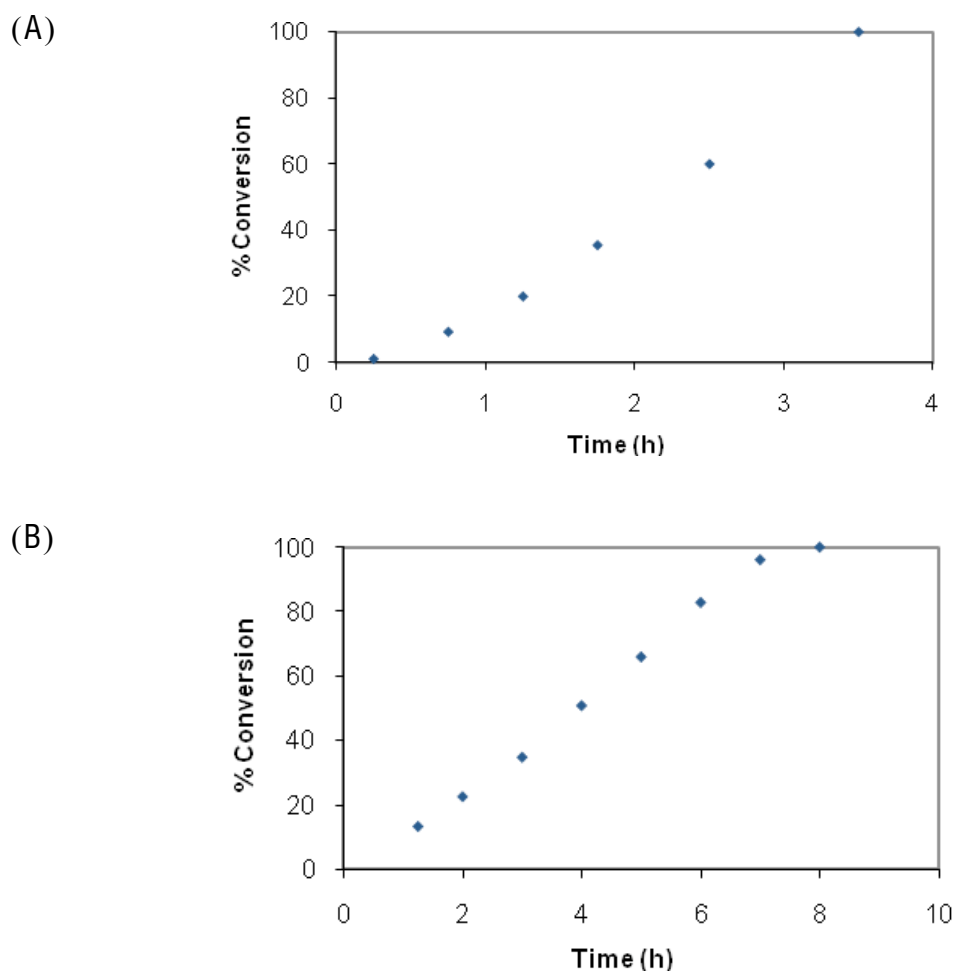
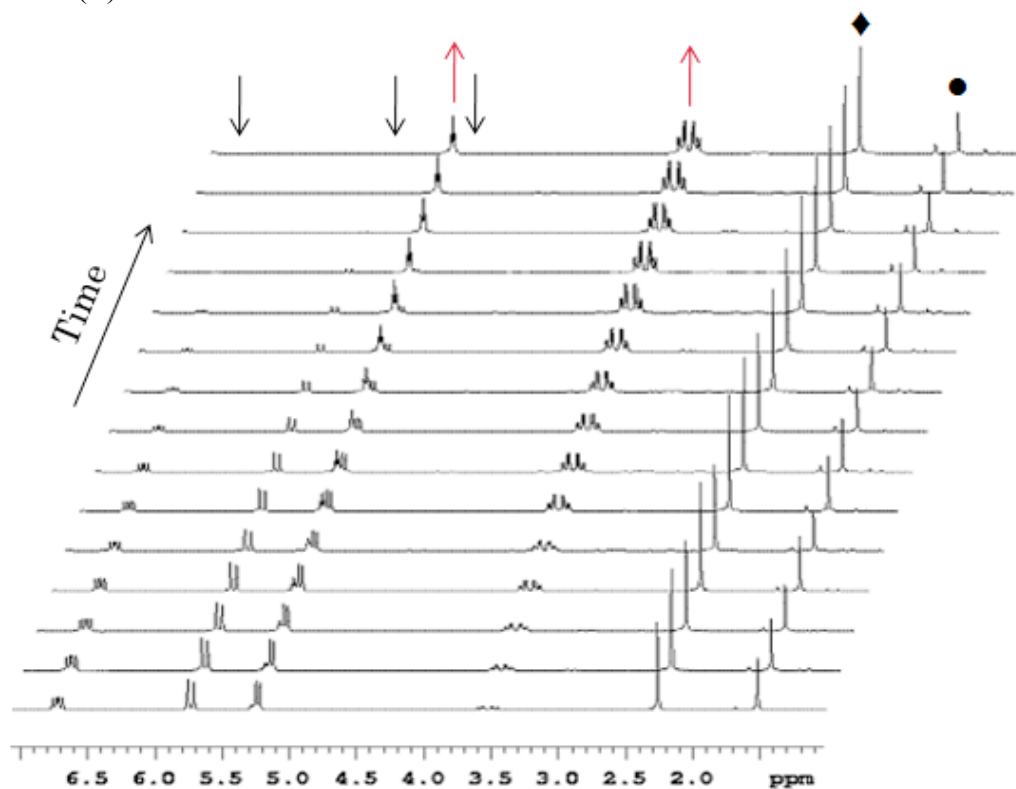


Figure 3.6: Array of ^1H NMR spectra in toluene- d_8 for the

IndRu(PTA)(PPh₃)Cl catalyzed CCl₄ addition to styrene. The spectra were recorded every half hour, at 60 °C, beginning at 1.25 h after the reaction started, and displayed from 1.2 ppm through 7.0 ppm; styrene peaks (↓), product peaks (↑), internal standard (◆), AIBN (●).

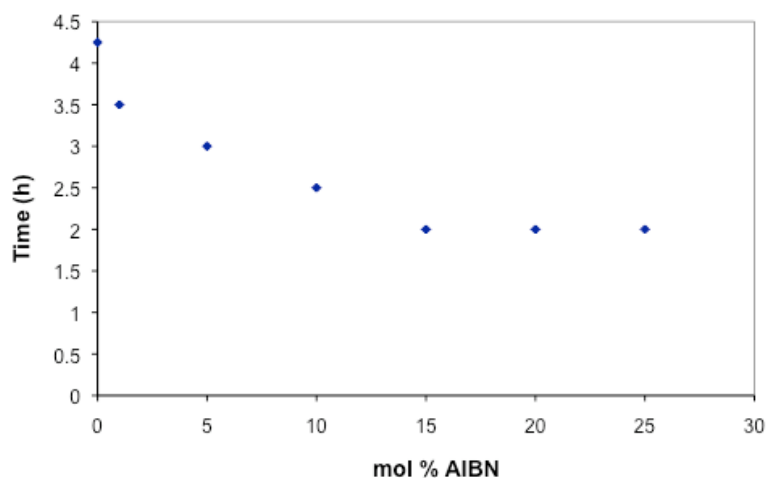


3.3.2 Role of AIBN

Severin and co-workers have recently reported the significance of AIBN in radical reactions.^{11a} As described in Chapter 1, the first step of the mechanism involves the abstraction of chloro atom from CCl₄ to give Ru^{III}-Cl complex and •CCl₃ radical. The possible side-reaction in ATRA is the combination of two •CCl₃ radicals to give C₂Cl₆. The formation of C₂Cl₆ would lead to the accretion of Ru^{III}-Cl complex, and hence the deactivation of the catalyst, particularly at low catalyst loading. Severin proposed that

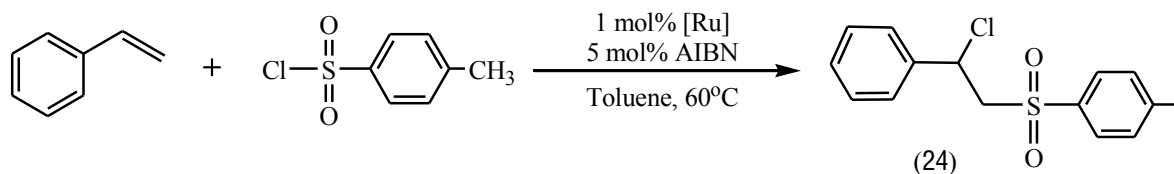
AIBN allows for the reduction of $\text{Ru}^{\text{III}}\text{-Cl}$ back to the active Ru^{II} catalyst. This hypothesis was confirmed by the reaction of CCl_4 with styrene using 0.005 mol% of the highly active catalyst $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$, which afforded only 3% product after 24 h. However, in the presence of 5 mol% AIBN, 83% product formation was observed.^{11a} Similar results were obtained with our catalytic systems. In the absence of AIBN a significant decrease in the reaction rate was observed for $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (TOF 415 h^{-1} ; Table 3.1, entry 3). We performed the addition of CCl_4 to styrene at different concentrations of AIBN using $\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ as catalyst, Figure 3.7. A slight decrease in the time required to reach >99% conversion was observed as the concentration of AIBN increased from 1 mol% to 15 mol%. With AIBN concentration >15 mol%, no further increase in the rate of reaction was observed. These results clearly indicate that AIBN provides a source of radicals and accelerates the reaction by regenerating the active Ru^{II} catalyst from $[\text{Ru}^{\text{III}}\text{-Cl}]$.

Figure 3.7: Plot of [AIBN] versus time for the addition of CCl_4 to styrene catalyzed by $\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$.



3.3.3 ATRA of *p*-toluenesulfonyl chloride to styrene

Scheme 3.3: Addition of *p*-TsCl to styrene.



The radical addition of sulfonyl chlorides to olefins has been reported by Kamagita and coworkers.³¹ These reactions were performed under harsh conditions (100-140°C) using $\text{RuCl}_2(\text{PPh}_3)_3$ as catalyst. We explored the efficiency of our catalytic system towards the addition of *p*-toluenesulfonyl chloride (*p*-TsCl) to styrene, Scheme 3.3. Using complexes 1-11, the reactions proceeded smoothly at 60 °C and the monoadducts were obtained in good to excellent yields, Table 3.4. The reactivity order for complexes 1-5 was similar to that observed for the addition of CCl_4 to styrene, with the exception of catalyst 3 (Table 3.4, entry 3). Unlike ATRA with CCl_4 , the PMe_3 complexes 6-10 exhibited lower reactivity towards the addition of *p*-TsCl to styrene as compared to their PTA analogues 1-5. Complex 3 exhibited a high TOF (53.4 h^{-1}) at short reaction time (~50% conversion); however, activity leveled off at 90% conversion, Figure 3.9 (C). The reaction could be brought to completion by addition of excess *p*-TsCl. Surprisingly, complex 8 showed very low activity with only 50% yield after 29h (TOF = 1.7 h^{-1} ; Table 3.4, entry 8). At this time, the reaction mixture had turned dark green in color and the reaction did not proceed any further. A bar graph comparing the rates of the reactions (TOFs) catalyzed by $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ 1-4 and their PMe_3 counterparts 6-9 is depicted in Figure 3.10. $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ 11 displayed the highest

activity with TOF of 131 h^{-1} (Table 3.4, entry 11). The PTA and PMe_3 analogues exhibited TOF's of 45.5 h^{-1} and 32.4 h^{-1} , respectively, (Table 3.4, entries 1 and 6). The TOF's of all three Cp^* complexes were significantly lower than those obtained for CCl_4 addition to styrene, indicating that the addition of *p*-TsCl to styrene is more difficult than that of CCl_4 . For other complexes in the series, the initial rates of addition were comparable to those of CCl_4 .

Table 3.4: Atom transfer radical addition of *p*-toluenesulfonyl chloride to styrene catalyzed by complexes 1-11.^a

Entry	Catalyst	Substrate	TOF ^b (h^{-1})	Time (h)	Yield ^c (%)
1	$\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1)	TsCl	45	3.8	96
2	$\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (2)	TsCl	23	5.8	95
3	$\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (3)	TsCl	53	4.8	90
4	$\text{CpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (4)	TsCl	20	7	95
5	$\text{TpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (5)	TsCl	1	52	66
6	$\text{Cp}^*\text{RuCl}(\text{PMe}_3)(\text{PPh}_3)$ (6)	TsCl	32	5	97
7	$\text{DpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (7)	TsCl	9	12	96
8	$\text{IndRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (8)	TsCl	1	29	50
9	$\text{CpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (9)	TsCl	15	6	99
10	$\text{TpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (10)	TsCl	--	75	40
11	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11)	TsCl	131	2.5	96

^a All reactions were performed in toluene-*d*₈ at 60°C using 1 mol% catalyst and 5 mol% AIBN; *p*-TsCl/styrene is 1.2:1; ^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene; ^c Yield is determined by ¹H NMR spectroscopy of product versus internal standard.

Of interest is that reactions involving *p*-TsCl with styrene exhibited no induction period, Figure 3.9. This may be due to the reaction of PPh_3 with *p*-TsCl as shown in Scheme 3.4.³² Such a reaction would prevent PPh_3 from coordinating back to ruthenium, thereby creating a vacant site on the metal. Hence, the induction time for C–Cl activation is reduced/eliminated.

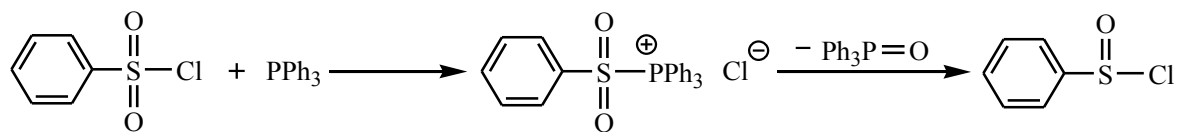
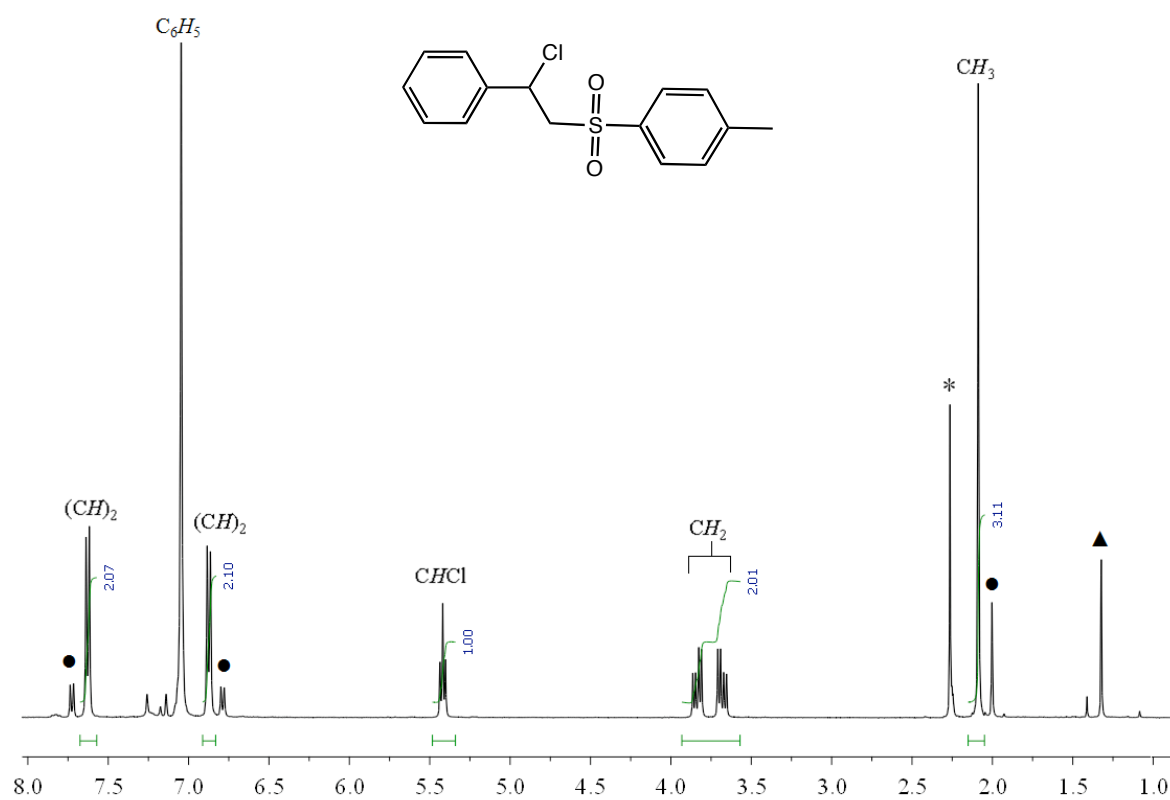
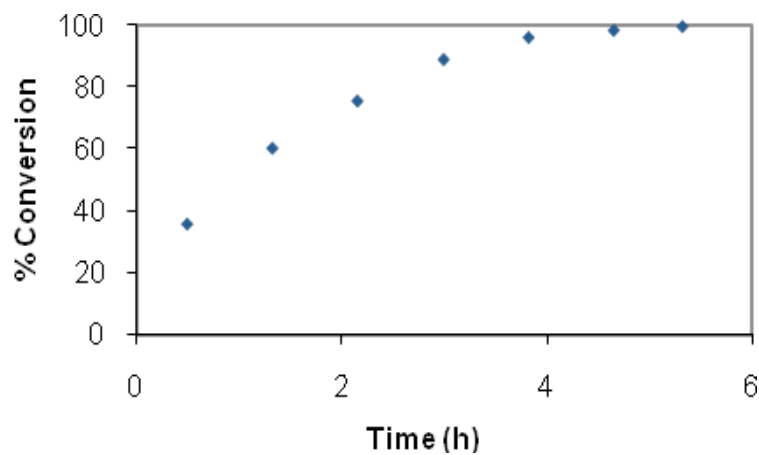
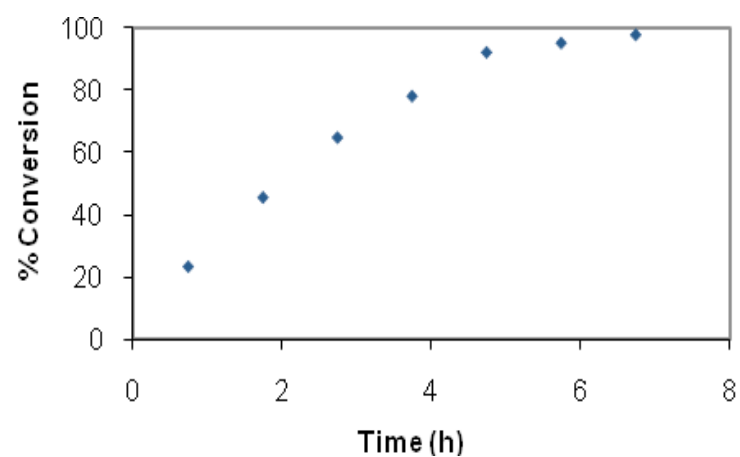
Scheme 3.4: Potential side-reaction of *p*-TsCl with styrene.³²Figure 3.8: ¹H NMR spectrum in toluene-*d*₈ of the reaction mixture, showing the 1:1 adduct **24** (2-chloro-2-phenylethyl *p*-tolyl sulfone) formed by the addition of *p*-TsCl to styrene; Internal standard (*), AIBN (▲), excess *p*-TsCl (●).

Figure 3.9: Kinetics plot for the addition of *p*-TsCl to styrene yielding the Kharasch product (♦) catalyzed by (A) Cp*Ru(PTA)(PPh₃)Cl, (B) DpRu(PTA)(PPh₃)Cl, (C) IndRu(PTA)(PPh₃)Cl, and (D) CpRu(PTA)(PPh₃)Cl followed by ¹H NMR spectroscopy.

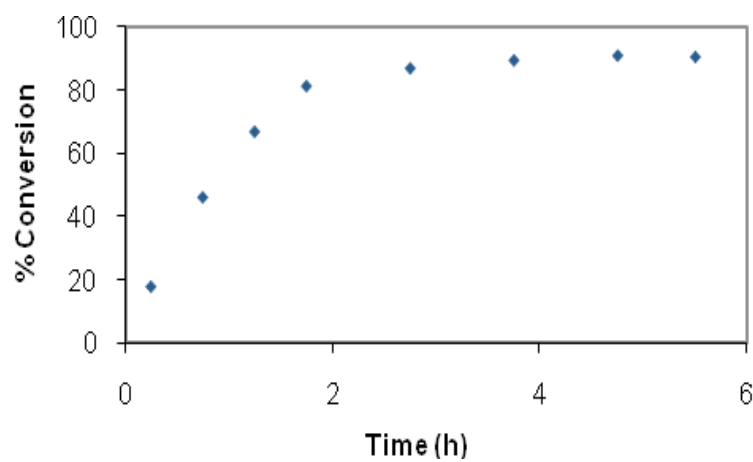
(A) Cp*Ru(PTA)(PPh₃)Cl



(B) DpRu(PTA)(PPh₃)Cl



(C) IndRu(PTA)(PPh₃)Cl



(D) CpRu(PTA)(PPh₃)Cl

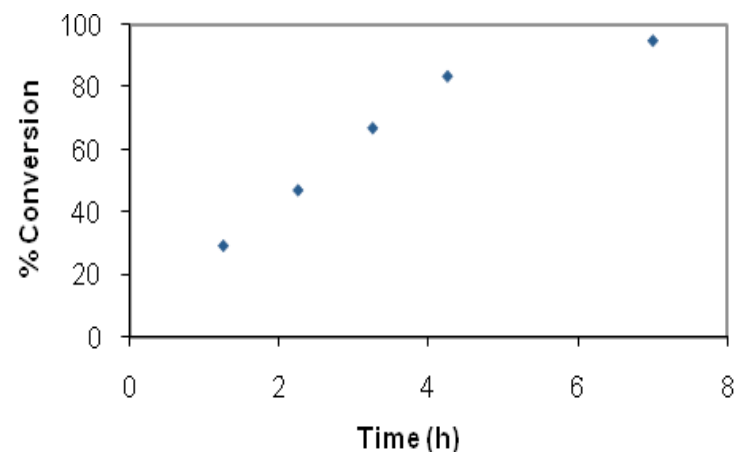
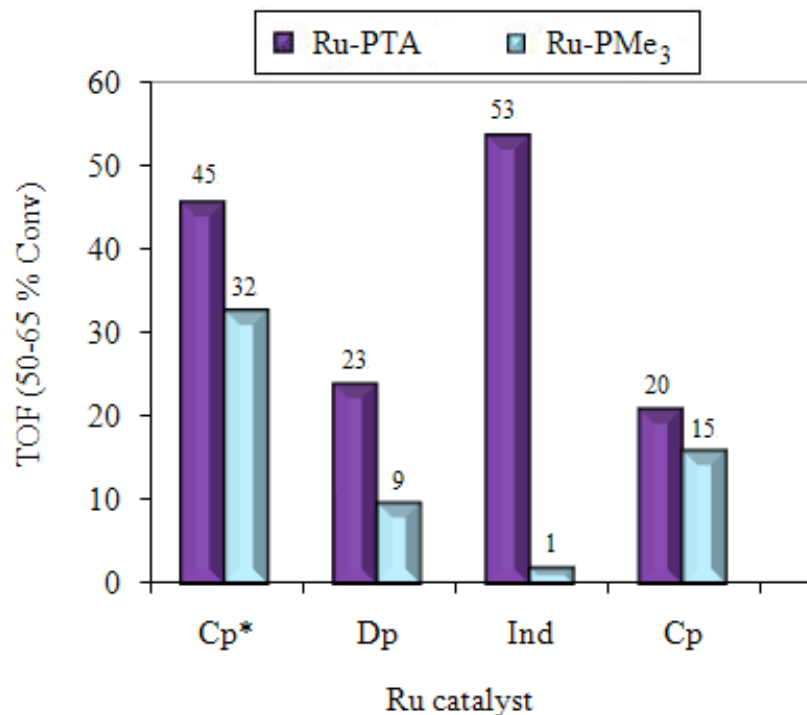
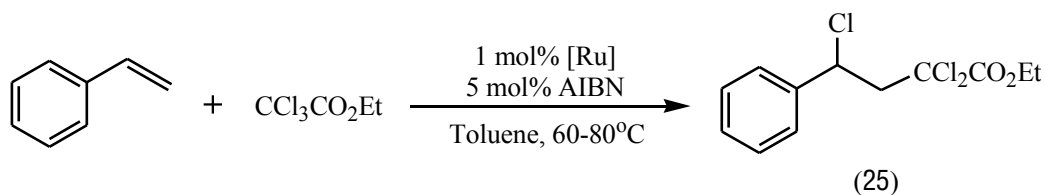


Figure 3.10: Comparison of the rates (TOF's in h^{-1}) of *p*-TsCl addition to styrene catalyzed by PTA complexes (1-4) and PMe_3 complexes (6-9).



3.3.4 ATRA of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene

Scheme 3.5: Addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene.



Next, we investigated the efficiency of complexes 1-11 towards the addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene, Scheme 3.5. The plots of Kharasch product formation versus time for the reaction of $\text{CCl}_3\text{CO}_2\text{Et}$ with styrene are shown in Figure 3.12. These reactions proceeded very efficiently at 60 °C and the desired 1:1 adduct 25 was obtained in

quantitative yields within 1-5 h, except for complexes 5 and 10, Table 3.5. Contrary to what was observed for the additions of CCl_4 and *p*-TsCl to styrene, the activity of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ 11 was slightly lower ($\text{TOF} = 226 \text{ h}^{-1}$) than that of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ 1 ($\text{TOF} = 251 \text{ h}^{-1}$) (Table 3.5, entries 1 and 11). The PMe_3 counterpart 6 also exhibited high reactivity in the series ($\text{TOF} = 132 \text{ h}^{-1}$). As expected, the order of reactivity was proportional to the electron-releasing ability of the ancillary ligand Cp' , with the exception of Dp complexes 2 and 7 which were slightly less efficient as compared to their Ind analogues 3 and 8, respectively, ($\text{Cp}^* > \text{Dp} < \text{Ind} > \text{Cp} > \text{Tp}$). Similar to what was observed for *p*-TsCl addition, the reaction catalyzed by complex 8 had turned green towards completion. A bar graph comparing the initial rates ($\text{TOF}'\text{s}$) of $\text{CCl}_3\text{CO}_2\text{Et}$ addition catalyzed by PTA complexes 1-4 and their PMe_3 analogues 6-9 is shown in Figure 3.13. The reactivity of our catalytic systems (except the Tp complexes 5 and 10) was higher than those reported in the literature. For example, the $\text{CCl}_3\text{CO}_2\text{Et}$ adduct of styrene was obtained in 60% yield using 1 mol% $\text{RuCl}_2(\text{PPh}_3)_2$ at 75°C after 24 h.²⁸ For the same reaction, 5 mol% of Grubbs catalyst $\text{P}(\text{Cy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ afforded only 57% yield at 75°C after 48 h.³³ As observed for CCl_4 and *p*-TsCl additions, the Tp-derivatives 5 and 10 were found to be least active with only 21-28% product formation after 24 h at 80°C (Table 3.5, entries 6 and 10). It is noteworthy that the catalytic performance of PTA complexes was similar to that of their PMe_3 counterparts, with the exception of $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ 7 which displayed a notably lower activity in comparison to $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ 2, Figure 3.13.

Table 3.5: Atom transfer radical addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene catalyzed by complexes 1-11.^a

Entry	Catalyst	Substrate	Temp (°C)	Time (h)	TOF ^b (h ⁻¹)	Yield ^c (%)
1	$\text{Cp}^*\text{RuCl}(\text{PTA})(\text{PPh}_3)$ (1)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	1.5	251	99
2	$\text{DpRuCl}(\text{PTA})(\text{PPh}_3)$ (2)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	3.25	40	98
3	$\text{IndRuCl}(\text{PTA})(\text{PPh}_3)$ (3)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	3.5	61	99
4	$\text{CpRuCl}(\text{PTA})(\text{PPh}_3)$ (4)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	4	34	98
5	$\text{TpRuCl}(\text{PTA})(\text{PPh}_3)$ (5)	$\text{CCl}_3\text{CO}_2\text{Et}$	80	24	---	21
6	$\text{Cp}^*\text{RuCl}(\text{PMe}_3)(\text{PPh}_3)$ (6)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	2	132	98
7	$\text{DpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (7)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	3.25	51	98
8	$\text{IndRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (8)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	5	54	99
9	$\text{CpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (9)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	4	38	99
10	$\text{TpRuCl}(\text{PMe}_3)(\text{PPh}_3)$ (10)	$\text{CCl}_3\text{CO}_2\text{Et}$	80	24	---	28
11	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11)	$\text{CCl}_3\text{CO}_2\text{Et}$	60	1.5	226	98

^a All reactions were performed in toluene- d_8 at 60-80°C using 1 mol% catalyst and 5 mol% AIBN; $\text{CCl}_3\text{CO}_2\text{Et}$ /styrene is 1.2:1; ^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene; ^c Yield is determined by ^1H NMR spectroscopy of product versus internal standard.

Figure 3.11: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 25 (2,2,4-trichloro-4-phenyl-butyric acid ethyl ester) formed by $\text{CCl}_3\text{CO}_2\text{Et}$ addition to styrene; Internal standard (*), AIBN (\blacktriangle), excess $\text{CCl}_3\text{CO}_2\text{Et}$ (\bullet).

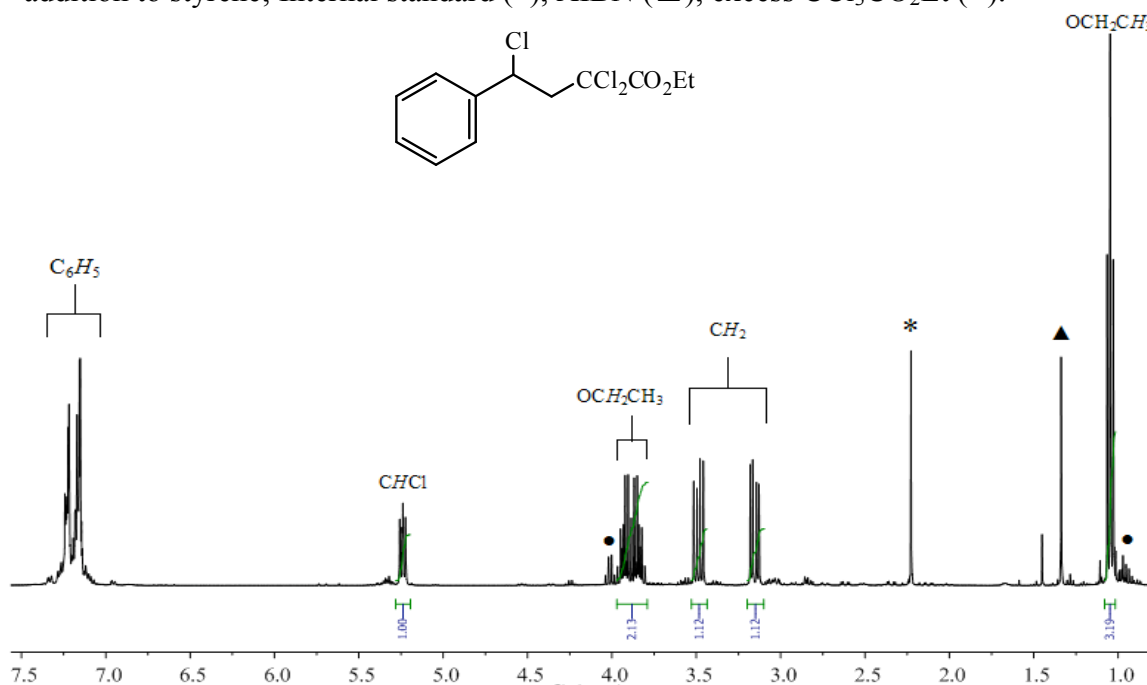
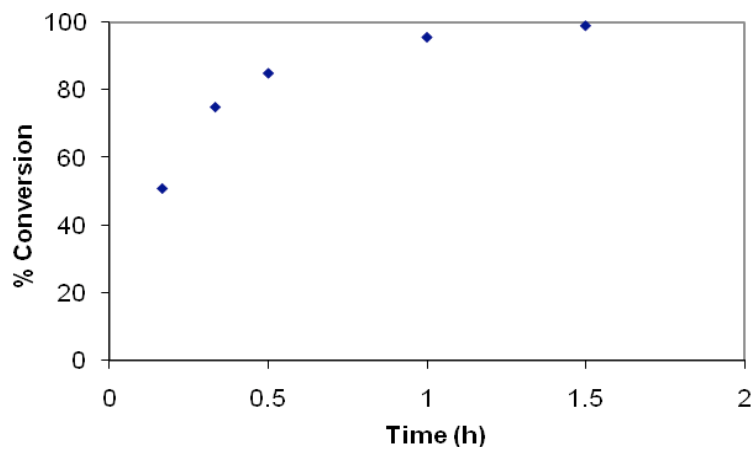
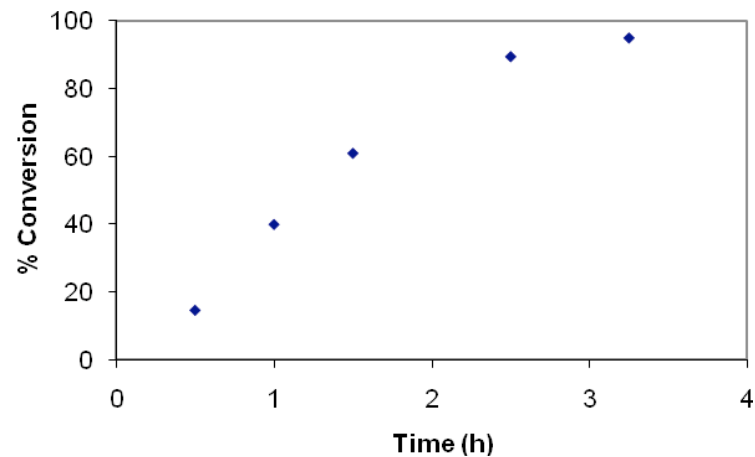


Figure 3.12. Kinetics plot for the addition of $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene yielding the Kharasch product (\blacklozenge) catalyzed by (A) $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$, (B) $\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$, (C) $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$, and (D) $\text{CpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ followed by ^1H NMR spectroscopy.

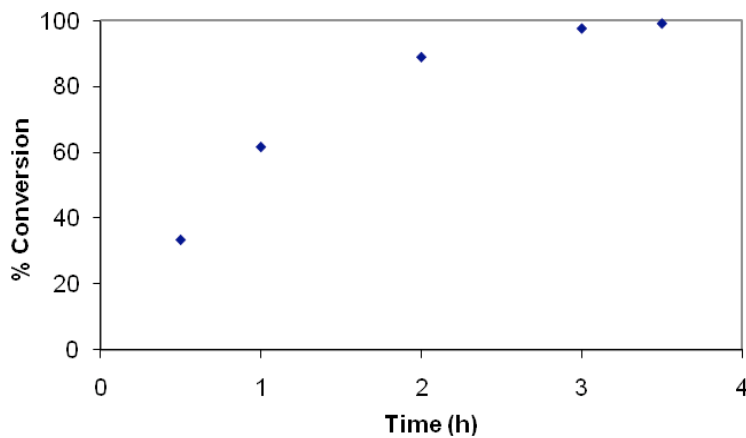
(A) $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$



(B) $\text{DpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$



(C) $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$



(D) $\text{CpRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$

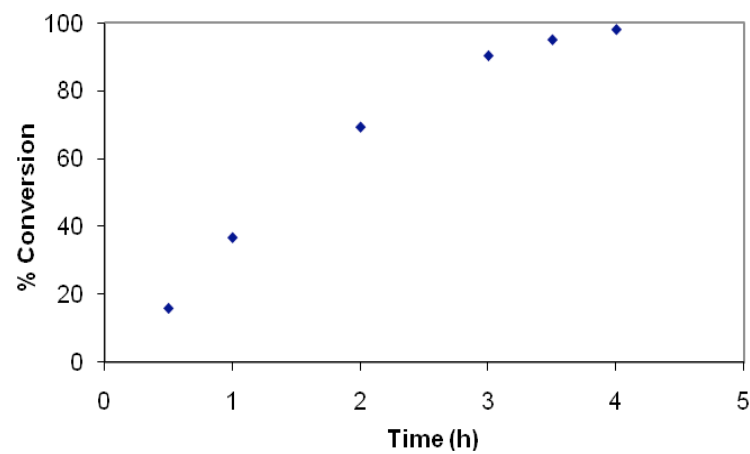
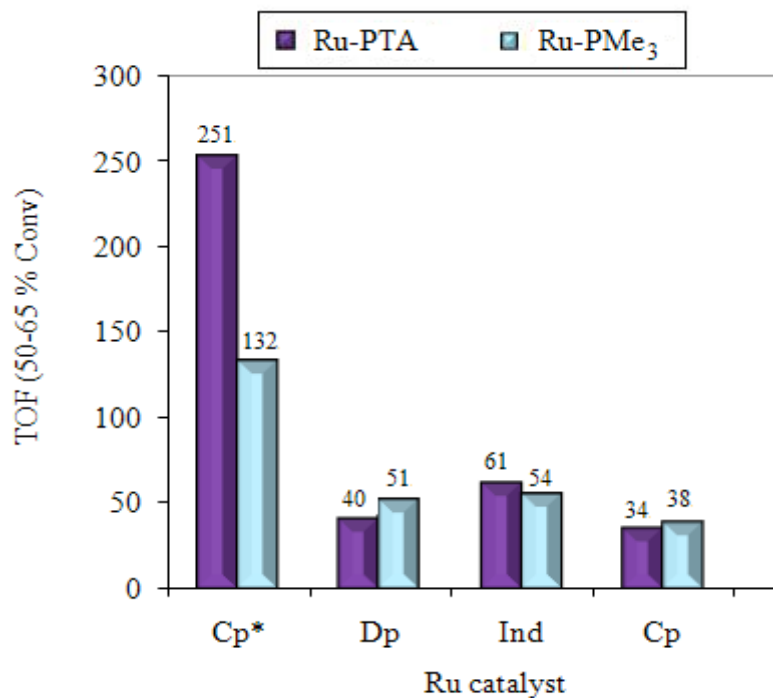
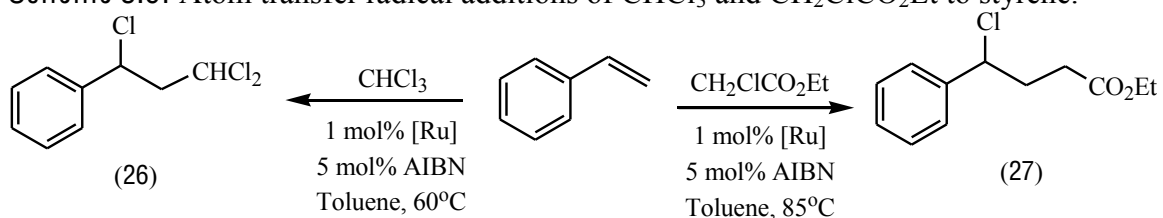


Figure 3.13: Comparison of the rates (TOF's in h^{-1}) of $\text{CCl}_3\text{CO}_2\text{Et}$ addition to styrene catalyzed by PTA complexes (1-4) and PMe_3 complexes (6-9).



3.3.5 ATRA of CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene

Scheme 3.6: Atom transfer radical additions of CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene.



The Cp* complexes 1, 6, and 11 were the most active catalysts among the series (1-11) for the addition of CCl_4 , $\text{CCl}_3\text{CO}_2\text{Et}$, and *p*-TsCl to styrene, and were therefore explored for the ATRA of more difficult chloro-substrates, CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$, to styrene, Scheme 3.6. For CHCl_3 addition, compound 11 was the most active with a TOF

of 272 h⁻¹ and 93% yield in 2 hours (Table 3.6, entry 3). Compound 6 has a faster initial rate with respect to 1 as evidenced by the higher TOF (62.6 h⁻¹ for 6 vs. 28.2 h⁻¹ for 1) with both complexes yielding >99% conversion at 60 °C in 3-4 h (Table 3.6, entries 1 and 2).

For the addition of CH₂ClCO₂Et to styrene, no product formation was observed at 60 °C. At an elevated temperature (85 °C), monoadduct 27 was obtained in very modest yields for all three complexes. Although the conversion of styrene was high (> 90%), only 21-28% of the product was formed after 24 h, presumably due to competing polymerization/oligomerization reactions (Table 3.6, entries 4-6). The reactions were significantly slower in comparison to the addition of the more halogenated ester CCl₃CO₂Et using 1, 6, and 11. Similar results have been reported previously for the RuCl₂(PPh₃)₃ catalyzed addition of CCl₃CO₂Et and CH₂ClCO₂Et to styrene.²⁸ The results obtained for the addition of CH₂ClCO₂Et and CHCl₃ to styrene suggest that the reactivity of polyhalogenated compounds is dependent on the degree of halogenation, i.e. CCl₃CO₂Et > CH₂ClCO₂Et, CCl₄ > CHCl₃.^{10,28}

Table 3.6: Additions of CHCl₃ and CH₂ClCO₂Et to styrene catalyzed by 1, 6 and 11.^a

Entry	Catalyst	Substrate	Temp (°C)	Time (h)	TOF ^b (h ⁻¹)	Yield ^c (%)
1 ^d	Cp*RuCl(PTA)(PPh ₃) (1)	CHCl ₃	60	4	28	>99
2 ^d	Cp*RuCl(PMe ₃)(PPh ₃) (6)	CHCl ₃	60	3.5	62	>99
3 ^d	Cp*Ru(PPh ₃) ₂ Cl (11)	CHCl ₃	60	2	272	93
4 ^e	Cp*RuCl(PTA)(PPh ₃) (1)	CH ₂ ClCO ₂ Et	85	24	--	21
5 ^e	Cp*RuCl(PMe ₃)(PPh ₃) (6)	CH ₂ ClCO ₂ Et	85	24	--	23
6 ^e	Cp*Ru(PPh ₃) ₂ Cl (11)	CH ₂ ClCO ₂ Et	85	24	--	28

^a All reactions were performed at 60-85°C using 1 mol% catalyst and 5 mol% AIBN; ^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene; ^c NMR yield determined by ¹H NMR spectroscopy of product versus internal standard. ^d 1.38 mmol styrene, Chloroform used as both solvent and substrate; ^e CH₂ClCO₂Et/styrene is 1.2:1.

Figure 3.14: ^1H NMR spectrum in CDCl_3 of the reaction mixture, showing the 1:1 adduct **26** (1,3,3-trichloropropyl-benzene) formed by the addition of CHCl_3 to styrene; Internal standard (*), AIBN (\blacktriangle), Solvent (S).

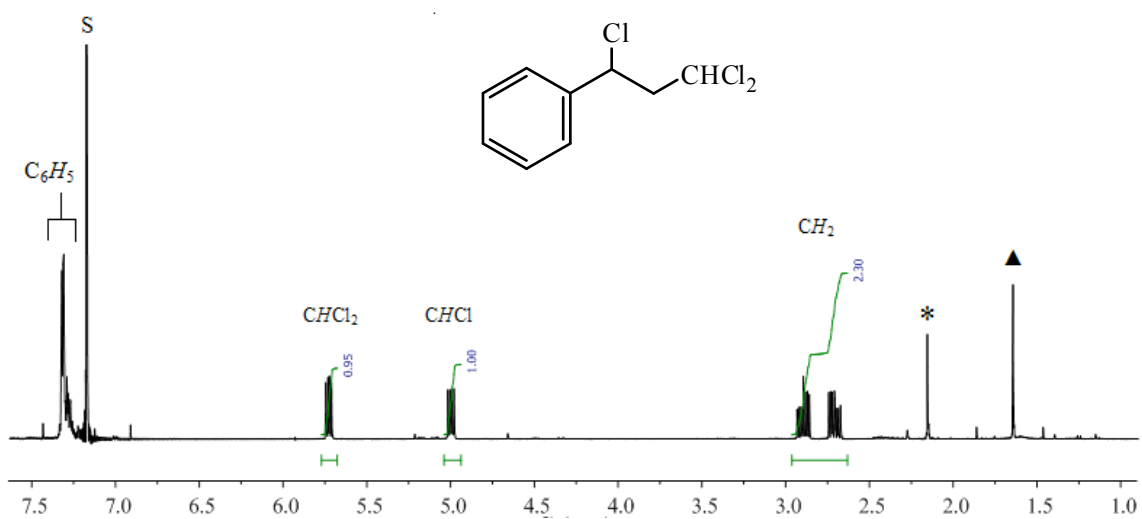
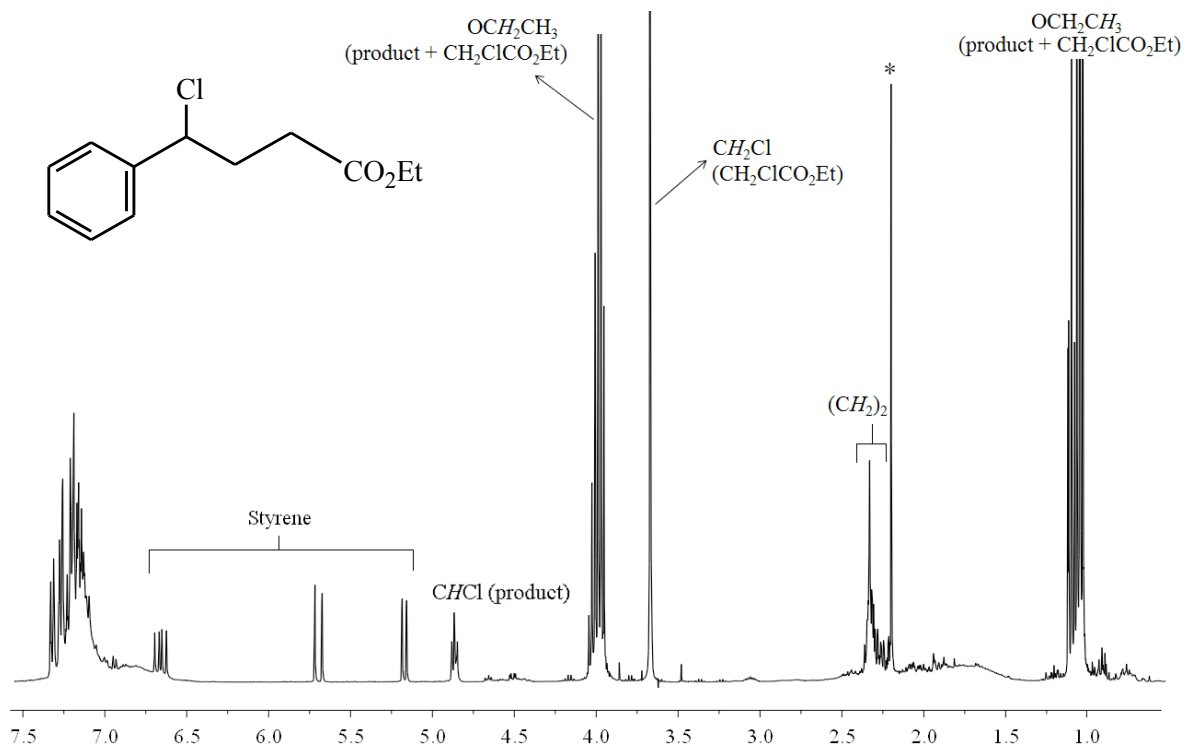


Figure 3.15: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **27** (4-chloro-4-phenyl-butyric acid ethyl ester) formed by the addition of $\text{CH}_2\text{ClCO}_2\text{Et}$ to styrene; Internal standard (*).



3.3.6 Variations in TOF values

Initial rates of the reactions (TOFs) were calculated at $\sim 50\%$ conversion for the following reasons: (i) to avoid induction period, if any, at earlier conversion, and (ii) at higher conversion, the reactions level off. Minor variations of TOFs with time were observed. The TOF values were fairly precise; $\sim 10\%$ error was calculated for the addition of CCl_4 and *p*-TsCl to styrene, Tables 3.7 and 3.8.

Table 3.7: TOFs calculated at different times for the addition of CCl_4 to styrene.

Entry	Catalyst	Time (h)	Yield ^c (%)	TOF (h^{-1})
1		0.49	46.3	945
2	Cp*RuCl(PTA)(PPh ₃) (1)	0.063	66.8	1060
3		0.080	77.6	970
4	DpRuCl(PTA)(PPh ₃) (2)	1.75	35.6	20.3
5		2.5	60.1	24.1
6	IndRuCl(PTA)(PPh ₃) (3)	4	50.75	12.7
7		5	65.9	13.2
8		6	82.8	13.8

Table 3.8: TOFs calculated at different times for the addition of *p*-TsCl to styrene.

Entry	Catalyst	Time (h)	Yield ^c (%)	TOF (h^{-1})
1		1.33	60.4	45.4
2	Cp*RuCl(PTA)(PPh ₃) (1)	2.16	75.6	35.0
3		3	88.9	29.6
4	DpRuCl(PTA)(PPh ₃) (2)	1.75	45.7	26.1
5		2.75	64.8	23.6
6		3.75	78.0	20.8
7	IndRuCl(PTA)(PPh ₃) (3)	0.75	46.1	61.5
8		1.25	66.8	53.4
9		1.75	81.2	46.4

The three important factors of these reactions are: (i) initial rate of the reaction, (ii) time required for the reaction to go to completion, and (iii) overall yield of the 1:1 adduct. Some reactions showed high initial rate, but did not go to completion. For instance, the addition of *p*-TsCl to styrene catalyzed by IndRu(PTA)(PPh₃)Cl exhibited highest TOF among the series of Cp'Ru(PR₃)(PPh₃)Cl catalysts (Figure 3.10), but the reaction leveled off at ~ 90% conversion.

3.3.7 Significance of phosphine dissociation in ATRA

The mechanistic studies of RuCl₂(PPh₃)₃ catalyzed ATRA reported by Davis and coworkers suggest phosphine dissociation as a prerequisite for ATRA (*see Chapter 1, section 1.3.2*). Our Cp'Ru(PR₃)(PPh₃)Cl catalytic systems are different from RuCl₂(PPh₃)₃, both sterically and electronically. The low reactivity of Cp'Ru(PR₃)(PPh₃)Cl in comparison to Cp'Ru(PPh₃)₂Cl indicate that dissociation of phosphine is crucial in the reaction. However, some other results obtained using our systems do not support phosphine-dissociation mechanism for ATRA. First, for the Cp*Ru(PTA)(PPh₃)Cl catalyzed addition of CCl₄ to styrene in the presence of ten-fold excess of free PPh₃, although the initial rate of the reaction was slower (TOF 444 h⁻¹ vs TOF 1060 h⁻¹ for the standard reaction), the reaction went to completion yielding > 99% product in 1.25 h. This is contrary to the results obtained for the RuCl₂(PPh₃)₃ catalyzed reaction that was completely inhibited in the presence of excess phosphine. Second, the substitutionally inert Cp'Ru(PTA)₂Cl and CpRu(dppe)Cl complexes showed some activity towards ATRA. In fact, Cp*Ru(PTA)₂Cl showed significant activity for the addition of CCl₄ to styrene. Third, one would expect to observe an induction period for all reactions due to phosphine-dissociation step. Using our catalysts, we found an

induction period for the addition of CCl_4 to styrene, but addition of p -TsCl and $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene lack an induction period. All these results suggest that for our catalytic systems, phosphine dissociation may not be crucial in the reaction mechanism.

3.4 Conclusion

In conclusion, we found that the air-stable and readily synthesized $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes ($\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}, \text{Tp}$; $\text{PR}_3 = \text{PTA}, \text{PMe}_3, \text{PPh}_3$) efficiently catalyzed the atom transfer radical addition of CCl_4 , $\text{CCl}_3\text{CO}_2\text{Et}$, and p -toluenesulfonyl chloride to styrene. The Cp^* analogues also catalyzed the addition of the difficult substrates, CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$, to styrene. Catalyst performance appears to depend mainly on the electron richness of the ruthenium center and on the nature of the phosphine ligand. The pronounced electron donating ability of Cp^* rendered $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11) an exceptional catalyst and both $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) and its PMe_3 counterpart (6) very efficient ATRA catalysts (the order of reactivity is $\text{Cp}^*\text{Ru} \gg \text{DpRu} > \text{IndRu} > \text{CpRu} > \text{TpRu}$). The catalytic activity of $\text{Cp}'\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ and $\text{Cp}'\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$, however, is significantly reduced as compared to the activity of the parent $\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl}$ complexes. This indicates to us that the efficiency of catalysis is hampered by replacement of PPh_3 with a stronger binding phosphine such as PTA or PMe_3 — a strong indication that phosphine dissociation is involved in the reaction mechanism. This was further confirmed by the lower catalytic activity of $\text{Cp}'\text{Ru}(\text{PTA})_2\text{Cl}$ complexes. The catalytic performance of the ruthenium complexes may be further tuned by modifications of ancillary ligands and phosphines, and awaits further study.

3.5 References

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Chapter 4

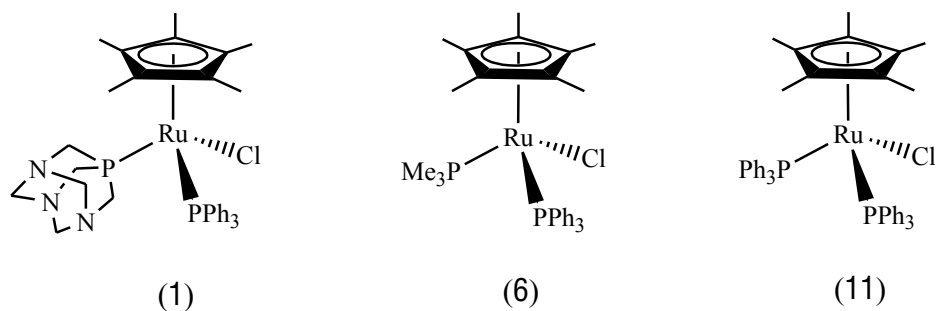
Atom transfer radical addition of CCl_4 to more challenging substrates catalyzed by $\text{Cp}^*\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ [$\text{PR}_3 = \text{PTA}, \text{PMe}_3, \text{PPh}_3$] complexes

4.1 Introduction

A variety of olefins are reported to undergo atom transfer radical addition with halogenated compounds (Kharasch addition or ATRA) to form the corresponding 1:1 adducts. Both aliphatic and aromatic olefins have been employed. In particular, styrenes and acrylates serve as excellent substrates for ATRA.^{1,2} Other commonly used substrates are hexene and higher α -olefins, and cycloalkenes.³⁻⁷ Only a few internal olefins and dienes have been employed as substrates for ATRA.^{6,8} Catalyst performance is strongly dependent on the nature of the substrates used. For instance, 1-octene and 1-decene are notoriously difficult substrates for Kharasch reactions.^{2d,9,10} In addition, isomerization of the α -olefins is observed in some cases leading to reduced yield of the desired product.¹¹ Similarly, with easily polymerizable substrates such as methyl methacrylate and *n*-butyl acrylate, the monoadducts are generally obtained in lower yields due to the formation of

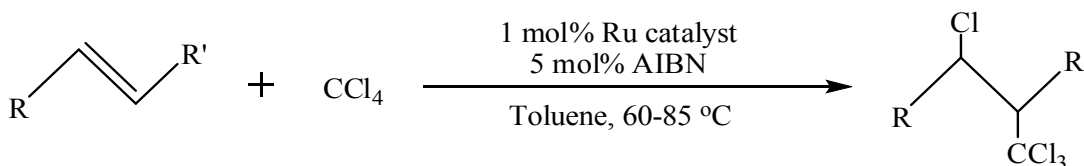
polymers/telomers.^{10,12} Using ruthenium catalysts, high regioselectivity⁶ and stereoselectivity⁷ has been achieved for CCl_4 addition to olefins.

Figure 4.1: Ruthenium complexes used as catalyst precursors for ATRA.



In chapter 3, we reported the efficiency of a series of $\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes, where $\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5^-, \text{Cp}^*)$, $(\eta^5\text{-C}_8\text{H}_9^-, \text{Dp})$, $(\eta^5\text{-C}_9\text{H}_7^-, \text{Ind})$, $(\eta^5\text{-C}_5\text{H}_5^-, \text{Cp})$ or $(\eta^3\text{-HB}(\text{N}_2\text{C}_3\text{H}_3)_3^-, \text{Tp})$; $\text{PR}_3 = \text{PTA}$, PMe_3 , or PPh_3 towards the addition of various halogenated compounds to styrene.¹³ In general, the monoaddition products were obtained in excellent yields at 60°C . Our previous studies revealed that the electron-donating ability of the ancillary ligand (Cp^*) and the relative facility of dissociation of the phosphine are crucial for good catalytic activity of the ruthenium complexes. Among the series of ruthenium (II) complexes investigated, the Cp^* complexes $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) and $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (6) exhibited high reactivity, (Figure 4.1). They were, however, less active in comparison to $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11), which set so far the standard in Kharasch chemistry (Figure 4.1).^{10,14} We then explored the effect of olefin structure on the Kharasch reactions. In this chapter, we report on the efficiency of complexes 1 and 6 towards the addition of CCl_4 to a variety of terminal and internal olefins in the presence of a radical source AIBN, Scheme 4.1. For comparative purposes, $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11) has also been employed under our reactions conditions.

Scheme 4.1: Atom transfer radical addition of CCl₄ to olefins catalyzed by Ru(II) complexes



4.2 Experimental Section

4.2.1 Materials and methods

All reactions were performed under a dry nitrogen atmosphere, using conventional Schlenk vacuum-line techniques and a glove-box. Reagents were purchased from commercial suppliers, and used as received. Solvents were dried with molecular sieves and degassed with N₂, prior to use. Column chromatography was performed using Silicycle silica gel (230-400 mesh). Synthesis of Cp*Ru(PTA)(PPh₃)Cl (1) and Cp*Ru(PMe₃)(PPh₃)Cl (6) are reported in Chapter 2. Cp*Ru(PPh₃)₂Cl was synthesized according to literature procedure.¹⁵ Kharasch addition reactions were carried out under nitrogen atmosphere in standard NMR tubes. Each catalytic run was repeated at least twice to ensure reproducibility. The following Kharasch adducts were identified by comparison of their spectral data with those reported in the literature: 1,1,1,3-tetrachloroheptane (28),¹⁶ 1,1,1,3-tetrachloro-undecane (29),¹⁷ 2,4,4,4-tetrachloro-butyric acid butyl ester (30),¹⁰ (1,3,3,3-tetrachloro-2-methyl-propyl)-benzene (31),¹⁷ and 4-chloro-4-phenyl-3-(trichloromethyl)-butan-2-one (32)⁶. The new compounds, 3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one (33) and 1,3,3,3-tetrachloro-1,2-diphenylpropane (34), were isolated and fully characterized. NMR spectra were recorded

with a Varian NMR System 400 spectrometer. ^1H and ^{13}C NMR spectra were referenced to a residual solvent relative to tetramethylsilane (TMS). APPI-MS data were recorded on a Waters Micromass 20 mass spectrometer.

4.2.2 *X-Ray Crystallography*

X-ray crystallographic data was collected at $100(\pm 1)$ K on a Bruker APEX CCD diffractometer with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and a detector-to-crystal distance of 4.94 cm. Data collection was optimized utilizing the APEX2 software with a 0.5° rotation about ω between frames, and an exposure time of 10 seconds per frame. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS, and corrected for absorption using SADABS. The structures were solved using direct methods followed by successive least squares refinement on F^2 using the SHELXTL 6.10 software package.¹⁸ All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions. Crystallographic data and data collection parameters are listed in Table 4.1. A complete list of bond lengths and angles may be found on the Appendix.

4.2.3 *Catalytic Experiments*

ATRA of CCl_4 to various olefins

To a 1.5 mL vial was added 1 mol % catalyst (0.0138 mmol), 5 mol % AIBN (11.3 mg, 0.069 mmol), olefin (1.38 mmol), CCl_4 (533 μL , 5.52 mmol) and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene- d_8 was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated at 60-85 $^\circ\text{C}$ in an oil-bath. The formation of product was monitored by ^1H NMR spectroscopy at predetermined intervals.

Synthesis of 3-Chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one (33)

To a Schlenk tube with Teflon cap was added Cp*Ru(PTA)(PPh₃)Cl (0.0288 g, 0.0414 mmol), AIBN (0.034 g, 0.207 mmol), chalcone (0.862 g, 4.14 mmol), CCl₄ (1.6 mL, 16.56 mmol), and 1.3 mL toluene-*d*₈. The reaction was stirred at 85 °C under nitrogen for 24 h. The reaction mixture was cooled to room temperature and purified by silica gel chromatography eluting with toluene to give compound **33** as a pale yellow crystalline solid in 29% yield (0.44 g). ¹H NMR (CDCl₃, 400 MHz, Figure 4.7) of major isomer: δ 4.8 (d, 1H, *CHCCl*₃, ³*J*_{HH} = 10.0 Hz); 5.2 (d, 1H, *CHCl*, ³*J*_{HH} = 10.0 Hz); 6.5-7.0 (m, 10H, PPh₃); minor isomer: δ 4.55 (d, 1H, *CHCCl*₃, ³*J*_{HH} = 8.0 Hz); 5.4 (d, 1H, *CHCl*, ³*J*_{HH} = 8.0 Hz); 6.5-7.0 (m, 10H, PPh₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz): 62.58 (*CHCl*), 66.97 (*CHCCl*₃), 96.0 (*CCl*₃), 129.06-129.55 (8 Ar-C); 130.06 (1 Ar-C), 134.35 (1 Ar-C), 138.19 (*C-CHCl*), 138.56 (*C-CO*), 194.11 (*C=O*). APPI-MS: *m/z* calcd, 362.08; found 363.12 for [5-H]⁺. M.P: 77-85°C. X-ray quality crystals were obtained by slow evaporation of hexane solution of **33**.

Synthesis of 1,3,3,3-tetrachloro-1,2-diphenylpropane (34)

To a Schlenk flask with Teflon cap was added Cp*Ru(PTA)(PPh₃)Cl (0.0288 g, 0.0414 mmol), AIBN (0.034 g, 0.207 mmol), cis-stilbene (740 μL, 4.14 mmol), CCl₄ (1.6 mL, 16.56 mmol), and 750 μL toluene-*d*₈. The reaction was stirred at 85 °C under nitrogen for 3 days. The reaction mixture was cooled to room temperature and purified by silica gel chromatography (solvent system: 5% toluene/hexane) to give compound **34** as a pale yellow crystalline solid in 43% yield (0.6 g). ¹H NMR (CDCl₃, 400 MHz, Figure 4.8) of major diastereomer: δ 4.17 (d, 1H, *CHCCl*₃, ³*J*_{HH} = 4.8 Hz); 5.91 (d, 1H, *CHCl*,

$^3J_{\text{HH}} = 4.8$ Hz); 7.0-7.6 (m, 10H, PPh₃); minor diastereomer: δ 4.48 (d, 1H, CHCl₃, $^3J_{\text{HH}} = 4.0$ Hz); 5.76 (d, 1H, CHCl, $^3J_{\text{HH}} = 4.0$ Hz); 7.0-7.6 (m, 10H, PPh₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 100 MHz): 62.25 (CHCl), 71.56 (CHCCl₃), 100.85 (CCl₃), 127.7-128.8 (8 Ar-C), 129.04 (1 Ar-C), 131.19 (1 Ar-C), 134.45 (C-CHCl), 140.07 (C-CHCCl₃). APPI-MS: m/z calcd, 334.07; found, 334.11. M.P: 62-70°C. X-ray quality crystals were obtained by slow evaporation of hexane solution of 34.

Table 4.1: Crystallographic data for compounds 33 and 34.

	Chalcone-CCl ₄ adduct (33)	<i>c/s</i> -stilbene-CCl ₄ adduct (34)
Empirical formula	C ₁₆ H ₁₂ Cl ₄ O	C ₁₅ H ₁₂ Cl ₄
Formula weight	362.06	334.05
Color	Light yellow	Colorless
Temperature (K)	100 (2)	100 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/c	Pna2(1)
a (Å)	10.83540(10)	11.7247(2)
b (Å)	8.01140(10)	19.7528(3)
c (Å)	18.1558(2)	6.09430(10)
α (deg)	90	90
β (deg)	97.5090(10)	90
γ (deg)	90	90
Volume (Å ³)	1562.53(3)	1411.41(4)
Z	4	4
Density _{calcd} (Mg/m ³)	1.539	1.572
Absorption coefficient (mm ⁻¹)	0.752	0.820
<i>F</i> (000)	736	680
Crystal size (mm ³)	0.56 x 0.23 x 0.12	0.518 x 0.065 x 0.06
θ range (deg)	1.90 to 32.56	2.02 to 31.01
	-16 ≤ h ≤ 16	-17 ≤ h ≤ 16
Index ranges	-12 ≤ k ≤ 11	-28 ≤ k ≤ 28
	-26 ≤ l ≤ 26	-8 ≤ l ≤ 8
Reflections collected	22693	33086
Independent reflections	5613	4366
	<i>R</i> _{int} = 0.0247	<i>R</i> _{int} = 0.0279
no. of data/restraints/params	5613 / 0 / 190	4366 / 1 / 220
GOF on <i>F</i> ²	1.097	1.064
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0311, w <i>R</i> ₂ = 0.0866	<i>R</i> ₁ = 0.0195, w <i>R</i> ₂ = 0.0530
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0345, w <i>R</i> ₂ = 0.0895	<i>R</i> ₁ = 0.0200, w <i>R</i> ₂ = 0.0534

4.3 Results and Discussion

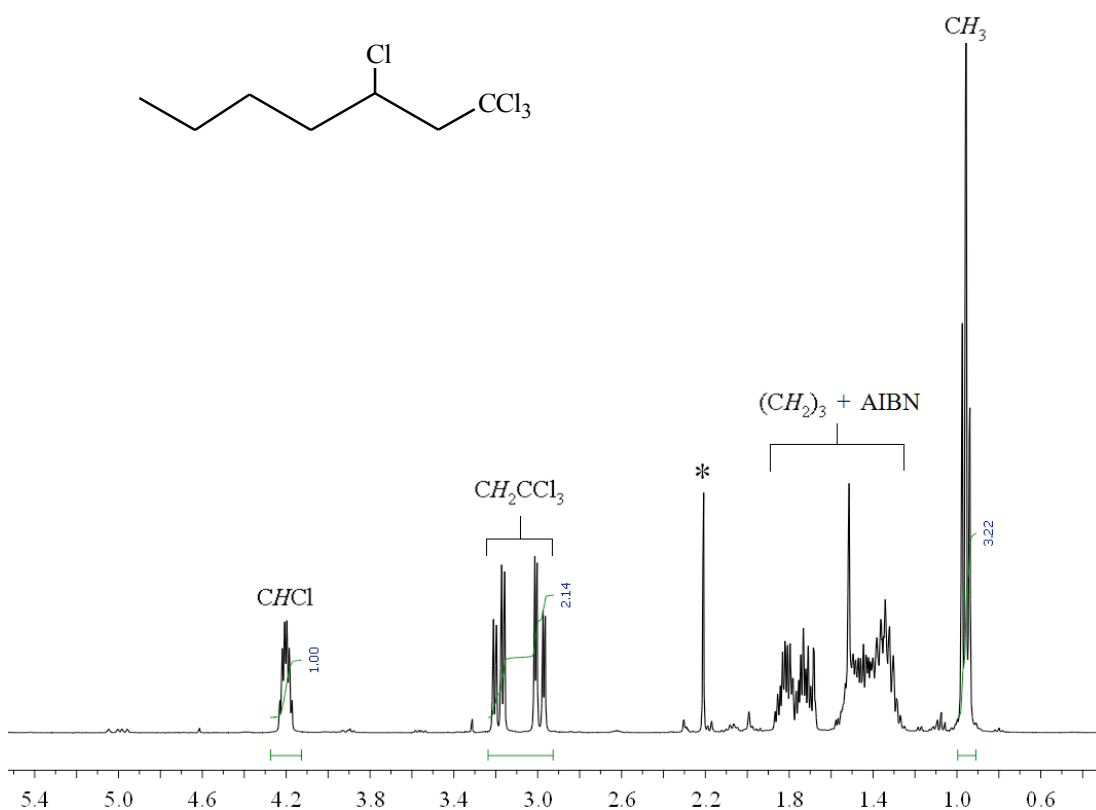
4.3.1 Catalytic activity

As mentioned earlier, the commonly used olefinic substrates in ATRA are styrenes, acrylates, and hexene. Other olefins (higher α -olefins, internal olefins, etc) have been reported as difficult substrates for Kharasch addition, the reasons for which remain unknown. Catalyst performance is found to be strongly dependent on the substrates employed.^{2a,10a} For example, with 1-decene as a substrate for CCl_4 addition, the best ATRA catalyst $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ afforded only 27% yield of the monoadduct after 24 h (60°C). Similar results have been reported for other ruthenium complexes.^{3,10b,12} With this in mind, we explored the potential of the catalyst precursors 1, 6, and 11 towards the addition of CCl_4 to various terminal and internal olefins, the results of which are summarized in Tables 4.2 and 4.3.

Addition of CCl_4 to terminal olefins: Hexene, octene, decene, and acrylates are some of the commonly used terminal olefins for ATRA. The terminal olefins that we employed were 1-hexene, 1-decene, and *n*-butyl acrylate. Hexene underwent CCl_4 addition to give the monoadduct 28 in almost quantitative yields within 4-7 h at 60°C (Table 4.2, entries 1-3); for ^1H NMR spectrum of 28, see Figure 4.2). The $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ catalyzed addition of CCl_4 to hexene proceeded rapidly ($\text{TOF } 202 \text{ h}^{-1}$) as compared to the PMe_3 analogue (53.3 h^{-1}) and PPh_3 analogue (100 h^{-1}). This is contrary to the results obtained for CCl_4 addition to styrene where $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ displayed highest activity (*see Chapter 3, section 3.3.1*). The total turnovers (TTOs) obtained using all three catalysts

were impressive; with catalyst loadings of 0.001 mol%, $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (1) exhibited a TTO of 79,000 in 48 hours, $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (6) was more impressive with a TTO of 88,000 after 48 h, and $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (11) was the most active with a TTO of 92,000 after 40 h. These are the highest TTOs reported to date. Prior to this work, the highest TTO reported for ATRA was 44,000 for the addition of CCl_4 to 1-hexene.¹⁹

Figure 4.2: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **28** (1,1,1,3-tetrachloro-heptane) formed by the addition of CCl_4 to hexene; internal standard (*).



With 1-decene, a difficult substrate for ATRA, the monoadduct **29** was obtained in > 90% yield in less than 4 h (Table 4.2, entries 4-6). These values are comparable to what is observed for other catalysts. Using $\text{Rh}^{\text{III}}\text{-Ru}^{\text{II}}$ system (*Chapter 1, Figure 6c*), for example, a yield of 88% was achieved after 10 h at 60°C.⁹ *n*-Butyl acrylate, an easily

polymerizable substrate, also underwent a fast and clean monoaddition of CCl_4 affording the 1:1 adduct **30** in > 90% yield within 2.5-3.5 h (Table 4.2, entries 7-9). With 1-decene and *n*-Butyl acrylate, the reactivity of complexes **1**, **6** and **11** was comparable. The ^1H NMR spectra of compounds **29** and **30** are shown in Figures 4.3 and 4.4, respectively.

Due to the exceptional activity of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**11**) for ATRA reactions, we performed the addition of CCl_4 to hexene, decene, and *n*-butyl-acrylate with complex **11** at room temperature. Unlike CCl_4 addition to styrene (96% yield in 6 min; Chapter 3, section 3.3.1), only 30-40% yield was observed in all three cases after ~10 minutes with no further reaction observed at longer times. These results indicate that the Kharasch additions not only depend on the nature of the catalyst, but also on the type of olefin employed.

Table 4.2: Atom transfer radical addition of CCl_4 to terminal olefins catalyzed by $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (**1**), $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**6**), and $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**11**).^a

Entry	Catalyst	Olefins	Time (h)	Product	Yield ^b (%)
1	1		4		93
2	2	Hexene	7		99
3	3		4.5		28
4	1		3.5		94
5	2	Decene	2.75		92
6	3		3.5		29
7	1		2.5		97
8	2	<i>n</i> -Butyl acrylate	2.5		99
9	3		3.5		30

^a All reactions were performed in toluene- d_8 at 60 °C using 1 mol% catalyst and 5 mol% AIBN; ^b Yield is determined by ^1H NMR spectroscopy of product versus internal standard.

Figure 4.3: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 29 (1,1,1,3-tetrachloro-undecane) formed by the addition of CCl_4 to decene; internal standard (*).

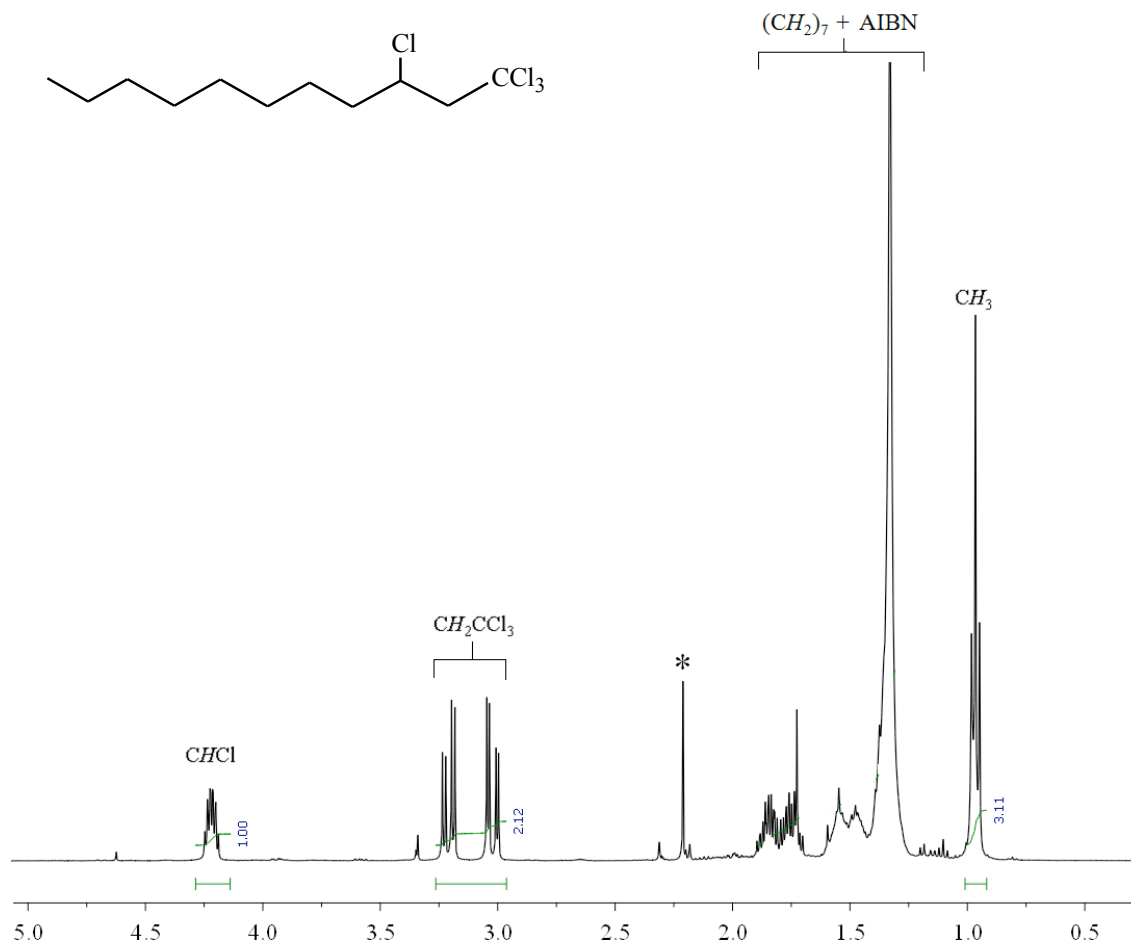
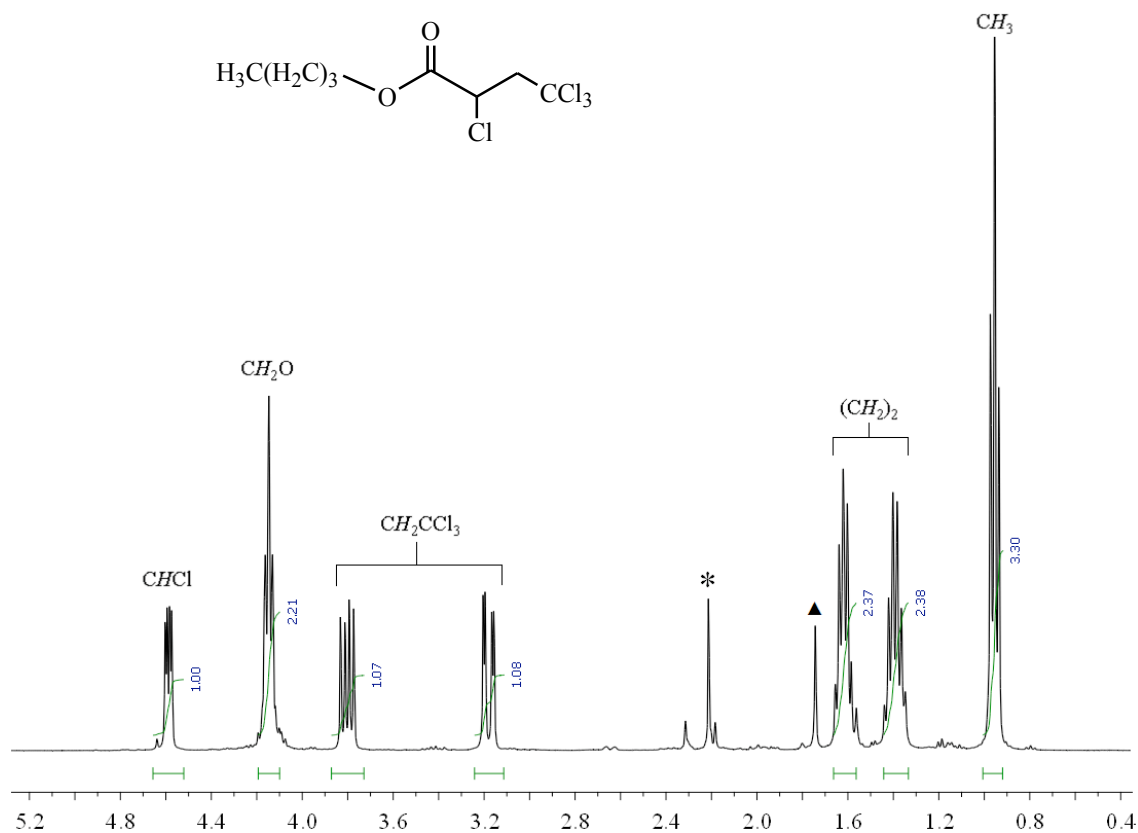


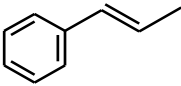
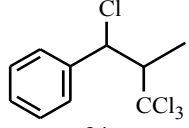
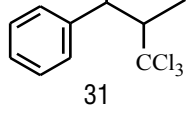
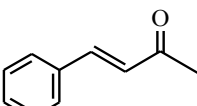
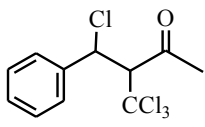
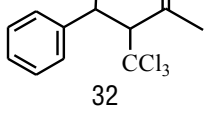
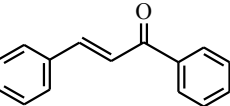
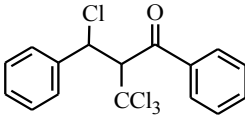
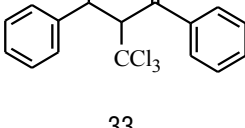
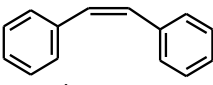
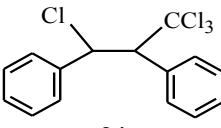
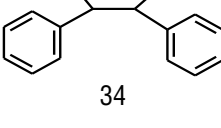
Figure 4.4: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct **30** (2,4,4,4-tetrachloro-butyl ester) formed by the addition of CCl_4 to *n*-butyl acrylate; internal standard (*), AIBN (\blacktriangle).



Addition of CCl_4 to internal olefins: For the reaction of CCl_4 with internal olefins, it has been reported that the Cl atom preferentially adds to the benzylic carbon.^{6,17} We obtained similar results for the addition of CCl_4 to *trans*- β -methyl styrene, benzylidene acetone, and chalcone (Table 4.3, entries 1-9). At 60°C, the reaction of *trans*- β -methyl styrene with CCl_4 afforded **31** in 91-95% yield after 5-7 h (Table 4.3, entries 1-3). The monoadduct **31** was obtained as a mixture of *anti/syn* isomers ($\sim 3:1$). The α,β -unsaturated ketones (benzylidene acetone and chalcone) were less prone to undergo the

addition of CCl_4 , yielding only 39-53% of **32** and **33** after 24 h at 60-85°C (Table 4.3, entries 4-9). With benzylidene acetone, the $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ catalyzed reaction had turned dark green in color after ~ 20 h, indicating the decomposition of catalyst. This is similar to what was observed for the additions of *p*-TscI and $\text{CCl}_3\text{CO}_2\text{Et}$ to styrene using $\text{IndRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ as catalyst (*discussed in chapter 3*). CCl_4 addition to *cis*-stilbene afforded the monoadduct **34** as a mixture of two diastereomers in < 50% yield (Table 4.3, entries 10-12). The ^1H NMR spectra of compounds **31-34** are shown in Figures 4.5-4.8.

Table 4.3: Atom transfer radical addition of CCl_4 to internal olefins catalyzed by $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (**1**), $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**6**), and $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**11**).^a

Entry	Catalyst	Olefins	Temp (°C)	Time (h)	Product	Yield ^b (%)
1	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$		60	5		94 (77:23) ^c
2	$\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$	<i>trans</i> - β -methyl styrene	60	6		95 (77:23) ^c
3	$\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$	styrene	60	7	31	91 (76:24) ^c
4	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$		60	24		49 (83:17) ^c
5	$\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$	Benzylidene acetone	60	24		53 (87:13) ^c
6	$\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$	Benzylidene acetone	60	24	32	39 (85:15) ^c
7	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$		85	24		41 (70:30) ^c
8	$\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$	Chalcone	85	24		58 (80:20) ^c
9	$\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$	Chalcone	85	24	33	44 (73:27) ^c
10	$\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$		85	24		43 (74:26) ^d
11	$\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$	<i>cis</i> -Stilbene	85	24		41 (73:27) ^d
12	$\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$	<i>cis</i> -Stilbene	85	24	34	28 (61:39) ^d

^a Toluene-*d*₈, 1 mol% catalyst, 5 mol% AIBN; ^b Yield determined by ^1H NMR spectroscopy of product versus internal standard; ^c The ratio of anti/syn isomers was determined from the ^1H NMR spectrum. ^d The diastereomeric ratio was determined from the ^1H NMR spectrum.

Interestingly, only subtle differences in the activities of catalytic systems 1, 6 and 11 were observed with all the substrates employed. With *trans*- β -methyl styrene, all three catalysts yielded > 90% of the 1:1 adduct. With benzylidene acetone, chalcone, and *cis*-stilbene, however, < 60% yield was obtained. Despite the superior catalytic performance in the ATRA of CCl₄ to styrene,^{10a,13,14} the activity of 11 towards the addition of CCl₄ to the aforementioned substrates was low and comparable to that of 1 and 6. These results clearly indicate that the rate of the addition reaction is strongly dependent on the substrates used.

Compounds 31-34 contain two stereogenic centers; a mixture of diastereomers was obtained as can be seen from the two sets of peaks in ¹H NMR spectra (Figures 4.5-4.8). Only minor variations in isomeric ratio were observed for each of the four substrates using all three catalysts. The diastereomeric ratio obtained for 31 and 32 were higher than those reported in the literature (literature data; 66:33 for 31, 64:36 for 32).^{6,17} In the case of chalcone-CCl₄ adduct 33, both % yield and isomeric ratio for Cp*Ru(PTA)(PPh₃)Cl catalyzed reaction were higher than those of PMe₃ and PPh₃ analogs.

Figure 4.5: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 31 (1,3,3,3-tetrachloro-2-methyl-propyl-benzene) formed by the addition of CCl_4 to *trans*- β -methyl styrene; internal standard (*), AIBN (\blacktriangle), minor isomer (\bullet).

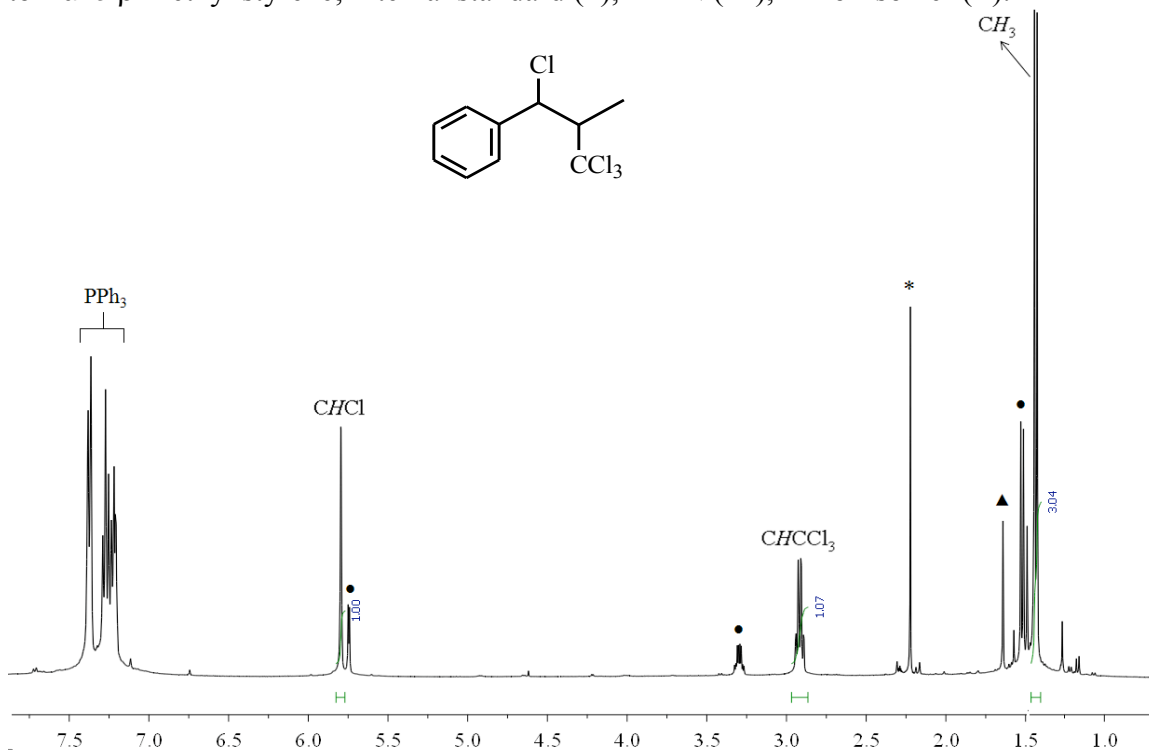


Figure 4.6: ^1H NMR spectrum in toluene- d_8 of the reaction mixture, showing the 1:1 adduct 32 (4-chloro-4-phenyl-3-(trichloromethyl)-butan-2-one) formed by the addition of CCl_4 to benzylidene acetone; internal standard (*), AIBN (\blacktriangle), minor isomer (\bullet), benzylidene acetone (\blacklozenge).

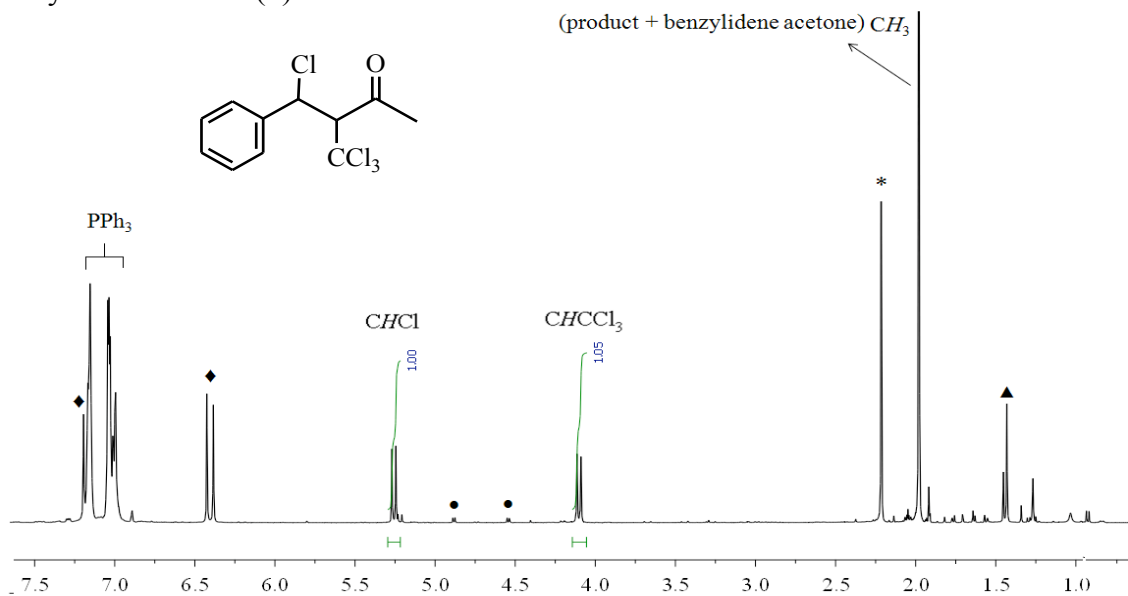


Figure 4.7: ^1H NMR spectrum in CDCl_3 of 3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one (**33**) formed by the addition of CCl_4 to chalcone; residual toluene (*), minor isomer (\bullet).

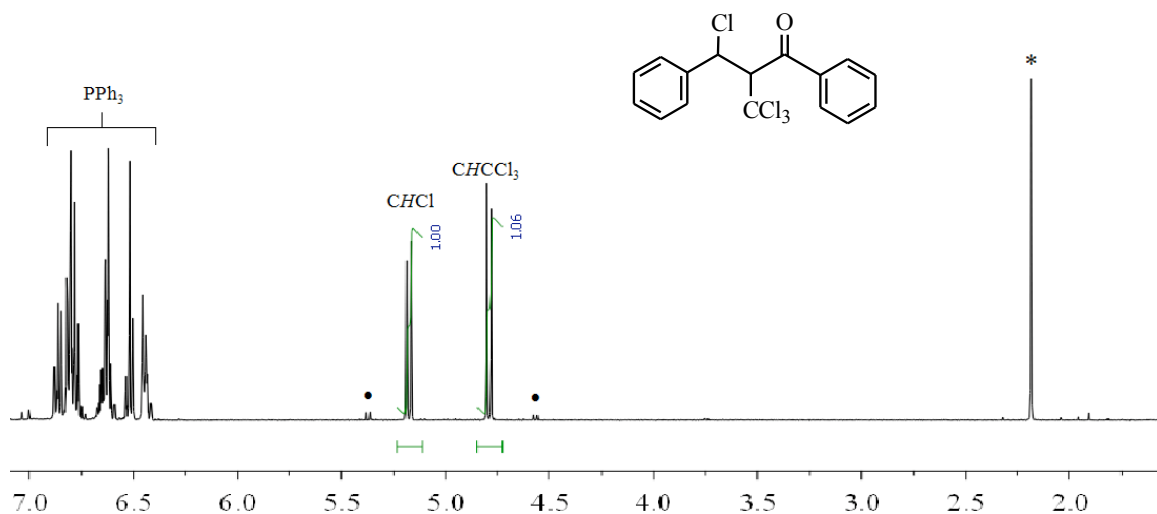
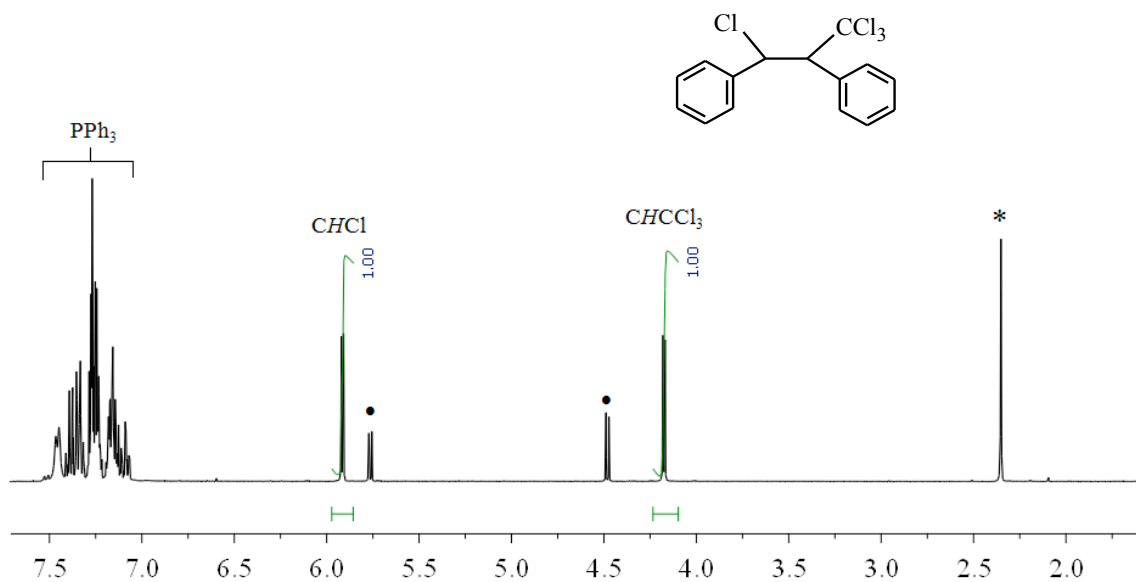


Figure 4.8: ^1H NMR spectrum in CDCl_3 of 1,3,3,3-tetrachloro-1,2-diphenylpropane (**34**) formed by the addition of CCl_4 to *c/s*-Stilbene; residual toluene (*), minor isomer (\bullet).



4.3.2 Characterization and structures of the Kharasch products (33) and (34)

^1H NMR spectrum of compound 33 in CDCl_3 exhibits two doublets at 5.30 and 5.33 ppm corresponding to aliphatic hydrogens of the *trans*-isomer. A second pair of doublets is observed at 4.55 and 5.80 ppm which is due to the minor isomer (Figure 4.7). Compound 34 also shows two pairs of doublets in the ^1H NMR spectrum, each of which corresponds to a diastereomer (Figure 4.8). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these compounds may be found in the Appendix. The mass spectra (APPI) obtained for compounds 33 and 34 are identical to their computer simulations, Figures 4.9 and 4.10.

Figure 4.9: Mass spectrum (bottom) along with computer simulation (top) of 33 (chalcone- CCl_4 adduct).

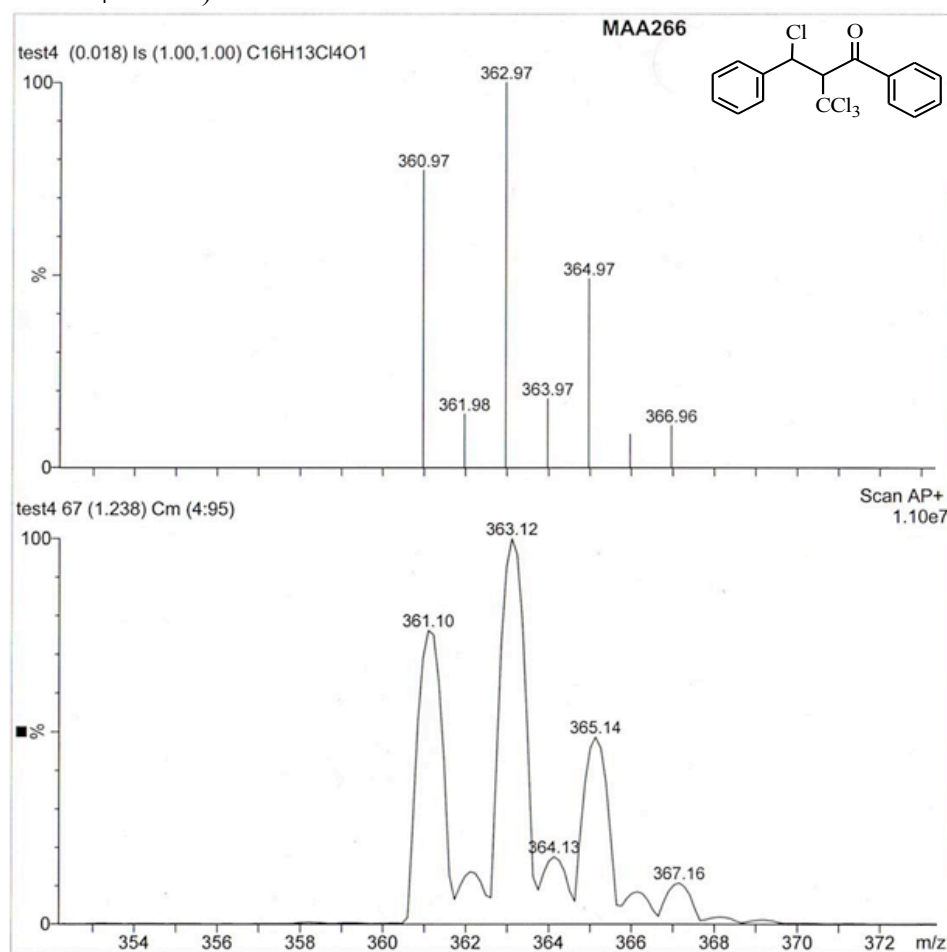
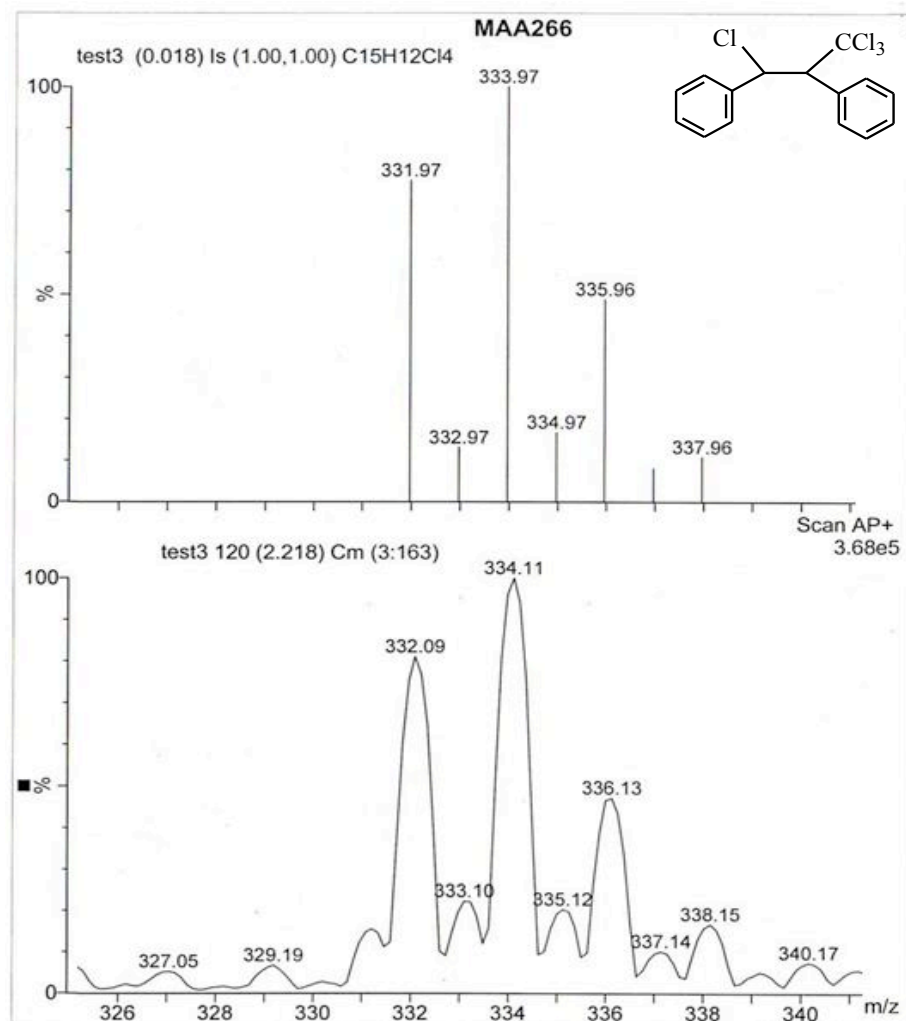


Figure 4.10: Mass spectrum (bottom) along with computer simulation (top) of 34 (*cis*-stilbene-CCl₄ adduct).



The solid-state structures of 33 and 34 were determined by X-ray crystallography. Crystals suitable for X-ray diffraction were obtained by slow evaporation of hexane solutions of 33 and 34. Thermal ellipsoid representations of 33 and 34 are depicted in Figures 4.9 and 4.10, respectively, along with atomic numbering schemes. The regioselectivity of CCl₄ addition to chalcone is confirmed from the structure of 33. As expected, Cl atom is bonded to the benzylic carbon. The structure of chalcone-CCl₄

adduct in Figure 4.11 represents (*RR*)-configuration. In the case of *cis*-stilbene-CCl₄ adduct, the structure of major diastereomer with (*SS*)-configuration is depicted in Figure 4.12.

Figure 4.11: Thermal ellipsoid (50% probability) representation of chalcone-CCl₄ adduct with the atomic numbering scheme.

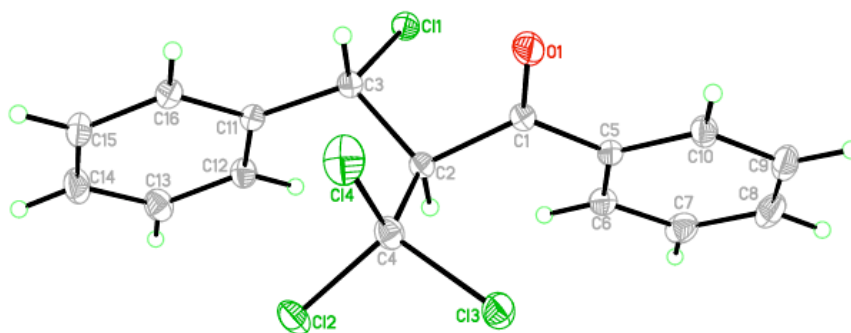
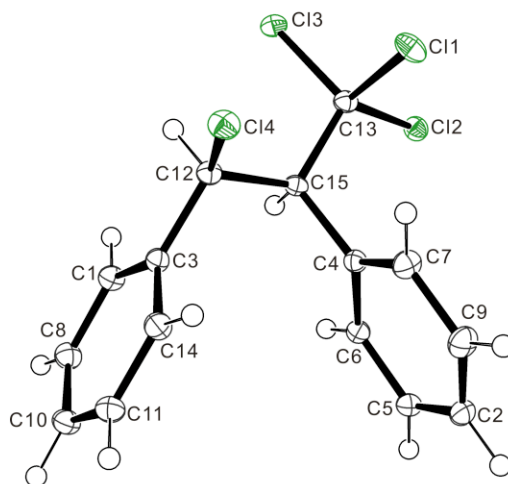


Figure 4.12: Thermal ellipsoid (50% probability) representation of *cis*-stilbene-CCl₄ adduct with the atomic numbering scheme.



4.4 Conclusion

In summary, we have presented here the activity of readily available and air-stable ruthenium Cp* complexes bearing PTA, PPh₃, or PMe₃ ligands towards the addition of carbon tetrachloride to a variety of olefins. The addition of CCl₄ to terminal olefins was almost quantitative with all three catalysts. The internal olefins employed in this study (except *trans*- β -methyl styrene) proved to be less reactive whatever the catalytic system may be. The activities of Cp*Ru(PTA)(PPh₃)Cl **1** and Cp*Ru(PMe₃)(PPh₃)Cl **6** were comparable to that of Cp*Ru(PPh₃)₂Cl **11**, which set so far the standard in Kharasch chemistry. These results indicate that the rate of the reaction depends not only on the type of catalyst, but also on the nature of substrate employed.

4.5 References

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Chapter 5

Conclusion

Half-sandwich ruthenium (II) complexes of the type $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ were synthesized and characterized, and their efficiency to catalyze the radical addition of various halogenated compounds to olefinic substrates was investigated.¹⁻³

The concluding remarks of Kharasch addition reactions catalyzed by $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes are summarized below.

The rate of the addition reactions depended largely on the following factors:

1. Nature of the catalyst
2. Type of the olefinic substrate employed
3. Nature of the chlorinated compound

Catalytic performance of the $\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes was determined by:

1. Nature of the Cp' ancillary ligands
2. Nature of the phosphine

A series of air stable $\text{Cp}'\text{Ru}(\text{PR}_3)(\text{PPh}_3)\text{Cl}$ complexes, where $\text{Cp}' = \text{Cp}^*, \text{Dp}, \text{Ind}, \text{Cp}, \text{Tp}$; $\text{PR}_3 = \text{PTA}$ or PMe_3 were synthesized in good to excellent yields by ligand exchange reactions with $\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl}$. The complexes were characterized by NMR

spectroscopy (^{31}P , ^1H) and X-ray crystallography. Solid-state structures revealed classic three-legged piano stool geometry of all the complexes. Attempts to synthesize $\text{IndRu}(\text{PTA})_2\text{Cl}$ resulted in the cationic complex $[\text{IndRu}(\text{PTA})_2\text{PPh}_3]\text{Cl}$. $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ was found to be moderately active towards the selective transfer hydrogenation of α,β -unsaturated carbonyl compounds. The synthesis and characterization of the air-sensitive hydride, $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$, was also described. The H/D exchange of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$ ($t_{1/2} \sim 5.5$ d) was found to be much slower than that of the Cp-analog ($t_{1/2} \ll 10$ min). Cyclic voltammetry measurements for the ruthenium complexes in dichloromethane indicated that the ease of oxidation of the metal center was proportional to the electron-donating ability of the ancillary ligand (Cp').

$\text{Cp}'\text{Ru}(\text{PPh}_3)(\text{PR}_3)\text{Cl}$ complexes (Cp' = Cp*, Dp, Ind, Cp, Tp; PR_3 = PTA, PMe_3 , PPh_3) were explored for the atom transfer radical addition of a variety of halogenated compounds (CCl_4 , $\text{CCl}_3\text{CO}_2\text{Et}$, *p*-TsCl, CHCl_3 , and $\text{CH}_2\text{ClCO}_2\text{Et}$) to styrene. These complexes proved to be efficient catalyst precursors for the addition of CCl_4 , $\text{CCl}_3\text{CO}_2\text{Et}$, and *p*-TsCl to styrene, affording the 1:1 adducts in almost quantitative yields at 60°C . The Cp* analogues also catalyzed the addition of the difficult substrates, CHCl_3 and $\text{CH}_2\text{ClCO}_2\text{Et}$, to styrene. The results revealed that the electron-donating ability of the ancillary ligand (Cp') and the relative facility of dissociation of the phosphine are crucial for good catalytic performance of the ruthenium complexes. From catalytic point of view, the most electron rich Cp* ligands played a major role. Based on the electron-donating ability of the Cp' ligand, the order of reactivity was: $\text{Cp}^*\text{Ru} \gg \text{DpRu} > \text{IndRu} > \text{CpRu} > \text{TpRu}$. A significant drop in the reactivity was observed upon replacing Cp* ligand with other Cp' ligands. The pronounced electron richness of Cp* rendered $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ an

exceptional catalyst, and both $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ and its PMe_3 counterpart highly efficient catalysts for ATRA. The catalytic activity of $\text{Cp}'\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$ and $\text{Cp}'\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$, however, was significantly lower than that of the parent $\text{Cp}'\text{Ru}(\text{PPh}_3)_2\text{Cl}$ complexes. This suggested that the efficiency of catalysts was hampered by replacement of PPh_3 with a stronger binding phosphine such as PTA or PMe_3 . These results are in accord with the phosphine-dissociation step, involved in the reaction mechanism. This was further confirmed by the lower catalytic activity of the substitutionally inert $\text{Cp}'\text{Ru}(\text{PTA})_2\text{Cl}$ complexes. Another evidence for the phosphine-dissociation mechanism was the retardation of the reaction rate upon addition of excess free PPh_3 to the reaction mixture.

The nature of the chlorinated reagent was also crucial for promoting Kharasch reactions. Using Cp^* complexes, the reactivity order was: $\text{CCl}_4 > \text{CHCl}_3$, and $\text{CCl}_3\text{CO}_2\text{Et} > \text{CH}_2\text{ClCO}_2\text{Et}$. This suggested that higher the level of halogenation, greater is the reactivity of the chloro-substrate. In most cases, the reactivity of PTA-complexes was comparable to that of their PMe_3 counterparts.

The activity of $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$, $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ and $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ towards the addition of CCl_4 to more challenging olefins was also studied. Both terminal (hexene, decene, *n*-butyl acrylate) and internal (*trans*- β -methyl styrene, benzylidene acetone, chalcone, *cis*-Stilbene) olefins were employed. The CCl_4 addition to 1-hexene was very impressive; total turnovers (TTO) in excess of 80,000 were obtained. These are the highest TTOs reported to date. Even with 1-decene (a difficult substrate for ATRA) and *n*-butyl acrylate (an easily polymerizable substrate), nearly quantitative yields were obtained with all three catalysts. With *trans*- β -methyl styrene as

substrate, high reactivity was observed. Other internal olefins, however, were less prone to the addition of CCl_4 , whatever the catalytic system may be. At elevated temperature (85°C), only $< 50\%$ of the desired products were obtained. Despite the superior catalytic performance in Kharasch chemistry, the activity of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ towards CCl_4 addition to the difficult internal olefins was low and comparable to that of PTA and PMe_3 analogs. These results clearly indicated that the rate of the reaction depended not only on the type of catalyst, but also on the nature of substrate employed. The chalcone- CCl_4 and *cis*-Stilbene- CCl_4 adducts were synthesized and fully characterized for the first time.

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Appendix

NMR spectra (^1H , ^{31}P , ^{13}C), Crystal data, and Tables for Bond distances and Angles.

Figure/ Table #	Title	Page
A1	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (3) in CD_2Cl_2 .	
A2	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{DpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (7) in CD_2Cl_2 .	
A3	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{CpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (9) in CD_2Cl_2 .	
A4	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (10) in CD_2Cl_2 .	
A5	^{31}P NMR spectrum of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$ (20) in CD_3OD .	
A6	^1H NMR spectrum of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19) in CD_2Cl_2 .	
A7	^{13}C NMR spectrum of (33) in CDCl_3 .	
A8	^{13}C NMR spectrum of (34) in CDCl_3 .	
A9	Bond lengths [\AA] and angles [$^\circ$] for $\text{CpRu}(\text{PTA})_2\text{SnCl}_3$.	
A10	Torsion angles [$^\circ$] for $\text{CpRu}(\text{PTA})_2\text{SnCl}_3$.	
A11	Bond lengths [\AA] and angles [$^\circ$] for $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$.	
A12	Torsion angles [$^\circ$] for $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$.	
A13	Bond lengths [\AA] and angles [$^\circ$] for $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{SnCl}_3$.	
A14	Torsion angles [$^\circ$] for $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{SnCl}_3$.	
A15	Bond lengths [\AA] and angles [$^\circ$] for $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$.	

- A16 Torsion angles [°] for IndRu(PTA)(PPh₃)Cl.
- A17 Bond lengths [Å] and angles [°] for Cp*Ru(PTA)(PPh₃)Cl.
- A18 Torsion angles [°] for Cp*Ru(PTA)(PPh₃)Cl.
- A19 Bond lengths [Å] and angles [°] for IndRu(PMe₃)(PPh₃)Cl.
- A20 Torsion angles [°] for IndRu(PMe₃)(PPh₃)Cl.
- A21 Bond lengths [Å] and angles [°] for TpRu(PMe₃)(PPh₃)Cl.
- A22 Torsion angles [°] for TpRu(PMe₃)(PPh₃)Cl.
- A23 Bond lengths [Å] and angles [°] for Cp*Ru(PMe₃)(PPh₃)Cl.
- A24 Torsion angles [°] for Cp*Ru(PMe₃)(PPh₃)Cl.
- A25 Bond lengths [Å] and angles [°] for chalcone-CCl₄ adduct.
- A26 Torsion angles [°] for chalcone-CCl₄ adduct.
- A27 Bond lengths [Å] and angles [°] for *cis*-stilbene-CCl₄ adduct.
- A28 Torsion angles [°] for *cis*-stilbene -CCl₄ adduct.

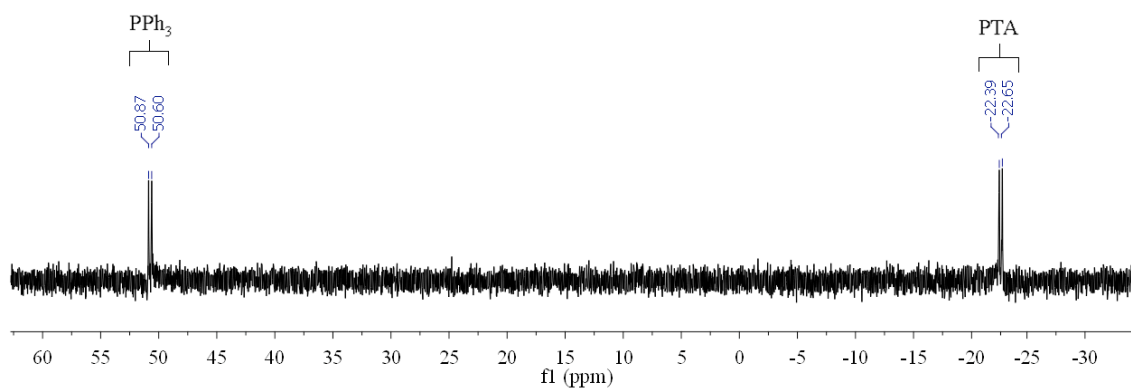
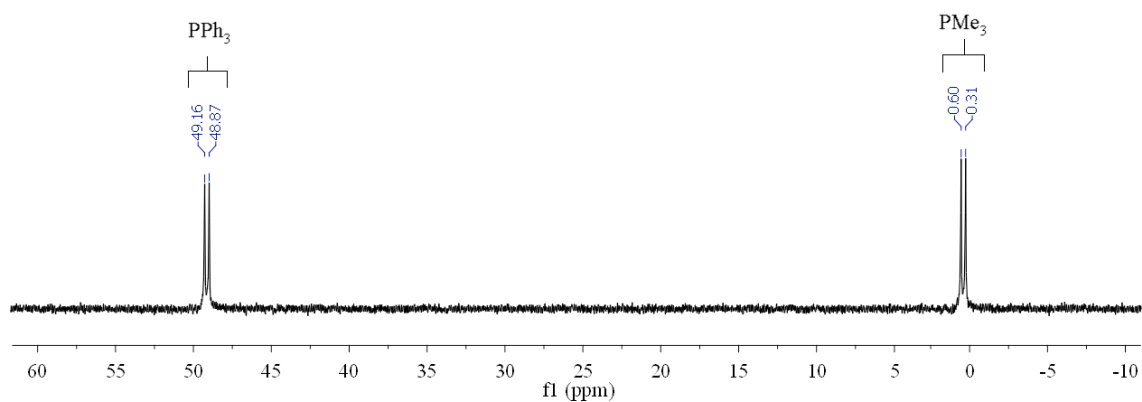
Figure A1: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{Cl}$ (**3**) in CD_2Cl_2 .Figure A2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{DpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (**7**) in CD_2Cl_2 .

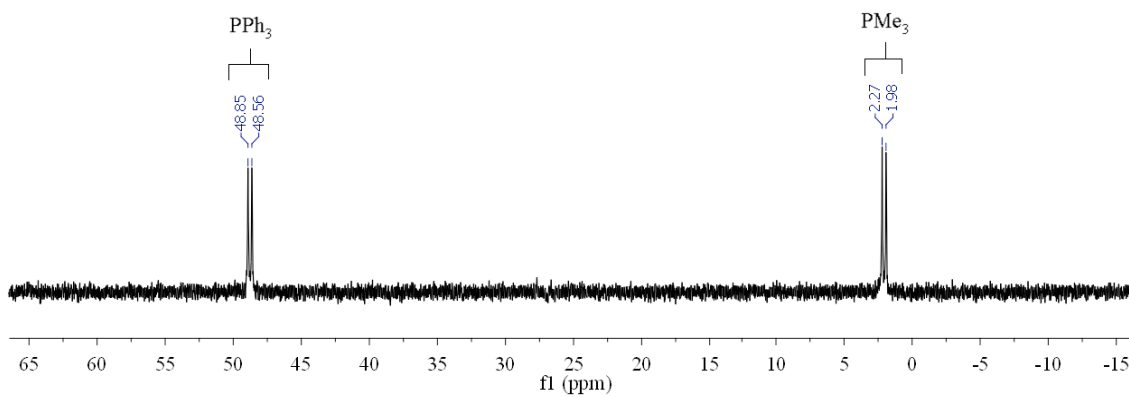
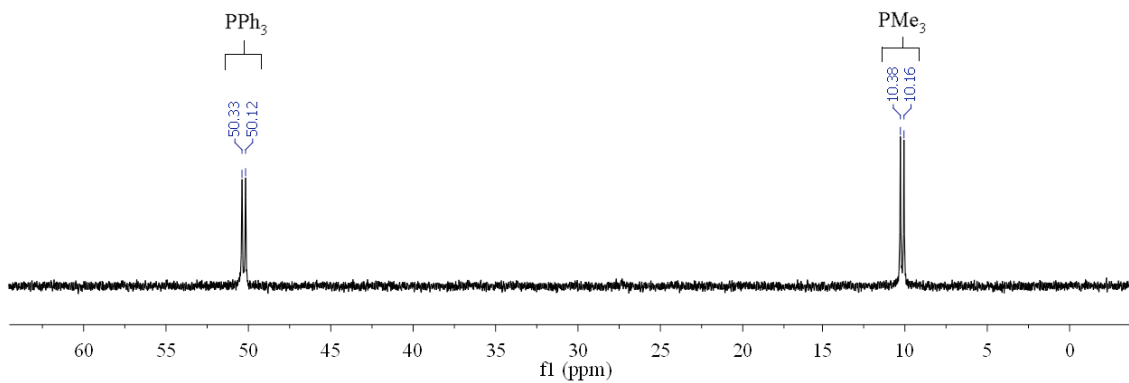
Figure A3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{CpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (9) in CD_2Cl_2 .Figure A4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{TpRu}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$ (10) in CD_2Cl_2 .

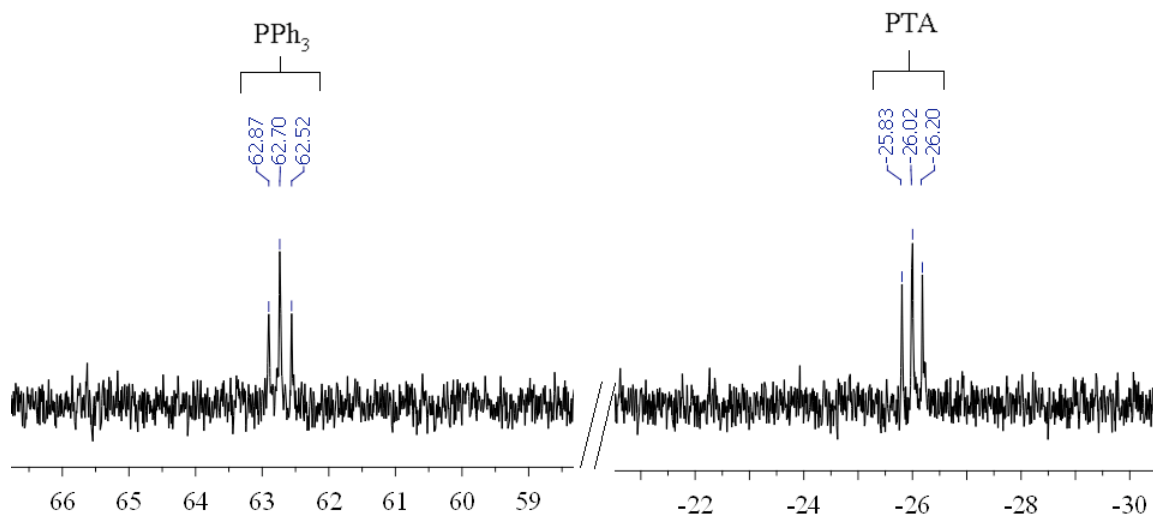
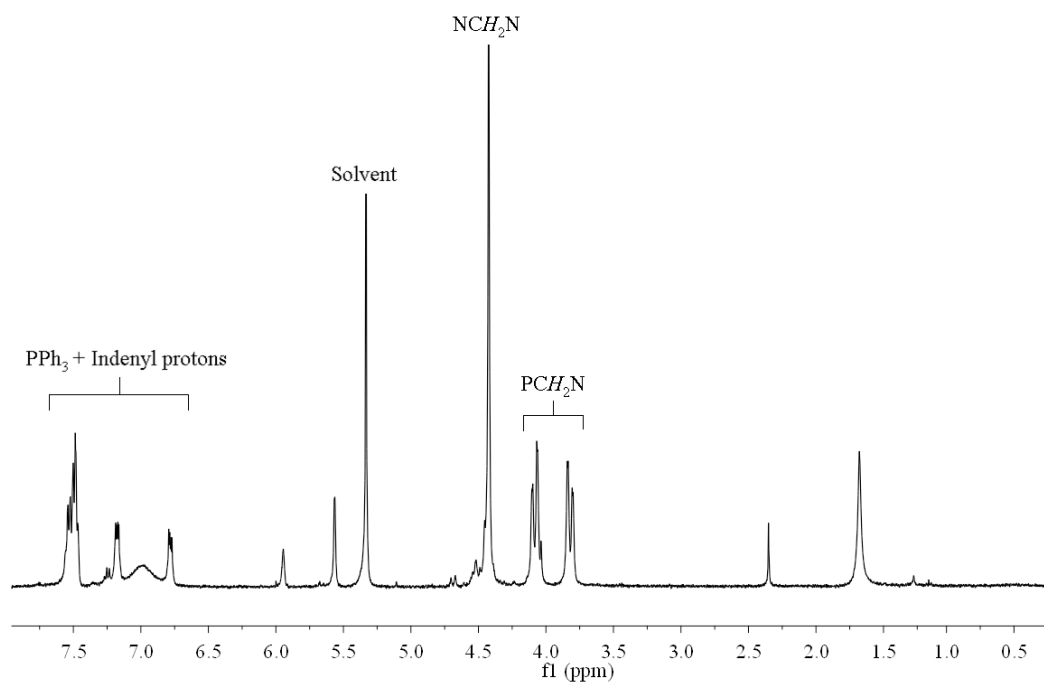
Figure A5: ^{31}P NMR spectrum of $\text{IndRu}(\text{PTA})(\text{PPh}_3)\text{H}$ (20) in CD_3OD .Figure A6: ^1H NMR spectrum of $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{Cl}$ (19) in CD_2Cl_2 .

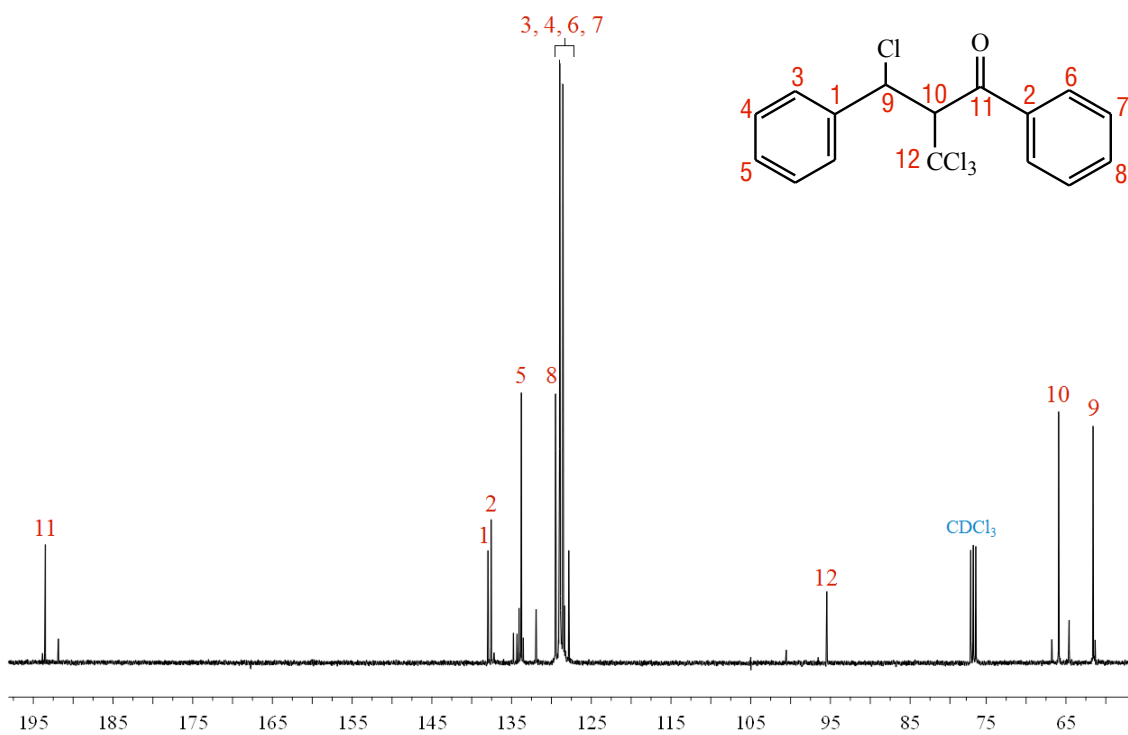
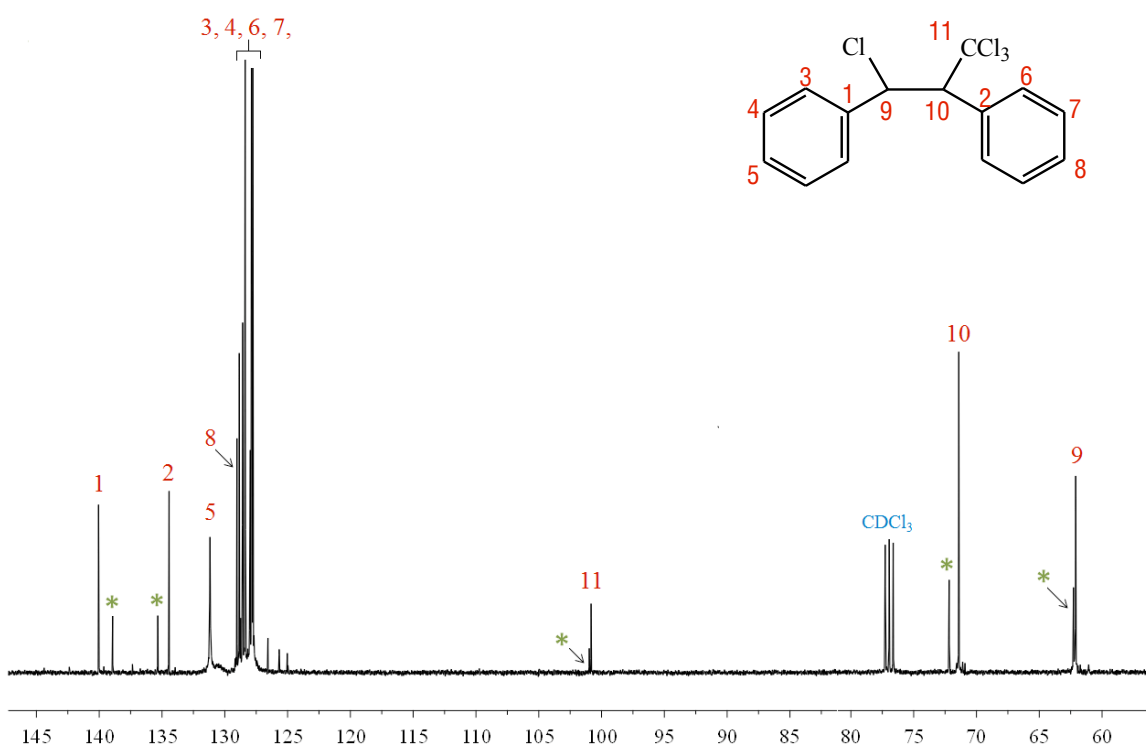
Figure A7: ^{13}C NMR spectrum of (33) in CDCl_3 .Figure A8: ^{13}C NMR spectrum of (34) in CDCl_3 ; minor isomer (*).

Table A9: Bond lengths [\AA] and angles [$^\circ$] for $\text{CpRu(PTA)}_2\text{SnCl}_3$.

Ru(1)-C(17)	2.2225(19)	C(8)-H(8B)	0.9900
Ru(1)-C(13)	2.223(2)	C(9)-H(9A)	0.9900
Ru(1)-C(16)	2.2385(19)	C(9)-H(9B)	0.9900
Ru(1)-C(14)	2.241(2)	C(10)-H(10A)	0.9900
Ru(1)-C(15)	2.246(2)	C(10)-H(10B)	0.9900
Ru(1)-P(1)	2.2747(5)	C(11)-H(11A)	0.9900
Ru(1)-P(2)	2.2805(5)	C(11)-H(11B)	0.9900
Ru(1)-Sn(1)	2.5319(2)	C(12)-H(12A)	0.9900
Sn(1)-Cl(2)	2.3865(6)	C(12)-H(12B)	0.9900
Sn(1)-Cl(1)	2.4125(5)	C(13)-C(17)	1.416(3)
Sn(1)-Cl(3)	2.4129(5)	C(13)-C(14)	1.442(4)
P(1)-C(2)	1.8479(19)	C(13)-H(13A)	1.0000
P(1)-C(1)	1.8507(19)	C(14)-C(15)	1.406(3)
P(1)-C(3)	1.8534(19)	C(14)-H(14A)	1.0000
P(2)-C(9)	1.8491(19)	C(15)-C(16)	1.421(3)
P(2)-C(8)	1.851(2)	C(15)-H(15A)	1.0000
P(2)-C(7)	1.8584(19)	C(16)-C(17)	1.421(3)
N(1)-C(4)	1.467(3)	C(16)-H(16A)	1.0000
N(1)-C(6)	1.474(3)	C(17)-H(17A)	1.0000
N(1)-C(1)	1.479(3)	Cl(1S)-C(1S)	1.770(2)
N(2)-C(4)	1.464(3)	C(1S)-Cl(1S)#1	1.770(2)
N(2)-C(5)	1.465(3)	C(1S)-H(1S)	0.92(3)
N(2)-C(2)	1.466(2)		
N(3)-C(5)	1.467(3)	C(17)-Ru(1)-C(13)	37.14(9)
N(3)-C(6)	1.467(3)	C(17)-Ru(1)-C(16)	37.14(8)
N(3)-C(3)	1.475(3)	C(13)-Ru(1)-C(16)	62.19(8)
N(4)-C(10)	1.465(3)	C(17)-Ru(1)-C(14)	62.02(8)
N(4)-C(12)	1.466(3)	C(13)-Ru(1)-C(14)	37.70(9)
N(4)-C(7)	1.476(2)	C(16)-Ru(1)-C(14)	61.65(8)
N(5)-C(11)	1.466(3)	C(17)-Ru(1)-C(15)	61.76(7)
N(5)-C(8)	1.473(3)	C(13)-Ru(1)-C(15)	62.07(8)
N(5)-C(10)	1.474(3)	C(16)-Ru(1)-C(15)	36.94(8)
N(6)-C(12)	1.471(3)	C(14)-Ru(1)-C(15)	36.52(9)
N(6)-C(9)	1.474(3)	C(17)-Ru(1)-P(1)	91.17(6)
N(6)-C(11)	1.477(3)	C(13)-Ru(1)-P(1)	115.11(7)
C(1)-H(1A)	0.9900	C(16)-Ru(1)-P(1)	102.78(6)
C(1)-H(1B)	0.9900	C(14)-Ru(1)-P(1)	151.85(6)
C(2)-H(2A)	0.9900	C(15)-Ru(1)-P(1)	138.68(6)
C(2)-H(2B)	0.9900	C(17)-Ru(1)-P(2)	127.92(6)
C(3)-H(3A)	0.9900	C(13)-Ru(1)-P(2)	96.36(6)
C(3)-H(3B)	0.9900	C(16)-Ru(1)-P(2)	157.08(6)
C(4)-H(4A)	0.9900	C(14)-Ru(1)-P(2)	96.70(6)
C(4)-H(4B)	0.9900	C(15)-Ru(1)-P(2)	127.60(6)
C(5)-H(5A)	0.9900	P(1)-Ru(1)-P(2)	93.474(17)
C(5)-H(5B)	0.9900	C(17)-Ru(1)-Sn(1)	140.01(6)
C(6)-H(6A)	0.9900	C(13)-Ru(1)-Sn(1)	149.27(7)
C(6)-H(6B)	0.9900	C(16)-Ru(1)-Sn(1)	103.39(6)
C(7)-H(7A)	0.9900	C(14)-Ru(1)-Sn(1)	111.90(7)
C(7)-H(7B)	0.9900	C(15)-Ru(1)-Sn(1)	89.81(6)
C(8)-H(8A)	0.9900	P(1)-Ru(1)-Sn(1)	93.964(13)

P(2)-Ru(1)-Sn(1)	91.336(13)	H(3A)-C(3)-H(3B)	107.8
Cl(2)-Sn(1)-Cl(1)	95.77(2)	N(2)-C(4)-N(1)	114.23(16)
Cl(2)-Sn(1)-Cl(3)	94.90(2)	N(2)-C(4)-H(4A)	108.7
Cl(1)-Sn(1)-Cl(3)	96.723(18)	N(1)-C(4)-H(4A)	108.7
Cl(2)-Sn(1)-Ru(1)	126.633(15)	N(2)-C(4)-H(4B)	108.7
Cl(1)-Sn(1)-Ru(1)	117.385(14)	N(1)-C(4)-H(4B)	108.7
Cl(3)-Sn(1)-Ru(1)	119.009(15)	H(4A)-C(4)-H(4B)	107.6
C(2)-P(1)-C(1)	97.43(9)	N(2)-C(5)-N(3)	114.09(16)
C(2)-P(1)-C(3)	96.77(9)	N(2)-C(5)-H(5A)	108.7
C(1)-P(1)-C(3)	97.73(9)	N(3)-C(5)-H(5A)	108.7
C(2)-P(1)-Ru(1)	124.53(6)	N(2)-C(5)-H(5B)	108.7
C(1)-P(1)-Ru(1)	117.36(7)	N(3)-C(5)-H(5B)	108.7
C(3)-P(1)-Ru(1)	117.70(7)	H(5A)-C(5)-H(5B)	107.6
C(9)-P(2)-C(8)	98.30(9)	N(3)-C(6)-N(1)	114.71(16)
C(9)-P(2)-C(7)	97.60(9)	N(3)-C(6)-H(6A)	108.6
C(8)-P(2)-C(7)	96.29(9)	N(1)-C(6)-H(6A)	108.6
C(9)-P(2)-Ru(1)	117.78(6)	N(3)-C(6)-H(6B)	108.6
C(8)-P(2)-Ru(1)	115.97(6)	N(1)-C(6)-H(6B)	108.6
C(7)-P(2)-Ru(1)	125.59(6)	H(6A)-C(6)-H(6B)	107.6
C(4)-N(1)-C(6)	108.44(17)	N(4)-C(7)-P(2)	112.47(13)
C(4)-N(1)-C(1)	110.46(16)	N(4)-C(7)-H(7A)	109.1
C(6)-N(1)-C(1)	110.87(17)	P(2)-C(7)-H(7A)	109.1
C(4)-N(2)-C(5)	109.27(16)	N(4)-C(7)-H(7B)	109.1
C(4)-N(2)-C(2)	111.40(15)	P(2)-C(7)-H(7B)	109.1
C(5)-N(2)-C(2)	110.61(15)	H(7A)-C(7)-H(7B)	107.8
C(5)-N(3)-C(6)	108.33(17)	N(5)-C(8)-P(2)	113.03(13)
C(5)-N(3)-C(3)	110.92(15)	N(5)-C(8)-H(8A)	109.0
C(6)-N(3)-C(3)	111.20(17)	P(2)-C(8)-H(8A)	109.0
C(10)-N(4)-C(12)	108.82(16)	N(5)-C(8)-H(8B)	109.0
C(10)-N(4)-C(7)	110.67(15)	P(2)-C(8)-H(8B)	109.0
C(12)-N(4)-C(7)	111.91(15)	H(8A)-C(8)-H(8B)	107.8
C(11)-N(5)-C(8)	110.54(17)	N(6)-C(9)-P(2)	112.72(13)
C(11)-N(5)-C(10)	108.74(16)	N(6)-C(9)-H(9A)	109.0
C(8)-N(5)-C(10)	111.23(16)	P(2)-C(9)-H(9A)	109.0
C(12)-N(6)-C(9)	110.41(16)	N(6)-C(9)-H(9B)	109.0
C(12)-N(6)-C(11)	108.10(16)	P(2)-C(9)-H(9B)	109.0
C(9)-N(6)-C(11)	111.46(16)	H(9A)-C(9)-H(9B)	107.8
N(1)-C(1)-P(1)	112.92(13)	N(4)-C(10)-N(5)	113.68(16)
N(1)-C(1)-H(1A)	109.0	N(4)-C(10)-H(10A)	108.8
P(1)-C(1)-H(1A)	109.0	N(5)-C(10)-H(10A)	108.8
N(1)-C(1)-H(1B)	109.0	N(4)-C(10)-H(10B)	108.8
P(1)-C(1)-H(1B)	109.0	N(5)-C(10)-H(10B)	108.8
H(1A)-C(1)-H(1B)	107.8	H(10A)-C(10)-H(10B)	107.7
N(2)-C(2)-P(1)	112.96(13)	N(5)-C(11)-N(6)	114.67(16)
N(2)-C(2)-H(2A)	109.0	N(5)-C(11)-H(11A)	108.6
P(1)-C(2)-H(2A)	109.0	N(6)-C(11)-H(11A)	108.6
N(2)-C(2)-H(2B)	109.0	N(5)-C(11)-H(11B)	108.6
P(1)-C(2)-H(2B)	109.0	N(6)-C(11)-H(11B)	108.6
H(2A)-C(2)-H(2B)	107.8	H(11A)-C(11)-H(11B)	107.6
N(3)-C(3)-P(1)	112.71(13)	N(4)-C(12)-N(6)	114.46(16)
N(3)-C(3)-H(3A)	109.0	N(4)-C(12)-H(12A)	108.6
P(1)-C(3)-H(3A)	109.0	N(6)-C(12)-H(12A)	108.6
N(3)-C(3)-H(3B)	109.0	N(4)-C(12)-H(12B)	108.6
P(1)-C(3)-H(3B)	109.0	N(6)-C(12)-H(12B)	108.6

H(12A)-C(12)-H(12B)	107.6	C(16)-C(15)-H(15A)	125.7
C(17)-C(13)-C(14)	107.14(19)	Ru(1)-C(15)-H(15A)	125.7
C(17)-C(13)-Ru(1)	71.43(12)	C(15)-C(16)-C(17)	107.64(19)
C(14)-C(13)-Ru(1)	71.83(12)	C(15)-C(16)-Ru(1)	71.83(11)
C(17)-C(13)-H(13A)	126.3	C(17)-C(16)-Ru(1)	70.82(11)
C(14)-C(13)-H(13A)	126.3	C(15)-C(16)-H(16A)	126.1
Ru(1)-C(13)-H(13A)	126.3	C(17)-C(16)-H(16A)	126.1
C(15)-C(14)-C(13)	107.99(19)	Ru(1)-C(16)-H(16A)	126.1
C(15)-C(14)-Ru(1)	71.96(12)	C(13)-C(17)-C(16)	108.65(19)
C(13)-C(14)-Ru(1)	70.47(12)	C(13)-C(17)-Ru(1)	71.43(12)
C(15)-C(14)-H(14A)	126.0	C(16)-C(17)-Ru(1)	72.04(11)
C(13)-C(14)-H(14A)	126.0	C(13)-C(17)-H(17A)	125.6
Ru(1)-C(14)-H(14A)	126.0	C(16)-C(17)-H(17A)	125.6
C(14)-C(15)-C(16)	108.57(19)	Ru(1)-C(17)-H(17A)	125.6
C(14)-C(15)-Ru(1)	71.52(12)	Cl(1S)#1-C(1S)-Cl(1S)	113.1(2)
C(16)-C(15)-Ru(1)	71.23(11)	Cl(1S)#1-C(1S)-H(1S)	108(2)
C(14)-C(15)-H(15A)	125.7	Cl(1S)-C(1S)-H(1S)	103(2)

Symmetry transformations used to generate equivalent atoms:

Table A10: Torsion angles [$^{\circ}$] for CpRu(PTA)₂SnCl₃.

C(17)-Ru(1)-Sn(1)-Cl(2)	108.56(9)	Sn(1)-Ru(1)-P(1)-C(2)	-55.98(8)
C(13)-Ru(1)-Sn(1)-Cl(2)	173.59(12)	C(17)-Ru(1)-P(1)-C(1)	-74.09(9)
C(16)-Ru(1)-Sn(1)-Cl(2)	116.14(6)	C(13)-Ru(1)-P(1)-C(1)	-103.52(10)
C(14)-Ru(1)-Sn(1)-Cl(2)	-179.35(7)	C(16)-Ru(1)-P(1)-C(1)	-38.48(9)
C(15)-Ru(1)-Sn(1)-Cl(2)	150.82(7)	C(14)-Ru(1)-P(1)-C(1)	-91.02(16)
P(1)-Ru(1)-Sn(1)-Cl(2)	11.99(3)	C(15)-Ru(1)-P(1)-C(1)	-28.01(12)
P(2)-Ru(1)-Sn(1)-Cl(2)	-81.58(3)	P(2)-Ru(1)-P(1)-C(1)	157.80(8)
C(17)-Ru(1)-Sn(1)-Cl(1)	-13.19(9)	Sn(1)-Ru(1)-P(1)-C(1)	66.22(7)
C(13)-Ru(1)-Sn(1)-Cl(1)	51.84(12)	C(17)-Ru(1)-P(1)-C(3)	42.19(10)
C(16)-Ru(1)-Sn(1)-Cl(1)	-5.61(6)	C(13)-Ru(1)-P(1)-C(3)	12.77(10)
C(14)-Ru(1)-Sn(1)-Cl(1)	58.90(7)	C(16)-Ru(1)-P(1)-C(3)	77.81(9)
C(15)-Ru(1)-Sn(1)-Cl(1)	29.07(6)	C(14)-Ru(1)-P(1)-C(3)	25.27(16)
P(1)-Ru(1)-Sn(1)-Cl(1)	-109.754(19)	C(15)-Ru(1)-P(1)-C(3)	88.27(11)
P(2)-Ru(1)-Sn(1)-Cl(1)	156.670(19)	P(2)-Ru(1)-P(1)-C(3)	-85.91(8)
C(17)-Ru(1)-Sn(1)-Cl(3)	-129.17(9)	Sn(1)-Ru(1)-P(1)-C(3)	-177.50(8)
C(13)-Ru(1)-Sn(1)-Cl(3)	-64.13(12)	C(17)-Ru(1)-P(2)-C(9)	-26.61(11)
C(16)-Ru(1)-Sn(1)-Cl(3)	-121.59(6)	C(13)-Ru(1)-P(2)-C(9)	-48.17(11)
C(14)-Ru(1)-Sn(1)-Cl(3)	-57.08(7)	C(16)-Ru(1)-P(2)-C(9)	-67.85(16)
C(15)-Ru(1)-Sn(1)-Cl(3)	-86.91(6)	C(14)-Ru(1)-P(2)-C(9)	-86.13(11)
P(1)-Ru(1)-Sn(1)-Cl(3)	134.27(2)	C(15)-Ru(1)-P(2)-C(9)	-107.57(10)
P(2)-Ru(1)-Sn(1)-Cl(3)	40.69(2)	P(1)-Ru(1)-P(2)-C(9)	67.58(8)
C(17)-Ru(1)-P(1)-C(2)	163.71(9)	Sn(1)-Ru(1)-P(2)-C(9)	161.64(8)
C(13)-Ru(1)-P(1)-C(2)	134.29(10)	C(17)-Ru(1)-P(2)-C(8)	89.38(10)
C(16)-Ru(1)-P(1)-C(2)	-160.67(9)	C(13)-Ru(1)-P(2)-C(8)	67.81(10)
C(14)-Ru(1)-P(1)-C(2)	146.79(15)	C(16)-Ru(1)-P(2)-C(8)	48.14(17)
C(15)-Ru(1)-P(1)-C(2)	-150.21(11)	C(14)-Ru(1)-P(2)-C(8)	29.86(10)
P(2)-Ru(1)-P(1)-C(2)	35.61(8)	C(15)-Ru(1)-P(2)-C(8)	8.41(11)
		P(1)-Ru(1)-P(2)-C(8)	-176.43(8)

Sn(1)-Ru(1)-P(2)-C(8)	-82.38(8)	C(8)-N(5)-C(11)-N(6)	-67.7(2)
C(17)-Ru(1)-P(2)-C(7)	-150.72(10)	C(10)-N(5)-C(11)-N(6)	54.7(2)
C(13)-Ru(1)-P(2)-C(7)	-172.28(10)	C(12)-N(6)-C(11)-N(5)	-54.1(2)
C(16)-Ru(1)-P(2)-C(7)	168.04(16)	C(9)-N(6)-C(11)-N(5)	67.4(2)
C(14)-Ru(1)-P(2)-C(7)	149.76(10)	C(10)-N(4)-C(12)-N(6)	-55.8(2)
C(15)-Ru(1)-P(2)-C(7)	128.32(10)	C(7)-N(4)-C(12)-N(6)	66.8(2)
P(1)-Ru(1)-P(2)-C(7)	-56.53(8)	C(9)-N(6)-C(12)-N(4)	-67.7(2)
Sn(1)-Ru(1)-P(2)-C(7)	37.53(8)	C(11)-N(6)-C(12)-N(4)	54.5(2)
C(4)-N(1)-C(1)-P(1)	60.48(19)	C(16)-Ru(1)-C(13)-C(17)	-37.22(12)
C(6)-N(1)-C(1)-P(1)	-59.76(19)	C(14)-Ru(1)-C(13)-C(17)	-115.95(18)
C(2)-P(1)-C(1)-N(1)	-48.93(16)	C(15)-Ru(1)-C(13)-C(17)	-79.22(13)
C(3)-P(1)-C(1)-N(1)	48.98(16)	P(1)-Ru(1)-C(13)-C(17)	54.44(13)
Ru(1)-P(1)-C(1)-N(1)	175.75(12)	P(2)-Ru(1)-C(13)-C(17)	151.31(12)
C(4)-N(2)-C(2)-P(1)	-60.09(18)	Sn(1)-Ru(1)-C(13)-C(17)	-105.21(15)
C(5)-N(2)-C(2)-P(1)	61.65(18)	C(17)-Ru(1)-C(13)-C(14)	115.95(18)
C(1)-P(1)-C(2)-N(2)	48.53(15)	C(16)-Ru(1)-C(13)-C(14)	78.73(14)
C(3)-P(1)-C(2)-N(2)	-50.22(15)	C(15)-Ru(1)-C(13)-C(14)	36.73(13)
Ru(1)-P(1)-C(2)-N(2)	179.25(10)	P(1)-Ru(1)-C(13)-C(14)	170.39(11)
C(5)-N(3)-C(3)-P(1)	-60.56(19)	P(2)-Ru(1)-C(13)-C(14)	-92.75(12)
C(6)-N(3)-C(3)-P(1)	60.06(19)	Sn(1)-Ru(1)-C(13)-C(14)	10.7(2)
C(2)-P(1)-C(3)-N(3)	49.53(15)	C(17)-C(13)-C(14)-C(15)	0.6(2)
C(1)-P(1)-C(3)-N(3)	-48.96(16)	Ru(1)-C(13)-C(14)-C(15)	-62.57(15)
Ru(1)-P(1)-C(3)-N(3)	-175.48(11)	C(17)-C(13)-C(14)-Ru(1)	63.13(14)
C(5)-N(2)-C(4)-N(1)	-54.7(2)	C(17)-Ru(1)-C(14)-C(15)	79.47(13)
C(2)-N(2)-C(4)-N(1)	67.8(2)	C(13)-Ru(1)-C(14)-C(15)	117.40(18)
C(6)-N(1)-C(4)-N(2)	54.0(2)	C(16)-Ru(1)-C(14)-C(15)	37.11(12)
C(1)-N(1)-C(4)-N(2)	-67.7(2)	P(1)-Ru(1)-C(14)-C(15)	98.71(18)
C(4)-N(2)-C(5)-N(3)	55.1(2)	P(2)-Ru(1)-C(14)-C(15)	-150.87(12)
C(2)-N(2)-C(5)-N(3)	-67.9(2)	Sn(1)-Ru(1)-C(14)-C(15)	-56.71(13)
C(6)-N(3)-C(5)-N(2)	-54.8(2)	C(17)-Ru(1)-C(14)-C(13)	-37.93(12)
C(3)-N(3)-C(5)-N(2)	67.5(2)	C(16)-Ru(1)-C(14)-C(13)	-80.29(14)
C(5)-N(3)-C(6)-N(1)	54.9(2)	C(15)-Ru(1)-C(14)-C(13)	-117.40(18)
C(3)-N(3)-C(6)-N(1)	-67.2(2)	P(1)-Ru(1)-C(14)-C(13)	-18.7(2)
C(4)-N(1)-C(6)-N(3)	-54.5(2)	P(2)-Ru(1)-C(14)-C(13)	91.73(12)
C(1)-N(1)-C(6)-N(3)	66.9(2)	Sn(1)-Ru(1)-C(14)-C(13)	-174.11(11)
C(10)-N(4)-C(7)-P(2)	62.58(18)	C(13)-C(14)-C(15)-C(16)	-0.3(2)
C(12)-N(4)-C(7)-P(2)	-58.97(19)	Ru(1)-C(14)-C(15)-C(16)	-61.95(14)
C(9)-P(2)-C(7)-N(4)	48.32(15)	C(13)-C(14)-C(15)-Ru(1)	61.61(14)
C(8)-P(2)-C(7)-N(4)	-50.97(15)	C(17)-Ru(1)-C(15)-C(14)	-80.23(14)
Ru(1)-P(2)-C(7)-N(4)	-179.33(10)	C(13)-Ru(1)-C(15)-C(14)	-37.92(14)
C(11)-N(5)-C(8)-P(2)	60.1(2)	C(16)-Ru(1)-C(15)-C(14)	-117.92(19)
C(10)-N(5)-C(8)-P(2)	-60.8(2)	P(1)-Ru(1)-C(15)-C(14)	-135.06(12)
C(9)-P(2)-C(8)-N(5)	-48.47(16)	P(2)-Ru(1)-C(15)-C(14)	37.60(15)
C(7)-P(2)-C(8)-N(5)	50.18(16)	Sn(1)-Ru(1)-C(15)-C(14)	129.14(13)
Ru(1)-P(2)-C(8)-N(5)	-174.98(12)	C(17)-Ru(1)-C(15)-C(16)	37.69(13)
C(12)-N(6)-C(9)-P(2)	61.48(19)	C(13)-Ru(1)-C(15)-C(16)	80.01(14)
C(11)-N(6)-C(9)-P(2)	-58.7(2)	C(14)-Ru(1)-C(15)-C(16)	117.92(19)
C(8)-P(2)-C(9)-N(6)	47.52(16)	P(1)-Ru(1)-C(15)-C(16)	-17.14(17)
C(7)-P(2)-C(9)-N(6)	-50.02(16)	P(2)-Ru(1)-C(15)-C(16)	155.53(10)
Ru(1)-P(2)-C(9)-N(6)	172.77(12)	Sn(1)-Ru(1)-C(15)-C(16)	-112.93(12)
C(12)-N(4)-C(10)-N(5)	55.5(2)	C(14)-C(15)-C(16)-C(17)	0.0(2)
C(7)-N(4)-C(10)-N(5)	-67.8(2)	Ru(1)-C(15)-C(16)-C(17)	-62.14(14)
C(11)-N(5)-C(10)-N(4)	-55.1(2)	C(14)-C(15)-C(16)-Ru(1)	62.13(15)
C(8)-N(5)-C(10)-N(4)	66.9(2)	C(17)-Ru(1)-C(16)-C(15)	-116.87(19)

C(13)-Ru(1)-C(16)-C(15)	-79.65(15)	Ru(1)-C(16)-C(17)-C(13)	-62.44(14)
C(14)-Ru(1)-C(16)-C(15)	-36.69(14)	C(15)-C(16)-C(17)-Ru(1)	62.80(14)
P(1)-Ru(1)-C(16)-C(15)	168.49(12)	C(16)-Ru(1)-C(17)-C(13)	117.61(18)
P(2)-Ru(1)-C(16)-C(15)	-57.4(2)	C(14)-Ru(1)-C(17)-C(13)	38.51(14)
Sn(1)-Ru(1)-C(16)-C(15)	71.21(13)	C(15)-Ru(1)-C(17)-C(13)	80.13(14)
C(13)-Ru(1)-C(16)-C(17)	37.22(13)	P(1)-Ru(1)-C(17)-C(13)	-132.54(12)
C(14)-Ru(1)-C(16)-C(17)	80.17(15)	P(2)-Ru(1)-C(17)-C(13)	-37.22(15)
C(15)-Ru(1)-C(16)-C(17)	116.87(19)	Sn(1)-Ru(1)-C(17)-C(13)	129.88(12)
P(1)-Ru(1)-C(16)-C(17)	-74.64(13)	C(13)-Ru(1)-C(17)-C(16)	-117.61(18)
P(2)-Ru(1)-C(16)-C(17)	59.4(2)	C(14)-Ru(1)-C(17)-C(16)	-79.10(14)
Sn(1)-Ru(1)-C(16)-C(17)	-171.93(11)	C(15)-Ru(1)-C(17)-C(16)	-37.48(13)
C(14)-C(13)-C(17)-C(16)	-0.6(2)	P(1)-Ru(1)-C(17)-C(16)	109.85(12)
Ru(1)-C(13)-C(17)-C(16)	62.83(14)	P(2)-Ru(1)-C(17)-C(16)	-154.84(10)
C(14)-C(13)-C(17)-Ru(1)	-63.39(14)	Sn(1)-Ru(1)-C(17)-C(16)	12.27(17)
C(15)-C(16)-C(17)-C(13)	0.4(2)		

Symmetry transformations used to generate equivalent atoms:

Table A11: Bond lengths [\AA] and angles [$^\circ$] for IndRu(PTA)(PPh₃)H.

Ru(1)-C(3)	2.217(3)	C(3)-H(3A)	1.0000
Ru(1)-C(2)	2.233(3)	C(4)-C(5)	1.444(5)
Ru(1)-C(4)	2.254(3)	C(4)-H(4A)	1.0000
Ru(1)-P(2)	2.2539(8)	C(5)-C(6)	1.421(5)
Ru(1)-P(1)	2.2564(8)	C(6)-C(7)	1.360(6)
Ru(1)-C(1)	2.350(3)	C(6)-H(6A)	0.9500
Ru(1)-C(5)	2.362(3)	C(7)-C(8)	1.424(6)
Ru(1)-H(1)	1.52(4)	C(7)-H(7A)	0.9500
P(1)-C(11)	1.856(3)	C(8)-C(9)	1.370(6)
P(1)-C(10)	1.861(3)	C(8)-H(8A)	0.9500
P(1)-C(12)	1.864(3)	C(9)-H(9A)	0.9500
P(2)-C(22)	1.781(3)	C(10)-H(10A)	0.9900
P(2)-C(16)	1.833(3)	C(10)-H(10B)	0.9900
P(2)-C(28)	1.8539(18)	C(11)-H(11A)	0.9900
P(2)-C(22A)	1.915(3)	C(11)-H(11B)	0.9900
N(1)-C(13)	1.459(4)	C(12)-H(12A)	0.9900
N(1)-C(15)	1.469(4)	C(12)-H(12B)	0.9900
N(1)-C(10)	1.482(4)	C(13)-H(13A)	0.9900
N(2)-C(14)	1.464(4)	C(13)-H(13B)	0.9900
N(2)-C(11)	1.471(4)	C(14)-H(14A)	0.9900
N(2)-C(13)	1.471(4)	C(14)-H(14B)	0.9900
N(3)-C(15)	1.462(4)	C(15)-H(15A)	0.9900
N(3)-C(14)	1.476(4)	C(15)-H(15B)	0.9900
N(3)-C(12)	1.485(4)	C(16)-C(17)	1.393(4)
C(1)-C(9)	1.405(5)	C(16)-C(21)	1.402(4)
C(1)-C(5)	1.444(5)	C(17)-C(18)	1.393(4)
C(1)-C(2)	1.463(5)	C(17)-H(17A)	0.9500
C(2)-C(3)	1.415(5)	C(18)-C(19)	1.389(5)
C(2)-H(2A)	1.0000	C(18)-H(18A)	0.9500
C(3)-C(4)	1.423(5)	C(19)-C(20)	1.381(5)

C(19)-H(19A)	0.9500	C(2)-Ru(1)-C(5)	61.01(12)
C(20)-C(21)	1.395(5)	C(4)-Ru(1)-C(5)	36.35(13)
C(20)-H(20A)	0.9500	P(2)-Ru(1)-C(5)	101.30(9)
C(21)-H(21A)	0.9500	P(1)-Ru(1)-C(5)	128.41(9)
C(22)-C(23)	1.3900	C(1)-Ru(1)-C(5)	35.70(11)
C(22)-C(27)	1.3900	C(3)-Ru(1)-H(1)	92.2(15)
C(23)-C(24)	1.3900	C(2)-Ru(1)-H(1)	109.9(15)
C(23)-H(23A)	0.9500	C(4)-Ru(1)-H(1)	110.1(15)
C(24)-C(25)	1.3900	P(2)-Ru(1)-H(1)	82.7(15)
C(24)-H(24A)	0.9500	P(1)-Ru(1)-H(1)	83.1(15)
C(25)-C(26)	1.3900	C(1)-Ru(1)-H(1)	147.0(15)
C(25)-H(25A)	0.9500	C(5)-Ru(1)-H(1)	146.4(15)
C(26)-C(27)	1.3900	C(11)-P(1)-C(10)	96.68(15)
C(26)-H(26A)	0.9500	C(11)-P(1)-C(12)	96.51(14)
C(27)-H(27A)	0.9500	C(10)-P(1)-C(12)	96.29(14)
C(22A)-C(23A)	1.3900	C(11)-P(1)-Ru(1)	113.00(10)
C(22A)-C(27A)	1.3900	C(10)-P(1)-Ru(1)	123.69(10)
C(23A)-C(24A)	1.3900	C(12)-P(1)-Ru(1)	124.44(11)
C(23A)-H(23B)	0.9500	C(22)-P(2)-C(16)	106.80(19)
C(24A)-C(25A)	1.3900	C(22)-P(2)-C(28)	97.7(2)
C(24A)-H(24B)	0.9500	C(16)-P(2)-C(28)	100.41(13)
C(25A)-C(26A)	1.3900	C(22)-P(2)-C(22A)	10.2(2)
C(25A)-H(25B)	0.9500	C(16)-P(2)-C(22A)	97.25(18)
C(26A)-C(27A)	1.3900	C(28)-P(2)-C(22A)	103.2(2)
C(26A)-H(26B)	0.9500	C(22)-P(2)-Ru(1)	112.7(2)
C(27A)-H(27B)	0.9500	C(16)-P(2)-Ru(1)	121.90(10)
C(28)-C(29)	1.3900	C(28)-P(2)-Ru(1)	114.10(8)
C(28)-C(33)	1.3900	C(22A)-P(2)-Ru(1)	116.8(2)
C(29)-C(30)	1.3900	C(13)-N(1)-C(15)	108.4(2)
C(29)-H(29A)	0.9500	C(13)-N(1)-C(10)	111.0(3)
C(30)-C(31)	1.3900	C(15)-N(1)-C(10)	110.5(2)
C(30)-H(30A)	0.9500	C(14)-N(2)-C(11)	110.4(2)
C(31)-C(32)	1.3900	C(14)-N(2)-C(13)	108.3(3)
C(31)-H(31A)	0.9500	C(11)-N(2)-C(13)	110.2(2)
C(32)-C(33)	1.3900	C(15)-N(3)-C(14)	107.8(3)
C(32)-H(32A)	0.9500	C(15)-N(3)-C(12)	111.0(3)
C(33)-H(33A)	0.9500	C(14)-N(3)-C(12)	111.4(3)
		C(9)-C(1)-C(5)	119.6(3)
C(3)-Ru(1)-C(2)	37.08(13)	C(9)-C(1)-C(2)	133.5(3)
C(3)-Ru(1)-C(4)	37.10(12)	C(5)-C(1)-C(2)	106.9(3)
C(2)-Ru(1)-C(4)	62.18(12)	C(9)-C(1)-Ru(1)	126.2(3)
C(3)-Ru(1)-P(2)	133.32(9)	C(5)-C(1)-Ru(1)	72.63(18)
C(2)-Ru(1)-P(2)	161.98(9)	C(2)-C(1)-Ru(1)	67.12(17)
C(4)-Ru(1)-P(2)	101.94(9)	C(3)-C(2)-C(1)	107.7(3)
C(3)-Ru(1)-P(1)	127.98(9)	C(3)-C(2)-Ru(1)	70.82(19)
C(2)-Ru(1)-P(1)	96.67(9)	C(1)-C(2)-Ru(1)	75.77(18)
C(4)-Ru(1)-P(1)	157.56(9)	C(3)-C(2)-H(2A)	125.9
P(2)-Ru(1)-P(1)	97.59(3)	C(1)-C(2)-H(2A)	125.9
C(3)-Ru(1)-C(1)	61.11(14)	Ru(1)-C(2)-H(2A)	125.9
C(2)-Ru(1)-C(1)	37.11(13)	C(2)-C(3)-C(4)	109.5(3)
C(4)-Ru(1)-C(1)	60.98(13)	C(2)-C(3)-Ru(1)	72.10(19)
P(2)-Ru(1)-C(1)	129.28(9)	C(4)-C(3)-Ru(1)	72.87(19)
P(1)-Ru(1)-C(1)	97.91(9)	C(2)-C(3)-H(3A)	125.2
C(3)-Ru(1)-C(5)	60.61(13)	C(4)-C(3)-H(3A)	125.2

Ru(1)-C(3)-H(3A)	125.2	H(14A)-C(14)-H(14B)	107.6
C(3)-C(4)-C(5)	107.7(3)	N(3)-C(15)-N(1)	114.9(3)
C(3)-C(4)-Ru(1)	70.03(18)	N(3)-C(15)-H(15A)	108.5
C(5)-C(4)-Ru(1)	75.92(19)	N(1)-C(15)-H(15A)	108.5
C(3)-C(4)-H(4A)	125.9	N(3)-C(15)-H(15B)	108.5
C(5)-C(4)-H(4A)	125.9	N(1)-C(15)-H(15B)	108.5
Ru(1)-C(4)-H(4A)	125.9	H(15A)-C(15)-H(15B)	107.5
C(6)-C(5)-C(4)	132.5(3)	C(17)-C(16)-C(21)	118.8(3)
C(6)-C(5)-C(1)	119.4(3)	C(17)-C(16)-P(2)	119.7(2)
C(4)-C(5)-C(1)	108.1(3)	C(21)-C(16)-P(2)	121.3(2)
C(6)-C(5)-Ru(1)	128.1(3)	C(16)-C(17)-C(18)	120.6(3)
C(4)-C(5)-Ru(1)	67.73(17)	C(16)-C(17)-H(17A)	119.7
C(1)-C(5)-Ru(1)	71.67(17)	C(18)-C(17)-H(17A)	119.7
C(7)-C(6)-C(5)	119.3(4)	C(19)-C(18)-C(17)	120.3(3)
C(7)-C(6)-H(6A)	120.4	C(19)-C(18)-H(18A)	119.9
C(5)-C(6)-H(6A)	120.4	C(17)-C(18)-H(18A)	119.9
C(6)-C(7)-C(8)	121.2(4)	C(20)-C(19)-C(18)	119.4(3)
C(6)-C(7)-H(7A)	119.4	C(20)-C(19)-H(19A)	120.3
C(8)-C(7)-H(7A)	119.4	C(18)-C(19)-H(19A)	120.3
C(9)-C(8)-C(7)	121.1(4)	C(19)-C(20)-C(21)	120.9(3)
C(9)-C(8)-H(8A)	119.5	C(19)-C(20)-H(20A)	119.6
C(7)-C(8)-H(8A)	119.5	C(21)-C(20)-H(20A)	119.6
C(8)-C(9)-C(1)	119.4(4)	C(20)-C(21)-C(16)	119.9(3)
C(8)-C(9)-H(9A)	120.3	C(20)-C(21)-H(21A)	120.0
C(1)-C(9)-H(9A)	120.3	C(16)-C(21)-H(21A)	120.0
N(1)-C(10)-P(1)	113.5(2)	C(23)-C(22)-C(27)	120.0
N(1)-C(10)-H(10A)	108.9	C(23)-C(22)-P(2)	114.9(3)
P(1)-C(10)-H(10A)	108.9	C(27)-C(22)-P(2)	125.1(3)
N(1)-C(10)-H(10B)	108.9	C(24)-C(23)-C(22)	120.0
P(1)-C(10)-H(10B)	108.9	C(24)-C(23)-H(23A)	120.0
H(10A)-C(10)-H(10B)	107.7	C(22)-C(23)-H(23A)	120.0
N(2)-C(11)-P(1)	114.7(2)	C(23)-C(24)-C(25)	120.0
N(2)-C(11)-H(11A)	108.6	C(23)-C(24)-H(24A)	120.0
P(1)-C(11)-H(11A)	108.6	C(25)-C(24)-H(24A)	120.0
N(2)-C(11)-H(11B)	108.6	C(26)-C(25)-C(24)	120.0
P(1)-C(11)-H(11B)	108.6	C(26)-C(25)-H(25A)	120.0
H(11A)-C(11)-H(11B)	107.6	C(24)-C(25)-H(25A)	120.0
N(3)-C(12)-P(1)	113.0(2)	C(25)-C(26)-C(27)	120.0
N(3)-C(12)-H(12A)	109.0	C(25)-C(26)-H(26A)	120.0
P(1)-C(12)-H(12A)	109.0	C(27)-C(26)-H(26A)	120.0
N(3)-C(12)-H(12B)	109.0	C(26)-C(27)-C(22)	120.0
P(1)-C(12)-H(12B)	109.0	C(26)-C(27)-H(27A)	120.0
H(12A)-C(12)-H(12B)	107.8	C(22)-C(27)-H(27A)	120.0
N(1)-C(13)-N(2)	115.1(3)	C(23A)-C(22A)-C(27A)	120.0
N(1)-C(13)-H(13A)	108.5	C(23A)-C(22A)-P(2)	115.6(3)
N(2)-C(13)-H(13A)	108.5	C(27A)-C(22A)-P(2)	124.4(3)
N(1)-C(13)-H(13B)	108.5	C(22A)-C(23A)-C(24A)	120.0
N(2)-C(13)-H(13B)	108.5	C(22A)-C(23A)-H(23B)	120.0
H(13A)-C(13)-H(13B)	107.5	C(24A)-C(23A)-H(23B)	120.0
N(2)-C(14)-N(3)	114.7(2)	C(25A)-C(24A)-C(23A)	120.0
N(2)-C(14)-H(14A)	108.6	C(25A)-C(24A)-H(24B)	120.0
N(3)-C(14)-H(14A)	108.6	C(23A)-C(24A)-H(24B)	120.0
N(2)-C(14)-H(14B)	108.6	C(26A)-C(25A)-C(24A)	120.0
N(3)-C(14)-H(14B)	108.6	C(26A)-C(25A)-H(25B)	120.0

C(24A)-C(25A)-H(25B)	120.0	C(29)-C(30)-C(31)	120.0
C(25A)-C(26A)-C(27A)	120.0	C(29)-C(30)-H(30A)	120.0
C(25A)-C(26A)-H(26B)	120.0	C(31)-C(30)-H(30A)	120.0
C(27A)-C(26A)-H(26B)	120.0	C(30)-C(31)-C(32)	120.0
C(26A)-C(27A)-C(22A)	120.0	C(30)-C(31)-H(31A)	120.0
C(26A)-C(27A)-H(27B)	120.0	C(32)-C(31)-H(31A)	120.0
C(22A)-C(27A)-H(27B)	120.0	C(31)-C(32)-C(33)	120.0
C(29)-C(28)-C(33)	120.0	C(31)-C(32)-H(32A)	120.0
C(29)-C(28)-P(2)	117.38(14)	C(33)-C(32)-H(32A)	120.0
C(33)-C(28)-P(2)	122.39(14)	C(32)-C(33)-C(28)	120.0
C(30)-C(29)-C(28)	120.0	C(32)-C(33)-H(33A)	120.0
C(30)-C(29)-H(29A)	120.0	C(28)-C(33)-H(33A)	120.0
C(28)-C(29)-H(29A)	120.0		

Symmetry transformations used to generate equivalent atoms:

Table A12: Torsion angles [°] for IndRu(PTA)(PPh₃)H.

C(3)-Ru(1)-P(1)-C(11)	16.31(17)	C(4)-Ru(1)-P(2)-C(28)	-9.15(13)
C(2)-Ru(1)-P(1)-C(11)	-5.59(14)	P(1)-Ru(1)-P(2)-C(28)	159.73(10)
C(4)-Ru(1)-P(1)-C(11)	-24.2(3)	C(1)-Ru(1)-P(2)-C(28)	52.98(16)
P(2)-Ru(1)-P(1)-C(11)	-174.55(11)	C(5)-Ru(1)-P(2)-C(28)	27.99(14)
C(1)-Ru(1)-P(1)-C(11)	-43.00(14)	C(3)-Ru(1)-P(2)-C(22A)	-152.5(2)
C(5)-Ru(1)-P(1)-C(11)	-63.58(16)	C(2)-Ru(1)-P(2)-C(22A)	-102.8(4)
C(3)-Ru(1)-P(1)-C(10)	132.09(17)	C(4)-Ru(1)-P(2)-C(22A)	-129.6(2)
C(2)-Ru(1)-P(1)-C(10)	110.19(16)	P(1)-Ru(1)-P(2)-C(22A)	39.26(19)
C(4)-Ru(1)-P(1)-C(10)	91.6(3)	C(1)-Ru(1)-P(2)-C(22A)	-67.5(2)
P(2)-Ru(1)-P(1)-C(10)	-58.77(13)	C(5)-Ru(1)-P(2)-C(22A)	-92.5(2)
C(1)-Ru(1)-P(1)-C(10)	72.78(16)	C(3)-Ru(1)-C(1)-C(9)	-166.7(3)
C(5)-Ru(1)-P(1)-C(10)	52.20(17)	C(2)-Ru(1)-C(1)-C(9)	-128.1(4)
C(3)-Ru(1)-P(1)-C(12)	-99.82(18)	C(4)-Ru(1)-C(1)-C(9)	150.6(3)
C(2)-Ru(1)-P(1)-C(12)	-121.73(16)	P(2)-Ru(1)-C(1)-C(9)	69.2(3)
C(4)-Ru(1)-P(1)-C(12)	-140.3(3)	P(1)-Ru(1)-C(1)-C(9)	-37.5(3)
P(2)-Ru(1)-P(1)-C(12)	69.31(14)	C(5)-Ru(1)-C(1)-C(9)	114.4(4)
C(1)-Ru(1)-P(1)-C(12)	-159.14(16)	C(3)-Ru(1)-C(1)-C(5)	78.9(2)
C(5)-Ru(1)-P(1)-C(12)	-179.71(17)	C(2)-Ru(1)-C(1)-C(5)	117.6(3)
C(3)-Ru(1)-P(2)-C(22)	-142.3(2)	C(4)-Ru(1)-C(1)-C(5)	36.3(2)
C(2)-Ru(1)-P(2)-C(22)	-92.5(4)	P(2)-Ru(1)-C(1)-C(5)	-45.2(3)
C(4)-Ru(1)-P(2)-C(22)	-119.4(2)	P(1)-Ru(1)-C(1)-C(5)	-151.8(2)
P(1)-Ru(1)-P(2)-C(22)	49.5(2)	C(3)-Ru(1)-C(1)-C(2)	-38.7(2)
C(1)-Ru(1)-P(2)-C(22)	-57.2(2)	C(4)-Ru(1)-C(1)-C(2)	-81.3(2)
C(5)-Ru(1)-P(2)-C(22)	-82.2(2)	P(2)-Ru(1)-C(1)-C(2)	-162.78(16)
C(3)-Ru(1)-P(2)-C(16)	88.72(18)	P(1)-Ru(1)-C(1)-C(2)	90.61(19)
C(2)-Ru(1)-P(2)-C(16)	138.5(3)	C(5)-Ru(1)-C(1)-C(2)	-117.6(3)
C(4)-Ru(1)-P(2)-C(16)	111.62(15)	C(9)-C(1)-C(2)-C(3)	-177.0(4)
P(1)-Ru(1)-P(2)-C(16)	-79.50(12)	C(5)-C(1)-C(2)-C(3)	1.9(4)
C(1)-Ru(1)-P(2)-C(16)	173.75(17)	Ru(1)-C(1)-C(2)-C(3)	64.1(2)
C(5)-Ru(1)-P(2)-C(16)	148.76(15)	C(9)-C(1)-C(2)-Ru(1)	118.9(4)
C(3)-Ru(1)-P(2)-C(28)	-32.05(16)	C(5)-C(1)-C(2)-Ru(1)	-62.2(2)
C(2)-Ru(1)-P(2)-C(28)	17.7(3)	C(4)-Ru(1)-C(2)-C(3)	-37.1(2)

P(2)-Ru(1)-C(2)-C(3)	-67.1(4)	C(3)-Ru(1)-C(5)-C(4)	38.8(2)
P(1)-Ru(1)-C(2)-C(3)	150.81(18)	C(2)-Ru(1)-C(5)-C(4)	81.5(2)
C(1)-Ru(1)-C(2)-C(3)	-114.9(3)	P(2)-Ru(1)-C(5)-C(4)	-94.83(19)
C(5)-Ru(1)-C(2)-C(3)	-78.6(2)	P(1)-Ru(1)-C(5)-C(4)	155.88(16)
C(3)-Ru(1)-C(2)-C(1)	114.9(3)	C(1)-Ru(1)-C(5)-C(4)	119.2(3)
C(4)-Ru(1)-C(2)-C(1)	77.8(2)	C(3)-Ru(1)-C(5)-C(1)	-80.4(2)
P(2)-Ru(1)-C(2)-C(1)	47.8(4)	C(2)-Ru(1)-C(5)-C(1)	-37.7(2)
P(1)-Ru(1)-C(2)-C(1)	-94.31(19)	C(4)-Ru(1)-C(5)-C(1)	-119.2(3)
C(5)-Ru(1)-C(2)-C(1)	36.3(2)	P(2)-Ru(1)-C(5)-C(1)	145.9(2)
C(1)-C(2)-C(3)-C(4)	-3.7(4)	P(1)-Ru(1)-C(5)-C(1)	36.6(3)
Ru(1)-C(2)-C(3)-C(4)	63.7(2)	C(4)-C(5)-C(6)-C(7)	-176.1(4)
C(1)-C(2)-C(3)-Ru(1)	-67.4(2)	C(1)-C(5)-C(6)-C(7)	1.0(5)
C(4)-Ru(1)-C(3)-C(2)	117.8(3)	Ru(1)-C(5)-C(6)-C(7)	90.1(4)
P(2)-Ru(1)-C(3)-C(2)	156.96(15)	C(5)-C(6)-C(7)-C(8)	-3.2(6)
P(1)-Ru(1)-C(3)-C(2)	-37.9(2)	C(6)-C(7)-C(8)-C(9)	2.6(7)
C(1)-Ru(1)-C(3)-C(2)	38.70(19)	C(7)-C(8)-C(9)-C(1)	0.3(6)
C(5)-Ru(1)-C(3)-C(2)	79.8(2)	C(5)-C(1)-C(9)-C(8)	-2.4(5)
C(2)-Ru(1)-C(3)-C(4)	-117.8(3)	C(2)-C(1)-C(9)-C(8)	176.4(4)
P(2)-Ru(1)-C(3)-C(4)	39.1(3)	Ru(1)-C(1)-C(9)-C(8)	-91.8(4)
P(1)-Ru(1)-C(3)-C(4)	-155.73(17)	C(13)-N(1)-C(10)-P(1)	59.6(3)
C(1)-Ru(1)-C(3)-C(4)	-79.1(2)	C(15)-N(1)-C(10)-P(1)	-60.7(3)
C(5)-Ru(1)-C(3)-C(4)	-38.0(2)	C(11)-P(1)-C(10)-N(1)	-47.5(2)
C(2)-C(3)-C(4)-C(5)	4.0(4)	C(12)-P(1)-C(10)-N(1)	49.9(2)
Ru(1)-C(3)-C(4)-C(5)	67.2(2)	Ru(1)-P(1)-C(10)-N(1)	-170.90(16)
C(2)-C(3)-C(4)-Ru(1)	-63.2(2)	C(14)-N(2)-C(11)-P(1)	60.3(3)
C(2)-Ru(1)-C(4)-C(3)	37.1(2)	C(13)-N(2)-C(11)-P(1)	-59.3(3)
P(2)-Ru(1)-C(4)-C(3)	-152.00(19)	C(10)-P(1)-C(11)-N(2)	48.1(2)
P(1)-Ru(1)-C(4)-C(3)	58.1(4)	C(12)-P(1)-C(11)-N(2)	-49.1(2)
C(1)-Ru(1)-C(4)-C(3)	79.5(2)	Ru(1)-P(1)-C(11)-N(2)	179.10(18)
C(5)-Ru(1)-C(4)-C(3)	115.1(3)	C(15)-N(3)-C(12)-P(1)	60.6(3)
C(3)-Ru(1)-C(4)-C(5)	-115.1(3)	C(14)-N(3)-C(12)-P(1)	-59.6(3)
C(2)-Ru(1)-C(4)-C(5)	-78.0(2)	C(11)-P(1)-C(12)-N(3)	48.0(3)
P(2)-Ru(1)-C(4)-C(5)	92.90(18)	C(10)-P(1)-C(12)-N(3)	-49.5(3)
P(1)-Ru(1)-C(4)-C(5)	-57.0(3)	Ru(1)-P(1)-C(12)-N(3)	171.72(17)
C(1)-Ru(1)-C(4)-C(5)	-35.61(19)	C(15)-N(1)-C(13)-N(2)	54.1(3)
C(3)-C(4)-C(5)-C(6)	174.7(4)	C(10)-N(1)-C(13)-N(2)	-67.5(3)
Ru(1)-C(4)-C(5)-C(6)	-122.0(4)	C(14)-N(2)-C(13)-N(1)	-54.0(3)
C(3)-C(4)-C(5)-C(1)	-2.7(4)	C(11)-N(2)-C(13)-N(1)	66.8(3)
Ru(1)-C(4)-C(5)-C(1)	60.6(2)	C(11)-N(2)-C(14)-N(3)	-66.4(3)
C(3)-C(4)-C(5)-Ru(1)	-63.3(2)	C(13)-N(2)-C(14)-N(3)	54.4(3)
C(9)-C(1)-C(5)-C(6)	1.8(5)	C(15)-N(3)-C(14)-N(2)	-55.1(3)
C(2)-C(1)-C(5)-C(6)	-177.3(3)	C(12)-N(3)-C(14)-N(2)	67.0(3)
Ru(1)-C(1)-C(5)-C(6)	124.0(3)	C(14)-N(3)-C(15)-N(1)	55.2(3)
C(9)-C(1)-C(5)-C(4)	179.6(3)	C(12)-N(3)-C(15)-N(1)	-67.1(3)
C(2)-C(1)-C(5)-C(4)	0.5(4)	C(13)-N(1)-C(15)-N(3)	-55.0(3)
Ru(1)-C(1)-C(5)-C(4)	-58.1(2)	C(10)-N(1)-C(15)-N(3)	66.9(3)
C(9)-C(1)-C(5)-Ru(1)	-122.3(3)	C(22)-P(2)-C(16)-C(17)	-106.9(4)
C(2)-C(1)-C(5)-Ru(1)	58.6(2)	C(28)-P(2)-C(16)-C(17)	151.7(2)
C(3)-Ru(1)-C(5)-C(6)	166.2(4)	C(22A)-P(2)-C(16)-C(17)	-103.3(3)
C(2)-Ru(1)-C(5)-C(6)	-151.1(4)	Ru(1)-P(2)-C(16)-C(17)	24.6(3)
C(4)-Ru(1)-C(5)-C(6)	127.4(4)	C(22)-P(2)-C(16)-C(21)	68.7(4)
P(2)-Ru(1)-C(5)-C(6)	32.6(4)	C(28)-P(2)-C(16)-C(21)	-32.6(3)
P(1)-Ru(1)-C(5)-C(6)	-76.7(3)	C(22A)-P(2)-C(16)-C(21)	72.3(4)
C(1)-Ru(1)-C(5)-C(6)	-113.4(4)	Ru(1)-P(2)-C(16)-C(21)	-159.7(2)

C(21)-C(16)-C(17)-C(18)	-0.6(5)	C(16)-P(2)-C(22A)-C(27A)	-3.0(3)
P(2)-C(16)-C(17)-C(18)	175.1(3)	C(28)-P(2)-C(22A)-C(27A)	99.5(3)
C(16)-C(17)-C(18)-C(19)	1.4(5)	Ru(1)-P(2)-C(22A)-C(27A)	-134.4(3)
C(17)-C(18)-C(19)-C(20)	-1.7(6)	C(27A)-C(22A)-C(23A)-C(24A)	0.0
C(18)-C(19)-C(20)-C(21)	1.2(6)	P(2)-C(22A)-C(23A)-C(24A)	178.6(5)
C(19)-C(20)-C(21)-C(16)	-0.4(6)	C(22A)-C(23A)-C(24A)-C(25A)	0.0
C(17)-C(16)-C(21)-C(20)	0.1(5)	C(23A)-C(24A)-C(25A)-C(26A)	0.0
P(2)-C(16)-C(21)-C(20)	-175.6(3)	C(24A)-C(25A)-C(26A)-C(27A)	0.0
C(16)-P(2)-C(22)-C(23)	178.7(3)	C(25A)-C(26A)-C(27A)-C(22A)	0.0
C(28)-P(2)-C(22)-C(23)	-78.0(3)	C(23A)-C(22A)-C(27A)-C(26A)	0.0
C(22A)-P(2)-C(22)-C(23)	158(3)	P(2)-C(22A)-C(27A)-C(26A)	-178.5(5)
Ru(1)-P(2)-C(22)-C(23)	42.2(4)	C(22)-P(2)-C(28)-C(29)	-177.4(2)
C(16)-P(2)-C(22)-C(27)	-2.1(4)	C(16)-P(2)-C(28)-C(29)	-68.71(17)
C(28)-P(2)-C(22)-C(27)	101.2(3)	C(22A)-P(2)-C(28)-C(29)	-168.8(2)
C(22A)-P(2)-C(22)-C(27)	-23(2)	Ru(1)-P(2)-C(28)-C(29)	63.42(16)
Ru(1)-P(2)-C(22)-C(27)	-138.6(3)	C(22)-P(2)-C(28)-C(33)	8.2(2)
C(27)-C(22)-C(23)-C(24)	0.0	C(16)-P(2)-C(28)-C(33)	116.92(18)
P(2)-C(22)-C(23)-C(24)	179.3(5)	C(22A)-P(2)-C(28)-C(33)	16.8(2)
C(22)-C(23)-C(24)-C(25)	0.0	Ru(1)-P(2)-C(28)-C(33)	-110.96(15)
C(23)-C(24)-C(25)-C(26)	0.0	C(33)-C(28)-C(29)-C(30)	0.0
C(24)-C(25)-C(26)-C(27)	0.0	P(2)-C(28)-C(29)-C(30)	-174.5(2)
C(25)-C(26)-C(27)-C(22)	0.0	C(28)-C(29)-C(30)-C(31)	0.0
C(23)-C(22)-C(27)-C(26)	0.0	C(29)-C(30)-C(31)-C(32)	0.0
P(2)-C(22)-C(27)-C(26)	-179.2(5)	C(30)-C(31)-C(32)-C(33)	0.0
C(22)-P(2)-C(22A)-C(23A)	-21(2)	C(31)-C(32)-C(33)-C(28)	0.0
C(16)-P(2)-C(22A)-C(23A)	178.4(3)	C(29)-C(28)-C(33)-C(32)	0.0
C(28)-P(2)-C(22A)-C(23A)	-79.1(3)	P(2)-C(28)-C(33)-C(32)	
Ru(1)-P(2)-C(22A)-C(23A)	47.0(4)		174.2(2)
C(22)-P(2)-C(22A)-C(27A)	157(3)		

Symmetry transformations used to generate equivalent atoms:

Table A13: Bond lengths [\AA] and angles [$^\circ$] for $[\text{IndRu}(\text{PTA})_2(\text{PPh}_3)]\text{SnCl}_3$.

Ru(1)-C(4)	2.213(7)	P(2)-C(18)	1.837(6)
Ru(1)-C(3)	2.226(7)	P(2)-C(17)	1.849(7)
Ru(1)-C(2)	2.247(7)	P(2)-C(16)	1.856(7)
Ru(1)-P(2)	2.2576(18)	P(3)-C(28)	1.845(7)
Ru(1)-P(1)	2.3076(19)	P(3)-C(22)	1.848(7)
Ru(1)-P(3)	2.3456(19)	P(3)-C(34)	1.860(7)
Ru(1)-C(5)	2.367(7)	N(1)-C(15)	1.462(9)
Ru(1)-C(1)	2.384(6)	N(1)-C(13)	1.473(9)
Sn(1)-Cl(3)	2.5016(18)	N(1)-C(10)	1.473(8)
Sn(1)-Cl(2)	2.5164(18)	N(2)-C(14)	1.463(9)
Sn(1)-Cl(1)	2.5716(19)	N(2)-C(13)	1.473(9)
Cl(1S)-C(1S)	1.753(7)	N(2)-C(11)	1.478(8)
Cl(2S)-C(1S)	1.764(7)	N(3)-C(12)	1.454(8)
P(1)-C(10)	1.857(6)	N(3)-C(14)	1.478(9)
P(1)-C(12)	1.861(7)	N(3)-C(15)	1.474(9)
P(1)-C(11)	1.877(7)	N(4)-C(17)	1.466(9)

N(4)-C(19)	1.472(8)	C(23)-H(23A)	0.9500
N(4)-C(20)	1.491(8)	C(24)-C(25)	1.388(10)
N(5)-C(19)	1.460(8)	C(24)-H(24A)	0.9500
N(5)-C(21)	1.468(8)	C(25)-C(26)	1.356(10)
N(5)-C(16)	1.467(8)	C(25)-H(25A)	0.9500
N(6)-C(20)	1.458(9)	C(26)-C(27)	1.392(10)
N(6)-C(18)	1.474(8)	C(26)-H(26A)	0.9500
N(6)-C(21)	1.484(8)	C(27)-H(27A)	0.9500
C(1)-C(2)	1.422(9)	C(28)-C(29)	1.378(9)
C(1)-C(9)	1.427(9)	C(28)-C(33)	1.403(9)
C(1)-C(5)	1.445(10)	C(29)-C(30)	1.384(9)
C(1S)-H(1SA)	0.9900	C(29)-H(29A)	0.9500
C(1S)-H(1SB)	0.9900	C(30)-C(31)	1.385(10)
C(2)-C(3)	1.439(10)	C(30)-H(30A)	0.9500
C(2)-H(2A)	1.0000	C(31)-C(32)	1.399(10)
C(3)-C(4)	1.412(10)	C(31)-H(31A)	0.9500
C(3)-H(3A)	1.0000	C(32)-C(33)	1.376(9)
C(4)-C(5)	1.457(10)	C(32)-H(32A)	0.9500
C(4)-H(4A)	1.0000	C(33)-H(33A)	0.9500
C(5)-C(6)	1.414(10)	C(34)-C(35)	1.374(9)
C(6)-C(7)	1.367(10)	C(34)-C(39)	1.399(10)
C(6)-H(6A)	0.9500	C(35)-C(36)	1.399(10)
C(7)-C(8)	1.421(10)	C(35)-H(35A)	0.9500
C(7)-H(7A)	0.9500	C(36)-C(37)	1.362(11)
C(8)-C(9)	1.332(10)	C(36)-H(36A)	0.9500
C(8)-H(8A)	0.9500	C(37)-C(38)	1.382(10)
C(9)-H(9A)	0.9500	C(37)-H(37A)	0.9500
C(10)-H(10A)	0.9900	C(38)-C(39)	1.396(9)
C(10)-H(10B)	0.9900	C(38)-H(38A)	0.9500
C(11)-H(11A)	0.9900	C(39)-H(39B)	0.9500
C(11)-H(11B)	0.9900		
C(12)-H(12A)	0.9900	C(4)-Ru(1)-C(3)	37.1(3)
C(12)-H(12B)	0.9900	C(4)-Ru(1)-C(2)	62.5(3)
C(13)-H(13A)	0.9900	C(3)-Ru(1)-C(2)	37.5(3)
C(13)-H(13B)	0.9900	C(4)-Ru(1)-P(2)	108.11(19)
C(14)-H(14A)	0.9900	C(3)-Ru(1)-P(2)	86.15(19)
C(14)-H(14B)	0.9900	C(2)-Ru(1)-P(2)	101.70(19)
C(15)-H(15A)	0.9900	C(4)-Ru(1)-P(1)	92.75(19)
C(15)-H(15B)	0.9900	C(3)-Ru(1)-P(1)	124.3(2)
C(16)-H(16A)	0.9900	C(2)-Ru(1)-P(1)	154.09(19)
C(16)-H(16B)	0.9900	P(2)-Ru(1)-P(1)	92.99(7)
C(17)-H(17A)	0.9900	C(4)-Ru(1)-P(3)	153.66(18)
C(17)-H(17B)	0.9900	C(3)-Ru(1)-P(3)	138.1(2)
C(18)-H(18A)	0.9900	C(2)-Ru(1)-P(3)	102.14(19)
C(18)-H(18B)	0.9900	P(2)-Ru(1)-P(3)	95.56(7)
C(19)-H(19A)	0.9900	P(1)-Ru(1)-P(3)	97.47(7)
C(19)-H(19B)	0.9900	C(4)-Ru(1)-C(5)	36.9(2)
C(20)-H(20A)	0.9900	C(3)-Ru(1)-C(5)	60.5(3)
C(20)-H(20B)	0.9900	C(2)-Ru(1)-C(5)	60.3(3)
C(21)-H(21A)	0.9900	P(2)-Ru(1)-C(5)	144.2(2)
C(21)-H(21B)	0.9900	P(1)-Ru(1)-C(5)	95.61(19)
C(22)-C(27)	1.386(9)	P(3)-Ru(1)-C(5)	117.55(18)
C(22)-C(23)	1.401(9)	C(4)-Ru(1)-C(1)	61.0(2)
C(23)-C(24)	1.388(10)	C(3)-Ru(1)-C(1)	60.2(2)

C(2)-Ru(1)-C(1)	35.6(2)	Cl(2S)-C(1S)-H(1SB)	109.3
P(2)-Ru(1)-C(1)	137.29(17)	H(1SA)-C(1S)-H(1SB)	108.0
P(1)-Ru(1)-C(1)	126.84(17)	C(1)-C(2)-C(3)	108.1(7)
P(3)-Ru(1)-C(1)	93.84(17)	C(1)-C(2)-Ru(1)	77.5(4)
C(5)-Ru(1)-C(1)	35.4(2)	C(3)-C(2)-Ru(1)	70.4(4)
Cl(3)-Sn(1)-Cl(2)	94.65(6)	C(1)-C(2)-H(2A)	125.6
Cl(3)-Sn(1)-Cl(1)	88.21(6)	C(3)-C(2)-H(2A)	125.6
Cl(2)-Sn(1)-Cl(1)	91.80(6)	Ru(1)-C(2)-H(2A)	125.6
C(10)-P(1)-C(12)	97.7(3)	C(4)-C(3)-C(2)	108.6(6)
C(10)-P(1)-C(11)	95.1(3)	C(4)-C(3)-Ru(1)	71.0(4)
C(12)-P(1)-C(11)	95.5(3)	C(2)-C(3)-Ru(1)	72.0(4)
C(10)-P(1)-Ru(1)	114.2(2)	C(4)-C(3)-H(3A)	125.7
C(12)-P(1)-Ru(1)	125.5(2)	C(2)-C(3)-H(3A)	125.7
C(11)-P(1)-Ru(1)	122.5(2)	Ru(1)-C(3)-H(3A)	125.7
C(18)-P(2)-C(17)	97.4(3)	C(3)-C(4)-C(5)	107.7(6)
C(18)-P(2)-C(16)	97.9(3)	C(3)-C(4)-Ru(1)	71.9(4)
C(17)-P(2)-C(16)	96.6(3)	C(5)-C(4)-Ru(1)	77.3(4)
C(18)-P(2)-Ru(1)	118.2(2)	C(3)-C(4)-H(4A)	125.7
C(17)-P(2)-Ru(1)	126.1(2)	C(5)-C(4)-H(4A)	125.7
C(16)-P(2)-Ru(1)	115.3(2)	Ru(1)-C(4)-H(4A)	125.7
C(28)-P(3)-C(22)	101.8(3)	C(6)-C(5)-C(1)	118.5(6)
C(28)-P(3)-C(34)	102.5(3)	C(6)-C(5)-C(4)	133.6(7)
C(22)-P(3)-C(34)	101.3(3)	C(1)-C(5)-C(4)	107.2(6)
C(28)-P(3)-Ru(1)	121.2(2)	C(6)-C(5)-Ru(1)	133.8(6)
C(22)-P(3)-Ru(1)	115.6(2)	C(1)-C(5)-Ru(1)	72.9(4)
C(34)-P(3)-Ru(1)	111.9(2)	C(4)-C(5)-Ru(1)	65.8(4)
C(15)-N(1)-C(13)	108.3(6)	C(7)-C(6)-C(5)	119.1(7)
C(15)-N(1)-C(10)	111.6(6)	C(7)-C(6)-H(6A)	120.4
C(13)-N(1)-C(10)	109.5(5)	C(5)-C(6)-H(6A)	120.4
C(14)-N(2)-C(13)	108.5(6)	C(6)-C(7)-C(8)	121.3(7)
C(14)-N(2)-C(11)	111.1(5)	C(6)-C(7)-H(7A)	119.3
C(13)-N(2)-C(11)	110.4(5)	C(8)-C(7)-H(7A)	119.3
C(12)-N(3)-C(14)	110.1(5)	C(9)-C(8)-C(7)	122.1(7)
C(12)-N(3)-C(15)	110.8(6)	C(9)-C(8)-H(8A)	118.9
C(14)-N(3)-C(15)	108.6(6)	C(7)-C(8)-H(8A)	118.9
C(17)-N(4)-C(19)	111.4(5)	C(8)-C(9)-C(1)	118.5(7)
C(17)-N(4)-C(20)	110.1(5)	C(8)-C(9)-H(9A)	120.7
C(19)-N(4)-C(20)	108.0(5)	C(1)-C(9)-H(9A)	120.7
C(19)-N(5)-C(21)	107.9(5)	N(1)-C(10)-P(1)	114.1(4)
C(19)-N(5)-C(16)	109.7(5)	N(1)-C(10)-H(10A)	108.7
C(21)-N(5)-C(16)	111.4(5)	P(1)-C(10)-H(10A)	108.7
C(20)-N(6)-C(18)	111.5(5)	N(1)-C(10)-H(10B)	108.7
C(20)-N(6)-C(21)	107.7(5)	P(1)-C(10)-H(10B)	108.7
C(18)-N(6)-C(21)	111.2(5)	H(10A)-C(10)-H(10B)	107.6
C(2)-C(1)-C(9)	131.7(7)	N(2)-C(11)-P(1)	113.6(5)
C(2)-C(1)-C(5)	107.9(6)	N(2)-C(11)-H(11A)	108.8
C(9)-C(1)-C(5)	120.2(6)	P(1)-C(11)-H(11A)	108.8
C(2)-C(1)-Ru(1)	66.9(4)	N(2)-C(11)-H(11B)	108.8
C(9)-C(1)-Ru(1)	129.8(5)	P(1)-C(11)-H(11B)	108.8
C(5)-C(1)-Ru(1)	71.7(4)	H(11A)-C(11)-H(11B)	107.7
Cl(1S)-C(1S)-Cl(2S)	111.6(4)	N(3)-C(12)-P(1)	114.7(5)
Cl(1S)-C(1S)-H(1SA)	109.3	N(3)-C(12)-H(12A)	108.6
Cl(2S)-C(1S)-H(1SA)	109.3	P(1)-C(12)-H(12A)	108.6
Cl(1S)-C(1S)-H(1SB)	109.3	N(3)-C(12)-H(12B)	108.6

P(1)-C(12)-H(12B)	108.6	N(6)-C(21)-H(21B)	108.5
H(12A)-C(12)-H(12B)	107.6	H(21A)-C(21)-H(21B)	107.5
N(2)-C(13)-N(1)	114.9(6)	C(27)-C(22)-C(23)	119.0(6)
N(2)-C(13)-H(13A)	108.6	C(27)-C(22)-P(3)	122.7(5)
N(1)-C(13)-H(13A)	108.6	C(23)-C(22)-P(3)	118.3(5)
N(2)-C(13)-H(13B)	108.6	C(24)-C(23)-C(22)	119.8(7)
N(1)-C(13)-H(13B)	108.6	C(24)-C(23)-H(23A)	120.1
H(13A)-C(13)-H(13B)	107.5	C(22)-C(23)-H(23A)	120.1
N(2)-C(14)-N(3)	114.5(6)	C(23)-C(24)-C(25)	119.4(7)
N(2)-C(14)-H(14A)	108.6	C(23)-C(24)-H(24A)	120.3
N(3)-C(14)-H(14A)	108.6	C(25)-C(24)-H(24A)	120.3
N(2)-C(14)-H(14B)	108.6	C(26)-C(25)-C(24)	121.6(7)
N(3)-C(14)-H(14B)	108.6	C(26)-C(25)-H(25A)	119.2
H(14A)-C(14)-H(14B)	107.6	C(24)-C(25)-H(25A)	119.2
N(1)-C(15)-N(3)	115.2(6)	C(25)-C(26)-C(27)	119.2(7)
N(1)-C(15)-H(15A)	108.5	C(25)-C(26)-H(26A)	120.4
N(3)-C(15)-H(15A)	108.5	C(27)-C(26)-H(26A)	120.4
N(1)-C(15)-H(15B)	108.5	C(22)-C(27)-C(26)	121.0(7)
N(3)-C(15)-H(15B)	108.5	C(22)-C(27)-H(27A)	119.5
H(15A)-C(15)-H(15B)	107.5	C(26)-C(27)-H(27A)	119.5
N(5)-C(16)-P(2)	113.7(4)	C(29)-C(28)-C(33)	117.2(7)
N(5)-C(16)-H(16A)	108.8	C(29)-C(28)-P(3)	121.8(6)
P(2)-C(16)-H(16A)	108.8	C(33)-C(28)-P(3)	120.9(5)
N(5)-C(16)-H(16B)	108.8	C(28)-C(29)-C(30)	122.0(7)
P(2)-C(16)-H(16B)	108.8	C(28)-C(29)-H(29A)	119.0
H(16A)-C(16)-H(16B)	107.7	C(30)-C(29)-H(29A)	119.0
N(4)-C(17)-P(2)	113.3(5)	C(29)-C(30)-C(31)	120.5(7)
N(4)-C(17)-H(17A)	108.9	C(29)-C(30)-H(30A)	119.8
P(2)-C(17)-H(17A)	108.9	C(31)-C(30)-H(30A)	119.8
N(4)-C(17)-H(17B)	108.9	C(30)-C(31)-C(32)	118.5(7)
P(2)-C(17)-H(17B)	108.9	C(30)-C(31)-H(31A)	120.7
H(17A)-C(17)-H(17B)	107.7	C(32)-C(31)-H(31A)	120.7
N(6)-C(18)-P(2)	112.9(4)	C(33)-C(32)-C(31)	120.2(7)
N(6)-C(18)-H(18A)	109.0	C(33)-C(32)-H(32A)	119.9
P(2)-C(18)-H(18A)	109.0	C(31)-C(32)-H(32A)	119.9
N(6)-C(18)-H(18B)	109.0	C(32)-C(33)-C(28)	121.6(7)
P(2)-C(18)-H(18B)	109.0	C(32)-C(33)-H(33A)	119.2
H(18A)-C(18)-H(18B)	107.8	C(28)-C(33)-H(33A)	119.2
N(5)-C(19)-N(4)	115.3(5)	C(35)-C(34)-C(39)	119.5(7)
N(5)-C(19)-H(19A)	108.5	C(35)-C(34)-P(3)	122.8(5)
N(4)-C(19)-H(19A)	108.5	C(39)-C(34)-P(3)	117.6(5)
N(5)-C(19)-H(19B)	108.5	C(34)-C(35)-C(36)	119.4(7)
N(4)-C(19)-H(19B)	108.5	C(34)-C(35)-H(35A)	120.3
H(19A)-C(19)-H(19B)	107.5	C(36)-C(35)-H(35A)	120.3
N(6)-C(20)-N(4)	114.3(6)	C(37)-C(36)-C(35)	120.8(7)
N(6)-C(20)-H(20A)	108.7	C(37)-C(36)-H(36A)	119.6
N(4)-C(20)-H(20A)	108.7	C(35)-C(36)-H(36A)	119.6
N(6)-C(20)-H(20B)	108.7	C(36)-C(37)-C(38)	120.9(7)
N(4)-C(20)-H(20B)	108.7	C(36)-C(37)-H(37A)	119.6
H(20A)-C(20)-H(20B)	107.6	C(38)-C(37)-H(37A)	119.6
N(5)-C(21)-N(6)	114.9(5)	C(37)-C(38)-C(39)	118.6(7)
N(5)-C(21)-H(21A)	108.5	C(37)-C(38)-H(38A)	120.7
N(6)-C(21)-H(21A)	108.5	C(39)-C(38)-H(38A)	120.7
N(5)-C(21)-H(21B)	108.5	C(38)-C(39)-C(34)	120.7(7)

C(38)-C(39)-H(39B)

119.7

C(34)-C(39)-H(39B)

119.7

Symmetry transformations used to generate equivalent atoms:

Table A14: Torsion angles [°] for [IndRu(PTA)₂(PPh₃)]SnCl₃.

C(4)-Ru(1)-P(1)-C(10)	45.1(3)	C(3)-Ru(1)-P(3)-C(22)	-126.1(4)
C(3)-Ru(1)-P(1)-C(10)	66.0(3)	C(2)-Ru(1)-P(3)-C(22)	-113.2(3)
C(2)-Ru(1)-P(1)-C(10)	28.4(5)	P(2)-Ru(1)-P(3)-C(22)	143.5(2)
P(2)-Ru(1)-P(1)-C(10)	153.4(3)	P(1)-Ru(1)-P(3)-C(22)	49.7(2)
P(3)-Ru(1)-P(1)-C(10)	-110.6(3)	C(5)-Ru(1)-P(3)-C(22)	-50.6(3)
C(5)-Ru(1)-P(1)-C(10)	8.2(3)	C(1)-Ru(1)-P(3)-C(22)	-78.2(3)
C(1)-Ru(1)-P(1)-C(10)	-10.1(3)	C(4)-Ru(1)-P(3)-C(34)	52.9(5)
C(4)-Ru(1)-P(1)-C(12)	165.1(3)	C(3)-Ru(1)-P(3)-C(34)	-10.9(4)
C(3)-Ru(1)-P(1)-C(12)	-174.0(4)	C(2)-Ru(1)-P(3)-C(34)	1.9(3)
C(2)-Ru(1)-P(1)-C(12)	148.5(5)	P(2)-Ru(1)-P(3)-C(34)	-101.3(2)
P(2)-Ru(1)-P(1)-C(12)	-86.6(3)	P(1)-Ru(1)-P(3)-C(34)	164.9(2)
P(3)-Ru(1)-P(1)-C(12)	9.4(3)	C(5)-Ru(1)-P(3)-C(34)	64.6(3)
C(5)-Ru(1)-P(1)-C(12)	128.2(3)	C(1)-Ru(1)-P(3)-C(34)	37.0(3)
C(1)-Ru(1)-P(1)-C(12)	110.0(4)	C(4)-Ru(1)-C(1)-C(2)	82.5(5)
C(4)-Ru(1)-P(1)-C(11)	-68.5(3)	C(3)-Ru(1)-C(1)-C(2)	39.7(4)
C(3)-Ru(1)-P(1)-C(11)	-47.6(4)	P(2)-Ru(1)-C(1)-C(2)	-3.1(5)
C(2)-Ru(1)-P(1)-C(11)	-85.2(5)	P(1)-Ru(1)-C(1)-C(2)	152.1(4)
P(2)-Ru(1)-P(1)-C(11)	39.8(3)	P(3)-Ru(1)-C(1)-C(2)	-105.6(4)
P(3)-Ru(1)-P(1)-C(11)	135.8(3)	C(5)-Ru(1)-C(1)-C(2)	119.6(6)
C(5)-Ru(1)-P(1)-C(11)	-105.4(3)	C(4)-Ru(1)-C(1)-C(9)	-151.6(7)
C(1)-Ru(1)-P(1)-C(11)	-123.7(3)	C(3)-Ru(1)-C(1)-C(9)	165.6(7)
C(4)-Ru(1)-P(2)-C(18)	-99.3(3)	C(2)-Ru(1)-C(1)-C(9)	125.9(9)
C(3)-Ru(1)-P(2)-C(18)	-69.0(3)	P(2)-Ru(1)-C(1)-C(9)	122.9(6)
C(2)-Ru(1)-P(2)-C(18)	-34.6(3)	P(1)-Ru(1)-C(1)-C(9)	-81.9(7)
P(1)-Ru(1)-P(2)-C(18)	166.8(2)	P(3)-Ru(1)-C(1)-C(9)	20.4(6)
P(3)-Ru(1)-P(2)-C(18)	69.0(2)	C(5)-Ru(1)-C(1)-C(9)	-114.5(8)
C(5)-Ru(1)-P(2)-C(18)	-89.3(4)	C(4)-Ru(1)-C(1)-C(5)	-37.1(4)
C(1)-Ru(1)-P(2)-C(18)	-32.8(4)	C(3)-Ru(1)-C(1)-C(5)	-79.9(5)
C(4)-Ru(1)-P(2)-C(17)	136.0(4)	C(2)-Ru(1)-C(1)-C(5)	-119.6(6)
C(3)-Ru(1)-P(2)-C(17)	166.3(4)	P(2)-Ru(1)-C(1)-C(5)	-122.7(4)
C(2)-Ru(1)-P(2)-C(17)	-159.4(4)	P(1)-Ru(1)-C(1)-C(5)	32.6(5)
P(1)-Ru(1)-P(2)-C(17)	42.1(3)	P(3)-Ru(1)-C(1)-C(5)	134.9(4)
P(3)-Ru(1)-P(2)-C(17)	-55.7(3)	C(9)-C(1)-C(2)-C(3)	172.2(7)
C(5)-Ru(1)-P(2)-C(17)	146.0(4)	C(5)-C(1)-C(2)-C(3)	-4.1(8)
C(1)-Ru(1)-P(2)-C(17)	-157.5(4)	Ru(1)-C(1)-C(2)-C(3)	-64.3(5)
C(4)-Ru(1)-P(2)-C(16)	15.9(3)	C(9)-C(1)-C(2)-Ru(1)	-123.5(8)
C(3)-Ru(1)-P(2)-C(16)	46.3(3)	C(5)-C(1)-C(2)-Ru(1)	60.2(5)
C(2)-Ru(1)-P(2)-C(16)	80.6(3)	C(4)-Ru(1)-C(2)-C(1)	-77.7(4)
P(1)-Ru(1)-P(2)-C(16)	-77.9(3)	C(3)-Ru(1)-C(2)-C(1)	-114.6(6)
P(3)-Ru(1)-P(2)-C(16)	-175.8(3)	P(2)-Ru(1)-C(2)-C(1)	177.9(4)
C(5)-Ru(1)-P(2)-C(16)	25.9(4)	P(1)-Ru(1)-C(2)-C(1)	-58.9(7)
C(1)-Ru(1)-P(2)-C(16)	82.4(4)	P(3)-Ru(1)-C(2)-C(1)	79.5(4)
C(4)-Ru(1)-P(3)-C(28)	174.0(5)	C(5)-Ru(1)-C(2)-C(1)	-35.5(4)
C(3)-Ru(1)-P(3)-C(28)	110.2(4)	C(4)-Ru(1)-C(2)-C(3)	37.0(4)
C(2)-Ru(1)-P(3)-C(28)	123.0(3)	P(2)-Ru(1)-C(2)-C(3)	-67.5(4)
P(2)-Ru(1)-P(3)-C(28)	19.7(3)	P(1)-Ru(1)-C(2)-C(3)	55.7(6)
P(1)-Ru(1)-P(3)-C(28)	-74.0(3)	P(3)-Ru(1)-C(2)-C(3)	-165.9(4)
C(5)-Ru(1)-P(3)-C(28)	-174.4(3)	C(5)-Ru(1)-C(2)-C(3)	79.1(4)
C(1)-Ru(1)-P(3)-C(28)	158.0(3)	C(1)-Ru(1)-C(2)-C(3)	114.6(6)
C(4)-Ru(1)-P(3)-C(22)	-62.2(5)	C(1)-C(2)-C(3)-C(4)	7.1(8)

Ru(1)-C(2)-C(3)-C(4)	-61.9(5)	P(3)-Ru(1)-C(5)-C(1)	-52.9(5)
C(1)-C(2)-C(3)-Ru(1)	69.0(5)	C(3)-Ru(1)-C(5)-C(4)	-39.4(4)
C(2)-Ru(1)-C(3)-C(4)	117.8(6)	C(2)-Ru(1)-C(5)-C(4)	-82.9(5)
P(2)-Ru(1)-C(3)-C(4)	-127.3(4)	P(2)-Ru(1)-C(5)-C(4)	-15.9(6)
P(1)-Ru(1)-C(3)-C(4)	-36.3(5)	P(1)-Ru(1)-C(5)-C(4)	87.1(4)
P(3)-Ru(1)-C(3)-C(4)	138.7(4)	P(3)-Ru(1)-C(5)-C(4)	-171.4(3)
C(5)-Ru(1)-C(3)-C(4)	39.2(4)	C(1)-Ru(1)-C(5)-C(4)	-118.5(6)
C(1)-Ru(1)-C(3)-C(4)	80.2(4)	C(1)-C(5)-C(6)-C(7)	2.9(11)
C(4)-Ru(1)-C(3)-C(2)	-117.8(6)	C(4)-C(5)-C(6)-C(7)	172.2(7)
P(2)-Ru(1)-C(3)-C(2)	114.9(4)	Ru(1)-C(5)-C(6)-C(7)	-90.4(9)
P(1)-Ru(1)-C(3)-C(2)	-154.1(3)	C(5)-C(6)-C(7)-C(8)	-0.7(11)
P(3)-Ru(1)-C(3)-C(2)	20.9(5)	C(6)-C(7)-C(8)-C(9)	0.7(11)
C(5)-Ru(1)-C(3)-C(2)	-78.6(4)	C(7)-C(8)-C(9)-C(1)	-2.8(11)
C(1)-Ru(1)-C(3)-C(2)	-37.6(4)	C(2)-C(1)-C(9)-C(8)	-170.9(7)
C(2)-C(3)-C(4)-C(5)	-7.1(7)	C(5)-C(1)-C(9)-C(8)	5.0(10)
Ru(1)-C(3)-C(4)-C(5)	-69.7(5)	Ru(1)-C(1)-C(9)-C(8)	95.7(8)
C(2)-C(3)-C(4)-Ru(1)	62.6(5)	C(15)-N(1)-C(10)-P(1)	-57.3(7)
C(2)-Ru(1)-C(4)-C(3)	-37.4(4)	C(13)-N(1)-C(10)-P(1)	62.6(7)
P(2)-Ru(1)-C(4)-C(3)	56.6(4)	C(12)-P(1)-C(10)-N(1)	44.8(6)
P(1)-Ru(1)-C(4)-C(3)	150.7(4)	C(11)-P(1)-C(10)-N(1)	-51.4(6)
P(3)-Ru(1)-C(4)-C(3)	-96.3(5)	Ru(1)-P(1)-C(10)-N(1)	179.5(4)
C(5)-Ru(1)-C(4)-C(3)	-113.6(6)	C(14)-N(2)-C(11)-P(1)	59.9(7)
C(1)-Ru(1)-C(4)-C(3)	-78.0(4)	C(13)-N(2)-C(11)-P(1)	-60.6(7)
C(3)-Ru(1)-C(4)-C(5)	113.6(6)	C(10)-P(1)-C(11)-N(2)	50.1(5)
C(2)-Ru(1)-C(4)-C(5)	76.2(4)	C(12)-P(1)-C(11)-N(2)	-48.1(5)
P(2)-Ru(1)-C(4)-C(5)	170.3(4)	Ru(1)-P(1)-C(11)-N(2)	173.1(4)
P(1)-Ru(1)-C(4)-C(5)	-95.7(4)	C(14)-N(3)-C(12)-P(1)	-61.7(7)
P(3)-Ru(1)-C(4)-C(5)	17.3(7)	C(15)-N(3)-C(12)-P(1)	58.5(7)
C(1)-Ru(1)-C(4)-C(5)	35.6(4)	C(10)-P(1)-C(12)-N(3)	-46.0(6)
C(2)-C(1)-C(5)-C(6)	171.7(7)	C(11)-P(1)-C(12)-N(3)	49.8(6)
C(9)-C(1)-C(5)-C(6)	-5.1(10)	Ru(1)-P(1)-C(12)-N(3)	-173.2(4)
Ru(1)-C(1)-C(5)-C(6)	-131.0(7)	C(14)-N(2)-C(13)-N(1)	-54.9(7)
C(2)-C(1)-C(5)-C(4)	-0.2(8)	C(11)-N(2)-C(13)-N(1)	67.1(7)
C(9)-C(1)-C(5)-C(4)	-177.0(6)	C(15)-N(1)-C(13)-N(2)	54.4(8)
Ru(1)-C(1)-C(5)-C(4)	57.0(5)	C(10)-N(1)-C(13)-N(2)	-67.6(7)
C(2)-C(1)-C(5)-Ru(1)	-57.2(5)	C(13)-N(2)-C(14)-N(3)	54.5(7)
C(9)-C(1)-C(5)-Ru(1)	126.0(6)	C(11)-N(2)-C(14)-N(3)	-67.0(7)
C(3)-C(4)-C(5)-C(6)	-165.6(8)	C(12)-N(3)-C(14)-N(2)	67.5(8)
Ru(1)-C(4)-C(5)-C(6)	128.3(9)	C(15)-N(3)-C(14)-N(2)	-54.0(8)
C(3)-C(4)-C(5)-C(1)	4.5(8)	C(13)-N(1)-C(15)-N(3)	-53.9(8)
Ru(1)-C(4)-C(5)-C(1)	-61.5(5)	C(10)-N(1)-C(15)-N(3)	66.7(8)
C(3)-C(4)-C(5)-Ru(1)	66.1(5)	C(12)-N(3)-C(15)-N(1)	-67.2(8)
C(4)-Ru(1)-C(5)-C(6)	-128.1(9)	C(14)-N(3)-C(15)-N(1)	53.9(8)
C(3)-Ru(1)-C(5)-C(6)	-167.5(8)	C(19)-N(5)-C(16)-P(2)	-61.2(6)
C(2)-Ru(1)-C(5)-C(6)	149.0(8)	C(21)-N(5)-C(16)-P(2)	58.2(6)
P(2)-Ru(1)-C(5)-C(6)	-144.0(6)	C(18)-P(2)-C(16)-N(5)	-48.1(5)
P(1)-Ru(1)-C(5)-C(6)	-41.0(7)	C(17)-P(2)-C(16)-N(5)	50.3(6)
P(3)-Ru(1)-C(5)-C(6)	60.5(8)	Ru(1)-P(2)-C(16)-N(5)	-174.5(4)
C(1)-Ru(1)-C(5)-C(6)	113.4(9)	C(19)-N(4)-C(17)-P(2)	59.1(6)
C(4)-Ru(1)-C(5)-C(1)	118.5(6)	C(20)-N(4)-C(17)-P(2)	-60.6(7)
C(3)-Ru(1)-C(5)-C(1)	79.1(5)	C(18)-P(2)-C(17)-N(4)	50.2(5)
C(2)-Ru(1)-C(5)-C(1)	35.7(4)	C(16)-P(2)-C(17)-N(4)	-48.7(6)
P(2)-Ru(1)-C(5)-C(1)	102.6(4)	Ru(1)-P(2)-C(17)-N(4)	-176.7(4)
P(1)-Ru(1)-C(5)-C(1)	-154.4(4)	C(20)-N(6)-C(18)-P(2)	60.2(6)

C(21)-N(6)-C(18)-P(2)	-60.0(6)	C(25)-C(26)-C(27)-C(22)	1.5(11)
C(17)-P(2)-C(18)-N(6)	-49.0(5)	C(22)-P(3)-C(28)-C(29)	141.4(6)
C(16)-P(2)-C(18)-N(6)	48.7(5)	C(34)-P(3)-C(28)-C(29)	36.9(6)
Ru(1)-P(2)-C(18)-N(6)	173.0(4)	Ru(1)-P(3)-C(28)-C(29)	-88.6(6)
C(21)-N(5)-C(19)-N(4)	-54.7(7)	C(22)-P(3)-C(28)-C(33)	-43.3(6)
C(16)-N(5)-C(19)-N(4)	66.8(7)	C(34)-P(3)-C(28)-C(33)	-147.8(6)
C(17)-N(4)-C(19)-N(5)	-66.5(7)	Ru(1)-P(3)-C(28)-C(33)	86.7(6)
C(20)-N(4)-C(19)-N(5)	54.5(7)	C(33)-C(28)-C(29)-C(30)	-3.0(10)
C(18)-N(6)-C(20)-N(4)	-66.8(7)	P(3)-C(28)-C(29)-C(30)	172.4(5)
C(21)-N(6)-C(20)-N(4)	55.4(7)	C(28)-C(29)-C(30)-C(31)	1.8(11)
C(17)-N(4)-C(20)-N(6)	66.9(7)	C(29)-C(30)-C(31)-C(32)	0.3(11)
C(19)-N(4)-C(20)-N(6)	-55.0(7)	C(30)-C(31)-C(32)-C(33)	-1.1(11)
C(19)-N(5)-C(21)-N(6)	55.2(7)	C(31)-C(32)-C(33)-C(28)	-0.2(11)
C(16)-N(5)-C(21)-N(6)	-65.3(7)	C(29)-C(28)-C(33)-C(32)	2.3(10)
C(20)-N(6)-C(21)-N(5)	-56.0(7)	P(3)-C(28)-C(33)-C(32)	-173.3(5)
C(18)-N(6)-C(21)-N(5)	66.4(7)	C(28)-P(3)-C(34)-C(35)	100.6(6)
C(28)-P(3)-C(22)-C(27)	-30.2(7)	C(22)-P(3)-C(34)-C(35)	-4.4(7)
C(34)-P(3)-C(22)-C(27)	75.3(6)	Ru(1)-P(3)-C(34)-C(35)	-128.0(5)
Ru(1)-P(3)-C(22)-C(27)	-163.6(5)	C(28)-P(3)-C(34)-C(39)	-84.1(6)
C(28)-P(3)-C(22)-C(23)	150.3(5)	C(22)-P(3)-C(34)-C(39)	170.9(5)
C(34)-P(3)-C(22)-C(23)	-104.3(6)	Ru(1)-P(3)-C(34)-C(39)	47.3(6)
Ru(1)-P(3)-C(22)-C(23)	16.8(6)	C(39)-C(34)-C(35)-C(36)	-0.7(10)
C(27)-C(22)-C(23)-C(24)	1.8(10)	P(3)-C(34)-C(35)-C(36)	174.5(5)
P(3)-C(22)-C(23)-C(24)	-178.7(5)	C(34)-C(35)-C(36)-C(37)	-1.1(11)
C(22)-C(23)-C(24)-C(25)	-1.5(10)	C(35)-C(36)-C(37)-C(38)	1.4(12)
C(23)-C(24)-C(25)-C(26)	1.2(10)	C(36)-C(37)-C(38)-C(39)	0.2(11)
C(24)-C(25)-C(26)-C(27)	-1.2(11)	C(37)-C(38)-C(39)-C(34)	-2.0(11)
C(23)-C(22)-C(27)-C(26)	-1.8(11)	C(35)-C(34)-C(39)-C(38)	2.3(10)
P(3)-C(22)-C(27)-C(26)	178.6(6)	P(3)-C(34)-C(39)-C(38)	-173.2(5)

Symmetry transformations used to generate equivalent atoms:

Table A15. Bond lengths [\AA] and angles [$^\circ$] for IndRu(PTA)(PPh₃)Cl.

Ru(1)-C(3)	2.164(4)	N(1)-C(13)	1.472(5)
Ru(1)-C(4)	2.176(4)	N(2)-C(13)	1.470(5)
Ru(1)-C(2)	2.215(4)	N(2)-C(14)	1.473(5)
Ru(1)-P(2)	2.2697(10)	N(2)-C(11)	1.476(5)
Ru(1)-P(1)	2.2931(10)	N(3)-C(15)	1.467(5)
Ru(1)-C(5)	2.338(4)	N(3)-C(14)	1.469(5)
Ru(1)-C(1)	2.343(4)	N(3)-C(12)	1.480(5)
Ru(1)-Cl(1)	2.4465(9)	C(1)-C(9)	1.420(5)
P(1)-C(12)	1.853(4)	C(1)-C(5)	1.432(5)
P(1)-C(11)	1.856(4)	C(1)-C(2)	1.443(5)
P(1)-C(10)	1.858(4)	C(2)-C(3)	1.423(5)
P(2)-C(16)	1.835(4)	C(2)-H(2A)	0.9999
P(2)-C(22)	1.845(4)	C(3)-C(4)	1.416(5)
P(2)-C(28)	1.852(4)	C(3)-H(3A)	0.9998
N(1)-C(10)	1.466(5)	C(4)-C(5)	1.453(5)
N(1)-C(15)	1.470(5)	C(4)-H(4A)	1.0001

C(5)-C(6)	1.420(5)	C(3)-Ru(1)-C(4)	38.08(14)
C(6)-C(7)	1.359(5)	C(3)-Ru(1)-C(2)	37.90(14)
C(6)-H(6A)	0.9498	C(4)-Ru(1)-C(2)	63.65(14)
C(7)-C(8)	1.420(5)	C(3)-Ru(1)-P(2)	90.51(11)
C(7)-H(7A)	0.9500	C(4)-Ru(1)-P(2)	115.57(10)
C(8)-C(9)	1.366(5)	C(2)-Ru(1)-P(2)	101.69(10)
C(8)-H(8A)	0.9498	C(3)-Ru(1)-P(1)	128.79(11)
C(9)-H(9A)	0.9500	C(4)-Ru(1)-P(1)	95.05(11)
C(10)-H(10A)	0.9899	C(2)-Ru(1)-P(1)	155.64(10)
C(10)-H(10B)	0.9902	P(2)-Ru(1)-P(1)	98.19(4)
C(11)-H(11A)	0.9903	C(3)-Ru(1)-C(5)	61.83(14)
C(11)-H(11B)	0.9899	C(4)-Ru(1)-C(5)	37.33(13)
C(12)-H(12A)	0.9898	C(2)-Ru(1)-C(5)	61.65(14)
C(12)-H(12B)	0.9900	P(2)-Ru(1)-C(5)	151.38(10)
C(13)-H(13A)	0.9900	P(1)-Ru(1)-C(5)	94.38(10)
C(13)-H(13B)	0.9899	C(3)-Ru(1)-C(1)	61.34(14)
C(14)-H(14A)	0.9900	C(4)-Ru(1)-C(1)	61.58(13)
C(14)-H(14B)	0.9899	C(2)-Ru(1)-C(1)	36.78(13)
C(15)-H(15A)	0.9901	P(2)-Ru(1)-C(1)	137.72(10)
C(15)-H(15B)	0.9899	P(1)-Ru(1)-C(1)	123.89(10)
C(16)-C(17)	1.397(5)	C(5)-Ru(1)-C(1)	35.63(13)
C(16)-C(21)	1.398(5)	C(3)-Ru(1)-Cl(1)	140.25(11)
C(17)-C(18)	1.394(5)	C(4)-Ru(1)-Cl(1)	150.80(10)
C(17)-H(17A)	0.9499	C(2)-Ru(1)-Cl(1)	103.12(10)
C(18)-C(19)	1.381(5)	P(2)-Ru(1)-Cl(1)	91.99(3)
C(18)-H(18A)	0.9500	P(1)-Ru(1)-Cl(1)	90.03(3)
C(19)-C(20)	1.386(6)	C(5)-Ru(1)-Cl(1)	113.68(10)
C(19)-H(19A)	0.9500	C(1)-Ru(1)-Cl(1)	91.88(9)
C(20)-C(21)	1.388(5)	C(12)-P(1)-C(11)	96.88(18)
C(20)-H(20A)	0.9501	C(12)-P(1)-C(10)	97.10(18)
C(21)-H(21A)	0.9501	C(11)-P(1)-C(10)	97.09(17)
C(22)-C(23)	1.400(5)	C(12)-P(1)-Ru(1)	127.55(13)
C(22)-C(27)	1.406(5)	C(11)-P(1)-Ru(1)	116.13(13)
C(23)-C(24)	1.387(6)	C(10)-P(1)-Ru(1)	116.30(13)
C(23)-H(23A)	0.9500	C(16)-P(2)-C(22)	100.97(17)
C(24)-C(25)	1.390(6)	C(16)-P(2)-C(28)	100.21(17)
C(24)-H(24A)	0.9500	C(22)-P(2)-C(28)	103.52(17)
C(25)-C(26)	1.384(6)	C(16)-P(2)-Ru(1)	115.81(13)
C(25)-H(25A)	0.9501	C(22)-P(2)-Ru(1)	121.23(12)
C(26)-C(27)	1.387(6)	C(28)-P(2)-Ru(1)	112.32(12)
C(26)-H(26A)	0.9498	C(10)-N(1)-C(15)	110.8(3)
C(27)-H(27A)	0.9499	C(10)-N(1)-C(13)	110.9(3)
C(28)-C(33)	1.390(5)	C(15)-N(1)-C(13)	108.1(3)
C(28)-C(29)	1.394(5)	C(13)-N(2)-C(14)	107.8(3)
C(29)-C(30)	1.389(6)	C(13)-N(2)-C(11)	110.3(3)
C(29)-H(29A)	0.9500	C(14)-N(2)-C(11)	110.4(3)
C(30)-C(31)	1.387(6)	C(15)-N(3)-C(14)	107.9(3)
C(30)-H(30A)	0.9500	C(15)-N(3)-C(12)	111.6(3)
C(31)-C(32)	1.379(6)	C(14)-N(3)-C(12)	111.2(3)
C(31)-H(31A)	0.9498	C(9)-C(1)-C(5)	120.0(3)
C(32)-C(33)	1.404(5)	C(9)-C(1)-C(2)	131.4(4)
C(32)-H(32A)	0.9498	C(5)-C(1)-C(2)	108.6(3)
C(33)-H(33A)	0.9500	C(9)-C(1)-Ru(1)	128.1(3)
		C(5)-C(1)-Ru(1)	72.0(2)

C(2)-C(1)-Ru(1)	66.8(2)	H(12A)-C(12)-H(12B)	107.8
C(3)-C(2)-C(1)	107.0(3)	N(2)-C(13)-N(1)	115.3(3)
C(3)-C(2)-Ru(1)	69.1(2)	N(2)-C(13)-H(13A)	108.5
C(1)-C(2)-Ru(1)	76.4(2)	N(1)-C(13)-H(13A)	108.6
C(3)-C(2)-H(2A)	126.3	N(2)-C(13)-H(13B)	108.3
C(1)-C(2)-H(2A)	126.2	N(1)-C(13)-H(13B)	108.3
Ru(1)-C(2)-H(2A)	126.1	H(13A)-C(13)-H(13B)	107.5
C(4)-C(3)-C(2)	109.4(3)	N(3)-C(14)-N(2)	115.0(3)
C(4)-C(3)-Ru(1)	71.4(2)	N(3)-C(14)-H(14A)	108.5
C(2)-C(3)-Ru(1)	73.0(2)	N(2)-C(14)-H(14A)	108.5
C(4)-C(3)-H(3A)	125.3	N(3)-C(14)-H(14B)	108.5
C(2)-C(3)-H(3A)	125.2	N(2)-C(14)-H(14B)	108.5
Ru(1)-C(3)-H(3A)	125.4	H(14A)-C(14)-H(14B)	107.5
C(3)-C(4)-C(5)	107.8(3)	N(3)-C(15)-N(1)	114.7(3)
C(3)-C(4)-Ru(1)	70.5(2)	N(3)-C(15)-H(15A)	108.5
C(5)-C(4)-Ru(1)	77.4(2)	N(1)-C(15)-H(15A)	108.6
C(3)-C(4)-H(4A)	125.8	N(3)-C(15)-H(15B)	108.7
C(5)-C(4)-H(4A)	125.6	N(1)-C(15)-H(15B)	108.6
Ru(1)-C(4)-H(4A)	125.8	H(15A)-C(15)-H(15B)	107.6
C(6)-C(5)-C(1)	119.1(3)	C(17)-C(16)-C(21)	119.1(4)
C(6)-C(5)-C(4)	134.0(4)	C(17)-C(16)-P(2)	118.9(3)
C(1)-C(5)-C(4)	106.9(3)	C(21)-C(16)-P(2)	122.0(3)
C(6)-C(5)-Ru(1)	127.9(3)	C(18)-C(17)-C(16)	120.1(4)
C(1)-C(5)-Ru(1)	72.4(2)	C(18)-C(17)-H(17A)	120.1
C(4)-C(5)-Ru(1)	65.3(2)	C(16)-C(17)-H(17A)	119.8
C(7)-C(6)-C(5)	119.4(4)	C(19)-C(18)-C(17)	120.4(4)
C(7)-C(6)-H(6A)	120.3	C(19)-C(18)-H(18A)	119.9
C(5)-C(6)-H(6A)	120.2	C(17)-C(18)-H(18A)	119.6
C(6)-C(7)-C(8)	121.5(4)	C(18)-C(19)-C(20)	119.7(4)
C(6)-C(7)-H(7A)	119.3	C(18)-C(19)-H(19A)	120.1
C(8)-C(7)-H(7A)	119.2	C(20)-C(19)-H(19A)	120.2
C(9)-C(8)-C(7)	121.0(4)	C(19)-C(20)-C(21)	120.6(4)
C(9)-C(8)-H(8A)	119.5	C(19)-C(20)-H(20A)	119.7
C(7)-C(8)-H(8A)	119.5	C(21)-C(20)-H(20A)	119.7
C(8)-C(9)-C(1)	119.0(4)	C(20)-C(21)-C(16)	120.1(4)
C(8)-C(9)-H(9A)	120.5	C(20)-C(21)-H(21A)	120.1
C(1)-C(9)-H(9A)	120.5	C(16)-C(21)-H(21A)	119.9
N(1)-C(10)-P(1)	113.5(3)	C(23)-C(22)-C(27)	118.2(4)
N(1)-C(10)-H(10A)	108.9	C(23)-C(22)-P(2)	121.9(3)
P(1)-C(10)-H(10A)	108.9	C(27)-C(22)-P(2)	119.9(3)
N(1)-C(10)-H(10B)	108.8	C(24)-C(23)-C(22)	120.3(4)
P(1)-C(10)-H(10B)	108.8	C(24)-C(23)-H(23A)	119.7
H(10A)-C(10)-H(10B)	107.7	C(22)-C(23)-H(23A)	119.9
N(2)-C(11)-P(1)	113.9(3)	C(23)-C(24)-C(25)	121.0(4)
N(2)-C(11)-H(11A)	109.0	C(23)-C(24)-H(24A)	119.4
P(1)-C(11)-H(11A)	108.9	C(25)-C(24)-H(24A)	119.6
N(2)-C(11)-H(11B)	108.6	C(26)-C(25)-C(24)	119.1(4)
P(1)-C(11)-H(11B)	108.6	C(26)-C(25)-H(25A)	120.2
H(11A)-C(11)-H(11B)	107.7	C(24)-C(25)-H(25A)	120.7
N(3)-C(12)-P(1)	112.7(3)	C(25)-C(26)-C(27)	120.5(4)
N(3)-C(12)-H(12A)	109.2	C(25)-C(26)-H(26A)	120.1
P(1)-C(12)-H(12A)	109.1	C(27)-C(26)-H(26A)	119.4
N(3)-C(12)-H(12B)	109.0	C(26)-C(27)-C(22)	120.8(4)
P(1)-C(12)-H(12B)	109.0	C(26)-C(27)-H(27A)	119.5

C(22)-C(27)-H(27A)	119.7	C(32)-C(31)-C(30)	119.6(4)
C(33)-C(28)-C(29)	118.0(4)	C(32)-C(31)-H(31A)	120.2
C(33)-C(28)-P(2)	123.3(3)	C(30)-C(31)-H(31A)	120.2
C(29)-C(28)-P(2)	118.6(3)	C(31)-C(32)-C(33)	120.1(4)
C(30)-C(29)-C(28)	121.2(4)	C(31)-C(32)-H(32A)	119.9
C(30)-C(29)-H(29A)	119.2	C(33)-C(32)-H(32A)	120.0
C(28)-C(29)-H(29A)	119.6	C(28)-C(33)-C(32)	120.9(4)
C(31)-C(30)-C(29)	120.2(4)	C(28)-C(33)-H(33A)	119.7
C(31)-C(30)-H(30A)	119.8	C(32)-C(33)-H(33A)	119.4
C(29)-C(30)-H(30A)	120.0		

Symmetry transformations used to generate equivalent atoms:

Table A16: Torsion angles [$^{\circ}$] for IndRu(PTA)(PPh₃)Cl.

C(3)-Ru(1)-P(1)-C(12)	110.6(2)	C(3)-Ru(1)-P(2)-C(28)	66.32(17)
C(4)-Ru(1)-P(1)-C(12)	130.0(2)	C(4)-Ru(1)-P(2)-C(28)	96.04(18)
C(2)-Ru(1)-P(1)-C(12)	157.8(3)	C(2)-Ru(1)-P(2)-C(28)	29.83(17)
P(2)-Ru(1)-P(1)-C(12)	13.25(17)	P(1)-Ru(1)-P(2)-C(28)	-164.32(14)
C(5)-Ru(1)-P(1)-C(12)	167.48(19)	C(5)-Ru(1)-P(2)-C(28)	80.5(2)
C(1)-Ru(1)-P(1)-C(12)	-171.0(2)	C(1)-Ru(1)-P(2)-C(28)	21.0(2)
Cl(1)-Ru(1)-P(1)-C(12)	-78.76(17)	Cl(1)-Ru(1)-P(2)-C(28)	-74.00(14)
C(3)-Ru(1)-P(1)-C(11)	-126.38(19)	C(3)-Ru(1)-C(1)-C(9)	-164.9(4)
C(4)-Ru(1)-P(1)-C(11)	-106.92(17)	C(4)-Ru(1)-C(1)-C(9)	151.5(4)
C(2)-Ru(1)-P(1)-C(11)	-79.2(3)	C(2)-Ru(1)-C(1)-C(9)	-125.3(4)
P(2)-Ru(1)-P(1)-C(11)	136.31(15)	P(2)-Ru(1)-C(1)-C(9)	-110.7(3)
C(5)-Ru(1)-P(1)-C(11)	-69.46(17)	P(1)-Ru(1)-C(1)-C(9)	75.6(4)
C(1)-Ru(1)-P(1)-C(11)	-47.99(18)	C(5)-Ru(1)-C(1)-C(9)	114.4(4)
Cl(1)-Ru(1)-P(1)-C(11)	44.29(15)	Cl(1)-Ru(1)-C(1)-C(9)	-15.7(3)
C(3)-Ru(1)-P(1)-C(10)	-13.1(2)	C(3)-Ru(1)-C(1)-C(5)	80.7(2)
C(4)-Ru(1)-P(1)-C(10)	6.40(17)	C(4)-Ru(1)-C(1)-C(5)	37.1(2)
C(2)-Ru(1)-P(1)-C(10)	34.1(3)	C(2)-Ru(1)-C(1)-C(5)	120.3(3)
P(2)-Ru(1)-P(1)-C(10)	-110.38(14)	P(2)-Ru(1)-C(1)-C(5)	134.87(19)
C(5)-Ru(1)-P(1)-C(10)	43.85(17)	P(1)-Ru(1)-C(1)-C(5)	-38.8(2)
C(1)-Ru(1)-P(1)-C(10)	65.33(18)	Cl(1)-Ru(1)-C(1)-C(5)	-130.1(2)
Cl(1)-Ru(1)-P(1)-C(10)	157.61(14)	C(3)-Ru(1)-C(1)-C(2)	-39.6(2)
C(3)-Ru(1)-P(2)-C(16)	-47.97(18)	C(4)-Ru(1)-C(1)-C(2)	-83.2(2)
C(4)-Ru(1)-P(2)-C(16)	-18.25(18)	P(2)-Ru(1)-C(1)-C(2)	14.6(3)
C(2)-Ru(1)-P(2)-C(16)	-84.46(17)	P(1)-Ru(1)-C(1)-C(2)	-159.11(18)
P(1)-Ru(1)-P(2)-C(16)	81.40(14)	C(5)-Ru(1)-C(1)-C(2)	-120.3(3)
C(5)-Ru(1)-P(2)-C(16)	-33.8(3)	Cl(1)-Ru(1)-C(1)-C(2)	109.6(2)
C(1)-Ru(1)-P(2)-C(16)	-93.3(2)	C(9)-C(1)-C(2)-C(3)	-176.1(4)
Cl(1)-Ru(1)-P(2)-C(16)	171.71(14)	C(5)-C(1)-C(2)-C(3)	2.7(4)
C(3)-Ru(1)-P(2)-C(22)	-170.69(18)	Ru(1)-C(1)-C(2)-C(3)	62.8(2)
C(4)-Ru(1)-P(2)-C(22)	-140.96(19)	C(9)-C(1)-C(2)-Ru(1)	121.1(4)
C(2)-Ru(1)-P(2)-C(22)	152.83(18)	C(5)-C(1)-C(2)-Ru(1)	-60.0(3)
P(1)-Ru(1)-P(2)-C(22)	-41.32(15)	C(4)-Ru(1)-C(2)-C(3)	-37.5(2)
C(5)-Ru(1)-P(2)-C(22)	-156.5(2)	P(2)-Ru(1)-C(2)-C(3)	75.5(2)
C(1)-Ru(1)-P(2)-C(22)	144.0(2)	P(1)-Ru(1)-C(2)-C(3)	-68.6(3)
Cl(1)-Ru(1)-P(2)-C(22)	48.99(15)	C(5)-Ru(1)-C(2)-C(3)	-79.6(2)

C(1)-Ru(1)-C(2)-C(3)	-114.5(3)	P(2)-Ru(1)-C(5)-C(6)	151.1(3)
Cl(1)-Ru(1)-C(2)-C(3)	170.3(2)	P(1)-Ru(1)-C(5)-C(6)	35.0(3)
C(3)-Ru(1)-C(2)-C(1)	114.5(3)	C(1)-Ru(1)-C(5)-C(6)	-113.5(4)
C(4)-Ru(1)-C(2)-C(1)	77.0(2)	Cl(1)-Ru(1)-C(5)-C(6)	-56.9(4)
P(2)-Ru(1)-C(2)-C(1)	-170.06(19)	C(3)-Ru(1)-C(5)-C(1)	-79.2(2)
P(1)-Ru(1)-C(2)-C(1)	45.9(4)	C(4)-Ru(1)-C(5)-C(1)	-118.9(3)
C(5)-Ru(1)-C(2)-C(1)	34.9(2)	C(2)-Ru(1)-C(5)-C(1)	-36.0(2)
Cl(1)-Ru(1)-C(2)-C(1)	-75.2(2)	P(2)-Ru(1)-C(5)-C(1)	-95.4(3)
C(1)-C(2)-C(3)-C(4)	-5.1(4)	P(1)-Ru(1)-C(5)-C(1)	148.6(2)
Ru(1)-C(2)-C(3)-C(4)	62.6(3)	Cl(1)-Ru(1)-C(5)-C(1)	56.6(2)
C(1)-C(2)-C(3)-Ru(1)	-67.7(3)	C(3)-Ru(1)-C(5)-C(4)	39.6(2)
C(2)-Ru(1)-C(3)-C(4)	-117.9(3)	C(2)-Ru(1)-C(5)-C(4)	82.9(2)
P(2)-Ru(1)-C(3)-C(4)	133.5(2)	P(2)-Ru(1)-C(5)-C(4)	23.4(3)
P(1)-Ru(1)-C(3)-C(4)	32.6(3)	P(1)-Ru(1)-C(5)-C(4)	-92.6(2)
C(5)-Ru(1)-C(3)-C(4)	-38.8(2)	C(1)-Ru(1)-C(5)-C(4)	118.9(3)
C(1)-Ru(1)-C(3)-C(4)	-79.5(2)	Cl(1)-Ru(1)-C(5)-C(4)	175.45(19)
Cl(1)-Ru(1)-C(3)-C(4)	-132.8(2)	C(1)-C(5)-C(6)-C(7)	0.2(6)
C(4)-Ru(1)-C(3)-C(2)	117.9(3)	C(4)-C(5)-C(6)-C(7)	-179.3(4)
P(2)-Ru(1)-C(3)-C(2)	-108.6(2)	Ru(1)-C(5)-C(6)-C(7)	89.9(4)
P(1)-Ru(1)-C(3)-C(2)	150.48(18)	C(5)-C(6)-C(7)-C(8)	-0.8(6)
C(5)-Ru(1)-C(3)-C(2)	79.1(2)	C(6)-C(7)-C(8)-C(9)	1.1(6)
C(1)-Ru(1)-C(3)-C(2)	38.4(2)	C(7)-C(8)-C(9)-C(1)	-0.9(6)
Cl(1)-Ru(1)-C(3)-C(2)	-14.8(3)	C(5)-C(1)-C(9)-C(8)	0.3(5)
C(2)-C(3)-C(4)-C(5)	5.5(4)	C(2)-C(1)-C(9)-C(8)	179.1(4)
Ru(1)-C(3)-C(4)-C(5)	69.1(3)	Ru(1)-C(1)-C(9)-C(8)	-89.6(4)
C(2)-C(3)-C(4)-Ru(1)	-63.6(3)	C(15)-N(1)-C(10)-P(1)	-60.3(4)
C(2)-Ru(1)-C(4)-C(3)	37.3(2)	C(13)-N(1)-C(10)-P(1)	59.7(4)
P(2)-Ru(1)-C(4)-C(3)	-53.5(2)	C(12)-P(1)-C(10)-N(1)	49.5(3)
P(1)-Ru(1)-C(4)-C(3)	-155.1(2)	C(11)-P(1)-C(10)-N(1)	-48.4(3)
C(5)-Ru(1)-C(4)-C(3)	114.3(3)	Ru(1)-P(1)-C(10)-N(1)	-172.2(2)
C(1)-Ru(1)-C(4)-C(3)	78.8(2)	C(13)-N(2)-C(11)-P(1)	-59.3(4)
Cl(1)-Ru(1)-C(4)-C(3)	105.7(3)	C(14)-N(2)-C(11)-P(1)	59.7(4)
C(3)-Ru(1)-C(4)-C(5)	-114.3(3)	C(12)-P(1)-C(11)-N(2)	-49.7(3)
C(2)-Ru(1)-C(4)-C(5)	-77.0(2)	C(10)-P(1)-C(11)-N(2)	48.4(3)
P(2)-Ru(1)-C(4)-C(5)	-167.81(18)	Ru(1)-P(1)-C(11)-N(2)	172.3(2)
P(1)-Ru(1)-C(4)-C(5)	90.6(2)	C(15)-N(3)-C(12)-P(1)	59.8(4)
C(1)-Ru(1)-C(4)-C(5)	-35.5(2)	C(14)-N(3)-C(12)-P(1)	-60.7(4)
Cl(1)-Ru(1)-C(4)-C(5)	-8.6(4)	C(11)-P(1)-C(12)-N(3)	49.5(3)
C(9)-C(1)-C(5)-C(6)	0.0(5)	C(10)-P(1)-C(12)-N(3)	-48.6(3)
C(2)-C(1)-C(5)-C(6)	-179.0(3)	Ru(1)-P(1)-C(12)-N(3)	-179.8(2)
Ru(1)-C(1)-C(5)-C(6)	124.2(3)	C(14)-N(2)-C(13)-N(1)	-53.9(4)
C(9)-C(1)-C(5)-C(4)	179.6(3)	C(11)-N(2)-C(13)-N(1)	66.7(4)
C(2)-C(1)-C(5)-C(4)	0.6(4)	C(10)-N(1)-C(13)-N(2)	-67.3(4)
Ru(1)-C(1)-C(5)-C(4)	-56.2(2)	C(15)-N(1)-C(13)-N(2)	54.3(4)
C(9)-C(1)-C(5)-Ru(1)	-124.1(3)	C(15)-N(3)-C(14)-N(2)	-55.6(4)
C(2)-C(1)-C(5)-Ru(1)	56.8(3)	C(12)-N(3)-C(14)-N(2)	67.1(4)
C(3)-C(4)-C(5)-C(6)	175.8(4)	C(13)-N(2)-C(14)-N(3)	54.6(4)
Ru(1)-C(4)-C(5)-C(6)	-119.7(4)	C(11)-N(2)-C(14)-N(3)	-66.0(4)
C(3)-C(4)-C(5)-C(1)	-3.7(4)	C(14)-N(3)-C(15)-N(1)	55.6(4)
Ru(1)-C(4)-C(5)-C(1)	60.8(3)	C(12)-N(3)-C(15)-N(1)	-66.8(4)
C(3)-C(4)-C(5)-Ru(1)	-64.5(2)	C(10)-N(1)-C(15)-N(3)	66.7(4)
C(3)-Ru(1)-C(5)-C(6)	167.2(4)	C(13)-N(1)-C(15)-N(3)	-55.0(4)
C(4)-Ru(1)-C(5)-C(6)	127.6(5)	C(22)-P(2)-C(16)-C(17)	108.3(3)
C(2)-Ru(1)-C(5)-C(6)	-149.5(4)	C(28)-P(2)-C(16)-C(17)	-145.6(3)

Ru(1)-P(2)-C(16)-C(17)	-24.6(4)	C(22)-C(23)-C(24)-C(25)	-2.3(6)
C(22)-P(2)-C(16)-C(21)	-71.3(4)	C(23)-C(24)-C(25)-C(26)	2.8(6)
C(28)-P(2)-C(16)-C(21)	34.8(4)	C(24)-C(25)-C(26)-C(27)	-0.7(6)
Ru(1)-P(2)-C(16)-C(21)	155.8(3)	C(25)-C(26)-C(27)-C(22)	-1.8(6)
C(21)-C(16)-C(17)-C(18)	1.3(6)	C(23)-C(22)-C(27)-C(26)	2.2(6)
P(2)-C(16)-C(17)-C(18)	-178.3(3)	P(2)-C(22)-C(27)-C(26)	-179.5(3)
C(16)-C(17)-C(18)-C(19)	-1.1(6)	C(16)-P(2)-C(28)-C(33)	-130.1(3)
C(17)-C(18)-C(19)-C(20)	0.4(6)	C(22)-P(2)-C(28)-C(33)	-26.1(4)
C(18)-C(19)-C(20)-C(21)	0.1(6)	Ru(1)-P(2)-C(28)-C(33)	106.4(3)
C(19)-C(20)-C(21)-C(16)	0.1(6)	C(16)-P(2)-C(28)-C(29)	52.4(3)
C(17)-C(16)-C(21)-C(20)	-0.8(6)	C(22)-P(2)-C(28)-C(29)	156.4(3)
P(2)-C(16)-C(21)-C(20)	178.8(3)	Ru(1)-P(2)-C(28)-C(29)	-71.1(3)
C(16)-P(2)-C(22)-C(23)	-10.9(4)	C(33)-C(28)-C(29)-C(30)	0.0(6)
C(28)-P(2)-C(22)-C(23)	-114.4(3)	P(2)-C(28)-C(29)-C(30)	177.6(3)
Ru(1)-P(2)-C(22)-C(23)	118.6(3)	C(28)-C(29)-C(30)-C(31)	0.5(6)
C(16)-P(2)-C(22)-C(27)	170.8(3)	C(29)-C(30)-C(31)-C(32)	-0.2(6)
C(28)-P(2)-C(22)-C(27)	67.4(3)	C(30)-C(31)-C(32)-C(33)	-0.7(6)
Ru(1)-P(2)-C(22)-C(27)	-59.7(3)	C(29)-C(28)-C(33)-C(32)	-0.9(6)
C(27)-C(22)-C(23)-C(24)	-0.2(6)	P(2)-C(28)-C(33)-C(32)	-178.3(3)
P(2)-C(22)-C(23)-C(24)	-178.5(3)	C(31)-C(32)-C(33)-C(28)	1.2(6)

Symmetry transformations used to generate equivalent atoms:

Table A17: Bond lengths [\AA] and angles [$^\circ$] for $\text{Cp}^*\text{Ru}(\text{PTA})(\text{PPh}_3)\text{Cl}$.

Ru(1)-Cp* _{cent}	1.868	C(1)-C(2)	1.430(4)
Ru(1)-C(3)	2.208(3)	C(1)-C(5)	1.447(4)
Ru(1)-C(1)	2.218(3)	C(1)-C(6)	1.499(4)
Ru(1)-C(5)	2.236(3)	C(2)-C(3)	1.433(4)
Ru(1)-C(2)	2.241(3)	C(2)-C(7)	1.504(4)
Ru(1)-C(4)	2.254(3)	C(3)-C(4)	1.449(4)
Ru(1)-P(2)	2.2853(7)	C(3)-C(8)	1.502(4)
Ru(1)-P(1)	2.3008(7)	C(4)-C(5)	1.415(4)
Ru(1)-Cl(1)	2.4494(6)	C(4)-C(9)	1.501(4)
P(1)-C(12)	1.853(3)	C(5)-C(10)	1.498(4)
P(1)-C(11)	1.855(3)	C(6)-H(6A)	0.9800
P(1)-C(13)	1.861(3)	C(6)-H(6B)	0.9800
P(2)-C(17)	1.842(3)	C(6)-H(6C)	0.9800
P(2)-C(29)	1.844(3)	C(7)-H(7A)	0.9800
P(2)-C(23)	1.846(3)	C(7)-H(7B)	0.9800
N(1)-C(16)	1.464(3)	C(7)-H(7C)	0.9800
N(1)-C(14)	1.470(4)	C(8)-H(8A)	0.9800
N(1)-C(11)	1.474(3)	C(8)-H(8B)	0.9800
N(2)-C(15)	1.467(3)	C(8)-H(8C)	0.9800
N(2)-C(14)	1.468(4)	C(9)-H(9A)	0.9800
N(2)-C(12)	1.480(3)	C(9)-H(9B)	0.9800
N(3)-C(15)	1.463(4)	C(9)-H(9C)	0.9800
N(3)-C(16)	1.465(3)	C(10)-H(10A)	0.9800
N(3)-C(13)	1.481(3)	C(10)-H(10B)	0.9800

C(10)-H(10C)	0.9800	C(1)-Ru(1)-C(4)	62.64(10)
C(11)-H(11A)	0.9900	C(5)-Ru(1)-C(4)	36.73(10)
C(11)-H(11B)	0.9900	C(2)-Ru(1)-C(4)	62.26(9)
C(12)-H(12A)	0.9900	C(3)-Ru(1)-P(2)	104.53(7)
C(12)-H(12B)	0.9900	C(1)-Ru(1)-P(2)	157.31(7)
C(13)-H(13A)	0.9900	C(5)-Ru(1)-P(2)	120.12(7)
C(13)-H(13B)	0.9900	C(2)-Ru(1)-P(2)	140.04(7)
C(14)-H(14A)	0.9900	C(4)-Ru(1)-P(2)	95.74(7)
C(14)-H(14B)	0.9900	C(3)-Ru(1)-P(1)	114.59(7)
C(15)-H(15A)	0.9900	C(1)-Ru(1)-P(1)	107.62(7)
C(15)-H(15B)	0.9900	C(5)-Ru(1)-P(1)	144.90(7)
C(16)-H(16A)	0.9900	C(2)-Ru(1)-P(1)	93.88(7)
C(16)-H(16B)	0.9900	C(4)-Ru(1)-P(1)	152.37(7)
C(17)-C(18)	1.396(4)	P(2)-Ru(1)-P(1)	94.81(2)
C(17)-C(22)	1.404(4)	C(3)-Ru(1)-Cl(1)	153.10(7)
C(18)-C(19)	1.385(4)	C(1)-Ru(1)-Cl(1)	93.49(7)
C(18)-H(18A)	0.9500	C(5)-Ru(1)-Cl(1)	90.65(7)
C(19)-C(20)	1.384(4)	C(2)-Ru(1)-Cl(1)	127.54(7)
C(19)-H(19A)	0.9500	C(4)-Ru(1)-Cl(1)	120.75(7)
C(20)-C(21)	1.379(4)	P(2)-Ru(1)-Cl(1)	92.14(2)
C(20)-H(20A)	0.9500	P(1)-Ru(1)-Cl(1)	84.22(2)
C(21)-C(22)	1.391(4)	C(12)-P(1)-C(11)	98.56(12)
C(21)-H(21A)	0.9500	C(12)-P(1)-C(13)	96.11(12)
C(22)-H(22A)	0.9500	C(11)-P(1)-C(13)	95.38(12)
C(23)-C(28)	1.389(4)	C(12)-P(1)-Ru(1)	124.11(9)
C(23)-C(24)	1.405(4)	C(11)-P(1)-Ru(1)	112.07(9)
C(24)-C(25)	1.385(4)	C(13)-P(1)-Ru(1)	124.48(9)
C(24)-H(24A)	0.9500	C(17)-P(2)-C(29)	103.75(12)
C(25)-C(26)	1.388(4)	C(17)-P(2)-C(23)	102.72(12)
C(25)-H(25A)	0.9500	C(29)-P(2)-C(23)	97.17(12)
C(26)-C(27)	1.384(4)	C(17)-P(2)-Ru(1)	114.57(9)
C(26)-H(26A)	0.9500	C(29)-P(2)-Ru(1)	118.95(8)
C(27)-C(28)	1.396(4)	C(23)-P(2)-Ru(1)	116.99(9)
C(27)-H(27A)	0.9500	C(16)-N(1)-C(14)	108.9(2)
C(28)-H(28A)	0.9500	C(16)-N(1)-C(11)	110.2(2)
C(29)-C(30)	1.393(4)	C(14)-N(1)-C(11)	110.3(2)
C(29)-C(34)	1.404(4)	C(15)-N(2)-C(14)	108.8(2)
C(30)-C(31)	1.391(4)	C(15)-N(2)-C(12)	110.5(2)
C(30)-H(30A)	0.9500	C(14)-N(2)-C(12)	110.6(2)
C(31)-C(32)	1.387(4)	C(15)-N(3)-C(16)	108.2(2)
C(31)-H(31A)	0.9500	C(15)-N(3)-C(13)	110.6(2)
C(32)-C(33)	1.388(4)	C(16)-N(3)-C(13)	111.9(2)
C(32)-H(32A)	0.9500	C(2)-C(1)-C(5)	107.2(2)
C(33)-C(34)	1.389(4)	C(2)-C(1)-C(6)	128.5(2)
C(33)-H(33A)	0.9500	C(5)-C(1)-C(6)	124.1(2)
C(34)-H(34A)	0.9500	C(2)-C(1)-Ru(1)	72.15(14)
		C(5)-C(1)-Ru(1)	71.71(15)
C(3)-Ru(1)-C(1)	63.32(10)	C(6)-C(1)-Ru(1)	124.53(18)
C(3)-Ru(1)-C(5)	62.79(10)	C(1)-C(2)-C(3)	108.5(2)
C(1)-Ru(1)-C(5)	37.91(9)	C(1)-C(2)-C(7)	128.7(2)
C(3)-Ru(1)-C(2)	37.57(10)	C(3)-C(2)-C(7)	122.1(2)
C(1)-Ru(1)-C(2)	37.41(9)	C(1)-C(2)-Ru(1)	70.45(14)
C(5)-Ru(1)-C(2)	62.32(9)	C(3)-C(2)-Ru(1)	70.00(14)
C(3)-Ru(1)-C(4)	37.87(9)	C(7)-C(2)-Ru(1)	132.84(18)

C(2)-C(3)-C(4)	107.5(2)	N(2)-C(12)-P(1)	113.10(18)
C(2)-C(3)-C(8)	123.9(2)	N(2)-C(12)-H(12A)	109.0
C(4)-C(3)-C(8)	126.9(2)	P(1)-C(12)-H(12A)	109.0
C(2)-C(3)-Ru(1)	72.44(14)	N(2)-C(12)-H(12B)	109.0
C(4)-C(3)-Ru(1)	72.76(14)	P(1)-C(12)-H(12B)	109.0
C(8)-C(3)-Ru(1)	132.07(19)	H(12A)-C(12)-H(12B)	107.8
C(5)-C(4)-C(3)	107.9(2)	N(3)-C(13)-P(1)	113.31(18)
C(5)-C(4)-C(9)	126.2(2)	N(3)-C(13)-H(13A)	108.9
C(3)-C(4)-C(9)	125.4(2)	P(1)-C(13)-H(13A)	108.9
C(5)-C(4)-Ru(1)	70.95(15)	N(3)-C(13)-H(13B)	108.9
C(3)-C(4)-Ru(1)	69.37(14)	P(1)-C(13)-H(13B)	108.9
C(9)-C(4)-Ru(1)	131.74(19)	H(13A)-C(13)-H(13B)	107.7
C(4)-C(5)-C(1)	108.6(2)	N(2)-C(14)-N(1)	115.0(2)
C(4)-C(5)-C(10)	127.3(2)	N(2)-C(14)-H(14A)	108.5
C(1)-C(5)-C(10)	123.8(2)	N(1)-C(14)-H(14A)	108.5
C(4)-C(5)-Ru(1)	72.31(15)	N(2)-C(14)-H(14B)	108.5
C(1)-C(5)-Ru(1)	70.38(14)	N(1)-C(14)-H(14B)	108.5
C(10)-C(5)-Ru(1)	128.08(19)	H(14A)-C(14)-H(14B)	107.5
C(1)-C(6)-H(6A)	109.5	N(3)-C(15)-N(2)	114.6(2)
C(1)-C(6)-H(6B)	109.5	N(3)-C(15)-H(15A)	108.6
H(6A)-C(6)-H(6B)	109.5	N(2)-C(15)-H(15A)	108.6
C(1)-C(6)-H(6C)	109.5	N(3)-C(15)-H(15B)	108.6
H(6A)-C(6)-H(6C)	109.5	N(2)-C(15)-H(15B)	108.6
H(6B)-C(6)-H(6C)	109.5	H(15A)-C(15)-H(15B)	107.6
C(2)-C(7)-H(7A)	109.5	N(1)-C(16)-N(3)	114.3(2)
C(2)-C(7)-H(7B)	109.5	N(1)-C(16)-H(16A)	108.7
H(7A)-C(7)-H(7B)	109.5	N(3)-C(16)-H(16A)	108.7
C(2)-C(7)-H(7C)	109.5	N(1)-C(16)-H(16B)	108.7
H(7A)-C(7)-H(7C)	109.5	N(3)-C(16)-H(16B)	108.7
H(7B)-C(7)-H(7C)	109.5	H(16A)-C(16)-H(16B)	107.6
C(3)-C(8)-H(8A)	109.5	C(18)-C(17)-C(22)	117.7(2)
C(3)-C(8)-H(8B)	109.5	C(18)-C(17)-P(2)	119.69(19)
H(8A)-C(8)-H(8B)	109.5	C(22)-C(17)-P(2)	122.4(2)
C(3)-C(8)-H(8C)	109.5	C(19)-C(18)-C(17)	121.1(2)
H(8A)-C(8)-H(8C)	109.5	C(19)-C(18)-H(18A)	119.5
H(8B)-C(8)-H(8C)	109.5	C(17)-C(18)-H(18A)	119.5
C(4)-C(9)-H(9A)	109.5	C(20)-C(19)-C(18)	120.3(3)
C(4)-C(9)-H(9B)	109.5	C(20)-C(19)-H(19A)	119.8
H(9A)-C(9)-H(9B)	109.5	C(18)-C(19)-H(19A)	119.8
C(4)-C(9)-H(9C)	109.5	C(21)-C(20)-C(19)	119.8(3)
H(9A)-C(9)-H(9C)	109.5	C(21)-C(20)-H(20A)	120.1
H(9B)-C(9)-H(9C)	109.5	C(19)-C(20)-H(20A)	120.1
C(5)-C(10)-H(10A)	109.5	C(20)-C(21)-C(22)	120.2(3)
C(5)-C(10)-H(10B)	109.5	C(20)-C(21)-H(21A)	119.9
H(10A)-C(10)-H(10B)	109.5	C(22)-C(21)-H(21A)	119.9
C(5)-C(10)-H(10C)	109.5	C(21)-C(22)-C(17)	120.9(2)
H(10A)-C(10)-H(10C)	109.5	C(21)-C(22)-H(22A)	119.6
H(10B)-C(10)-H(10C)	109.5	C(17)-C(22)-H(22A)	119.6
N(1)-C(11)-P(1)	114.10(18)	C(28)-C(23)-C(24)	118.7(2)
N(1)-C(11)-H(11A)	108.7	C(28)-C(23)-P(2)	120.1(2)
P(1)-C(11)-H(11A)	108.7	C(24)-C(23)-P(2)	121.0(2)
N(1)-C(11)-H(11B)	108.7	C(25)-C(24)-C(23)	120.6(3)
P(1)-C(11)-H(11B)	108.7	C(25)-C(24)-H(24A)	119.7
H(11A)-C(11)-H(11B)	107.6	C(23)-C(24)-H(24A)	119.7

C(24)-C(25)-C(26)	119.9(3)	C(31)-C(30)-C(29)	120.9(2)
C(24)-C(25)-H(25A)	120.0	C(31)-C(30)-H(30A)	119.5
C(26)-C(25)-H(25A)	120.0	C(29)-C(30)-H(30A)	119.5
C(27)-C(26)-C(25)	120.2(3)	C(32)-C(31)-C(30)	120.2(3)
C(27)-C(26)-H(26A)	119.9	C(32)-C(31)-H(31A)	119.9
C(25)-C(26)-H(26A)	119.9	C(30)-C(31)-H(31A)	119.9
C(26)-C(27)-C(28)	120.0(3)	C(31)-C(32)-C(33)	119.6(2)
C(26)-C(27)-H(27A)	120.0	C(31)-C(32)-H(32A)	120.2
C(28)-C(27)-H(27A)	120.0	C(33)-C(32)-H(32A)	120.2
C(23)-C(28)-C(27)	120.5(3)	C(32)-C(33)-C(34)	120.2(2)
C(23)-C(28)-H(28A)	119.7	C(32)-C(33)-H(33A)	119.9
C(27)-C(28)-H(28A)	119.7	C(34)-C(33)-H(33A)	119.9
C(30)-C(29)-C(34)	118.2(2)	C(33)-C(34)-C(29)	120.8(2)
C(30)-C(29)-P(2)	125.4(2)	C(33)-C(34)-H(34A)	119.6
C(34)-C(29)-P(2)	116.35(19)	C(29)-C(34)-H(34A)	119.6

Symmetry transformations used to generate equivalent atoms:

Table A18: Torsion angles [°] for Cp*Ru(PTA)(PPh₃)Cl.

C(3)-Ru(1)-P(1)-C(12)	39.44(14)	C(3)-Ru(1)-P(2)-C(29)	-142.26(12)
C(1)-Ru(1)-P(1)-C(12)	107.55(13)	C(1)-Ru(1)-P(2)-C(29)	163.38(19)
C(5)-Ru(1)-P(1)-C(12)	116.53(16)	C(5)-Ru(1)-P(2)-C(29)	151.05(12)
C(2)-Ru(1)-P(1)-C(12)	72.02(13)	C(2)-Ru(1)-P(2)-C(29)	-127.22(14)
C(4)-Ru(1)-P(1)-C(12)	43.22(19)	C(4)-Ru(1)-P(2)-C(29)	-179.75(12)
P(2)-Ru(1)-P(1)-C(12)	-68.94(11)	P(1)-Ru(1)-P(2)-C(29)	-25.32(10)
Cl(1)-Ru(1)-P(1)-C(12)	-160.61(11)	Cl(1)-Ru(1)-P(2)-C(29)	59.06(10)
C(3)-Ru(1)-P(1)-C(11)	-78.51(13)	C(3)-Ru(1)-P(2)-C(23)	101.52(12)
C(1)-Ru(1)-P(1)-C(11)	-10.40(12)	C(1)-Ru(1)-P(2)-C(23)	47.2(2)
C(5)-Ru(1)-P(1)-C(11)	-1.42(16)	C(5)-Ru(1)-P(2)-C(23)	34.83(12)
C(2)-Ru(1)-P(1)-C(11)	-45.93(12)	C(2)-Ru(1)-P(2)-C(23)	116.56(14)
C(4)-Ru(1)-P(1)-C(11)	-74.73(18)	C(4)-Ru(1)-P(2)-C(23)	64.03(11)
P(2)-Ru(1)-P(1)-C(11)	173.11(10)	P(1)-Ru(1)-P(2)-C(23)	-141.54(9)
Cl(1)-Ru(1)-P(1)-C(11)	81.44(10)	Cl(1)-Ru(1)-P(2)-C(23)	-57.16(9)
C(3)-Ru(1)-P(1)-C(13)	167.84(13)	C(3)-Ru(1)-C(1)-C(2)	36.56(15)
C(1)-Ru(1)-P(1)-C(13)	-124.05(13)	C(5)-Ru(1)-C(1)-C(2)	115.8(2)
C(5)-Ru(1)-P(1)-C(13)	-115.07(16)	C(4)-Ru(1)-C(1)-C(2)	79.28(16)
C(2)-Ru(1)-P(1)-C(13)	-159.58(13)	P(2)-Ru(1)-C(1)-C(2)	98.3(2)
C(4)-Ru(1)-P(1)-C(13)	171.62(18)	P(1)-Ru(1)-C(1)-C(2)	-72.65(15)
P(2)-Ru(1)-P(1)-C(13)	59.46(11)	Cl(1)-Ru(1)-C(1)-C(2)	-157.68(14)
Cl(1)-Ru(1)-P(1)-C(13)	-32.21(11)	C(3)-Ru(1)-C(1)-C(5)	-79.19(16)
C(3)-Ru(1)-P(2)-C(17)	-18.79(12)	C(2)-Ru(1)-C(1)-C(5)	-115.8(2)
C(1)-Ru(1)-P(2)-C(17)	-73.1(2)	C(4)-Ru(1)-C(1)-C(5)	-36.47(15)
C(5)-Ru(1)-P(2)-C(17)	-85.48(12)	P(2)-Ru(1)-C(1)-C(5)	-17.5(3)
C(2)-Ru(1)-P(2)-C(17)	-3.75(14)	P(1)-Ru(1)-C(1)-C(5)	171.60(13)
C(4)-Ru(1)-P(2)-C(17)	-56.28(11)	Cl(1)-Ru(1)-C(1)-C(5)	86.57(14)
P(1)-Ru(1)-P(2)-C(17)	98.15(9)	C(3)-Ru(1)-C(1)-C(6)	161.5(2)
Cl(1)-Ru(1)-P(2)-C(17)	-177.47(9)	C(5)-Ru(1)-C(1)-C(6)	-119.4(3)

C(2)-Ru(1)-C(1)-C(6)	124.9(3)	C(2)-Ru(1)-C(3)-C(8)	-120.1(3)
C(4)-Ru(1)-C(1)-C(6)	-155.8(2)	C(4)-Ru(1)-C(3)-C(8)	124.5(3)
P(2)-Ru(1)-C(1)-C(6)	-136.85(19)	P(2)-Ru(1)-C(3)-C(8)	44.0(3)
P(1)-Ru(1)-C(1)-C(6)	52.2(2)	P(1)-Ru(1)-C(3)-C(8)	-58.4(3)
Cl(1)-Ru(1)-C(1)-C(6)	-32.8(2)	Cl(1)-Ru(1)-C(3)-C(8)	170.57(17)
C(5)-C(1)-C(2)-C(3)	3.7(3)	C(2)-C(3)-C(4)-C(5)	3.8(3)
C(6)-C(1)-C(2)-C(3)	179.8(3)	C(8)-C(3)-C(4)-C(5)	169.1(3)
Ru(1)-C(1)-C(2)-C(3)	-59.89(18)	Ru(1)-C(3)-C(4)-C(5)	-60.78(18)
C(5)-C(1)-C(2)-C(7)	-166.6(3)	C(2)-C(3)-C(4)-C(9)	-168.2(2)
C(6)-C(1)-C(2)-C(7)	9.5(4)	C(8)-C(3)-C(4)-C(9)	-2.9(4)
Ru(1)-C(1)-C(2)-C(7)	129.8(3)	Ru(1)-C(3)-C(4)-C(9)	127.2(3)
C(5)-C(1)-C(2)-Ru(1)	63.56(17)	C(2)-C(3)-C(4)-Ru(1)	64.59(17)
C(6)-C(1)-C(2)-Ru(1)	-120.3(3)	C(8)-C(3)-C(4)-Ru(1)	-130.1(3)
C(3)-Ru(1)-C(2)-C(1)	-119.2(2)	C(3)-Ru(1)-C(4)-C(5)	118.5(2)
C(5)-Ru(1)-C(2)-C(1)	-38.68(15)	C(1)-Ru(1)-C(4)-C(5)	37.64(15)
C(4)-Ru(1)-C(2)-C(1)	-80.38(16)	C(2)-Ru(1)-C(4)-C(5)	80.04(16)
P(2)-Ru(1)-C(2)-C(1)	-143.53(13)	P(2)-Ru(1)-C(4)-C(5)	-135.12(14)
P(1)-Ru(1)-C(2)-C(1)	114.24(14)	P(1)-Ru(1)-C(4)-C(5)	112.93(18)
Cl(1)-Ru(1)-C(2)-C(1)	28.56(17)	Cl(1)-Ru(1)-C(4)-C(5)	-39.18(17)
C(1)-Ru(1)-C(2)-C(3)	119.2(2)	C(1)-Ru(1)-C(4)-C(3)	-80.90(16)
C(5)-Ru(1)-C(2)-C(3)	80.51(16)	C(5)-Ru(1)-C(4)-C(3)	-118.5(2)
C(4)-Ru(1)-C(2)-C(3)	38.81(15)	C(2)-Ru(1)-C(4)-C(3)	-38.49(15)
P(2)-Ru(1)-C(2)-C(3)	-24.34(19)	P(2)-Ru(1)-C(4)-C(3)	106.34(15)
P(1)-Ru(1)-C(2)-C(3)	-126.57(14)	P(1)-Ru(1)-C(4)-C(3)	-5.6(3)
Cl(1)-Ru(1)-C(2)-C(3)	147.74(12)	Cl(1)-Ru(1)-C(4)-C(3)	-157.71(13)
C(3)-Ru(1)-C(2)-C(7)	115.7(3)	C(3)-Ru(1)-C(4)-C(9)	-119.6(3)
C(1)-Ru(1)-C(2)-C(7)	-125.1(3)	C(1)-Ru(1)-C(4)-C(9)	159.5(3)
C(5)-Ru(1)-C(2)-C(7)	-163.8(3)	C(5)-Ru(1)-C(4)-C(9)	121.9(3)
C(4)-Ru(1)-C(2)-C(7)	154.5(3)	C(2)-Ru(1)-C(4)-C(9)	-158.1(3)
P(2)-Ru(1)-C(2)-C(7)	91.3(3)	P(2)-Ru(1)-C(4)-C(9)	-13.2(3)
P(1)-Ru(1)-C(2)-C(7)	-10.9(3)	P(1)-Ru(1)-C(4)-C(9)	-125.2(2)
Cl(1)-Ru(1)-C(2)-C(7)	-96.6(3)	Cl(1)-Ru(1)-C(4)-C(9)	82.7(3)
C(1)-C(2)-C(3)-C(4)	-4.6(3)	C(3)-C(4)-C(5)-C(1)	-1.6(3)
C(7)-C(2)-C(3)-C(4)	166.5(2)	C(9)-C(4)-C(5)-C(1)	170.3(3)
Ru(1)-C(2)-C(3)-C(4)	-64.80(17)	Ru(1)-C(4)-C(5)-C(1)	-61.34(18)
C(1)-C(2)-C(3)-C(8)	-170.5(2)	C(3)-C(4)-C(5)-C(10)	-175.4(2)
C(7)-C(2)-C(3)-C(8)	0.6(4)	C(9)-C(4)-C(5)-C(10)	-3.5(4)
Ru(1)-C(2)-C(3)-C(8)	129.3(3)	Ru(1)-C(4)-C(5)-C(10)	124.8(3)
C(1)-C(2)-C(3)-Ru(1)	60.17(18)	C(3)-C(4)-C(5)-Ru(1)	59.78(18)
C(7)-C(2)-C(3)-Ru(1)	-128.7(2)	C(9)-C(4)-C(5)-Ru(1)	-128.3(3)
C(1)-Ru(1)-C(3)-C(2)	-36.41(14)	C(2)-C(1)-C(5)-C(4)	-1.3(3)
C(5)-Ru(1)-C(3)-C(2)	-79.15(16)	C(6)-C(1)-C(5)-C(4)	-177.6(2)
C(4)-Ru(1)-C(3)-C(2)	-115.4(2)	Ru(1)-C(1)-C(5)-C(4)	62.57(18)
P(2)-Ru(1)-C(3)-C(2)	164.13(13)	C(2)-C(1)-C(5)-C(10)	172.8(2)
P(1)-Ru(1)-C(3)-C(2)	61.78(15)	C(6)-C(1)-C(5)-C(10)	-3.5(4)
Cl(1)-Ru(1)-C(3)-C(2)	-69.3(2)	Ru(1)-C(1)-C(5)-C(10)	-123.3(3)
C(1)-Ru(1)-C(3)-C(4)	78.95(16)	C(2)-C(1)-C(5)-Ru(1)	-63.85(17)
C(5)-Ru(1)-C(3)-C(4)	36.21(15)	C(6)-C(1)-C(5)-Ru(1)	119.8(3)
C(2)-Ru(1)-C(3)-C(4)	115.4(2)	C(3)-Ru(1)-C(5)-C(4)	-37.33(15)
P(2)-Ru(1)-C(3)-C(4)	-80.51(15)	C(1)-Ru(1)-C(5)-C(4)	-118.0(2)
P(1)-Ru(1)-C(3)-C(4)	177.15(13)	C(2)-Ru(1)-C(5)-C(4)	-79.88(16)
Cl(1)-Ru(1)-C(3)-C(4)	46.1(2)	P(2)-Ru(1)-C(5)-C(4)	54.26(16)
C(1)-Ru(1)-C(3)-C(8)	-156.6(3)	P(1)-Ru(1)-C(5)-C(4)	-132.04(14)
C(5)-Ru(1)-C(3)-C(8)	160.7(3)	Cl(1)-Ru(1)-C(5)-C(4)	147.11(14)

C(3)-Ru(1)-C(5)-C(1)	80.70(16)	C(23)-P(2)-C(17)-C(18)	169.8(2)
C(2)-Ru(1)-C(5)-C(1)	38.16(15)	Ru(1)-P(2)-C(17)-C(18)	-62.3(2)
C(4)-Ru(1)-C(5)-C(1)	118.0(2)	C(29)-P(2)-C(17)-C(22)	-115.5(2)
P(2)-Ru(1)-C(5)-C(1)	172.30(12)	C(23)-P(2)-C(17)-C(22)	-14.8(3)
P(1)-Ru(1)-C(5)-C(1)	-14.0(2)	Ru(1)-P(2)-C(17)-C(22)	113.2(2)
Cl(1)-Ru(1)-C(5)-C(1)	-94.85(14)	C(22)-C(17)-C(18)-C(19)	3.3(4)
C(3)-Ru(1)-C(5)-C(10)	-161.2(3)	P(2)-C(17)-C(18)-C(19)	179.0(2)
C(1)-Ru(1)-C(5)-C(10)	118.1(3)	C(17)-C(18)-C(19)-C(20)	-2.6(4)
C(2)-Ru(1)-C(5)-C(10)	156.3(3)	C(18)-C(19)-C(20)-C(21)	0.0(4)
C(4)-Ru(1)-C(5)-C(10)	-123.9(3)	C(19)-C(20)-C(21)-C(22)	1.7(4)
P(2)-Ru(1)-C(5)-C(10)	-69.6(3)	C(20)-C(21)-C(22)-C(17)	-0.8(4)
P(1)-Ru(1)-C(5)-C(10)	104.1(2)	C(18)-C(17)-C(22)-C(21)	-1.6(4)
Cl(1)-Ru(1)-C(5)-C(10)	23.2(2)	P(2)-C(17)-C(22)-C(21)	-177.2(2)
C(16)-N(1)-C(11)-P(1)	62.4(3)	C(17)-P(2)-C(23)-C(28)	131.4(2)
C(14)-N(1)-C(11)-P(1)	-57.9(3)	C(29)-P(2)-C(23)-C(28)	-122.7(2)
C(12)-P(1)-C(11)-N(1)	45.9(2)	Ru(1)-P(2)-C(23)-C(28)	5.0(2)
C(13)-P(1)-C(11)-N(1)	-51.1(2)	C(17)-P(2)-C(23)-C(24)	-53.4(2)
Ru(1)-P(1)-C(11)-N(1)	178.21(16)	C(29)-P(2)-C(23)-C(24)	52.5(2)
C(15)-N(2)-C(12)-P(1)	-61.6(3)	Ru(1)-P(2)-C(23)-C(24)	-179.79(18)
C(14)-N(2)-C(12)-P(1)	58.9(3)	C(28)-C(23)-C(24)-C(25)	-1.2(4)
C(11)-P(1)-C(12)-N(2)	-46.0(2)	P(2)-C(23)-C(24)-C(25)	-176.5(2)
C(13)-P(1)-C(12)-N(2)	50.4(2)	C(23)-C(24)-C(25)-C(26)	1.2(4)
Ru(1)-P(1)-C(12)-N(2)	-170.07(14)	C(24)-C(25)-C(26)-C(27)	-0.8(4)
C(15)-N(3)-C(13)-P(1)	60.6(3)	C(25)-C(26)-C(27)-C(28)	0.5(4)
C(16)-N(3)-C(13)-P(1)	-60.1(3)	C(24)-C(23)-C(28)-C(27)	0.8(4)
C(12)-P(1)-C(13)-N(3)	-50.0(2)	P(2)-C(23)-C(28)-C(27)	176.1(2)
C(11)-P(1)-C(13)-N(3)	49.3(2)	C(26)-C(27)-C(28)-C(23)	-0.5(4)
Ru(1)-P(1)-C(13)-N(3)	170.75(14)	C(17)-P(2)-C(29)-C(30)	-24.8(2)
C(15)-N(2)-C(14)-N(1)	52.3(3)	C(23)-P(2)-C(29)-C(30)	-129.9(2)
C(12)-N(2)-C(14)-N(1)	-69.2(3)	Ru(1)-P(2)-C(29)-C(30)	103.8(2)
C(16)-N(1)-C(14)-N(2)	-52.8(3)	C(17)-P(2)-C(29)-C(34)	158.44(19)
C(11)-N(1)-C(14)-N(2)	68.3(3)	C(23)-P(2)-C(29)-C(34)	53.4(2)
C(16)-N(3)-C(15)-N(2)	55.9(3)	Ru(1)-P(2)-C(29)-C(34)	-72.9(2)
C(13)-N(3)-C(15)-N(2)	-67.0(3)	C(34)-C(29)-C(30)-C(31)	-0.2(4)
C(14)-N(2)-C(15)-N(3)	-54.1(3)	P(2)-C(29)-C(30)-C(31)	-176.8(2)
C(12)-N(2)-C(15)-N(3)	67.6(3)	C(29)-C(30)-C(31)-C(32)	-0.2(4)
C(14)-N(1)-C(16)-N(3)	54.7(3)	C(30)-C(31)-C(32)-C(33)	0.5(4)
C(11)-N(1)-C(16)-N(3)	-66.4(3)	C(31)-C(32)-C(33)-C(34)	-0.5(4)
C(15)-N(3)-C(16)-N(1)	-56.2(3)	C(32)-C(33)-C(34)-C(29)	0.2(4)
C(13)-N(3)-C(16)-N(1)	66.0(3)	C(30)-C(29)-C(34)-C(33)	0.2(4)
C(29)-P(2)-C(17)-C(18)	69.0(2)	P(2)-C(29)-C(34)-C(33)	177.11(19)

Symmetry transformations used to generate equivalent atoms:

Table A19: Bond lengths [\AA] and angles [$^\circ$] for IndRu(PMe₃)(PPh₃)Cl.

Ru(1)-C(3)	2.165(2)	Ru(1)-P(1)	2.2608(7)
Ru(1)-C(4)	2.175(2)	Ru(1)-P(2)	2.3077(6)
Ru(1)-C(2)	2.210(3)	Ru(1)-C(5)	2.348(3)

Ru(1)-C(1)	2.362(3)	C(16)-C(17)	1.382(4)
Ru(1)-Cl(1)	2.4399(6)	C(16)-H(16)	0.9500
Ru(2)-C(33)	2.155(3)	C(17)-C(18)	1.397(3)
Ru(2)-C(32)	2.181(3)	C(17)-H(17)	0.9500
Ru(2)-C(34)	2.203(3)	C(18)-H(18)	0.9500
Ru(2)-P(3)	2.2546(7)	C(19)-C(20)	1.388(4)
Ru(2)-P(4)	2.3042(7)	C(19)-C(24)	1.408(3)
Ru(2)-C(35)	2.364(3)	C(20)-C(21)	1.398(4)
Ru(2)-C(31)	2.367(3)	C(20)-H(20)	0.9500
Ru(2)-Cl(2)	2.4414(6)	C(21)-C(22)	1.387(4)
P(1)-C(11)	1.816(3)	C(21)-H(21)	0.9500
P(1)-C(10)	1.823(3)	C(22)-C(23)	1.381(4)
P(1)-C(12)	1.827(3)	C(22)-H(22)	0.9500
P(2)-C(19)	1.836(3)	C(23)-C(24)	1.389(4)
P(2)-C(25)	1.839(3)	C(23)-H(23)	0.9500
P(2)-C(13)	1.842(2)	C(24)-H(24)	0.9500
P(3)-C(41)	1.812(3)	C(25)-C(30)	1.386(4)
P(3)-C(40)	1.818(3)	C(25)-C(26)	1.399(3)
P(3)-C(42)	1.826(3)	C(26)-C(27)	1.387(4)
P(4)-C(49)	1.830(3)	C(26)-H(26)	0.9500
P(4)-C(55)	1.837(2)	C(27)-C(28)	1.397(4)
P(4)-C(43)	1.840(2)	C(27)-H(27)	0.9500
C(1)-C(9)	1.414(4)	C(28)-C(29)	1.387(4)
C(1)-C(5)	1.436(3)	C(28)-H(28)	0.9500
C(1)-C(2)	1.456(3)	C(29)-C(30)	1.401(3)
C(2)-C(3)	1.425(4)	C(29)-H(29)	0.9500
C(2)-H(2)	1.0000	C(30)-H(30)	0.9500
C(3)-C(4)	1.427(4)	C(31)-C(39)	1.411(4)
C(3)-H(3)	1.0000	C(31)-C(35)	1.439(3)
C(4)-C(5)	1.433(4)	C(31)-C(32)	1.446(3)
C(4)-H(4)	1.0000	C(32)-C(33)	1.421(4)
C(5)-C(6)	1.415(4)	C(32)-H(32)	1.0000
C(6)-C(7)	1.373(4)	C(33)-C(34)	1.426(4)
C(6)-H(6)	0.9500	C(33)-H(33)	1.0000
C(7)-C(8)	1.412(4)	C(34)-C(35)	1.447(3)
C(7)-H(7)	0.9500	C(34)-H(34)	1.0000
C(8)-C(9)	1.371(4)	C(35)-C(36)	1.418(3)
C(8)-H(8)	0.9500	C(36)-C(37)	1.368(4)
C(9)-H(9)	0.9500	C(36)-H(36)	0.9500
C(10)-H(10A)	0.9800	C(37)-C(38)	1.418(4)
C(10)-H(10B)	0.9800	C(37)-H(37)	0.9500
C(10)-H(10C)	0.9800	C(38)-C(39)	1.374(3)
C(11)-H(11A)	0.9800	C(38)-H(38)	0.9500
C(11)-H(11B)	0.9800	C(39)-H(39)	0.9500
C(11)-H(11C)	0.9800	C(40)-H(40A)	0.9800
C(12)-H(12A)	0.9800	C(40)-H(40B)	0.9800
C(12)-H(12B)	0.9800	C(40)-H(40C)	0.9800
C(12)-H(12C)	0.9800	C(41)-H(41A)	0.9800
C(13)-C(18)	1.396(3)	C(41)-H(41B)	0.9800
C(13)-C(14)	1.406(3)	C(41)-H(41C)	0.9800
C(14)-C(15)	1.385(3)	C(42)-H(42A)	0.9800
C(14)-H(14)	0.9500	C(42)-H(42B)	0.9800
C(15)-C(16)	1.391(4)	C(42)-H(42C)	0.9800
C(15)-H(15)	0.9500	C(43)-C(44)	1.387(3)

C(43)-C(48)	1.403(3)	C(3)-Ru(1)-Cl(1)	133.38(8)
C(44)-C(45)	1.398(3)	C(4)-Ru(1)-Cl(1)	157.40(7)
C(44)-H(44)	0.9500	C(2)-Ru(1)-Cl(1)	98.94(7)
C(45)-C(46)	1.381(4)	P(1)-Ru(1)-Cl(1)	87.03(2)
C(45)-H(45)	0.9500	P(2)-Ru(1)-Cl(1)	92.54(2)
C(46)-C(47)	1.393(4)	C(5)-Ru(1)-Cl(1)	123.12(6)
C(46)-H(46)	0.9500	C(1)-Ru(1)-Cl(1)	95.94(6)
C(47)-C(48)	1.393(3)	C(33)-Ru(2)-C(32)	38.27(10)
C(47)-H(47)	0.9500	C(33)-Ru(2)-C(34)	38.18(9)
C(48)-H(48)	0.9500	C(32)-Ru(2)-C(34)	64.15(10)
C(49)-C(54)	1.394(3)	C(33)-Ru(2)-P(3)	86.36(8)
C(49)-C(50)	1.405(3)	C(32)-Ru(2)-P(3)	109.15(7)
C(50)-C(51)	1.383(4)	C(34)-Ru(2)-P(3)	101.64(7)
C(50)-H(50)	0.9500	C(33)-Ru(2)-P(4)	133.62(8)
C(51)-C(52)	1.388(4)	C(32)-Ru(2)-P(4)	98.89(7)
C(51)-H(51)	0.9500	C(34)-Ru(2)-P(4)	157.52(7)
C(52)-C(53)	1.385(4)	P(3)-Ru(2)-P(4)	97.85(2)
C(52)-H(52)	0.9500	C(33)-Ru(2)-C(35)	61.20(9)
C(53)-C(54)	1.397(4)	C(32)-Ru(2)-C(35)	61.54(9)
C(53)-H(53)	0.9500	C(34)-Ru(2)-C(35)	36.73(9)
C(54)-H(54)	0.9500	P(3)-Ru(2)-C(35)	138.33(6)
C(55)-C(56)	1.392(3)	P(4)-Ru(2)-C(35)	123.22(6)
C(55)-C(60)	1.398(3)	C(33)-Ru(2)-C(31)	61.15(10)
C(56)-C(57)	1.395(3)	C(32)-Ru(2)-C(31)	36.79(9)
C(56)-H(56)	0.9500	C(34)-Ru(2)-C(31)	61.33(9)
C(57)-C(58)	1.381(4)	P(3)-Ru(2)-C(31)	145.06(6)
C(57)-H(57)	0.9500	P(4)-Ru(2)-C(31)	96.20(6)
C(58)-C(59)	1.393(4)	C(35)-Ru(2)-C(31)	35.41(8)
C(58)-H(58)	0.9500	C(33)-Ru(2)-Cl(2)	133.28(8)
C(59)-C(60)	1.384(3)	C(32)-Ru(2)-Cl(2)	157.18(7)
C(59)-H(59)	0.9500	C(34)-Ru(2)-Cl(2)	98.59(7)
C(60)-H(60)	0.9500	P(3)-Ru(2)-Cl(2)	88.18(3)
		P(4)-Ru(2)-Cl(2)	93.09(2)
C(3)-Ru(1)-C(4)	38.39(10)	C(35)-Ru(2)-Cl(2)	95.66(6)
C(3)-Ru(1)-C(2)	37.99(10)	C(31)-Ru(2)-Cl(2)	122.82(6)
C(4)-Ru(1)-C(2)	64.05(10)	C(11)-P(1)-C(10)	99.98(14)
C(3)-Ru(1)-P(1)	86.87(8)	C(11)-P(1)-C(12)	100.91(15)
C(4)-Ru(1)-P(1)	110.11(7)	C(10)-P(1)-C(12)	102.26(13)
C(2)-Ru(1)-P(1)	101.55(7)	C(11)-P(1)-Ru(1)	122.78(10)
C(3)-Ru(1)-P(2)	134.06(7)	C(10)-P(1)-Ru(1)	110.22(10)
C(4)-Ru(1)-P(2)	99.00(7)	C(12)-P(1)-Ru(1)	117.61(10)
C(2)-Ru(1)-P(2)	157.13(7)	C(19)-P(2)-C(25)	98.47(11)
P(1)-Ru(1)-P(2)	98.72(2)	C(19)-P(2)-C(13)	103.79(11)
C(3)-Ru(1)-C(5)	61.32(9)	C(25)-P(2)-C(13)	103.03(11)
C(4)-Ru(1)-C(5)	36.69(9)	C(19)-P(2)-Ru(1)	122.08(8)
C(2)-Ru(1)-C(5)	61.52(9)	C(25)-P(2)-Ru(1)	115.64(8)
P(1)-Ru(1)-C(5)	145.89(6)	C(13)-P(2)-Ru(1)	111.41(8)
P(2)-Ru(1)-C(5)	95.65(6)	C(41)-P(3)-C(40)	100.98(17)
C(3)-Ru(1)-C(1)	61.30(9)	C(41)-P(3)-C(42)	100.37(14)
C(4)-Ru(1)-C(1)	61.47(9)	C(40)-P(3)-C(42)	102.55(13)
C(2)-Ru(1)-C(1)	36.95(9)	C(41)-P(3)-Ru(2)	122.53(10)
P(1)-Ru(1)-C(1)	138.41(6)	C(40)-P(3)-Ru(2)	117.36(11)
P(2)-Ru(1)-C(1)	122.46(6)	C(42)-P(3)-Ru(2)	110.14(9)
C(5)-Ru(1)-C(1)	35.50(8)	C(49)-P(4)-C(55)	104.96(11)

C(49)-P(4)-C(43)	98.97(11)	P(1)-C(11)-H(11B)	109.5
C(55)-P(4)-C(43)	102.47(11)	H(11A)-C(11)-H(11B)	109.5
C(49)-P(4)-Ru(2)	122.95(8)	P(1)-C(11)-H(11C)	109.5
C(55)-P(4)-Ru(2)	109.66(8)	H(11A)-C(11)-H(11C)	109.5
C(43)-P(4)-Ru(2)	115.46(8)	H(11B)-C(11)-H(11C)	109.5
C(9)-C(1)-C(5)	119.8(2)	P(1)-C(12)-H(12A)	109.5
C(9)-C(1)-C(2)	132.5(2)	P(1)-C(12)-H(12B)	109.5
C(5)-C(1)-C(2)	107.6(2)	H(12A)-C(12)-H(12B)	109.5
C(9)-C(1)-Ru(1)	128.49(17)	P(1)-C(12)-H(12C)	109.5
C(5)-C(1)-Ru(1)	71.71(15)	H(12A)-C(12)-H(12C)	109.5
C(2)-C(1)-Ru(1)	65.82(14)	H(12B)-C(12)-H(12C)	109.5
C(3)-C(2)-C(1)	106.9(2)	C(18)-C(13)-C(14)	118.3(2)
C(3)-C(2)-Ru(1)	69.32(14)	C(18)-C(13)-P(2)	123.87(19)
C(1)-C(2)-Ru(1)	77.23(14)	C(14)-C(13)-P(2)	117.55(19)
C(3)-C(2)-H(2)	126.2	C(15)-C(14)-C(13)	121.1(2)
C(1)-C(2)-H(2)	126.2	C(15)-C(14)-H(14)	119.5
Ru(1)-C(2)-H(2)	126.2	C(13)-C(14)-H(14)	119.5
C(2)-C(3)-C(4)	109.2(2)	C(14)-C(15)-C(16)	119.9(3)
C(2)-C(3)-Ru(1)	72.69(14)	C(14)-C(15)-H(15)	120.0
C(4)-C(3)-Ru(1)	71.16(14)	C(16)-C(15)-H(15)	120.0
C(2)-C(3)-H(3)	125.3	C(17)-C(16)-C(15)	119.8(2)
C(4)-C(3)-H(3)	125.3	C(17)-C(16)-H(16)	120.1
Ru(1)-C(3)-H(3)	125.3	C(15)-C(16)-H(16)	120.1
C(3)-C(4)-C(5)	107.5(2)	C(16)-C(17)-C(18)	120.6(3)
C(3)-C(4)-Ru(1)	70.45(14)	C(16)-C(17)-H(17)	119.7
C(5)-C(4)-Ru(1)	78.25(14)	C(18)-C(17)-H(17)	119.7
C(3)-C(4)-H(4)	125.8	C(13)-C(18)-C(17)	120.3(3)
C(5)-C(4)-H(4)	125.8	C(13)-C(18)-H(18)	119.8
Ru(1)-C(4)-H(4)	125.8	C(17)-C(18)-H(18)	119.8
C(6)-C(5)-C(4)	132.0(2)	C(20)-C(19)-C(24)	118.9(2)
C(6)-C(5)-C(1)	119.8(2)	C(20)-C(19)-P(2)	124.72(19)
C(4)-C(5)-C(1)	108.2(2)	C(24)-C(19)-P(2)	116.4(2)
C(6)-C(5)-Ru(1)	128.94(17)	C(19)-C(20)-C(21)	120.3(2)
C(4)-C(5)-Ru(1)	65.05(14)	C(19)-C(20)-H(20)	119.8
C(1)-C(5)-Ru(1)	72.79(14)	C(21)-C(20)-H(20)	119.8
C(7)-C(6)-C(5)	118.6(2)	C(22)-C(21)-C(20)	120.3(3)
C(7)-C(6)-H(6)	120.7	C(22)-C(21)-H(21)	119.8
C(5)-C(6)-H(6)	120.7	C(20)-C(21)-H(21)	119.8
C(6)-C(7)-C(8)	121.6(2)	C(23)-C(22)-C(21)	119.6(3)
C(6)-C(7)-H(7)	119.2	C(23)-C(22)-H(22)	120.2
C(8)-C(7)-H(7)	119.2	C(21)-C(22)-H(22)	120.2
C(9)-C(8)-C(7)	121.2(3)	C(22)-C(23)-C(24)	120.7(2)
C(9)-C(8)-H(8)	119.4	C(22)-C(23)-H(23)	119.7
C(7)-C(8)-H(8)	119.4	C(24)-C(23)-H(23)	119.7
C(8)-C(9)-C(1)	118.8(2)	C(23)-C(24)-C(19)	120.1(3)
C(8)-C(9)-H(9)	120.6	C(23)-C(24)-H(24)	120.0
C(1)-C(9)-H(9)	120.6	C(19)-C(24)-H(24)	120.0
P(1)-C(10)-H(10A)	109.5	C(30)-C(25)-C(26)	119.0(2)
P(1)-C(10)-H(10B)	109.5	C(30)-C(25)-P(2)	120.42(19)
H(10A)-C(10)-H(10B)	109.5	C(26)-C(25)-P(2)	120.5(2)
P(1)-C(10)-H(10C)	109.5	C(27)-C(26)-C(25)	120.5(3)
H(10A)-C(10)-H(10C)	109.5	C(27)-C(26)-H(26)	119.7
H(10B)-C(10)-H(10C)	109.5	C(25)-C(26)-H(26)	119.7
P(1)-C(11)-H(11A)	109.5	C(26)-C(27)-C(28)	120.3(2)

C(26)-C(27)-H(27)	119.9	P(3)-C(40)-H(40B)	109.5
C(28)-C(27)-H(27)	119.9	H(40A)-C(40)-H(40B)	109.5
C(29)-C(28)-C(27)	119.6(2)	P(3)-C(40)-H(40C)	109.5
C(29)-C(28)-H(28)	120.2	H(40A)-C(40)-H(40C)	109.5
C(27)-C(28)-H(28)	120.2	H(40B)-C(40)-H(40C)	109.5
C(28)-C(29)-C(30)	120.0(3)	P(3)-C(41)-H(41A)	109.5
C(28)-C(29)-H(29)	120.0	P(3)-C(41)-H(41B)	109.5
C(30)-C(29)-H(29)	120.0	H(41A)-C(41)-H(41B)	109.5
C(25)-C(30)-C(29)	120.7(2)	P(3)-C(41)-H(41C)	109.5
C(25)-C(30)-H(30)	119.7	H(41A)-C(41)-H(41C)	109.5
C(29)-C(30)-H(30)	119.7	H(41B)-C(41)-H(41C)	109.5
C(39)-C(31)-C(35)	120.1(2)	P(3)-C(42)-H(42A)	109.5
C(39)-C(31)-C(32)	132.1(2)	P(3)-C(42)-H(42B)	109.5
C(35)-C(31)-C(32)	107.8(2)	H(42A)-C(42)-H(42B)	109.5
C(39)-C(31)-Ru(2)	129.63(18)	P(3)-C(42)-H(42C)	109.5
C(35)-C(31)-Ru(2)	72.19(15)	H(42A)-C(42)-H(42C)	109.5
C(32)-C(31)-Ru(2)	64.59(14)	H(42B)-C(42)-H(42C)	109.5
C(33)-C(32)-C(31)	107.2(2)	C(44)-C(43)-C(48)	119.4(2)
C(33)-C(32)-Ru(2)	69.88(15)	C(44)-C(43)-P(4)	120.37(19)
C(31)-C(32)-Ru(2)	78.62(15)	C(48)-C(43)-P(4)	120.22(18)
C(33)-C(32)-H(32)	125.9	C(43)-C(44)-C(45)	119.9(2)
C(31)-C(32)-H(32)	125.9	C(43)-C(44)-H(44)	120.0
Ru(2)-C(32)-H(32)	125.9	C(45)-C(44)-H(44)	120.0
C(32)-C(33)-C(34)	109.7(2)	C(46)-C(45)-C(44)	120.5(2)
C(32)-C(33)-Ru(2)	71.85(15)	C(46)-C(45)-H(45)	119.7
C(34)-C(33)-Ru(2)	72.73(15)	C(44)-C(45)-H(45)	119.7
C(32)-C(33)-H(33)	125.1	C(45)-C(46)-C(47)	120.1(2)
C(34)-C(33)-H(33)	125.1	C(45)-C(46)-H(46)	119.9
Ru(2)-C(33)-H(33)	125.1	C(47)-C(46)-H(46)	119.9
C(33)-C(34)-C(35)	106.9(2)	C(46)-C(47)-C(48)	119.5(2)
C(33)-C(34)-Ru(2)	69.09(15)	C(46)-C(47)-H(47)	120.2
C(35)-C(34)-Ru(2)	77.71(15)	C(48)-C(47)-H(47)	120.2
C(33)-C(34)-H(34)	126.2	C(47)-C(48)-C(43)	120.4(2)
C(35)-C(34)-H(34)	126.2	C(47)-C(48)-H(48)	119.8
Ru(2)-C(34)-H(34)	126.2	C(43)-C(48)-H(48)	119.8
C(36)-C(35)-C(31)	119.2(2)	C(54)-C(49)-C(50)	118.4(2)
C(36)-C(35)-C(34)	132.8(2)	C(54)-C(49)-P(4)	125.1(2)
C(31)-C(35)-C(34)	108.0(2)	C(50)-C(49)-P(4)	116.56(19)
C(36)-C(35)-Ru(2)	128.16(19)	C(51)-C(50)-C(49)	121.2(2)
C(31)-C(35)-Ru(2)	72.40(14)	C(51)-C(50)-H(50)	119.4
C(34)-C(35)-Ru(2)	65.57(14)	C(49)-C(50)-H(50)	119.4
C(37)-C(36)-C(35)	119.3(2)	C(50)-C(51)-C(52)	119.9(3)
C(37)-C(36)-H(36)	120.3	C(50)-C(51)-H(51)	120.1
C(35)-C(36)-H(36)	120.3	C(52)-C(51)-H(51)	120.1
C(36)-C(37)-C(38)	121.3(2)	C(53)-C(52)-C(51)	119.8(3)
C(36)-C(37)-H(37)	119.4	C(53)-C(52)-H(52)	120.1
C(38)-C(37)-H(37)	119.4	C(51)-C(52)-H(52)	120.1
C(39)-C(38)-C(37)	121.1(2)	C(52)-C(53)-C(54)	120.6(3)
C(39)-C(38)-H(38)	119.5	C(52)-C(53)-H(53)	119.7
C(37)-C(38)-H(38)	119.5	C(54)-C(53)-H(53)	119.7
C(38)-C(39)-C(31)	118.9(2)	C(49)-C(54)-C(53)	120.1(3)
C(38)-C(39)-H(39)	120.5	C(49)-C(54)-H(54)	119.9
C(31)-C(39)-H(39)	120.5	C(53)-C(54)-H(54)	119.9
P(3)-C(40)-H(40A)	109.5	C(56)-C(55)-C(60)	118.3(2)

C(56)-C(55)-P(4)	122.42(18)	C(57)-C(58)-H(58)	120.0
C(60)-C(55)-P(4)	118.65(19)	C(59)-C(58)-H(58)	120.0
C(55)-C(56)-C(57)	120.8(2)	C(60)-C(59)-C(58)	119.8(2)
C(55)-C(56)-H(56)	119.6	C(60)-C(59)-H(59)	120.1
C(57)-C(56)-H(56)	119.6	C(58)-C(59)-H(59)	120.1
C(58)-C(57)-C(56)	120.0(2)	C(59)-C(60)-C(55)	121.1(2)
C(58)-C(57)-H(57)	120.0	C(59)-C(60)-H(60)	119.4
C(56)-C(57)-H(57)	120.0	C(55)-C(60)-H(60)	119.4
C(57)-C(58)-C(59)	119.9(2)		

Symmetry transformations used to generate equivalent atoms:

Table A20: Torsion angles [°] for IndRu(PMe₃)(PPh₃)Cl.

C(3)-Ru(1)-P(1)-C(11)	-179.57(15)	C(1)-Ru(1)-P(2)-C(25)	39.85(11)
C(4)-Ru(1)-P(1)-C(11)	149.29(15)	Cl(1)-Ru(1)-P(2)-C(25)	-58.83(9)
C(2)-Ru(1)-P(1)-C(11)	-144.34(15)	C(3)-Ru(1)-P(2)-C(13)	2.49(14)
P(2)-Ru(1)-P(1)-C(11)	46.31(13)	C(4)-Ru(1)-P(2)-C(13)	-15.52(12)
C(5)-Ru(1)-P(1)-C(11)	160.15(17)	C(2)-Ru(1)-P(2)-C(13)	-55.6(2)
C(1)-Ru(1)-P(1)-C(11)	-141.42(16)	P(1)-Ru(1)-P(2)-C(13)	96.59(9)
Cl(1)-Ru(1)-P(1)-C(11)	-45.82(13)	C(5)-Ru(1)-P(2)-C(13)	-52.38(11)
C(3)-Ru(1)-P(1)-C(10)	-62.39(13)	C(1)-Ru(1)-P(2)-C(13)	-77.34(12)
C(4)-Ru(1)-P(1)-C(10)	-93.53(13)	Cl(1)-Ru(1)-P(2)-C(13)	-176.02(9)
C(2)-Ru(1)-P(1)-C(10)	-27.16(12)	C(33)-Ru(2)-P(3)-C(41)	178.32(16)
P(2)-Ru(1)-P(1)-C(10)	163.49(10)	C(32)-Ru(2)-P(3)-C(41)	-150.43(16)
C(5)-Ru(1)-P(1)-C(10)	-82.67(15)	C(34)-Ru(2)-P(3)-C(41)	143.14(16)
C(1)-Ru(1)-P(1)-C(10)	-24.23(14)	P(4)-Ru(2)-P(3)-C(41)	-48.13(15)
Cl(1)-Ru(1)-P(1)-C(10)	71.37(10)	C(35)-Ru(2)-P(3)-C(41)	141.21(17)
C(3)-Ru(1)-P(1)-C(12)	54.22(13)	C(31)-Ru(2)-P(3)-C(41)	-160.94(18)
C(4)-Ru(1)-P(1)-C(12)	23.08(14)	Cl(2)-Ru(2)-P(3)-C(41)	44.74(14)
C(2)-Ru(1)-P(1)-C(12)	89.46(13)	C(33)-Ru(2)-P(3)-C(40)	-55.92(15)
P(2)-Ru(1)-P(1)-C(12)	-79.90(12)	C(32)-Ru(2)-P(3)-C(40)	-24.66(15)
C(5)-Ru(1)-P(1)-C(12)	33.94(17)	C(34)-Ru(2)-P(3)-C(40)	-91.10(15)
C(1)-Ru(1)-P(1)-C(12)	92.38(15)	P(4)-Ru(2)-P(3)-C(40)	77.63(13)
Cl(1)-Ru(1)-P(1)-C(12)	-172.02(12)	C(35)-Ru(2)-P(3)-C(40)	-93.03(16)
C(3)-Ru(1)-P(2)-C(19)	-120.72(14)	C(31)-Ru(2)-P(3)-C(40)	-35.18(17)
C(4)-Ru(1)-P(2)-C(19)	-138.74(12)	Cl(2)-Ru(2)-P(3)-C(40)	170.50(13)
C(2)-Ru(1)-P(2)-C(19)	-178.9(2)	C(33)-Ru(2)-P(3)-C(42)	60.84(13)
P(1)-Ru(1)-P(2)-C(19)	-26.62(10)	C(32)-Ru(2)-P(3)-C(42)	92.10(13)
C(5)-Ru(1)-P(2)-C(19)	-175.60(11)	C(34)-Ru(2)-P(3)-C(42)	25.66(13)
C(1)-Ru(1)-P(2)-C(19)	159.44(12)	P(4)-Ru(2)-P(3)-C(42)	-165.60(11)
Cl(1)-Ru(1)-P(2)-C(19)	60.76(10)	C(35)-Ru(2)-P(3)-C(42)	23.74(14)
C(3)-Ru(1)-P(2)-C(25)	119.68(13)	C(31)-Ru(2)-P(3)-C(42)	81.59(15)
C(4)-Ru(1)-P(2)-C(25)	101.67(11)	Cl(2)-Ru(2)-P(3)-C(42)	-72.73(11)
C(2)-Ru(1)-P(2)-C(25)	61.5(2)	C(33)-Ru(2)-P(4)-C(49)	120.03(14)
P(1)-Ru(1)-P(2)-C(25)	-146.22(8)	C(32)-Ru(2)-P(4)-C(49)	138.47(11)
C(5)-Ru(1)-P(2)-C(25)	64.81(10)	C(34)-Ru(2)-P(4)-C(49)	177.55(19)

P(3)-Ru(2)-P(4)-C(49)	27.58(10)	C(1)-C(2)-C(3)-C(4)	6.6(3)
C(35)-Ru(2)-P(4)-C(49)	-159.84(12)	Ru(1)-C(2)-C(3)-C(4)	-62.15(18)
C(31)-Ru(2)-P(4)-C(49)	175.50(11)	C(1)-C(2)-C(3)-Ru(1)	68.79(17)
Cl(2)-Ru(2)-P(4)-C(49)	-61.01(10)	C(4)-Ru(1)-C(3)-C(2)	-118.1(2)
C(33)-Ru(2)-P(4)-C(55)	-3.91(13)	P(1)-Ru(1)-C(3)-C(2)	113.32(15)
C(32)-Ru(2)-P(4)-C(55)	14.53(11)	P(2)-Ru(1)-C(3)-C(2)	-147.57(13)
C(34)-Ru(2)-P(4)-C(55)	53.6(2)	C(5)-Ru(1)-C(3)-C(2)	-79.48(17)
P(3)-Ru(2)-P(4)-C(55)	-96.37(9)	C(1)-Ru(1)-C(3)-C(2)	-38.81(15)
C(35)-Ru(2)-P(4)-C(55)	76.22(11)	Cl(1)-Ru(1)-C(3)-C(2)	30.4(2)
C(31)-Ru(2)-P(4)-C(55)	51.55(10)	C(2)-Ru(1)-C(3)-C(4)	118.1(2)
Cl(2)-Ru(2)-P(4)-C(55)	175.05(8)	P(1)-Ru(1)-C(3)-C(4)	-128.58(15)
C(33)-Ru(2)-P(4)-C(43)	-119.01(13)	P(2)-Ru(1)-C(3)-C(4)	-29.5(2)
C(32)-Ru(2)-P(4)-C(43)	-100.56(11)	C(5)-Ru(1)-C(3)-C(4)	38.63(15)
C(34)-Ru(2)-P(4)-C(43)	-61.5(2)	C(1)-Ru(1)-C(3)-C(4)	79.30(17)
P(3)-Ru(2)-P(4)-C(43)	148.54(9)	Cl(1)-Ru(1)-C(3)-C(4)	148.50(13)
C(35)-Ru(2)-P(4)-C(43)	-38.87(12)	C(2)-C(3)-C(4)-C(5)	-7.1(3)
C(31)-Ru(2)-P(4)-C(43)	-63.54(11)	Ru(1)-C(3)-C(4)-C(5)	-70.20(17)
Cl(2)-Ru(2)-P(4)-C(43)	59.96(9)	C(2)-C(3)-C(4)-Ru(1)	63.12(18)
C(3)-Ru(1)-C(1)-C(9)	166.1(3)	C(2)-Ru(1)-C(4)-C(3)	-37.14(16)
C(4)-Ru(1)-C(1)-C(9)	-149.9(3)	P(1)-Ru(1)-C(4)-C(3)	56.23(16)
C(2)-Ru(1)-C(1)-C(9)	126.1(3)	P(2)-Ru(1)-C(4)-C(3)	159.03(15)
P(1)-Ru(1)-C(1)-C(9)	121.4(2)	C(5)-Ru(1)-C(4)-C(3)	-113.6(2)
P(2)-Ru(1)-C(1)-C(9)	-67.7(2)	C(1)-Ru(1)-C(4)-C(3)	-78.80(17)
C(5)-Ru(1)-C(1)-C(9)	-114.0(3)	Cl(1)-Ru(1)-C(4)-C(3)	-81.2(2)
Cl(1)-Ru(1)-C(1)-C(9)	29.1(2)	C(3)-Ru(1)-C(4)-C(5)	113.6(2)
C(3)-Ru(1)-C(1)-C(5)	-79.94(16)	C(2)-Ru(1)-C(4)-C(5)	76.44(16)
C(4)-Ru(1)-C(1)-C(5)	-35.95(14)	P(1)-Ru(1)-C(4)-C(5)	169.82(13)
C(2)-Ru(1)-C(1)-C(5)	-119.9(2)	P(2)-Ru(1)-C(4)-C(5)	-87.39(14)
P(1)-Ru(1)-C(1)-C(5)	-124.64(13)	C(1)-Ru(1)-C(4)-C(5)	34.78(14)
P(2)-Ru(1)-C(1)-C(5)	46.31(15)	Cl(1)-Ru(1)-C(4)-C(5)	32.4(3)
Cl(1)-Ru(1)-C(1)-C(5)	143.15(13)	C(3)-C(4)-C(5)-C(6)	-174.2(3)
C(3)-Ru(1)-C(1)-C(2)	39.93(15)	Ru(1)-C(4)-C(5)-C(6)	120.9(3)
C(4)-Ru(1)-C(1)-C(2)	83.92(16)	C(3)-C(4)-C(5)-C(1)	4.7(3)
P(1)-Ru(1)-C(1)-C(2)	-4.77(19)	Ru(1)-C(4)-C(5)-C(1)	-60.22(18)
P(2)-Ru(1)-C(1)-C(2)	166.18(12)	C(3)-C(4)-C(5)-Ru(1)	64.91(17)
C(5)-Ru(1)-C(1)-C(2)	119.9(2)	C(9)-C(1)-C(5)-C(6)	-1.0(4)
Cl(1)-Ru(1)-C(1)-C(2)	-96.99(14)	C(2)-C(1)-C(5)-C(6)	178.4(2)
C(9)-C(1)-C(2)-C(3)	175.6(3)	Ru(1)-C(1)-C(5)-C(6)	-125.5(2)
C(5)-C(1)-C(2)-C(3)	-3.7(3)	C(9)-C(1)-C(5)-C(4)	180.0(2)
Ru(1)-C(1)-C(2)-C(3)	-63.42(17)	C(2)-C(1)-C(5)-C(4)	-0.6(3)
C(9)-C(1)-C(2)-Ru(1)	-120.9(3)	Ru(1)-C(1)-C(5)-C(4)	55.48(17)
C(5)-C(1)-C(2)-Ru(1)	59.77(17)	C(9)-C(1)-C(5)-Ru(1)	124.5(2)
C(4)-Ru(1)-C(2)-C(3)	37.53(16)	C(2)-C(1)-C(5)-Ru(1)	-56.11(17)
P(1)-Ru(1)-C(2)-C(3)	-69.38(16)	C(3)-Ru(1)-C(5)-C(6)	-165.4(3)
P(2)-Ru(1)-C(2)-C(3)	82.6(2)	C(4)-Ru(1)-C(5)-C(6)	-124.9(3)
C(5)-Ru(1)-C(2)-C(3)	78.90(17)	C(2)-Ru(1)-C(5)-C(6)	151.1(3)
C(1)-Ru(1)-C(2)-C(3)	113.9(2)	P(1)-Ru(1)-C(5)-C(6)	-142.17(19)
Cl(1)-Ru(1)-C(2)-C(3)	-158.15(15)	P(2)-Ru(1)-C(5)-C(6)	-27.5(2)
C(3)-Ru(1)-C(2)-C(1)	-113.9(2)	C(1)-Ru(1)-C(5)-C(6)	114.7(3)
C(4)-Ru(1)-C(2)-C(1)	-76.32(15)	Cl(1)-Ru(1)-C(5)-C(6)	69.3(2)
P(1)-Ru(1)-C(2)-C(1)	176.77(13)	C(3)-Ru(1)-C(5)-C(4)	-40.45(16)
P(2)-Ru(1)-C(2)-C(1)	-31.3(3)	C(2)-Ru(1)-C(5)-C(4)	-83.96(17)
C(5)-Ru(1)-C(2)-C(1)	-34.95(14)	P(1)-Ru(1)-C(5)-C(4)	-17.2(2)
Cl(1)-Ru(1)-C(2)-C(1)	88.00(14)	P(2)-Ru(1)-C(5)-C(4)	97.48(15)

C(1)-Ru(1)-C(5)-C(4)	-120.3(2)	C(26)-C(27)-C(28)-C(29)	0.2(4)
Cl(1)-Ru(1)-C(5)-C(4)	-165.75(13)	C(27)-C(28)-C(29)-C(30)	-0.6(4)
C(3)-Ru(1)-C(5)-C(1)	79.88(16)	C(26)-C(25)-C(30)-C(29)	1.3(4)
C(4)-Ru(1)-C(5)-C(1)	120.3(2)	P(2)-C(25)-C(30)-C(29)	-179.10(18)
C(2)-Ru(1)-C(5)-C(1)	36.37(14)	C(28)-C(29)-C(30)-C(25)	-0.2(4)
P(1)-Ru(1)-C(5)-C(1)	103.11(16)	C(33)-Ru(2)-C(31)-C(39)	165.3(3)
P(2)-Ru(1)-C(5)-C(1)	-142.19(13)	C(32)-Ru(2)-C(31)-C(39)	124.8(3)
Cl(1)-Ru(1)-C(5)-C(1)	-45.42(16)	C(34)-Ru(2)-C(31)-C(39)	-150.9(3)
C(4)-C(5)-C(6)-C(7)	176.8(3)	P(3)-Ru(2)-C(31)-C(39)	141.49(18)
C(1)-C(5)-C(6)-C(7)	-1.9(4)	P(4)-Ru(2)-C(31)-C(39)	28.2(2)
Ru(1)-C(5)-C(6)-C(7)	-93.3(3)	C(35)-Ru(2)-C(31)-C(39)	-114.7(3)
C(5)-C(6)-C(7)-C(8)	2.5(4)	Cl(2)-Ru(2)-C(31)-C(39)	-69.5(2)
C(6)-C(7)-C(8)-C(9)	-0.1(4)	C(33)-Ru(2)-C(31)-C(35)	-79.97(16)
C(7)-C(8)-C(9)-C(1)	-2.9(4)	C(32)-Ru(2)-C(31)-C(35)	-120.5(2)
C(5)-C(1)-C(9)-C(8)	3.4(4)	C(34)-Ru(2)-C(31)-C(35)	-36.16(14)
C(2)-C(1)-C(9)-C(8)	-175.8(3)	P(3)-Ru(2)-C(31)-C(35)	-103.77(15)
Ru(1)-C(1)-C(9)-C(8)	93.0(3)	P(4)-Ru(2)-C(31)-C(35)	142.95(13)
C(19)-P(2)-C(13)-C(18)	-110.9(2)	Cl(2)-Ru(2)-C(31)-C(35)	45.21(16)
C(25)-P(2)-C(13)-C(18)	-8.6(2)	C(33)-Ru(2)-C(31)-C(32)	40.53(16)
Ru(1)-P(2)-C(13)-C(18)	116.0(2)	C(34)-Ru(2)-C(31)-C(32)	84.34(17)
C(19)-P(2)-C(13)-C(14)	75.0(2)	P(3)-Ru(2)-C(31)-C(32)	16.7(2)
C(25)-P(2)-C(13)-C(14)	177.2(2)	P(4)-Ru(2)-C(31)-C(32)	-96.56(15)
Ru(1)-P(2)-C(13)-C(14)	-58.2(2)	C(35)-Ru(2)-C(31)-C(32)	120.5(2)
C(18)-C(13)-C(14)-C(15)	0.8(4)	Cl(2)-Ru(2)-C(31)-C(32)	165.70(13)
P(2)-C(13)-C(14)-C(15)	175.2(2)	C(39)-C(31)-C(32)-C(33)	173.9(3)
C(13)-C(14)-C(15)-C(16)	-0.8(4)	C(35)-C(31)-C(32)-C(33)	-5.1(3)
C(14)-C(15)-C(16)-C(17)	0.7(4)	Ru(2)-C(31)-C(32)-C(33)	-64.57(18)
C(15)-C(16)-C(17)-C(18)	-0.6(4)	C(39)-C(31)-C(32)-Ru(2)	-121.5(3)
C(14)-C(13)-C(18)-C(17)	-0.6(4)	C(35)-C(31)-C(32)-Ru(2)	59.48(19)
P(2)-C(13)-C(18)-C(17)	-174.7(2)	C(34)-Ru(2)-C(32)-C(33)	37.24(15)
C(16)-C(17)-C(18)-C(13)	0.6(4)	P(3)-Ru(2)-C(32)-C(33)	-56.73(15)
C(25)-P(2)-C(19)-C(20)	-119.2(2)	P(4)-Ru(2)-C(32)-C(33)	-158.30(13)
C(13)-P(2)-C(19)-C(20)	-13.5(2)	C(35)-Ru(2)-C(32)-C(33)	78.61(16)
Ru(1)-P(2)-C(19)-C(20)	113.2(2)	C(31)-Ru(2)-C(32)-C(33)	113.2(2)
C(25)-P(2)-C(19)-C(24)	62.3(2)	Cl(2)-Ru(2)-C(32)-C(33)	80.9(2)
C(13)-P(2)-C(19)-C(24)	168.02(19)	C(33)-Ru(2)-C(32)-C(31)	-113.2(2)
Ru(1)-P(2)-C(19)-C(24)	-65.3(2)	C(34)-Ru(2)-C(32)-C(31)	-75.98(16)
C(24)-C(19)-C(20)-C(21)	0.8(4)	P(3)-Ru(2)-C(32)-C(31)	-169.95(13)
P(2)-C(19)-C(20)-C(21)	-177.7(2)	P(4)-Ru(2)-C(32)-C(31)	88.48(14)
C(19)-C(20)-C(21)-C(22)	-0.7(4)	C(35)-Ru(2)-C(32)-C(31)	-34.61(14)
C(20)-C(21)-C(22)-C(23)	0.1(4)	Cl(2)-Ru(2)-C(32)-C(31)	-32.4(3)
C(21)-C(22)-C(23)-C(24)	0.3(4)	C(31)-C(32)-C(33)-C(34)	7.2(3)
C(22)-C(23)-C(24)-C(19)	-0.2(4)	Ru(2)-C(32)-C(33)-C(34)	-63.3(2)
C(20)-C(19)-C(24)-C(23)	-0.4(4)	C(31)-C(32)-C(33)-Ru(2)	70.54(18)
P(2)-C(19)-C(24)-C(23)	178.2(2)	C(34)-Ru(2)-C(33)-C(32)	-118.2(2)
C(19)-P(2)-C(25)-C(30)	-130.1(2)	P(3)-Ru(2)-C(33)-C(32)	127.68(14)
C(13)-P(2)-C(25)-C(30)	123.6(2)	P(4)-Ru(2)-C(33)-C(32)	30.31(19)
Ru(1)-P(2)-C(25)-C(30)	1.8(2)	C(35)-Ru(2)-C(33)-C(32)	-79.55(16)
C(19)-P(2)-C(25)-C(26)	49.5(2)	C(31)-Ru(2)-C(33)-C(32)	-38.92(14)
C(13)-P(2)-C(25)-C(26)	-56.9(2)	Cl(2)-Ru(2)-C(33)-C(32)	-148.27(12)
Ru(1)-P(2)-C(25)-C(26)	-178.69(16)	C(32)-Ru(2)-C(33)-C(34)	118.2(2)
C(30)-C(25)-C(26)-C(27)	-1.7(4)	P(3)-Ru(2)-C(33)-C(34)	-114.09(15)
P(2)-C(25)-C(26)-C(27)	178.70(18)	P(4)-Ru(2)-C(33)-C(34)	148.54(13)
C(25)-C(26)-C(27)-C(28)	1.0(4)	C(35)-Ru(2)-C(33)-C(34)	38.68(15)

C(31)-Ru(2)-C(33)-C(34)	79.31(16)	C(34)-C(35)-C(36)-C(37)	176.2(3)
Cl(2)-Ru(2)-C(33)-C(34)	-30.0(2)	Ru(2)-C(35)-C(36)-C(37)	-93.2(3)
C(32)-C(33)-C(34)-C(35)	-6.5(3)	C(35)-C(36)-C(37)-C(38)	2.5(4)
Ru(2)-C(33)-C(34)-C(35)	-69.26(18)	C(36)-C(37)-C(38)-C(39)	0.0(4)
C(32)-C(33)-C(34)-Ru(2)	62.77(19)	C(37)-C(38)-C(39)-C(31)	-1.8(4)
C(32)-Ru(2)-C(34)-C(33)	-37.33(16)	C(35)-C(31)-C(39)-C(38)	0.9(4)
P(3)-Ru(2)-C(34)-C(33)	68.47(16)	C(32)-C(31)-C(39)-C(38)	-178.0(3)
P(4)-Ru(2)-C(34)-C(33)	-81.1(2)	Ru(2)-C(31)-C(39)-C(38)	92.2(3)
C(35)-Ru(2)-C(34)-C(33)	-113.7(2)	C(49)-P(4)-C(43)-C(44)	131.2(2)
C(31)-Ru(2)-C(34)-C(33)	-78.79(17)	C(55)-P(4)-C(43)-C(44)	-121.2(2)
Cl(2)-Ru(2)-C(34)-C(33)	158.37(15)	Ru(2)-P(4)-C(43)-C(44)	-2.0(2)
C(33)-Ru(2)-C(34)-C(35)	113.7(2)	C(49)-P(4)-C(43)-C(48)	-48.4(2)
C(32)-Ru(2)-C(34)-C(35)	76.34(16)	C(55)-P(4)-C(43)-C(48)	59.2(2)
P(3)-Ru(2)-C(34)-C(35)	-177.86(13)	Ru(2)-P(4)-C(43)-C(48)	178.37(18)
P(4)-Ru(2)-C(34)-C(35)	32.5(3)	C(48)-C(43)-C(44)-C(45)	-2.0(4)
C(31)-Ru(2)-C(34)-C(35)	34.87(14)	P(4)-C(43)-C(44)-C(45)	178.4(2)
Cl(2)-Ru(2)-C(34)-C(35)	-87.96(14)	C(43)-C(44)-C(45)-C(46)	0.5(4)
C(39)-C(31)-C(35)-C(36)	1.6(4)	C(44)-C(45)-C(46)-C(47)	0.5(4)
C(32)-C(31)-C(35)-C(36)	-179.2(2)	C(45)-C(46)-C(47)-C(48)	-0.1(4)
Ru(2)-C(31)-C(35)-C(36)	-124.4(2)	C(46)-C(47)-C(48)-C(43)	-1.3(4)
C(39)-C(31)-C(35)-C(34)	-178.0(2)	C(44)-C(43)-C(48)-C(47)	2.4(4)
C(32)-C(31)-C(35)-C(34)	1.2(3)	P(4)-C(43)-C(48)-C(47)	-178.0(2)
Ru(2)-C(31)-C(35)-C(34)	55.98(18)	C(55)-P(4)-C(49)-C(54)	9.0(2)
C(39)-C(31)-C(35)-Ru(2)	126.0(2)	C(43)-P(4)-C(49)-C(54)	114.6(2)
C(32)-C(31)-C(35)-Ru(2)	-54.82(18)	Ru(2)-P(4)-C(49)-C(54)	-117.0(2)
C(33)-C(34)-C(35)-C(36)	-176.3(3)	C(55)-P(4)-C(49)-C(50)	-171.07(18)
Ru(2)-C(34)-C(35)-C(36)	120.3(3)	C(43)-P(4)-C(49)-C(50)	-65.5(2)
C(33)-C(34)-C(35)-C(31)	3.2(3)	Ru(2)-P(4)-C(49)-C(50)	62.9(2)
Ru(2)-C(34)-C(35)-C(31)	-60.20(19)	C(54)-C(49)-C(50)-C(51)	0.8(4)
C(33)-C(34)-C(35)-Ru(2)	63.39(18)	P(4)-C(49)-C(50)-C(51)	-179.15(19)
C(33)-Ru(2)-C(35)-C(36)	-166.6(3)	C(49)-C(50)-C(51)-C(52)	0.5(4)
C(32)-Ru(2)-C(35)-C(36)	149.6(3)	C(50)-C(51)-C(52)-C(53)	-1.1(4)
C(34)-Ru(2)-C(35)-C(36)	-126.3(3)	C(51)-C(52)-C(53)-C(54)	0.4(4)
P(3)-Ru(2)-C(35)-C(36)	-123.2(2)	C(50)-C(49)-C(54)-C(53)	-1.4(4)
P(4)-Ru(2)-C(35)-C(36)	67.9(2)	P(4)-C(49)-C(54)-C(53)	178.5(2)
C(31)-Ru(2)-C(35)-C(36)	113.6(3)	C(52)-C(53)-C(54)-C(49)	0.8(4)
Cl(2)-Ru(2)-C(35)-C(36)	-29.6(2)	C(49)-P(4)-C(55)-C(56)	121.5(2)
C(33)-Ru(2)-C(35)-C(31)	79.80(16)	C(43)-P(4)-C(55)-C(56)	18.5(2)
C(32)-Ru(2)-C(35)-C(31)	35.94(14)	Ru(2)-P(4)-C(55)-C(56)	-104.6(2)
C(34)-Ru(2)-C(35)-C(31)	120.0(2)	C(49)-P(4)-C(55)-C(60)	-67.6(2)
P(3)-Ru(2)-C(35)-C(31)	123.19(13)	C(43)-P(4)-C(55)-C(60)	-170.6(2)
P(4)-Ru(2)-C(35)-C(31)	-45.73(16)	Ru(2)-P(4)-C(55)-C(60)	66.3(2)
Cl(2)-Ru(2)-C(35)-C(31)	-143.18(13)	C(60)-C(55)-C(56)-C(57)	-2.0(4)
C(33)-Ru(2)-C(35)-C(34)	-40.24(16)	P(4)-C(55)-C(56)-C(57)	169.0(2)
C(32)-Ru(2)-C(35)-C(34)	-84.10(16)	C(55)-C(56)-C(57)-C(58)	1.8(4)
P(3)-Ru(2)-C(35)-C(34)	3.15(19)	C(56)-C(57)-C(58)-C(59)	-0.1(4)
P(4)-Ru(2)-C(35)-C(34)	-165.76(13)	C(57)-C(58)-C(59)-C(60)	-1.4(4)
C(31)-Ru(2)-C(35)-C(34)	-120.0(2)	C(58)-C(59)-C(60)-C(55)	1.2(4)
Cl(2)-Ru(2)-C(35)-C(34)	96.78(14)	C(56)-C(55)-C(60)-C(59)	0.5(4)
C(31)-C(35)-C(36)-C(37)	-3.3(4)	P(4)-C(55)-C(60)-C(59)	-170.8(2)

Symmetry transformations used to generate equivalent atoms:

Table A21: Bond lengths [Å] and angles [°] for TpRu(PMe₃)(PPh₃)Cl.

Ru(1)-N(1)	2.097(3)	C(12)-H(12)	0.9500
Ru(1)-N(5)	2.132(3)	C(13)-C(14)	1.378(5)
Ru(1)-N(3)	2.162(3)	C(13)-H(13)	0.9500
Ru(1)-P(1)	2.2993(11)	C(14)-C(15)	1.381(5)
Ru(1)-P(2)	2.3125(9)	C(14)-H(14)	0.9500
Ru(1)-Cl(1)	2.4046(8)	C(15)-H(15)	0.9500
B(1)-N(2)	1.524(5)	C(16)-C(21)	1.388(5)
B(1)-N(6)	1.533(5)	C(16)-C(17)	1.405(5)
B(1)-N(4)	1.549(5)	C(17)-C(18)	1.388(5)
B(1)-H(1)	1.0000	C(17)-H(17)	0.9500
P(1)-C(1)	1.824(3)	C(18)-C(19)	1.378(6)
P(1)-C(3)	1.831(4)	C(18)-H(18)	0.9500
P(1)-C(2)	1.832(4)	C(19)-C(20)	1.385(5)
P(2)-C(10)	1.832(3)	C(19)-H(19)	0.9500
P(2)-C(4)	1.839(3)	C(20)-C(21)	1.382(5)
P(2)-C(16)	1.855(4)	C(20)-H(20)	0.9500
N(1)-C(22)	1.336(4)	C(21)-H(21)	0.9500
N(1)-N(2)	1.373(4)	C(22)-C(23)	1.395(5)
N(2)-C(24)	1.348(4)	C(22)-H(22)	0.9500
N(3)-C(25)	1.329(4)	C(23)-C(24)	1.367(5)
N(3)-N(4)	1.377(4)	C(23)-H(23)	0.9500
N(4)-C(27)	1.351(5)	C(24)-H(24)	0.9500
N(5)-C(28)	1.342(4)	C(25)-C(26)	1.401(5)
N(5)-N(6)	1.364(4)	C(25)-H(25)	0.9500
N(6)-C(30)	1.351(4)	C(26)-C(27)	1.367(5)
C(1)-H(1A)	0.9800	C(26)-H(26)	0.9500
C(1)-H(1B)	0.9800	C(27)-H(27)	0.9500
C(1)-H(1C)	0.9800	C(28)-C(29)	1.394(5)
C(2)-H(2A)	0.9800	C(28)-H(28)	0.9500
C(2)-H(2B)	0.9800	C(29)-C(30)	1.373(5)
C(2)-H(2C)	0.9800	C(29)-H(29)	0.9500
C(3)-H(3A)	0.9800	C(30)-H(30)	0.9500
C(3)-H(3B)	0.9800		
C(3)-H(3C)	0.9800	N(1)-Ru(1)-N(5)	88.29(10)
C(4)-C(9)	1.390(5)	N(1)-Ru(1)-N(3)	86.41(11)
C(4)-C(5)	1.394(5)	N(5)-Ru(1)-N(3)	81.88(11)
C(5)-C(6)	1.383(5)	N(1)-Ru(1)-P(1)	88.80(9)
C(5)-H(5)	0.9500	N(5)-Ru(1)-P(1)	86.65(8)
C(6)-C(7)	1.388(5)	N(3)-Ru(1)-P(1)	167.68(8)
C(6)-H(6)	0.9500	N(1)-Ru(1)-P(2)	96.28(8)
C(7)-C(8)	1.378(5)	N(5)-Ru(1)-P(2)	174.59(8)
C(7)-H(7)	0.9500	N(3)-Ru(1)-P(2)	95.49(8)
C(8)-C(9)	1.381(5)	P(1)-Ru(1)-P(2)	96.31(3)
C(8)-H(8)	0.9500	N(1)-Ru(1)-Cl(1)	171.71(7)
C(9)-H(9)	0.9500	N(5)-Ru(1)-Cl(1)	84.56(8)
C(10)-C(15)	1.391(5)	N(3)-Ru(1)-Cl(1)	88.41(7)
C(10)-C(11)	1.406(5)	P(1)-Ru(1)-Cl(1)	94.98(3)
C(11)-C(12)	1.386(5)	P(2)-Ru(1)-Cl(1)	90.66(3)
C(11)-H(11)	0.9500	N(2)-B(1)-N(6)	109.4(3)
C(12)-C(13)	1.383(5)	N(2)-B(1)-N(4)	109.4(3)

N(6)-B(1)-N(4)	106.8(3)	C(5)-C(4)-P(2)	120.8(3)
N(2)-B(1)-H(1)	110.4	C(6)-C(5)-C(4)	120.8(4)
N(6)-B(1)-H(1)	110.4	C(6)-C(5)-H(5)	119.6
N(4)-B(1)-H(1)	110.4	C(4)-C(5)-H(5)	119.6
C(1)-P(1)-C(3)	99.71(17)	C(5)-C(6)-C(7)	120.2(3)
C(1)-P(1)-C(2)	100.08(17)	C(5)-C(6)-H(6)	119.9
C(3)-P(1)-C(2)	99.71(18)	C(7)-C(6)-H(6)	119.9
C(1)-P(1)-Ru(1)	123.03(13)	C(8)-C(7)-C(6)	119.4(4)
C(3)-P(1)-Ru(1)	109.91(13)	C(8)-C(7)-H(7)	120.3
C(2)-P(1)-Ru(1)	120.33(13)	C(6)-C(7)-H(7)	120.3
C(10)-P(2)-C(4)	102.20(15)	C(7)-C(8)-C(9)	120.4(4)
C(10)-P(2)-C(16)	103.76(16)	C(7)-C(8)-H(8)	119.8
C(4)-P(2)-C(16)	95.58(16)	C(9)-C(8)-H(8)	119.8
C(10)-P(2)-Ru(1)	115.37(11)	C(8)-C(9)-C(4)	121.0(3)
C(4)-P(2)-Ru(1)	119.83(12)	C(8)-C(9)-H(9)	119.5
C(16)-P(2)-Ru(1)	117.02(11)	C(4)-C(9)-H(9)	119.5
C(22)-N(1)-N(2)	106.1(3)	C(15)-C(10)-C(11)	117.9(3)
C(22)-N(1)-Ru(1)	135.4(2)	C(15)-C(10)-P(2)	122.9(3)
N(2)-N(1)-Ru(1)	118.1(2)	C(11)-C(10)-P(2)	118.8(3)
C(24)-N(2)-N(1)	109.3(3)	C(12)-C(11)-C(10)	120.6(3)
C(24)-N(2)-B(1)	128.9(3)	C(12)-C(11)-H(11)	119.7
N(1)-N(2)-B(1)	121.4(3)	C(10)-C(11)-H(11)	119.7
C(25)-N(3)-N(4)	106.5(3)	C(13)-C(12)-C(11)	120.0(3)
C(25)-N(3)-Ru(1)	135.7(2)	C(13)-C(12)-H(12)	120.0
N(4)-N(3)-Ru(1)	116.7(2)	C(11)-C(12)-H(12)	120.0
C(27)-N(4)-N(3)	108.8(3)	C(14)-C(13)-C(12)	120.1(3)
C(27)-N(4)-B(1)	129.7(3)	C(14)-C(13)-H(13)	120.0
N(3)-N(4)-B(1)	120.9(3)	C(12)-C(13)-H(13)	120.0
C(28)-N(5)-N(6)	106.0(3)	C(13)-C(14)-C(15)	120.1(3)
C(28)-N(5)-Ru(1)	133.6(2)	C(13)-C(14)-H(14)	119.9
N(6)-N(5)-Ru(1)	120.4(2)	C(15)-C(14)-H(14)	119.9
C(30)-N(6)-N(5)	109.9(3)	C(14)-C(15)-C(10)	121.2(3)
C(30)-N(6)-B(1)	131.3(3)	C(14)-C(15)-H(15)	119.4
N(5)-N(6)-B(1)	117.6(3)	C(10)-C(15)-H(15)	119.4
P(1)-C(1)-H(1A)	109.5	C(21)-C(16)-C(17)	117.6(3)
P(1)-C(1)-H(1B)	109.5	C(21)-C(16)-P(2)	126.8(3)
H(1A)-C(1)-H(1B)	109.5	C(17)-C(16)-P(2)	115.6(3)
P(1)-C(1)-H(1C)	109.5	C(18)-C(17)-C(16)	120.9(4)
H(1A)-C(1)-H(1C)	109.5	C(18)-C(17)-H(17)	119.5
H(1B)-C(1)-H(1C)	109.5	C(16)-C(17)-H(17)	119.5
P(1)-C(2)-H(2A)	109.5	C(19)-C(18)-C(17)	120.6(4)
P(1)-C(2)-H(2B)	109.5	C(19)-C(18)-H(18)	119.7
H(2A)-C(2)-H(2B)	109.5	C(17)-C(18)-H(18)	119.7
P(1)-C(2)-H(2C)	109.5	C(18)-C(19)-C(20)	118.8(4)
H(2A)-C(2)-H(2C)	109.5	C(18)-C(19)-H(19)	120.6
H(2B)-C(2)-H(2C)	109.5	C(20)-C(19)-H(19)	120.6
P(1)-C(3)-H(3A)	109.5	C(21)-C(20)-C(19)	121.0(4)
P(1)-C(3)-H(3B)	109.5	C(21)-C(20)-H(20)	119.5
H(3A)-C(3)-H(3B)	109.5	C(19)-C(20)-H(20)	119.5
P(1)-C(3)-H(3C)	109.5	C(20)-C(21)-C(16)	121.1(4)
H(3A)-C(3)-H(3C)	109.5	C(20)-C(21)-H(21)	119.5
H(3B)-C(3)-H(3C)	109.5	C(16)-C(21)-H(21)	119.5
C(9)-C(4)-C(5)	118.1(3)	N(1)-C(22)-C(23)	110.8(3)
C(9)-C(4)-P(2)	120.9(3)	N(1)-C(22)-H(22)	124.6

C(23)-C(22)-H(22)	124.6	N(4)-C(27)-C(26)	109.4(3)
C(24)-C(23)-C(22)	104.8(3)	N(4)-C(27)-H(27)	125.3
C(24)-C(23)-H(23)	127.6	C(26)-C(27)-H(27)	125.3
C(22)-C(23)-H(23)	127.6	N(5)-C(28)-C(29)	110.6(3)
N(2)-C(24)-C(23)	109.1(3)	N(5)-C(28)-H(28)	124.7
N(2)-C(24)-H(24)	125.5	C(29)-C(28)-H(28)	124.7
C(23)-C(24)-H(24)	125.5	C(30)-C(29)-C(28)	105.0(3)
N(3)-C(25)-C(26)	110.9(3)	C(30)-C(29)-H(29)	127.5
N(3)-C(25)-H(25)	124.6	C(28)-C(29)-H(29)	127.5
C(26)-C(25)-H(25)	124.6	N(6)-C(30)-C(29)	108.4(3)
C(27)-C(26)-C(25)	104.5(3)	N(6)-C(30)-H(30)	125.8
C(27)-C(26)-H(26)	127.8	C(29)-C(30)-H(30)	125.8
C(25)-C(26)-H(26)	127.8		

Symmetry transformations used to generate equivalent atoms:

Table A22: Torsion angles [°] for TpRu(PMe₃)(PPh₃)Cl.

N(1)-Ru(1)-P(1)-C(1)	-73.77(16)	Cl(1)-Ru(1)-P(2)-C(16)	63.07(13)
N(5)-Ru(1)-P(1)-C(1)	-162.13(16)	N(5)-Ru(1)-N(1)-C(22)	133.7(4)
N(3)-Ru(1)-P(1)-C(1)	-140.8(4)	N(3)-Ru(1)-N(1)-C(22)	-144.3(4)
P(2)-Ru(1)-P(1)-C(1)	22.42(14)	P(1)-Ru(1)-N(1)-C(22)	47.0(3)
Cl(1)-Ru(1)-P(1)-C(1)	113.63(14)	P(2)-Ru(1)-N(1)-C(22)	-49.2(4)
N(1)-Ru(1)-P(1)-C(3)	42.94(15)	Cl(1)-Ru(1)-N(1)-C(22)	164.2(4)
N(5)-Ru(1)-P(1)-C(3)	-45.42(15)	N(5)-Ru(1)-N(1)-N(2)	-38.4(3)
N(3)-Ru(1)-P(1)-C(3)	-24.1(4)	N(3)-Ru(1)-N(1)-N(2)	43.6(3)
P(2)-Ru(1)-P(1)-C(3)	139.12(13)	P(1)-Ru(1)-N(1)-N(2)	-125.1(2)
Cl(1)-Ru(1)-P(1)-C(3)	-129.66(13)	P(2)-Ru(1)-N(1)-N(2)	138.7(2)
N(1)-Ru(1)-P(1)-C(2)	157.76(16)	Cl(1)-Ru(1)-N(1)-N(2)	-7.8(8)
N(5)-Ru(1)-P(1)-C(2)	69.40(16)	C(22)-N(1)-N(2)-C(24)	-0.8(4)
N(3)-Ru(1)-P(1)-C(2)	90.7(4)	Ru(1)-N(1)-N(2)-C(24)	173.5(2)
P(2)-Ru(1)-P(1)-C(2)	-106.06(14)	C(22)-N(1)-N(2)-B(1)	-174.6(3)
Cl(1)-Ru(1)-P(1)-C(2)	-14.84(15)	Ru(1)-N(1)-N(2)-B(1)	-0.4(4)
N(1)-Ru(1)-P(2)-C(10)	10.12(16)	N(6)-B(1)-N(2)-C(24)	-113.5(4)
N(5)-Ru(1)-P(2)-C(10)	157.7(9)	N(4)-B(1)-N(2)-C(24)	129.8(4)
N(3)-Ru(1)-P(2)-C(10)	97.10(15)	N(6)-B(1)-N(2)-N(1)	59.1(4)
P(1)-Ru(1)-P(2)-C(10)	-79.36(13)	N(4)-B(1)-N(2)-N(1)	-57.6(4)
Cl(1)-Ru(1)-P(2)-C(10)	-174.44(13)	N(1)-Ru(1)-N(3)-C(25)	149.3(3)
N(1)-Ru(1)-P(2)-C(4)	132.91(15)	N(5)-Ru(1)-N(3)-C(25)	-121.9(3)
N(5)-Ru(1)-P(2)-C(4)	-79.5(9)	P(1)-Ru(1)-N(3)-C(25)	-143.4(3)
N(3)-Ru(1)-P(2)-C(4)	-140.11(15)	P(2)-Ru(1)-N(3)-C(25)	53.4(3)
P(1)-Ru(1)-P(2)-C(4)	43.43(13)	Cl(1)-Ru(1)-N(3)-C(25)	-37.1(3)
Cl(1)-Ru(1)-P(2)-C(4)	-51.65(13)	N(1)-Ru(1)-N(3)-N(4)	-44.8(2)
N(1)-Ru(1)-P(2)-C(16)	-112.38(15)	N(5)-Ru(1)-N(3)-N(4)	44.0(2)
N(5)-Ru(1)-P(2)-C(16)	35.2(9)	P(1)-Ru(1)-N(3)-N(4)	22.5(5)
N(3)-Ru(1)-P(2)-C(16)	-25.40(15)	P(2)-Ru(1)-N(3)-N(4)	-140.8(2)
P(1)-Ru(1)-P(2)-C(16)	158.14(13)	Cl(1)-Ru(1)-N(3)-N(4)	128.7(2)

C(25)-N(3)-N(4)-C(27)	1.3(4)	C(4)-P(2)-C(10)-C(11)	162.2(3)
Ru(1)-N(3)-N(4)-C(27)	-168.5(2)	C(16)-P(2)-C(10)-C(11)	63.3(3)
C(25)-N(3)-N(4)-B(1)	173.0(3)	Ru(1)-P(2)-C(10)-C(11)	-66.1(3)
Ru(1)-N(3)-N(4)-B(1)	3.3(4)	C(15)-C(10)-C(11)-C(12)	2.5(5)
N(2)-B(1)-N(4)-C(27)	-135.3(4)	P(2)-C(10)-C(11)-C(12)	176.0(3)
N(6)-B(1)-N(4)-C(27)	106.4(4)	C(10)-C(11)-C(12)-C(13)	-2.1(6)
N(2)-B(1)-N(4)-N(3)	54.9(4)	C(11)-C(12)-C(13)-C(14)	0.2(6)
N(6)-B(1)-N(4)-N(3)	-63.4(4)	C(12)-C(13)-C(14)-C(15)	1.2(6)
N(1)-Ru(1)-N(5)-C(28)	-146.4(3)	C(13)-C(14)-C(15)-C(10)	-0.8(6)
N(3)-Ru(1)-N(5)-C(28)	126.9(3)	C(11)-C(10)-C(15)-C(14)	-1.1(5)
P(1)-Ru(1)-N(5)-C(28)	-57.5(3)	P(2)-C(10)-C(15)-C(14)	-174.3(3)
P(2)-Ru(1)-N(5)-C(28)	65.8(11)	C(10)-P(2)-C(16)-C(21)	-17.7(3)
Cl(1)-Ru(1)-N(5)-C(28)	37.8(3)	C(4)-P(2)-C(16)-C(21)	-121.7(3)
N(1)-Ru(1)-N(5)-N(6)	33.3(3)	Ru(1)-P(2)-C(16)-C(21)	110.6(3)
N(3)-Ru(1)-N(5)-N(6)	-53.3(2)	C(10)-P(2)-C(16)-C(17)	160.8(3)
P(1)-Ru(1)-N(5)-N(6)	122.2(2)	C(4)-P(2)-C(16)-C(17)	56.7(3)
P(2)-Ru(1)-N(5)-N(6)	-114.4(8)	Ru(1)-P(2)-C(16)-C(17)	-70.9(3)
Cl(1)-Ru(1)-N(5)-N(6)	-142.4(2)	C(21)-C(16)-C(17)-C(18)	-1.5(5)
C(28)-N(5)-N(6)-C(30)	-0.2(4)	P(2)-C(16)-C(17)-C(18)	179.9(3)
Ru(1)-N(5)-N(6)-C(30)	179.9(2)	C(16)-C(17)-C(18)-C(19)	0.3(6)
C(28)-N(5)-N(6)-B(1)	-169.0(3)	C(17)-C(18)-C(19)-C(20)	1.0(6)
Ru(1)-N(5)-N(6)-B(1)	11.2(4)	C(18)-C(19)-C(20)-C(21)	-1.1(5)
N(2)-B(1)-N(6)-C(30)	129.8(4)	C(19)-C(20)-C(21)-C(16)	-0.2(5)
N(4)-B(1)-N(6)-C(30)	-111.8(4)	C(17)-C(16)-C(21)-C(20)	1.5(5)
N(2)-B(1)-N(6)-N(5)	-64.3(4)	P(2)-C(16)-C(21)-C(20)	179.9(3)
N(4)-B(1)-N(6)-N(5)	54.0(4)	N(2)-N(1)-C(22)-C(23)	0.5(4)
C(10)-P(2)-C(4)-C(9)	138.5(3)	Ru(1)-N(1)-C(22)-C(23)	-172.3(3)
C(16)-P(2)-C(4)-C(9)	-116.1(3)	N(1)-C(22)-C(23)-C(24)	0.0(4)
Ru(1)-P(2)-C(4)-C(9)	9.5(3)	N(1)-N(2)-C(24)-C(23)	0.8(4)
C(10)-P(2)-C(4)-C(5)	-46.3(3)	B(1)-N(2)-C(24)-C(23)	174.0(4)
C(16)-P(2)-C(4)-C(5)	59.1(3)	C(22)-C(23)-C(24)-N(2)	-0.5(4)
Ru(1)-P(2)-C(4)-C(5)	-175.3(2)	N(4)-N(3)-C(25)-C(26)	-1.2(4)
C(9)-C(4)-C(5)-C(6)	-3.2(5)	Ru(1)-N(3)-C(25)-C(26)	165.6(2)
P(2)-C(4)-C(5)-C(6)	-178.5(3)	N(3)-C(25)-C(26)-C(27)	0.7(4)
C(4)-C(5)-C(6)-C(7)	1.7(6)	N(3)-N(4)-C(27)-C(26)	-0.9(4)
C(5)-C(6)-C(7)-C(8)	0.3(6)	B(1)-N(4)-C(27)-C(26)	-171.7(3)
C(6)-C(7)-C(8)-C(9)	-0.5(6)	C(25)-C(26)-C(27)-N(4)	0.2(4)
C(7)-C(8)-C(9)-C(4)	-1.2(6)	N(6)-N(5)-C(28)-C(29)	0.2(4)
C(5)-C(4)-C(9)-C(8)	3.0(5)	Ru(1)-N(5)-C(28)-C(29)	180.0(3)
P(2)-C(4)-C(9)-C(8)	178.3(3)	N(5)-C(28)-C(29)-C(30)	0.0(4)
C(4)-P(2)-C(10)-C(15)	-24.6(3)	N(5)-N(6)-C(30)-C(29)	0.2(4)
C(16)-P(2)-C(10)-C(15)	-123.6(3)	B(1)-N(6)-C(30)-C(29)	166.9(4)
Ru(1)-P(2)-C(10)-C(15)	107.1(3)	C(28)-C(29)-C(30)-N(6)	-0.1(4)

Symmetry transformations used to generate equivalent atoms:

Table A23: Bond lengths [\AA] and angles [$^\circ$] for $\text{Cp}^*\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}$.

Ru(1)-C(5)	2.206(3)	C(15)-H(15)	0.9500
Ru(1)-C(3)	2.221(2)	C(16)-C(17)	1.372(4)
Ru(1)-C(1)	2.226(3)	C(16)-H(16)	0.9500
Ru(1)-C(4)	2.240(2)	C(17)-C(18)	1.392(4)
Ru(1)-C(2)	2.254(2)	C(17)-H(17)	0.9500
Ru(1)-P(1)	2.3006(7)	C(18)-C(19)	1.386(4)
Ru(1)-P(2)	2.3049(7)	C(18)-H(18)	0.9500
Ru(1)-Cl(1)	2.4583(6)	C(19)-H(19)	0.9500
P(1)-C(13)	1.818(3)	C(20)-C(21)	1.393(3)
P(1)-C(11)	1.826(3)	C(20)-C(25)	1.405(4)
P(1)-C(12)	1.836(3)	C(21)-C(22)	1.395(4)
P(2)-C(20)	1.828(3)	C(21)-H(21)	0.9500
P(2)-C(14)	1.848(3)	C(22)-C(23)	1.382(4)
P(2)-C(26)	1.852(3)	C(22)-H(22)	0.9500
C(1)-C(2)	1.410(4)	C(23)-C(24)	1.383(4)
C(1)-C(5)	1.442(4)	C(23)-H(23)	0.9500
C(1)-C(6)	1.498(4)	C(24)-C(25)	1.383(4)
C(2)-C(3)	1.439(4)	C(24)-H(24)	0.9500
C(2)-C(7)	1.500(3)	C(25)-H(25)	0.9500
C(3)-C(4)	1.434(4)	C(26)-C(31)	1.396(4)
C(3)-C(8)	1.510(4)	C(26)-C(27)	1.403(4)
C(4)-C(5)	1.412(4)	C(27)-C(28)	1.390(4)
C(4)-C(9)	1.495(4)	C(27)-H(27)	0.9500
C(5)-C(10)	1.500(4)	C(28)-C(29)	1.383(4)
C(6)-H(6A)	0.9800	C(28)-H(28)	0.9500
C(6)-H(6B)	0.9800	C(29)-C(30)	1.382(4)
C(6)-H(6C)	0.9800	C(29)-H(29)	0.9500
C(7)-H(7A)	0.9800	C(30)-C(31)	1.394(4)
C(7)-H(7B)	0.9800	C(30)-H(30)	0.9500
C(7)-H(7C)	0.9800	C(31)-H(31)	0.9500
C(8)-H(8A)	0.9800		
C(8)-H(8B)	0.9800	C(5)-Ru(1)-C(3)	62.81(9)
C(8)-H(8C)	0.9800	C(5)-Ru(1)-C(1)	37.97(9)
C(9)-H(9A)	0.9800	C(3)-Ru(1)-C(1)	62.42(10)
C(9)-H(9B)	0.9800	C(5)-Ru(1)-C(4)	37.04(9)
C(9)-H(9C)	0.9800	C(3)-Ru(1)-C(4)	37.48(9)
C(10)-H(10A)	0.9800	C(1)-Ru(1)-C(4)	62.18(9)
C(10)-H(10B)	0.9800	C(5)-Ru(1)-C(2)	62.44(9)
C(10)-H(10C)	0.9800	C(3)-Ru(1)-C(2)	37.50(9)
C(11)-H(11A)	0.9800	C(1)-Ru(1)-C(2)	36.69(10)
C(11)-H(11B)	0.9800	C(4)-Ru(1)-C(2)	62.06(9)
C(11)-H(11C)	0.9800	C(5)-Ru(1)-P(1)	107.93(7)
C(12)-H(12A)	0.9800	C(3)-Ru(1)-P(1)	113.57(7)
C(12)-H(12B)	0.9800	C(1)-Ru(1)-P(1)	145.45(7)
C(12)-H(12C)	0.9800	C(4)-Ru(1)-P(1)	93.39(7)
C(13)-H(13A)	0.9800	C(2)-Ru(1)-P(1)	151.04(7)
C(13)-H(13B)	0.9800	C(5)-Ru(1)-P(2)	155.09(7)
C(13)-H(13C)	0.9800	C(3)-Ru(1)-P(2)	104.66(7)
C(14)-C(15)	1.387(4)	C(1)-Ru(1)-P(2)	117.66(7)
C(14)-C(19)	1.399(4)	C(4)-Ru(1)-P(2)	140.70(7)
C(15)-C(16)	1.391(4)	C(2)-Ru(1)-P(2)	94.21(7)

P(1)-Ru(1)-P(2)	96.78(2)	H(6A)-C(6)-H(6C)	109.5
C(5)-Ru(1)-Cl(1)	93.03(7)	H(6B)-C(6)-H(6C)	109.5
C(3)-Ru(1)-Cl(1)	153.12(7)	C(2)-C(7)-H(7A)	109.5
C(1)-Ru(1)-Cl(1)	91.46(7)	C(2)-C(7)-H(7B)	109.5
C(4)-Ru(1)-Cl(1)	126.12(7)	H(7A)-C(7)-H(7B)	109.5
C(2)-Ru(1)-Cl(1)	122.36(7)	C(2)-C(7)-H(7C)	109.5
P(1)-Ru(1)-Cl(1)	83.82(2)	H(7A)-C(7)-H(7C)	109.5
P(2)-Ru(1)-Cl(1)	92.75(2)	H(7B)-C(7)-H(7C)	109.5
C(13)-P(1)-C(11)	99.38(15)	C(3)-C(8)-H(8A)	109.5
C(13)-P(1)-C(12)	98.13(14)	C(3)-C(8)-H(8B)	109.5
C(11)-P(1)-C(12)	102.50(14)	H(8A)-C(8)-H(8B)	109.5
C(13)-P(1)-Ru(1)	121.81(10)	C(3)-C(8)-H(8C)	109.5
C(11)-P(1)-Ru(1)	120.12(9)	H(8A)-C(8)-H(8C)	109.5
C(12)-P(1)-Ru(1)	111.25(10)	H(8B)-C(8)-H(8C)	109.5
C(20)-P(2)-C(14)	105.01(11)	C(4)-C(9)-H(9A)	109.5
C(20)-P(2)-C(26)	101.48(12)	C(4)-C(9)-H(9B)	109.5
C(14)-P(2)-C(26)	94.95(11)	H(9A)-C(9)-H(9B)	109.5
C(20)-P(2)-Ru(1)	112.18(8)	C(4)-C(9)-H(9C)	109.5
C(14)-P(2)-Ru(1)	115.88(9)	H(9A)-C(9)-H(9C)	109.5
C(26)-P(2)-Ru(1)	124.48(8)	H(9B)-C(9)-H(9C)	109.5
C(2)-C(1)-C(5)	108.3(2)	C(5)-C(10)-H(10A)	109.5
C(2)-C(1)-C(6)	127.5(2)	C(5)-C(10)-H(10B)	109.5
C(5)-C(1)-C(6)	123.9(3)	H(10A)-C(10)-H(10B)	109.5
C(2)-C(1)-Ru(1)	72.75(15)	C(5)-C(10)-H(10C)	109.5
C(5)-C(1)-Ru(1)	70.26(15)	H(10A)-C(10)-H(10C)	109.5
C(6)-C(1)-Ru(1)	127.10(19)	H(10B)-C(10)-H(10C)	109.5
C(1)-C(2)-C(3)	107.9(2)	P(1)-C(11)-H(11A)	109.5
C(1)-C(2)-C(7)	125.8(2)	P(1)-C(11)-H(11B)	109.5
C(3)-C(2)-C(7)	125.8(3)	H(11A)-C(11)-H(11B)	109.5
C(1)-C(2)-Ru(1)	70.56(15)	P(1)-C(11)-H(11C)	109.5
C(3)-C(2)-Ru(1)	69.99(14)	H(11A)-C(11)-H(11C)	109.5
C(7)-C(2)-Ru(1)	131.37(18)	H(11B)-C(11)-H(11C)	109.5
C(4)-C(3)-C(2)	107.5(2)	P(1)-C(12)-H(12A)	109.5
C(4)-C(3)-C(8)	124.6(2)	P(1)-C(12)-H(12B)	109.5
C(2)-C(3)-C(8)	125.9(2)	H(12A)-C(12)-H(12B)	109.5
C(4)-C(3)-Ru(1)	72.00(14)	P(1)-C(12)-H(12C)	109.5
C(2)-C(3)-Ru(1)	72.50(14)	H(12A)-C(12)-H(12C)	109.5
C(8)-C(3)-Ru(1)	133.48(18)	H(12B)-C(12)-H(12C)	109.5
C(5)-C(4)-C(3)	108.3(2)	P(1)-C(13)-H(13A)	109.5
C(5)-C(4)-C(9)	126.6(2)	P(1)-C(13)-H(13B)	109.5
C(3)-C(4)-C(9)	124.2(2)	H(13A)-C(13)-H(13B)	109.5
C(5)-C(4)-Ru(1)	70.14(14)	P(1)-C(13)-H(13C)	109.5
C(3)-C(4)-Ru(1)	70.52(14)	H(13A)-C(13)-H(13C)	109.5
C(9)-C(4)-Ru(1)	133.65(19)	H(13B)-C(13)-H(13C)	109.5
C(4)-C(5)-C(1)	107.8(2)	C(15)-C(14)-C(19)	118.6(2)
C(4)-C(5)-C(10)	128.0(2)	C(15)-C(14)-P(2)	119.0(2)
C(1)-C(5)-C(10)	123.8(3)	C(19)-C(14)-P(2)	122.0(2)
C(4)-C(5)-Ru(1)	72.82(15)	C(14)-C(15)-C(16)	120.6(3)
C(1)-C(5)-Ru(1)	71.77(15)	C(14)-C(15)-H(15)	119.7
C(10)-C(5)-Ru(1)	126.48(19)	C(16)-C(15)-H(15)	119.7
C(1)-C(6)-H(6A)	109.5	C(17)-C(16)-C(15)	120.1(3)
C(1)-C(6)-H(6B)	109.5	C(17)-C(16)-H(16)	119.9
H(6A)-C(6)-H(6B)	109.5	C(15)-C(16)-H(16)	119.9
C(1)-C(6)-H(6C)	109.5	C(16)-C(17)-C(18)	120.4(3)

C(16)-C(17)-H(17)	119.8	C(25)-C(24)-H(24)	120.1
C(18)-C(17)-H(17)	119.8	C(24)-C(25)-C(20)	121.4(2)
C(19)-C(18)-C(17)	119.4(3)	C(24)-C(25)-H(25)	119.3
C(19)-C(18)-H(18)	120.3	C(20)-C(25)-H(25)	119.3
C(17)-C(18)-H(18)	120.3	C(31)-C(26)-C(27)	118.8(2)
C(18)-C(19)-C(14)	120.8(3)	C(31)-C(26)-P(2)	123.9(2)
C(18)-C(19)-H(19)	119.6	C(27)-C(26)-P(2)	117.3(2)
C(14)-C(19)-H(19)	119.6	C(28)-C(27)-C(26)	119.7(3)
C(21)-C(20)-C(25)	117.8(2)	C(28)-C(27)-H(27)	120.1
C(21)-C(20)-P(2)	125.3(2)	C(26)-C(27)-H(27)	120.1
C(25)-C(20)-P(2)	116.79(19)	C(29)-C(28)-C(27)	120.9(3)
C(20)-C(21)-C(22)	120.6(2)	C(29)-C(28)-H(28)	119.5
C(20)-C(21)-H(21)	119.7	C(27)-C(28)-H(28)	119.5
C(22)-C(21)-H(21)	119.7	C(30)-C(29)-C(28)	119.9(3)
C(23)-C(22)-C(21)	120.4(2)	C(30)-C(29)-H(29)	120.0
C(23)-C(22)-H(22)	119.8	C(28)-C(29)-H(29)	120.0
C(21)-C(22)-H(22)	119.8	C(29)-C(30)-C(31)	119.8(3)
C(22)-C(23)-C(24)	119.9(3)	C(29)-C(30)-H(30)	120.1
C(22)-C(23)-H(23)	120.1	C(31)-C(30)-H(30)	120.1
C(24)-C(23)-H(23)	120.1	C(30)-C(31)-C(26)	120.9(3)
C(23)-C(24)-C(25)	119.9(3)	C(30)-C(31)-H(31)	119.6
C(23)-C(24)-H(24)	120.1	C(26)-C(31)-H(31)	119.6

Symmetry transformations used to generate equivalent atoms:

Table A24: Torsion angles [°] for Cp*Ru(PMe₃)(PPh₃)Cl.

C(5)-Ru(1)-P(1)-C(13)	138.00(16)	C(1)-Ru(1)-P(2)-C(20)	86.76(12)
C(3)-Ru(1)-P(1)-C(13)	-154.51(16)	C(4)-Ru(1)-P(2)-C(20)	7.79(14)
C(1)-Ru(1)-P(1)-C(13)	130.38(19)	C(2)-Ru(1)-P(2)-C(20)	57.12(11)
C(4)-Ru(1)-P(1)-C(13)	172.78(16)	P(1)-Ru(1)-P(2)-C(20)	-96.04(9)
C(2)-Ru(1)-P(1)-C(13)	-156.8(2)	Cl(1)-Ru(1)-P(2)-C(20)	179.85(9)
P(2)-Ru(1)-P(1)-C(13)	-45.25(14)	C(5)-Ru(1)-P(2)-C(14)	-43.96(19)
Cl(1)-Ru(1)-P(1)-C(13)	46.80(14)	C(3)-Ru(1)-P(2)-C(14)	-100.04(11)
C(5)-Ru(1)-P(1)-C(11)	-96.44(13)	C(1)-Ru(1)-P(2)-C(14)	-33.82(12)
C(3)-Ru(1)-P(1)-C(11)	-28.95(14)	C(4)-Ru(1)-P(2)-C(14)	-112.78(13)
C(1)-Ru(1)-P(1)-C(11)	-104.06(17)	C(2)-Ru(1)-P(2)-C(14)	-63.46(11)
C(4)-Ru(1)-P(1)-C(11)	-61.66(13)	P(1)-Ru(1)-P(2)-C(14)	143.38(9)
C(2)-Ru(1)-P(1)-C(11)	-31.3(2)	Cl(1)-Ru(1)-P(2)-C(14)	59.28(9)
P(2)-Ru(1)-P(1)-C(11)	80.32(12)	C(5)-Ru(1)-P(2)-C(26)	-160.67(19)
Cl(1)-Ru(1)-P(1)-C(11)	172.36(12)	C(3)-Ru(1)-P(2)-C(26)	143.25(12)
C(5)-Ru(1)-P(1)-C(12)	23.17(13)	C(1)-Ru(1)-P(2)-C(26)	-150.52(13)
C(3)-Ru(1)-P(1)-C(12)	90.66(13)	C(4)-Ru(1)-P(2)-C(26)	130.51(14)
C(1)-Ru(1)-P(1)-C(12)	15.55(17)	C(2)-Ru(1)-P(2)-C(26)	179.84(12)
C(4)-Ru(1)-P(1)-C(12)	57.95(13)	P(1)-Ru(1)-P(2)-C(26)	26.68(11)
C(2)-Ru(1)-P(1)-C(12)	88.35(19)	Cl(1)-Ru(1)-P(2)-C(26)	-57.42(11)
P(2)-Ru(1)-P(1)-C(12)	-160.08(11)	C(5)-Ru(1)-C(1)-C(2)	117.4(2)
Cl(1)-Ru(1)-P(1)-C(12)	-68.03(11)	C(3)-Ru(1)-C(1)-C(2)	37.16(14)
C(5)-Ru(1)-P(2)-C(20)	76.61(19)	C(4)-Ru(1)-C(1)-C(2)	79.72(16)
C(3)-Ru(1)-P(2)-C(20)	20.53(11)	P(1)-Ru(1)-C(1)-C(2)	129.28(14)

P(2)-Ru(1)-C(1)-C(2)	-55.63(16)	P(2)-Ru(1)-C(3)-C(4)	-166.73(13)
Cl(1)-Ru(1)-C(1)-C(2)	-149.50(14)	Cl(1)-Ru(1)-C(3)-C(4)	64.5(2)
C(3)-Ru(1)-C(1)-C(5)	-80.29(16)	C(5)-Ru(1)-C(3)-C(2)	-79.34(16)
C(4)-Ru(1)-C(1)-C(5)	-37.73(14)	C(1)-Ru(1)-C(3)-C(2)	-36.36(15)
C(2)-Ru(1)-C(1)-C(5)	-117.4(2)	C(4)-Ru(1)-C(3)-C(2)	-115.8(2)
P(1)-Ru(1)-C(1)-C(5)	11.8(2)	P(1)-Ru(1)-C(3)-C(2)	-178.17(13)
P(2)-Ru(1)-C(1)-C(5)	-173.07(12)	P(2)-Ru(1)-C(3)-C(2)	77.51(15)
Cl(1)-Ru(1)-C(1)-C(5)	93.05(14)	Cl(1)-Ru(1)-C(3)-C(2)	-51.2(2)
C(5)-Ru(1)-C(1)-C(6)	-118.1(3)	C(5)-Ru(1)-C(3)-C(8)	157.4(3)
C(3)-Ru(1)-C(1)-C(6)	161.6(3)	C(1)-Ru(1)-C(3)-C(8)	-159.7(3)
C(4)-Ru(1)-C(1)-C(6)	-155.9(3)	C(4)-Ru(1)-C(3)-C(8)	121.0(3)
C(2)-Ru(1)-C(1)-C(6)	124.4(3)	C(2)-Ru(1)-C(3)-C(8)	-123.3(3)
P(1)-Ru(1)-C(1)-C(6)	-106.3(2)	P(1)-Ru(1)-C(3)-C(8)	58.5(3)
P(2)-Ru(1)-C(1)-C(6)	68.8(3)	P(2)-Ru(1)-C(3)-C(8)	-45.8(3)
Cl(1)-Ru(1)-C(1)-C(6)	-25.1(2)	Cl(1)-Ru(1)-C(3)-C(8)	-174.51(18)
C(5)-C(1)-C(2)-C(3)	1.3(3)	C(2)-C(3)-C(4)-C(5)	4.0(3)
C(6)-C(1)-C(2)-C(3)	175.8(3)	C(8)-C(3)-C(4)-C(5)	168.9(2)
Ru(1)-C(1)-C(2)-C(3)	-60.29(17)	Ru(1)-C(3)-C(4)-C(5)	-60.25(18)
C(5)-C(1)-C(2)-C(7)	-170.8(2)	C(2)-C(3)-C(4)-C(9)	-165.6(2)
C(6)-C(1)-C(2)-C(7)	3.6(4)	C(8)-C(3)-C(4)-C(9)	-0.8(4)
Ru(1)-C(1)-C(2)-C(7)	127.6(3)	Ru(1)-C(3)-C(4)-C(9)	130.1(3)
C(5)-C(1)-C(2)-Ru(1)	61.62(18)	C(2)-C(3)-C(4)-Ru(1)	64.27(17)
C(6)-C(1)-C(2)-Ru(1)	-123.9(3)	C(8)-C(3)-C(4)-Ru(1)	-130.9(2)
C(5)-Ru(1)-C(2)-C(1)	-38.01(15)	C(3)-Ru(1)-C(4)-C(5)	118.8(2)
C(3)-Ru(1)-C(2)-C(1)	-118.4(2)	C(1)-Ru(1)-C(4)-C(5)	38.69(15)
C(4)-Ru(1)-C(2)-C(1)	-80.08(16)	C(2)-Ru(1)-C(4)-C(5)	80.41(16)
P(1)-Ru(1)-C(2)-C(1)	-114.95(17)	P(1)-Ru(1)-C(4)-C(5)	-115.69(14)
P(2)-Ru(1)-C(2)-C(1)	132.86(14)	P(2)-Ru(1)-C(4)-C(5)	139.30(13)
Cl(1)-Ru(1)-C(2)-C(1)	36.91(16)	Cl(1)-Ru(1)-C(4)-C(5)	-30.87(17)
C(5)-Ru(1)-C(2)-C(3)	80.41(16)	C(5)-Ru(1)-C(4)-C(3)	-118.8(2)
C(1)-Ru(1)-C(2)-C(3)	118.4(2)	C(1)-Ru(1)-C(4)-C(3)	-80.09(16)
C(4)-Ru(1)-C(2)-C(3)	38.35(15)	C(2)-Ru(1)-C(4)-C(3)	-38.37(15)
P(1)-Ru(1)-C(2)-C(3)	3.5(3)	P(1)-Ru(1)-C(4)-C(3)	125.53(14)
P(2)-Ru(1)-C(2)-C(3)	-108.72(14)	P(2)-Ru(1)-C(4)-C(3)	20.5(2)
Cl(1)-Ru(1)-C(2)-C(3)	155.34(12)	Cl(1)-Ru(1)-C(4)-C(3)	-149.65(12)
C(5)-Ru(1)-C(2)-C(7)	-159.0(3)	C(5)-Ru(1)-C(4)-C(9)	122.2(3)
C(3)-Ru(1)-C(2)-C(7)	120.6(3)	C(3)-Ru(1)-C(4)-C(9)	-119.1(3)
C(1)-Ru(1)-C(2)-C(7)	-121.0(3)	C(1)-Ru(1)-C(4)-C(9)	160.9(3)
C(4)-Ru(1)-C(2)-C(7)	158.9(3)	C(2)-Ru(1)-C(4)-C(9)	-157.4(3)
P(1)-Ru(1)-C(2)-C(7)	124.1(2)	P(1)-Ru(1)-C(4)-C(9)	6.5(3)
P(2)-Ru(1)-C(2)-C(7)	11.9(3)	P(2)-Ru(1)-C(4)-C(9)	-98.5(3)
Cl(1)-Ru(1)-C(2)-C(7)	-84.1(3)	Cl(1)-Ru(1)-C(4)-C(9)	91.3(3)
C(1)-C(2)-C(3)-C(4)	-3.3(3)	C(3)-C(4)-C(5)-C(1)	-3.2(3)
C(7)-C(2)-C(3)-C(4)	168.9(2)	C(9)-C(4)-C(5)-C(1)	166.1(3)
Ru(1)-C(2)-C(3)-C(4)	-63.93(17)	Ru(1)-C(4)-C(5)-C(1)	-63.69(18)
C(1)-C(2)-C(3)-C(8)	-167.9(2)	C(3)-C(4)-C(5)-C(10)	-176.3(3)
C(7)-C(2)-C(3)-C(8)	4.3(4)	C(9)-C(4)-C(5)-C(10)	-7.0(4)
Ru(1)-C(2)-C(3)-C(8)	131.5(2)	Ru(1)-C(4)-C(5)-C(10)	123.2(3)
C(1)-C(2)-C(3)-Ru(1)	60.65(18)	C(3)-C(4)-C(5)-Ru(1)	60.48(17)
C(7)-C(2)-C(3)-Ru(1)	-127.2(3)	C(9)-C(4)-C(5)-Ru(1)	-130.2(3)
C(5)-Ru(1)-C(3)-C(4)	36.41(15)	C(2)-C(1)-C(5)-C(4)	1.2(3)
C(1)-Ru(1)-C(3)-C(4)	79.39(16)	C(6)-C(1)-C(5)-C(4)	-173.5(2)
C(2)-Ru(1)-C(3)-C(4)	115.8(2)	Ru(1)-C(1)-C(5)-C(4)	64.38(18)
P(1)-Ru(1)-C(3)-C(4)	-62.42(15)	C(2)-C(1)-C(5)-C(10)	174.6(3)

C(6)-C(1)-C(5)-C(10)	-0.1(4)	C(16)-C(17)-C(18)-C(19)	-0.4(4)
Ru(1)-C(1)-C(5)-C(10)	-122.2(3)	C(17)-C(18)-C(19)-C(14)	-0.5(4)
C(2)-C(1)-C(5)-Ru(1)	-63.22(18)	C(15)-C(14)-C(19)-C(18)	1.3(4)
C(6)-C(1)-C(5)-Ru(1)	122.1(3)	P(2)-C(14)-C(19)-C(18)	174.4(2)
C(3)-Ru(1)-C(5)-C(4)	-36.85(14)	C(14)-P(2)-C(20)-C(21)	12.9(3)
C(1)-Ru(1)-C(5)-C(4)	-116.0(2)	C(26)-P(2)-C(20)-C(21)	111.2(2)
C(2)-Ru(1)-C(5)-C(4)	-79.29(15)	Ru(1)-P(2)-C(20)-C(21)	-113.8(2)
P(1)-Ru(1)-C(5)-C(4)	70.99(14)	C(14)-P(2)-C(20)-C(25)	-170.79(19)
P(2)-Ru(1)-C(5)-C(4)	-101.3(2)	C(26)-P(2)-C(20)-C(25)	-72.4(2)
Cl(1)-Ru(1)-C(5)-C(4)	155.48(14)	Ru(1)-P(2)-C(20)-C(25)	62.5(2)
C(3)-Ru(1)-C(5)-C(1)	79.18(16)	C(25)-C(20)-C(21)-C(22)	-1.6(4)
C(4)-Ru(1)-C(5)-C(1)	116.0(2)	P(2)-C(20)-C(21)-C(22)	174.7(2)
C(2)-Ru(1)-C(5)-C(1)	36.74(15)	C(20)-C(21)-C(22)-C(23)	1.9(4)
P(1)-Ru(1)-C(5)-C(1)	-172.98(13)	C(21)-C(22)-C(23)-C(24)	-0.4(4)
P(2)-Ru(1)-C(5)-C(1)	14.7(3)	C(22)-C(23)-C(24)-C(25)	-1.5(4)
Cl(1)-Ru(1)-C(5)-C(1)	-88.50(14)	C(23)-C(24)-C(25)-C(20)	1.7(4)
C(3)-Ru(1)-C(5)-C(10)	-161.8(3)	C(21)-C(20)-C(25)-C(24)	-0.2(4)
C(1)-Ru(1)-C(5)-C(10)	119.0(3)	P(2)-C(20)-C(25)-C(24)	-176.8(2)
C(4)-Ru(1)-C(5)-C(10)	-124.9(3)	C(20)-P(2)-C(26)-C(31)	8.8(2)
C(2)-Ru(1)-C(5)-C(10)	155.8(3)	C(14)-P(2)-C(26)-C(31)	115.2(2)
P(1)-Ru(1)-C(5)-C(10)	-53.9(2)	Ru(1)-P(2)-C(26)-C(31)	-118.6(2)
P(2)-Ru(1)-C(5)-C(10)	133.7(2)	C(20)-P(2)-C(26)-C(27)	-169.3(2)
Cl(1)-Ru(1)-C(5)-C(10)	30.5(2)	C(14)-P(2)-C(26)-C(27)	-62.8(2)
C(20)-P(2)-C(14)-C(15)	-133.5(2)	Ru(1)-P(2)-C(26)-C(27)	63.4(2)
C(26)-P(2)-C(14)-C(15)	123.2(2)	C(31)-C(26)-C(27)-C(28)	0.2(4)
Ru(1)-P(2)-C(14)-C(15)	-9.2(2)	P(2)-C(26)-C(27)-C(28)	178.3(2)
C(20)-P(2)-C(14)-C(19)	53.4(2)	C(26)-C(27)-C(28)-C(29)	0.2(4)
C(26)-P(2)-C(14)-C(19)	-49.9(2)	C(27)-C(28)-C(29)-C(30)	0.1(4)
Ru(1)-P(2)-C(14)-C(19)	177.74(18)	C(28)-C(29)-C(30)-C(31)	-0.7(4)
C(19)-C(14)-C(15)-C(16)	-1.1(4)	C(29)-C(30)-C(31)-C(26)	1.1(4)
P(2)-C(14)-C(15)-C(16)	-174.4(2)	C(27)-C(26)-C(31)-C(30)	-0.8(4)
C(14)-C(15)-C(16)-C(17)	0.2(4)	P(2)-C(26)-C(31)-C(30)	-178.8(2)
C(15)-C(16)-C(17)-C(18)	0.6(4)		

Symmetry transformations used to generate equivalent atoms:

Table A25: Bond lengths [\AA] and angles [$^\circ$] for chalcone- CCl_4 adduct.

Cl(1)-C(3)	1.8219(11)	C(5)-C(10)	1.4015(14)
Cl(2)-C(4)	1.7749(11)	C(6)-C(7)	1.3955(15)
Cl(3)-C(4)	1.7907(11)	C(6)-H(6A)	0.9500
Cl(4)-C(4)	1.7671(12)	C(7)-C(8)	1.3902(18)
O(1)-C(1)	1.2165(13)	C(7)-H(7A)	0.9500
C(1)-C(5)	1.4907(14)	C(8)-C(9)	1.3857(19)
C(1)-C(2)	1.5482(14)	C(8)-H(8A)	0.9500
C(2)-C(3)	1.5438(14)	C(9)-C(10)	1.3894(16)
C(2)-C(4)	1.5499(15)	C(9)-H(9A)	0.9500
C(2)-H(2A)	1.0000	C(10)-H(10A)	0.9500
C(3)-C(11)	1.5050(14)	C(11)-C(12)	1.3958(15)
C(3)-H(3A)	1.0000	C(11)-C(16)	1.3966(15)
C(5)-C(6)	1.3968(15)	C(12)-C(13)	1.3873(15)

C(12)-H(12A)	0.9500	C(7)-C(6)-C(5)	120.08(10)
C(13)-C(14)	1.3939(17)	C(7)-C(6)-H(6A)	120.0
C(13)-H(13A)	0.9500	C(5)-C(6)-H(6A)	120.0
C(14)-C(15)	1.3872(17)	C(8)-C(7)-C(6)	119.78(11)
C(14)-H(14A)	0.9500	C(8)-C(7)-H(7A)	120.1
C(15)-C(16)	1.3970(15)	C(6)-C(7)-H(7A)	120.1
C(15)-H(15A)	0.9500	C(9)-C(8)-C(7)	120.48(11)
C(16)-H(16A)	0.9500	C(9)-C(8)-H(8A)	119.8
		C(7)-C(8)-H(8A)	119.8
O(1)-C(1)-C(5)	121.14(9)	C(8)-C(9)-C(10)	120.03(11)
O(1)-C(1)-C(2)	118.40(9)	C(8)-C(9)-H(9A)	120.0
C(5)-C(1)-C(2)	120.44(9)	C(10)-C(9)-H(9A)	120.0
C(3)-C(2)-C(1)	108.41(8)	C(9)-C(10)-C(5)	120.12(11)
C(3)-C(2)-C(4)	114.48(8)	C(9)-C(10)-H(10A)	119.9
C(1)-C(2)-C(4)	108.52(8)	C(5)-C(10)-H(10A)	119.9
C(3)-C(2)-H(2A)	108.4	C(12)-C(11)-C(16)	119.59(9)
C(1)-C(2)-H(2A)	108.4	C(12)-C(11)-C(3)	121.30(9)
C(4)-C(2)-H(2A)	108.4	C(16)-C(11)-C(3)	119.03(9)
C(11)-C(3)-C(2)	115.72(8)	C(13)-C(12)-C(11)	120.28(10)
C(11)-C(3)-Cl(1)	109.79(7)	C(13)-C(12)-H(12A)	119.9
C(2)-C(3)-Cl(1)	105.26(7)	C(11)-C(12)-H(12A)	119.9
C(11)-C(3)-H(3A)	108.6	C(12)-C(13)-C(14)	120.17(11)
C(2)-C(3)-H(3A)	108.6	C(12)-C(13)-H(13A)	119.9
Cl(1)-C(3)-H(3A)	108.6	C(14)-C(13)-H(13A)	119.9
C(2)-C(4)-Cl(4)	112.67(7)	C(15)-C(14)-C(13)	119.82(10)
C(2)-C(4)-Cl(2)	111.55(7)	C(15)-C(14)-H(14A)	120.1
Cl(4)-C(4)-Cl(2)	108.89(6)	C(13)-C(14)-H(14A)	120.1
C(2)-C(4)-Cl(3)	107.89(7)	C(14)-C(15)-C(16)	120.29(10)
Cl(4)-C(4)-Cl(3)	108.88(6)	C(14)-C(15)-H(15A)	119.9
Cl(2)-C(4)-Cl(3)	106.77(6)	C(16)-C(15)-H(15A)	119.9
C(6)-C(5)-C(10)	119.49(10)	C(11)-C(16)-C(15)	119.84(10)
C(6)-C(5)-C(1)	123.28(9)	C(11)-C(16)-H(16A)	120.1
C(10)-C(5)-C(1)	117.22(9)	C(15)-C(16)-H(16A)	120.1

Symmetry transformations used to generate equivalent atoms:

Table A26: Torsion angles [°] for chalcone-CCl₄ adduct.

O(1)-C(1)-C(2)-C(3)	53.28(13)	C(1)-C(2)-C(4)-Cl(3)	-46.39(9)
C(5)-C(1)-C(2)-C(3)	-128.53(10)	O(1)-C(1)-C(5)-C(6)	-160.39(11)
O(1)-C(1)-C(2)-C(4)	-71.62(12)	C(2)-C(1)-C(5)-C(6)	21.47(15)
C(5)-C(1)-C(2)-C(4)	106.58(11)	O(1)-C(1)-C(5)-C(10)	18.91(15)
C(1)-C(2)-C(3)-C(11)	178.72(9)	C(2)-C(1)-C(5)-C(10)	-159.24(9)
C(4)-C(2)-C(3)-C(11)	-59.99(12)	C(10)-C(5)-C(6)-C(7)	-0.25(16)
C(1)-C(2)-C(3)-Cl(1)	57.32(9)	C(1)-C(5)-C(6)-C(7)	179.04(10)
C(4)-C(2)-C(3)-Cl(1)	178.60(7)	C(5)-C(6)-C(7)-C(8)	1.44(17)
C(3)-C(2)-C(4)-Cl(4)	-47.40(10)	C(6)-C(7)-C(8)-C(9)	-1.20(18)
C(1)-C(2)-C(4)-Cl(4)	73.83(9)	C(7)-C(8)-C(9)-C(10)	-0.25(18)
C(3)-C(2)-C(4)-Cl(2)	75.42(10)	C(8)-C(9)-C(10)-C(5)	1.45(17)
C(1)-C(2)-C(4)-Cl(2)	-163.35(7)	C(6)-C(5)-C(10)-C(9)	-1.20(16)
C(3)-C(2)-C(4)-Cl(3)	-167.62(7)	C(1)-C(5)-C(10)-C(9)	179.47(10)

C(2)-C(3)-C(11)-C(12)	-63.84(13)	C(11)-C(12)-C(13)-C(14)	-0.36(17)
Cl(1)-C(3)-C(11)-C(12)	55.11(12)	C(12)-C(13)-C(14)-C(15)	0.84(18)
C(2)-C(3)-C(11)-C(16)	112.87(11)	C(13)-C(14)-C(15)-C(16)	-0.43(18)
Cl(1)-C(3)-C(11)-C(16)	-128.19(9)	C(12)-C(11)-C(16)-C(15)	0.94(16)
C(16)-C(11)-C(12)-C(13)	-0.53(16)	C(3)-C(11)-C(16)-C(15)	-175.82(10)
C(3)-C(11)-C(12)-C(13)	176.16(10)	C(14)-C(15)-C(16)-C(11)	-0.46(17)

Symmetry transformations used to generate equivalent atoms:

Table A27: Bond lengths [\AA] and angles [$^\circ$] for *cis*-Stilbene- CCl_4 adduct.

Cl(1)-C(1)	1.7735(11)	C(10)-C(2)-C(3)	114.99(9)
Cl(2)-C(1)	1.7893(12)	C(1)-C(2)-C(3)	115.77(9)
Cl(3)-C(1)	1.7755(11)	C(10)-C(2)-H(2)	105.0(8)
Cl(4)-C(3)	1.7998(12)	C(1)-C(2)-H(2)	102.1(9)
C(1)-C(2)	1.5518(15)	C(3)-C(2)-H(2)	102.7(8)
C(2)-C(10)	1.5201(15)	C(4)-C(3)-C(2)	109.86(8)
C(2)-C(3)	1.5533(15)	C(4)-C(3)-Cl(4)	111.63(8)
C(2)-H(2)	1.007(17)	C(2)-C(3)-Cl(4)	113.99(7)
C(3)-C(4)	1.5164(15)	C(4)-C(3)-H(3)	109.5(10)
C(3)-H(3)	0.929(17)	C(2)-C(3)-H(3)	110.1(11)
C(4)-C(9)	1.3929(16)	Cl(4)-C(3)-H(3)	101.4(11)
C(4)-C(5)	1.3971(17)	C(9)-C(4)-C(5)	119.22(10)
C(5)-C(6)	1.3958(15)	C(9)-C(4)-C(3)	123.25(10)
C(5)-H(5)	0.92(2)	C(5)-C(4)-C(3)	117.48(10)
C(6)-C(7)	1.3919(18)	C(6)-C(5)-C(4)	120.55(11)
C(6)-H(6)	0.92(2)	C(6)-C(5)-H(5)	118.3(12)
C(7)-C(8)	1.3845(18)	C(4)-C(5)-H(5)	121.1(12)
C(7)-H(7)	0.920(16)	C(7)-C(6)-C(5)	119.78(11)
C(8)-C(9)	1.3973(15)	C(7)-C(6)-H(6)	120.1(11)
C(8)-H(8)	0.938(18)	C(5)-C(6)-H(6)	120.2(11)
C(9)-H(9)	0.907(17)	C(8)-C(7)-C(6)	119.91(10)
C(10)-C(15)	1.3972(16)	C(8)-C(7)-H(7)	116.7(11)
C(10)-C(11)	1.3974(15)	C(6)-C(7)-H(7)	123.4(11)
C(11)-C(12)	1.3921(15)	C(7)-C(8)-C(9)	120.44(12)
C(11)-H(11)	0.943(19)	C(7)-C(8)-H(8)	123.0(10)
C(12)-C(13)	1.3884(18)	C(9)-C(8)-H(8)	116.5(11)
C(12)-H(12)	0.91(2)	C(4)-C(9)-C(8)	120.09(12)
C(13)-C(14)	1.3863(18)	C(4)-C(9)-H(9)	117.6(10)
C(13)-H(13)	0.909(18)	C(8)-C(9)-H(9)	122.3(10)
C(14)-C(15)	1.3956(15)	C(15)-C(10)-C(11)	118.63(10)
C(14)-H(14)	0.98(2)	C(15)-C(10)-C(2)	123.61(10)
C(15)-H(15)	0.927(18)	C(11)-C(10)-C(2)	117.72(10)
		C(12)-C(11)-C(10)	120.97(11)
C(2)-C(1)-Cl(1)	115.86(8)	C(12)-C(11)-H(11)	120.7(10)
C(2)-C(1)-Cl(3)	110.13(7)	C(10)-C(11)-H(11)	118.3(11)
Cl(1)-C(1)-Cl(3)	107.79(6)	C(13)-C(12)-C(11)	119.96(11)
C(2)-C(1)-Cl(2)	108.10(7)	C(13)-C(12)-H(12)	120.2(13)
Cl(1)-C(1)-Cl(2)	106.90(6)	C(11)-C(12)-H(12)	119.8(13)
Cl(3)-C(1)-Cl(2)	107.74(6)	C(14)-C(13)-C(12)	119.60(10)
C(10)-C(2)-C(1)	113.96(8)	C(14)-C(13)-H(13)	118.5(12)

C(12)-C(13)-H(13)	121.6(12)	C(14)-C(15)-C(10)	120.18(11)
C(13)-C(14)-C(15)	120.64(12)	C(14)-C(15)-H(15)	120.7(11)
C(13)-C(14)-H(14)	118.8(11)	C(10)-C(15)-H(15)	119.1(11)
C(15)-C(14)-H(14)	120.4(11)		

Symmetry transformations used to generate equivalent atoms:

Table A28: Torsion angles [°] for *cis*-stilbene-CCl₄ adduct.

Cl(1)-C(1)-C(2)-C(10)	-61.48(11)	C(5)-C(6)-C(7)-C(8)	0.17(17)
Cl(3)-C(1)-C(2)-C(10)	175.88(8)	C(6)-C(7)-C(8)-C(9)	-0.88(18)
Cl(2)-C(1)-C(2)-C(10)	58.42(11)	C(5)-C(4)-C(9)-C(8)	0.09(17)
Cl(1)-C(1)-C(2)-C(3)	75.23(11)	C(3)-C(4)-C(9)-C(8)	-177.15(10)
Cl(3)-C(1)-C(2)-C(3)	-47.41(12)	C(7)-C(8)-C(9)-C(4)	0.75(18)
Cl(2)-C(1)-C(2)-C(3)	-164.87(8)	C(1)-C(2)-C(10)-C(15)	68.33(14)
C(10)-C(2)-C(3)-C(4)	-54.34(12)	C(3)-C(2)-C(10)-C(15)	-68.73(13)
C(1)-C(2)-C(3)-C(4)	169.39(9)	C(1)-C(2)-C(10)-C(11)	-114.15(11)
C(10)-C(2)-C(3)-Cl(4)	71.80(11)	C(3)-C(2)-C(10)-C(11)	108.79(12)
C(1)-C(2)-C(3)-Cl(4)	-64.47(11)	C(15)-C(10)-C(11)-C(12)	-0.67(16)
C(2)-C(3)-C(4)-C(9)	96.79(13)	C(2)-C(10)-C(11)-C(12)	-178.32(10)
Cl(4)-C(3)-C(4)-C(9)	-30.67(13)	C(10)-C(11)-C(12)-C(13)	-0.50(17)
C(2)-C(3)-C(4)-C(5)	-80.49(12)	C(11)-C(12)-C(13)-C(14)	0.96(17)
Cl(4)-C(3)-C(4)-C(5)	152.04(8)	C(12)-C(13)-C(14)-C(15)	-0.23(18)
C(9)-C(4)-C(5)-C(6)	-0.80(16)	C(13)-C(14)-C(15)-C(10)	-0.96(18)
C(3)-C(4)-C(5)-C(6)	176.60(10)	C(11)-C(10)-C(15)-C(14)	1.40(17)
C(4)-C(5)-C(6)-C(7)	0.68(17)	C(2)-C(10)-C(15)-C(14)	178.89(11)

Symmetry transformations used to generate equivalent atoms: