Shiraz University

Faculty of Science

Ph.D. Dissertation In Inorganic Chemistry

Study of Fundamental Organometallic Reactions

By

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Supervised by

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July 2012

In The Name of God

In the Name of God

Declaration

Hereby, Hamid Reza Shahsavari (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 Shahsavari

21.07.2012

IN THE NAME OF GOD

STUDY OF FUNDAMENTAL ORGANOMETALLIC REACTIONS
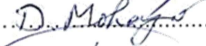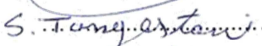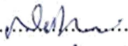

BY

HAMID REZA SHAHSAVARI

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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

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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.

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Hamid Reza Shahsavari

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Abstract

Study of Fundamental Organometallic Reactions

By

Hamid Reza Shahsavari

A complex [PtMe$_4$(dppf)], **2**, dppf = 1,1'-bis(diphenylphosphino)ferrocene, which contains a chelating dppf ligand, has been prepared by the reaction of complex *cis,cis*-[PtMe$_4$(μ-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$_3$COOH and first gave methane, followed by C-C coupling reaction to give ethane and the complex [PtMe(OCOCF$_3$)(dppf)], **5**, and reaction of the complex [PtMe$_2$(dppf)], **1**, with 1 equiv of CF$_3$COOH gave methane and the complex **5**.

Substitution reaction of the labile SMe$_2$ ligand in the cyclometalated platinum(II) complexes with general formula [PtAr(ppy)(SMe$_2$)], **10**, in which ppy = deprotonated 2-phenylpyridyl and Ar = *p*-MeC$_6$H$_4$ or *p*-MeOC$_6$H$_4$, by several P donor reagents were studied; the P-donors, L, are phosphines or phosphites, L = P(OPh)$_3$, P(O-^{i}Pr)$_3$, PPh$_3$ and L$_2$ = Ph$_2$PCH$_2$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 [Pt(*p*-MeC$_6$H$_4$)$_2$(NN)], **12**, (NN = 1,10-phenanthroline (phen) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bpy)) with MeI in ionic liquids 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][bta]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][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 S$_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.

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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 $[Pt(C_2H_4)Cl_2]_2$, 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, $K[Pt(C_2H_4)Cl_3].H_2O$.

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 isotope which has a nuclear spin of ½ , 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**).

(1) Square-planar

(2) Tetrahedral

Cy = Cyclohexyl

(3) Octahedral

(4) Trigonal-bipyramidal
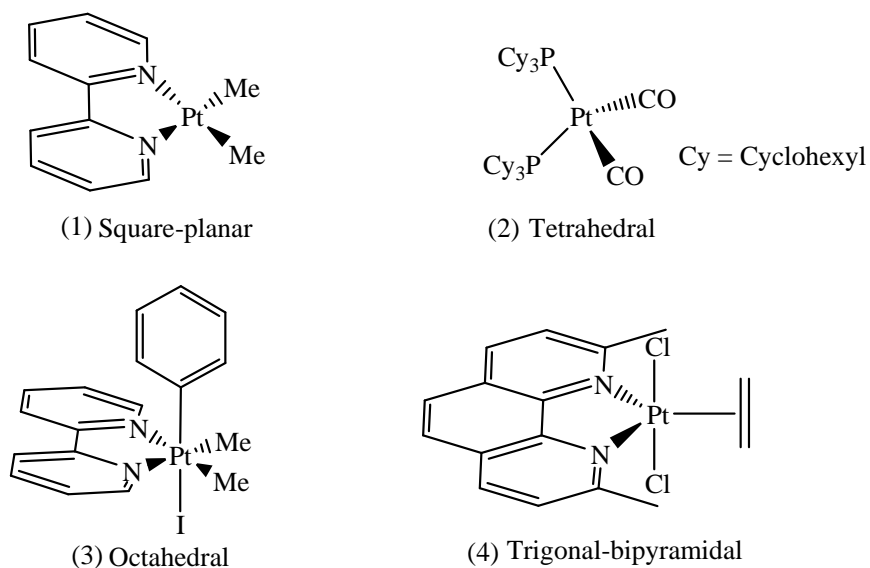
Scheme 1.1

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]

Phosphine Phosphinite Phosphonite Phosphite
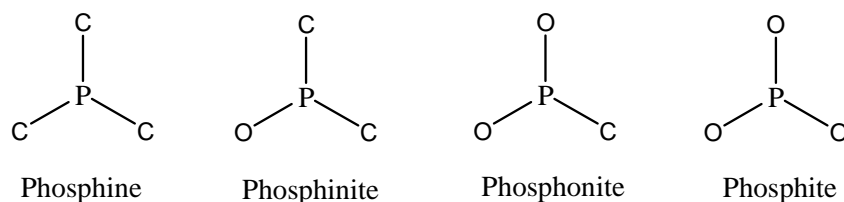
Scheme 1.2. Various trivalent phosphorus ligand families.

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]

monodentate bidentate   polydentate   mixed bidentate
                     X = O, N, S, etc.
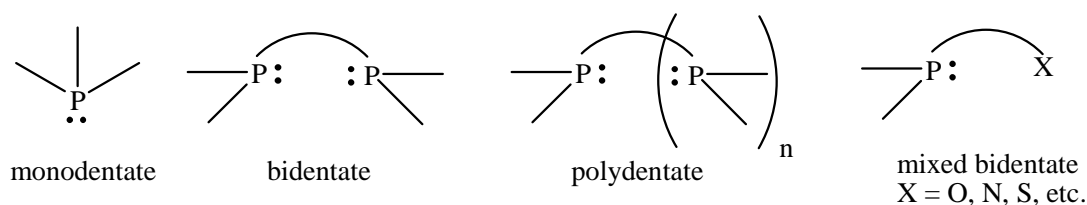
Scheme 1.3. Trivalent phosphorus ligands classified by coordination mode

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

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