In the Name of God

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Shiraz University

Faculty of Science

M. Sc. Thesis in Inorganic Chemistry

SYMMETRICAL AND UNSYMMETRICAL BINUCLEAR CYCLOMETALATED ORGANOPLATINUM (II) COMPLEXES

By

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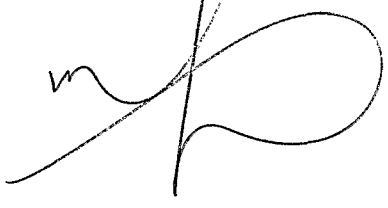

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BY:

MOHSEN GOLBON HAGHIGHI

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Dedicted to

My Dear Family Especially

My Lovely Mother

Acknowledgement

Laudation to the the God of majesty and glory obedience to him is cause of approch and gratitude in increase of benefits. Every inhalation of the breath prolongs life and every expiration of it gladdens our nature. Wherefore every breath confers two benefits and for every benefit gratitiude is due.

Thanks God for patient family, nice teachers and lovely friends that help me to pass succesfully from this part of my life.

I hope never forget to thanks him !

Prase is for God, that is created all the world

ABSTRACT

SYMMETRICAL AND UNSYMMETRICAL BINUCLEAR CYCLOMETALATED ORGANOPLATINUM (II) COMPLEXES

BY:

MOHSEN GOLBON HAGHIGHI

A versatile general synthetic approach has been designed to synthesize a series of symmetrical and unsymmetrical binuclear cyclometalated platinum(II) complexes each containing a bridging dppm, bis(diphenylphosphino)methane, ligand. Reaction of *cis*-[Pt(Ar)$_2$(SMe$_2$)$_2$], in which Ar= *para*-tolyl (*p*-T) or *para*-anisole (*p*-A), with 1 equiv of C^N ligand, in which C^N= 2-phenylpyridine (C N) or benzo[h]quinoline (C*N) , in acetone gave [Pt(Ar)(C^N)(SMe$_2$)]. When [Pt(Ar)(C^N)(SMe$_2$)] was reacted with 1 equiv of dppm ligand in acetone, the complex [Pt(Ar)(C^N)(η^1-dppm)] containing a monodentate dppm ligand was obtained by displacement of SMe$_2$ with dppm ligand. The reaction of 0.5 equiv of dppm in acetone with [Pt(Ar)(C^N)(SMe$_2$)] gave a symmetrical binuclear complex [Pt$_2$(Ar)$_2$(C^N)$_2$(μ-dppm)]. This complex was also prepared by reaction of complex [Pt(Ar)(C^N)(η^1-dppm)] with complex [Pt(Ar)(C^N)(SMe$_2$)]. The unsymmetrical complex [(Ar)(CN)Pt(μ-dppm)Pt(Ar')(C*N)], was prepared by reaction of [Pt(Ar)(CN)(SMe$_2$)], with 1 equiv of complex [Pt(Ar')(C*N)(η^1-dppm)]. All the complexes were fully characterized using multinuclear (^{1}H, ^{13}C, ^{31}P and ^{195}Pt) NMR spectroscopy and elemental analysis

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CHAPTER ONE

Introduction and Literature Review

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1. General introduction

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. In addition to the traditional metals and semimetals, elements such as boron, silicon, arsenic and selenium are considered to form organometallic compounds. Examples include organomagnesium compounds such as iodo(methyl)magnesium MeMgI, diethylmagnesium (Et_2Mg); organolithium compounds such as butyllithium (BuLi), organozinc compounds such as chloro(ethoxycarbonylmethyl)zinc ($ClZnCH_2C(=O)OEt$); organocopper compounds such as lithium dimethylcuprate ($Li^+[CuMe_2]^-$); and organoborane compounds such as triethylborane (Et_3B).

The status of compounds in which the canonical anion has a delocalized structure in which the negative charge is shared with an atom more electronegative than carbon, as in enolates, may vary with the nature of the anionic moiety, the metal ion, and possibly the medium; in the absence of direct structural evidence for a carbon-metal bond, such compounds are not considered to be organometallic.

Depending mostly on the nature of metallic ion and somewhat on the nature of the organic compound, the character of the bond may either be ionic or covalent. Organic compounds bonded to sodium or potassium are primarily ionic. Those bonded to lead, tin, mercury, etc. are considered to have covalent bonds, and those bonded to magnesium or lithium have bonds with intermediate properties.

Organometallic compounds with bonds that have characters in between ionic and covalent are very important in industry, as they are both relatively stable in solutions and relatively ionic to undergo reactions. Two important classes are organolithium and organomagnesium compounds.

Binuclear complexes are of great importance in chemistry, catalysis and medicine. In recent years, there has been a great interest in investigating binuclear platinum (II) complexes as a new and exciting area in the effort to improve platinum chemotherapy. These compounds containing two or more metal atoms are of great interest because they can be used as models for mimicking the behaviors of heterogeneous catalytic systems. Although synthetic aspects of binuclear palladium and platinum complexes and their use in organic reactions are now fairly well demonstrated, their role in material's science, as liquid crystals (e.g., cyclometallated derivatives), preparation of metal (e.g., Pd) films and bioinorganic chemistry is emerging.

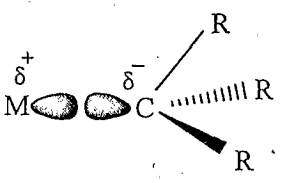
1.2. Metal Alkyl Complexes

Alkyl complexes play a critical role in a variety of important organometallic reactions such as olefin polymerization and hydroformylation. Early attempts to synthesize these complexes were unsuccessful, so it was originally thought that such species were inherently unstable due to weak metal-carbon bonds. In fact, the issue is not their thermodynamic stability (M-C bond dissociation energies are typically 40-60 kcal/mol with 20-70 kcal/mol being a practical range), but their kinetic stability.

1.2.1. Structure and Bonding

Simple alkyls are simple sigma donors that can be considered to donate one or two electrons to the metal center depending on which electron counting formalism we use (Fig.1.1).

Fig.1.1. Orbital interaction in metal-alkyl bond.



For simple metal alkyls, the M-R bond distance is typically 190 to 220 pm. This is approximately the sum of the covalent radii of carbon and metal, (r_c = 77 pm and r_m ~120 pm). Note that the first row transition metals are smaller, so any M-X bond distance will usually be smaller by 10-20 pm or so. Alkyls can bridge two metal centers, something that is well known from aluminum-alkyl chemistry. For example, consider the condensed phase structure of this Al-alkyls.[1]

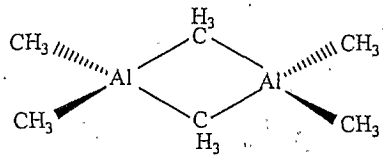


Fig.1.2. Bridging alkyl in Al_2Me_6

For Al_2Me_6, Fig.1.2, we see sharp resonances for bridging and terminal Me groups at -75 °C in the ^{1}H-NMR, but these coalesce and give one average signal at room temperature. This indicates a very low barrier to interconversion of the two groups.

1.3. 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. More recently, with the development of NMR, platinum, 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.

A number of platinum systems are of catalytic interest. These include the chloroplatinic acid catalyzed hydrosilation of olefins and the platinum (II)-tin (II) catalysts for the selective hydrogenation of polyolefines to monoolefins. However, the great interest in organoplatinum chemistry is the possibility of isolating stable complexes. In many cases, the 'stability' of these complexes is kinetic rather than thermodynamic and arises because the reactions of platinum are generally rather slow. Thus whilst nickel and palladium have a richer catalytic chemistry than platinum, in many instances it is only possible to understand what is going on in nickel and palladium chemistry by analogy with the known stable organoplatinum complexes that have been prepared and characterized.[2]

1.3.1. Bonding

A number of useful reviews on complexes containing metal-carbon σ-bonds have been published.[3-14]

In platinum(II)-alkyl σ-bonds, the σ-bond from the alkyl group to platinum is formed by overlap of a filled sp^3 hybrid orbital on the alkyl carbon atom with an empty $sp_x d_{x^2-y^2}$ hybrid orbital on platinum[2] (the platinum-carbon bond is taken as the x-axis).

Although it was originally thought that there was little π–back-donation of charge from platinum to the alkyl group because the p_y and p_z orbitals of the carbon atom were believed to be fully involved in bonding to the other atoms bound to this carbon atom, NMR evidence has suggested that even in methyl complexes there is some π–back donation from platinum (II) to the methyl group.[15]

In platinum (II)-aryl complexes the σ-bonds are formed by overlap of a filled sp^2 hybrid orbital on the carbon with an empty $sp_xp_yd_x^2-_y^2$ hybrid orbital on platinum. In addition there is the possibility of forming π–bonds by overlap of the filled pπ-orbitals of the aryl ligand with empty hybrid orbitals on platinum, as well as π–back bonds from filled platinum hybrid orbitals to the empty pπ*-orbitals of the aryl ligand. It is thus not surprising to find that aryl complexes are more easily prepared and purified and are more stable than alkyl complexes.[16,17]

1.3.2. Stability

One of the greater problems in determining the stability of a complex is to decide what the stability is in relation to. The phrase is often loosely applied in respect of one or all the thermal, oxidative, hydrolytic or solvolytic factors. The platinum (II) complexes are fairly stable in respect of all of these terms. Thus methyl platinum (II) complexes are not hydrolyzed by dilute acids or oxidized by moist air, and *cis*-$[Pt(PEt_3)_2Me_2]$ can be distilled without decomposition at 85 °C (at 10^{-4} mmHg). Again, in these terms, the stability order of organic ligands is *o*-subs[18]:

phenyl > PhC≡C > *p*-subs. phenyl ≈ phenyl > Me > higher alkyl > HC≡C

Discussion of stability becomes more meaningful when the stability is divided into its thermodynamic and kinetic components. The thermodynamic stability depends on the relative energies of the metal-carbon and either the carbon-carbon or the carbon-hydrogen bonds. Although there is very little quantitative evidence on this, it is known that the Pt-C_6H_5 and Pt-CPh=CHPh σ–bonds have energies of 264 ±15 and 215 ±23 kJ/mol, respectively.[19, 20]

This is rather less than that of the carbon-carbon single bond (347 kJ/mol)[21] or the carbon-hydrogen bond (364 kJ/mol)[22], which are the main products of thermal decomposition. The platinum(II)-methyl bond is of comparable strength to the platinum(II)-iodide bond.[23] Hence it appears that the stability of platinum(II)-carbon σ–bonds must be kinetic rather than thermodynamic origin.

An important difference between the behavior of alkyls and aryls as ligands and that of the more familiar ligands of transition metal chemistry is that the latter complexes decompose with the formation of ions (*e.g.* Cl^-, NO_3^-) or of neutral molecules (*e.g.* H_2O, NH_3, PEt_3), all of which are stable species.

Dissociation of these ligands from a complex is therefore quite likely to be reversible. By contrast, dissociation of metal-carbon σ–bonds yields very reactive products such as free radicals, or less likely carbanions. This is an irreversible process, so that for stability a metal-carbon σ–bond must have a high activation energy barrier towards decomposition. The kinetic stability of a compound decreases with increasing temperature, which accounts for the low temperature necessary in the preparation of most complexes containing metal-carbon σ–bonds.

As a rule, aryl platinum compounds show a greater resistance to thermal decomposition and cleavage reactions than their alkyl analogous. Overlap between the platinum 5d orbitals and those of the aromatic system are almost certainly responsible. This can lead to a greater stability by effectively increasing the Pt-C bond strength and reducing the energy of the 5d orbitals.[18]

Aryl derivatives containing bulky *ortho*-substituent are particularly nonreactive.[24] For steric reasons, those groups will tend to lie perpendicular to the plane of the molecule. This position allows maximum overlap between the orbitals of the benzene nucleus and the metal $5d_{xy}$ orbital, thus lowering its energy and increasing the energy gap between this and lowest energy antibonding orbital. This effect is particularly pronounced in the aryl complexes of nickel.[25]

A second reason for the increased stability of these compounds is that the ortho groups will hinder the attack of reagents at platinum. Cleavage and decomposition reactions are slower with *o*-MeC_6H_4 derivatives than with phenyl or *p*-MeC_6H_4 or *m*-MeC_6H_4 complexes[18], and under similar conditions penta flourophenyl compounds often fail to react at all.[24]

In connection with these steric arrangements, Chatt and Shaw have pointed that the existence of syn and anti forms of *trans*-[Pt $(PEt_3)_2$(*o*-$MeC_6H_4)_2$] should be possible, as the phosphine ligands will prevent rotation about the Pt-C bonds.[18] Only one compound has been isolated, however, and this is assumed to be anti-form.