



**Shiraz University
Faculty of Science**

Ph.D. Dissertation In Inorganic Chemistry

Study of Fundamental Organometallic Reactions

By

Hamid Reza Shamsavari

Supervised by

Prof. Dr. Mehdi Rashidi

July 2012

In The
Name of
God

In the Name of God

Declaration

Hereby, Hamid Reza Shamsavari (871241) student of Inorganic Chemistry, college of science, Shiraz University, certify that this thesis results of my own research and whenever I have utilized other resources, I have mentioned clearly references for them. Also, I declare that this research content and the title of my thesis are new and I promise without the permission of Shiraz University the results of it never be published or bring to someone else. The copyright of this thesis is the property of Shiraz University.



Hamid Reza Shamsavari

21.07.2012

IN THE NAME OF GOD

STUDY OF FUNDAMENTAL ORGANOMETALLIC REACTIONS

BY

HAMID REZA SHAHSAVARI


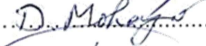

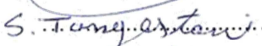
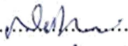

THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILSOPHY (PhD)

IN

INORGANIC CHEMISTRY
SHIRAZ UNIVERSITY
SHIRAZ
ISLAMIC REPUBLIC OF IRAN

EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS: EXCELLENT

.....M. RASHIDI, Ph.D., PROF. OF CHEMISTRY (SUPERVISOR)
.....D. MOHAJER, Ph.D., PROF. OF CHEMISTRY
.....M. ASADI, Ph.D., PROF. OF CHEMISTRY
.....S. TANGESTANINEJAD, Ph.D., PROF. OF CHEMISTRY
.....S. M. NABAVIZADEH, Ph.D., ASSOCI. PROF OF CHEMISTRY
.....A. R. ESMAILBEIG, Ph.D., ASSIST. PROF OF CHEMISTRY

JULY 2012

Dedicated to:

My Dear Family

&

My Nephew (Sina)

and

My Best Professors in My Life

Prof. Dr. M. Rashidi

&

Prof. Dr. E. Lalinde

Acknowledgments

Within this short acknowledgement, I hope to thank some of the people who have pushed me and given me the support and guidance I truly needed to get through this.

First, I cannot thank my dearest and excellent supervisor, Prof. Dr. Mehdi Rashidi. Without his support, advice, encouragement and extreme patience, I never would have been able to complete such a demanding task. I am fortunate to have such a great supervisor whose enthusiasm for science and kindness to people set the norm for me in my future career.

I also eager to acknowledge all the former and current members of Prof. Rashidi research group who have helped and contributed to my projects. Specifically, Dr. S. Masoud Nabavizadeh taught me many tricks of kinetic study and gave me instructions, etc. Dr. Ahmad Reza Esmaeilbeig has been a wonderful guidance in my career and my life. I give my thanks to my best friends Hashem and Mohsen for their great helps and willings. I would like to thank my committee members, Prof. Daryoush Mohajer, Prof. Mozaffar Asadi and Prof. Shahram Tangestaninejad for their helpful suggestions.

I would also like to take this opportunity to appreciate Prof. Dr. Elena Lalinde, my graet advisor during my Visiting Period at Universidad de La Rioja, Spain. Her enthusiasm in science encouraged me to keep on studying; her advice and suggestions made my projects go more smoothly; and her kind help made the life there in a totally different country a lot easier. Special thanks go to Dr. María Teresa Moreno, who was like my mother and has played an important role in my research. Dr. Jesús Rubén Berenguer, who was always nice to talk to whenever I had got questions. I also thank all the other members; Sergio, Ángel, Santiago, Patricia and Julio; in the Prof. Lalinde research group.

I would like to express my heart-felt gratitude to my family. My parents are a constant source of support as they provided me with the best condition for education.

Since I was very young, they have taught me how to face challenges, how to discover my potentials, how to be responsible. I thank my brother and his family, who never ceased to share their love, understanding, advice, and support.

Lastly, I thank God for giving me the gifts to do what I do and the initiative to actually use the gifts once I discover them. With his blessing, I pray my life that will continue to grow and prosper both inside and outside of the chemistry lab.

Hamid Reza Shamsavari

July 2012

Abstract

Study of Fundamental Organometallic Reactions

By

Hamid Reza Shahsavari

A complex $[\text{PtMe}_4(\text{dppf})]$, **2**, $\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene, which contains a chelating dppf ligand, has been prepared by the reaction of complex $\text{cis,cis-}[\text{PtMe}_4(\mu\text{-SMe}_2)]_2$ with 2 equiv of the biphosphine ligand dppf at room temperature by replacement of SMe_2 ligands with the P ligating atoms of dppf . The complex **2** reacted with 1 equiv of the strong acid CF_3COOH and first gave methane, followed by C-C coupling reaction to give ethane and the complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, **5**, and reaction of the complex $[\text{PtMe}_2(\text{dppf})]$, **1**, with 1 equiv of CF_3COOH gave methane and the complex **5**.

Substitution reaction of the labile SMe_2 ligand in the cyclometalated platinum(II) complexes with general formula $[\text{PtAr}(\text{ppy})(\text{SMe}_2)]$, **10**, in which $\text{ppy} =$ deprotonated 2-phenylpyridyl and $\text{Ar} = p\text{-MeC}_6\text{H}_4$ or $p\text{-MeOC}_6\text{H}_4$, by several P donor reagents were studied; the P-donors, L, are phosphines or phosphites, $\text{L} = \text{P}(\text{OPh})_3$, $\text{P}(\text{O}^i\text{Pr})_3$, PPh_3 and $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{PPh}_2$. Complexes **10** have a MLCT band in the visible region which was used to easily follow the kinetics of the ligand substitution reactions by UV-vis spectroscopy. Although the complexes **10** contain 2 *cis* Pt–C bonds, the substitution reactions followed a normal associative mechanism. The rates of reactions were dependent on the concentration and the nature of the entering group.

Kinetic study of the oxidative addition reaction of diarylplatinum(II) complexes $[\text{Pt}(p\text{-MeC}_6\text{H}_4)_2(\text{NN})]$, **12**, ($\text{NN} = 1,10$ -phenanthroline (phen) and 4,4'-di-*tert*-butyl-2,2'-bipyridine ($^t\text{Bu}_2\text{bpy}$)) with MeI in ionic liquids 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($[\text{bmim}][\text{bta}]$) or 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}][\text{BF}_4]$) are described. The reactions were investigated as a function of MeI concentration and temperature under pseudo-first-order conditions using UV-vis spectroscopy. In general, the oxidative addition reactions in ionic liquids followed an $\text{S}_{\text{N}}2$ mechanism, similar to that reported for the related reactions in conventional solvents, *e.g.* benzene or acetone. The reaction rates in different solvents followed the order acetone > ionic liquids > benzene. Therefore no particular 'ionic liquid effect' was detected in this kind of reactions. Effect of solvent on the reactions was examined using a linear solvation energy relationship (LSER) based on the Kamlet–Taft solvent scale.

Table of Contents

Chapter One.....	1
Introduction	1
1.1. General Remarks	2
1.2. Organoplatinum Complexes	2
1.3. Phosphorus Ligands.....	3
1.4 Cyclometalation Reactions	8
1.5. Fundamental Organometallic Reactions.....	11
1.5.1 Substitution Reaction	12
1.5.2. Oxidative Addition Reaction	15
1.5.3. Reductive Elimination Reaction	19
1.5.4. Electrophilic Reaction.....	22
1.6. Ionic Liquid	22
1.6.1 Types of Ionic Liquids	26
1.6.2. History and New Developments	26
1.6.3. Preparation of Ionic Liquids	28
16.4. Properties of Ionic Liquids.....	29
1.6.5. Organometallic Reaction in Ionic Liquids	35
1.6.6. Application of Ionic Liquids	36
Chapter Two	39
Experimental	39
Part I.....	40
A tetramethylplatinum(IV) complex with 1,1'-bis(diphenylphosphino)ferrocene ligand: reaction with Trifluoroacetic Acid	40

2.1.1. Instrumentation	40
2.1.2. Materials.....	40
2.1.3. Synthesis of precursor complexes.....	41
2.1.4. Synthesis of complexes with donor ligands	42
2.1.5. Synthesis of complexes by electrophiles	44
2.1.6. Attempted reaction of MeI with complex [PtMe ₂ (dppf)], 1.	46
2.1.7. X-ray crystal structure determination	46
Part II	48
Substitution reactions involving cyclometalated platinum(II) complexes: kinetic investigations.....	48
2.2.1. Instrumentation	48
2.2.2. Materials.....	48
2.2.3. Synthesis of complexes with donor ligands.....	48
2.2.4. Kinetic studies of reaction of [PtAr(ppy)(SMe ₂)], 10, (Ar = <i>p</i> -MeC ₆ H ₄ or <i>p</i> -MeOC ₆ H ₄), with P-donors ligands in CH ₂ Cl ₂	50
Part III.....	51
Oxidative addition reaction of diarylplatinum(II) complexes with MeI in ionic liquid media: a kinetic study	51
2.3.1. Instrumentation	51
2.3.2. Materials.....	51
2.3.3. Kinetic studies of reaction of [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (NN)], 12, (NN = ^t Bu ₂ bpy, phen) with MeI in Ionic liquids as solvent.....	51
Chapter Three	53
Results and Discussions	53
Part I.....	54

A tetramethylplatinum(IV) complex with 1,1'-bis(diphenylphosphino)ferrocene ligand: reaction with Trifluoroacetic Acid	54
3.1.1. Overview	54
3.1.2. Synthesis of complexes and reactions with electrophiles	55
3.1.3. Characterization of the complexes	58
3.1.4. Crystal structure determination of complexes	71
3.1.5. Conclusions	74
Part II	76
Substitution reactions involving cyclometalated platinum(II) complexes: kinetic investigations	76
3.2.1. Overview	76
3.3.2. Synthesis and characterization of the complexes	77
3.2.3. Kinetics of the reaction of complex [PtAr(ppy)(SMe ₂)], 10, with P-donor nucleophiles	86
3.2.4. Conclusions	90
Part III	92
Oxidative addition reaction of diarylplatinum(II) complexes with MeI in ionic liquid media: a kinetic study	92
3.3.1. Overview	92
3.3.2. Kinetic and mechanistic studies of oxidative addition reaction of MeI to diimine-diaryllplatinum(II) complexes	93
3.3.3. Conclusions	102
References	103
Appendix	108

List of Figures

Figure 1.1 Difference between an ionic solution and an ionic liquid	24
Figure 3.1 ^{31}P NMR spectrum (202 MHz) of complex $[\text{PtMe}_4(\text{dppf})]$, 2 , in CDCl_3	60
Figure 3.2 ^1H NMR spectrum (250 MHz) of complex $[\text{PtMe}_4(\text{dppf})]$, 2 , in CDCl_3	61
Figure 3.3 ^{31}P NMR spectrum (202 MHz) of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5 , in CDCl_3	63
Figure 3.4 ^{195}Pt NMR spectrum (107 MHz) of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5 , in CDCl_3	64
Figure 3.5 ^1H NMR spectrum (250 MHz) of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5 , in CDCl_3	65
Figure 3.6 ^1H NMR spectrum (250 MHz) of complex $[\text{PtMe}_3(\text{OCOCF}_3)(\text{bpy})]$, 7 , in CDCl_3	67
Figure 3.7 ^{13}C NMR spectrum (69 MHz) of complex $[\text{PtMe}_3(\text{OCOCF}_3)(\text{bpy})]$, 7 , in CDCl_3	68
Figure 3.8 Expansion of -20–2.5 ppm region of ^{13}C NMR spectrum (69 MHz) of complex $[\text{PtMe}_3(\text{OCOCF}_3)(\text{bpy})]$, 7 , in CDCl_3	69
Figure 3.9 Expansion of 120–160 ppm region of ^{13}C NMR spectrum (69 MHz) of complex $[\text{PtMe}_3(\text{OCOCF}_3)(\text{bpy})]$, 7 , in CDCl_3	70
Figure 3.10 Molecular structure of complex $[\text{PtMe}_4(\text{dppf})]$, 2	72
Figure 3.11 Molecular structure of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5	73
Figure 3.12 ^{31}P NMR spectrum (202 MHz) of complex $[\text{Pt}(p\text{-MeC}_6\text{H}_4)(\text{ppy})(\text{P}(\text{O}^i\text{Pr})_3)]$, 11d , in CDCl_3	79
Figure 3.13 ^1H NMR spectrum (250 MHz) of complex $[\text{Pt}(p\text{-MeC}_6\text{H}_4)(\text{ppy})(\text{P}(\text{O}^i\text{Pr})_3)]$, 11d , in CDCl_3	80
Figure 3.14 ^{31}P NMR spectrum (202 MHz) of complex $[\text{Pt}(p\text{-MeC}_6\text{H}_4)(\text{ppy})(\text{P}(\text{O}^i\text{Pr})_3)]$, 11e , in CDCl_3	81
Figure 3.15 ^{195}Pt NMR spectrum (107 MHz) of complex $[\text{Pt}(p\text{-MeC}_6\text{H}_4)(\text{ppy})(\text{P}(\text{O}^i\text{Pr})_3)]$, 11e , in CDCl_3	82

Figure 3.16 ^1H NMR spectrum (250 MHz) of complex [Pt(<i>p</i> -MeC ₆ H ₄)(ppy)(P(O- ^{<i>i</i>} Pr) ₃)], 11e , in CDCl ₃	83
Figure 3.17 ^{31}P NMR spectrum (202 MHz) of complex [Pt(<i>p</i> -MeOC ₆ H ₄)(ppy)(PPh ₃)], 11f , in CDCl ₃	84
Figure 3.18 ^1H NMR spectrum (250 MHz) of complex [Pt(<i>p</i> -MeOC ₆ H ₄)(ppy)(PPh ₃)], 11f , in CDCl ₃	85
Figure 3.19 Changes in the UV-vis spectrum during the reaction of complex [Pt(<i>p</i> -MeC ₆ H ₄)(ppy)SMe ₂], 10b , (2.6×10^{-4} M) and dppm, under second-order 1:1 stoichiometric conditions, in CH ₂ Cl ₂ at T = 25 °C: (a) initial spectrum (before adding dppm) and (b) spectrum at t = 30 s; successive spectra were recorded at intervals of 1 min	86
Figure 3.20 Absorbance-time curves for the reaction of complex 10b with PPh ₃ (2.6×10^{-4} M), under second order 1:1 stoichiometric condition, in CH ₂ Cl ₂ at different temperatures 20, 25, 30, 35 °C (increases reading downward)	87
Figure 3.21 Eyring plots for the reaction of complex 10b with: (a) P(OPh) ₃ ; (b) PPh ₃ ; (c) P(O- ^{<i>i</i>} Pr) ₃ in CH ₂ Cl ₂	87
Figure 3.22 The $\Delta H^\ddagger/\Delta S^\ddagger$ compensation plots of reaction of complex 10b with the P-donor nucleophiles L in CH ₂ Cl ₂	88
Figure 3.23 Changes in the UV-vis spectrum during the reaction of complex [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (phen)], 12a , (3×10^{-4} M) and MeI in [bmim][bta] at T = 25 °C: (a) initial spectrum (before adding MeI) and (b) spectrum at t = 30 s; successive spectra were recorded at intervals of 45 s	95
Figure 3.24 Absorbance-time curves for the reaction of [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (phen)], 12a , with MeI (0.022-0.057 M; [MeI] increases reading downward) in [bmim][bta] at 25 °C	95
Figure 3.25 Plots of first-order rate constants for the reaction of complex [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (phen)], 12a , with MeI at different temperatures (a, 15 °C; b, 20 °C; c, 25 °C; d, 30 °C, e, 40 °C) versus the concentration of MeI in [bmim][bta]	96
Figure 3.26 Eyring plots for the reaction of MeI with (a) [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (phen)], 12a , in [bmim][bta], (b) [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (^{<i>t</i>} Bu ₂ bpy)], 12b , in [bmim][bta] and (c) [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (phen)], 12a , in [bmim][BF ₄]	97

Figure 3.27 Plot of ΔS^\ddagger vs. ΔH^\ddagger for the oxidative addition of MeI with (a) complex 12a and (b) complex 12b in different solvents	98
Figure 3.28 Plot showing a correlation between the experimental rate constants ($\ln k_2$) for the reaction of (a) complex 12a and (b) complex 12b with MeI at 25°C in different solvents and calculated rate constants based on Kamlet-Taft LSER fit	102
Figure A.1 ^1H -NMR spectrum (250 MHz) of mixture complex <i>trans-cis</i> -[PtCl ₂ (SMe ₂) ₂] in CDCl ₃	109
Figure A.2 ^1H NMR spectrum (250 MHz) of complex <i>cis,cis</i> -[PtMe ₂ (μ -SMe ₂) ₂] in CDCl ₃	110
Figure A.3 ^1H NMR spectrum (250 MHz) of complex <i>cis,cis</i> -[PtMe ₄ (μ -SMe ₂) ₂] in CDCl ₃	111
Figure A.4 ^1H -NMR spectrum (250 MHz) of complex [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (SMe ₂) ₂] in CDCl ₃	112
Figure A.5 ^1H -NMR spectrum (250 MHz) of complex [Pt(<i>p</i> -MeOC ₆ H ₄) ₂ (SMe ₂) ₂] in CDCl ₃	113
Figure A.6 ^{31}P NMR spectrum (202 MHz) of complex [PtMe ₂ (dppf)], 1 , in CDCl ₃	114
Figure A.7 ^{195}Pt NMR spectrum (107 MHz) of complex [PtMe ₂ (dppf)], 1 , in CDCl ₃	115
Figure A.8 ^1H NMR spectrum (250 MHz) of complex [PtMe ₂ (dppf)], 1 , in CDCl ₃	116
Figure A.9 Reaction of complex [PtMe ₄ (dppf)], 2 , with CF ₃ CO ₂ H as monitored by ^1H NMR spectroscopy at room temperature. Up view: After reaction in NMR tube. Down view: After reaction and removing solvent and adding new solvent	117
Figure A.10 ^1H NMR spectrum (250 MHz) of complex [PtMe ₄ (dppm)], 3 , in CDCl ₃	118
Figure A.11 ^1H NMR spectrum (250 MHz) of complex [PtMe ₄ (bipy)], 4 , in CDCl ₃	119

Figure A.12 ^1H NMR spectrum (250 MHz) of complex $[\text{PtMe}_3(\text{OCOCF}_3)(\text{dppm})]$, 6 , in CDCl_3	120
Figure A.13 ^1H NMR spectrum (250 MHz) of complex $[\text{Pt}(p\text{-MeC}_6\text{H}_4)(\text{ppy})(\text{SMe}_2)]$ in CDCl_3	121
Figure A.14 ^1H NMR spectrum (250 MHz) of complex $[\text{Pt}(p\text{-MeOC}_6\text{H}_4)(\text{ppy})(\text{SMe}_2)]$ in CDCl_3	122
Figure A.15 Packing diagram of complex $[\text{PtMe}_4(\text{dppf})]$, 2	123
Figure A.16 Packing diagram of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5	124
Figure A.17 ^{19}F NMR spectrum (470 MHz) of complex $[\text{PtMe}(\text{OCOCF}_3)(\text{dppf})]$, 5 , in CDCl_3	125

List of Tables

Table 1.1 Brief comparison of organic solvents with ionic liquids	37
Table 2.1. Crystal data, data collection and structure refinement details for complex [PtMe ₄ (dppf)], 2 , or complex [PtMe(OCOCF ₃)(dppf)], 5	.47
Table 3.1 Selected bond distances (Å) and angles (°) for complex [PtMe ₄ (dppf)], 2	72
Table 3.2 Selected bond distances (Å) and angles (°) for complex [PtMe(OCOCF ₃)(dppf)], 5	74
Table 3.3 Second-order rate constants and activation parameters for reaction of the complex [Pt(<i>p</i> -MeC ₆ H ₄)(ppy)(SMe ₂)], 10b , with the P-donor nucleophiles, L, in dichloromethane	88
Table 3.4 Second-order rate constants and activation parameters for reaction of [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (NN)], 12 , with MeI in different solvents	98
Table 3.5 The property parameters of solvents and the second-order rate constants ($k_2 / \text{L mol}^{-1} \text{s}^{-1}$) for the reaction of [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (NN)], 12 , with MeI in different solvents at 25 °C	99
Table 3.6 Parametric solvent coefficients of the reaction of [Pt(<i>p</i> -MeC ₆ H ₄) ₂ (NN)], 12 , with MeI obtained from the different multi-parametric equations (LSER)	101

Chapter One

Introduction

1.1. General Remarks

Organometallic compounds are those compounds having bonds between one or more metal atoms and one or more carbon atoms of an organyl group. They are classified by prefixing the metal with *organo-*, e.g. organoplatinum compounds. Organometallic compounds, with their metal–carbon bonds, lie at the interface between classical organic and inorganic chemistry in dealing with the interaction between inorganic metal species and organic molecules. In the related metal–organic compound area, in contrast, the organic fragment is bound only by metal–heteroatom bonds.

The organometallic field has provided a series of important conceptual insights, surprising structures, and useful catalysts both for industrial processes and for organic synthesis. The field is beginning to make links with biochemistry with the discovery of enzymes that carry out organometallic catalysis. The field is also creating links with the chemistry of materials because organometallic compounds are increasingly preferred as the precursors for depositing materials on various substrates via thermal decomposition of the metal compound.

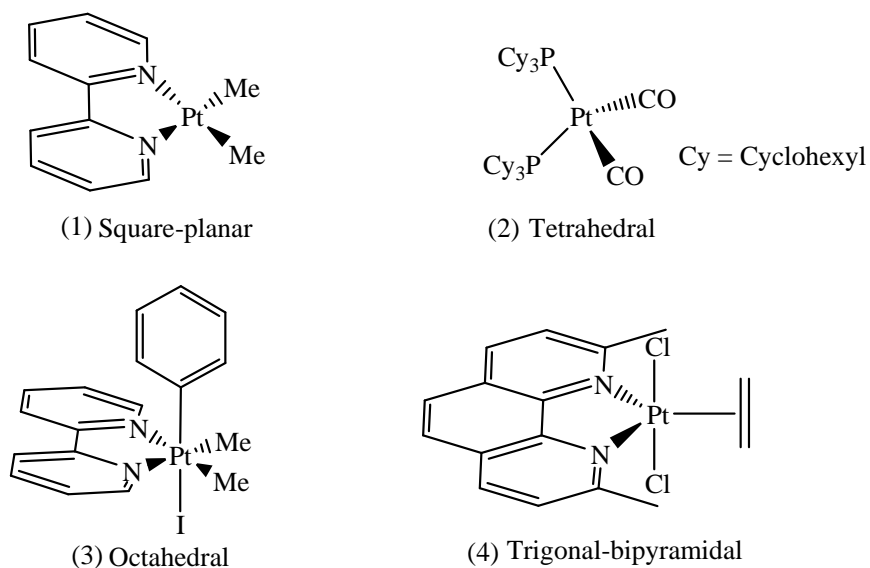
1.2. Organoplatinum Complexes

The first compound containing an unsaturated hydrocarbon attached to a metal, and indeed the first organometallic compound, if one excludes the cyanides, was $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, discovered by the Danish chemist W. C. Zeise as long ago as 1827 and followed 4 years later by the salt which bears his name, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$.

Ever since that time, platinum has been an important element in organometallic chemistry because it forms a wide range of organometallic compounds that are kinetically sufficiently inert to enable them to be isolated and characterized. The development of NMR for platinum, that 33.7% of which is present in nature as the ^{195}Pt isotope which has a nuclear spin of $\frac{1}{2}$, has been attractive because of the possibility of observing coupling between the metal and other nuclei. The presence, or absence, of such coupling provides valuable evidence on which to base structural

conclusions as well as to make mechanistic suggestions for the reactions of organoplatinum complexes.

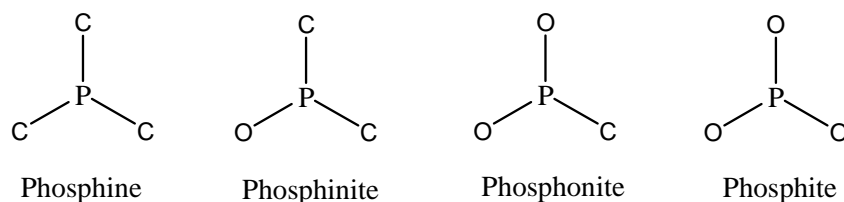
The common geometries for platinum complexes are four (square-planar (1)¹ and in some cases tetrahedral (2)²) and six (octahedral (3)³) coordinations. However, other geometry like uncommon five (trigonal-bipyramidal (4)⁴) coordination is desirable (Scheme 1.1).



Scheme 1.1

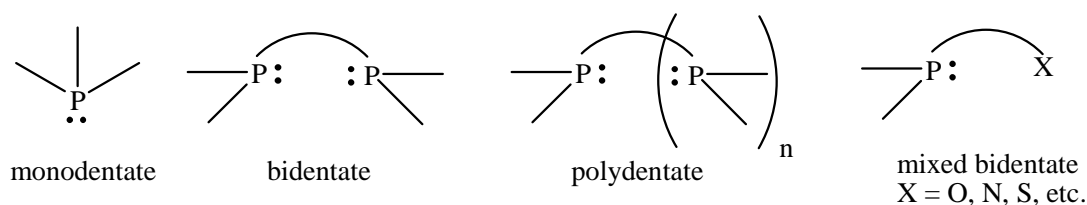
1.3. Phosphorus Ligands

Owing to the special metal ligation properties of phosphorus derivatives, trivalent phosphorus ligands have played and still play an important role as metal binders in organometallic chemistry. These trivalent phosphorus compounds offer chemists the unique opportunity to modify the steric and electronic properties of the ligands. In terms of electronic structure, the π -accepting properties of the phosphorus group can be strongly modified via replacement of the P-C bonds with P-O (Scheme 1.2), leading to phosphinites, phosphonites, or phosphites.⁵



Scheme 1.2. Various trivalent phosphorus ligand families.

Ligands, in general, and more specifically P-derivatives can also be differentiated according to their coordinating mode (*i.e.*, monodentate, bidentate, or polydentate; see Scheme 1.3).⁵



Scheme 1.3. Trivalent phosphorus ligands classified by coordination mode

Phosphines (PR_3) are one of the most important classes of ligands in chemistry, in both the industrial and academic spheres. Phosphine ligands are soft, strong σ -donors, and their electronic, steric, and stereochemical properties vary based on the substituents attached to the phosphorus atoms. Thus, choosing the correct phosphine ligands for a metal complex allows control over the electronic and steric environment of the complex.⁶

^{31}P NMR spectroscopy is routinely used to study of metal–phosphine complexes. When the substrates are phosphines, this technique becomes even more valuable for monitoring reactions and characterizing intermediates and products. However, ^{31}P NMR spectroscopic data on several related platinum complexes provided useful information on structure and bonding in this functional group.⁷

The electronic effect of various PR_3 ligands can be adjusted by changing the R group as a result of transmission of electron density along chemical bonds, quantified by Tolman.⁸ The second important feature of PR_3 is the variable steric size, as a result of forces between parts of a molecule. Tolman has proposed to measure the size of a