PLATINUM-CARBON BOND FORMATION BY CYCLOMETALLATION AND OXIDATIVE ADDITION REACTIVITY OF ORGANOPLATINUM COMPOUNDS.

by

Ronald Thomas Honeyman B.Sc., M.Sc., Dip.Ed.

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Chemistry Department,
University of Tasmania,
Hobart, Tasmania,
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This thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge, contains no copy or paraphrase of material previously presented by another person, except where due reference is made in the text.

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Commonly Used Abbreviations

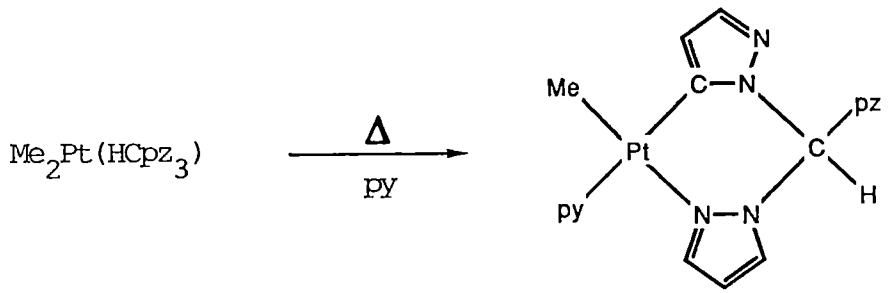
bipy - 2,2'-bipyridyl
COD - 1,5 cyclooctadiene
im - imidazolyl
Me - methyl group
mim - N-methylimidazolyl substituent
NBD - norbornadiene
OAc - acetate group
Ph - phenyl group
py - pyridine, or pyridin-2-yl substituent
pz - pyrazolyl substituent
R - alkyl or aryl group

NMR

ax - axial
co, c - coordinated
eq - equatorial
met, m - metallated
unco, u - uncoordinated

ABSTRACT

The work described in this thesis stems from the observation that a pyrazolyl group in $Me_2Pt(HCpz_3)$ undergoes a cyclometallation reaction when heated in neat pyridine, giving rise to a NC^- coordination mode, which is uncommon for flexible carbon bridged multidentate ligands.



The chemistry of this novel cyclometallation system has been explored, together with related polydentate ligand systems and the oxidative addition reactivity of platinum(II) complexes, in order to extend our knowledge of reactivity of platinum(II) toward formation of organoplatinum(II) and platinum(IV) complexes with new structural features.

A range of polydentate pyrazolyl ligands were chosen, or designed and synthesized, according to their ability to possibly undergo cyclometallation reactions. New ligands utilized in this work include the bidentate donors $H_2C(py)pz$, $H_2C(mim)pz$, and 1,3-$(pzCH_2)_2C_6H_4$ and tridentate donors $MeCpz_3$, $HC(mim)pz_2$, $HC(py)pz_2$ and $HC(thio)pz_2$.

A range of $Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes of these and other ligands were synthesized. The cyclometallation reaction was found to be feasible only for $Me_2Pt(II)$ complexes containing tridentate N-donor groups, except for the two bidentate ligands H_2Cpz_2 and $Ph(H)Cpz_2$. The reaction also proceeded in cold pyridine and in other N-donor solvents, eg. α and γ-picoline and N-methylimidazole.

Oxidative addition reactions using simple organohalides (MeI, EtI, $PhCH_2Br$) converted the cyclometallated tridentate systems (NC^-) into

platinum(IV) complexes displaying N_2C^- coordination geometry for the cyclometallated ligands. Remarkably, addition of these simple organohalides directly to Me_2Pt(tridentate) complexes caused a sequence of metallation and oxidative addition to occur, also resulting in the isolation of complexes with the N_2C^- ligand coordination geometry. Oxidative addition reactions involving bidentate ligands resulted in the isolation of N,N-coordinated platinum(IV) species.

Diphenylplatinum(II) did not participate in the cyclometallation reaction and upon addition of organohalides neutral or cationic complexes were formed depending on whether the substrate contained a bidentate or tridentate ligand respectively.

A more general route to complexes exhibiting the N_2C^- coordination geometry was sought, and thus N,N bidentate ligands possessing a halogen atom were synthesized, eg. $MeCpz_2CH_2Cl$, $2\text{-}PhXCpz_2H$, (X = Cl, Br) and their reactions with Me_2Pt(II) and Ph_2Pt(II) complexes investigated. In both instances Pt(IV) complexes with the ligand present as a N_2C^- tripodal tridentate were isolated and the first X-ray structural studies obtained for ligand systems of this type.

The new ligands, and halogen containing reagents used in oxidative addition reactions, appear to be suitable for applications in other areas of coordination and organometallic chemistry.

CHAPTER 1

INTRODUCTION

CHAPTER ONE

1.1 Introduction

Platinum is a member of the 5d transition series, and is the third member of the nickel triad, below palladium and adjacent to both gold and iridium. This proximity is reflected in the similarity of chemical properties of these elements. Thus, in the divalent state platinum is isoelectronic with palladium(II) and gold(III), and these ions often form closely related compounds, eg. $Me_2Pt(bipy)$, $Me_2Pd(bipy)$ and $[Me_2Au(bipy)]NO_3$.

Platinum(II),[1] like iridium(I)[2] often participates in facile oxidative addition reactions with alkyl halides, increasing both its formal oxidation number and coordination number by two.

$$\underline{trans}\text{-}Me(I)Pt(PEt_3)_2 + MeI \longrightarrow Me_2I_2Pt(PEt_3)_2 \qquad (1)$$

$$\underline{trans}\text{-}IIr(PPh_3)_2(CO) + MeI \longrightarrow MeI_2Ir(PPh_3)_2(CO) \qquad (2)$$

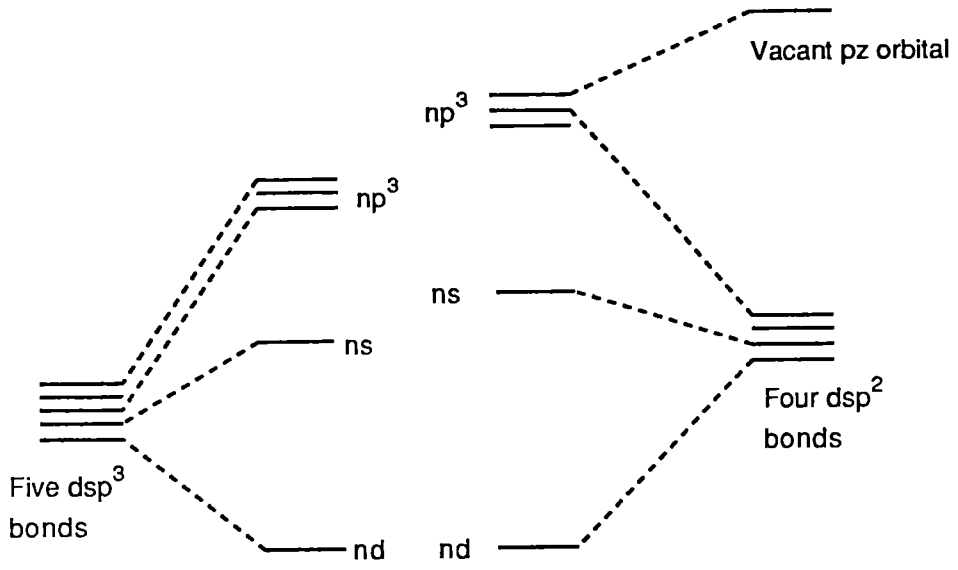
Owing to a combination of a high sublimation energy and a high ionization potential, platinum is a noble metal. However, it will dissolve in warm aqua regia, and when the nitrogen oxides are removed from this solution, hexachloroplatinic acid forms and this acid may be regarded as the starting material for most investigations of platinum chemistry.

Platinum is an important element in organometallic chemistry because it forms a wide range of organometallic compounds, in various oxidation states, that are sufficiently inert kinetically to enable them to be isolated and fully characterised. Furthermore, 33.8% of platinum occurs as the isotope ^{195}Pt which has nuclear spin $I = {}^1/_2$, and thus offers the possibility of exhibiting spin-spin coupling with other appropriate nuclei (viz. ^1H, ^{31}P, ^{19}F) in compounds. The presence or absence of such couplings can provide valuable evidence on which to base structural conclusions.

In its compounds, platinum exhibits a distinct preference for three oxidation states, platinum(0) with a d^{10} electronic configuration, platinum(II) [d^8] and platinum(IV) [d^6]. Platinum is able to form stable, isolable metal-carbon σ bonded (η bonding) complexes in its (II) and (IV) oxidation states.[3] Oxidation states of (I) and (III) are rare,[4] although a range of stable homo- and hetero-dinuclear platinum(I) complexes with a variety of bridging ligands have been isolated,[5] whilst the literature reports now include a smaller number of stable, dinuclear metal-metal bonded platinum(III) complexes.[6]

Zerovalent platinum complexes exhibit a range of coordination geometries, including linear, tetrahedral, and distorted trigonal bipyramidal including cationic complexes. For example, the phosphine complex $Pt(PPh_3)_4$ is tetra-coordinate, however if bulky substituents are placed on the phosphine the complexes are two coordinate, eg. $Pt(PBu^t_3)_2$. The dominant geometry of platinum(II) compounds is square planar, with both inorganic and organometallic compounds exhibiting this characteristic geometry, although distorted five coordinate trigonal bipyramidal platinum(II) complexes have also been isolated.

Of the nine orbitals available for forming bonds, namely 5d, 6s, 6p, for a valence bond approach to bonding for a $5d^8$ square planar complex, those used to form σ bonds are, by symmetry requirements, and assuming bonding in the xy plane, the $5d_{x^2-y^2}$, $6p_x$, $6p_y$ and a combination of 6s and $5d_{z^2}$. Since the $5d_{z^2}$ orbital is perpendicular to the xy plane, its overlap in the xy plane is relatively small, and as a consequence the 6s-$5d_{z^2}$ combination orbital has predominant s character, with the hybridization for square planar described as dsp^2. If a noble gas configuration is to be achieved in these complexes, then the remaining p orbital ($6p_z$) must be incorporated into the hybridization scheme, resulting in dsp^3 hybridization and five coordination, presumably square pyramidal. Incorporation of the $6p_z$ orbital into the overall hybridization will only be facilitated if the 5d-6p energy difference is relatively small. The effect of energy separation on hybridization is illustrated in figure 1.1.



small overall separation — large overall separation

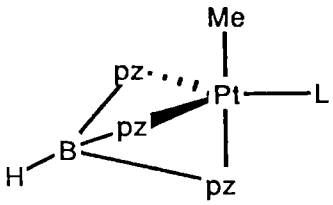
5 coordination — 4 coordination

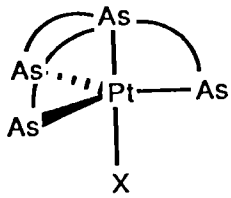
Figure 1.1 Effect of Energy Separation on Hybridization and Complex Geometry

On downward progression through the nickel triad the energy separation between the 5d and 6p orbitals increases in the order Ni(II)< Pd(II)< Pt(II).[7] Five coordination is therefore not favoured for platinum(II).

This simple valence bond approach to square-planar versus five coordinate geometry for platinum(II) neglects π-bonding interactions between a coordinated ligand and metal d and p orbitals, and any stereochemical requirements of the ligand. Indeed, five coordinate platinum(II) complexes have been isolated with π-bonding ligands[8] and polydentate ligands.[9] (See figure 1.2)

Tetravalent platinum exhibits only octahedral geometries in its complexes, although the regular octahedral structure may be distorted depending on the properties of the donor ligands and the presence of bulky substituents.





L = CO, alkyne, alkene

As_4 = tris-(o-diphenylarsinophenyl) arsine

X = Cl, Br, I, SCN

Figure 1.2

Between the three major oxidation states, platinum complexes are relatively easily oxidised or reduced in well defined two electron processes. Because all oxidation states differ by two electrons, there has been a wide range of oxidative addition chemistry in both oxidation states (0) and (II). In some instances reductive elimination follows oxidative addition if the intermediate platinum(IV) complex is not sufficiently inert. For example, methyl iodide reacts with cis-$Ph_2Pt(PMe_2Ph)_2$ to yield trans-$Ph(I)Pt(PMe_2Ph)_2$ and toluene, with platinum(IV) intermediates detected by NMR, but not isolated.[10]

The ability of platinum compounds to exist in a range of oxidation states, coupled with the ability to change its oxidation state by (often) facile reaction are important properties required for the role of platinum compounds in catalytic processes.

Although palladium complexes exhibit a richer catalytic chemistry than platinum, in many instances studies of closely related platinum chemistry has contributed to an understanding of the role of palladium in catalytic processes because the greater stability of platinum complexes has allowed the synthesis of model intermediates, and kinetic studies of slower reactions involving platinum substrates.

1.2 Platinum(0) Complexes

Although zerovalent platinum does not form any complexes with metal-carbon σ bonds, and thus falls outside the scope of the investigation reported in this thesis, some platinum(0) compounds are useful substrates for the preparation of platinum (II) and (IV) complexes which do contain metal-carbon σ bonds, eg. monoalkyl complexes can be prepared by oxidative addition of alkyl halides to zerovalent platinum complexes,[11,12,13] with the order of reactivity RI > RBr > RCl.[14]

$$Pt(PEt_3)_3 + PhCl \longrightarrow \underline{trans}\text{-}Ph(Cl)Pt(PEt_3)_2 + PEt_3 \quad (3)$$

$$Pt(PPh_3)_2(C_2H_4) + CH_2ClI \longrightarrow \underline{cis}\text{-}Cl(CH_2I)Pt(PPh_3)_2 + C_2H_4 \quad (4)$$

$$Pt(PPh_3)_2(C_2H_4) + MeI \longrightarrow \underline{trans}\text{-}Me(I)Pt(PPh_3)_2 + C_2H_4 \quad (5)$$

Of the various zerovalent platinum complexes studied, those containing a tertiary phosphine, eg. $Pt(PR_3)_4$ and $Pt(PR_3)_2(C_2H_4)$, are most numerous. This is due mainly to their inherent stability and the fact that they are soluble in a number of common organic solvents. $Pt(PPh_3)_4$ dissociates in benzene solution:

$$Pt(PPh_3)_4 \rightleftharpoons Pt(PPh_3)_3 + PPh_3 \quad (6)$$

$$Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3 \quad (7)$$

Kinetic evidence suggests that the chemically reactive intermediate in reactions of $Pt(PPh_3)_4$ is $Pt(PPh_3)_2$.[15,16] Thus, analysis of the kinetics of the oxidative addition of MeI to $Pt(PPh_3)_3$ showed that reactions (8) to (10) represent the mechanism.[15]

$$Pt(PPh_3)_3 \overset{k_1}{\rightleftharpoons} Pt(PPh_3)_2 + PPh_3 \quad (8)$$

$$Pt(PPh_3)_3 + MeI \xrightarrow{k_2} \underline{trans}\text{-}Me(I)Pt(PPh_3)_2 + PPh_3 \quad (9)$$

$$Pt(PPh_3)_2 + MeI \xrightarrow{k_3} \underline{trans}\text{-}Me(I)Pt(PPh_3)_2 \qquad (10)$$

In benzene at 25^0C $k_1 = 1.8 \times 10^{-4}$ l mol^{-1} sec^{-1}
$k_2 = 3.5 \times 10^{-3}$ l mol^{-1} sec^{-1}
$k_3 = 2.0 \times 10^{-2}$ l mol^{-1} sec^{-1}
indicating that the dissociated species $Pt(PPh_3)_2$ is 17.5 times more reactive than the undissociated species $Pt(PPh_3)_3$.

Other platinum(0) precursors studied in oxidative addition reactions have included $Pt(COD)_2$.[17]

1.3 Platinum(II) Complexes

Divalent platinum forms stable mononuclear complexes with anionic and neutral monodentate ligands. Bidentate ligands can form either mononuclear chelates or bridging dinuclear complexes. Mononuclear, four coordinate planar complexes are normally isolated from reactions of platinum(II) substrates with tridentate ligands (the tridentate ligands acting in a bidentate mode). Appreciable tendency toward higher coordination number is manifested when tetradentate ligands, particularly of the heavier donor atoms (eg. As, Sb), are utilized.

Organoplatinum(II) complexes can be derived from a variety of sources, including oxidative addition of organohalides to zerovalent platinum complexes, transmetallation of platinum(II) halide complexes, and cyclometallation. These methods of synthesis will be reviewed in Chapter 2.

The first methylplatinum(II) complexes were synthesized by Chatt and Shaw.[1]

$$\underline{cis/trans}\text{-}X_2Pt(PR_3)_2 + \text{xs MeMgI} \longrightarrow \underline{cis}\text{-}Me_2Pt(PR_3)_2 + \underline{trans}\text{-}Me(I)Pt(PR_3)_2 \qquad (11)$$

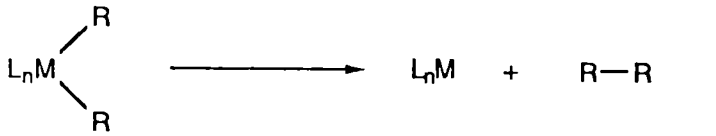
$$\underline{cis}\text{-}Cl_2Pt(PR_3)_2 + 2MeLi \longrightarrow \underline{cis}\text{-}Me_2Pt(PR_3)_2 + 2LiCl \qquad (12)$$

Dialkylplatinum(II) complexes exist exclusively as the cis isomer.[18] The universal adoption of the cis configuration is a consequence of the fact that strong σ bonding anionic groups, such as methyl groups, will require bonding orbitals which are of least energy, and these will be orbitals which are directed at 90^{o} to each other in the square plane. In general, arylplatinum(II) complexes are more thermodynamically stable than their alkyl analogues. With alkylplatinum(II) σ bonds, the bond 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 the metal atom. In the case of an arylplatinum(II) bond, overlap is between a filled sp^2 hybrid orbital on the aryl carbon atom with an appropriate $sp_x d_{x^2-y^2}$ hybrid orbital on the platinum atom. However, in addition to this direct overlap of orbitals, there exists the possibility of forming π bonds by overlap of the filled p_π orbitals of the aryl ligand with the appropriate empty hybrid orbitals on platinum, as well as π back bonds from the filled platinum hybrid orbitals to the empty p_π^* antibonding orbitals of the aryl ligand. Thus, it is not surprising to find that arylplatinum complexes are more easily prepared and purified, and in general are more stable, than corresponding alkyl complexes.

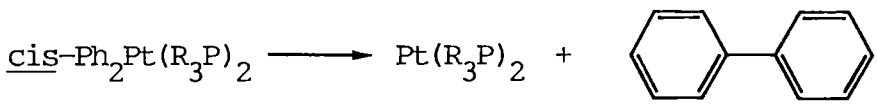
Although scant quantitative evidence exists, it is known that the $Pt-C_6H_5$ σ bond has an energy of 264 ± 15 kJ mol^{-1}.[19] The methyl-platinum bond energy has been determined from thermal decomposition reactions of various methylplatinum complexes, and is considered to be of the same order as a platinum-iodine bond.[20a] Values range from 144 kJ mol^{-1} [20b] to 163 ± 20 kJ mol^{-1}.[20c]

Both Pt-C aryl and alkyl σ bond energies are rather less than that of the C-C σ single bond, 347 kJ mol^{-1},[21] and the C-H σ bond 364 kJ mol^{-1},[22] which are the bonds formed in the main products of thermal decomposition. Thus, the stability of the platinum-carbon bond appears to be of kinetic rather than thermodynamic origin. The kinetic stability of a compound decreases with increasing temperature, which accounts for the low temperatures necessary in the preparation of most complexes containing metal-carbon σ bonds.

Initially, the observed instability of simple organotransition metal derivatives was ascribed to the inherent weakness of the metal-carbon σ bond.[1] Currently, it is accepted that the instability of a metal-carbon σ bond arises from the availability of low energy pathways for decomposition. Common cleavage mechanisms include reductive elimination[23] and β-hydrogen elimination from the ligand.[24] (equations (13) - (16))

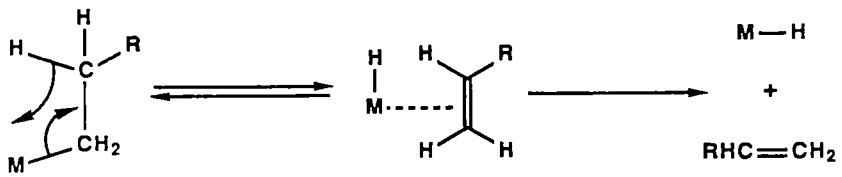


(13)

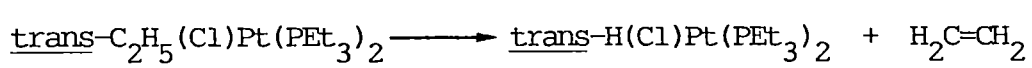


(14)

Reductive elimination:



(15)



(16)

β-hydrogen elimination:

Usually, after β-hydrogen elimination, the metal hydride formed is not stable enough to be isolated and decomposes to the metal.

Stabilization of metal-carbon σ bonds can be achieved by blocking of these concerted decomposition pathways, eg. occupation of neighbouring coordination sites can suppress β-hydrogen elimination. Ortho-substituted aryl ligands provide a good example of a series of very stable complexes whose extra stability relative to complexes involving meta, para or unsubstituted aryl ligands is largely of kinetic origin. Bulky ortho substituents prevent the aryl rings from

rotating about the platinum-carbon σ bond. This ensures that the ortho group remains in a position where it can most effectively hinder attack at the platinum atom.[25]

The importance of β-elimination as a decomposition mechanism for platinum(II) alkyls is emphasized by the much higher stability of methylplatinum(II) than ethyl or higher n-alkyl derivatives.

A very large number of X-ray diffraction studies of complexes containing platinum(II)-carbon σ bonds have been reported. The mean covalent radii for carbon atoms have been given as 0.772 Å (sp^3), 0.667 Å (sp^2) and 0.603 Å (sp),[26] which together with a covalent radius of 1.31 for platinum(II)[27] suggests typical bond lengths of 2.08 Å (Pt-C sp^3), 1.98 Å (Pt-C sp^2) and 1.91 Å (Pt-C sp). Examination of the structure of a range of complexes, containing platinum(II)-carbon σ bonds trans to ligands of moderate trans influence, yield bond lengths near the expected value (Table 1-1), consistent with a typical σ bond with no appreciable π character.

Table 1-1

Typical Pt(II)-C (sp^3) Bond Lengths

Complex	Pt-C, Å	trans to	Reference
$Me(Cl)Pt(PPh_3)_2$	2.08 (1)	Cl	28
$Me(Cl)Pt(PMePh_2)_2$	2.081 (6)	Cl	30
$Me(C_5H_5)Pt(COD)$	2.068 (8)	COD	29
$Me(C_2F_4)Pt(HBpz_3\text{-}N,N',N'')$	2.058 (14)	pz	31

The reactions of organoplatinum(II) complexes can be broadly subdivided into four categories:

(i) Reactions which rely on the variable oxidation states of platinum. This class of reactions includes oxidative addition and reductive elimination reactions.
Oxidative-addition and reductive-elimination reactions will be reviewed in Chapter 4.

(ii) Insertion reactions in which the Pt-C σ bond is modified,eg.

$$\underline{\text{trans}}\text{-Me(Cl)Pt(PEt}_3)_2 + \text{CO} \underset{140^{\circ}}{\overset{90^{\circ},\ 80\text{atm}}{\rightleftharpoons}} \underline{\text{trans}}\text{-MeCO(Cl)Pt(PEt}_3)_2 \quad (17)$$

Carbonylation of alkylplatinum(II) complexes usually requires vigorous conditions and the reactions are reversible on further heating.[22] They are considered to proceed via a five-coordinate intermediate, which has been observed during NMR studies, and a complex actually isolated for $Ph(Cl)Pt(CO)(P(C_6H_4NMe_2)_3)_2$.[32] The lower tendency of platinum(II) to expand its coordination number to five in comparison to palladium(II) accounts for the more vigorous conditions required in carbonylation of platinum(II) compared with organopalladium(II) complexes.

Other molecules which insert into the organoplatinum(II)-carbon bond include sulphur dioxide, isocyanides, olefins and acetylenes.[33]

(iii) Reactions which involve a strong dependence on the strength of the platinum-carbon σ bond, of which both chemical and thermal cleavage are examples.

Reaction of organoplatinum(II) complexes with electrophiles such as anhydrous hydrogen chloride can cause cleavage and reduce the number of organo groups bound to platinum. For example, anhydrous hydrogen chloride cleaves the methyl-platinum bond in $\underline{\text{cis}}\text{-Me}_2\text{Pt(PEt}_3)_2$.[1]

$$Me_2Pt(PEt_3)_2 \xrightarrow[\text{benzene}]{1\ HCl} Me(Cl)Pt(PEt_3)_2 + CH_4 \qquad (18)$$

$$Me(Cl)Pt(PEt_3)_2 \xrightarrow[\text{benzene}]{1\ HCl} \underline{cis}\text{-}Cl_2Pt(PEt_3)_2 + CH_4 \qquad (19)$$

The cleavage reaction may occur by either an S_E2 mechanism;

$$Pt\text{-}R + H\text{-}Cl \longrightarrow \begin{matrix} Pt\text{---}R \\ | \quad | \\ Cl\text{---}H \end{matrix} \longrightarrow Pt\text{-}Cl + RH \qquad (20)$$

an oxidative addition - reductive elimination sequence;

$$Pt(II)\text{-}R + H\text{-}Cl \xrightarrow{k_1} [Cl\text{-}\overset{H}{\overset{|}{Pt}}\text{-}R] \xrightarrow{k_2} Pt(II)\text{-}Cl + HR \qquad (21)$$

(if $k_1 >> k_2$ then the intermediate platinum(IV) complex may be isolable), or by direct attack by the electrophile on the platinum-carbon bond.

$$Pt\text{-}R + H^+ \longrightarrow \begin{matrix} & H & \\ Pt & \cdots & R \end{matrix}^+ \longrightarrow Pt^+ + HR \qquad (22)$$

The mechanism followed depends on such factors as the nature of the ligands surrounding platinum, and the nature of the electrophilic reagent and the organo group bound to platinum, eg. powerful electron donors such as bipy favour an oxidative addition - reductive elimination sequence, whilst sterically demanding and modest ligands such as COD favour the S_E2 mechanism.

Thermal decomposition of acyclic organoplatinum(II) complexes results in cleavage of the platinum-carbon σ bond and formation of alkanes and alkenes.[34]

$$(Bu^n)_2Pt(PPh_3)_2 \xrightarrow{\Delta} \underset{1}{n\text{-}C_4H_{10}} + \underset{1}{CH_3CH_2CH{=}CH_2} + Pt \qquad (23)$$

In mixed alkyl complexes, the elimination may take place from either the α, β, or γ carbon atoms, but it is the hydrogens bound to the β-carbons which are particularly susceptible to this reaction. The distribution of alkane and alkene indicates that the relative ease of β-hydrogen elimination depends on the number of β-hydrogens present in the two alkyl groups.[35]

$$Me(Et)Pt(PPh_3)_2 \xrightarrow{\Delta} \underset{1}{CH_4} + \underset{1}{C_2H_4} \qquad (24)$$

$$Et(C_3H_7)Pt(PPh_3)_2 \xrightarrow{\Delta} \underset{1}{C_2H_4} + \underset{0.61}{C_2H_6} + \underset{0.64}{C_3H_6} + \underset{0.95}{C_3H_8} \qquad (25)$$

Photolytic cleavage of organoplatinum(II) complexes yields products different than those formed by thermolysis, and is consistent with the formation of radicals.[35]

(iv) Replacement reactions which involve entities other than bonded organo groups which are bound to platinum. This class of reaction is very important and is responsible for the synthesis of an enormous number of organoplatinum(II) complexes.[36]

$$Me_2Pt(COD) + L \longrightarrow Me_2PtL + COD \qquad (26)$$

L = $2PPh_3$, 2py, bipy, $2AsMe_3$, $Me_2NCH_2CH_2NMe_2$

$$[Me_2Pt(Me_2S)]_2 + 2L \longrightarrow 2Me_2PtL + 2Me_2S \qquad (27)$$

L = bipy, phen

1.4 Platinum(IV) Complexes

All tetravalent platinum complexes exhibit regular octahedral structures, except where chelating or bulky ligands cause minor

distortions. Both solid-state X-ray diffraction studies and solution ^1H NMR results support the exclusive octahedral structure for platinum(IV). Because of the considerable ligand field splitting which renders the d^6 metal ion low-spin, all complexes are diamagnetic.

The general preparative methods for platinum(IV) complexes containing a Pt–C bond are based on either oxidative addition of an appropriate reagent to square-planar platinum(II) complexes (equations (28), (29), (30)),[1,37,38] or ligand exchange processes.[39,40]

$$\underline{\text{trans}}\text{-Me(I)Pt(PEt}_3)_2 + \text{MeI} \longrightarrow \text{Me}_2\text{I}_2\text{Pt(PEt}_3)_2 \qquad (28)$$

$$\text{Me}_2\text{Pt(COD)} + \text{H}_2\text{Cpz}_2 + \text{I}_2 \longrightarrow \text{Me}_2\text{I}_2\text{Pt(H}_2\text{Cpz}_2) + \text{COD} \qquad (29)$$

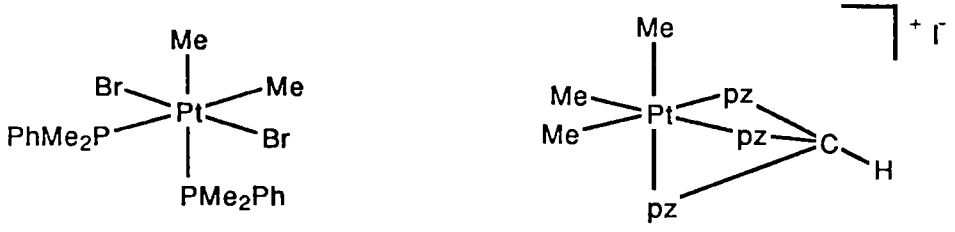
$$\text{Me}_2\text{Pt(bipy)} + \text{MeI} \longrightarrow \text{Me}_3\text{IPt(bipy)} \qquad (30)$$

$$[\text{Me}_3\text{PtI}]_4 + \text{L} \longrightarrow \text{Me}_3\text{IPt(L)} \qquad (31)$$

L = bipy, $HBpz_3$, 2py

$$[\text{Me}_3\text{PtI}]_4 + \text{KBpz}_3 \longrightarrow \text{Me}_3\text{Pt(Bpz}_3) \qquad (32)$$

Methylplatinum(IV) complexes are normally classified as containing the MePt, Me_2Pt, Me_3Pt or Me_4Pt unit. Regardless of ancillary ligands, the methyl groups are always in a cis or fac arrangement, emphasizing the high trans influence of the methyl group (Figure 1.3)



cis fac

Figure 1.3

It is noteworthy that despite a number of claims, Me_4Pt has not been isolated as a simple complex, although tetramethylplatinum(IV) complexes do exist, and are usually synthesized by transmetallation of the appropriate trialkylplatinum(IV) precursor.[39]

$$Me_3IPt(bipy) + MeLi \longrightarrow Me_4Pt(bipy) + LiI \qquad (33)$$

Recently,[41] the first binuclear tetramethylplatinum(IV) complex, $[Me_4Pt_2(Me_2S)]_2$, was synthesized.

$$2Cl_2Pt(Me_2S)_2 + 6MeLi + 2MeLi \xrightarrow[-2Me_2S]{-4LiCl,\ -2LiI} [Me_4Pt_2(Me_2S)]_2 \qquad (34)$$

The complex slowly decomposes in acetone at room temperature to $[Me_3Pt(OH)]_4$, and rapidly undergoes displacement reactions with bidentate ligands to yield mononuclear tetramethyl complexes.[41]

$$[Me_4Pt_2(Me_2S)]_2 + 2L \longrightarrow 2Me_4PtL + 2Me_2S \qquad (35)$$

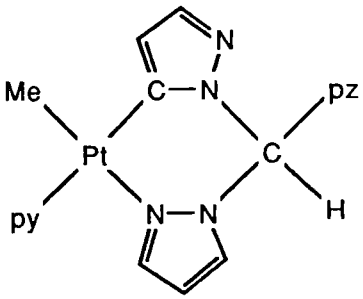
L = bipy, 1.10-phen, $Ph_2PCH_2PPh_2$

Homoleptic platinum(IV) lithium alkyls, eg $Li_2[PtMe_6]$, have been synthesized.[42] They are unstable to heat, and are violently hydrolyzed when exposed to moisture.

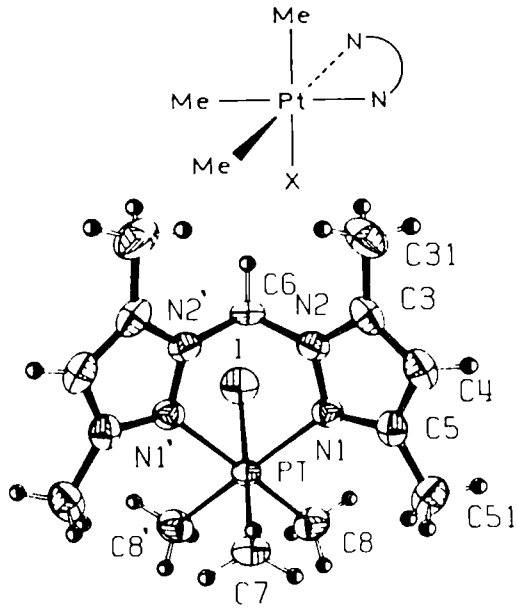
Alkylplatinum(IV) complexes are fairly stable with respect to hydrolysis, but on thermolysis undergo elimination reactions, an intermediate platinum(II) complex often being isolated, eg. when many fac-Me_3Pt(IV) complexes are heated they eliminate ethane cleanly.[20b]

$$fac\text{-}Me_3IPt(PMe_2Ph)_2 \longrightarrow trans\text{-}Me(I)Pt(PMe_2Ph)_2 + C_2H_6 \qquad (36)$$

X-ray diffraction studies carried out on methyl complexes of platinum(IV) indicate that the methyl bond lengths are almost identical to methylplatinum(II) bond distances (Figure 1.4)



MePt(II) 2.024(9)

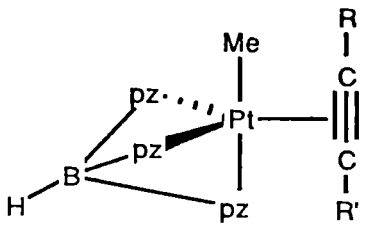


MePt(IV)
trans to N 2.032(5)
trans to I 2.077(6)

Figure 1.4

1.5 Platinum Complexes of Interest to this Investigation

The poly(1-pyrazolyl)borate ligands, $K[H_{4-n}B(pz)_n]$ (n=2-4), first developed as ligands by Trofimenko,[43] have been found to confer considerable stability on many organometallic complexes. Five coordinate complexes of platinum(II) are sufficiently rare that Clark[44] investigated the possibility of stabilizing such species using the tridentate poly(1-pyrazolyl)borate ligand, $HBpz_3^-$. In particular, he was interested in the formation of five coordinate olefin and acetylene complexes, since often such complexes have been postulated as intermediates in the transition metal catalyzed polymerization and hydrogenation of olefins and acetylenes. He found that by utilizing tris(1-pyrazolyl)borate as a tridentate ligand, a number of five coordinate methylplatinum(II) complexes of acetylenes, olefins and allenes could be stabilized and isolated, eg. spectroscopic studies support the structure (figure 1.5) shown for several acetylenes.

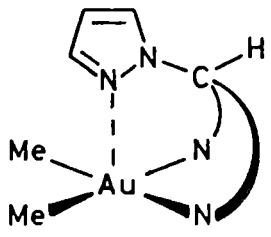


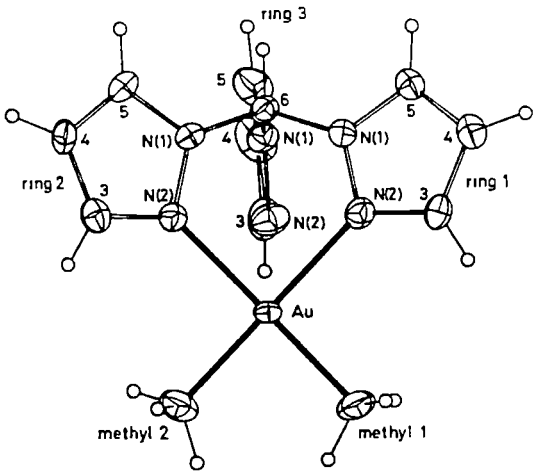
R, R' = CF_3, $(CH_3)O_2C$

Figure 1.5

This approach to the development of higher coordinate geometries for d^8 methylmetal systems has been applied in our laboratory, with the additional utilization of the neutral and isoelectronic poly(1-pyrazolyl)methanes.

Thus, dimethylgold(III) nitrate reacts with tris(1-pyrazolyl) methane to form a square planar complex with an additional weak axial interaction (figure 1.6).[45]





Au...N = 3.139(7)

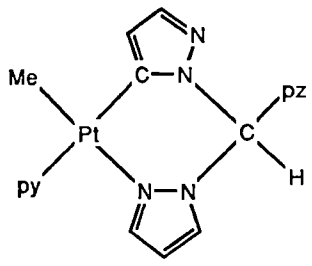
Figure 1.6

The gold atom is slightly above the square plane defined by the two methyl groups and the two strongly bonding nitrogen atoms of the tris(1-pyrazolyl)methane, and is close to (0.33Å) the mean plane of the axial pyrazolyl group.[45]

Dimethylplatinum(II) is isoelectronic with dimethylgold(III), and also exhibits square-planar geometries in its complexes, and thus a tris(1-pyrazolyl)methane derivative of dimethylplatinum(II) was synthesized to compare its behaviour with dimethylgold(III).

Reaction between $Me_2Pt(COD)$ and tris(1-pyrazolyl)methane yielded an intractable white powder. During preliminary characterization of this intractable solid, a "crystallization" from hot pyridine gave a microcrystalline product. Microanalysis, spectroscopic and physical data showed that a cyclometallation reaction had occurred.[46]

$$Me_2Pt(HCpz_3) \xrightarrow[\text{pyridine}]{\text{hot}} \underline{A} \qquad (37)$$



($\underline{A}$) $MePt(HCpz_2(C_3N_2H_2)\text{-}C,N)(py)$

The authors assumed that methane was eliminated from the cyclometallation reaction.[46]

The occurrence of cyclometallation reactions for reagents containing more than one donor group has been reported for two classes of reagent. The most common are those for which polydentate coordination by the donor group encourages or requires metallation at an additional site(s), eg. for nitrogen donor ligands palladation of phenyl rings of $[PhCH_2(Me)NCH_2]_2$ and $1,3\text{-}[py(Me)CH]_2C_6H_4$ results in formation of $Pd[PhCH_2(Me)NCH_2CH_2CH_2N(Me)CH_2C_6H_4\text{-}N,N,C]Cl$ (figure 1.7)[47] and $Pd[2,6\text{-}(py(Me)CH)_2C_6H_3\text{-}N,C,N](O_2CMe)$ (figure 1.8)[48] respectively.

However, cyclometallation of a donor ring(s) of a polydentate ligand, rather than simple donor atom chelation by the ring(s), has been reported for only a limited number of reagents, eg. 2,2'-bipyridyl in $[Ir(C_{10}H_8N_2\text{-}N,N')_2(C_{10}H_7N(NH)\text{-}N,C)(H_2O)]^{3+}$ [49] and $[(PtPh(4\text{-}Bu^tpy))_2(\mu\text{-}C_{10}H_6N_2\text{-}N,C,N',C')]$ (figure 1.9)[50] and 2-(2'-thienyl)pyridine[pyC_4H_3S], in $[Pd(py(C_4H_2S)\text{-}N,)C(\mu\text{-}Cl)]_2$.[51]

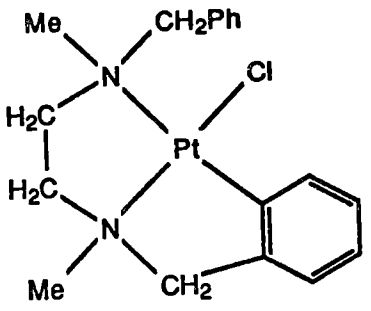


Figure 1.7

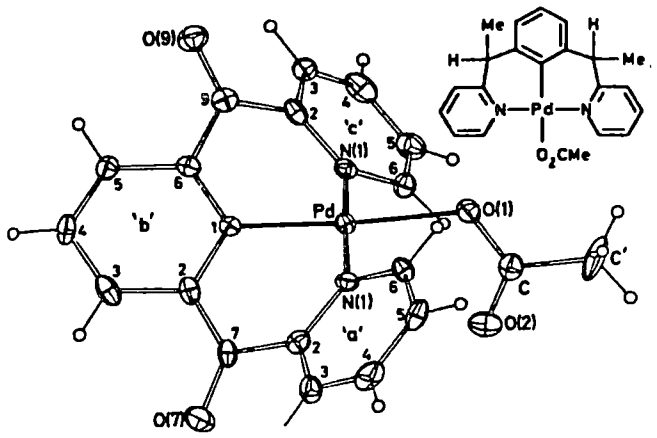


Figure 1.8

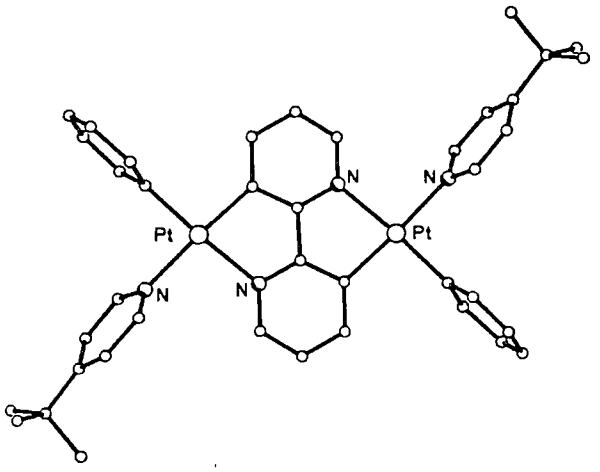
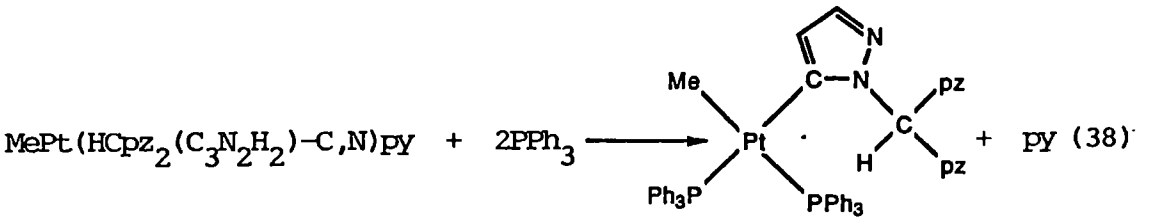


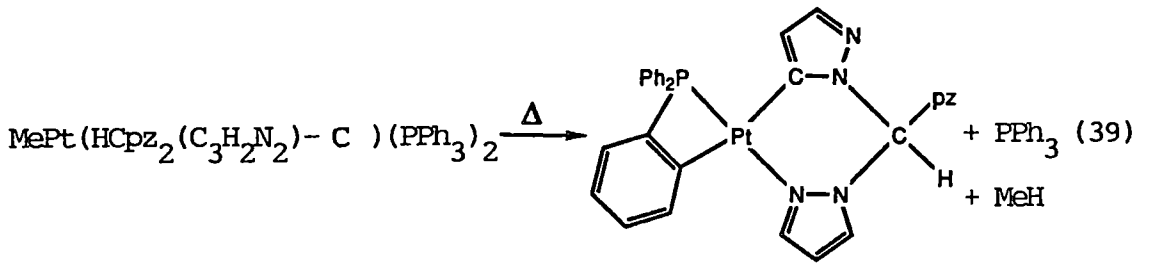
Figure 1.9

Complex (A) (equation (37)) is the only reported example of cyclometallation of a potential donor ring in which the rings are linked by a bridging group (CH), rather than linked directly as in 2,2'-bipyridyl or 2-(2'-thienyl)pyridine. Reaction of palladium(II) acetate with pyridine groups linked in this manner, eg. with py_2CH_2, $py_2(Ph)CH$ and py_3CH, results in isolation of N,N'-coordination complexes.[52]

Complex A reacts with triphenylphosphine to form a bis(phosphine) complex in which the tris(1-pyrazolyl)methane ligand acts as a unidentate C-donor.[46]



On heating this phosphine derivative, an additional cyclometallation reaction occurs to form the doubly cyclometallated complex $[Pt(HCpz_2(C_3H_2N_2)-N,C)(PPh_2(C_6H_4)-P,C)]$.[46]



In view of the unusual features exhibited by these complexes, further studies have been undertaken to ascertain the tendency of $HCpz_3$ and related poly(1-pyrazolyl) ligands to undergo cyclometallation. The reactivity of some of these complexes toward other phosphine ligands and carbon monoxide has also been studied, together with oxidative addition reactions to give, for example, methylplatinum(IV) complexes with metallated tris(1-pyrazolyl)methane as a tripodal $[N-C-N]^-$ group formally isoelectronic with tridentate $[pz_3BH-N,N',N'']^-$.

The aim of this study is to investigate factors affecting cyclometallation reactions of ligands containing at least one pyrazolyl group, and to develop the chemistry of cyclometallated complexes.

Within these two broad aims, and with methine bridged $HCpz_3$ as the basic 'model' ligand, specific aims initially included:

(i) to determine whether the cyclometallation reaction can be extended to related ligand systems, in particular ligands

containing less than three donor groups where at least one of these is pz, to ascertain effects of donor ring basicity and ligand geometry, and ligands containing other potential metallating groups and substituents on the carbon.

(ii) to develop the chemistry of cyclometallated complexes to include a range of ancillary ligands to encourage various modes of coordination of the cyclometallated group, eg. C,N-bidentate and C-unidentate, and oxidative addition chemistry to generate examples of C,N,N'-tripodal systems.

These aims were sought in several ways, but the general strategy relied on development of an improved procedure for synthesis of cycloplatinated $HCpz_3$ in $MePt(HCpz_2(C_3H_2N_2)-C,N)(py)$, to give a better potential route to other cycloplatinated systems, and extensive development of ligand synthesis to generate a series of ligands considered appropriate for investigation of the general aims. Precise reasons for choice of ligand, and reactions with Pt(II) to form cyclometallated complexes are given in the appropriate chapters.

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CHAPTER 2

STARTING MATERIALS

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2.1 Preparative Techniques

Since the first synthesis of stable platinum(II)-carbon σ bonded complexes by Chatt and Shaw some thirty years ago,[1] numerous diverse complexes have been synthesised by a variety of methods. However, only a few of these preparative methods are of general synthetic applicability.

2.1.1 Transmetallation

Transmetallation is the most widely utilized preparative technique and involves the reaction of a metal salt with a preformed organometallic reagent. Most typically, a dihalometal(II) complex is reacted with a Grignard or organolithium reagent. The reaction can lead to mono- or disubstituted organoplatinum(II) complexes depending upon the nature of the metal precursor, relative amount of organometallic reagent and whether it is a Grignard or an organolithium reagent. This is illustrated in the following equations (1 - 5).[2a,b,c,d.]

$$I_2Pt(COD) + \text{xs } MeMgI \longrightarrow Me_2Pt(COD) + MgI_2 \quad (71\%) \quad (1)$$

$$I_2Pt(NBD) + \text{xs } MeMgI \longrightarrow Me(I)Pt(NBD) + MgI_2 \quad (45\%) \quad (2)$$

$$I_2Pt(COD) + 2MeLi \longrightarrow Me_2Pt(COD) + 2MeLi \quad (84\%) \quad (3)$$

$$Cl_2Pt(NBD) + 2MeLi \longrightarrow Me_2Pt(NBD) + 2LiCl \quad (94\%) \quad (4)$$

$$2Cl_2Pt(Me_2S)_2 + 4MeLi \longrightarrow [Me_2Pt(Me_2S)]_2 + 2Me_2S + 4LiCl \quad (71\%) \quad (5)$$

Organolithium reagents are more powerful alkylating agents than the corresponding Grignard reagents, and Grignard reagents can participate in reversible equilibria and lead to a mixture of products in varying yields, and thus organolithium reagents are more often than not the reagent of choice.

Organometallic reagents other than organolithium and Grignard reagents have been used to transfer an organo group to platinum(II) complexes, eg. organomercurials may be used in essentially the same manner as Grignard reagents.[3]

$$Ph_2Hg + Cl_2Pt(PR_3)_2 \xrightarrow[\text{reflux}]{\text{benzene}} \underline{\text{trans}}\text{-}Ph(Cl)Pt(PR_3)_2 + PhHgCl \qquad (6)$$

The reaction of organomercurials with platinum(0) complexes provides a versatile route to alkyl-, aryl- and vinylplatinum(II) complexes.[4]

$$Pt(PPh_3)_4 + R_2Hg \longrightarrow R_2Pt(PPh_3)_2 + 2PPh_3 + Hg \qquad (7)$$

Organotin reagents, such as Me_3ArSn where Ar is aryl or another unsaturated group (vinyl or alkynyl), have been employed to transfer the Ar group to platinum.[5]

$$Cl_2Pt(COD) + Me_3ArSn \longrightarrow Ar(Cl)Pt(COD) + Me_3SnCl \qquad (8)$$

$$Ar(Cl)Pt(COD) + Me_3ArSn \longrightarrow Ar_2Pt(COD) + Me_3SnCl \qquad (9)$$

When tetramethyltin is used, methylplatinum(II) complexes may be formed, although the product of substitution is highly dependent upon the experimental conditions employed.[6,7]

$$Cl_2Pt(COD) + SnMe_4 \xrightarrow[Cl_2CHCHCl_2]{100^{\circ}C} Me(Cl)Pt(COD) \qquad (10)$$

$$Cl_2Pt(COD) + SnMe_4 \xrightarrow{DMSO} Me_2Pt(DMSO)_2 \qquad (11)$$

Other metals which have been employed as transmetallating reagents include sodium, potassium, copper and thallium.[8]

These routes to organoplatinum(II) complexes are generally employed when the corresponding lithio derivative has the potential to react with another substituent in the platinum substrate.

The use of organolithium reagents derived from ligands containing a heteroatom can lead to products which are analogous to those derived from cyclometallation reactions, and these will be discussed in Chapter 3.

2.1.2 Oxidative Addition of Organohalides to Platinum(0) Complexes

Both platinum(0) and platinum(II) complexes undergo a wide range of oxidative addition reactions, many of which are quite facile when a simple organohalide, eg. MeI, is employed. Thus, platinum(0) complexes can oxidatively add organohalides to form monoalkylplatinum(II) complexes[1,9]

$$Pt(PPh_3)_3 + MeI \longrightarrow \underline{trans}\text{-}Me(I)Pt(PPh_3)_2 + 2PPh_3 \qquad (12)$$

$$Pt(PPh_3)_3 + C_6H_5CH{=}CHBr \longrightarrow (C_6H_5CH{=}CH)BrPt(PPh_3)_2 + PPh_3 \qquad (13)$$

The product from these oxidative addition reactions may subsequently be reacted with a transmetallating reagent to yield higher organosubstituted complexes.

2.1.3 Cleavage Reactions

Cleavage reactions do not generate new platinum-carbon bonds, but instead reduce the number of platinum-carbon bonds,[10] and reaction stoichiometry must be carefully controlled to ensure that cleavage is stopped at the required point.[2b]

$$Me_2Pt(COD) \xrightarrow[\text{methanol}]{1\ HCl} Me(Cl)Pt(COD) + CH_4 \quad (14)$$

$$Me(Cl)Pt(COD) \xrightarrow{1\ HCl} Cl_2Pt(COD) + CH_4 \quad (15)$$

After single cleavage from a diorganoplatinum(II) complex with formation of a new R(Cl)Pt(II) complex, the product can then be made to undergo a transmetallation reaction to produce a new mixed diorgano complex. Unsymmetrical cis-dialkylplatinum(II) complexes can be produced by this method.[11]

$$(PhCH_2CH_2)_2Pt(COD) + HCl \longrightarrow PhCH_2CH_2(Cl)Pt(COD) \quad (16)$$

$$PhCH_2CH_2(Cl)Pt(COD) + EtMgBr \longrightarrow PhCH_2CH_2(Et)Pt(COD) \quad (17)$$

2.1.4 Cyclometallation

A method of metal-carbon σ bond formation used in this work involves direct reaction of a carbon-hydrogen bond with a metal when the organic group has a donor atom, and is termed cyclometallation. This type of reaction is reviewed in Chapter 3.

Other examples of reactions which result in new or modified metal-carbon σ bonds include insertion[12] and elimination[13] reactions, eg. reactions (18) and (19) respectively

$$trans\text{-}H(Cl)Pt(PEt_3)_2 + C_2H_4 \longrightarrow trans\text{-}C_2H_5(Cl)Pt(PEt_3)_2 \quad (18)$$

$$trans\text{-}Ph_3Sn(Cl)Pt(PPh_3)_2 \xrightarrow[\text{reflux}]{\text{acetone}} trans\text{-}Ph(Cl)Pt(PPh_3)_2 + Ph_2Sn \quad (19)$$

2.2 Synthetic Considerations in the Formation of $R_2Pt(II)L$ Complexes

Two general synthetic routes are preferred for the formation of $R_2Pt(II)L$ complexes (R = Me, Ph, L = 2 mono-, or 1 polydentate ligand).

(i) Transmetallation of the appropriate dihaloplatinum(II) ligand complex, X_2PtL.

Chatt and Shaw employed this method in their original preparation of R_2PtL complexes,[1]

$$Cl_2Pt(PPh_3)_2 + \text{xs } MeMgI \longrightarrow Me_2Pt(PPh_3)_2 + 2MgICl \qquad (20)$$

This method is applicable in instances where the platinum(II) substrate exhibits some solubility in the reaction solvent, where the reaction is not reversible or leads to a mixture of products, and where L is not susceptible to reaction with the transmetallating reagent.

(ii) Substitution reaction between a preformed diorganoplatinum complex and the required ligand.

A diorganoplatinum(II) precursor containing a labile ligand is made to undergo a substitution reaction with the ligand of interest. Clark and Manzer[2b] synthesised a large range of complexes by this method, employing $Me_2Pt(COD)$ as the precursor, eg.

$$Me_2Pt(COD) + bipy \longrightarrow Me_2Pt(bipy) + COD \qquad (21)$$

The cyclooctadiene ligand is strongly bound to platinum, and thus displacement of COD is difficult for ligands of low <u>trans</u> influence, and high temperatures are often required for weak donor ligands, in particular N-donors.

Dimethylplatinum(II) complexes of the related diolefin, norbornadiene, NBD, have also been synthesised and studied as reagents for synthesis. The coordination bite angle of COD in platinum(II) complexes is reported to be about 86^{o}.[14] Although crystal structures of platinum(II) complexes with NBD have not been reported, structures of the isoelectronic rhodium(I) complexes of NBD show that the coordination bite of this diolefin is approximately 66^{o}.[15] Thus, the overlap between the orbitals of the platinum atom

and the NBD ligand is expected to be much less in comparison with that of $Me_2Pt(COD)$. Consequently, the bonds between the metal atom and NBD should be weaker, and it is thus proposed that NBD should be more labile than COD in substitution reactions.

This is indeed the case, and $Me_2Pt(NBD)$[2c] has been used to synthesise complexes of donor ligands which showed little or no reactivity toward $Me_2Pt(COD)$, eg.

$$Me_2Pt(NBD) + 2py \xrightarrow{\text{benzene}} Me_2Pt(py)_2 + NBD \qquad (23)$$

A further series of alkyl- and arylplatinum(II) complexes which have proven useful as precursors for the preparation of various R_2PtL complexes are the dialkylsulphide complexes.[16,17] Reaction of the simple complexes $Cl_2Pt(R_2S)_2$ (R = Me, Et, Pr^n, Pr^i) with MeLi or PhLi have been reported to yield a variety of compounds.[16,18] With careful control of reagent stoichiometry dimeric organoplatinum(II) dialkylsulphide bridged complexes are obtained.[2d,16]

$$2(\underline{cis}\text{- or } \underline{trans}\text{-})Cl_2Pt(R^1{}_2S)_2 + 4R^2Li \longrightarrow [R^2{}_2Pt(R^1{}_2S)]_2 + 4LiCl \qquad (24)$$

(R^1= Me, Et, R^2= Me, Ph)

The bridging dialkylsulphide ligands are quite labile and can be replaced, in bridge splitting reactions, by various donor reagents.[2b,16,19]

$$[Me_2Pt(Me_2S)]_2 + 2bipy \longrightarrow 2Me_2Pt(bipy) + 2Me_2S \qquad (25)$$

$$[Me_2Pt(Me_2S)]_2 + 4L \longrightarrow 2Me_2PtL_2 + 2Me_2S \qquad (26)$$

(L= PPh_3, 0.5 $PPh_2(CH_2)_2PPh_2$,....)

Both $[Me_2Pt(Me_2S)]_2$ and $[Me_2Pt(Et_2S)]_2$ have been employed as precursors for substitution reactions, resulting in near quantitative yields of products.

An analogous diphenylplatinum(II)dialkylsulphide complex, $[Ph_2Pt(R_2S)]_2$, can be employed as a precursor in the formation of diphenylplatinum(II) complexes.[17,18]

$$[Ph_2Pt(Et_2S)]_2 + 2bipy \longrightarrow 2Ph_2Pt(bipy) + 2Et_2S \quad (27)$$

2.3 Results

2.3.1 Preparation of Cl_2PtL Complexes

Neutral, inorganic complexes of the ligands containing pyrazolyl groups H_2Cpz_2, $Me(H)Cpz_2$, Me_2Cpz_2, $HCpz_3$, and Cpz_4, were all obtained, in high yield, by direct reaction between equimolar amounts of ligand and potassium tetrachloroplatinate(II) in a 1:1 aqueous acetone mixture.

$$K_2PtCl_4 + L \longrightarrow Cl_2PtL + 2KCl \quad (28)$$

The reaction was complete when the red coloration of the solution (due to $PtCl_4^{2-}$) had disappeared. This was achieved by 0.5 hour reflux or by standing at ambient temperature for 6-8 hours. All complexes were deposited as yellow microcrystalline solids which were very insoluble in common solvents, except for $Cl_2Pt(Me_2Cpz_2)$ which exhibited solubility in most solvents.

2.3.2 Reaction of MeLi with $Cl_2Pt(HCpz_3)$

Reaction between $Cl_2Pt(HCpz_3)$ in anhydrous THF and MeLi in anhydrous ether, gave an insoluble purple product, which when heated with nitric acid evolved iodine vapour. It was assumed that some halide metathesis had occurred and that the product was $I_2Pt(HCpz_3)$ and/or $I(Cl)Pt(HCpz_3)$. Reaction of $Cl_2Pt(HCpz_3)$ with halide free MeLi resulted in isolation of unreacted susbtrate, and it was concluded that synthesis of $Me_2Pt(HCpz_3)$ by this method is unlikely to be feasible or of general applicability.

2.3.3 Synthesis of $Me_2Pt(HCpz_3)$

The complex $Me_2Pt(HCpz_3)$ was initially synthesised by the displacement reaction between $Me_2Pt(COD)$ and $HCpz_3$ in refluxing benzene.[20]

$$Me_2Pt(COD) + HCpz_3 \xrightarrow[30\ hours]{refluxing\ benzene} Me_2Pt(HCpz_3) + COD \quad (30)$$
(58%)

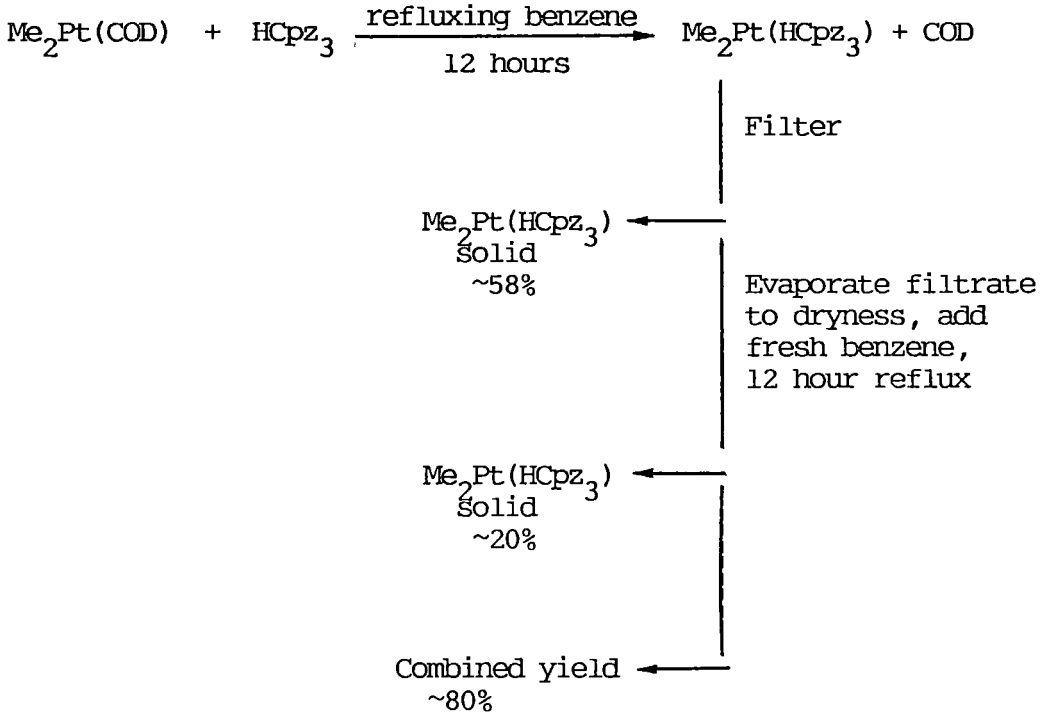
$Me_2Pt(HCpz_3)$ is insoluble in hot or cold benzene, and the appearance of it as a white precipitate during its synthesis indicates the extent of the reaction.

As this complex is a key reagent in the studies reported in this thesis, extensive efforts were made to improve the yield for its synthesis. In addition, it was anticipated that determination of the ideal conditions for synthesis would improve opportunities for the synthesis of complexes with ligands related to $HCpz_3$.

Increasing the reflux time of reaction (30) to 48 hours in benzene increases the yield only marginally, and removal of the product by filtration followed by further reflux of the filtrate does not increase the yield. However, the yield from reaction (30) can be increased, up to approximately 80%, by the procedure outlined in Scheme 2.1

As an appreciable additional yield of product is obtained after initial filtration, followed by removal of volatile substances and further reflux, it appears that displaced COD, present after initial substitution, interferes in the reaction. When present in comparable concentrations, free COD may compete with the $HCpz_3$ ligand.

Although this procedure (Scheme 2.1) allows for an increase in product yield, reaction time is still quite lengthy (30 hours). Thus, other dimethylplatinum(II) precursors were investigated for their reaction with $HCpz_3$. Results from these investigations are given in Table 2-1



Scheme 2.1

Table 2-1

Preparation of $Me_2Pt(HCpz_3)$ from Various $Me_2Pt(II)$ Precursors

Precursor	Solvent[1]	Time (hrs)	Yield (%)
$Me_2Pt(COD)$	Benzene	30	58
$Me_2Pt(NBD)$	Benzene	12	72
$[Me_2Pt(Me_2S)]_2$	Benzene	0.5	>90
$[Me_2Pt(Et_2S)]_2$	Benzene	0.5	>90

1. At reflux no reaction was apparent after 3 hrs when either acetone or chloroform were employed as solvents.

Higher yields are obtained with $Me_2Pt(NBD)$, presumably for the reasons outlined earlier, but the highly successful syntheses using

the dialkylsulphide complexes as substrates lead to the use of $[Me_2Pt(Et_2S)]_2$ as a reagent for all further studies.

$$[Me_2Pt(Et_2S)]_2 + 2HCpz_3 \xrightarrow[\text{benzene}\ 0.5\ hr]{\text{hot}} 2Me_2Pt(HCpz_3) + 2Et_2S \qquad (31)$$

It was noticed during this work that $[Me_2Pt(Et_2S)]_2$ appears to be more stable than $[Me_2Pt(Me_2S)]_2$, and it can be kept at room temperature under normal atmospheric conditions for at least 6 months, whereas $[Me_2Pt(Me_2S)]_2$ requires storage at ca $-20^{o}C$, and thus $[Me_2Pt(Et_2S)]_2$ was chosen as the preferred reagent.

2.3.4 Preparation of $[Me_2Pt(Et_2S)]_2$

In the first reported[16] preparation of $[Me_2Pt(Et_2S)]_2$ it was noted that at least three and preferably four equivalents of MeLi (halide free) were required to avoid extensive decomposition during reaction with $Cl_2Pt(Et_2S)_2$. Under the experimental conditions employed in our procedure it was found that if three to four equivalents of MeLi were used the mixture darkened considerably during the hydrolysis step, and the final yield of product was very low. This may be attributed to the formation of the homoleptic tetramethyl complex Li_2PtMe_4, formed in the presence of a large excess of MeLi. Indeed, if $Cl_2Pt(Pr^i{}_2S)_2$ is reacted with four equivalents of MeLi, colourless crystals formulated as Li_2PtMe_4.ether are isolated as the major product.[16]

On hydrolysis, Li_2PtMe_4.ether rapidly decomposes. Thus, in the synthesis of $[Me_2Pt(Et_2S)]_2$, 2.1 equivalents of halide free MeLi were employed, resulting in yields on isolation of product consistently between 70-80%.

If MeLi made from lithium wire and MeI, and thus containing LiI, was employed in the synthesis, $[Me_2Pt(Et_2S)]_2$ was not isolated, but an iodide complex is obtained, presumably $Me(I)Pt(Et_2S)_2$, since a complex of this stoichiometry is observed from the reaction of

$Cl_2Pt(Et_2S)_2$ with MeMgI.[16] Alternatively, if the MeLi solution contains MeI then it is possible that the binuclear tetramethylplatinum complex $[Pt_2Me_8(Et_2S)_2]$, is formed, in an analogous manner to that reported by Lashanizadehgan et al.[21]

2.3.4.1 Conclusion

Of the two general methods available for the synthesis of dialkylplatinum(II) complexes containing $HCpz_3$, the substitution reaction between a preformed diorganoplatinum(II) complex and ligand was found to be the only successful route. The dimeric complex $[Me_2Pt(Et_2S)]_2$ is preferred as the precursor.

2.3.5 Preparation of Me_2PtL Complexes

A major aim of this work was to investigate the cyclometallating behaviour of the $Me_2Pt(II)$ moiety with a range of ligands containing at least one pyrazolyl group, but with a minimum of two donor atoms per ligand. To this end a range of bidentate and tridentate pyrazolyl ligands were synthesized, and their $Me_2Pt(II)$ and in some cases their $Ph_2Pt(II)$ complexes, obtained. The ligands were either chosen or designed with essentially three factors in mind

(i) a comparison of bidentate versus tridentate ligands, eg. H_2Cpz_2 versus $HCpz_3$

(ii) pyrazolyl group metallation versus other donor group metallation, eg. H_2Cpz_2 versus $H_2C(py)pz$

(iii) pyrazolyl metallation versus other, non-donor group metallation, eg. $HCpz_3$ versus $Ph(H)Cpz_2$

Table 2-2 lists the ligands used to prepare Me_2PtL complexes together with the method of preparation

Table 2-2

Preparation of Me_2PtL Complexes

Ligand	Method of Preparation	Yield (%)
H_2Cpz_2	A	89
$Me(H)Cpz_2$	B	88
Me_2Cpz_2	B	82
$Ph(H)Cpz_2$	A	90
$H_2C(mim)pz$	B	91
$H_2C(py)pz$	B	84
$HCpz_3$	A	93
$HC(mim)pz_2$	A	86
$HC(thio)pz_2$	A	82
Cpz_4	B	91

Method A

$[Me_2Pt(Et_2S)]_2$ and ligand in 1:2 mole ratio were heated with stirring in anhydrous benzene under a nitrogen atmosphere. After 2-5 minutes of gentle warming the platinum precursor dissolved and the solution generally exhibited a yellow coloration. After a further 10-15 minutes heating the required complex was deposited as an insoluble, whitish solid. The product was filtered from the hot solution, washed with ether and air dried.

Method B

$[Me_2Pt(Et_2S)]_2$ and ligand in a 1:2 mole ratio were stirred and refluxed in anhydrous acetone, under nitrogen, for 15 minutes to yield a clear solution. Hexane was added (2 cm^3 per 10 cm^3 of acetone) and the acetone removed by rotary evaporation. As the volume decreased, white solids precipitated. These were collected and air dried.

2.3.6 Preparation of Ph_2PtL Complexes

Some representative Ph_2PtL complexes were synthesized in order to compare both their cyclometallating and oxidative addition behaviour with their dimethyl analogues. The complexes synthesized are listed in Table 2-3.

All complexes were prepared by method A in 2.3.5, utilizing $[Ph_2Pt(Et_2S)]_2$ in place of $[Me_2Pt(Et_2S)]_2$.

Table 2-3

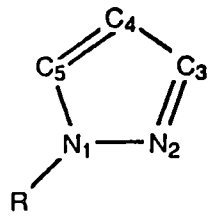
Preparation of Ph_2PtL Complexes

Complex	Yield (%)
$Ph_2Pt(HCpz_3)$	94
$Ph_2Pt(H_2Cpz_2)$	92
$Ph_2Pt(Me_2Cpz_2)$	92
$Ph_2Pt(Me(H)Cpz_2)$	90
$Ph_2Pt(H_2C(py)pz)$	90
$Ph_2Pt(H_2C(mim)pz)$	87
$Ph_2Pt(HC(py)pz_2)$	84
$Ph_2Pt(HC(thio)pz_2)$	88
$Ph_2Pt(HC(mim)pz_2)$	83

2.4 ^1H NMR Spectra of Pt(II) Complexes of Pyrazolyl Ligands

2.4.1 Proton Assignment in Substituted Pyrazoles

In the ^1H NMR spectrum of N-substituted pyrazoles (figure 2.1), the H4 proton resonance is well separated from both the H3 and H5 proton signals, occurring 1-2 ppm upfield.



R = organic group (not H)

Figure 2.1

It appears as a pseudo-triplet due to coupling with neighbouring H3 and H5 protons. The H3 and H5 proton resonances appear as doublets due to coupling with the H4 proton (close examination sometimes reveals further splitting due to long range ^{4}J coupling with the H3 and H5 protons). The published literature on organometallic derivatives of pyrazoles has lead to some ambiguity in the assignments of H3 and H5 proton signals. Observations which assist in the assignment of these signals include,[22]

(i) $J_{4,5}$ is always larger than $J_{3,4}$

(ii) The H3 signal is broadened by the nuclear quadrupole relaxation effect of N(2). Thus, if the H3 signal is a singlet (4 ≠ H), it is broader than H5, if it is a doublet (4 = H), it is less well resolved than H5.

(iii) H5 is more sensitive to solvent effects than H3.

Figures 2.2(a) and 2.2(b) illustrate the ^{1}H NMR spectrum of tris-(1-pyrazolyl)methane, $HCpz_3$, in $CDCl_3$ and D6 acetone respectively.

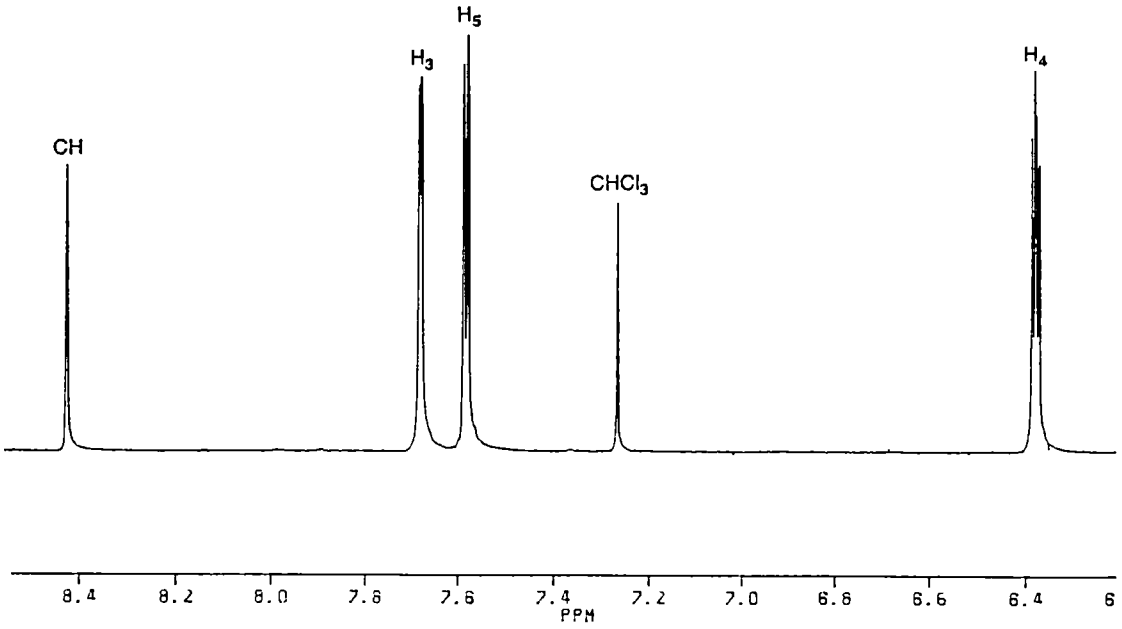


Figure 2.2(a) ^{1}H NMR spectrum of $HCpz_3$ in $CDCl_3$

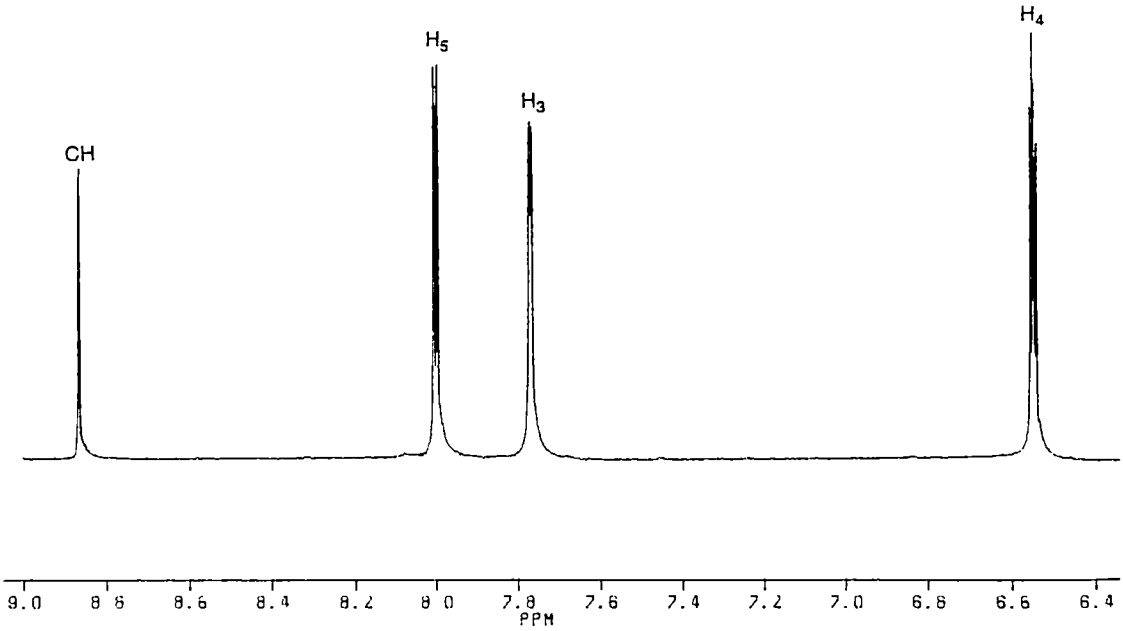


Figure 2.2(b) ^{1}H NMR spectrum of $HCpz_3$ in Acetone

From the magnitude of the coupling constants and the degree of resolution the H3 and H5 resonances can be assigned. Note that the relative positions of H3 and H5 are reversed in acetone and chloroform. The remaining low field resonance is due to the apical $\underline{H}Cpz_3$ proton.

Criterion (i), $J_{4,5} > J_{3,4}$ has been supported by a 2D heteronuclear COSY spectrum for a tris(1-pyrazolyl)methane rhodium complex.[23] This showed unambiguously that the proton signal with the largest coupling constant was bonded to the C5 position of the pyrazole ring.

To illustrate the generality of this assignment procedure, Table 2-4 contains the proton assignments of some pyrazole based ligands which will be utilized in complexes.

Table 2-4
^{1}H NMR Ligand Assignments

Ligand	Solvent	H4 (ppm)	Proton Assignment H3 $^3J_{(3,4)}$	H5 $^3J_{(4,5)}$
H_2Cpz_2	$CDCl_3$	6.26	7.55 (1.8)	7.63 (2.4)
	$(CD_3)_2CO$	6.39	7.61 (1.5)	7.98 (1.8)
$Me(H)Cpz_2$	$CDCl_3$	6.35	7.53 (2.0)	7.57 (2.4)
Me_2Cpz_2	$CDCl_3$	6.30	7.6 (1.8)	7.43 (2.5)
$Ph(H)Cpz_2$	$CDCl_3$	6.40	7.63 (1.8)	7.51 (2.4)

Note that in the ligands Me_2Cpz_2 and $Ph(H)Cpz_2$, the relative chemical shift positions are reversed with respect to other ligands.

2.4.2 Proton Assignment in Metal-Pyrazolyl Complexes

The proton resonances for a ligand bound to a metal generally exhibit a downfield shift on coordination. In simple coordination complexes the multiplicity of ligand resonances is not normally altered significantly, and unambiguous proton assignment is generally

straightforward. For example, consider the simple complexes $X_2Hg(H_2Cpz_2)$ (X = Cl, NO_3) and $Cl_2Pd(H_2Cpz_2)$ whose ^1H NMR data are given in Table 2-5.

Table 2-5

^1H NMR Assignment of Simple Inorganic Metal-Pyrazolyl Complexes

Complex[a]	^1H Assignment (ppm) H4	H3 $^3J_{(3,4)}$	H5 $^3J_{(4,5)}$	Reference
pz_2CH_2[b]	6.77	7.47 (1.78)	7.85 (2.40)	31
$Cl_2Hg(H_2Cpz_2)$	6.52	7.79 (1.9)	8.17 (2.5)	24
$(NO_3)_2Hg(H_2Cpz_2)$	6.45	7.66 (1.5)	8.12 (2.0)	24
$Cl_2Pd(H_2Cpz_2)$[b]	6.56	8.69 (2.4)	8.22 (2.7)	20

(a) Solvent D6 acetone

(b) Further splitting of the H3 and H5 is observed (^4J) and is in the order of 0.5 - 0.7 Hz.

Platinum occurs as several isotopes, and the isotope ^{195}Pt with nuclear spin I = $^1/_2$ occurs in 33.8% abundance. This nucleus can couple with ^1H in its complexes, and this coupling is often seen in NMR spectra as a central resonance flanked by symmetrical smaller resonances. The distance between these ^{195}Pt satellites is a measure of the ^1H-^{195}Pt coupling constant.

Clark has observed ^1H-^{195}Pt coupling in the spectra of tris(1-pyrazolyl)borate complexes of platinum.[25] Coupling was observed for all of the three pyrazole protons, confirming that the pyrazolyl rings are coordinated. ^1H-^{195}Pt coupling constants are of more value when the ligand donor atom is also bonded to a proton, eg. the MePt(II) group.

For Me_nPt complexes the value of the coupling constant is dependent upon the electronic properties of the platinum atom, including its oxidation state.

2.4.3 Characterization of Complexes

Characterization of complexes is based on microanalytical data, ^1H NMR spectra, molecular weights where solubility permitted, and IR spectral measurements if solubility precluded solution studies. The relevant data is listed with the respective complexes in the Experimental section, Chapter 7.

Included below is a discussion on the NMR aspects of the various complexes.

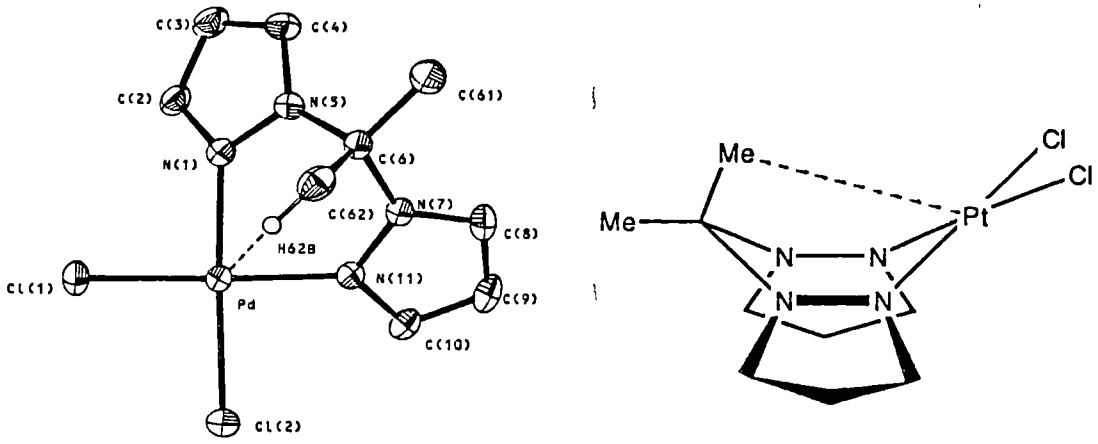
2.4.3.1 Cl_2PtL Complexes

Complete characterisation of this series of complexes was difficult due to their insolubility, although infrared spectra exhibit bands in the appropriate position for ($PtCl_2$) in a cis-Cl_2PtN_2 arrangement (See experimental).

The platinum(II) and palladium(II) complexes of Me_2Cpz_2 have been reported[26] during this thesis work, although the Pt complex was not well characterized. The complexes were formed by reaction between the appropriate benzonitrile substrate and ligand in refluxing chloroform.

$$Cl_2Pt(PhCN)_2 + L \longrightarrow Cl_2ML + 2PhCN \qquad (29)$$
M = Pd, Pt

An X-ray diffraction determination for the soluble palladium complex $Cl_2Pd(Me_2Cpz_2)$, revealed the structure shown in figure 2.3,



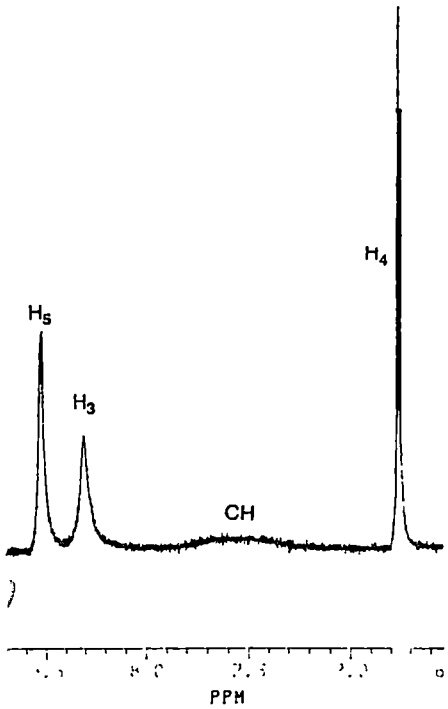
(a) (b)

Figure 2.3

with the chelate ring adopting the boat conformation. An agostic interaction is proposed for a proton of the axial methyl bridgehead group (Pd....H 2.57Å).[26]

The ^{1}H NMR spectrum of this complex exhibits typical pyrazolyl resonances in the expected positions. Care should be exercised in reading the interpretation of the NMR data contained in this reference[26] as the assignment procedure outlined earlier has not always been strictly adhered to.

Although most $Cl_2Pt(II)$ complexes prepared in this work exhibited poor solubility in deuterated solvents, it was possible in some instances to obtain low quality spectra using DMSO as solvent, although resonances were broad. The aromatic portion of a typical spectrum, for $Cl_2Pt(Me(H)Cpz_2)$, in DMSO is shown in figure 2.4. The extremely broad, low intensity signal suggests that inversion of the metallocycle is occurring and that this process is fast on the NMR time scale. Minghetti et al.[26] also observed this process for some closely related palladium complexes, and they were able to resolve this at low temperature.



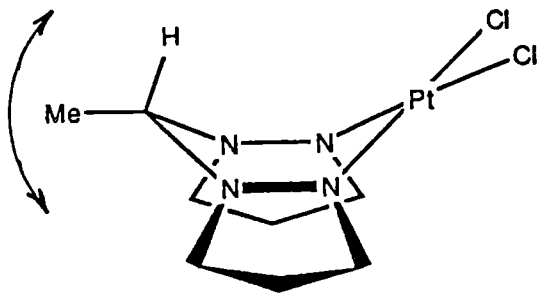


Figure 2.4 ^{1}H NMR spectrum of the Aromatic Region of $Cl_2Pt(Me(H)Cpz_2)$ in DMSO

2.4.3.2 Me_2PtL Complexes

Not all complexes exhibited sufficient solubility in common solvents for their ^{1}H NMR spectra to be recorded. The use of DMSO as a solvent resulted in low intensity, broad, unresolved signals and thus this was not employed. Where solubility permitted, the ^{1}H NMR spectra were recorded in either $CDCl_3$ or D6 acetone, and if the complex was soluble in both solvents the solvent which gave the best recorded resonances was employed. It is simplest to discuss the spectra of these complexes in four groups.

(i) Me_2PtL where L is a bidentate ligand and contains a single pyrazole group.

(L = $H_2C(py)pz$, $H_2C(mim)pz$)

The assigned ^{1}H NMR spectrum of $Me_2Pt(H_2C(py)pz)$ is shown in figure 2.5.

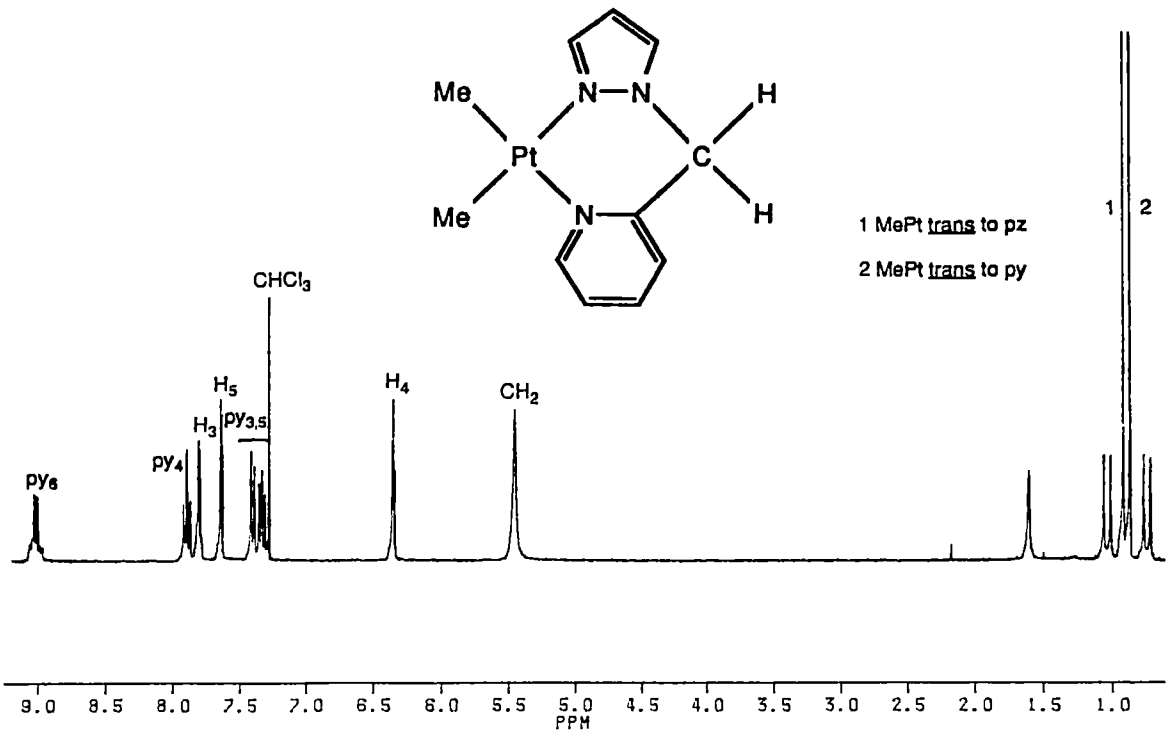


Figure 2.5 ^{1}H NMR spectrum of $Me_2Pt(H_2C(py)pz)$ in $CDCl_3$

As would be expected, two inequivalent MePt resonances are observed. In accordance with later MePt assignments (see Chapter 3,4), the MePt resonance with the largest $^{2}J(^{1}H-^{195}Pt)$ is assigned as trans to coordinated pyrazolyl. Apart from a general downfield shift, the ligand resonances are not altered significantly compared with the free ligand except that platinum satellites are observed for some resonances.

The most notable feature of this spectrum (figure 2.5) is the broad geminal apical ligand resonance at 5.45 ppm. This broadness is due to ring inversion, which is rapid on the NMR time scale, making the axial and equatorial protons equivalent. Low temperature spectra resolve this broad resonance into two sharp doublets, with the coalescence temperature estimated as ca. $-15^{o}C$ (figure 2.6).

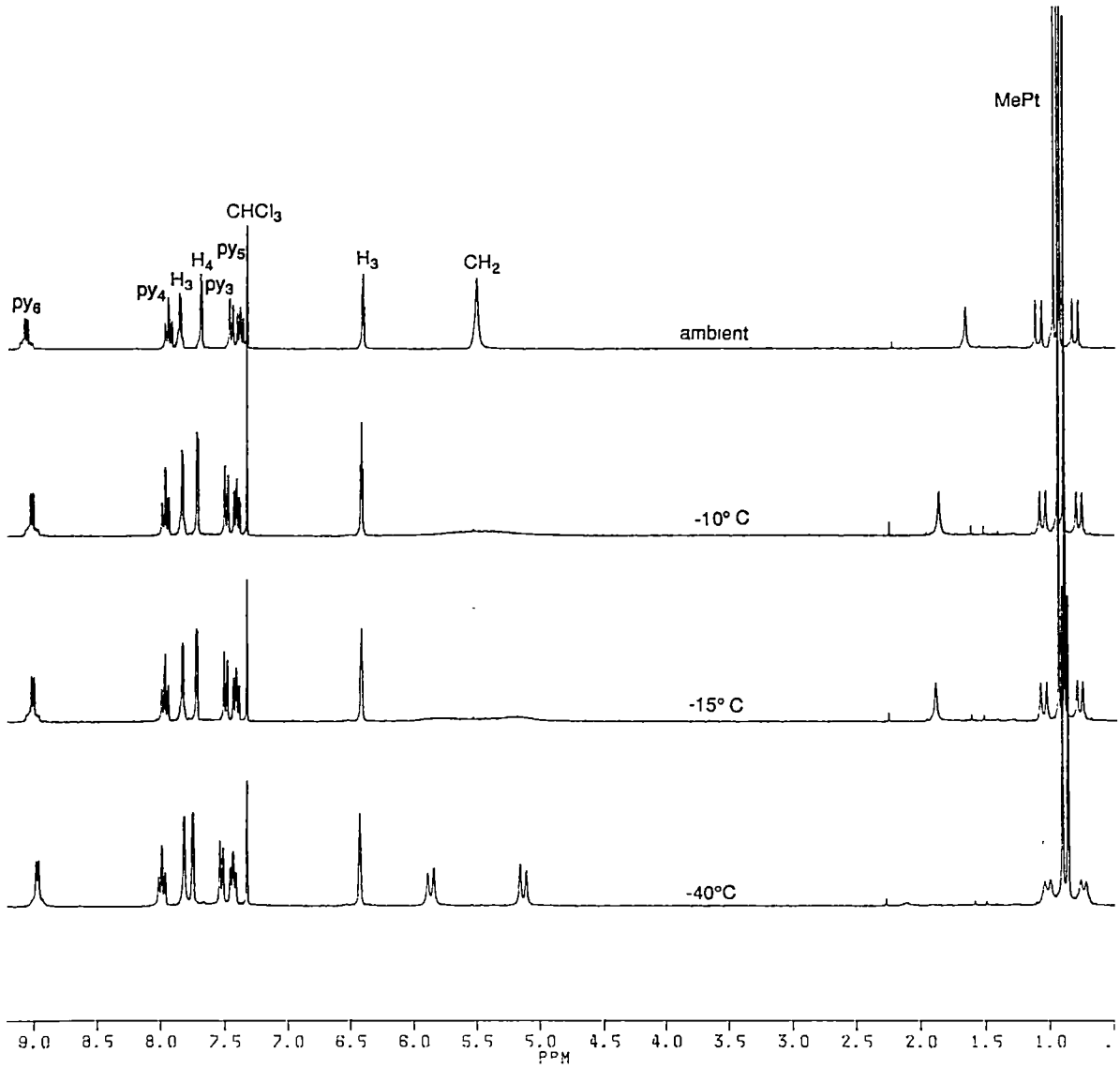


Figure 2.6 Variable Temperature ^{1}H NMR Spectra of $Me_2Pt(H_2C(py)pz)$ in $CDCl_3$

It is generally accepted that a geminal axial proton appears at higher field compared with an equatorial proton due to shielding of the former by the adjacent aromatic rings.[27] Thus, in the low-temperature limiting spectrum of $Me_2Pt(H_2C(py)pz)$ (figure 2.6) the upfield doublet (5.12 ppm) has been assigned to the axial proton, and the downfield doublet (5.86 ppm) assigned to the equatorial proton.

$Me_2Pt(H_2C(mim)pz)$ does not exhibit variable temperature behaviour in the range 45 to $-60^{o}C$, with only a sharp singlet being observed

for the apical protons even at -60°C. This is indicative of boat to boat ring inversion which is very rapid (NMR time scale) and not resolved under the conditions employed here.

(ii) Me_2PtL where L is bidentate and contains two pyrazolyl groups (L = H_2Cpz_2, $Me(H)Cpz_2$, Me_2Cpz_2, $Ph(H)Cpz_2$, $PhOMe(H)Cpz_2$)

The only complexes which exhibited sufficient solubility for ^1H NMR characterization were L = $Me(H)Cpz_2$, Me_2Cpz_2, and $PhOMe(H)Cpz_2$.

The ambient temperature ^1H NMR spectrum of $Me_2Pt(Me(H)Cpz_2)$ is shown in figure 2.7.

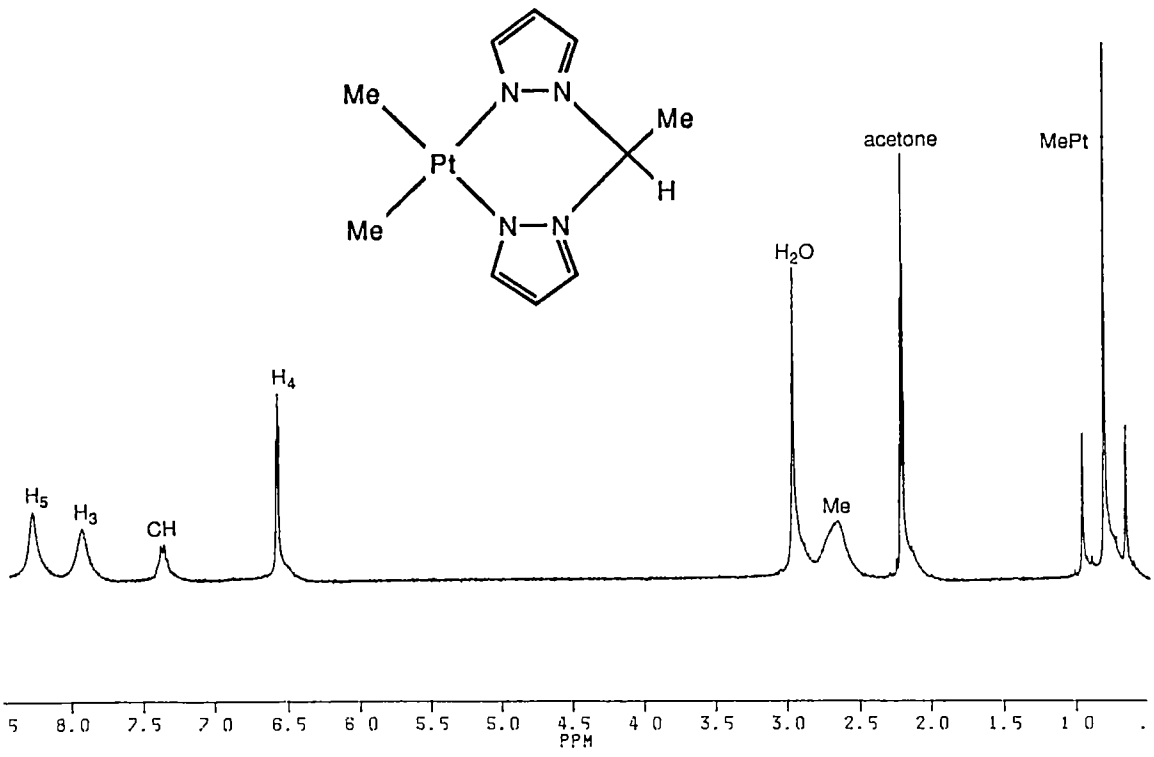


Figure 2.7 ^1H NMR Spectrum of $Me_2Pt(Me(H)Cpz_2)$ in D6 Acetone

All resonances are as expected for the structure shown above (a single MePt, and 3-, 4-, 5- pyrazolyl resonances), except that the signals are broadened appreciably. Both the apical proton and methyl group resonances are broadened considerably due to rapid (NMR time scale) ring inversion. Unlike the case of $Me_2Pt(H_2C(py)pz)$, ring inversion can lead to two conformers (A, B) (figure 2.8)

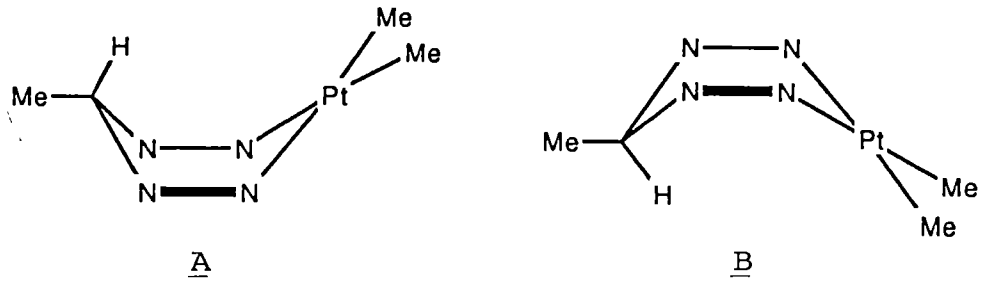


Figure 2.8

The existence of these conformers explains the broadened signals observed for the pyrazolyl ring protons. A variable temperature study was undertaken to establish if one configuration (A or B) was preferred over the other. On decreasing the temperature, all signals began to resolve and sharpen (figure 2.9).

The apical methyl group appears as a doublet due to coupling with the apical proton, which itself appears as a quartet. From the relative intensity (integration) of the two apical methyl resonances (and apical proton) it is apparent that one conformer is preferred relative to the other, in the approximate ratio 3:2. On the basis established previously, the furthest upfield apical proton (7.28 ppm) is assigned to the axial position and the resonance at 7.41 ppm to the equatorial position. These resonances are coupled to the apical methyl resonances at 2.60 ppm (equatorial) and 2.75 ppm (axial) respectively. Thus, at low temperature the preferred conformation is conformer A, with the apical proton in the axial position.

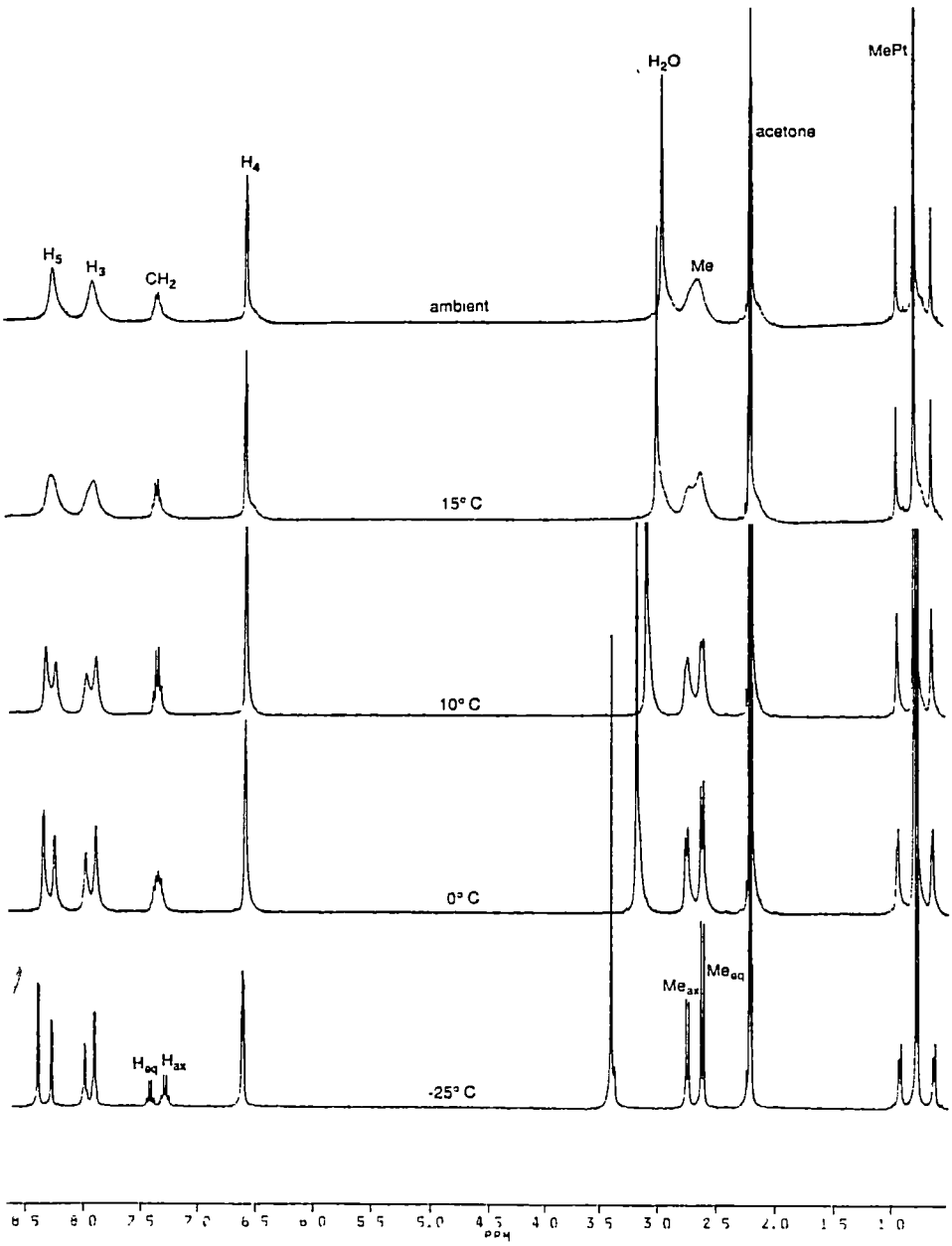


Figure 2.9 Variable Temperature ^{1}H NMR Spectra of $Me_2Pt(Me(H)Cpz_2)$ in D6 Acetone

$Me_2Pt(Me_2Cpz_2)$also exhibits rapid ring inversion on the NMR time scale with a corresponding average apical methyl environment being observed (2.20 ppm). On cooling, this signal resolves and exhibits axial and equatorial methyl environments (figure 2.10). By comparison with $Me_2Pt(Me(H)Cpz_2)$ the upfield resonance is tentatively assigned to the equatorial position.

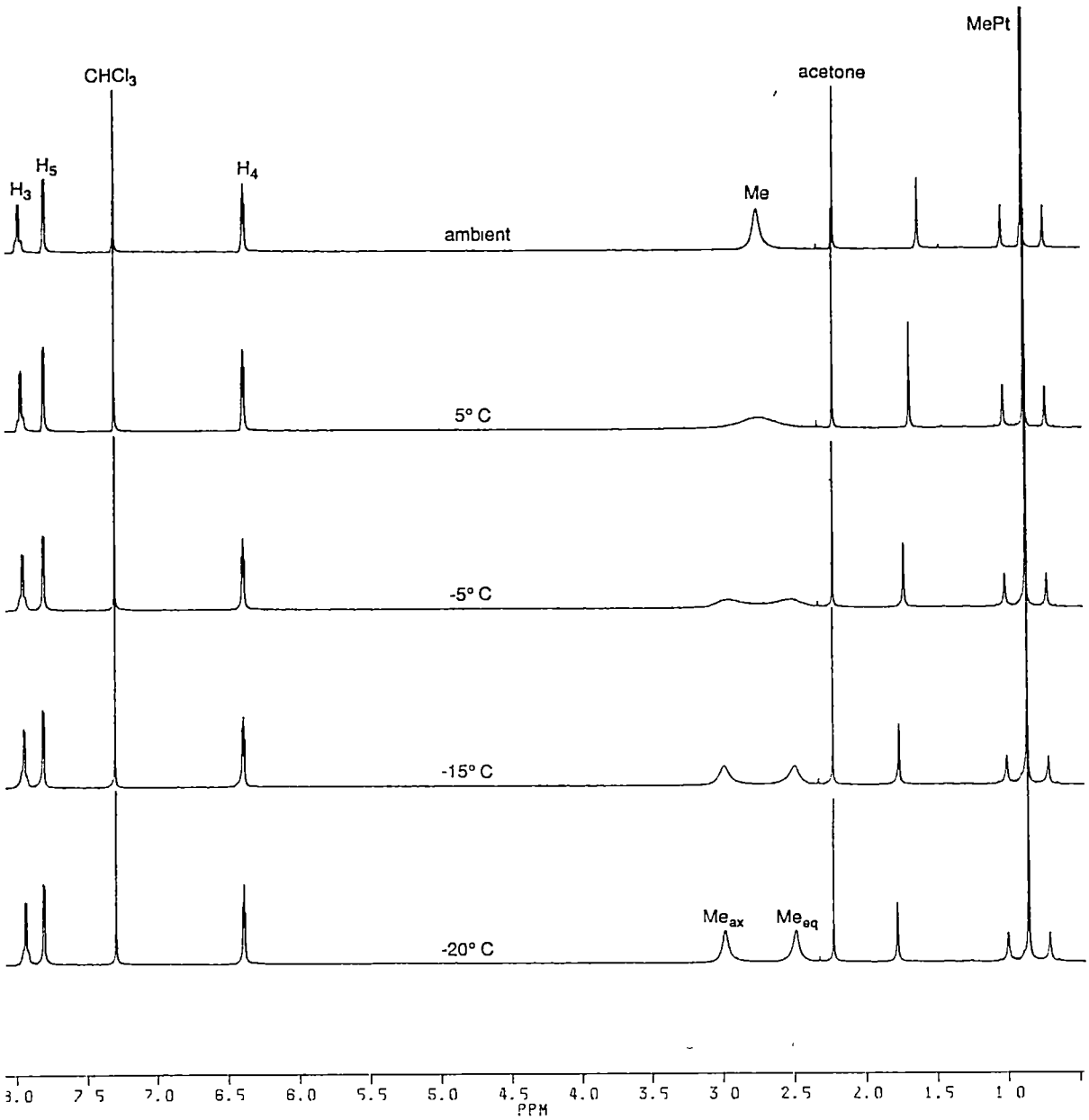


Figure 2.10 Variable Temperature ^{1}H NMR Spectra of $Me_2Pt(Me_2Cpz_2)$ in $CDCl_3$

(iii) Where L is tridentate and contains 2 pyrazolyl groups
(L = $HC(mim)pz_2$, $HC(py)pz_2$, $HC(thio)pz_2$)

$Me_2Pt(HC(mim)pz_2)$ exhibits slight solubility in D6 acetone, allowing a ^{1}H NMR spectrum (figure 2.11) to be recorded.

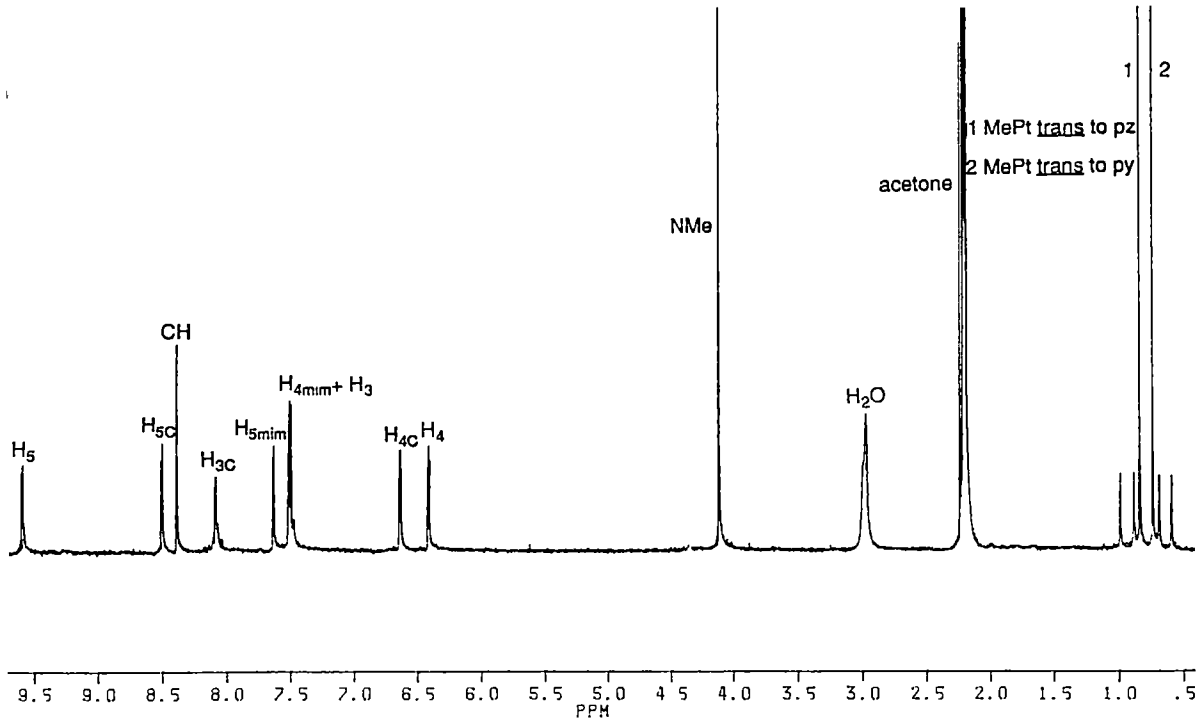


Figure 2.11 ^{1}H NMR Spectrum of $Me_2Pt(HC(mim)pz_2)$ in D6 Acetone

Two MePt resonances are observed, with the resonance exhibiting the largest MePt coupling constant attributed to the methyl trans to the coordinated pyrazolyl group (0.84 ppm, $^{2}J(^{1}H-^{195}Pt)$ 89.98 Hz). A difficulty in assignment arises in the aromatic region, in attempting to differentiate between pyrazolyl protons belonging to the coordinated ring and those of the uncoordinated ring.

Double resonance irradiation decoupling experiments have been used to assist in the assignment of ring protons in poly(pyrazolyl)borate complexes, but become tentative particularly where signals are coincident or near coincident. The use of two dimensional COSY spectra eliminates these problems.

Two dimensional homonuclear correlated (COSY) spectra manifest connectivities between spin coupled nuclei and provide assignments of individual spin systems in complex ^{1}H NMR spectra.

The COSY spectrum for $Me_2Pt(HC(mim)pz_2)$ in the region 6-10 ppm is shown.

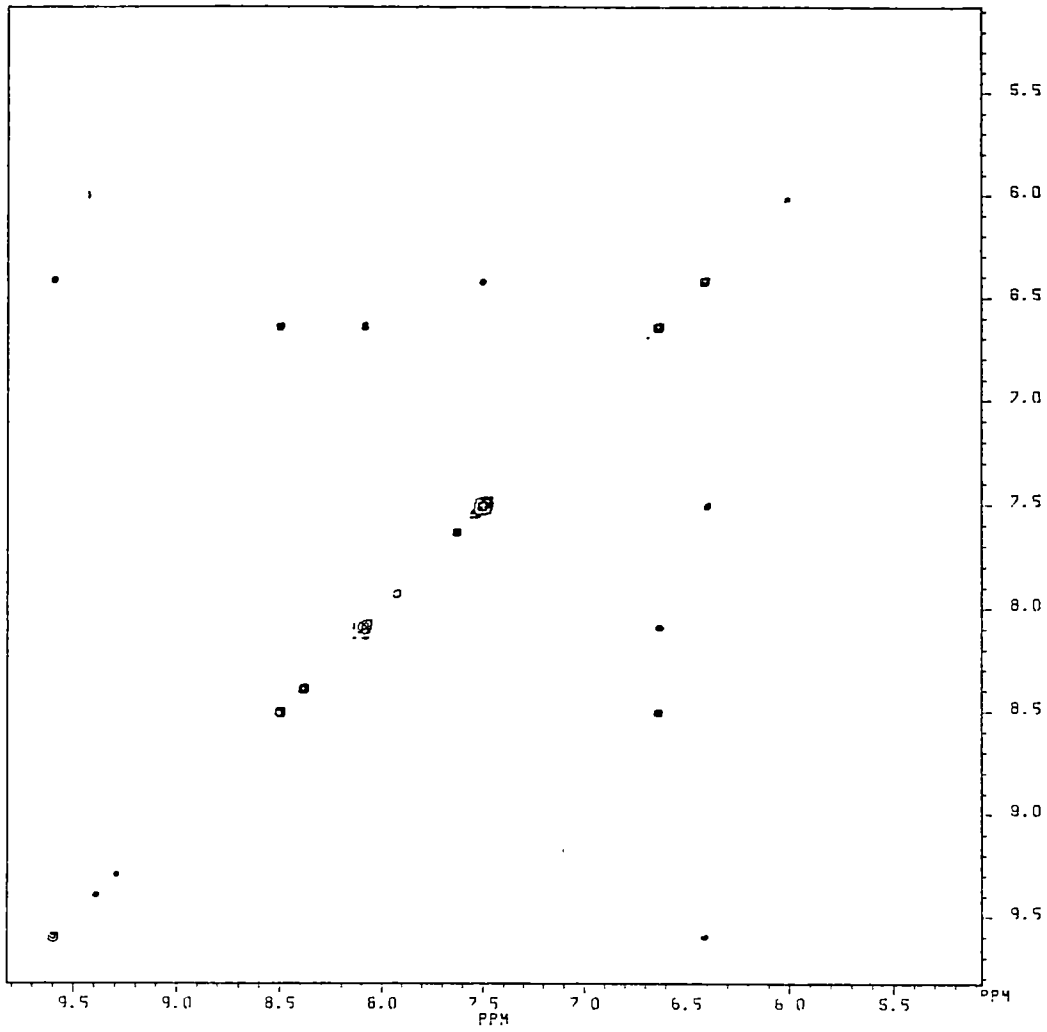


Figure 2.12 COSY Spectrum of $Me_2Pt(HC(mim)pz_2)$

The diagonal line from lower left to upper right represents the normal frequency versus intensity spectrum, with peak intensity represented by concentric contours. Those contoured regions off the diagonal indicate protons related by proton-proton coupling; uncoupled resonances do not exhibit cross peaks. For example, the H4 resonance at 6.41 ppm is coupled to the protons at 7.63 ppm and 9.6 ppm, and this constitutes a single spin connected system - a pyrazolyl ring (ring A). The other pyrazolyl ring resonances are 6.64 ppm, 8.09 ppm and 8.50 ppm (ring B). Protons H3 and H5 within a ring are then assigned according to $^2J(^1H-^1H)$ values and physical characteristics, eg. the H3 proton of a coordinated pyrazolyl ring often exhibits $^1H-^{195}Pt$ coupled sidebands. Thus, ring A is assigned to the uncoordinated pyrazolyl ring, with the large downfield shift

of the H5 proton, compared with the H5 of the coordinated ring, ascribed to its close proximity to the metal. Ring B is the coordinated pyrazolyl ring, with the H3 proton exhibiting platinum coupling.

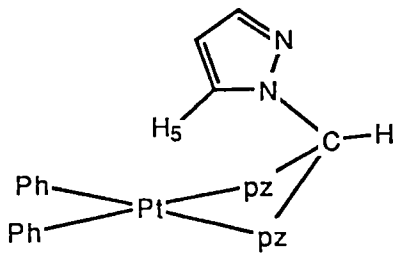


Figure 2.13

This structure is further supported by inspection of molecular models, which reveal unfavourable steric interactions between the uncoordinated pyrazolyl group and methyl group of the N-methyl imidazolyl when the pyrazolyl ring is placed in the equatorial position. An identical structure has been assigned to the $Me_2Pd(II)$ analogue $Me_2Pd(HC(mim)pz_2)$.[28]

$Me_2Pt(HC(thio)pz_2)$ exhibits enough solubility in deuterated acetone to allow a low quality ^1H NMR spectrum to be recorded. The spectrum exhibits a single MePt resonance (0.75 ppm, $^2J(^1H-^{195}Pt)$ 89.4 Hz, 6H), equivalent pyrazolyl resonances with all resonances being moved downfield by approximately 0.35 ppm (coordination shift), and thienyl resonances essentially unmoved from those in the free ligand. This information supports a structure with the uncoordinated thienyl group in an axial position and orientated such that the thienyl H3 is neither pointing toward the metal or over either coordinated pyrazolyl ring.

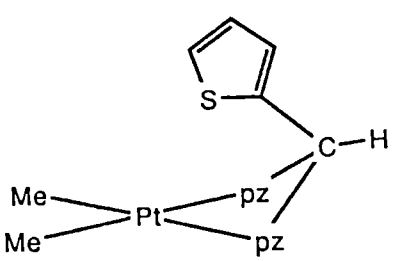


Figure 2.14

(iv) Where L is a tridentate or tetradentate ligand with all coordinating groups being pyrazolyl
(L = $HCpz_3$, $MeCpz_3$, Cpz_4)

$Me_2Pt(HCpz_3)$ does not exhibit enough solubility in common solvents to allow a ^1H NMR spectrum to be recorded. This insolubility is either an inherent characteristic of the complex or is due to the complex existing in a polymeric form via intermolecular coordination of the free pyrazolyl group.

The ambient temperature spectrum of $Me_2Pt(Cpz_4)$ (figure 2.15) shows two distinct sets of pyrazolyl resonances with the H4 resonances coincident.

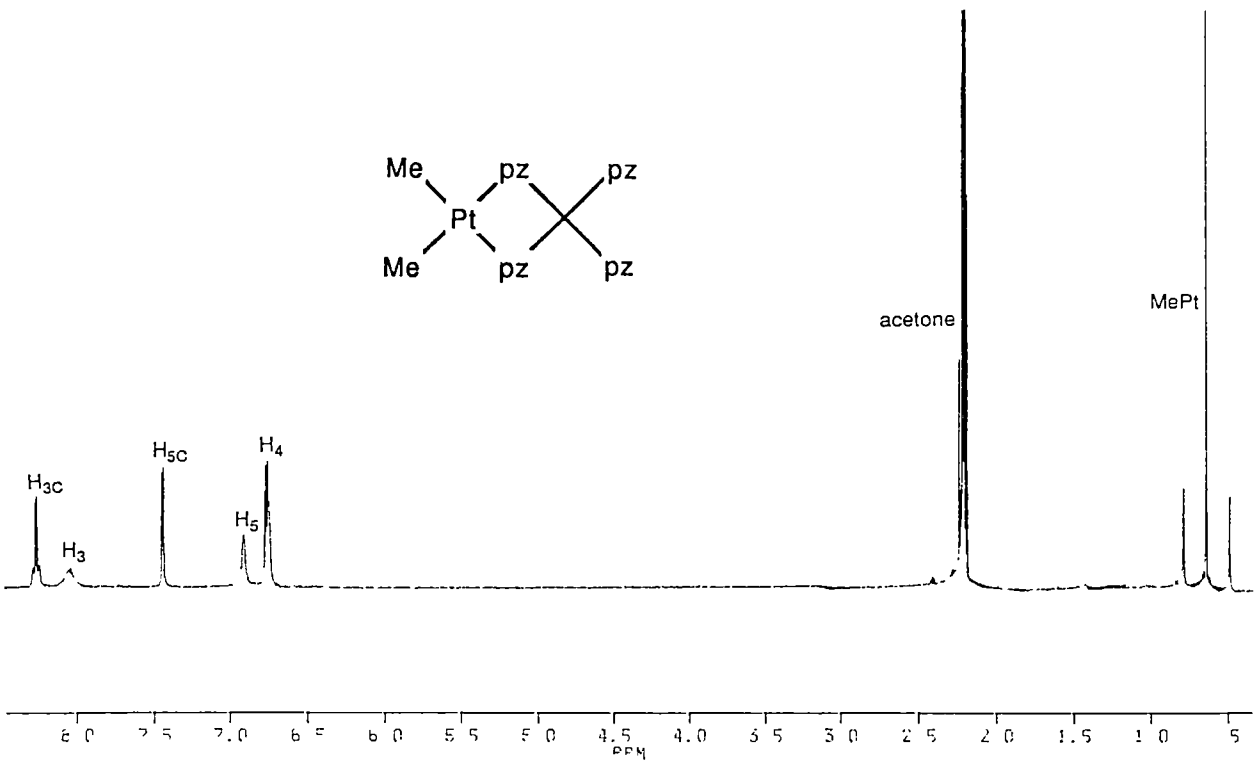


Figure 2.15 Ambient Temperature ^1H NMR spectrum of $Me_2Pt(Cpz_4)$ in D6 Acetone

Protons of the two coordinated pyrazolyl rings give sharp resonances, while those belonging to the uncoordinated rings are appreciably broadened, suggesting that an exchange process is occurring between the axial and equatorial positions.

This process is slowed appreciably on cooling and all resonances are fully resolved at $-40^{o}C$. Coupling constant values allow identification of individual resonances as either belonging to H5 or H3 protons, but a COSY spectrum is required to allow individual pyrazolyl ring assignments.

Both the low temperature spectrum (aromatic region) and associated COSY spectrum are shown in figures 2.16 and 2.17.

Four distinct pyrazolyl rings are evident, with the coordinated rings (denoted as H_C and $H_{C'}$) being inequivalent. The inequivalence of the coordinated rings can be rationalized by considering the orientation of the axial pyrazolyl ring, which is facial to and shielding a trans methyl, thus making the methyl groups inequivalent. Two methyl platinum resonances are seen in the appropriate region. In this orientation the H5 proton of the axial pyrazolyl ring is directly over one of the coordinated rings and strongly shielded. This proton is assigned to the resonance at 6.72 ppm to the axial pyrazolyl ring. The equatorial pyrazolyl ring (denoted H_{eq}) is not in a shielding environment and as its H5 proton is at 7.65 ppm it is assumed to be pointing downward, and not shielded by the axial pyrazolyl group. It is difficult to assign the remaining rings (rings H_C + $H_{C'}$) other than to say that they are the coordinated rings.

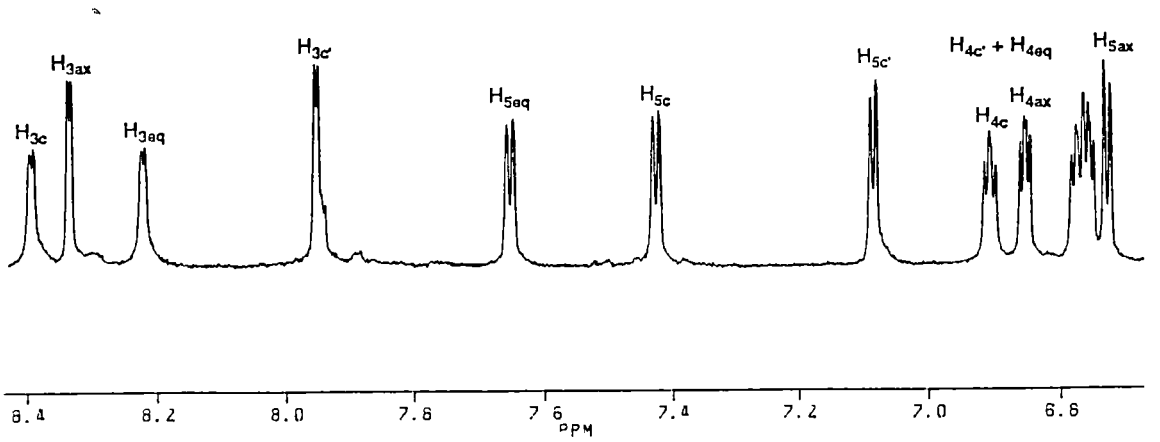


Figure 2.16 ^{1}H NMR spectrum of $Me_2Pt(Cpz_4)$ in D6 Acetone $-40^{o}C$

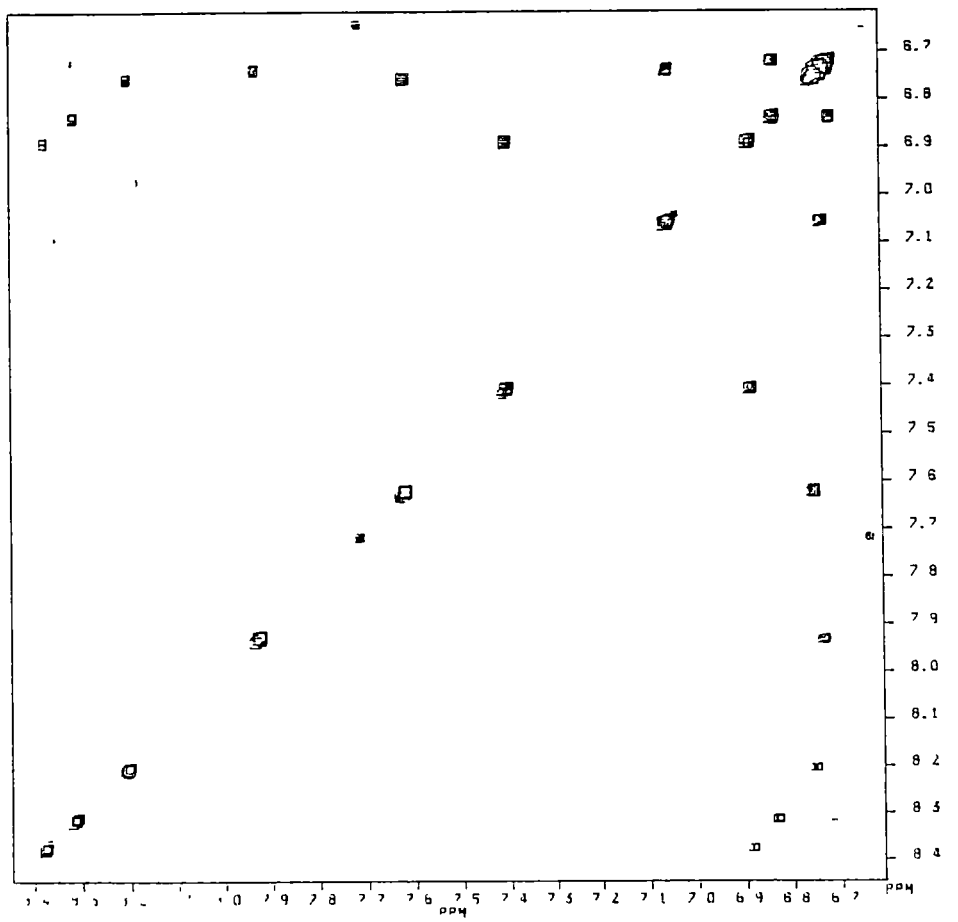


Figure 2.17 2D COSY Spectrum of Aromatic Region of $Me_2Pt(Cpz_4)$at $-40^{o}C$

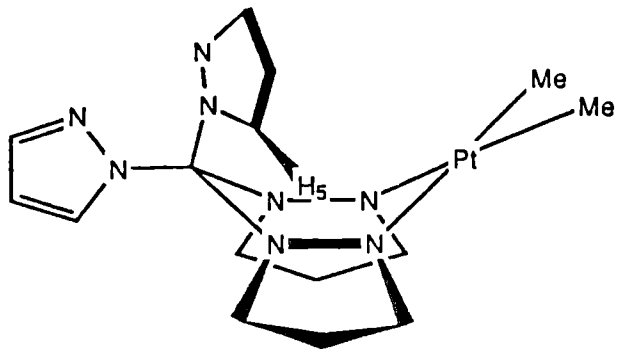


Figure 2.18 Proposed Structure of $Me_2Pt(Cpz_4)$ at $-40^{o}C$

2.4.3.3 Ph_2PtL Complexes

Diphenylplatinum(II) complexes of a representative range of pyrazolyl based ligands were synthesized in order to compare their behaviour with that of their $Me_2Pt(II)$ analogues.

Typically, $[Ph_2Pt(Et_2S)]_2$ and ligand in 1:2 mole ratio were warmed in dry benzene under a nitrogen atmosphere for 5 to 10 minutes, by which time the benzene had almost reached reflux. If the reaction was carried out on a large scale (> 0.2g $[Ph_2Pt(Et_2S)]_2$ in 20 cm^3 benzene) then the product precipitated as a white solid, but in smaller scale reactions (< 0.1g $[Ph_2Pt(Et_2S)]_2$ in 20 cm^3 benzene) the product remained in solution and required addition of hexane and/or cooling of the benzene solution for precipitation to occur.

Most of the $Ph_2Pt(II)$ complexes exhibited greater solubility than their $Me_2Pt(II)$ analogues in common NMR solvents, allowing ^1H spectra to be obtained for some ligands forming insoluble $Me_2Pt(II)$ complexes.

A ^1H NMR spectrum of $Ph_2Pt(HCpz_3)$ (figure 2.19) shows two pyrazolyl ring environments in the ratio 2:1 (H4 pyrazolyl resonances are coincident) as expected for $HCpz_3$ acting in a bidentate coordination mode.

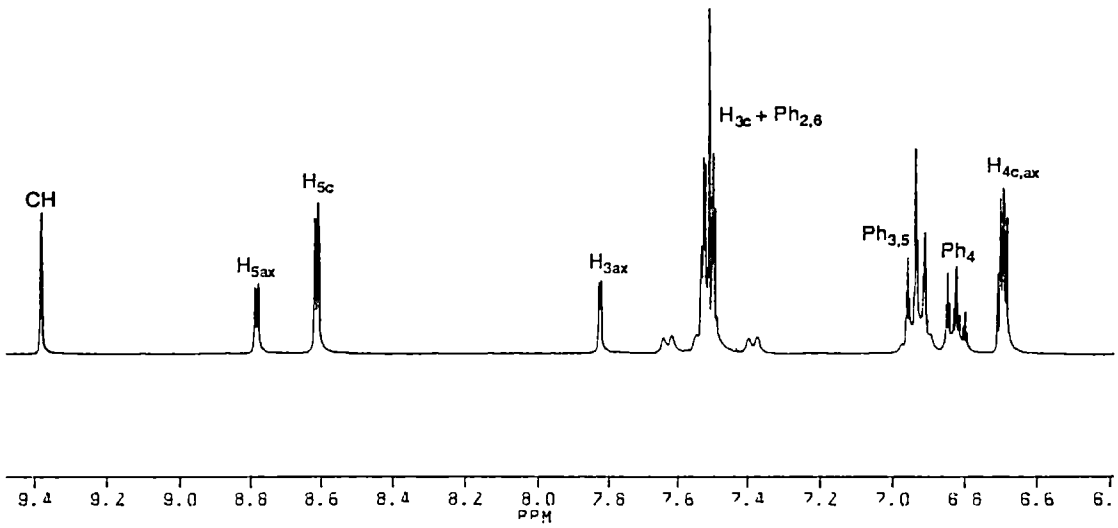


Figure 2.19 ^{1}H NMR spectrum of $Ph_2Pt(HCpz_3)$ in D6 Acetone

The separation and sharpness of the H5 and H3 ring protons indicates that exchange of coordinated and uncoordinated pyrazolyl groups is not occurring at ambient temperature, or that if it is it is extremely rapid on the NMR time scale.

The coordinated H3 protons are coincident with the 2,6-phenyl ring protons (7.50 ppm, COSY), and are upfield of both the uncoordinated ring H3 protons (7.82 ppm) and H3 for the free ligand (7.76 ppm). This upfield shift is due to shielding by the phenyl rings. The orientation of the uncoordinated pyrazolyl ring, axial or equatorial, can be determined by examining the resonances of the H5 pyrazolyl protons. With complexes in which this ring is in the equatorial position, eg. $Me_2I_2Pt(HCpz_3)$ (see Chapter 3), the H5 protons of the coordinated rings are strongly shielded and occur well upfield of the normal position for both H5 and H3 protons. However, with the ring in the axial position the H5 proton of this ring is deshielded by its proximity to the metal centre, and moved downfield from its normal position. From the downfield position of the H5 resonance relative to the coordinated H5 protons (figure 2.19), and from the position of this resonance relative to all H3 protons of the complex, a structure with the uncoordinated pyrazolyl group in an axial position can be deduced.

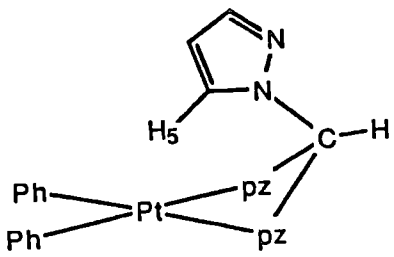


Figure 2.20

Although the ^1H NMR spectrum of $Ph_2Pt(HC(mim)pz_2)$ (figure 2.21) is slightly more complicated than that for $Ph_2Pt(HCpz_3)$, it supports a structure with the uncoordinated pyrazolyl ring in a similar axial orientation.

The individual pyrazolyl rings are labelled as C (coordinated) and as ax (uncoordinated) with the downfield H5 proton assigned to the axial ring. N-Methyl imidazolyl resonances are coincident with the 2,6-phenyl resonances centred at approximately 7.65 ppm, and phenyl resonances are more complex than for $Ph_2Pt(HCpz_3)$, owing to their inequivalence.

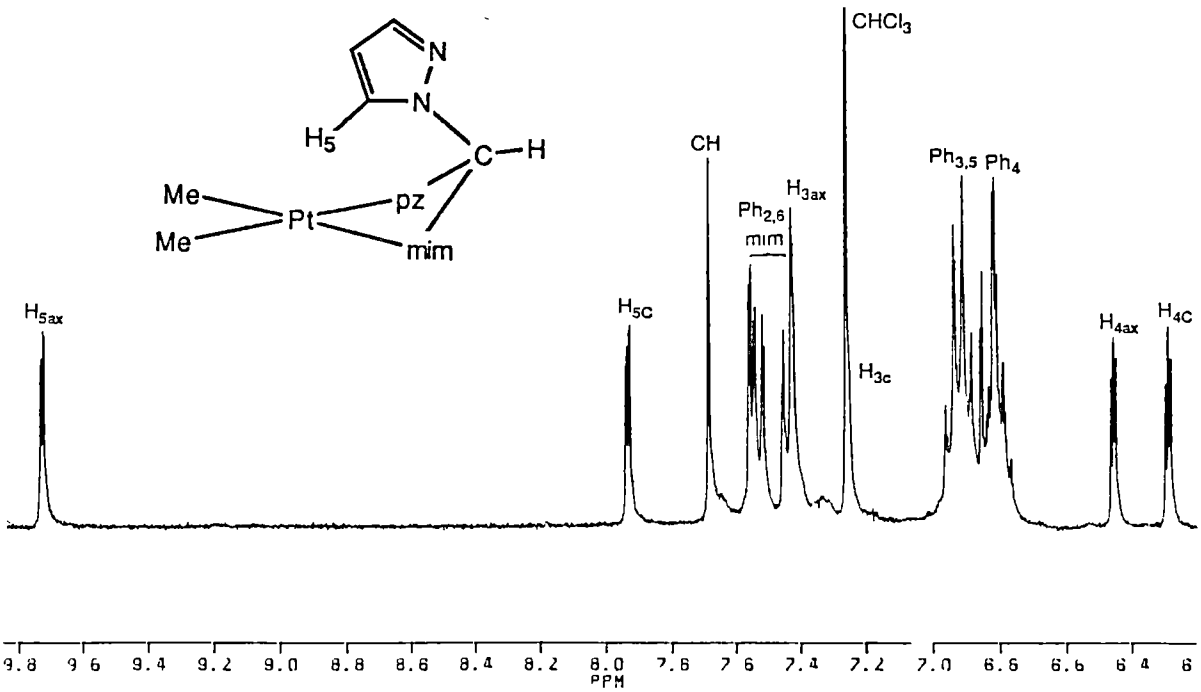


Figure 2.21 ^1H NMR spectrum of $Ph_2Pt(HC(mim)pz_2)$ in $CDCl_3$.

A comparison between the position of the H5 proton of the uncoordinated pyrazolyl ring in $Ph_2Pt(HCpz_3)$ (figure 2.19) and $Ph_2Pt(HC(mim)pz_2)$ (figure 2.21), 8.75 and 9.75 ppm respectively, suggests that closer interaction between the H5 proton and metal centre occurs in the latter complex. The methyl resonance of N-Methyl imidazolyl occurs at 4.66 ppm.

The complex $Ph_2Pt(HC(thio)pz_2)$ exhibits a ^1H NMR spectrum (figure 2.22) which allows for the position (axial/equatorial) of the uncoordinated ring to be determined, but not its orientation.

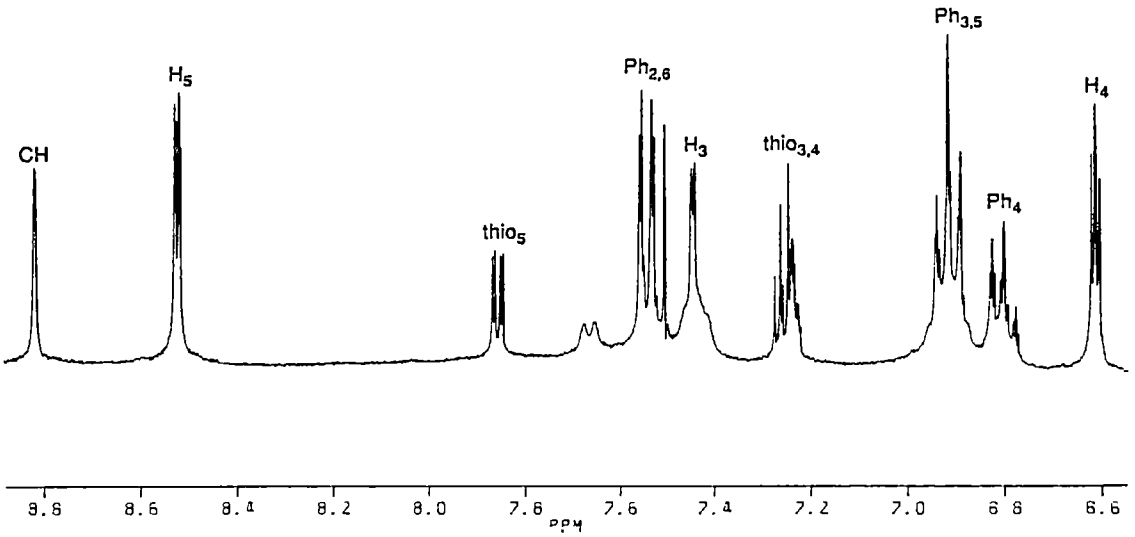


Figure 2.22 ^1H NMR of $Ph_2Pt(HC(thio)pz_2)$ in D6 Acetone.

As would be expected from the stronger donor ability of the nitrogen atom, the pyrazolyl groups are coordinated, resulting in a single pyrazolyl environment, with the H3 protons accidentally coincident with a platinum satellite of the 2,6-phenyl protons. The thiophene resonances have been assigned on the basis of $J_{4,5}$ and $J_{3,5}$ coupling constant values.[29] From the position of the H5 pyrazolyl resonance (8.52 ppm), the thienyl ring is in the axial position (vide supra). The H5 (thienyl) proton (7.85 ppm) is essentially unshifted from its position in the free ligand (7.75 ppm), and thus the orientation may involve sulphur directed toward the metal atom (figure 2.23), although a definite assignment is not attempted as spectra of only two thienyl ring containing complexes have been obtained in this work.

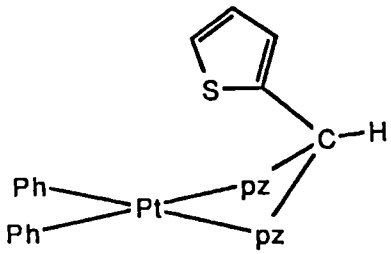
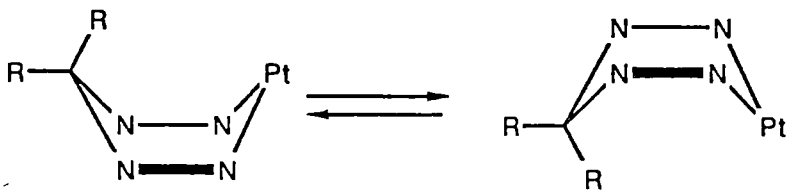


Figure 2.23

Ph_2Pt(bidentate) Complexes

Like their $Me_2Pt(II)$ analogues, the Ph_2Pt(bidentate) (bidentate = H_2Cpz_2, Me(H)Cpz, Me_2Cpz_2, $H_2C(py)pz$) complexes exhibit NMR spectra that vary with temperature due to boat to boat ring inversion of the 6 membered chelate ring:



For example, the ambient spectrum of $Ph_2Pt(Me_2Cpz_2)$ (figure 2.24) exhibits a very broad ligand methyl resonance (5.85 ppm) at ambient temperature. On cooling to $-30^{o}C$ this resonance is fully resolved into pairs of doublets at 5.90 ppm and 4.42 ppm, with the upfield resonance assigned to the equatorial methyl (vide supra).

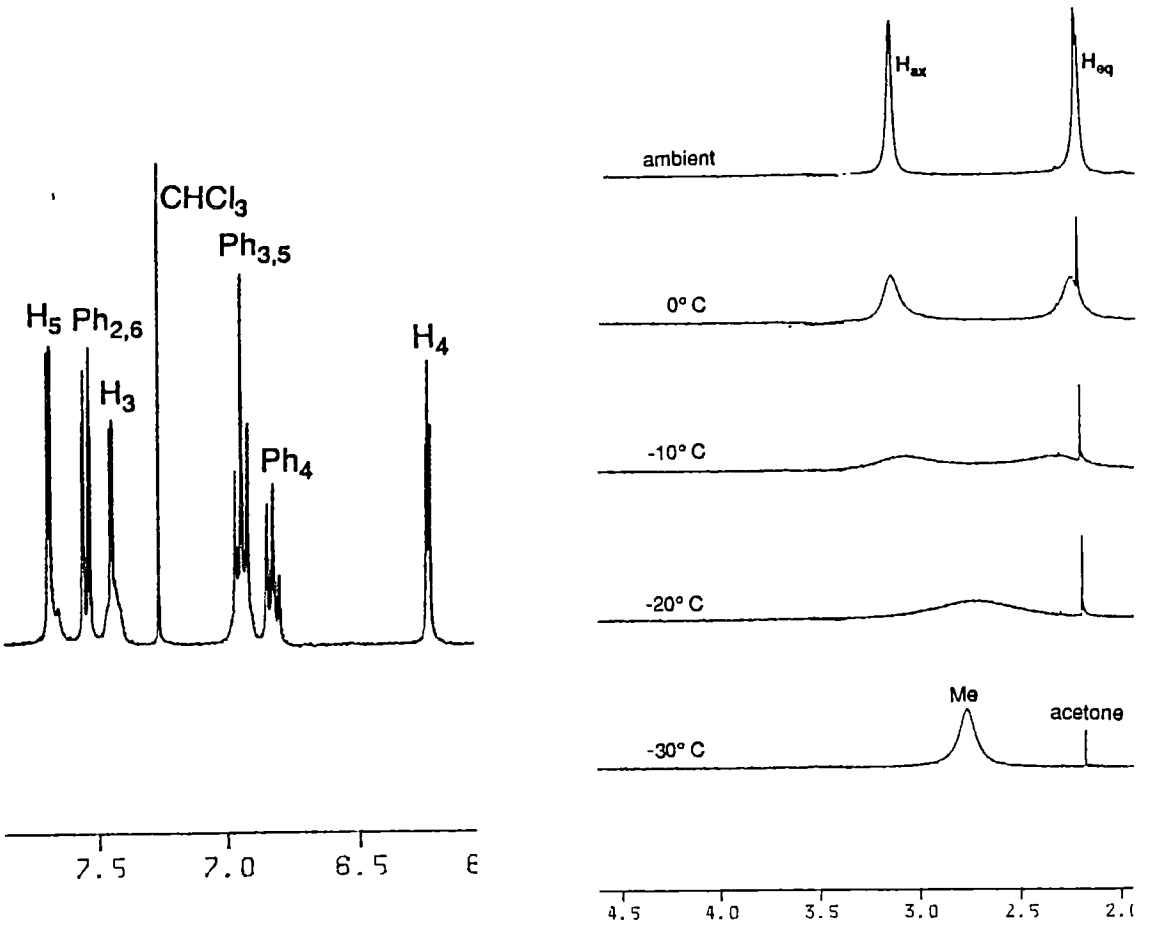


Figure 2.24 Variable Temperature ^1H NMR spectrum of $Ph_2Pt(Me_2Cpz_2)$ in $CDCl_3$.

2.5 Discussion

Reflux of $HCpz_3$ and $[Me_2Pt(Et_2S)]_2$ in acetone solution for an extended period of time failed to produce the expected complex, $Me_2Pt(HCpz_3)$, and unreacted starting material was isolated. However, reaction did proceed smoothly in hot benzene (not reflux) over a period of 10-15 minutes. An induction period for the reaction seems evident, as the solution remains clear on warming and suddenly after a certain time interval, massive precipitation occurs. Presumably benzene serves as a medium for a higher temperature which is required for reaction to proceed.

$Me(H)Cpz_2$ forms the very soluble white crystalline complex $Me_2Pt(Me(H)Cpz_2)$ when warmed with $[Me_2Pt(Et_2S)]_2$ in acetone solution for 5 minutes. If benzene is substituted as solvent, the solution

turns a deep yellow colour after 5-10 minutes warming and a tan decomposition product is isolated in low yield. Presumably the required complex is formed in benzene, but decomposes at the higher temperature.

Consequently, the preparation of the $Me_2Pt(II)$ complexes required the use of two solvents. In general, complexes which exhibited insolubility in common organic solvents required the use of benzene, while more soluble complexes could easily be prepared in acetone solution.

All of the $Ph_2Pt(II)$ complexes reported were prepared in benzene solution as they precipitate from benzene after approximately 5 minutes warming. Presumably these complexes could also be prepared in acetone solution, as the temperature of the benzene at the point of precipitation was under $50^{o}C$.

Both $Me_2Pt(II)$ and $Ph_2Pt(II)$complexes containing bidentate ligands (except for $H_2C(mim)pz$) exhibit temperature variable NMR behaviour due to rapid inversion of the chelate ring giving average environments for the apical ligand groups. On cooling, the rate of ring inversion decreases and becomes "visible" on the NMR time scale and specific axial and equatorial conformations can be observed. Polyakov and Ryabov[27] have investigated the dynamic system chloro(L)[2-(2'-pyridylmethyl)phenyl]palladium (L = substituted pyridine, particularly 2,4,6 Me_3-py, and 2-pyridylmethyl benzene is cyclometallated) and have proposed that chelate ring inversion occurs via a planar intermediate without any bond breaking (figure 2.25).

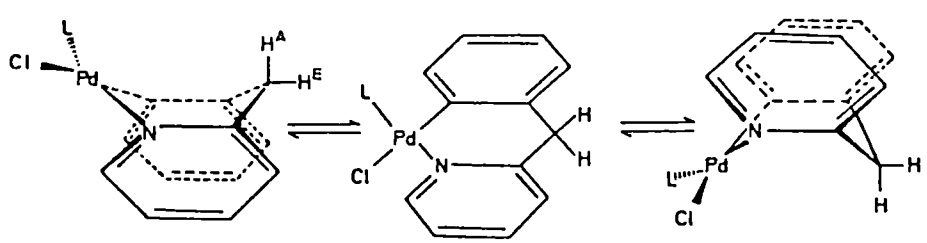


Figure 2.25

This same process has been used to account for the fluxional processes observed in $Me(PPh_3)Pt(Me_2Gapz_2)$.[30]

Molecular models indicate that the pyrazolyl complexes studied here can also invert through a planar intermediate similar to that in figure 2.25. Coalescence temperatures for the various $Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes are listed in Table 2-6.

Table 2-6

Coalescence Temperature of Various Me_2Pt & Ph_2Pt Complexes

Complex	Coalescence Temperature (^oC)	Solvent
$Me_2Pt(H_2C(py)pz)$	-15	$CDCl_3$
$Me_2Pt(Me(H)Cpz_2)$	15, -10	$CDCl_3$
$Me_2Pt(Me_2Cpz_2)$	-5	$CDCl_3$
$Ph_2Pt(H_2C(py)pz)$	-20	$CDCl_3$
$Ph_2Pt(H_2Cpz_2)$	-20	$CDCl_3$
$Ph_2Pt(Me(H)Cpz_2)$	0	$CDCl_3$
$Ph_2Pt(Me_2Cpz_2)$	-5	$CDCl_3$

An interesting comparison exists between $Me_2Pt(Me(H)Cpz_2)$ and $Ph_2Pt(Me(H)Cpz_2)$, in that on cooling the $Me_2Pt(II)$ complex exhibits two conformers with one being preferred over the other (p. 57), while for $Ph_2Pt(II)$ only a single conformer, presumably the conformer with the methyl group in the equatorial position, is observed.

$Me_2Pd(II)$ analogues of these complexes have been synthesized and their ^1H NMR spectral behaviour investigated and they have been found to exhibit similar variable temperature behaviour.[28]

For $R_2Pt(II)$ (R = Me, Ph) complexes containing tridentate ligands, a specific conformation, with the uncoordinated donor ring in the axial position, was observed. This conformation persisted even at temperatures of 50°C. When a pyrazolyl group was uncoordinated and in the axial position, its orientation was such that a ring proton (H_5) was directed toward the metal. This may have implications for the cyclometallation reaction of $Me_2Pt(HCpz_3)$ and will be discussed further in Chapter 3.

By comparing the MePt region of a number of complexes containing pyrazolyl donors only, mixed pyrazolyl-imidazolyl donors, and mixed pyrazolyl-pyridine donors, an order of MePt resonances trans to pyrazolyl, imidazolyl and pyridine can be established. Table 2-7 lists selected complexes with the accompanying MePt data

Table 2-7

MePt(II) Resonances for Pyrazolyl and mixed N Donor Ligand Complexes

Complex	MePt ppm; $^2J(^1H-^{195}Pt)$Hz	Solvent
$Me_2Pt(Me(H)Cpz_2)$	0.80; 89.71	acetone
$Me_2Pt(Cpz_4)$	0.64; 89.70	acetone
$Me_2Pt(HC(thio)pz_2)$	0.75; 89.44	acetone
$Me_2Pt(H_2C(mim)pz)$	0.76; 89.66 0.69; 86.98	acetone
$Me_2Pt(HC(mim)pz_2)$	0.86; 89.98 0.74; 87.28	acetone
$Me_2Pt(H_2C(py)pz)$	0.91; 86.16 0.86; 85.63	acetone

In D6 acetone solution a MePt trans to a pyrazolyl ring exhibits a resonance at a lower field than either an MePt trans to imidazolyl or pyridine, and has a larger $^{2}J(^{1}H-^{195}Pt)$ coupling constant. In $CDCl_3$, the same trend is observed.

Table 2-8 lists the pyrazolyl resonances for some $Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes containing bidentate and tridentate ligands.

Table 2-8

Pyrazolyl Resonances in $Me_2Pt(II)$ & $Ph_2Pt(II)$ Complexes

Complex	Pyrazolyl Resonances (ppm)						Solvent
	H3		H4		H5		
	Coord	Unco	Coord	Unco	Coord	Unco	
$Me_2Pt(H_2C(mim)pz)$	7.87	-	6.33	-	7.58	-	$CDCl_3$
$Me_2Pt(H_2C(mim)pz)$	7.88	-	6.50	-	8.17	-	acetone
$Me_2Pt(HC(mim)pz_2)$	8.10	7.50	6.64	6.41	8.5	9.6	acetone
$Me_2Pt(HC(thio)Cpz_2)$	8.07	-	6.67	-	8.44	-	acetone
$Ph_2Pt(HC(thio)pz_2)$	7.44	-	6.61	-	8.52	-	acetone
$Ph_2Pt(HCpz_3)$	7.51	7.82	6.55	6.65	8.61	8.78	acetone
$Ph_2Pt(HC(mim)pz_2)$	7.45	7.68	6.20	6.45	7.93	9.73	$CDCl_3$
$Ph_2Pt(HC(mim)pz_2)$	7.41	7.75	6.56	6.66	8.54	9.23	acetone

In $Me_2Pt(II)$ complexes a change of NMR solvent reverses the position of the pyrazolyl H3 and H5 protons, however this is not the case with $Ph_2Pt(II)$ complexes. Molecular models show that the phenyl rings strongly shield adjacent H3 pyrazolyl protons resulting in an upfield shift, and regardless of solvent, these protons are always found upfield of H5 pyrazolyl resonances.

For complexes which contain an axial uncoordinated pyrazolyl ring two sets of resonances are observed. For $Me_2Pt(II)$ complexes the uncoordinated H3 and H4 ring protons are found upfield in comparison to the coordinated rings (D6 acetone), with the H5 proton well downfield (compared with the coordinated rings) due to deshielding by the platinum atom.

The order of coordinated and uncoordinated H3 and H5 pyrazolyl protons is reversed in $Ph_2Pt(II)$ complexes and this can be explained by phenyl ring shielding. As expected the H5 proton of the uncoordinated pyrazolyl ring is still found furthest downfield. This is true for $Ph_2Pt(II)$ complexes regardless of solvent.

2.6 Conclusion

$Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes of a range of bidentate, tridentate and tetradentate pyrazolyl ligands can be readily prepared by reaction between the ligand and the $Me_2Pt(II)$ precursor $[Me_2Pt(Et_2S)]_2$.

$[Me_2Pt(Et_2S)]_2$ has the advantage over $[Me_2Pt(Me_2S)]_2$ in that it is very stable and can be stored at ambient temperature and does not require special storage conditions.

All soluble complexes are easily identified by their characteristic ^1H NMR spectra, with bidentate ligands exhibiting variable temperature behaviour, while tridentate ligands show a preference for a single conformer up to temperatures of 50^oC.

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CHAPTER 3

CYCLOMETALLATION

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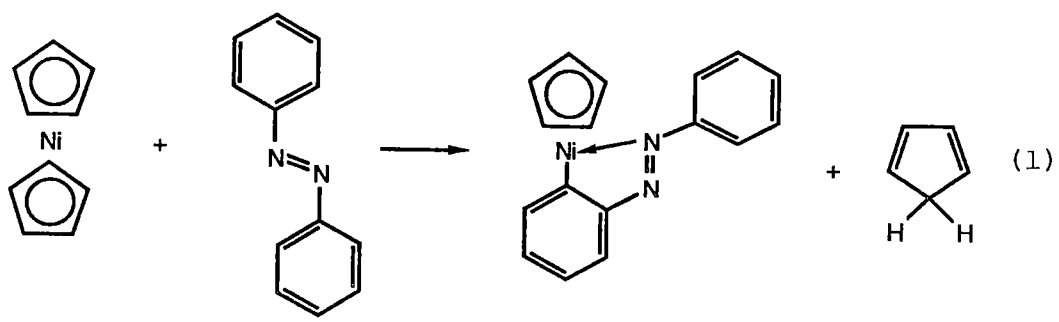
CYCLOMETALLATION

3.1 Introduction

Most organic molecules, in particular hydrocarbons, must be functionalized in some fashion prior to the formation of a metal-carbon bond, eg. formation of an organolithium reagent and application of it in transmetallation reactions. Direct metallation of a C-H bond is possible for some combinations of organic and inorganic substrates, eg. mercuration.

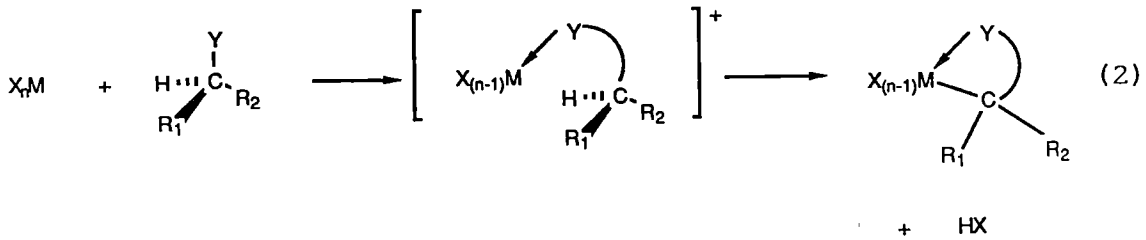
The first example of a "non-functionalized" metallation was discovered by Kleimann in 1963.[1] Nickelocene reacts with azobenzene affording a metallocyclic complex (I).



(1)

This type of intramolecular metallation, called orthometallation, is more commonly termed cyclometallation due to the formation of the chelate ring.

Apparently, prior coordination of the azo group leads to oxidative-addition of the ortho C-H group with subsequent reductive-elimination of cyclopentadiene. The general cyclometallation reaction is shown in equation 2.



(2)

M = metal

Y = donor atom, eg. N, P, O, S,

X = leaving group

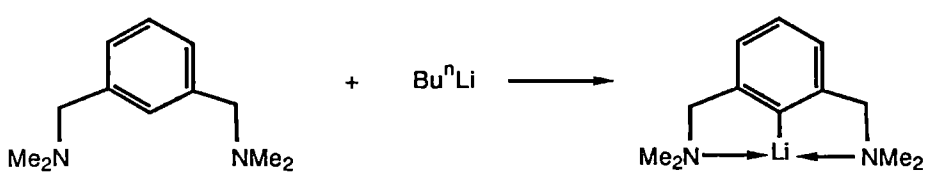
R_1,R_2 = appropriate organic groups

The formation of an initial simple coordination compound, A, (equation 2) allows favourable energetic and entropic contributions which facilitate the cyclometallation of an appropriately orientated C-H bond, with the concomitant elimination of a small molecule, HX. The hydrogen atom of the metallating C-H bond is not always eliminated and may remain as (formally) a hydrido ligand, eg. stable octahedral cyclometallated complexes involving a hydrido ligand have been isolated with iridium(I) substrates.[2,3]

$$\underline{trans}\text{-}Cl(CO)Ir(PPh_3)_2 + PhN{=}NPh \longrightarrow Cl(H)Ir(C_6H_4N{=}NPh)(PPh_3)_2 \quad (3)$$

$$ClIr(PPh_3)_3 \longrightarrow Cl(H)Ir(C_6H_4PPh_2)(PPh_3)_2 \quad (4)$$

Cyclometallated species have been proposed as intermediates in the formation of organolithium reagents from heterocyclic compounds,[4] eg. the reaction of Bu^nLi with 1,3-$(Me_2NCH_2)_2C_6H_4$ forms the stabilized cyclo 2-lithio derivative (C).



(5)

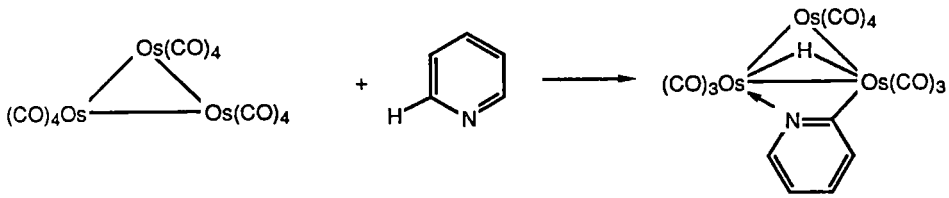
C

In syntheses prior to 1980, the C-donor atom metallated was sp^2 hybridized and usually part of an aromatic ring. However, the literature now includes numerous examples of non-aromatic olefinic sp^2 carbon atoms. Reviews on the cyclometallation reaction have been published.[5] In spite of the fact that aryl C-H bonds are stronger than aliphatic C-H bonds, aromatic groups are generally more reactive in the cyclometallation reaction.

In general, cyclometallation reactions are thermally activated and occur on or near pyrolysis, whether by direct heating of the metal and ligand as a solid mixture or solution, or a coordination compound as a solid or in an inert solvent.

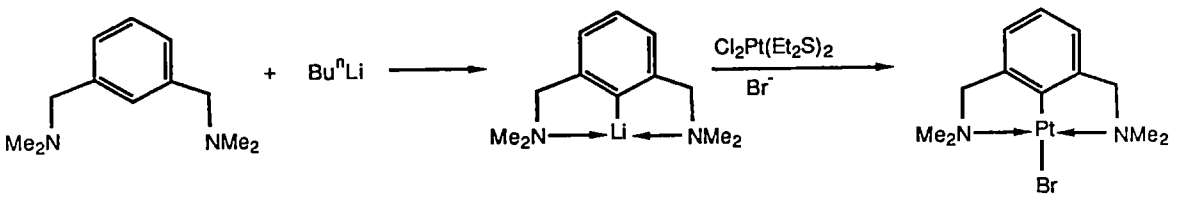
Variations on this strategy involve addition of a simple base, eg. sodium acetate or pyridine, to the mixture to help facilitate metallation.[6] For example, when Na_2PdCl_4 is treated with $PhCH_2(Me)NCH_2CH_2N(Me)CH_2Ph$ in methanol, the N,N-chelate dichloride is formed, and on prolonged heating no tendency to undergo cyclometallation is observed. However, addition of sodium acetate promotes metallation, which is observed in thirty minutes in refluxing ethanol.[7]

As well as monodentate complexes, cyclometallation reactions have been reported for metal clusters, notably carbonyl clusters of iron, ruthenium and osmium.[8] In these clusters the metallated ligand is coordinated to one metal and C-bonded to another metal atom of the cluster.[9]



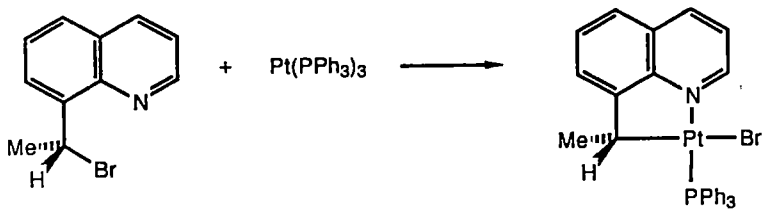
(6)

Apart from the direct activation of C-H bonds, complexes analogous to those formed in the cyclometallation reaction can be derived from two other sources. The most common involves a transmetallation reaction between a preformed lithio-heterocycle and metal ion to yield a new metal-carbon bond.[10]



(7)

Metallocycles can also be formed by the oxidative addition of an appropriate halo-heterocycle to a low-valent metal centre.[11]



(8)

3.2 Requirements for Metallation

Historically, the first cyclometallations centred on azobenzenes. Subsequent investigations have essentially remained with group Vb donor atoms, particularly nitrogen and phosphorus, although other donor atoms have been investigated and include oxygen, sulphur and arsenic.[5]

Basic ligand requirements for cyclometallation include:

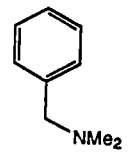
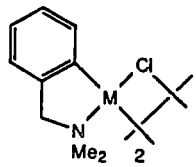
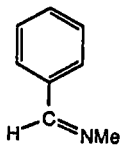
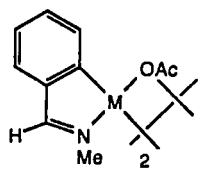
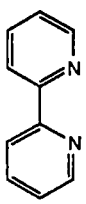
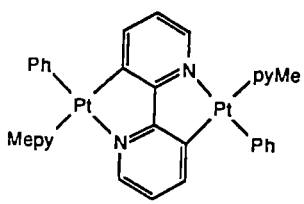
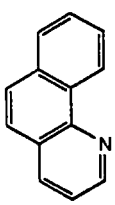
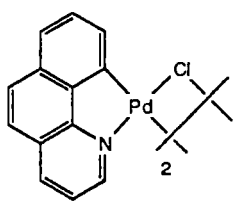
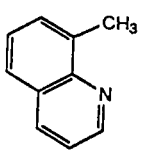
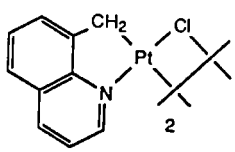
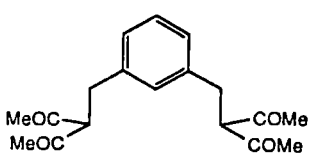
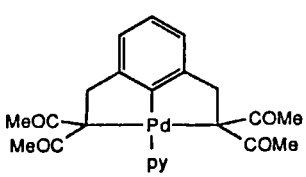
(i) the presence of a donor atom of sufficient strength to displace a ligand in the metal substrate.

(ii) such dimensions that it can orientate itself in an appropriate fashion to bring the required C-H bond into the metal sphere of influence and form a stable chelate ring.

Ligands which have been utilized in cyclometallation reactions have been quite diverse, varying in their carbon atom hybridization, donor atom strength, flexibility and denticity. Table 3-1 illustrates some typical examples for platinum and palladium with N-donor ligands.

Table 3-1

Cyclometallated N-Donor Ligands of Pt and Pd

Ligand	Metal	Complex	Reference
	Pt, Pd		12
	Pd		13
	Pt		14
	Pd		15, 16
	Pt		15
	Pd		17

Cope[12] proposed a set of empirical requirements to which a ligand must conform before a successful cyclometallation could proceed. One

of these basic requirements was that the ligand must be able to form a planar five membered ring in a bidentate ligation mode with the metal atom. The five membered cyclic core, M-C-Y occurs in the vast majority of tabulated cyclometallated complexes. The rationale for the enhanced stability imparted by a five membered ring is based on the necessity for such a system to possess a $\overset{\frown}{C\text{-}M\text{-}Y}$ bond angle of approximately 90^{o} (ideal geometry). Whilst this simple premise appears to have general validity, it by no means precludes other stable multi-membered cyclometallated rings. Formation of rings of greater or lesser size generally occurs when the ligand geometry precludes five-membered ring formation. Indeed, complexes containing four and six membered chelate rings are now common.[5k-m]

The C-H bond to be metallated must come into close proximity to the metal centre. This can be achieved either by the presence of a vacant coordination site on the metal, or by the presence of sterically bulky groups on the donor atom of the ligand. An illustration[19] which supports the premise of steric crowding promoting metallation is the observation that the phosphine PMe_2Ph is not metallated by either platinum(II) or palladium(II), whilst the higher substituted $PBu^{t}(Me)Ph$ is metallated, but less readily than the very crowded PBu^{t}_2Ph. The manner by which steric crowding can encourage an interaction between a C-H bond and metal atom is derived from both energetic and entropic contributions, and has been likened to the Thorpe-Ingold gem-dialkyl effect.[20] The sheer bulk of the substituted groups force one of their number sufficiently close to the metal atom so that metallation can occur, with the resultant loss of internal rotational entropy being much reduced on cyclization.

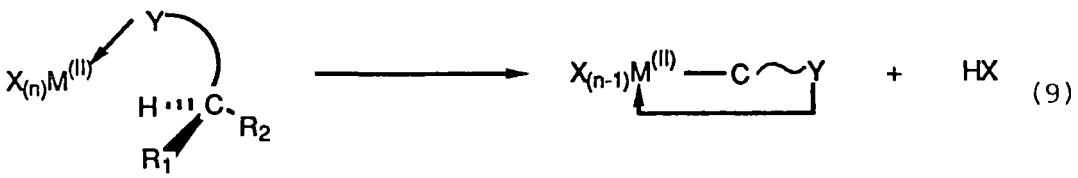
Whilst steric crowding is an important factor in promoting metallation, excessive overcrowding can produce a negative effect. For example, it has been reported[21] that $I_2Pt(P(o\text{-}tolyl)_3)_2$ does not cycloplatinate and this is attributed to such over congestion that the ligand cannot properly orientate itself for metallation to occur. However, tri-o-tolylphosphine has been reported[22] to undergo metallation of a methyl group in a ruthenium complex, but the same authors failed to detect metallation with a number of platinum(II)

and palladium(II) substrates.

3.3 Mechanism of Metallation

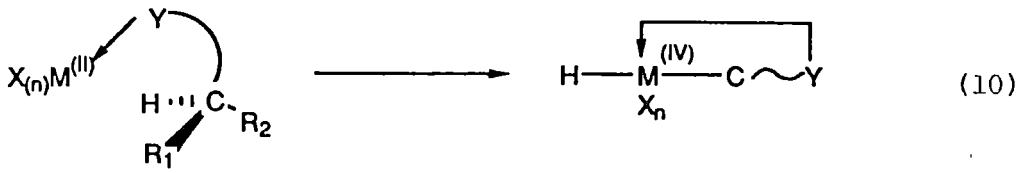
After the initial simple coordination compound is formed between the metal substrate and ligand, cyclometallation is considered to occur by one of two major activation mechanisms (excluding radical processes).

(i) Attack on the C-H bond by an electrophilic metal ion, with loss of H^+.



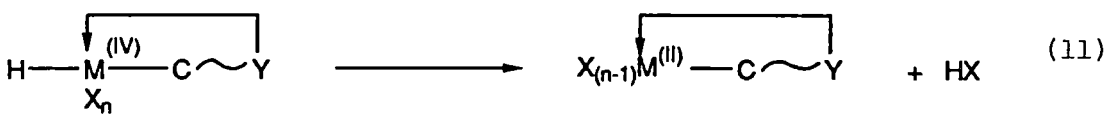
(9)

(ii) Oxidative addition of the C-H bond to an electron-rich metal centre.



(10)

The product from the oxidative addition reaction, formally a hydride, may spontaneously reductively eliminate if unstable.



(11)

Thus, via an oxidative-addition mechanism two products are possible depending upon the stability of the hydrido complex. After reductive-elimination the resultant product is identical to that formed via an electrophilic attack mechanism.

To obtain an understanding of the mechanistic pathways in which platinum(II) can participate in C-H bond activation, it is of interest to review:

(i) Reaction paths for related d^8 metal complexes, namely palladium(II) in cyclometallation reactions.

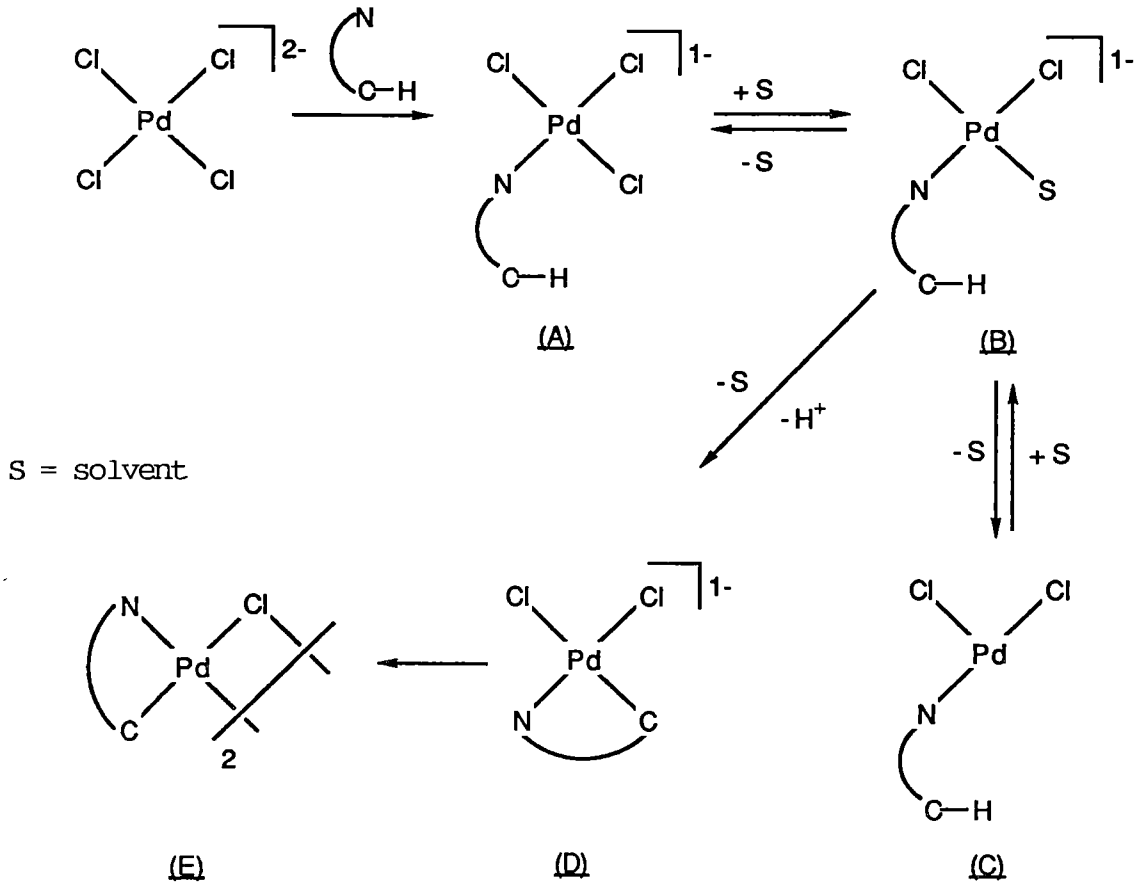
(ii) Cyclometallation by related low-valent transition metals, which, like platinum(II) can exist in a higher stable oxidation state.

(iii) the catalytic activity of platinum(II) in the activation of aromatic and aliphatic C-H bonds toward H-D exchange (intermolecular reactions).

3.3.1 Cyclometallation by Palladium(II)

Many workers have studied the electronic preferences for the palladation of ligands containing two or more aromatic rings, each possessing a different electron density. For example, Bruce et al.[23] studied the palladation of asymmetrically meta-fluoro-substituted azobenzenes. The results were consistent with an electrophilic attack by the palladium, in that 80% of the mixture was metallated in the non-fluorinated ring. Further, where palladation had occurred in the fluoro-substituted ring, reaction occurred in the position most favoured for electrophilic attack (ie. para to fluorine). Thus, cyclopalladation is considered to be electrophilic in character. These results support those of Parshall,[24] who studied the palladation of azobenzenes bearing a para substituent on only one of the two aromatic rings, and agree with those of Hietkamp et al.[25] who studied the cyclopalladation of meta-fluorophosphines.

Ryabov[26] has proposed the following general scheme for cyclo-palladation (Scheme 3.1).



Scheme 3.1 Proposed Reaction Sequence for Cyclopalladation

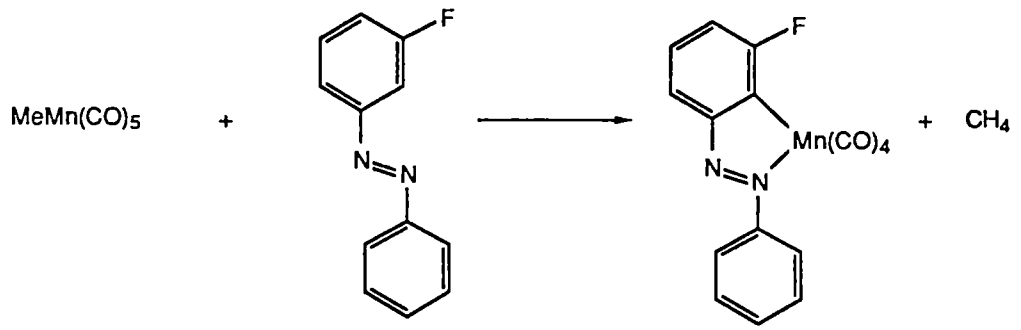
Addition of ligand to $PdCl_4^{2-}$ can give the anionic complex (A). The stronger kinetic trans effect of chloride compared with a N-donor ligand would result in cis solvation to give the uncharged intermediate (B). Either this solvated intermediate, or a coordinatively unsaturated species (C), is electrophilic in nature and it is at this stage that cyclometallation to yield (D) can occur. The isolated bridging chloro dimer (E) can be formed in subsequent steps. Deeming and Rothwell[27] have demonstrated that cyclopalladation would occur in the coordination plane of palladium(II) and have suggested the existence of a three coordinate intermediate (viz. (C) in Scheme 3.1). This mechanism is consistent with the original proposal by Parshall,[24] although for aryl ligands Parshall proposed the formation of an intermediate π-arene-palladium complex prior to cyclization. Planar ligands such as benzo[h]quinoline[15,16] and 8-methylquinoline[15] cyclometallate with $PdCl_4^{2-}$, the ligand geometry excluding the formation of a π-arene

complex, and thus its existence is not a prequisite for metallation to occur.

3.3.2 Cyclometallation by Low-Valent Electron Rich Metals

The electrophilic cyclometallation mechanism proposed for palladium(II) complexes seems unlikely for related reactions involving low-valent electron rich metal complexes. Indeed, with Fe(0), Ru(0), Os(0), Rh(I) and Ir(I), the isolated cyclometallated product generally contains oxidized metal. It has been suggested that for complexes of these metals, the metal may act as a nucleophile toward the ligand.[24]

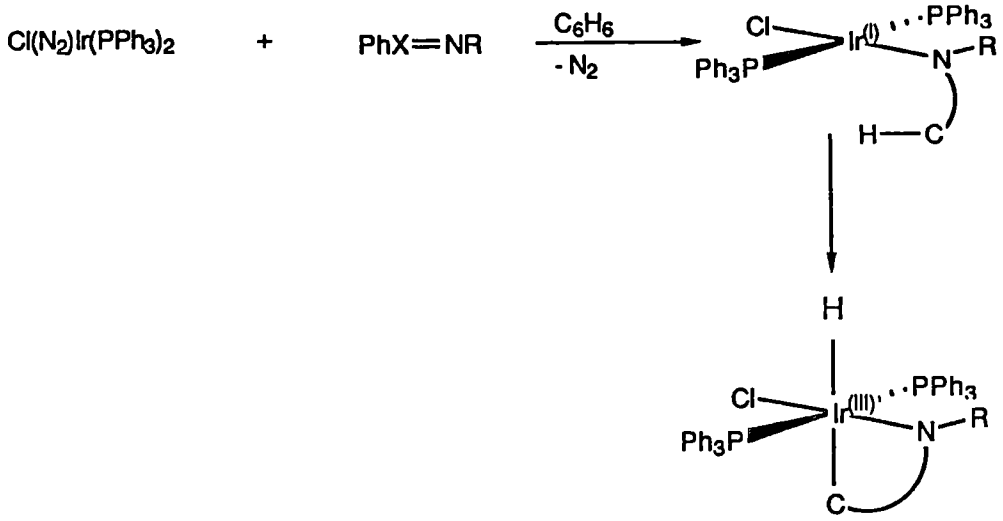
Bruce et al.[23] expanded their studies on the metallation of the asymmetrical meta-fluoro substituted azobenzenes, and included the reaction with the low-valent electron rich complex $MeMn(CO)_5$.



(12)

The major product is that with managanese substituted ortho to fluorine, which is consistent with nucleophilic attack on the carbon atom (powerfully activated by the inductive effect of fluorine).

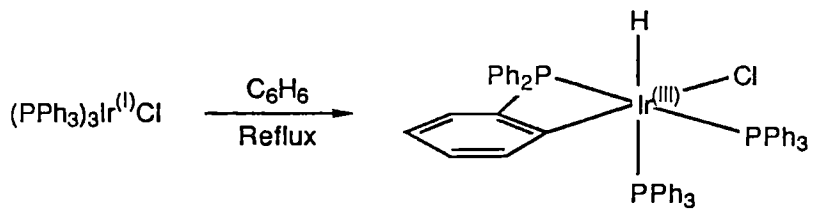
van Baar et al.[28] have investigated the metallation reactions of iridium(I) and rhodium(I) with aromatic and olefinic C-H bonds in azo- and imine- ligands. For reaction of the ligands PhX=NR (X = N or CH, R = aryl or alkyl) and H_2C=C(Me)-N=NMe with $ClIr(N_2)(PPh_3)_2$ the following reaction sequence was proposed.



(13)

Iridium(I) was found to be more reactive than rhodium(I). Thus, van Baar proposed that the mechanism involved a formal oxidative-addition of the appropriate C-H bond.

A further example for iridium(I),[3] and a comparison with the related rhodium(I) reaction,[29] are illustrated.



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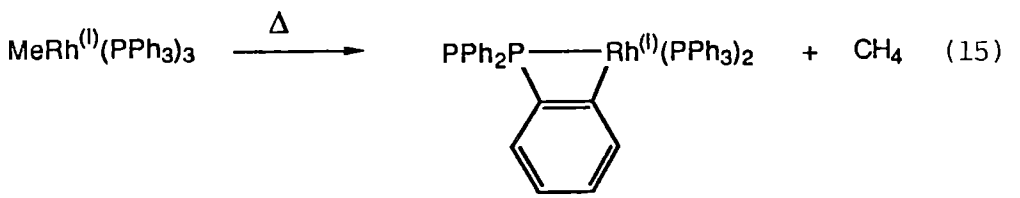


(15)

Only in the case of iridium is the trivalent hydrido complex stable and isolable under the experimental conditions. After oxidative-addition of an aryl C-H bond the intermediate Rh(III) complex undergoes reductive-elimination of methane. Consistent with this reaction sequence, pyrolysis of the deuterated complex $MeRh(P(C_6D_5)_3)_3$ produces CH_3D.[24]

Other metal complexes investigated which appear to undergo cyclometallation via a nucleophilic mechanism include ruthenium and osmium clusters.[8]

The less electron-rich high valent iridium(III) and rhodium(III) complexes have been reported to cyclometallate via an electrophilic mechanism.[30]

3.3.3 Platinum(II) Catalyzed H-D Exchange in Aliphatic and Aromatic Compounds

Although cyclometallation is an intramolecular process, and the Pt(II) H-D catalyzed exchange[8a,29] is an intermolecular process, some important conclusions can be stated which may be of relevance to cyclometallation.

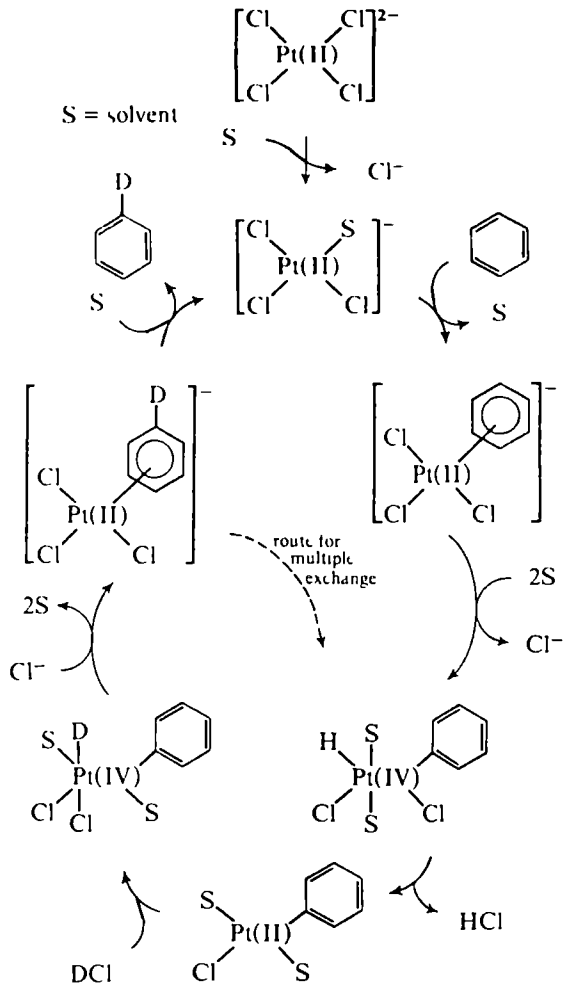
Two important observations reported from the platinum(II) H-D exchange of aromatic solvents are:

(i) the H-D exchange occurs via a dissociative mechanism,

(ii) this mechanism involves a proposed π (η^2) complexed metal-arene intermediate leading to a subsequent platinum(IV)-carbon σ bonded aromatic complex.

These observations are illustrated in Scheme 3.2.

This mechanism, originally proposed by Garnett,[32] is based on hydrogen transfer from a π - complexed arene to the metal atom, a formal oxidative addition of platinum(II) to platinum(IV), with formation of a platinum(IV)-carbon σ bond, which is unstable and reductively eliminates.



Scheme 3.2 Dissociative mechanism involving a Pt(IV) C bonded intermediate for H-D exchange on benzene.[31]

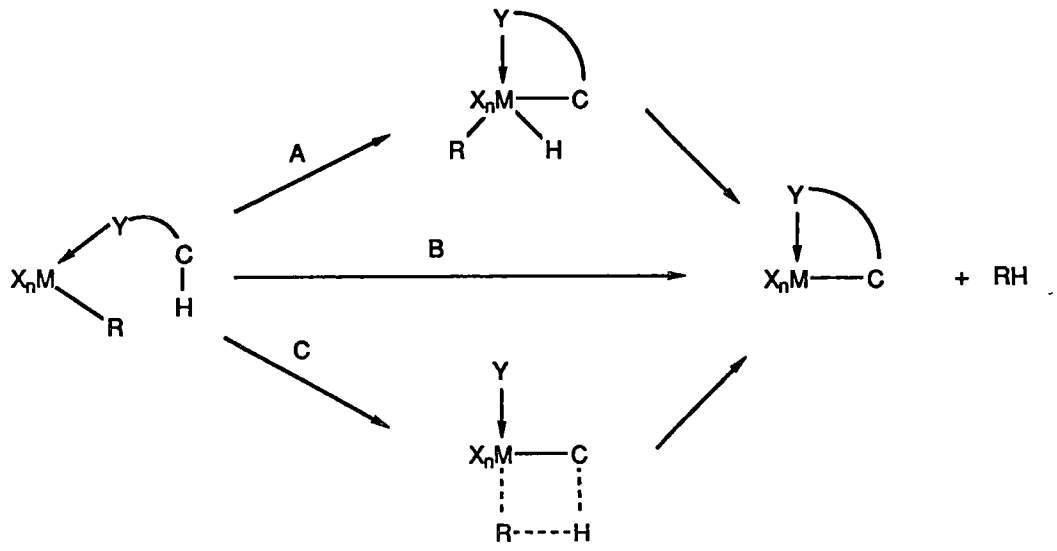
3.3.4 Electrophilic Substitution versus Nucleophilic Addition for Platinum(II) in Cyclometallation Reactions

Studies to elucidate the mechanism by which platinum(II) undergoes cyclometallation have established conflicting results, with platinum appearing to mimic Pd(II) in some instances, whilst mimicking Ir(I) and Rh(I) in others.

In the metallation of a wide range of phosphines, it has been proposed that platinum acts as a nucleophile, whilst if the number of phosphine ligands per complex is reduced, platinum can act

essentially as an electrophile in a proposed four-centre transition state mechanism. If the platinum substrate is $PtCl_4^{2-}$, an electrophilic mechanism, analogous to $PdCl_4^{2-}$, has been proposed.

The possible mechanisms by which platinum(II) can cyclometallate are shown in Scheme 3.3



A - Direct oxidative addition/reductive elimination

B - Electrophilic attack by metal

C - Four-centre transition state

Scheme 3.3 Mechanisms of Metallation.

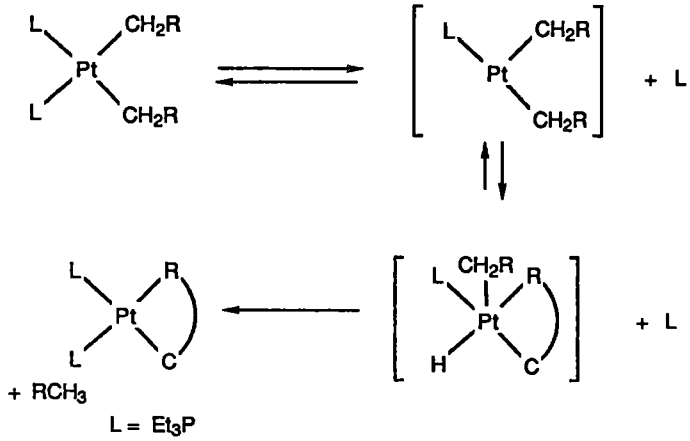
Although pathway C has not been discussed previously, it cannot be dismissed, as this allows for concerted metal-carbon bond making and breaking with no formal change in the oxidation state of the metal.

These results suggest that platinum(II) is a borderline case, and that cyclometallation may proceed via different mechanisms, according to the metal substrate and ligand, and is a manifestation of the balance between steric and electronic factors. Three general cases appear to be evident.

(i) where the electron density on platinum is high. This is achieved by surrounding platinum with strong electron donor

ligands, such as basic phosphines and strongly bonding alkyl groups. Whitesides et al.[33] have proposed a mechanism for the cyclometallation of dineopentylbis(triethylphosphine) platinum(II) which involves cleavage of the C-H bond by intramolecular oxidative addition.

The mechanism (Scheme 3.4) is analogous to that shown for electrophilic cleavage (equation 2), only differing in the mode of cleavage.



Scheme 3.4 Mechanism for Cyclometallation of Dineopentylbis(triethylphosphine)platinum(II)

If the platinum substrate contains the $Me_2Pt(II)$ unit, eg. $Me_2Pt(COD)$, then metallation is also considered to proceed via an oxidative addition of the ligand C-H bond.[34]

(ii) where the electron density on platinum is low. This is the situation generally encountered for metallation of nitrogen based ligands by the $Cl_2Pt(II)$ unit (particularly $PtCl_4^{2-}$), or where a very low basicity phosphorus donor ligand is being metallated utilizing a $Cl_2Pt(II)$ unit.
In this case, metallation usually proceeds via electrophilic attack of platinum on the appropriate C-H bond.

(iii) where the electron density on platinum is intermediate.
This situation generally exists when a nitrogen based ligand is being metallated by $Cl_2Pt(II)$ and the complex also contains a

phosphorus donor, or where the complex to be metallated contains only a single phosphine of intermediate basicity. Metallation in this instance is reported to favour an electrophilic mechanism, but it probably occurs via mechanism C, involving a four-centre transition state.[35]

The mode of metallation favoured for a particular system depends intimately on the system, and thus any generalization is not possible, as it is in the case with palladium(II).

3.4 Metallation of $Me_2Pt(HCpz_3)$

The cyclometallation of $Me_2Pt(HCpz_3)$ was serendipitously discovered by Minchin[36] while attempting to recrystallize the intractable complex from hot pyridine.

$$Me_2Pt(HCpz_3) + \text{xs pyridine} \longrightarrow MePt(HCpz_2(C_3N_2H_2)\text{-}C,N)(py) + CH_4 \qquad (16)$$

The authors assumed that methane was eliminated, without attempts at detection.

During the metallation reaction the pyridine solution turns a yellow-green colouration, and on additon of hexane the metallated complex is isolated as a white crystalline solid in 60% yield. If, after isolation of product, the filtrate is reduced in volume in an attempt to isolate more product, an off-white solid is obtained, but on filtration the solid darkens and oils on contact with the atmosphere.

Canty et al.[36] reported $Me_2Pt(HCpz_3)$ to be insoluble in cold pyridine, but in initial studies of this reaction it has been found that if a suspension in cold pyridine is allowed to stand at ambient temperature, it slowly "dissolves" over a period of hours during which time the solution turns a light yellow colour. The metallated product can be isolated from this solution (dropwise addition of hexane) in approximately 80% yield. Two competing reactions may be

occurring in the $Me_2Pt(HCpz_3)$/pyridine suspension, metallation (equation 16) and substitution (equation 17).

$$Me_2Pt(HCpz_3) + \text{xs pyridine} \longrightarrow Me_2Pt(py)_2 + HCpz_3 \quad (17)$$

The synthesis of $Me_2Pt(py)_2$, by heating $Me_2Pt(COD)$ in neat pyridine, was reported by Kistner et al.[37] in 1963, although the yield on isolation was only 5%. We, and others,[38] have not been able to reproduce this synthesis, but Williams et al.[38] have reported a facile preparation of $Me_2Pt(py)_2$ from $Me_2Pt(NBD)$ and pyridine in benzene solution. ^1H NMR studies indicate that when $Me_2Pt(NBD)$ is dissolved in neat pyridine, NBD is displaced from the $Me_2Pt(II)$ moiety (resonances due to free NBD are observed). Only when stringent experimental conditions (temperature, stoichiometry, rate of addition of pyridine) are exercised can $Me_2Pt(py)_2$ be isolated,[38] and it is stable as a solid if kept under a nitrogen atmosphere in the dark at 0^oC. If such experimental controls are not exercised, an off-white solid is produced, the ^1H NMR spectrum of which shows the presence of a variety of uncharacterized species.[38] The yields of $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ from hot and cold pyridine, 60 and 80% respectively, suggest that the competing reaction (17), if it occurs, is less important at ambient temperature.

It is observed that as $Me_2Pt(HCpz_3)$ metallates in pyridine, minute bubbles rise from the bulk of the solid to the surface. NMR studies in deuterated pyridine failed to detect any resonance due to methane, however this is not entirely unexpected as the reaction proceeds very slowly in the cold, and thus the concentration of methane in solution at any particular time may be miniscule. G.C./M.S. analysis of the expelled gas identifies it as methane.

Although Canty et al.[36] reported full characterization data for $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, their ^1H NMR spectra were recorded with a continuous wave instrument with low resolution, and a complete assignment was not given. A 300 MHz FT ^1H NMR spectrum is shown in figure 3.1, together with an expansion of the aromatic region (figure 3.2), with atom numbering shown in figure 3.3.

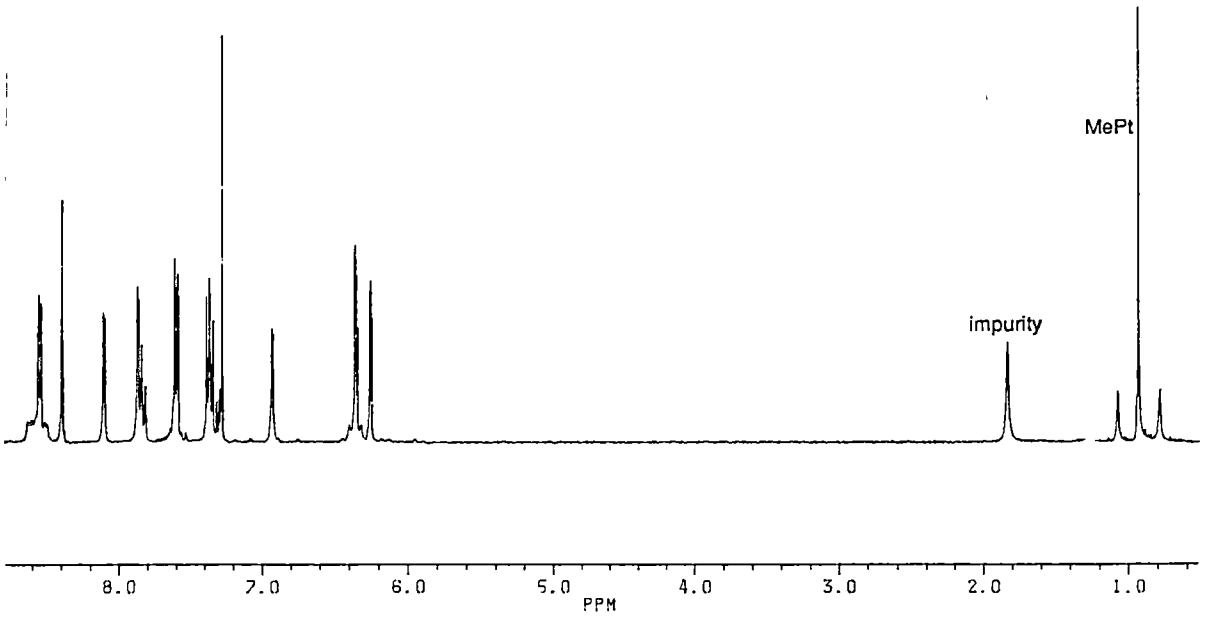


Figure 3.1 ^{1}H NMR Spectrum of MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(py)

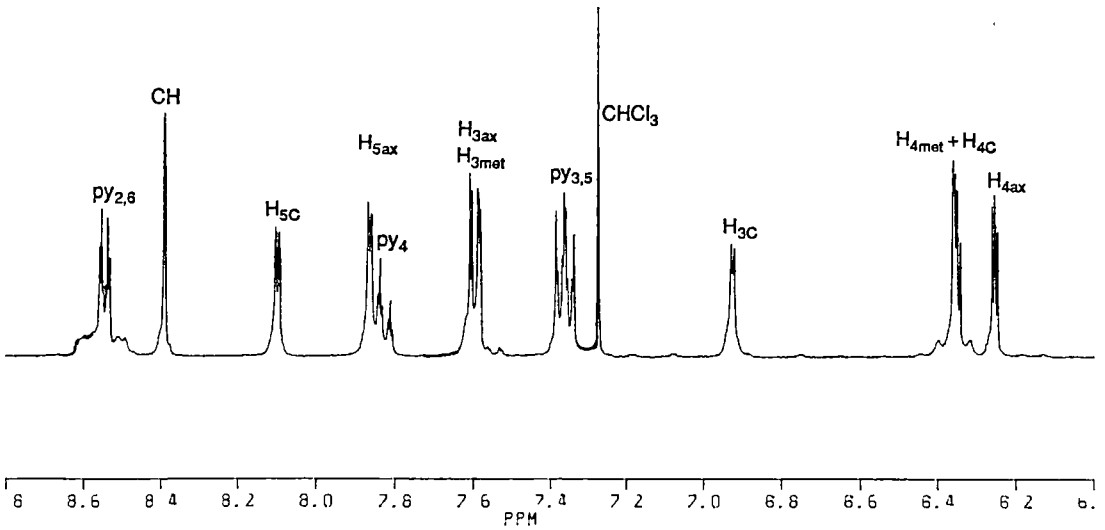


Figure 3.2 Aromatic Region of MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(py)

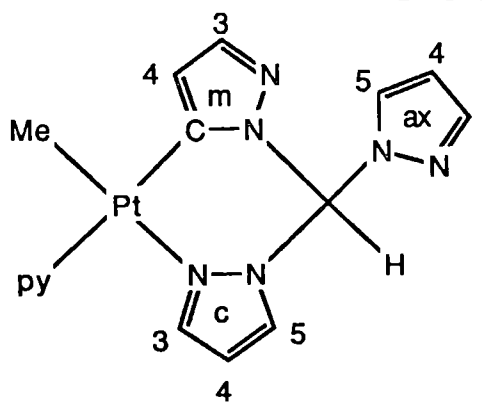


Figure 3.3

The complex exhibits major differences from N,N-chelated complexes in the aromatic region of the spectrum, showing three inequivalent pyrazolyl rings, with the H4 metallated and H4 N-coordinated proton resonances coincident (6.35 ppm), and at lower field than H4 uncoordinated (although this may result from shielding of this proton by the coordinated pyridine group), two H5 signals (7.86 ppm uncoordinated, 8.10 ppm coordinated) and three H3 resonances (7.60 ppm metallated, 6.92 ppm coordinated and 7.58 ppm uncoordinated), with assignment relying on integration and COSY spectra. The H3 proton belonging to the coordinated pyrazolyl ring (6.92 ppm) is shielded by the coordinated pyridine ring and is moved upfield relative to the H3 signals of the other rings. The H5 proton of the uncoordinated ring is upfield in comparison with the H5 proton of the coordinated ring. This upfield shift is attributed to shielding by a pyrazolyl ring, with the uncoordinated group in an axial position with its H5 proton directed away from the metal.

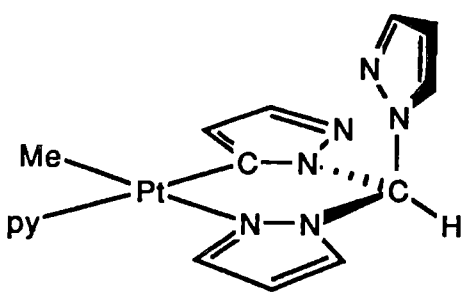


Figure 3.4

The ^{1}H NMR spectra of $Ph_2Pt(HCpz_3)$ (Chapter 2) and $Me_2Pd(HCpz_3)$[39] indicate that the free pyrazolyl group is in the axial position, but with the H5 proton adjacent to the metal.

Two extreme mechanisms are available for cyclometallation, electrophilic attack by the metal or oxidative addition of the C-H bond to the metal.

An electrophilic attack mechanism is unlikely since the $Me_2Pt(II)$ unit is expected to be nucleophilic in character, and in neat pyridine this nucleophilic character is expected to be enhanced if pyridine becomes coordinated to the platinum atom. Thus, cyclometallation is likely to proceed via oxidative addition, for which two possible pathways are envisaged.

The first involves an intermediate (figure 3.5) with the interaction occurring between the H5 proton of the uncoordinated axial pyrazolyl ring and the metal centre.

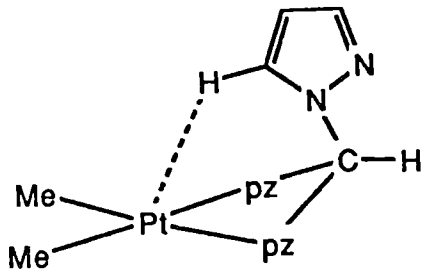


Figure 3.5

This interaction, perhaps agostic in nature, leads to a formal oxidative addition with formation of an unstable platinum(IV) hydride complex, followed by reductive elimination of methane and rearrangement of the pyrazolyl ligand and incorporation of pyridine to form the observed square planar platinum(II) complex. The role of pyridine in this reaction sequence is restricted to providing an ancillary ligand to complete the square-plane of the final product, or perhaps to coordinate axially to assist the initial step(s) in oxidative addition.

The other possible pathway involves a square-planar pyridine complex as an intermediate.

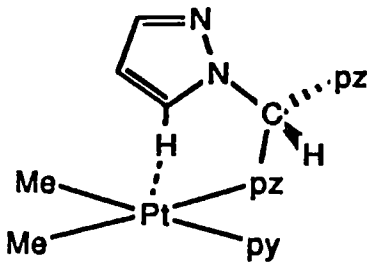


Figure 3.6

Pyridine displaces one coordinated pyrazolyl ring, thereby increasing the nucleophilic character of the complex, and either allowing the ligand greater flexibility to orientate itself in such a geometry that metallation can occur, or reducing the flexibility of the ligand in such a way that cyclometallation is favoured. Again, metallation would be expected to proceed via oxidative addition.

If a suspension of $Me_2Pt(HCpz_3)$ is refluxed in toluene cyclometallation is not observed and starting material is recovered unchanged, indicating that pyridine may be involved in the mechanism of cyclometallation. As $Me_2Pt(py)_2$ is thought to be formed (as a by product) during the metallation reaction, then pyridine substitution seems likely at some stage prior to metallation.

If solid $Me_2Pt(HCpz_3)$ is suspended in deuterated pyridine and its ^1H NMR spectrum recorded at successive time intervals, reliable reproducible spectra are not obtained until the solid has "dissolved" and mixing has occurred. However, in the initial stages of the reaction more than one MePt signal is observed and a number of H4 pyrazolyl resonances are apparent, perhaps indicating that a pyridine coordinated complex is indeed an intermediate in the reaction.

Crystalline metallated complexes are also formed from $Me_2Pt(HCpz_3)$ with other N-donor solvents such as N-methylimidazole and substituted pyridines, eg. α-and γ-picoline and 2,6-lutidine.

$MePt(HCpz_2(C_3N_2H_2)$-C,N)(py) slowly decomposes in $CDCl_3$, eg. an NMR sample left in $CDCl_3$ for 8 hours showed no MePt(II) resonance,

but a number of MePt(IV) resonances with a very complicated aromatic region. Thus, MePt($HCpz_2(C_3N_2H_2)$-C,N)(py) would appear to be reactive toward oxidative addition reactions, and aspects of this reactivity are discussed in Chapter 4.

Reactions of MePt($HCpz_2(C_3N_2H_2)$-C,N)(py)

When crystalline MePt($HCpz_2(C_3N_2H_2)$-C,N)(py) is refluxed as a suspension in benzene for 1 hour an amorphous white solid is obtained. This solid is insoluble in common organic solvents, and an infrared spectrum shows the absence of pyridine. The solid is assumed to be a polymer, $[MePt(HCpz_2(C_3N_2H_2)-N,C)]_n$, similar to the 'isoelectronic' polymer $[MePt(HBpz_3)]_n$.[40]

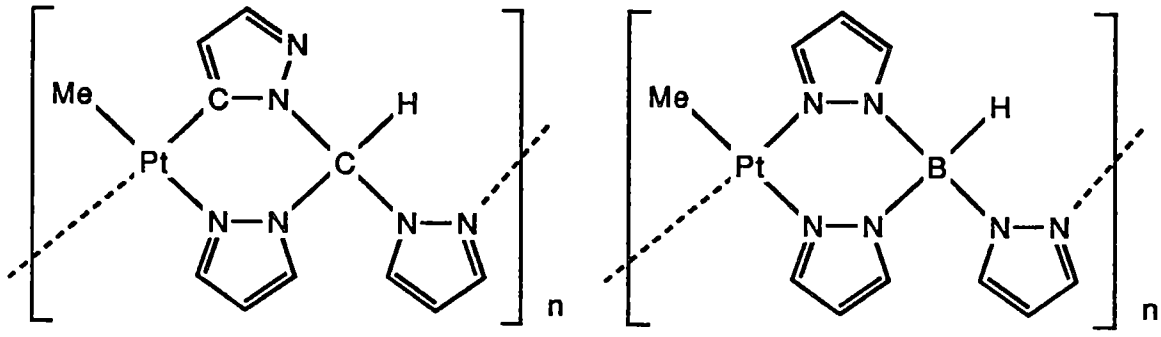


Figure 3.7

If MePt($HCpz_2(C_3N_2H_2)$-N,C)(py) is refluxed in acetone, the solid dissolves to give a clear solution, from which the polymer is obtained on addition of hexane. In acetone solution the complex is assumed to be present as a monomeric adduct, and if carbon monoxide is bubbled through this solution and hexane added, a carbon monoxide adduct is obtained. The infrared spectrum of the solid complex exhibits a strong band at 2074 cm^{-1}, consistent with coordinated CO, and a ^1H NMR spectrum (figure 3.8) is also consistent with this structure.

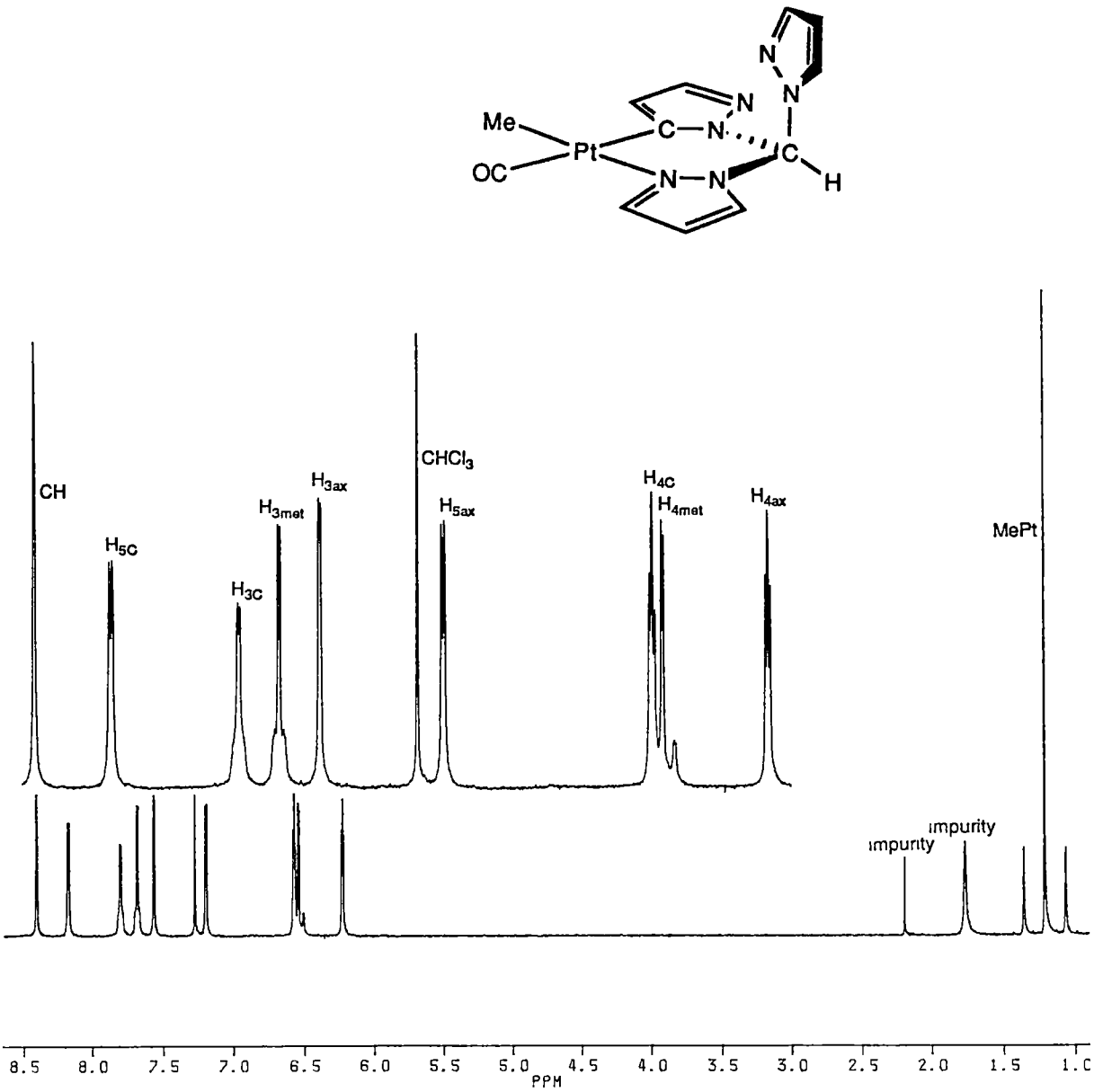


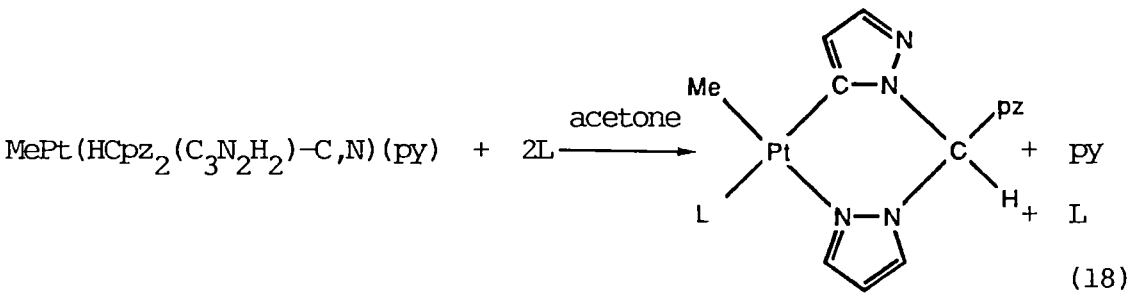
Figure 3.8 ^{1}H NMR Spectrum of $MePt(HCpz_2(C_3N_2H_2)-C,N)(CO)$.

The H5 pyrazolyl proton resonance occurs 1.1 ppm upfield (7.26 ppm) from that in $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, suggesting that the uncoordinated axial pyrazolyl ring adopts a conformation with the H5 proton away from the metal and in a shielding cone of one of the coordinated pyrazolyl rings.

Carbon monoxide was not observed to insert into the MePt bond, even after prolonged bubbling of CO into the soluble polymeric

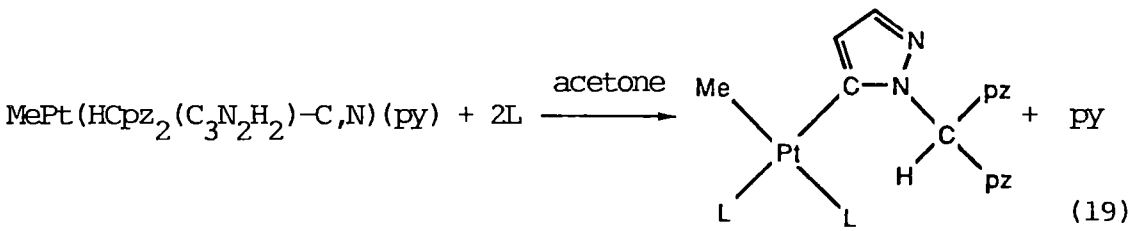
acetone solution.

$MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ also undergoes ligand exchange reactions with phosphine ligands, with the degree of incorporation of phosphine dependent upon the bulk of the phosphine. Thus, refluxing $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ with various phosphine ligands in either benzene or acetone resulted in displacement of pyridine, and in some cases the N-coordinated pyrazolyl group also.



(18)

L = $PPh_2(PhOMe)$, $PPh_2(o\text{-tolyl})$,



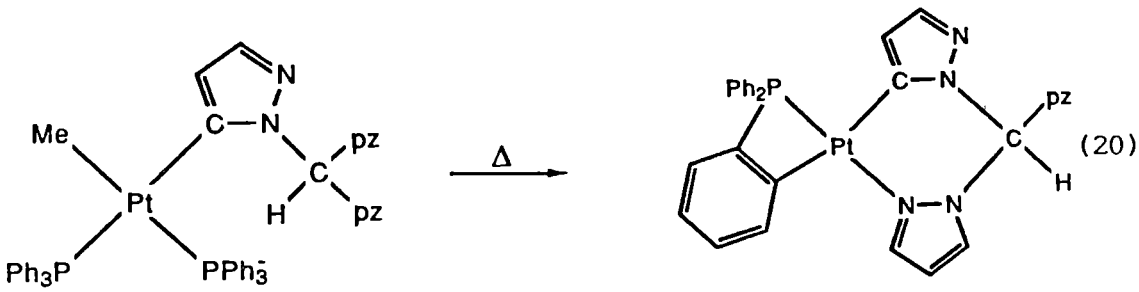
(19)

L = PPh_3, PPh_2Me, $PPhMe_2$, PPh_2Et, $PPh_2(CH_2Ph)$, $P(PhO)_3$
$^1/_2PPh_2(CH_2)_nPh_2P$ (n = 1, 2),

The phosphine ligands trimesitylphosphine and tri-o-tolyl phosphine failed to react with $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, presumably due to their bulkiness, and polymeric $[MePt(HCpz_2(C_3N_2H_2)-C,N]_n$ was isolated from the reaction mixture. Likewise, the arsine ligands $AsPh_3$ and $AsPh_2CH_2Ph_2As$ also failed to undergo reaction.

Canty et al.[36] have shown that the phosphine complex $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ undergoes metallation of a phosphine

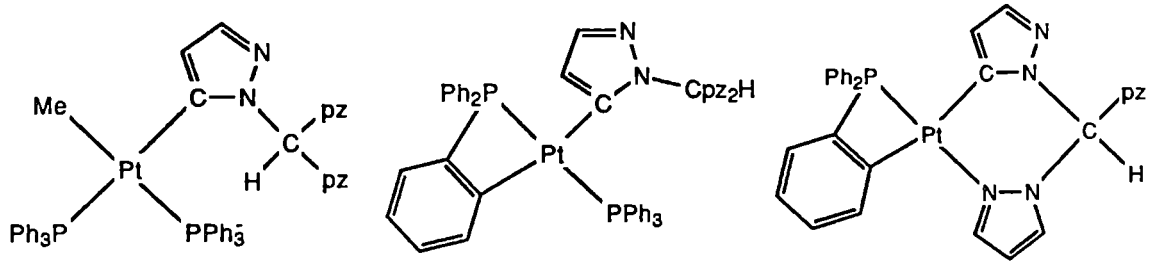
ligand upon heating the solid complex, with expulsion of the other phosphine ligand.



(20)

This doubly metallated complex contains both six (pyrazolyl) and four (phosphine) membered metallated chelate rings. To explore the ease of this type of reaction, the effect of heat on the phosphine complexes above was investigated, and the effect of heat on $MePt(HCpz_2(C_3N_2H_2)\text{-}C)(PPh_3)_2$ reinvestigated as only scant information was published earlier.

The mass spectrum of $MePt(HCpz_2(C_3N_2H_2)\text{-}C)(PPh_3)_2$ shows fragments with m/e values consistent with a parent ion of molecular weight 947, a fragment which has lost methane (931), and a fragment which has lost both methane and a single phosphine ligand, (669).



Mwt 947 931 669

Figure 3.9

Thus, the phosphine metallation appears to occur in two distinct steps, metallation of triphenylphosphine with concomitant loss of methane, followed by loss of triphenylphosphine

A T.G.A. for $MePt(HCpz_2(C_3N_2H_2)\text{-}C)(PPh_3)_2$ is shown in figure 3.10A.

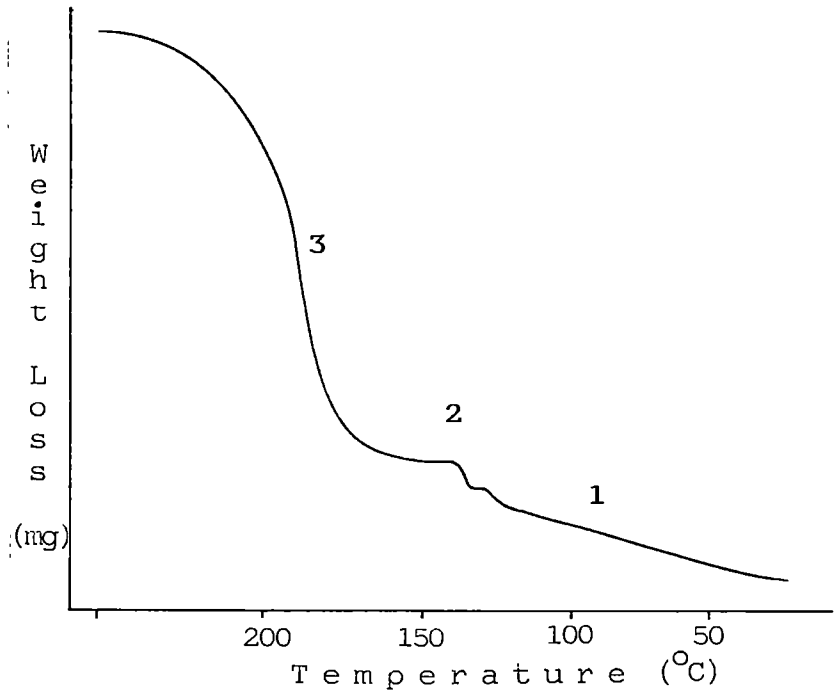


Figure 3.10A T,G.A. of $MePt(HCpz_2(C_3N_2H_2)-C,N)(PPh_3)_2$.

The initial weight loss (1), corresponds to the loss of acetone, as the complex (recrystallized from acetone/hexane, vacuum dried at 80°C for 2 hrs) is a 1:1 acetone solvate. The second weight loss (2) is rapid and is due to expulsion of methane gas (metallation step) while the third weight loss (3), occurring over the temperature range 160 - 200°C, is due to loss of PPh_3. The calculations for these weight losses are given in appendix 1. This is interpreted as indicating that PPh_3 is not lost until after CH_4 expulsion, i.e. after phosphine metallation has occurred.

Two other basic types of thermogravimetric curves were obtained for the other complexes, depending upon the phosphine present (figure 3.10 B, C).

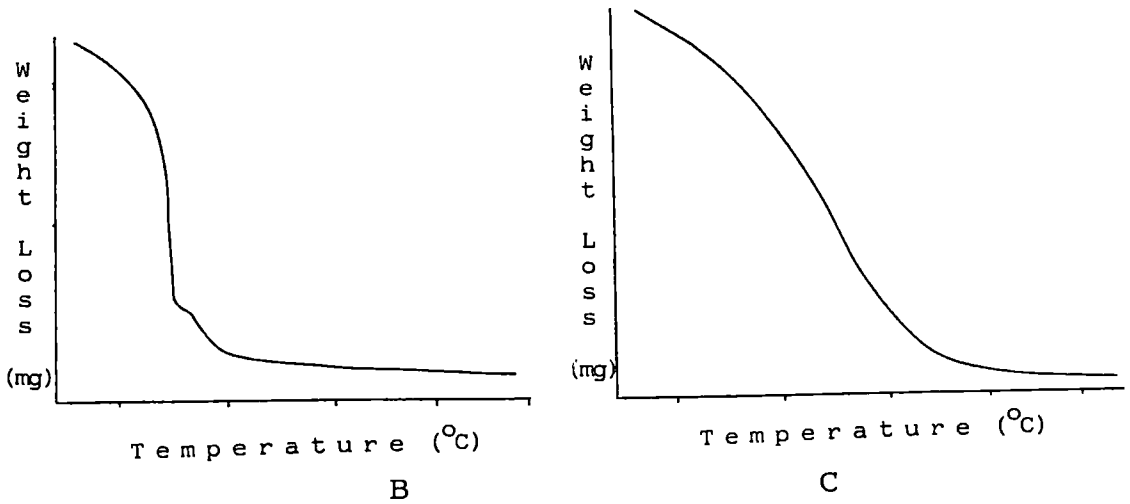


Figure 3.10 B, C General T.G.A. Curves for Various Phosphine Complexes

Curve A was observed for $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ only. This curve shows loss of CH_4 with subsequent gradual weight loss, presumably of phosphine, occurring as independent processes. Curve B, exhibited for complexes 2 - 6, shows a rapid expulsion of gas, immediately followed by gradual weight loss, again presumably of phosphine. However this weight loss is not stoichiometric and thus decomposition occurs as part of or at least during loss of phosphine. Curve C (complexes 7 - 10) is indicative of slow non-stoichiometric decomposition.

The mass spectral results (Table 3-2) for $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ are interesting in that they show a peak with m/e 16 (m.wt. CH_4) less than the parent ion, and presumably this indicates the presence of a metallation reaction. From these results, the metallation reaction for complexes 2 - 6 could be considered to occur as part of the thermal decomposition process, with the metallated complex not stable enough to be isolable.

Table 3-2

Mass Spectral and Thermal Analysis Results for Phosphine Complexes Containing Cyclometallated $HCpz_3$

Number	Complex $MePt(HCpz_2(C_3N_2H_2-C)(L)$	Mass Spectrum Observed, Calc. Fragment Loss			Thermogravimetric Behaviour (a)
1.	$2PPh_3$	947	947	m.wt.	
		931	931	CH_4	A
		669	669	$(CH_4 + PPh_3)$	
2.	$2PPh_2Me$	823	823	m.wt.	
		614	807	CH_4	B
			607	$(CH_4 + PPh_2Me)$	
3.	$2PPh_2Et$		851	m.wt.	
			835	CH_4	B
		621	621	$(CH_4 + PPh_2Et)$	
4.	$PPh_2(PhOMe)$		715	m.wt.	
		699	699	CH_4	B
5.	$2PPh_2(CH_2Ph)$		975	m.wt	
			959	CH_4	B
		683	683	$(CH_4 + PPh_2(CH_2Ph)$	
6.	$PPh_2(o\text{-tolyl})$		699	m.wt.	B
		683	683	CH_4	
7.	$2PPh_2Me$		699	m.wt	
		683	683	CH_4	C
		545	545	$(CH_4 + PPh_2Me)$	
8.	$PPh_2CH_2Ph_2P$		807	m.wt.	
		791	791	CH_4	C
9.	$PPh_2CH_2CH_2Ph_2P$		821	m.wt.	
		805	805	CH_4	C
10.	$2P(OPh)_3$		1043	m.wt	
			1027	CH_4	C
		717	717	$(CH_4 + P(PhO)_3)$	

(a) A, B, C. refer to the curves A, B, C shown in figure 3.10 p.106-7

The only complex which exhibits thermogravimetric behaviour exemplified by curve A was the PPh_3 complex, accounting for the observation that only this complex could be isolated after heating.

$Me_2Pt(L)$ $(L = H_2Cpz_2, Ph(H)Cpz_2)$

$Me_2Pt(H_2Cpz_2)$ and $Me_2Pt(Ph(H)Cpz_2)$ dissolve rapidly in neat pyridine to yield a deep golden solution, from which white solids can be precipiated by the addition of hexane. These solids oil on contact with air and are difficult to isolate as pure substances. Addition of triphenylphosphine allows the phosphine complexes to be isolated as white solids. In both cases ^1H NMR spectrum show the presence of a single MePt resonance (I = 3H) and a H4 pyrazolyl resonance flanked with well defined platinum satellites, consistent with cyclometallation having occurrred in the pyrazolyl ring. ^{31}P NMR show that in the case of $Me_2Pt(H_2Cpz_2)$ a bis(phosphine) complex is formed (figure 3.11 (A)) but with $Me_2Pt(Ph(H)Cpz_2)$ a monophosphine (figure 3.11 (B)) is isolated even though the ratio of phosphine : complex was 2:1. By analogy with the phosphine complexes of metallated $HCpz_3$ and $HC(mim)pz_2$, the following structures are proposed.

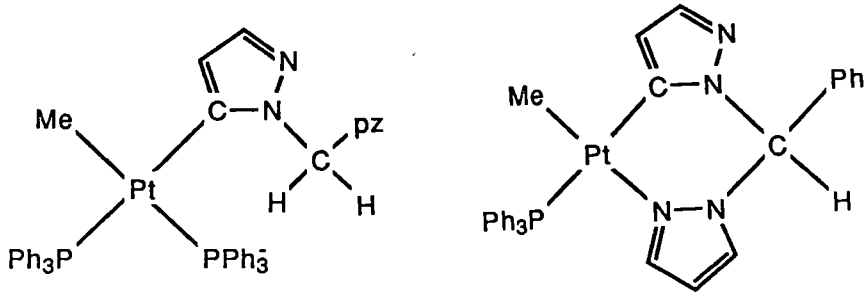


Figure 3.11

Whether a bis or monophosphine complex is formed is presumably determined by steric factors, as the C-bound pyrazolyl ligands differ in size although their Pt-N and Pt-C bonding character are expected to be very similar.

For the complex $Me_2Pt(Ph(H)Cpz_2)$, a pyrazolyl ring is metallated in preference to a non-donor phenyl ring, and this may be a

reflection of either differing ring reactivities or a preferred ligand orientation such that a pyrazolyl ring is in the most favoured orientation for metallation to occur.

In both of these metallation reactions, only the pyridine displacement mechanism would seem to be applicable for cyclometallation. Thus, at least with these bidentate complexes, metallation can be assumed to proceed via an intermediate pyridine complex.

On heating either of the phosphine complexes metallation of the phosphine ligand was not observed to occur. Mass spectral results gave a m/e value consistent with a metallation reaction occurring, but this is assumed to be concurrent with decomposition.

Reaction of the other Me_2PtL (L = eg. $Me(H)Cpz_2$) complexes with pyridine, followed by phosphine addition shows that metallation does not occur. For example, $Me_2Pt(H_2(mim)pz)$ dissolves in pyridine on warming to yield a deep yellow solution, from which a white crystalline phosphine derivative can be readily isolated on addition of PPh_3. The ^1H NMR spectrum of this complex shows that $Me_2Pt(PPh_3)_2$ has been formed and metallation has not occurred. This is surprising since related $Me_2Pt(H_2Cpz_2)$ and $Me_2Pt(HC(mim)pz_2)$ do cyclometallate, and $Me_2Pt(H_2C(mim)pz)$ has a strong donor group (mim) to 'anchor' the ligand during initial reaction with pyridine.

$\underline{Me_2Pt(HC(mim)pz_2)}$

On addition of pyridine to solid $Me_2Pt(HC(mim)pz_2)$ rapid evolution of bubbles is observed and the solid dissolves immediately to yield a deep yellow solution. Addition of hexane to this solution precipitates a white solid, which on attempted isolation oils in contact with air to produce a tan decomposition product. If pyridine is removed by rotary evaporation, acetone added and the suspension stirred for 5 minutes and filtered, an off-white solid is obtained which gives an ill-defined ^1H NMR spectrum.

The complex formed from $Me_2Pt(HC(mim)pz_2)$ in pyridine is best isolated as the phosphine derivative by addition of triphenylphosphine to the pyridine solution and stirring for 10 minutes. Removal of pyridine, addition of acetone and dropwise addition of hexane yields a crystalline complex , the ^1H NMR spectrum (figure 3.12) of which shows that a monophosphine complex is formed.

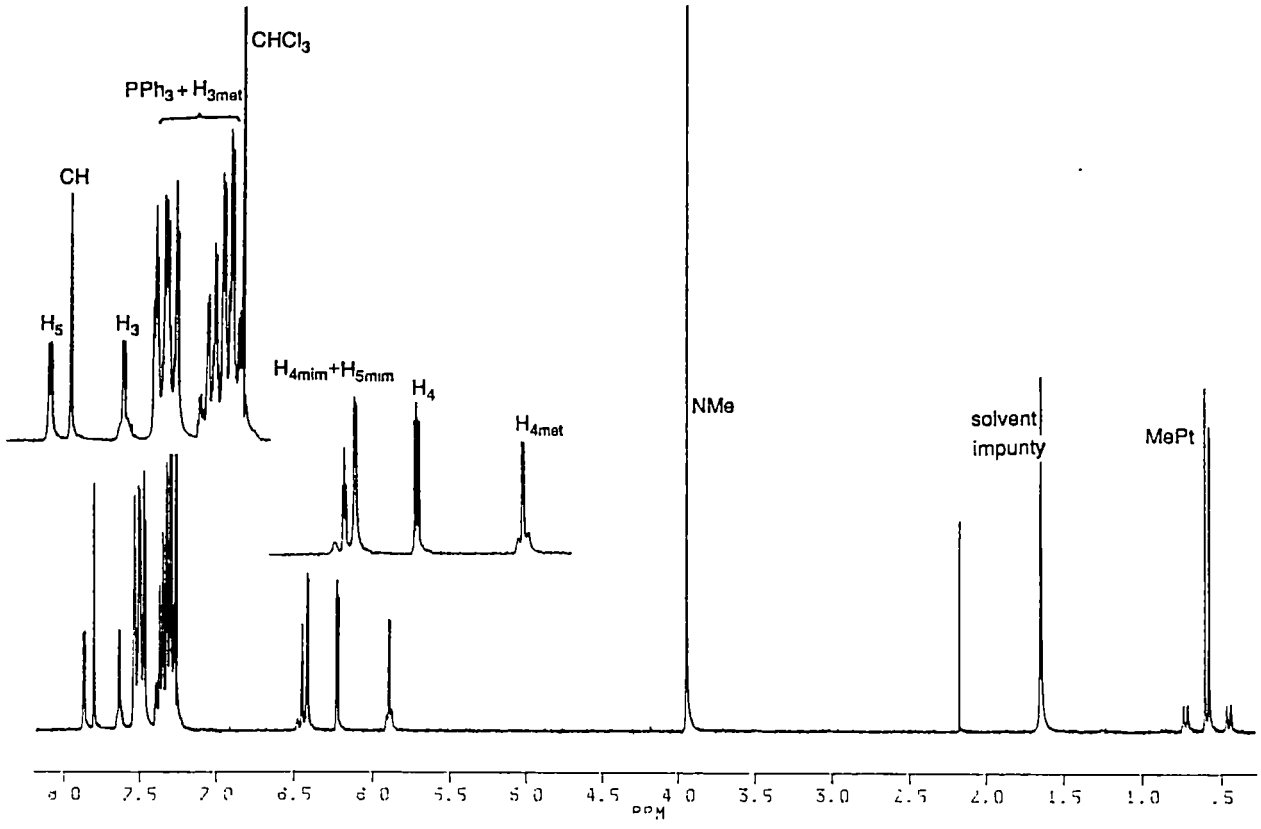


Figure 3.12 ^1H NMR Spectrum of $MePt(HC(mim)pz(C_3N_2H_2)-C,N)(PPh_3)$.

Features of interest which confirm that metallation has occurred are seen in the MePt resonance at 0.64 ppm ($^2J(^1H-^{195}Pt)$ 82.9 Hz, $J(^{31}P-^{195}Pt)$7.90 Hz), which integrates for a single methyl group, and the H4 resonance at 6.10 ppm which shows Pt coupling, $^3J(^1H-^{195}Pt)$ 11.9 Hz, typical of a metallated pyrazolyl ring.

This complex differs from that obtained on metallation of $Me_2Pt(HCpz_3)$ in that only a single phosphine group coordinates, and this is most probably due to the stronger donor ability of the N-methylimidazolyl ring forming a strong chelate ring which the

phosphine is unable to cleave.

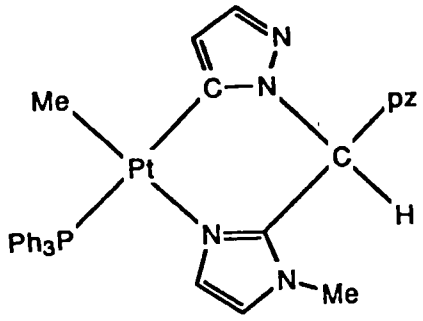


Figure 3.13

During an X-ray crystallographic study[36] of $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ an impurity crystal was found to contain a single phosphine, which was <u>trans</u> to methyl (figure 3.14).

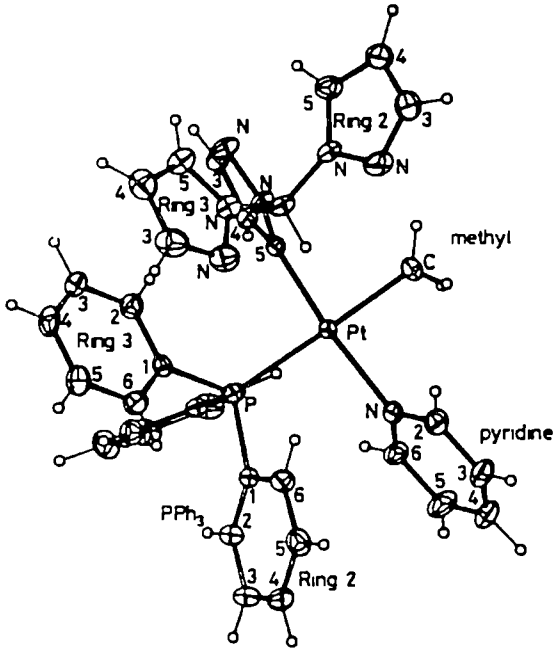


Figure 3.14

This monophosphine is in contrast to that obtained from the $MePt(H(mim)Cpz(C_3N_2H_2)-C,N)(py)$ system in which PPh_3 replaces pyridine and must reflect the relative strengths of the $^{-}CN(pz)$, $^{-}CN(mim)$ chelate bonds.

If $MePt(H(mim)Cpz(C_3N_2H_2)-C,N)(py)$ is prepared in situ (neat py), pyridine removed, benzene added and the solution refluxed, a precipitate is not obtained. After addition of hexane and isolation, an IR spectrum of the whitish solid obtained shows the presence of coordinated pyridine (starting material), and thus a polymeric substance analogous to $[MePt(HCpz_2(C_3N_2H_2)-C,N)]_n$ is not obtained.

Attempted Metallation Reactions

Other ligands synthesized which contain sites/geometries appropriate for metallation reactions include $pzCH_2CH_2CH_2pz$, $1,3-(pzCH_2)_2C_6H_4)$, $(PhOMe)(H)Cpz_2$ and $1,3-(pz_2CH_2)_2C_6H_4)$ (figure 3.15), with the appropriate metallation sites marked (*).

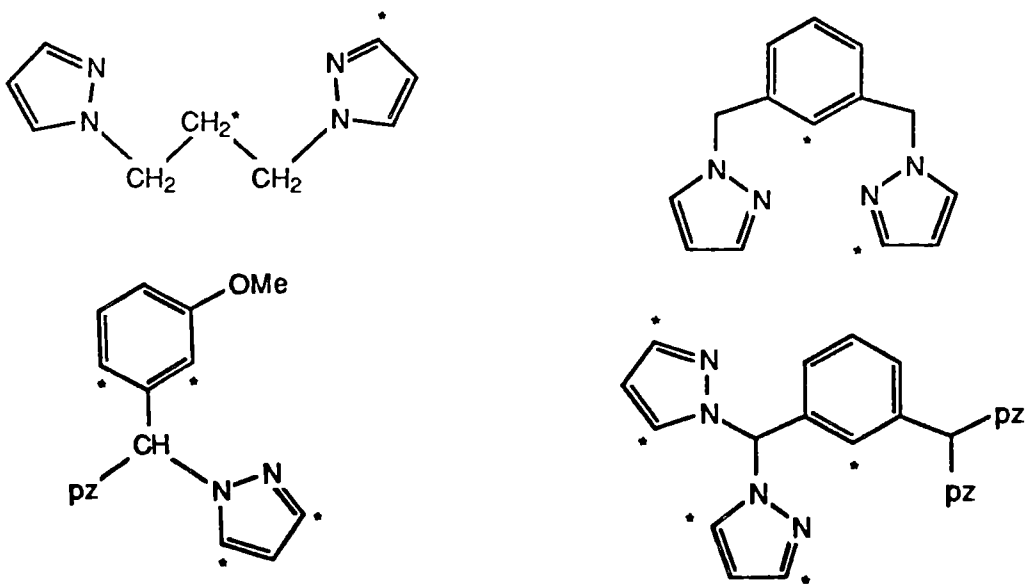


Figure 3.15

These ligands contain potential metallating sites, either in the pyrazolyl ring, in the carbon skeleton supporting the ring or in the non-donor groups attached to the ligand.

Reaction of $pzCH_2CH_2CH_2pz$ with $[Me_2Pt(Et_2S)]_2$ resulted in the isolation of an oil from which a solid complex could not be isolated. This oil was reacted with MeI to give a Pt(IV) complex which showed that metallation had not occurred. The closely related ligand $py(CH_2)_3py$ has been reported to undergo a metallation at the central

methylene C atom with $Pd(OAc)_2$ to form a doubly chelated cyclopalladated complex (figure 3.16), isolated as the chloride.[41]

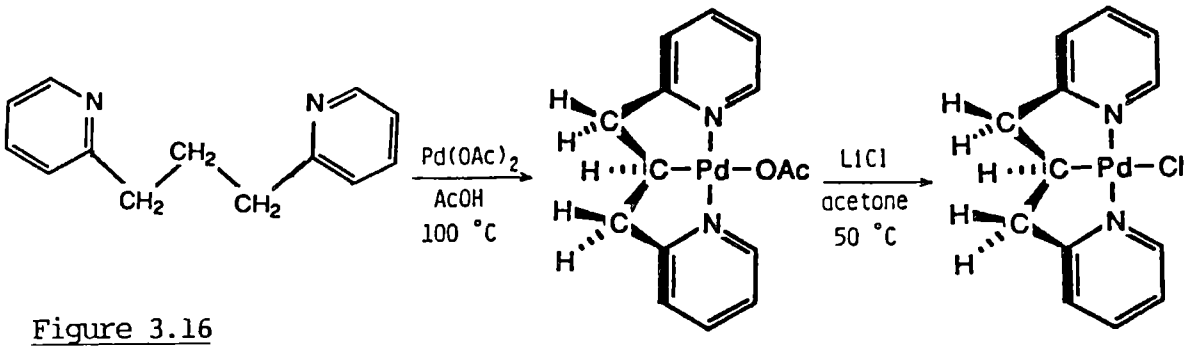


Figure 3.16

Thus, $pzCH_2CH_2CH_2pz$ was treated with $Pd(OAc)_2$ in acetic acid at 100°C for 2 hours after which time a yellow solution had formed and reduction to palladium was visibly evident. The solution was filtered, acetic acid removed and acetone added, from which a crystalline yellow solid precipitated. This solid was insoluble in common organic solvents, but dissolved in warm pyridine from which yellow crystals of a very soluble complex were obtained by addition of hexane. The ^1H NMR spectrum and melting point of this product identify it as diacetato-bispyridinepalladium(II). Thus, the ligand $pzCH_2CH_2CH_2pz$ is not metallated by palladium, the isolated complex after reflux in acetic acid being the simple N,N-chelated coordination compound.

Extended heating of this compound in acetic acid (100°C) resulted in reduction to palladium metal.

$Pd(OAc)_2$ was treated with a stoichiometric amount of $1,3-(pzCH_2)_2C_6H_4$ in acetic acid at 100°C. During the reaction the solution turned a deep purple colour which slowly faded resulting in a bright yellow solution from which a white crystalline complex could be isolated. The ^1H NMR spectrum of this complex shows the presence of equivalent pyrazolyl rings, equivalent methylene protons, an acetate methyl resonance, and integration for 3 phenyl protons, all consistent with palladation at the C1 position of the phenyl ring. The complex (figure 3.17) is planar and contains 6 membered NC^- chelate rings.

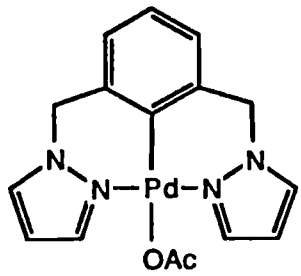


Figure 3.17

A ^{13}C NMR spectrum shows that the metallated carbon of the phenyl ring occurs at 139 ppm and a proton-carbon correlation spectrum shows that this resonance is not connected to any proton.

This complex undergoes metathesis with NaCl in acetone at ambient temperature to afford the chloro complex, $ClPd((pzCH_2)_2C_6H_3)$, which exhibits similar NMR features to that of the acetate complex.

Cyclopalladation of related pyridine donor ligands, eg. 1,3-$(pyCH(Me)_2C_6H_4)$, has been reported to form planar tridentate N_2C^- tridentate complexes.[42]

$1,3\text{-}(pzCH_2)_2C_6H_4$ reacted with $[Me_2Pt(Et_2S)]_2$ to form an intractable white solid. Addition of pyridine to this solid resulted in isolation of a solid which oiled and decomposed on contact with the atmosphere, and this may be $Me_2Pt(py)_2$. $PtCl_4^{2-}$ reacts with 1,3-$((pzCH_2)_2C_6H_4)$ to form a simple coordination compound which is highly insoluble in common solvents. Heating this compound in 2-methoxyethanol, even with the addition of base (NaOAc) failed to cause metallation to occur.

The related ligand $1,3\text{-}((pz_2CH)_2C_6H_4)$ also reacts with both $Me_2Pt(II)$ and $PtCl_4^{2-}$ but neither system yields a cyclometallated complex. Reaction of this ligand with $Pd(OAc)_2$ resulted in the isolation of an unmetallated complex, and this behaviour has been observed before.[42] $(PhOMe)HCpz_2$ reacts in an analogous fashion to $Ph(H)Cpz_2$, viz. metallation occurring in the pyrazolyl ring.

Ph_2PtL Complexes

The pyridine metallation reaction was investigated for a small number of Ph_2PtL (L = $HCpz_3$, $Ph(H)Cpz_2$, H_2Cpz_2) complexes since metallation of a $Ph_2Pt(II)$ complex containing the ligand (bipy) has been reported (figure 3.18)

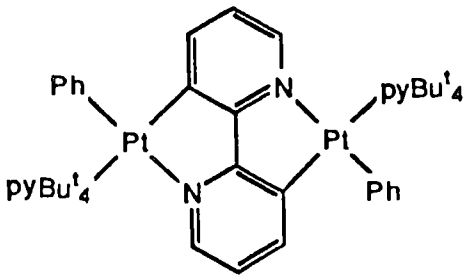


Figure 3.18

Reaction occurred between $Ph_2Pt(bipy)$ and 4Bu^{t}py (solvent) by a proposed 'roll-over' mechanism.

Reaction of $Ph_2Pt(HCpz_3)$ with pyridine (neat) yielded a yellow solution from which an off-white solid could be isolated with difficulty. An IR spectrum of this solid showed the presence of coordinated pyridine, but no absorptions indicative of $HCpz_3$. Extraction of the reaction mixture yielded a white crystalline solid identified as $HCpz_3$ (NMR). Thus, $Ph_2Pt(HCpz_3)$ does not appear to cyclometallate by this route, and most probably forms the bis pyridine complex $Ph_2Pt(py)_2$ in neat pyridine. This substantiates the idea that a first step to metallation for the Me_2PtL complexes is a pyridine displacement of a pyrazolyl group. In the case of Ph_2PtL the Pt atom in the expected intermediate may be less able to undergo an oxidative addition reaction with a C-H bond, eg. $Ph_2Pt(bipy)$ reacts approximately 100 times slower than $Me_2Pt(bipy)$ in the oxidative addition reaction.[43]

3.5 Conclusion

Cyclometallation of a pyrazolyl ring in Me_2PtL complexes has been shown for the complexes with L = $HCpz_3$, H_2Cpz_2, $Ph(H)Cpz_2$ and $HC(mim)pz_2$ by reaction with pyridine. Metallation is considered to

occur via a pyridine displacement mechanism with the actual C-H addition to the metal occurring via a conventional oxidative addition.

With some complexes (L = $H_2C(mim)pz$, $Me(H)Cpz_2$, Me_2Cpz_2) complete displacement rather than cyclometallation was favoured, presumably due to steric properties of the system.

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CHAPTER 4

OXIDATIVE ADDITION REACTIONS

CHAPTER FOUR

OXIDATIVE ADDITION REACTIONS OF R_2PtL COMPLEXES

4.1 Introduction

Oxidative addition of alkyl halides to the platinum(II) complex containing metallated tris(1-pyrazolyl)methane, $MePt(HCpz_2(C_3N_2H_2)$-C,N)(py), has been explored in order to attempt synthesis of platinum(IV) complexes containing tripodal N_2C^- donors. This approach was successful (Chapter 4, section 4.4.3), and it was subsequently found that reaction of iodomethane with the non-metallated complex, $Me_2Pt(HCpz_3)$, also gave the cyclometallated platinum(IV) complex directly. In view of this unexpected result, a range of oxidative addition reactions of alkyl halides and iodine with $Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes containing pyrazolyl based ligands has been investigated.

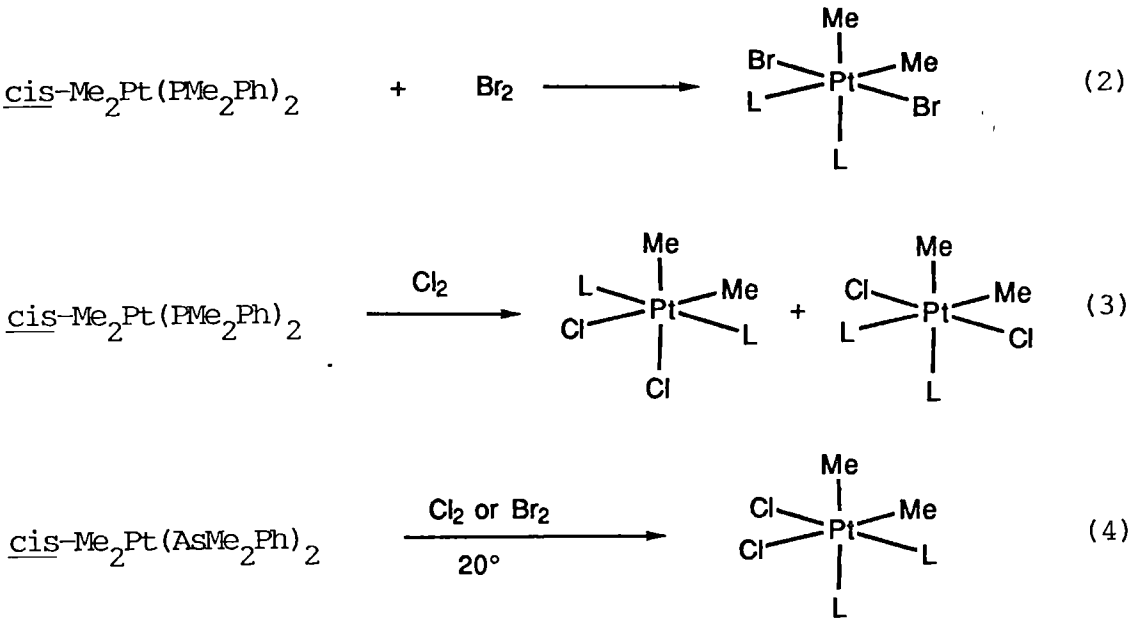
4.2 General

Organoplatinum(II) complexes are readily oxidized to platinum(IV) complexes by the addition of halogens and organohalides, and the oxidative addition reaction has become an important synthetic method for the synthesis of organoplatinum(IV) complexes. Clark et al.[1] have reported the oxidative addition of I_2 to a stoichiometric mixture of $Me_2Pt(COD)$ and pyrazolyl based ligands in CH_2Cl_2 to yield diorganoplatinum(IV) complexes, eg.

$$Me_2Pt(COD) + H_2C(3,5Mepz)_2) + I_2 \longrightarrow Me_2I_2Pt(H_2C(3,5Mepz)_2) \quad (1)$$

A crystallographic determination of the structure of this complex showed the methyl groups to be in the square plane defined by the platinum and H_2Cpz_2 ligand, with <u>trans</u> iodo donors. (Figure 1.4, Chapter 1)

If the platinum(II) substrate contains tertiary phosphine or arsine ligands, the nature of the ligand and halogen has a significant effect on the stereochemistry of the product.[2]



If the oxidizing agent is an alkylhalide, then a triorganoplatinum(IV) complex can be formed,[2,3] eg.

$$Me_2Pt(LMe_2Ph) + MeCl \longrightarrow Me_3(Cl)Pt(LMe_2Ph)_2 \quad (5)$$

L = As, P

$$Me_2Pt(PEt_3)_2 + MeI \longrightarrow Me_3(I)Pt(PEt_3)_2 \quad (6)$$

The only report[4] of the oxidative addition of MeI to form a tetramethylplatinum(IV) complex involves the synthesis of the dimeric dimethyl sulphide bridged complex $[Me_4Pt(Me_2S)]_2$.

$$2Cl_2Pt(Me_2S)_2 + 6MeLi + 2MeI \longrightarrow [Me_4Pt(Me_2S)]_2 \quad (7)$$

Up until about the last fifteen years, most oxidative addition reactions had been carried out using platinum(II) substrates containing phosphine or arsine ligands,[2,5] as it was thought that

these types of ligands were required to impart stability to organoplatinum complexes.

However, $Me_2Pt(bipy)$ has since been shown to be very reactive towards oxidative addition,[6] together with other imine and diimine complexes such as $Me_2Pt(py)_2$[7] and $Me_2Pt(phen)$.[8]

Oxidative addition of alkyl halides to diorganoplatinum(II) substrates containing diimine ligands generally produce trans addition products.[6a,7b,8]

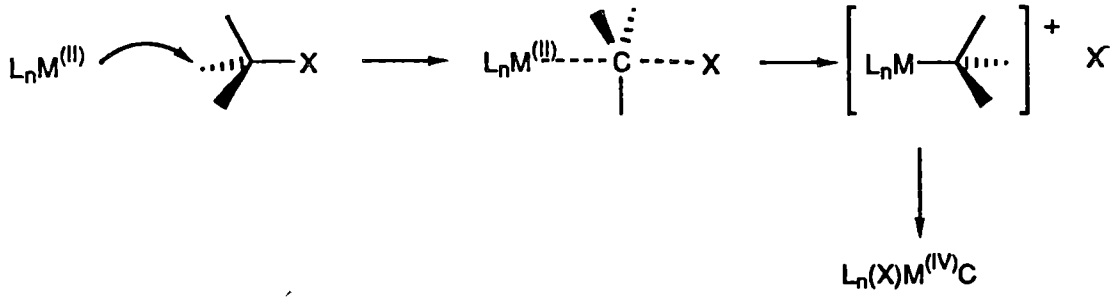
$$Me_2Pt(bipy) + RX \longrightarrow \underline{fac}\text{-}Me_2R(X)Pt(bipy) \quad (8)$$
(RX = MeI, EtI, allyl bromide, benzyl bromide

$$Me_2Pt(phen) + RX \longrightarrow \underline{fac}\text{-}Me_2R(X)Pt(phen) \quad (9)$$
(R = Me, Et, Pr^n, Bu^n; X = Br, I)

$$Me_2Pt(py)_2 + MeI \longrightarrow \underline{fac}\text{-}Me_3IPt(py)_2 \quad (10)$$

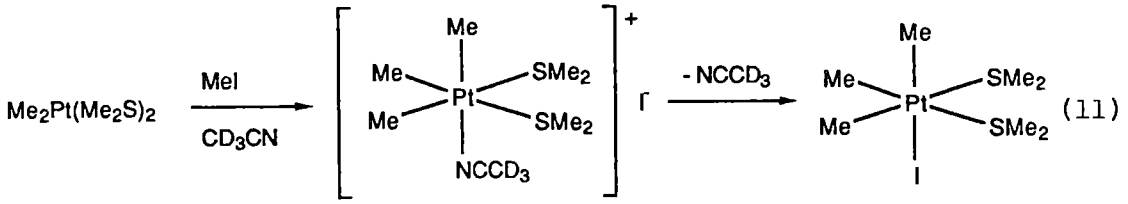
4.2.1 Mechanism of Oxidative Addition to Pt(II)

Two different mechanisms have been proposed for the reaction of organohalides with organoplatinum(II) substrates.[9] The more classical involves an S_N2 mechanism, in which the metal acts as the nucleophile displacing halide from the organohalide to form an intermediate cationic five coordinate complex, which then forms the final product (Scheme 4.1).



Scheme 4.1 S_N2 Mechanism for Oxidative Addition of RX to Pt(II)

A cationic intermediate has been observed during an NMR experiment of the reaction of $Me_2Pt(Me_2S)_2$ and MeI to form fac-$Me_3IPt(SMe_2)_2$.[10] If the reaction was carried out in CD_3CN, rather than the more commonly used solvent acetone, an intermediate assigned structure (A) (equation 11) was observed, and the intermediate disappeared as the final product formed.



(11)

A

The S_N2 mechanism for oxidative addition is supported principally by the following evidence:

(i) Reaction kinetics are overall second order.

(ii) The rate of oxidative addition increases in solvents of increasing polarity.

(iii) Classical RX reactivity patterns, Me > 1^O > 2^O > 3^O and I > Br > Cl >> F.

(iv) Inversion of configuration of chiral carbon.

The other established mechanism involves generation of free radicals, which can react by either a chain mechanism, or a non-chain mechanism involving paired or caged free radicals. The essential steps which produce the required product are shown in Scheme 4.2.

$$L_nM^{(II)} + R^{\cdot} \xrightarrow{RX} [L_nMR]^{\cdot} \xrightarrow{RX} L_nM^{(IV)}XR + R^{\cdot}$$

2A Free-Radical Chain Mechanism

$$L_nM^{(II)} + RX \longrightarrow [L_nM]^{+\cdot}[RX]^{-\cdot} \longrightarrow [L_nMX]^{\cdot} + R^{\cdot}$$

$$[L_nMX]^{\cdot} \longrightarrow L_nM^{(IV)}XR$$

2B Free-Radical Non-Chain Mechanism

Scheme 4.2 Free Radical Mechanisms for Oxidative Addition of RX to Pt(II).

The two free radical reaction paths result in different reaction kinetics. The radical non-chain mechanism follows second order kinetics (as for the S_N2 mechanism), while for the radical chain mechanism overall kinetics are difficult to predict due to the complex set of initiation, propagation and termination steps involved. Free-radical mechanisms are generally recognized by determining the effect that free-radical initiators and scavengers have on the course of the reaction, and the reaction of halides follows the order tertiary > secondary > primary. Also, the detection of radicals by ESR and radical trapping experiments provides evidence for radical intermediacy, but does not define whether radicals represent the main mechanism.

Little is known about the factors which influence whether an oxidative addition will proceed by the S_N2 mechanism or a free radical pathway, although these factors are becoming clearer.[11] For d^8 complexes in which ligand steric effects are low (eg. Me_2PtL where L = bipy, phen), primary alkyl halides oxidatively add via an S_N2 mechanism. The point at which free-radical mechanisms can compete with the S_N2 mechanism is realized when isopropyl iodide is used as the oxidizing reagent.[12] For example, $Me_2Pt(phen)$ reacts with primary halides and isopropyl bromide via an S_N2 mechanism, but with

isopropyliodide and tert-butyliodide the reaction occurs mainly by a free-radical mechanism.[12]

4.2.2 ^{1}H NMR Spectroscopy of Platinum(IV) Complexes

Methylplatinum(II) and IV complexes generally exhibit well resolved $^{2}J(^{1}H-^{195}Pt)$ couplings in their ^{1}H NMR spectra, with the magnitude of the coupling constant serving as a definitive tool in differentiating between the II and IV oxidation states. The magnitude of the coupling constant is reduced by approximately 20% on oxidation of methylplatinum(II) complexes,[13] eg. Figure 4.1 illustrates the MePt region for the related complexes $Me_2Pt^{(II)}$(bipy) and fac-$Me_3IPt^{(IV)}$(bipy).

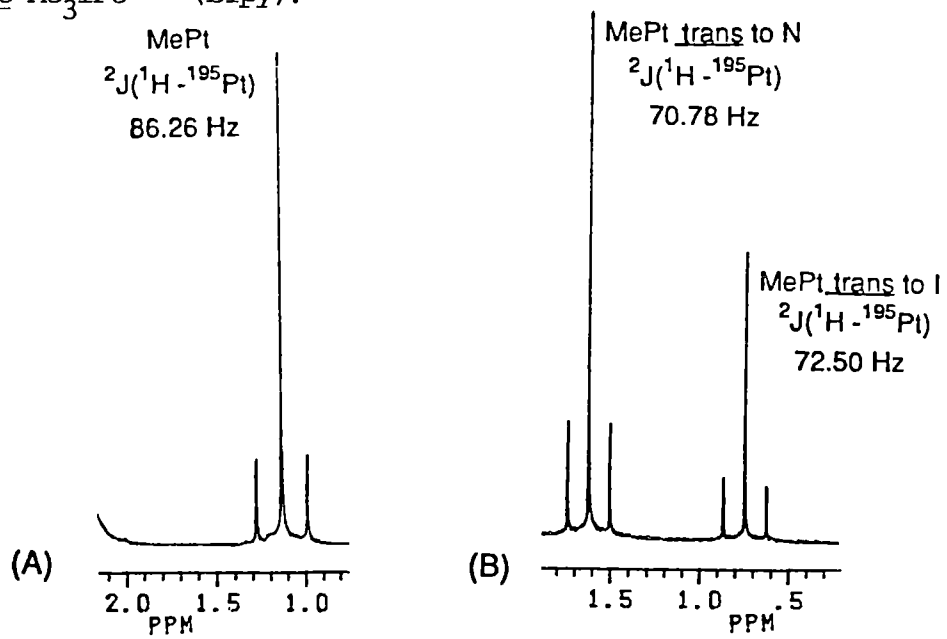


Figure 4.1 MePt Resonances for a) Me_2Pt(bipy) and b) Me_3IPt(bipy) in D6 Acetone.

Monomeric trimethylplatinum(IV) complexes derived from dimethylplatinum(II) substrates containing neutral bidentate nitrogen donor ligands may potentially have two configurations (A and B).

A B

Figure 4.2

Configuration A is the preferred isomer, as it has the methyl groups in positions which are not mutually trans to one another.

4.3 Oxidative Addition of Iodine to Me_2Pt(tridentate) Complexes

Dimethylplatinum(II) complexes of the tridentate ligands $HCpz_3$, $HC(py)pz_2$, $HC(mim)pz_2$ and $HC(thio)pz_2$ exhibit limited solubility in common organic solvents, and on addition of I_2 to acetone suspensions of these complexes black, difficult to characterize solids are obtained, and thus the method of oxidative addition of iodine to a stoichiometric mixture of soluble reagents $Me_2Pt(COD)$ and ligand, as developed by Clark et al.,[1] was adopted. This method was developed by Clark primarily because complexes such as $Me_2Pt(H_2Cpz_2)$ could not be obtained by reaction between $Me_2Pt(COD)$ and H_2Cpz_2 under reflux in chloroform.

Stoichiometric quantities of $Me_2Pt(COD)$ and tridentate ligand were stirred in acetone at ambient temperature, and iodine (in acetone) added dropwise until the iodine colour persisted. After removal of excess iodine by hexane extraction, and recrystallization from a suitable mixture of solvents, yellow to orange crystalline complexes of the above ligands were obtained.

The reaction most probably proceeds via reaction of ligand with an intermediate platinum(IV) complex of formulation $[Me_2PtI_2]_x$, since on addition of I_2 to $Me_2Pt(COD)$ in dichloromethane the solution is

immediately decolorized and an insoluble powder of composition $[Me_2PtI_2]_x$ is obtained in nearly quantitative yield.[14]

This reaction also proceeds if $[Me_2Pt(Et_2S)]_2$ is used in place of $Me_2Pt(COD)$ - most probably by the same mechanism involving a $[Me_2I_2Pt(Et_2S)]_2$ intermediate.

The complexes were characterized by elemental analysis, ^1H NMR spectroscopy, molecular weight (in chloroform) and conductivity (in acetone) measurements. All of the complexes were found to be non-conducting. Figure 4.3 shows the ^1H NMR spectrum for $Me_2I_2Pt(HCpz_3)$.

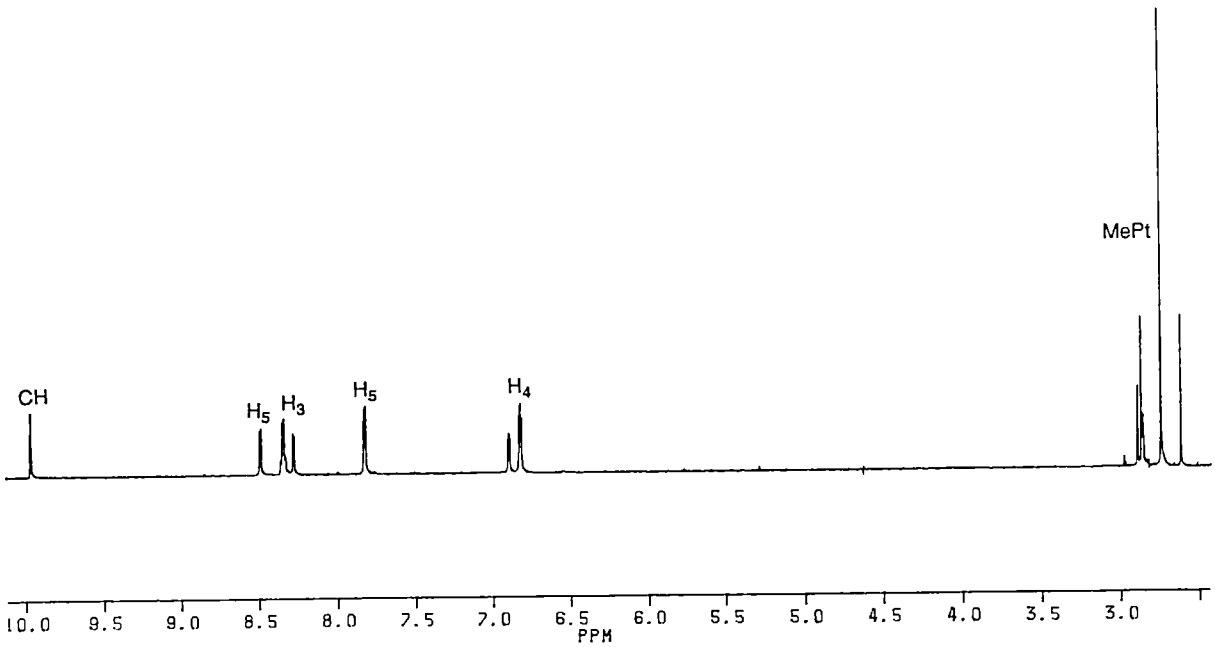


Figure 4.3 ^1H NMR spectrum of $Me_2I_2Pt(HCpz_3)$ in D6 Acetone.

The single methylplatinum resonance and pyrazolyl ring environments in the ratio 2:1 are consistent with the ligand acting as if in a bidentate mode with nitrogen *trans* to methyl, and *trans* iodo groups. Close examination of the aromatic region (figure 4.3B) provides evidence consistent with the orientation of the uncoordinated pyrazolyl ring in an equatorial position, as shown in figure 4.4.

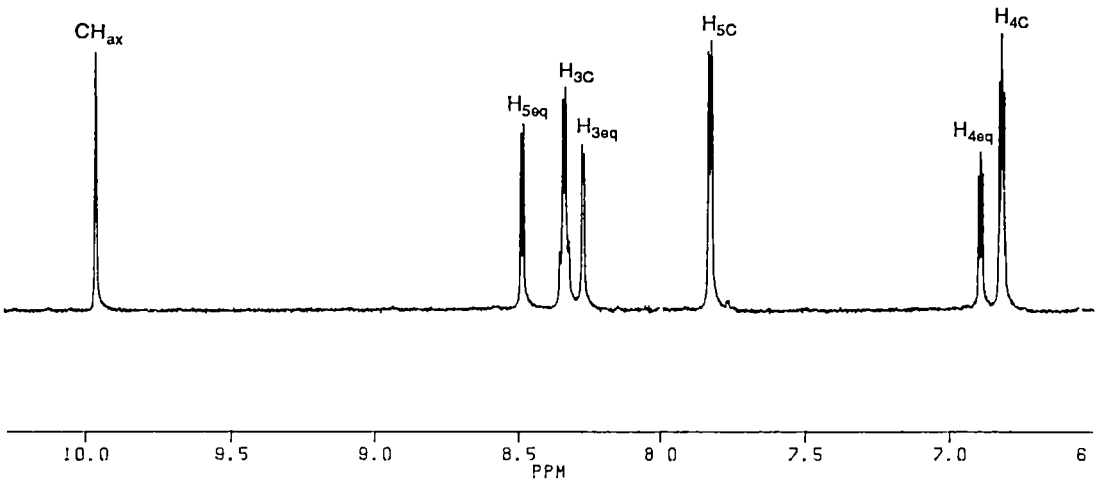


Figure 4.3B Aromatic Region of $Me_2I_2Pt(HCpz_3)$.

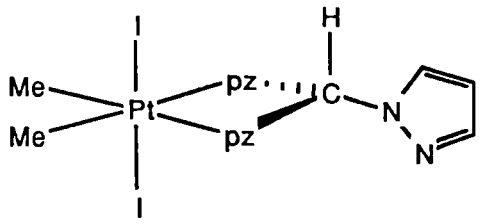


Figure 4.4

Uncoordinated H3 and H5 pyrazolyl ring resonances occur with the H5 proton furthest downfield. Compared with the free ligand these protons are deshielded, eg. H3 (7.77_{free}, 8.35_{unco}) H5 (8.00_{free}, 8.55_{unco}), but for the coordinated pyrazolyl rings the H5 protons show a pronounced upfield shift compared with the free ligand, eg. H5 (8.00_{free}, 7.75_{coord}). This upfield shift results from anisotropic shielding by the equatorial pyrazolyl group, since it is expected to be approximately perpendicular to the planes of the coordinated rings.

In contrast, reaction of $[Me_3PtI]_4$ with $HCpz_3$ gives a cationic complex with $HCpz_3$ acting as a tripodal tridentate ligand.[15]

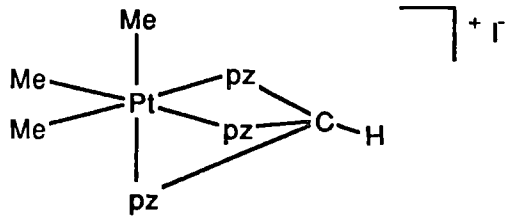


Figure 4.5

X-ray crystallographic studies of the complexes $Me_2I_2Pt(H_2Cpz_2)$[1] and $Me_3IPt(H_2C(3,5Mepz)_2)$[15] reveal Pt-I bond lengths of 2.65 Å (trans to I) and 2.84 Å (trans to Me), respectively, and thus iodide trans to another iodide is more strongly bound than iodide trans to a methyl group. Thus, the reason for the difference in product formation between $Me_2Pt(COD)/I_2/HCpz_3$ and $[Me_3PtI]_4/HCpz_3$, may at least partly result from the strong trans effect of the methyl group.

On heating solid $Me_2I_2Pt(HCpz_3)$ to ~140°C the orange-brown crystals suddenly change to bright yellow, which on further heating decompose above ~230°C. A ^1H NMR spectrum of these yellow crystals is shown below.

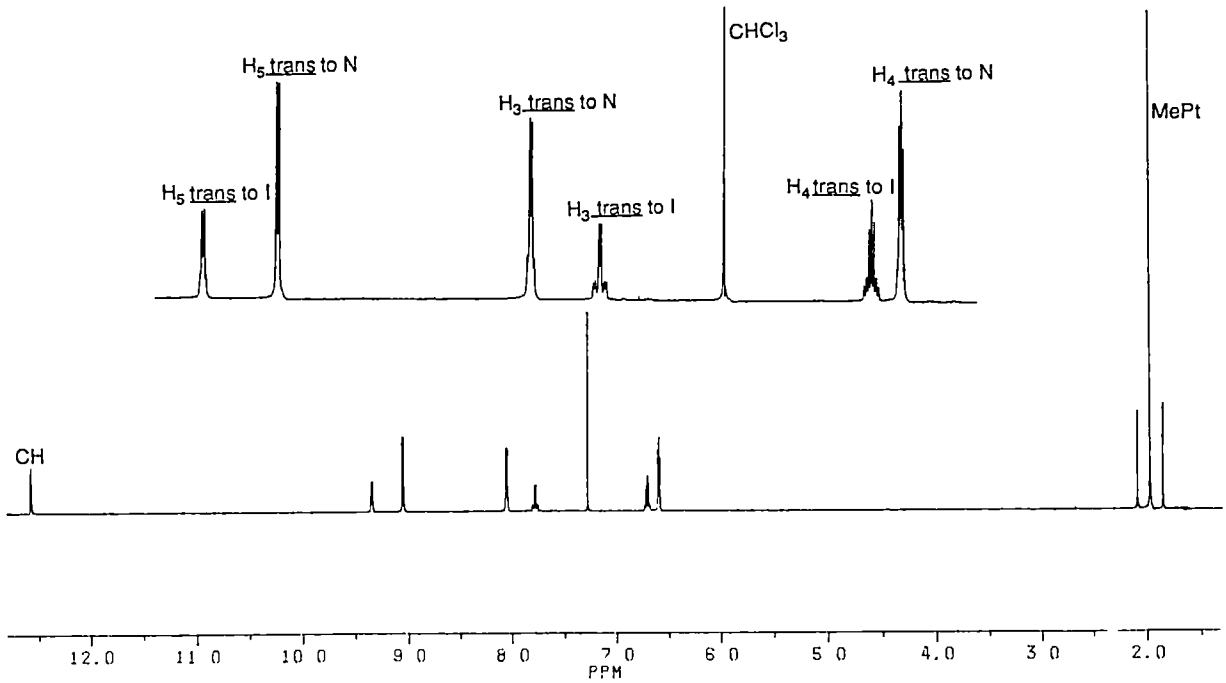


Figure 4.6 $Me_2I_2Pt(HCpz_3)$ heated to ~140°C.

The spectrum is considerably different than that of $Me_2I_2Pt(HCpz_3)$ (Figure 4.3). The methylplatinum(IV) resonance is moved significantly upfield (1.97 ppm, (by 0.7) $^2J(^1H-^{195}Pt)$ 70.38 Hz), the apical C-H proton is moved downfield (12.5 ppm, by 2.5 ppm), and the H3 and H4 proton resonances of the unique pyrazolyl ring are flanked by platinum satellites, which is indicative of coordination, although coupling is often not seen in spectra. These changes suggest that an isomerization has occurred in which a cationic complex is formed with $HCpz_3$ acting as a tripodal tridentate ligand.

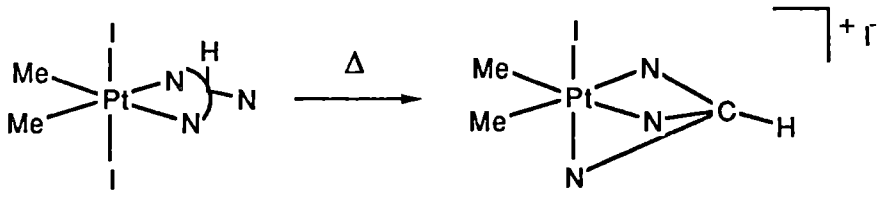


Figure 4.7

The large downfield shift of the apical C-H proton has been found to be indicative of $HCpz_3$ in a tripodal tridentate geometry.[16]

A high temperature study was undertaken to see if this isomerization occurs in solution. Thus, $Me_2I_2Pt(HCpz_3)$ was dissolved in $CDCl_3$ and the resultant spectra recorded at room temperature and successive temperatures up to 55°C (Figure 4.8).

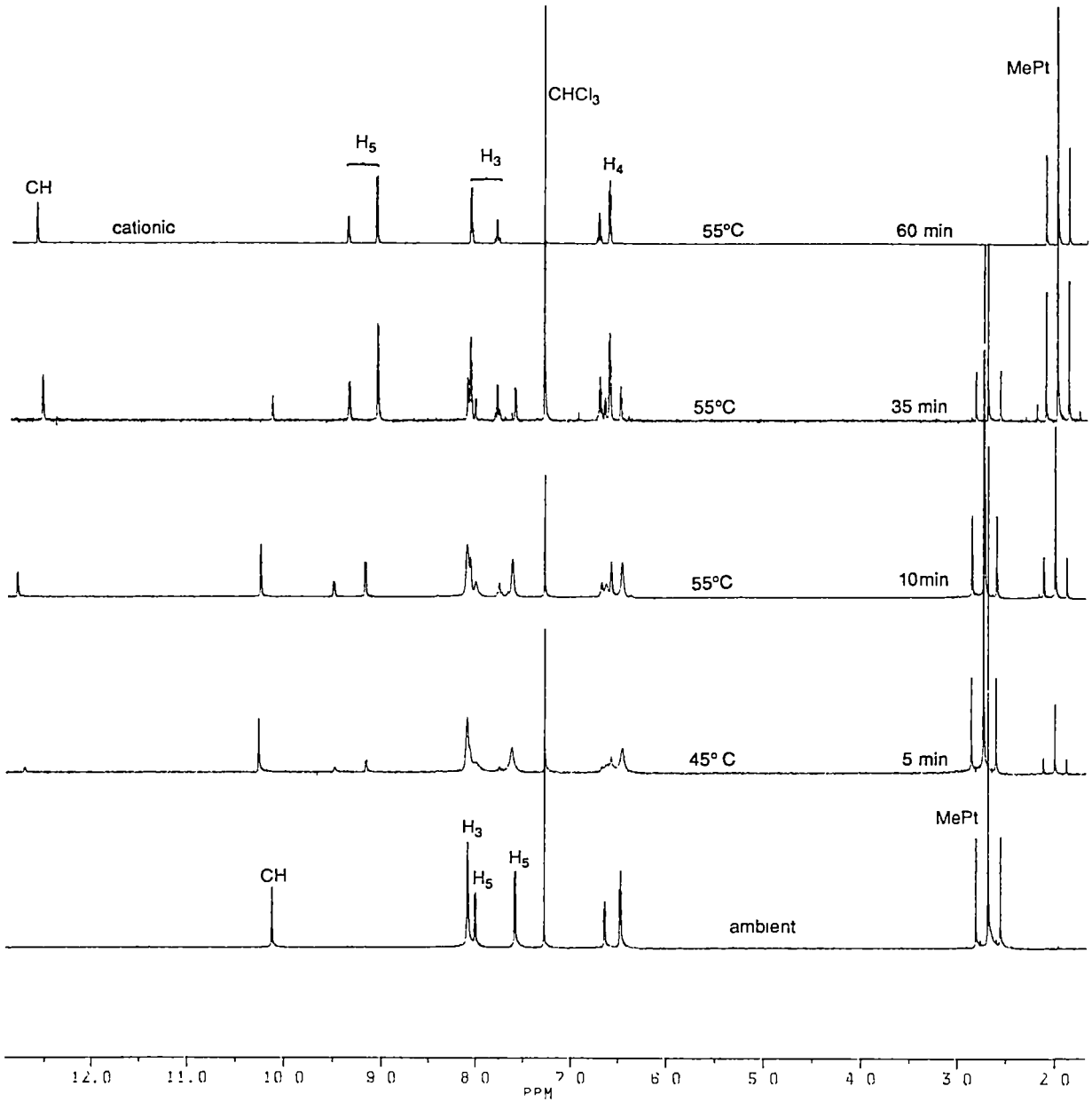


Figure 4.8 High Temperature Study of $Me_2I_2Pt(HCpz_3)$ in $CDCl_3$.

At 45^{o}C a new low intensity MePt resonance is observed at 1.97 ppm ($^{2}J(^{1}H-^{195}Pt)$ 70.38 Hz), and an apical C-H resonance at 12.5 ppm. The resonances due to the unique pyrazolyl ring are broadened considerably and coupling is no longer observed for resonances of the coordinated pyrazolyl rings. At 55^{o}C considerable conversion has occurred, and resonances due to both neutral and cationic complexes are clearly discernible. If the solution is heated strongly for 45 -

60 minutes then only resonances due to the cationic complex are observed. On standing and cooling, a NMR spectrum shows that the cationic complex persists, and it is clearly the favoured isomer thermodynamically. Conductivity measurements were not possible as this complex does not exhibit sufficient solubility in acetone. Isomerization was not observed in acetone.

Both $Me_2I_2Pt(HC(mim)pz_2)$ and $Me_2I_2Pt(HC(py)pz_2)$ exhibit similar NMR behaviour and only $Me_2I_2Pt(HC(mim)pz_2)$ will be discussed in detail. The ^1H NMR behaviour of $Me_2I_2Pt(HC(mim)pz_2)$ is different in different solvents. The spectrum in acetone is shown below.

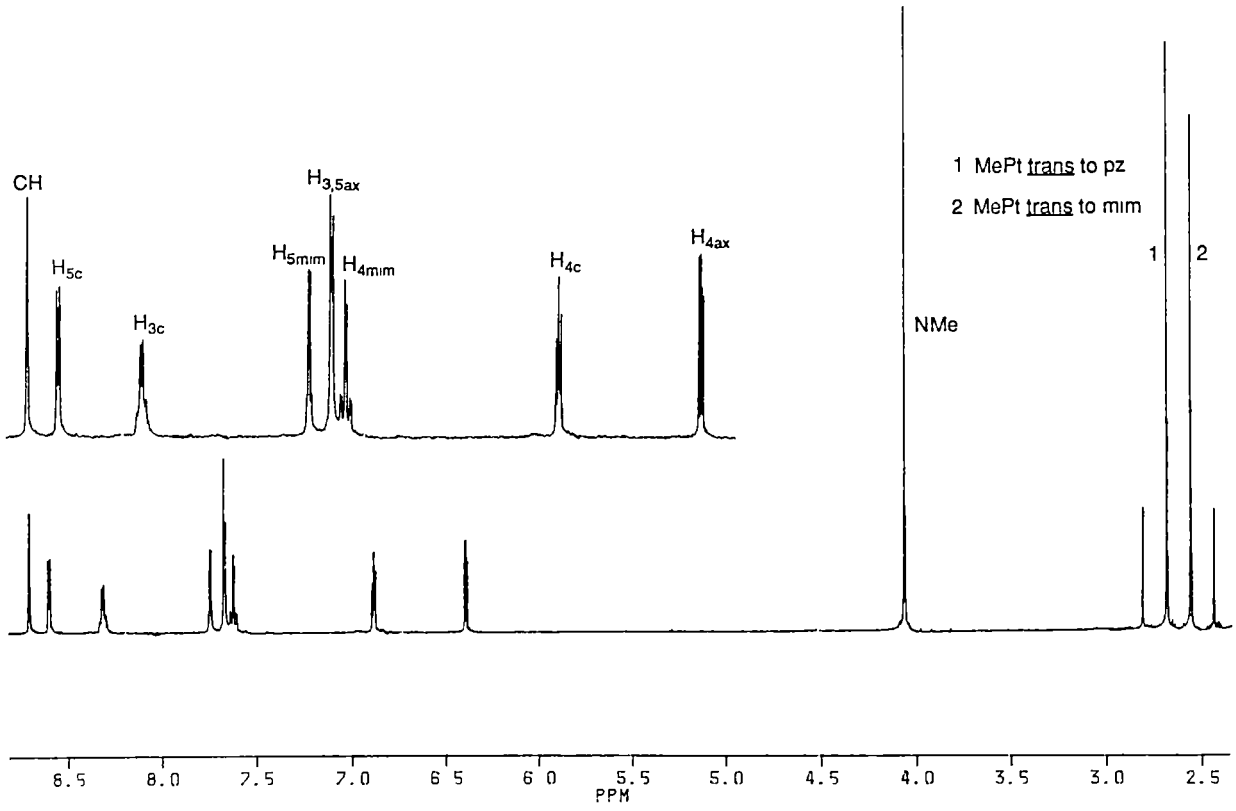


Figure 4.9 ^1H NMR spectrum of $Me_2I_2Pt(HC(mim)pz_2)$ in D6 Acetone.

The two methylplatinum resonances are indicative of methyl trans to a pyrazolyl group (2.68 ppm, $^2J(^1H-^{195}Pt)$ 76.05 Hz) and trans to a N-methylimidazolyl group (2.55 ppm, $^2J(^1H-^{195}Pt)$ 73.40 Hz). This structural assignment (figure 4.10) is also consistent with occurrence of resonances in the 1:1 ratio, for coordinated and uncoordinated pyrazolyl rings, and the H4 resonance of the

coordinated imidazolyl is clearly evident (inset) with well defined platinum satellites ($^{2}J(^{1}H-^{195}Pt)$ 9.44 Hz).

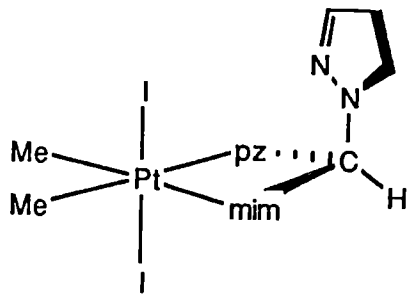


Figure 4.10

Variable temperature NMR experiments do not indicate a neutral -> cationic isomerization in the temperature range 25 - 60°C.

The ^{1}H NMR spectrum of this complex in $CDCl_3$ (figure 4.11) is quite different from that in $(CD_3)_2CO$ (figure 4.9), but may still be interpreted in terms of a neutral complex.

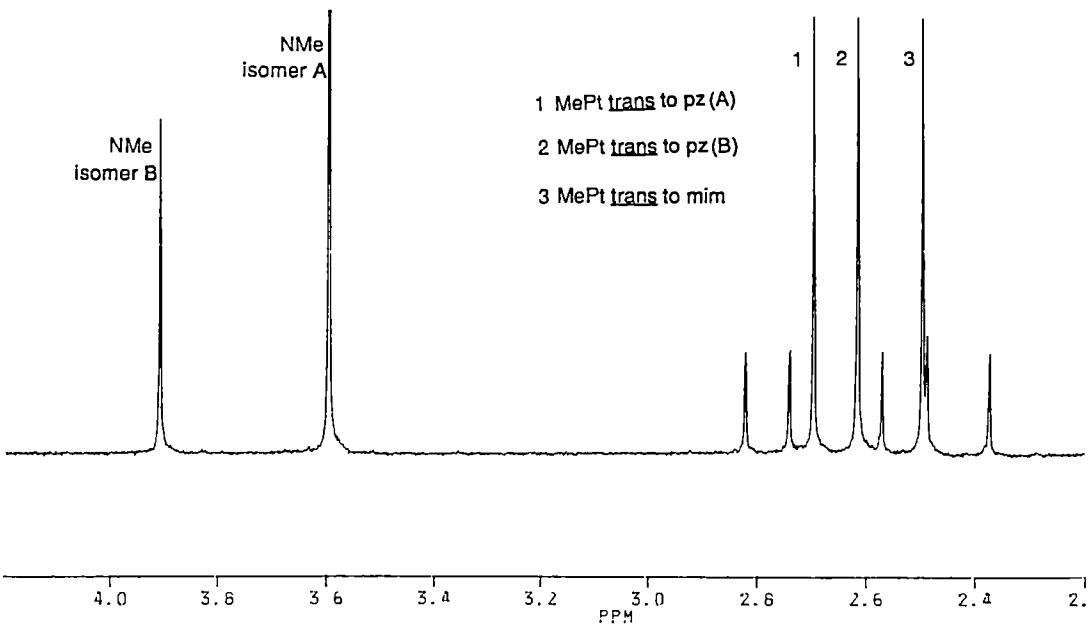


Figure 4.11 A ^{1}H NMR Spectrum of $Me_2I_2Pt(HC(mim)pz_2)$ in $CDCl_3$ - Aliphatic Region

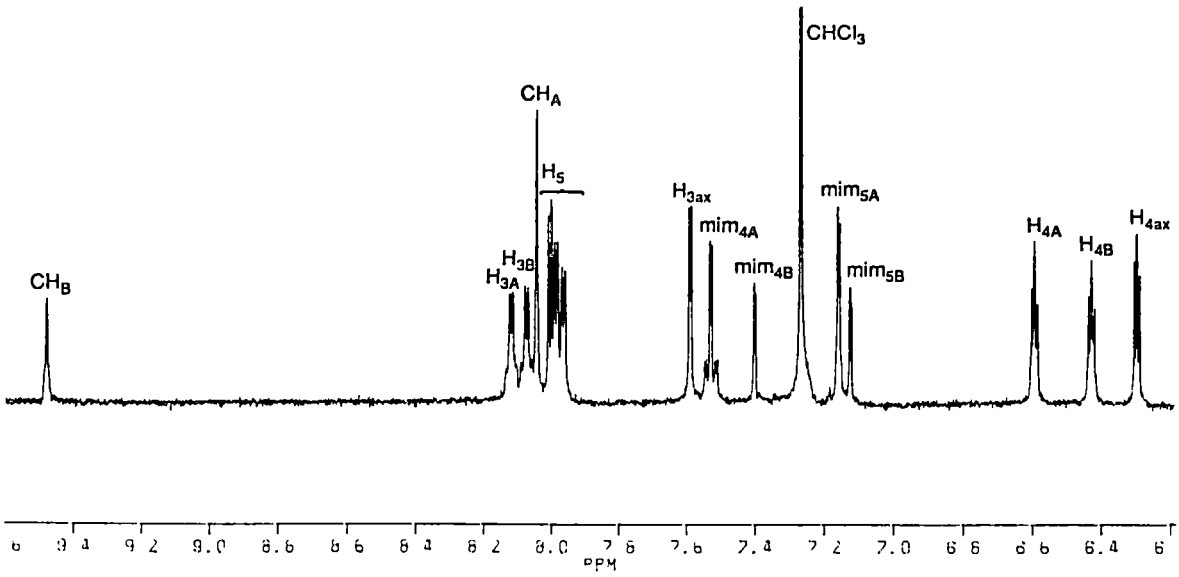
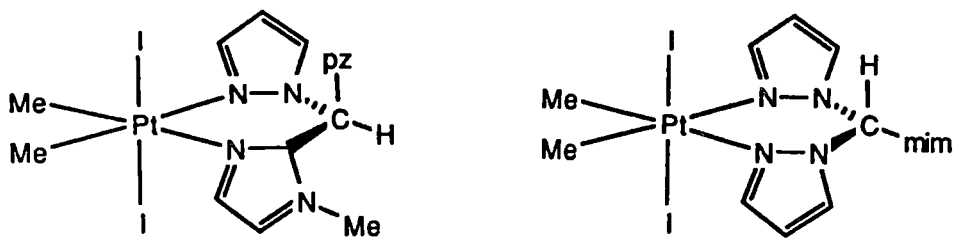


Figure 4.11 B ^{1}H NMR Spectrum of $Me_2I_2Pt(HC(mim)pz_2)$ in $CDCl_3$- Aromatic Region

The spectrum exhibits three methylplatinum(IV) resonances in the ratio 1:1:1, three pyrazolyl resonances in the ratio 1:1:1, two imidazolyl resonances in ratio 2:1, and two resonances in ratio 2:1 for the apical C-H proton. This evidence suggests a mixture of two isomers in the approximate ratio 2:1 (figure 4.12), with isomer A predominant.



A 2 : 1 B

Figure 4.12

Isomer A is shown with the uncoordinated pyrazolyl group in the axial position as molecular models show that steric crowding will not allow it in an equatorial position adjacent to the N-methyl of the imidazolyl group. In this position the H5 pyrazolyl proton of this group is expected to be shielded by one of the coordinated rings and

moved upfield, accounting for the equatorial proton resonance at 8.07 ppm.

Isomer B has a different configuration for the imidazolyl group, since the methine CH occurs 1.4 ppm downfield of isomer A, consistent with the methine proton oriented adjacent to the iodo group. The H5 pyrazolyl ring protons of isomer B are upfield from those of isomer A, consistent with shielding by an equatorial imidazolyl.

If a solid sample of $Me_2I_2Pt(HC(mim)pz_2)$ is heated to 180°C its colour suddenly changes from a deep yellow to very light yellow, and a ^1H NMR spectrum (figure 4.13) of the light yellow product in $CDCl_3$ is different from the initial deep yellow complex.

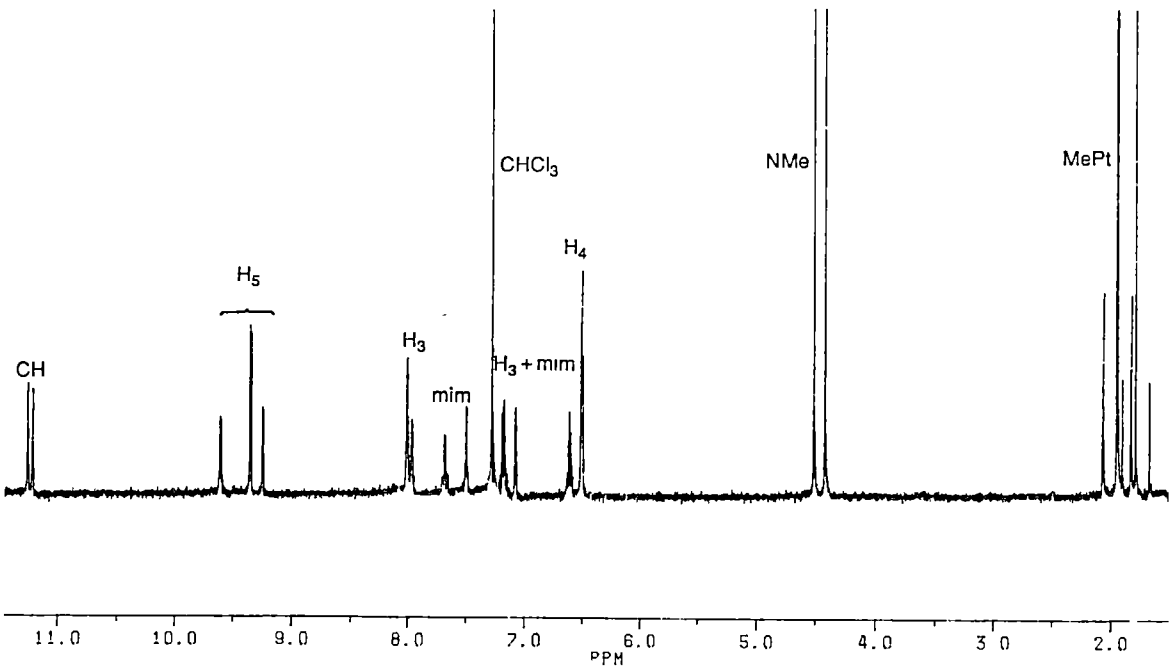


Figure 4.13 ^1H NMR Spectrum $Me_2I_2Pt(HC(mim)pz_2)$ heated to 180°C

The large downfield shift of the apical C-H protons compared with those in the parent complex are indicative of formation of a cationic complex with the ligand in a tripodal tridentate geometry. Two isomers are present in the ratio ca 1:1, as the spectrum displays 2 N-methylimidazolyl methyl resonances and 2 apical C-H resonances in a 1:1 ratio. The methylplatinum resonances (figure 4.13 B) in the

ratio 1:2:1 (1.93 ppm, $^{2}J(^{1}H-^{195}Pt)$ 70.77 Hz; 1.94 ppm, $^{2}J(^{1}H-^{195}Pt)$ 71.24 Hz; 1.78 ppm, $^{2}J(^{1}H-^{195}Pt)$ 68.34 Hz) are consistent with the structures A and B.

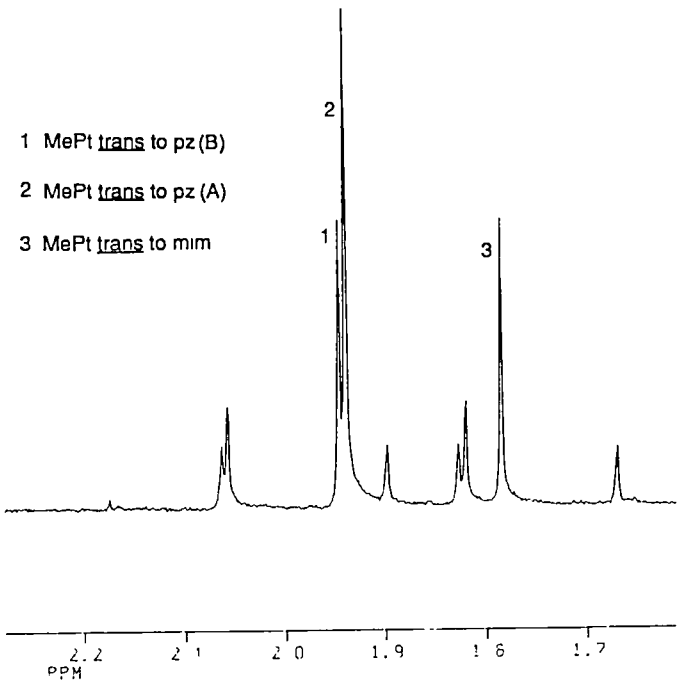


Figure 4.13 B MePt Region of $[Me_2IPt(HC(mim)pz_2)]I$ in D6 Acetone.

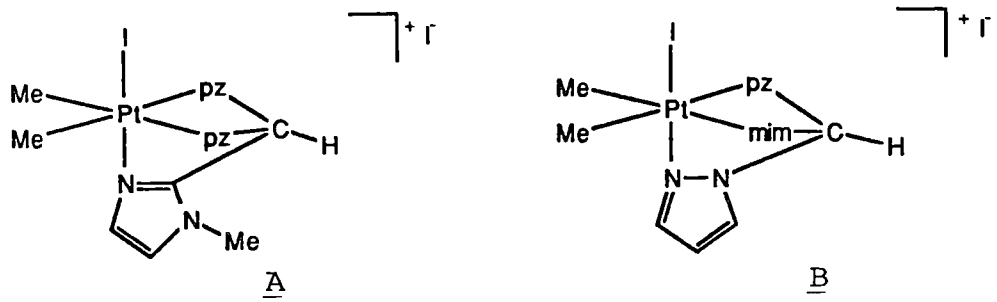


Figure 4.14

Thus, the methylplatinum signal at 1.93 ppm is assigned to the methyl groups trans to pyrazolyl rings in isomer A, the methylplatinum signal at 1.94 ppm represents the methyl group trans to the pyrazolyl ring in isomer B, and the methylplatinum resonance at 1.78 ppm is the methyl trans to the imidazolyl group. Resonances for the ligand ring protons exhibit the expected relative intensities.

High temperature NMR experiments for neutral $Me_2I_2Pt(HC(mim)pz_2)$ up to 60^oC in both acetone and $CDCl_3$ failed to detect any neutral-cationic isomerization, in contrast to the closely related complex $Me_2I_2Pt(HCpz_3)$. As for $Me_2I_2Pt(HCpz_3)$, once $Me_2I_2Pt(HC(mim)pz_2)$ had been rendered cationic it did not revert back to the neutral species in solution.

For the neutral complex $Me_2I_2Pt(HC(py)Cpz_2)$ the isomer ratio was also approximately 2:1, with bound pyridine predominating, based on integration of the characteristic bound and unbound pyridine H6 resonances and the two distinct apical C-H resonances. The remainder of the aromatic region is complex and a definitive assignment was not attempted. The MePt region (figure 4.15) shows three resonances with the downfield resonances (2.76 ppm, $^2J(^1H-^{195}Pt)$ 74.33 Hz (isomer A) and 2.71 ppm, $^2J(^1H-^{195}Pt)$ 75.06 Hz (isomer B)) being assigned to Me trans to pyrazolyl and the furthest upfield resonance (2.58 ppm, $^2J(^1H-^{195}Pt)$ 72.90 Hz) as Me trans to pyridine. The two isomers are shown in figure 4.16.

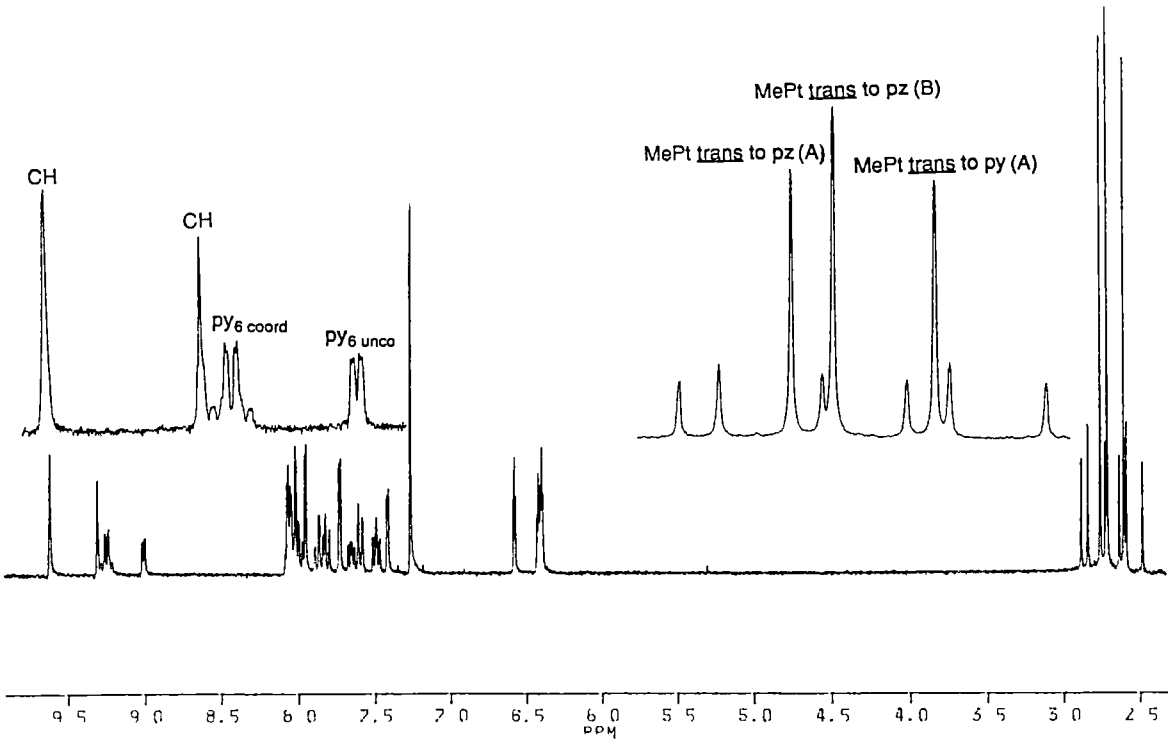
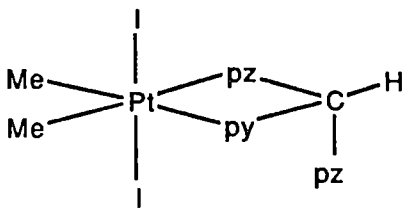
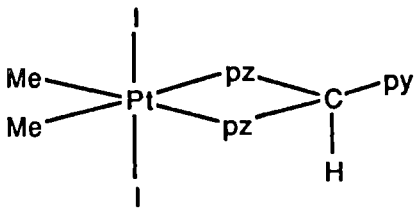


Figure 4.15 ^1H NMR Spectrum of $Me_2I_2Pt(HC(py)pz_2)$ in $CDCl_3$.



Isomer A



Isomer B

Figure 4.16

On heating (190^{o}C) similar conversion to a cationic species was observed as already described.

The ^{1}H NMR spectrum of $Me_2I_2Pt(HC(thio)pz_2)$ exhibits resonances (see experimental) consistent with the structure shown in figure 4.17.

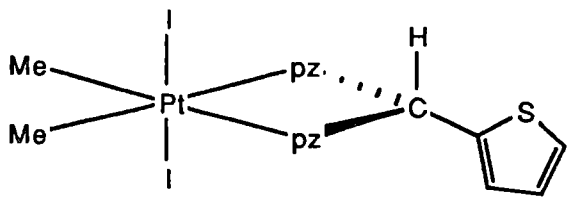


Figure 4.17

The pyrazolyl ring H3 resonances are shifted downfield from the free ligand (~ 0.5 ppm), while the H5 resonances are essentially unaffected. Any downfield shift of these protons is negated by shielding from the thienyl ring. On heating, both in solution and the solid state, no tendency to cationic formation is observed, perhaps owing to the weak donor ability of the thienyl ring.

The reaction of $[Ph_2Pt(Et_2S)]_2$ with I_2 in the presence of $HCpz_3$ yielded an orange-yellow complex, for which a ^{1}H NMR spectrum displayed pyrazolyl resonances in the ratio 2:1 with the apical proton well downfield (11.70 ppm). An acetone solution of this complex was conducting ($\Lambda = 87\ \Omega^{-1}\ cm^{2}\ mole^{-1}$) and thus the complex is ionic with the unique pyrazolyl ring coordinated and trans to I. This is in contrast to the $Me_2Pt(II)$ analogue which forms the neutral

species and requires strong heating to convert to the cationic complex.

If MeI is used in place of iodine in these in situ reactions, cationic $Me_3Pt(IV)$ complexes are formed for the tridentate ligands $HCpz_3$, $MeCpz_3$ and $HC(mim)pz_2$, in which the ligand acts as a N_3 donor, eg. $[Me_3Pt(HCpz_3)]I$.

^1H NMR results for these tridentate complexes (Table 4-1) show resonances appropriate for a single MePt(IV) and single equivalent ligand resonances, and in the case of $HCpz_3$ and $HC(mim)pz_2$ apical resonances consistent with an ionic complex formation, eg. $[Me_3Pt(RCpz_3)]I$, where R = H, Me.

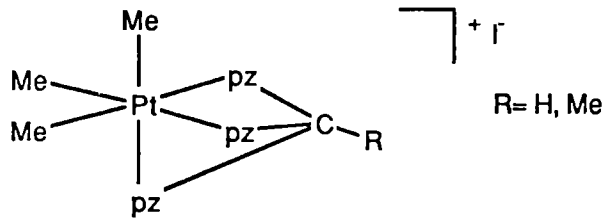


Figure 4.18

As $HCpz_3$ is known to not react with $[Me_2Pt(Et_2S)]_2$ in acetone at ambient temperature, these reactions are consistent with initial oxidative addition of MeI to $[Me_2Pt(Et_2S)]_2$, to form $[Me_3IPt(Et_2S)]_2$ or a monomer, followed by rapid ligand replacement to form $Me_3IPt(L)$ species.

Other alkyl halides can be used in place of MeI. For example, propargyl bromide reacts readily with $[Me_2Pt(Et_2S)]_2$ in the presence of $HCpz_3$ to form the complex $[Me_2(prop)Pt(HCpz_3)]Br$ ($\Lambda = 70\Omega^{-1}$ cm^2 $mole^{-1}$). The ^1H NMR spectrum of this complex (figure 4.19) shows the presence of both allenyl and alkynyl groups in the ratio 2:1 respectively. This ratio does not change, even on prolonged (1 hour) reflux in acetone or chloroform. Collman et al.[20] have reported the reaction of α-haloacetylenes with Ir(I) and Pt(0) complexes to yield products in which the acetylene group has rearranged to an allene.

Table 4-1

$Me_3Pt(IV)$ Complexes Formed by "In Situ" Reactions of $Me_2Pt(II)$, MeI and Tridentate Ligand

Complex	MePt ppm (^2J)	Pyrazolyl ppm (^2J) H_3	H_4	H_5	Other ppm	Λ Ω^{-1} cm^2 mole^{-1}
$[Me_3Pt(HCpz_3)]I$	1.14 (72.24)	7.72 (2.34)	6.55	9.08 (2.76)	apical 12.23	83
$[Me_3Pt(MeCpz_3)]I$	1.26 (72.07)	8.35 (2.30)	6.92	9.04 (3.02)	Methyl 4.04	78
$[Me_3Pt(HC(mim)pz_2)]I$						
<u>trans</u> to mim	1.12 (70.22)	9.44 (2.24)	6.78	8.16 (2.42)	apical 10.88	82
<u>trans</u> to pz	1.29 (73.29)				mim 7.58 7.64	

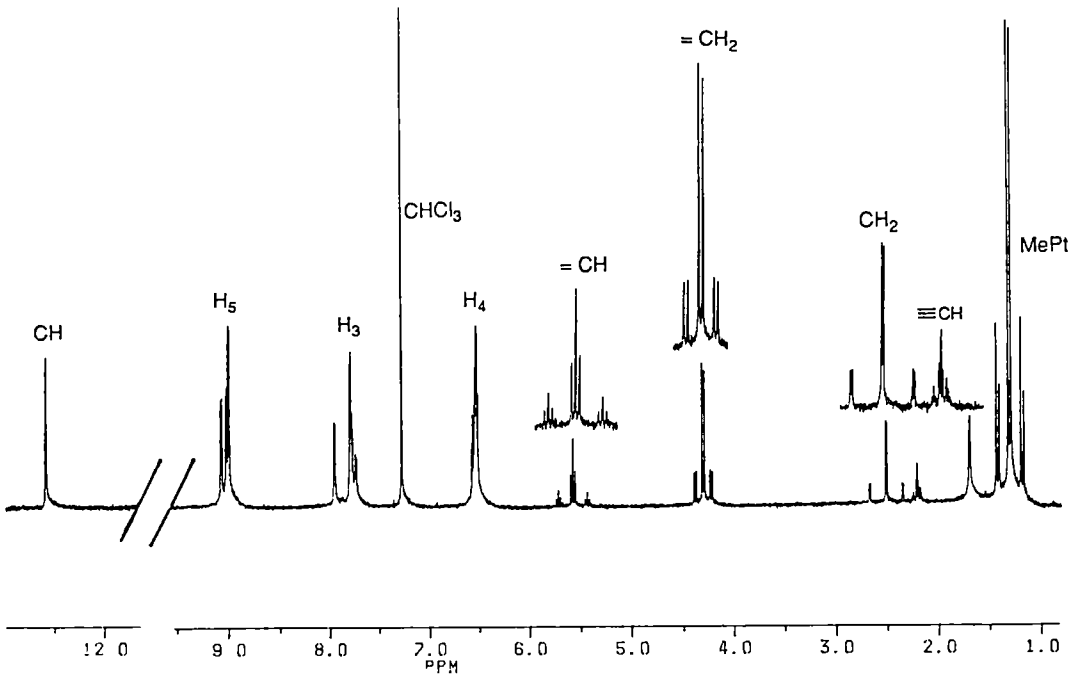


Figure 4.19 ^1H NMR Spectrum of Product from "In Situ" reaction of $[Me_2Pt(Et_2S)]_2$, $HCpz_3$ + Propargyl Bromide.

4.3.1 Reaction of Neutral and Cationic "Me_2I_2PtL" Complexes with Pyridine

If deuterated pyridine is added to an acetone solution of $Me_2I_2Pt(HCpz_3)$, resonances due to the free ligand are observed and the methylplatinum resonance is consistent with retention of the $Me_2I_2Pt(IV)$ unit. A pyridine complex of formulation $Me_2I_2Pt(py)_2$ is assumed to form by displacement of $HCpz_3$. Indeed, if $Me_2I_2Pt(HCpz_3)$ is dissolved in pyridine, taken to dryness and recrystallized from acetone, a bright orange complex is obtained. An infrared spectrum shows absorption at 1601 cm^{-1} (coordinated pyridine) and the ^1H NMR spectrum (figure 4.20) is consistent with the formulation cis-$Me_2I_2Pt(py)_2$.

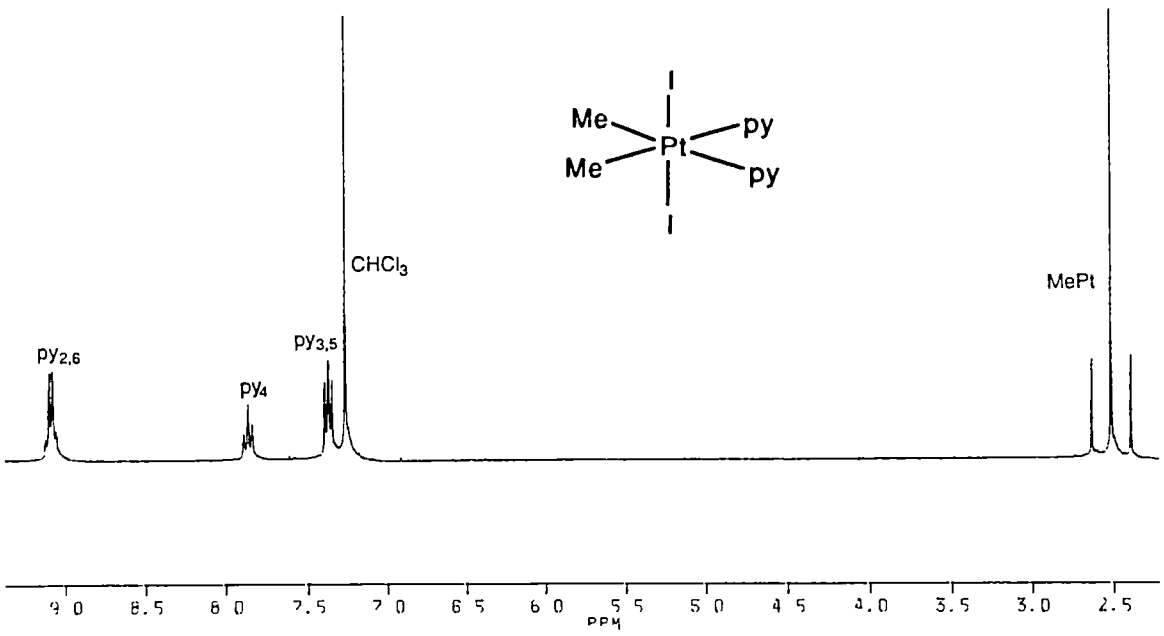


Figure 4.20 ^1H NMR Spectrum of $Me_2I_2Pt(py)_2$ from $Me_2I_2Pt(HCpz_3)$ + pyridine

The other complexes, Me_2I_2PtL (L = $HC(mim)pz_2$, $HC(py)pz_2$, $HC(thio)pz_2$), also react with pyridine to yield $Me_2I_2Pt(py)_2$. However, in the case of the cationic complexes, $[Me_2IPtL]I$ (L = $HC(mim)pz_2$, $HC(py)pz_2$, $HCpz_3$), where the ligands are present as tridentates, pyridine fails to displace the ligand even on heating to 60^oC.

Summary

The reaction of tridentate N donor ligands with $Me_2Pt(II)$, either $Me_2Pt(COD)$ or $[Me_2Pt(Et_2S)]_2$, in the presence of I_2, gives monomeric six coordinate $Me_2I_2Pt(N\sim N)$ complexes with the ligand acting in a bidentate mode. This can be rationalized in terms of I_2 reacting with the $Me_2Pt(II)$ unit to form a transient $Me_2I_2Pt(IV)$ species, which reacts with the chelating ligand present.

The preferred orientation of the uncoordinated donor group is equatorial, but in the case of $Me_2I_2Pt(HC(mim)pz_2)$, the uncoordinated pyrazolyl ring is axial due to the steric effect of the N-methyl group of the coordinated imidazolyl ring.

A single species appears to be present in a solution of $Me_2I_2Pt(HCpz_3)$, and if exchange is occurring it is too rapid to be seen on the NMR time scale. A single isomer is preferred for $Me_2I_2Pt(HC(thio)pz_2)$, presumably because the thienyl ring is too weak a donor to compete with the pyrazolyl rings for coordination. The ^1H NMR spectrum of $Me_2I_2Pt(HC(mim)pz_2)$ is solvent dependent, with a single species in acetone D6 (mim coordinated) but a mixture of two isomers in the ratio 2:1 in $CDCl_3$ solution. The preferred isomer is the chelating pz-mim bidentate with the uncoordinated pyrazolyl ring axial, and the minor isomer involves the pz-pz bidentate with the uncoordinated imidazolyl ring in an equatorial position. $Me_2I_2Pt(HC(py)pz_2)$ also yields a mixture of isomers, approx. 2:1, but in both isomers the uncoordinated group (pyrazolyl or pyridine) is in an equatorial position.

Heating solid $Me_2I_2Pt(N_2\text{-tridentate})$ complexes results in displacement of an iodo ligand by the free donor ring and formation of a cationic complex with the ligand acting as a chelating tripodal N_3 tridentate. To our knowledge replacement of iodo ligands by a neutral donor ring is unknown. This reaction is general to all tridentate N donor ligands, it is rapid, clean (no reduction) and quantitative. Solution studies showed that, at least in the case of $Me_2I_2Pt(HCpz_3)$, isomerization occurred and could be followed by ^1H

NMR. Presumably the other isomerizations could not be achieved in solution as a high enough temperature could not be attained in the solvents used.

Pyridine reacts with the neutral complexes Me_2I_2PtL (L = $HCpz_3$, $HC(mim)pz_2$, $HC(py)pz_2$, $HC(thio)pz_2$) to displace L and form the bis pyridine complex $Me_2I_2Pt(py)_2$. With the tridentate cations $[Me_2IPtL]^+$ (L = $HCpz_3$, $HC(mim)pz_2$, $HC(py)pz_2$) pyridine fails to displace the ligand.

The general reaction sequence, of simultaneously reacting a dimethylplatinum(II) precursor, ligand and iodine, is also successful if an alkyl halide, eg. MeI, is used in place of iodine. In this case a $Me_3Pt(IV)$ cationic complex, with ligand present as a tridentate, is isolated from the reaction mixture. More complex halides other than MeI, eg. propargyl bromide and benzyl bromide, undergo a similar reaction.

This synthetic strategy allows $Me_3Pt(IV)$ complexes to be made starting from $Me_2Pt(II)$ precursors which are easy to prepare and which can be made in high yield, it negates the need to make $[Me_3IPt]_4$, and avoids the formation of cyclometallated ligands (see Section 4.4)

4.4 Reaction of Organohalides with $Me_2Pt(HCpz_3)$ and Related Compounds

4.4.1 $Me_2Pt(HCpz_3)$

If $Me_2Pt(HCpz_3)$ is suspended in acetone in a stoppered flask with a five fold excess of MeI, and allowed to stand for 4-6 hours in the dark, $Me_2Pt(HCpz_3)$ 'dissolves' and a yellow solution results. Upon removal of excess MeI (rotary evaporation) and addition of hexane, a white solid precipitates. This solid is readily soluble in common organic solvents, and after filtration and vacuum drying, gives the ^1H NMR spectrum shown in figure 4.21.

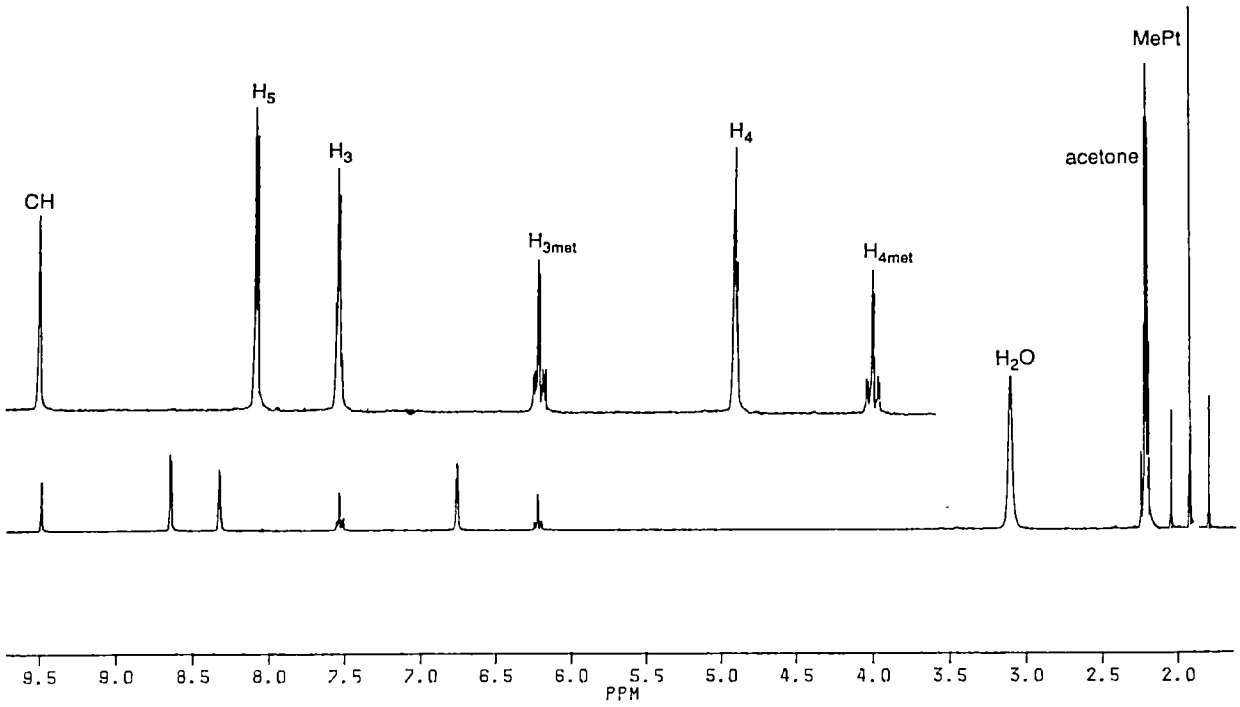


Figure 4.21 ^{1}H NMR Spectrum of $Me_2IPt(HCpz_2(C_3N_2H_2)-C,N)$.

The MePt resonance at 1.87 ppm ($^{2}J(^{1}H-^{195}Pt)$ 74.10 Hz) demonstrates that the complex is in oxidation state IV, but the signal only integrates for two methyl groups, not three as expected for oxidative addition of MeI. The aromatic portion of the spectrum integrates for 9 protons, not the expected 10. Resonances at 6.18 ppm and 7.54 ppm show well defined $^{1}H-^{195}Pt$ couplings, and, from the COSY spectrum, these protons belong to the same pyrazolyl ring but neither exhibit connectivity to a H5 pyrazolyl proton. Thus, the spectrum is consistent with metallation at C5, exhibiting $H4_{met}$ $^{3}J(^{1}H-^{195}Pt)$ 14.02 Hz and $H3_{met}$ $^{4}J(^{1}H-^{195}Pt)$ 10.80 Hz, similar to $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, and the single methylplatinum(IV) environment is consistent with the fac-C_3Pt geometry as expected for platinum(IV).

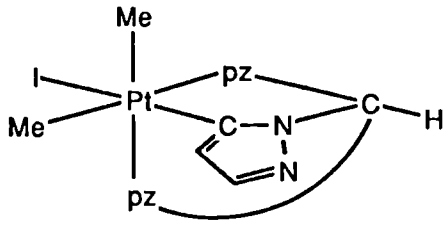


Figure 4.22

This assignment is supported by a ^{13}C NMR spectrum, which exhibits platinum-carbon satellites for the 3 and 4 carbon atoms of the metallated pyrazolyl ring.

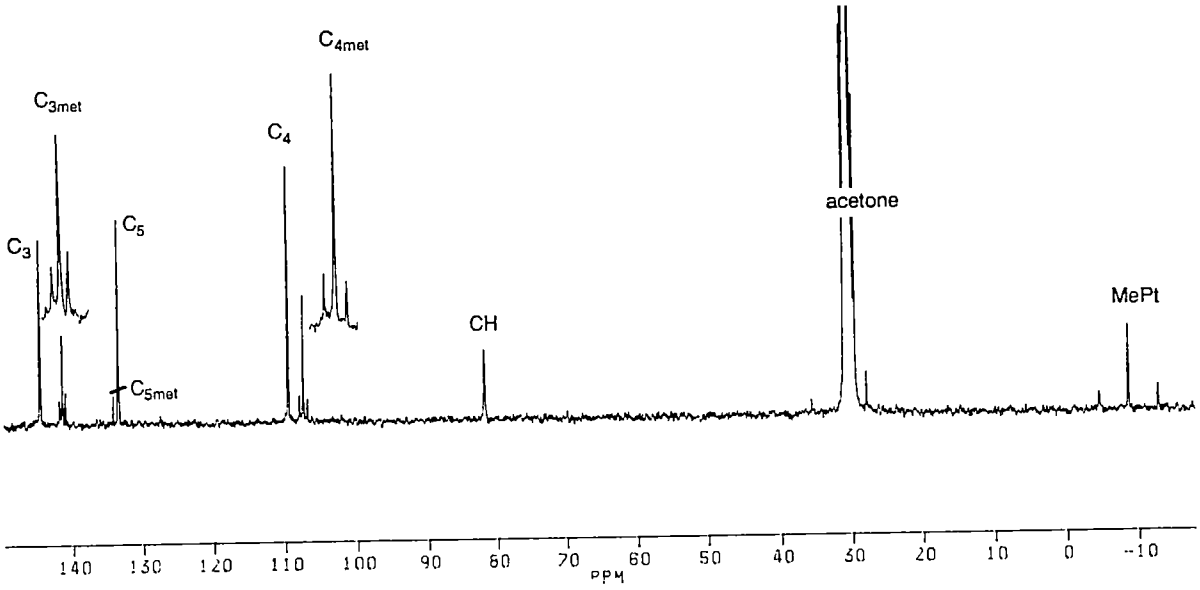


Figure 4.23 ^{13}C of $Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)$

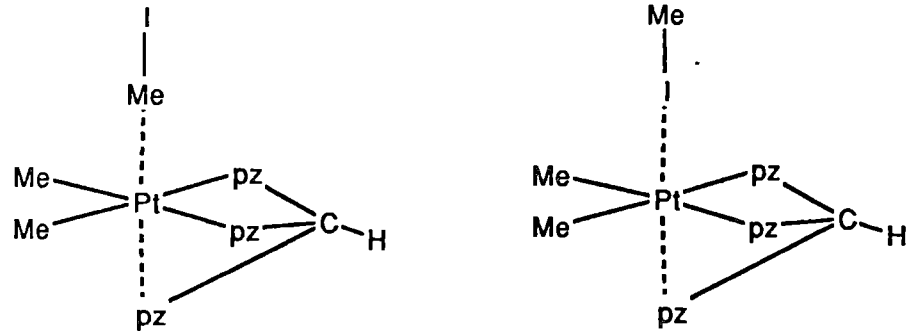
This reaction also occurs in the presence of a stoichiometric amount of MeI (in acetone), although the reaction appears to be slower, and in other solvents, eg. $CHCl_3$ and neat MeI, and on reaction with CD_3I the product formed is $Me(CD_3)IPt(HCpz_2(C_3N_2H_2)-C,N,N)$ (^1H, ^2H spectra).

The reaction of $Me_2Pt(HCpz_3)$ with MeI (equation 12) is remarkable, and although oxidative addition of alkyl halides to diorganoplatinum(II) complexes of tridentate ligands have not been reported, oxidative addition was expected to give $[Me_3Pt(HCpz_3)]I$, since $HCpz_3$ reacts with $[Me_3PtI]_4$ to form this ionic complex.

$$Me_2Pt(HCpz_3) \xrightarrow[acetone]{MeI} Me_2IPt(HCpz_2(C_3N_2H_2)\text{-}C,N,N) + CH_4 \quad (12)$$

The metallated complex reacts with pyridine to form the well characterized $[Me_2Pt(HCpz_2(C_3N_2H_2)\text{-}C,N,N)(py)]I$ (section 4.4.3).

The mechanism of metallation under these conditions is not clear, although it would be expected to be different from the pyridine induced metallation, since the first step in the latter appears to involve pyridine coordination with displacement of one pyrazolyl donor (Chapter 3). MeI can act as a ligand in its own right, and may be a stronger ligand than acetone,[19] but at the concentration used it is not expected to disrupt the N,N-chelated $HCpz_3$. Metallation is expected to occur while platinum is in oxidation state II, and if the mechanism followed for oxidative addition of MeI is S_N2, then it is possible that a metallation favoured orientation could be achieved during formation of the cationic intermediate or via MeI coordination at Pt(II) to increase the nucleophilic character of Pt(II). Representations of these possibilities are shown in figure 4.24.



(A) (B)

Figure 4.24

Of these two possible intermediates, (B) is favoured since the Pt atom in (A) will be less nucleophilic (toward H5 oxidative addition), although direct evidence for (B) has not been obtained and the reaction mechanism may be different from either (A) or (B).

This metallation/oxidative addition reaction is not restricted to MeI, since both EtI and $PhCH_2Br$ react in the same fashion, although the reaction of EtI is much slower and requires reflux for completion.

The ^1H NMR spectrum (see experimental) of the product formed on reaction of $Me_2Pt(HCpz_3)$ with EtI exhibits aromatic resonances consistent with one metallated pyrazolyl ring and two N bound pyrazolyl groups, while a single methylplatinum triplet is observed with a coupling constant $^2J(^1H-^{195}Pt)$ 75.00 Hz, consistent with platinum(IV). By comparison with $Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)$, the structure of this complex is expected to be as shown below.

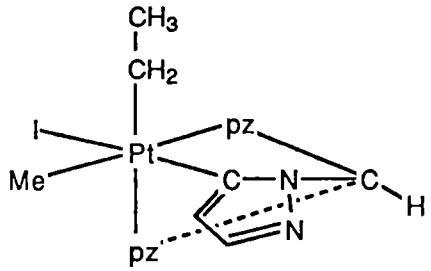


Figure 4.25

The aliphatic portion of the NMR spectrum shows inequivalent methylene protons, and these exhibit different $^2J(^1H-^{195}Pt)$ coupling values of ^2J_A 55.54 and ^2J_B 91.55 Hz, and it seems most likely that the ethyl group is in a specific orientation rather than in rapid rotation about the platinum-carbon bond. Molecular models show that of the orientations available to the ethyl group, that shown in figure 4.26 appears favourable, and would account for the pronounced downfield shift for one of the methylene protons (H_B) owing to its orientation near the iodo group.

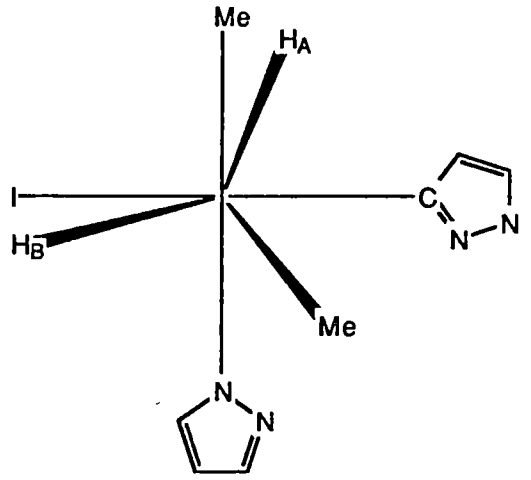


Figure 4.26

The ^1H NMR spectrum (figure 4.27) of the complex $Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)$, formed by reaction of $PhCH_2Br$ with $Me_2Pt(HCpz_3)$ may be similarly interpreted.

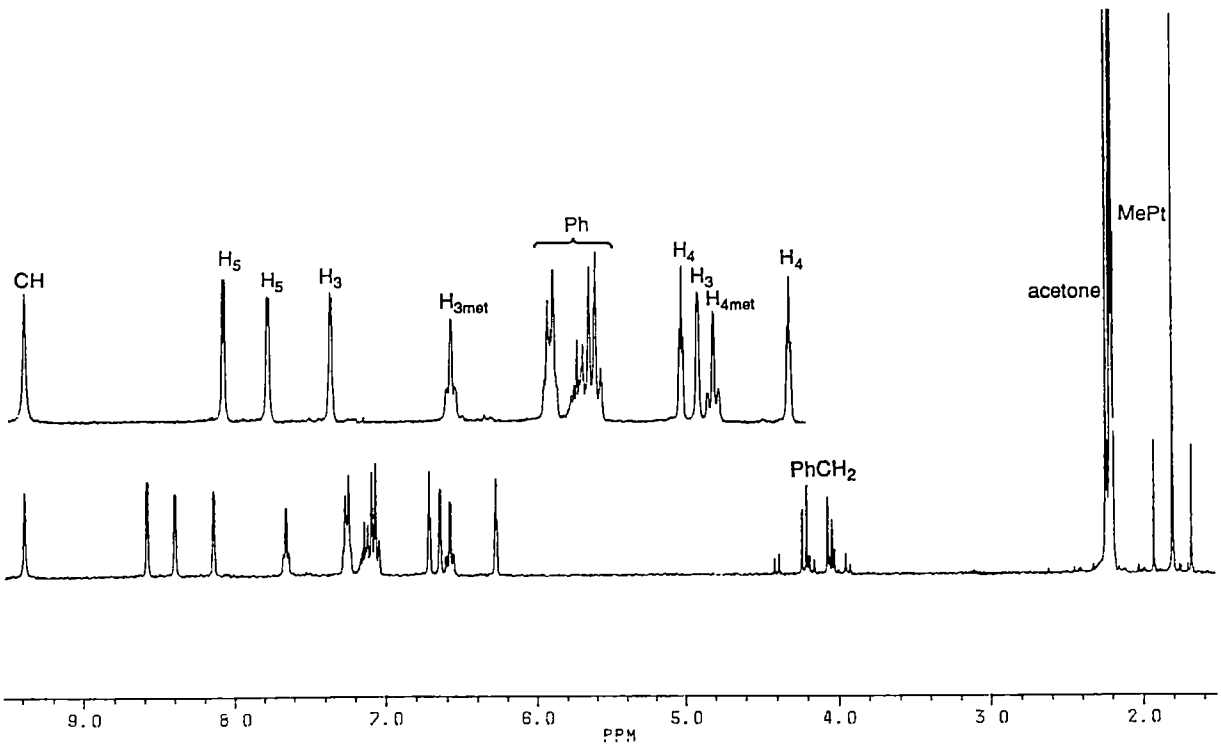


Figure 4.27 ^1H NMR Spectrum of $Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)$.

The aromatic region shows that one H3 proton of a N-coordinated pyrazolyl ring is strongly shielded and moved well upfield (6.65 ppm) from the other two H3 pyrazolyl ring resonances ($H3_{coord}$ 8.15 ppm, $H3_{met}$ 7.65 ppm). This shielding is assumed to result from the benzyl ring being situated over the H3 proton of the N-coordinated pyrazolyl group <u>trans</u> to methyl (figure 4.28). An expansion of the NMR spectrum showing the benzylic protons is given below.

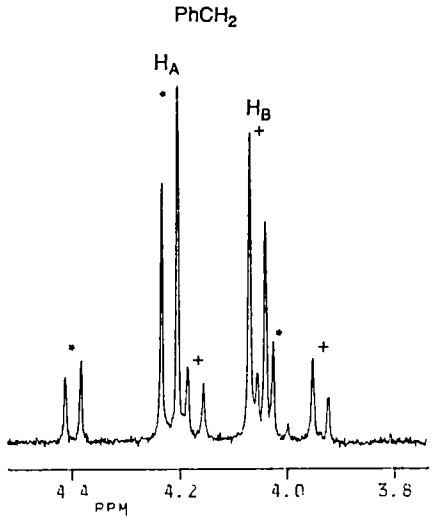
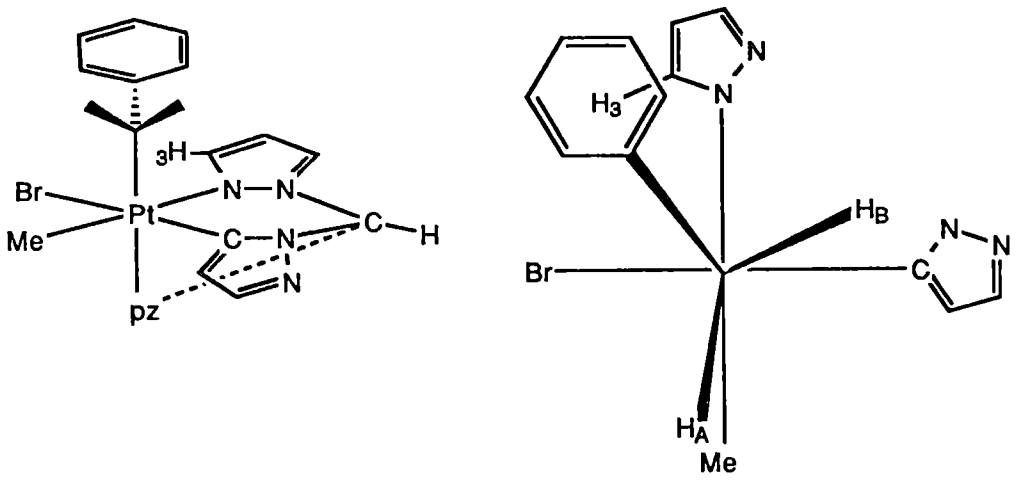


Figure 4.28 Benzylic Protons in $Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)$.

The benzylic protons are inequivalent and are split into doublets with each doublet showing the expected platinum satellites, eg. H_A 4.21 ppm, $^2J(^1H-^{195}Pt)$ 107.31 Hz, H_B 4.04 ppm, $^2J(^1H-^{195}Pt)$ 69.77 Hz.

In the orientation proposed, (figure 4.29) H_B is in a shielding environment (pyrazolyl rings) compared with H_A, accounting for its upfield position relative to H_A.



A B

Figure 4.29

In contrast to the reaction of $Me_2Pt(HCpz_3)$ with organohalides, $Me_2Pt(MeCpz_3)$ reacts with MeI to form the cationic oxidative addition compound $[Me_3Pt(MeCpz_3)]I$, in which the $MeCpz_3$ is acting as a N_3 tripodal tridentate ligand. A reason for this difference is not apparent, although it is possible that the apical methyl group does not permit the uncoordinated pyrazolyl group to adopt the required conformation for metallation to occur.

4.4.2 $[MePt(HCpz_2(C_3N_2H_2)-C,N)]_n$

When polymeric $[MePt(HCpz_2(C_3N_2H_2)-C,N]_n$ is suspended in acetone and excess MeI added the suspension clarifies to give a pale yellow solution from which the neutral complex $Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)$ can be isolated.

$$[MePt(HCpz_2(C_3N_2H_2)-C,N]_n + MeI \longrightarrow Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N) \quad (13)$$

This complex is identical to that obtained from the reaction of $Me_2Pt(HCpz_3)$ with MeI (section 4.4.1, figure 4.21). Reaction of EtI and $PhCH_2Br$ also resulted in isolation of the same complexes as those formed in the reaction of $Me_2Pt(HCpz_3)$ with RX.

The carbon monoxide adduct, $MePt(HCpz_2(C_3N_2H_2)-C,N)(CO)$, formed by bubbling CO through an acetone solution of $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, does not react with alkyl halide to yield platinum(IV) complexes. This is attributed to the lower nucleophilic character of the metal owing to the π acid character and low donor ability of carbon monoxide as a ligand.

4.4.3 $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$

The metallated complex $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, as a suspension in acetone, reacts rapidly (15–20 minutes) with simple organohalides (MeI, $PhCH_2Br$, or propargyl bromide) to form cationic complexes in which $HCpz_3$ acts as a tripodal tridentate N_2C^- ligand and pyridine remains coordinated in the cationic complexes. The complexes give ^1H NMR spectra similar to the neutral analogues, $Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)$, as discussed above.

Excess MeI reacts in 5 minutes to give a complex which may be readily isolated, and which has a molar conductance (in acetone) of 89 $^{-1}$ cm^2 mol^{-1} (1:1 electrolyte). A ^1H NMR spectrum (figure 4.30) shows a single MePt(IV) environment (1.55 ppm, $^2J(^1H-^{195}Pt)$ 69.20 Hz), and a metallated pyrazolyl ring (H3 7.45 ppm, $^4J(^1H-^{195}Pt)$ 10.71 Hz; H4 6.10 ppm, $^3J(^1H-^{195}Pt)$ 14.34 Hz). The other two pyrazolyl rings are equivalent (H4 6.50 ppm, H3 7.35 ppm, H5 9.60 ppm) and are coordinated to platinum.

The large downfield shift of the apical C–H ligand proton is consistent with the ligand acting as a tripod, and the H3 protons of the N-coordinated pyrazolyl groups occur upfield of the metallated ring H3 proton, and are assumed to be shielded by the pyridine ring (figure 4.31). The pyridine group shows the expected coupling between platinum and the ortho protons ($^3J(^1H-^{195}Pt)$ 23.90 Hz).

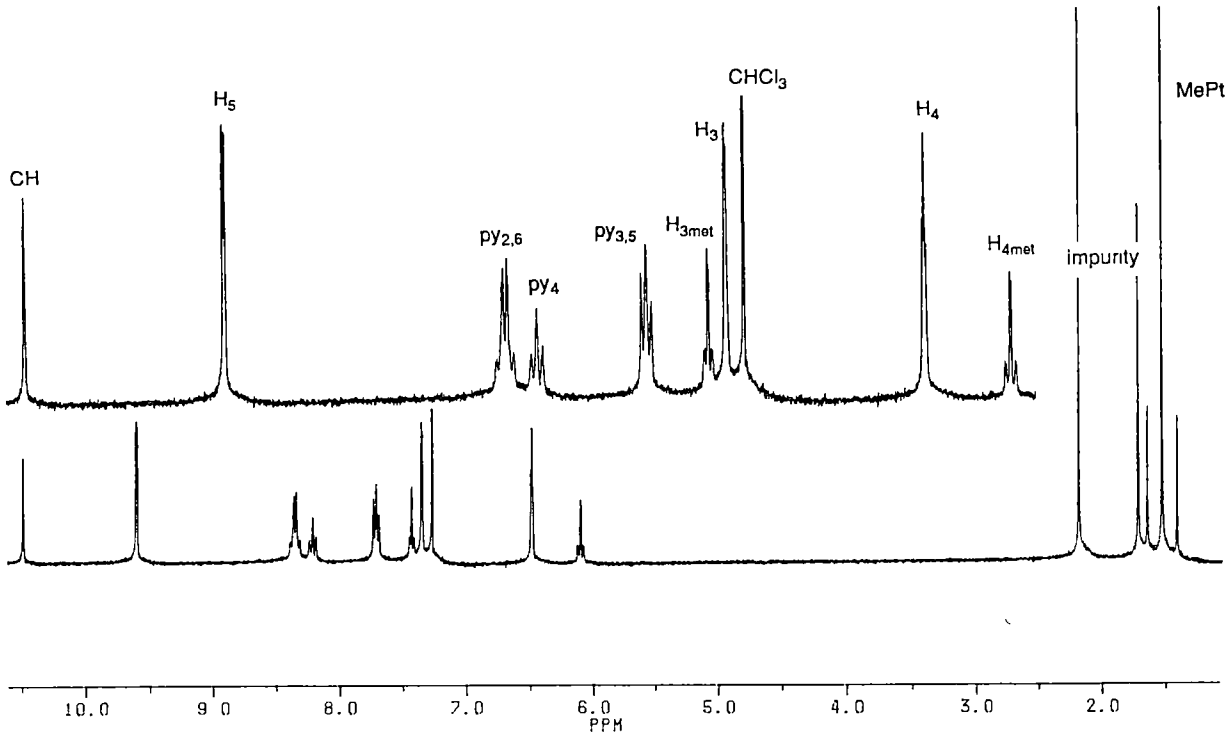


Figure 4.30 ^{1}H NMR Spectrum of $[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]I$.

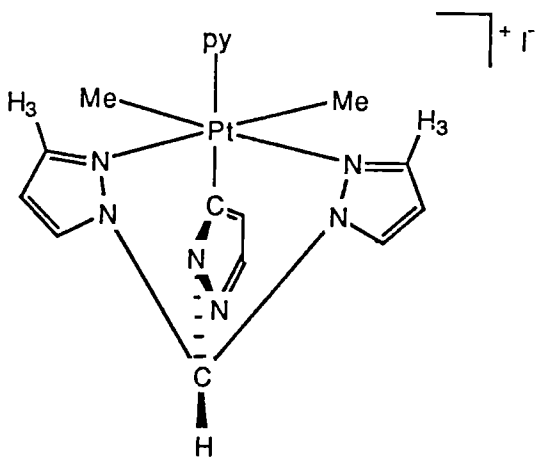


Figure 4.31

If the reaction proceeds via an S_N2 mechanism then this complex may be regarded as a coordination stabilized form of the ionic intermediate formed during the oxidative addition reaction.

The iodo ligand in $[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]I$ can undergo metathesis with $AgBF_4$.

$$[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]I \xrightarrow[\text{acetone}]{AgBF_4} [Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]BF_4 + AgI \qquad (13)$$

As for neutral $Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)$, the cation $[Me(PhCH_2)Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]Br$ exhibits a ^1H NMR spectrum (figure 4.32) permitting assignment of the preferred orientation of the benzyl group.

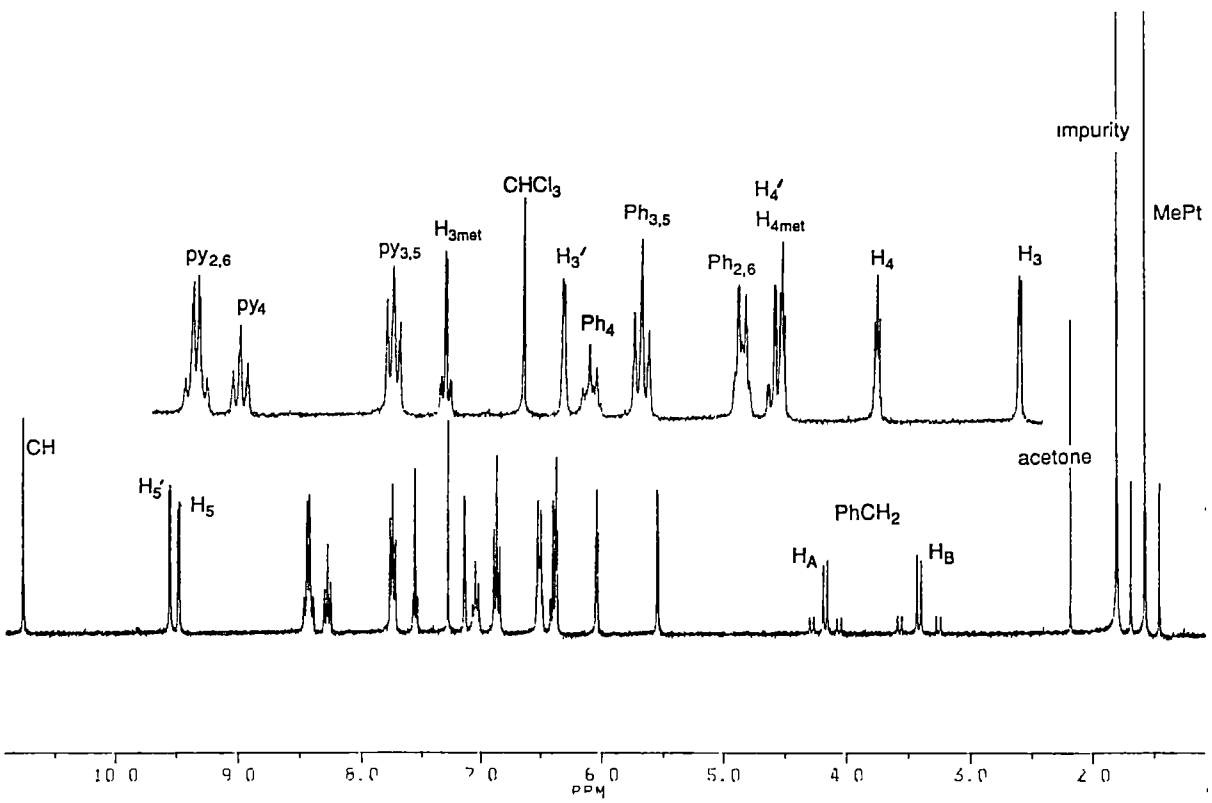
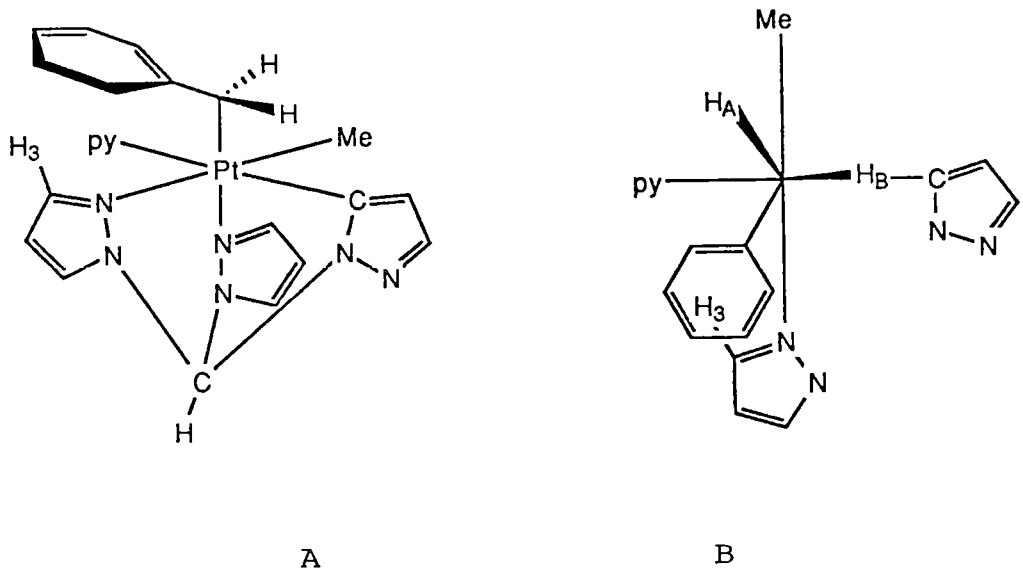


Figure 4.32 ^1H NMR of $[Me(PhCH_2)Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]Br$

Thus, the H3 proton of the N-coordinated pyrazolyl ring (5.55 ppm) occurs well upfield of all other pyrazolyl protons, and appears to be strongly shielded by the benzyl group in an orientation over this proton (figure 4.33 A,B). The ortho benzyl protons (6.38 ppm) are also upfield compared with their position in the neutral complex $Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)$ (p. 152) (7.10 ppm), and with the orientation proposed these protons would appear to be shielded by a N-coordinated pyrazolyl group and the coordinated pyridine.



A B

Figure 4.33

The benzylic protons give well defined doublets ($^2J(^1H-^1H)$ 9.80 Hz) at 4.18 ppm (H_A) and 3.40 ppm (H_B) flanked by platinum satellites with $^2J(^1H-^{195}Pt)$ 78.87 Hz and 94.05 Hz respectively.

For the allyl bromide oxidative addition product, $[Me(allyl)Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]Br$, the methylene resonances are separated, 2.96 ppm and 3.37 ppm, and have slightly different platinum coupling constants, $^2J(^1H-^{195}Pt)$ 91.54 Hz and $^2J(^1H-^{195}Pt)$ 88.24 Hz respectively.

An interesting situation arises with the oxidative addition of propargyl bromide to $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$, since the NMR

spectrum (figure 4.34) does not show the expected resonance pattern for a bound propargyl group, but rather an allenyl group.

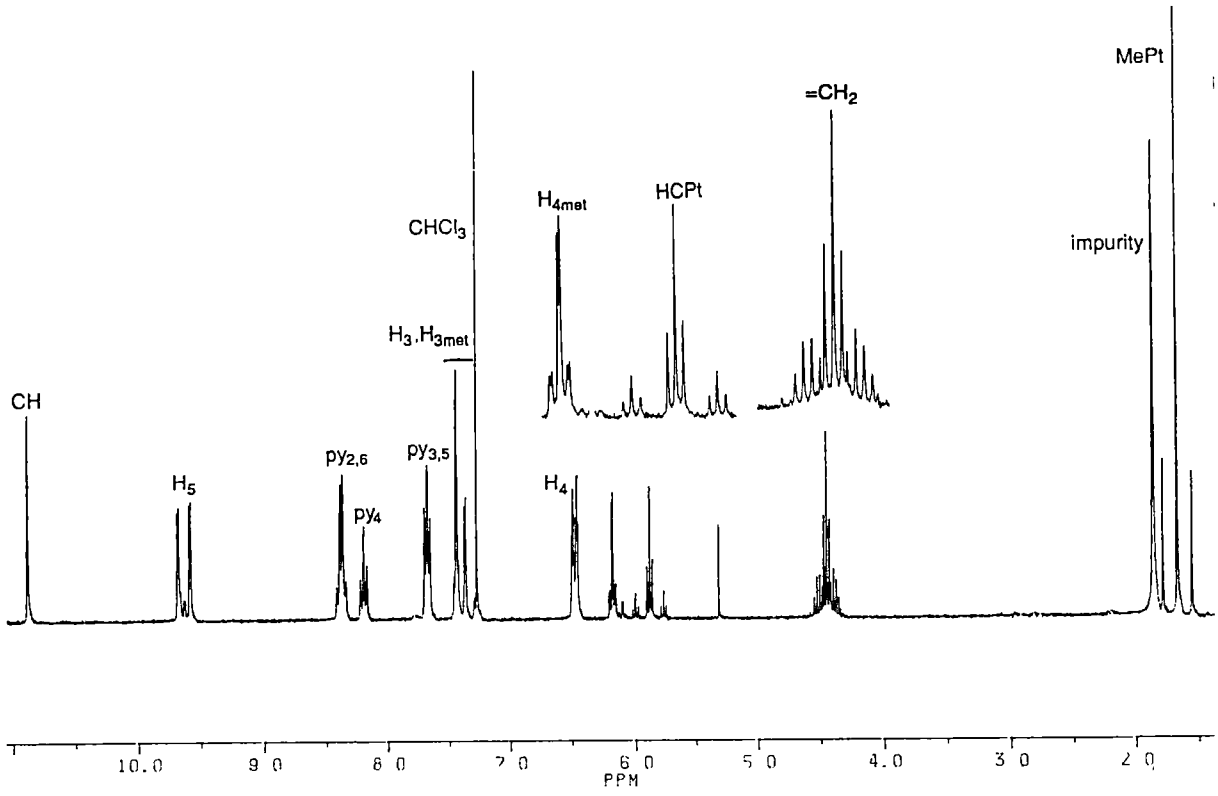


Figure 4.34 $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ + Propargyl Bromide

The resonance at 5.78 ppm, $^2J(^1H-^{195}Pt)$ 67.11 Hz, is assigned to H_A (figure 4.35) while the resonance centred at 4.45 ppm is assigned to the protons H_B.

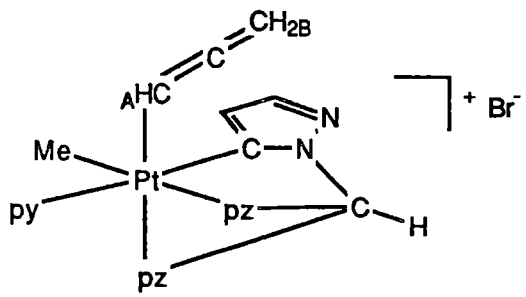


Figure 4.35

Infrared spectroscopy shows an absorption characteristic of an allenyl group, and well removed from the region expected for a propargyl group. The isomerization of a propargyl group to an allenyl group is not uncommon during oxidative addition reactions and has been observed.[20]

$MePt(HCpz_2(C_3N_2H_2)-C,N)(py) + pzCH_2CH_2Br$

$MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ was heated with a slight excess of $pzCH_2CH_2Br$ in acetone until a clear solution resulted (10 minutes). The solution volume was reduced and hexane added, giving a white solid. The product was insoluble in common organic solvents but exhibited enough solubility ($CDCl_3$) for its ^1H NMR to be recorded.

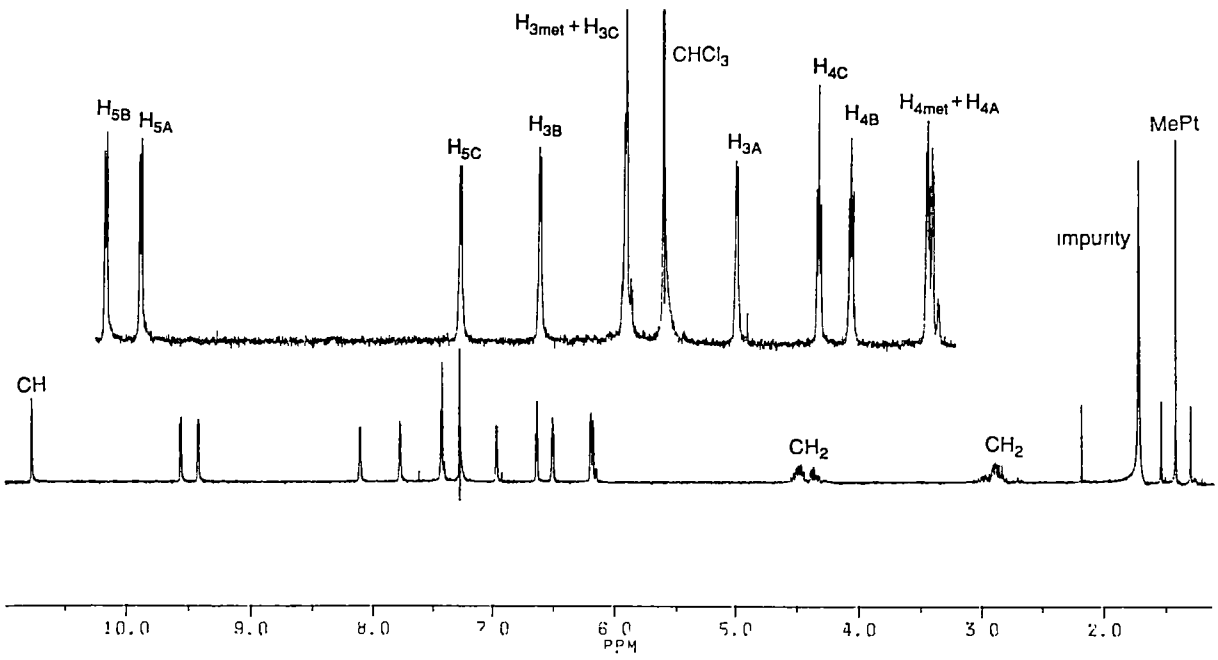


Figure 4.36 ^1H NMR Spectrum of $[Me(pzCH_2CH_2)Pt(HCpz_2(C_3N_2H_2)-C,N,N)]Br$.

The MePt resonance (1.44 ppm, $^2J(^1H-^{195}Pt)$ 70.23 Hz) illustrates that oxidative addition has occurred, while the downfield apical resonance (10.79 ppm) is consistent with the complex being ionic. The aromatic region of the spectrum shows no evidence for the presence of pyridine, and this is confirmed in the IR spectrum of the complex which does not exhibit the characteristic absorption for

coordinated pyridine. The following structure is proposed in which all pyrazolyl groups are coordinated with C bonding groups in a fac arrangement and the complex contains both five and six membered NC^- and N_2C^- chelate rings.

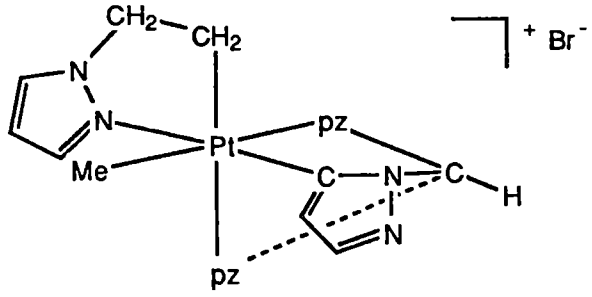


Figure 4.37

This is an example of a complex in which three pyrazolyl groups are trans to different bonded carbon atoms, and in which there are three types of chelate ring; a five membered and a six membered NC^- ring, and a six membered NN chelate ring. The NMR assignment for individual pyrazolyl rings relies on a COSY spectum while the assignment of rings trans to the various C donors is arrived at through molecular models and ring shielding arguments. The individual rings are labelled as ring A (trans to Me), ring B (trans to CH_2) and ring C (trans to metallated pyrazolyl).

The five membered NC^- chelate ring can be formed by several processes. Oxidative addition of $pzCH_2CH_2Br$ would bring the pyrazolyl group into a position where it could displace pyridine, or initial heating of the reaction mixture may form the de-pyridinated polymeric complex, $[MePt(HCpz_2(C_3N_2H_2)\text{-}C,N)]_n$, which then oxidatively adds $pzCH_2CH_2Br$ and the pyrazolyl group coordinates to satisfy the geometrical requirements of platinum. Alternatively, although unlikely since $pzCH_2CH_2Br$ is expected to be a weaker donor than pyridine, it may coordinate via nitrogen, to form square planar $[MePt(HCpz_2(C_3N_2H_2)\text{-}C,N)(pzCH_2CH_2Br)]$ followed by intramolecular oxidative addition.

4.4.4 Phosphine Complexes $MePt(HCpz_2(C_3N_2H_2)-C)(L)$ (L = $2PPh_3$, $PPh_2(PhOMe)$, $PPh_2(o\text{-tolyl})$)

The bis(phosphine) complex $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ reacts with MeI in acetone to yield $Ph_3PMe^+I^-$ and a platinum (IV) complex, for which the ^1H NMR spectrum shows a single coordinated Ph_3P. This complex can be made free from contamination of phosphonium salts by reacting $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ with one mole of Ph_3P in warm acetone, removing the solvent to dryness (to remove displaced pyridine), redissolving in acetone and addition of excess MeI. The ^1H NMR spectrum (experimental) is consistent with the structure shown in figure 4.38, with the Ph_3P ligand trans to the metallated pyrazolyl ring to give a fac-C_3Pt moiety. Triphenylphosphine shields the H3 and H4 protons of the N-coordinated pyrazolyl rings giving an upfield shift (6.61 ppm and 6.15 ppm respectively) for these resonances compared with other neutral complexes containing $HCpz_3$ as a N_2C^- tripod ligand, eg. for $Me_2PtI(HCpz_2(C_3N_2H_2)-C,N,N)$ (section 4.4.1).

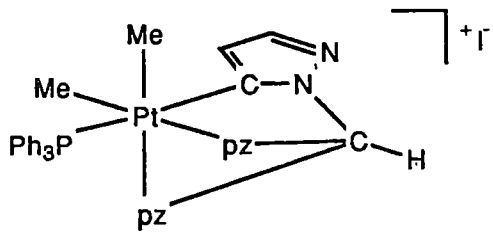


Figure 4.38

Other phosphine complexes $MePt(HCpz_2(C_3N_2H_2)-C,)L_2$ (L = PPh_2Me, $PPhMe_2$, PPh_2Et) and $MePt(HCpz_2(C_3N_2H_2)-C,N)L$ (L = $PPh_2(o\text{-tolyl})$, $PPh_2(PhOMe)$) reacted similarly to form $[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)L]I$ and, for the bisphosphine complexes, a phosphonium salt. Bidentate phosphine complexes (L = $0.5PPh_2(CH_2)_nPh_2P$, n = 1,2) failed to react with MeI.

$MePt(HC(mim)pz(C_3N_2H_2)-C,N)(py)$

$MePt(HC(mim)pz(C_3N_2H_2)-C,N)(py)$ reacts with MeI in much the same way as $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ does, to form an ionic (Λ = 78 Ω^{-1}

cm^2 $mole^{-1}$) $Me_2Pt(IV)$ complex, $[Me_2Pt(HC(mim)pz(C_3N_2H_2)-C,N,N)(py)]I$. The ^1H NMR spectrum (figure 4.39) shows two MePt resonances consistent with methyl trans to pyrazolyl (1.47 ppm, $^2J(^1H-^{195}Pt)$ 69.39 Hz) and methyl trans to imidazolyl (1.36 ppm, $^2J(^1H-^{195}Pt)$ 67.80 Hz) with part of each resonance coincident.

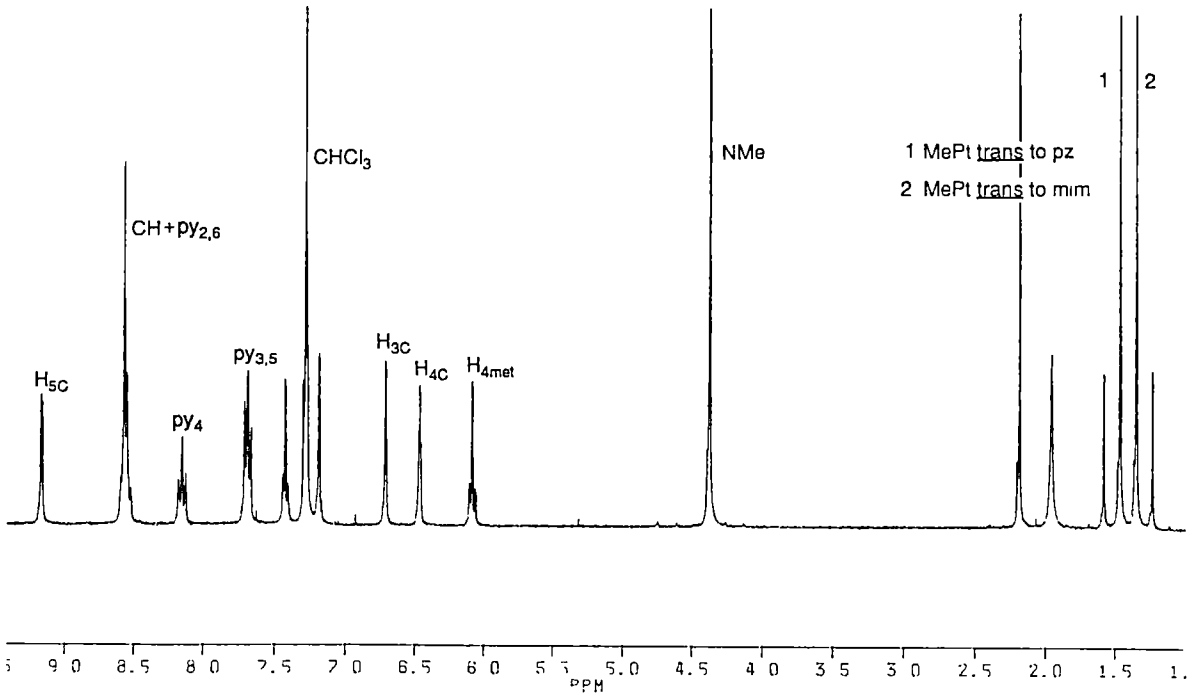


Figure 4.39 ^1H NMR Spectrum of $[Me_2Pt(HC(mim)pz(C_3N_2H_2)-C,N,N)(py)]I$

The absence of a low field MePt resonance (eg. ~1 ppm expected for trans to I) supports the complex being ionic with the ligand acting as a N_2C^- tridentate.

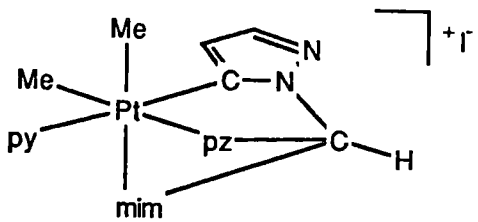


Figure 4.40

Metallated ring pyrazolyl resonances exhibit the expected platinum couplings (H4, 6.08 ppm, $^{3}J(^{1}H-^{195}Pt)$ 14.34 Hz; H3, 7.41 ppm $^{4}J(^{1}H-^{195}Pt)$ 10.68 Hz, $^{3}J(^{1}H-^{1}H)$ 1.78 Hz), while other resonances (pyrazolyl, pyridine) parallel those in the closely related complex $[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]I$. However, the apical proton is well upfield in this complex (8.60 ppm) compared with that in $[Me_2Pt(HCpz_2(C_3N_2H_2)-C,N,N)(py)]I$ (10.45 ppm), and this may be a consequence of the proximity to the imidazolyl N-methyl group. An imidazolyl proton resonance is near coincident with the $CHCl_3$ peak.

$MePt(HC(mim)pz(C_3N_2H_2)-C,N)(py)$ (formed in situ) reacts with PPh_3 to form the monophosphine complex $MePt(HC(mim)pz(C_3N_2H_2)-C,N)(PPh_3)$ which is readily isolated as a crystalline solid. This complex reacts with MeI to form an ionic complex with the tridentate ligand acting as a N_2C^- tripod, giving rise to inequivalent MePt groups (figure 4.41).

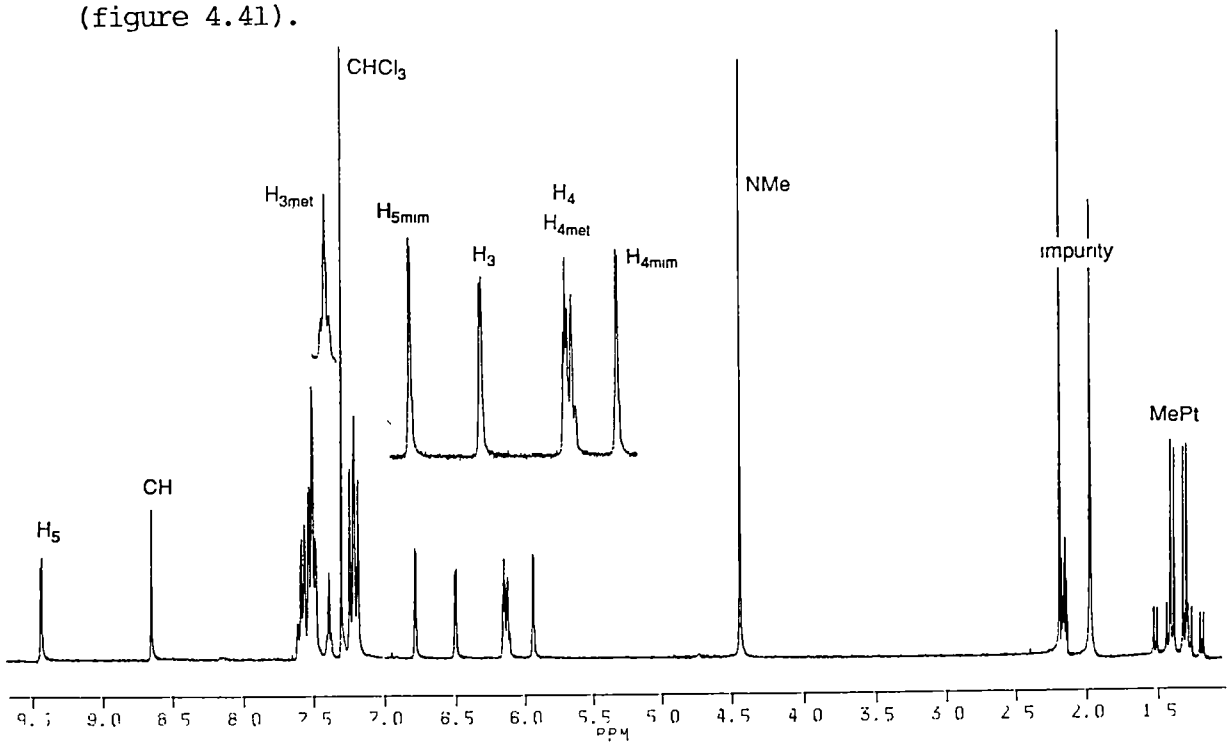


Figure 4.41 ^{1}H NMR Spectrum of $[Me_2Pt(HC(mim)pz(C_3N_2H_2)-C,N,N)(PPh_3)]I$.

4.5 Reaction of Me_2PtL Complexes with Alkyl Halides Where L is a Bidentate Ligand

Alkyl halides react with Me_2PtL (L = bidentate) to give simple neutral platinum(IV) complexes. Four classes of complexes were chosen for study and included:

(i) $Me_2Pt(H_2Cpz_2)$ and $Me_2Pt(Ph(H)Cpz_2)$ which like $Me_2Pt(HCpz_3)$ metallate in pyridine.

(ii) $Me_2Pt(Me(H)Cpz_2)$, which is an example of one of the few $Me_2Pt(II)$ complexes isolated and found to be soluble in common organic solvents.

(iii) Me_2PtL (L= $H_2C(mim)pz$, $H_2C(py)pz$),which are examples of typical $Me_2Pt(II)$ complexes with unsymmetrical bidentate ligands.

(iv) $Me_2Pt(Me_2Cpz_2)$ and $Me_2Pt(Cpz_4)$ which would be expected to exhibit severe steric crowding in a platinum(IV) environment if the complex forms.

(i)

$Me_2Pt(H_2Cpz_2)$

When $Me_2Pt(H_2Cpz_2)$ is suspended in acetone, excess MeI added and the solution stirred for 12 hours, either in the dark or in light, a pale yellow solution with much suspended white solid is obtained. After filtration and vacuum drying the white solid was identified (IR spectrum) as unreacted starting material. If the reaction is repeated in $CHCl_3$ as solvent, then after 8 hours a pale yellow solution results, but with much less unreacted starting material present. On filtration, reduction of volume and addition of hexane, a pale white solid is obtained. The solid gives an ill-defined ^1H NMR spectrum with MePt(IV) groups in the ratio 2:1, identical environments for the pyrazolyl rings, and two bridgehead proton

doublets separated by ~1.2 ppm, with the low field doublet considerably broader than the upfield one. These results are consistent with the formulation fac-Me_3IPtL. $Me_3IPt(H_2Cpz_2)$ is more readily made by the "in situ" reaction between $[Me_2Pt(Et_2S)]_2$ /H_2Cpz_2/MeI which yields a microcrystalline solid (p. 186).

This complex reacts with silver acetate in acetone to precipitate AgI, and from this solution the acetate complex can be isolated as a white powder. The acetate complex is far more soluble, and gives an NMR spectrum (figure 4.42) as expected for the same structure, exhibiting resonances attributable to methyl trans to nitrogen (1.45 ppm, $^2J(^1H-^{195}Pt)$ 72.05 Hz), methyl trans to acetate (0.70 ppm, $^2J(^1H-^{195}Pt)$ 73.42 Hz), equivalent pyrazolyl rings and two ligand bridging protons.

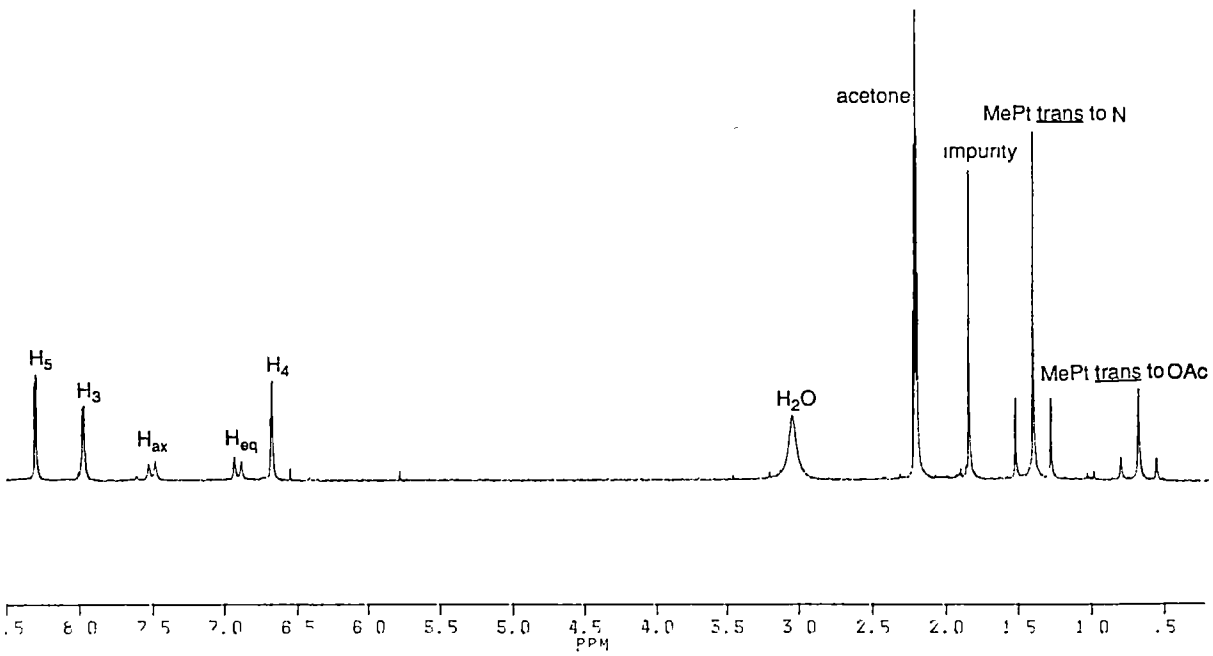
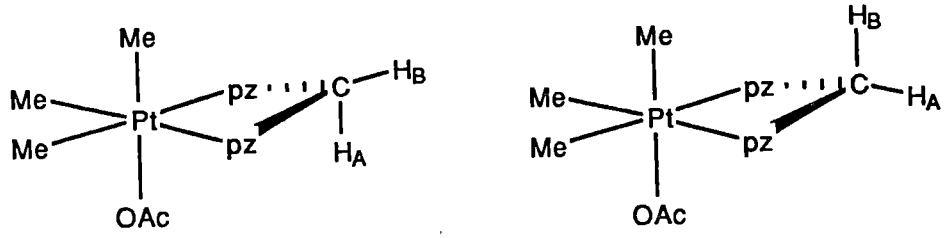


Figure 4.42 ^1H NMR Spectrum of $Me_3(OAc)Pt(H_2Cpz_2)$

Two configurations are possible for this complex.



Configuration 1 Configuration 2

Figure 4.43

Both configurations would result in inequivalent apical proton resonances, but configuration 1, with proton A in the axial position and adjacent to acetate is considered more likely, as it would result in lower steric interaction, H_A....O, H_B....Me. Thus, the downfield apical proton resonance (7.5 ppm) is assigned to H_A (configuration 1) and the resonance at 6.9 ppm to H_B (configuration 1). This assignment is further supported by a comparison of the apical regions of the ^1H NMR spectra of $Me_3IPt(H_2Cpz_2)$ and $Me_2(OAc)Pt(H_2Cpz_2)$ (figure 4.44), in which the downfield resonance is significantly moved on substituting acetate for iodo, and this proton is thus adjacent to the acetate coordination site.

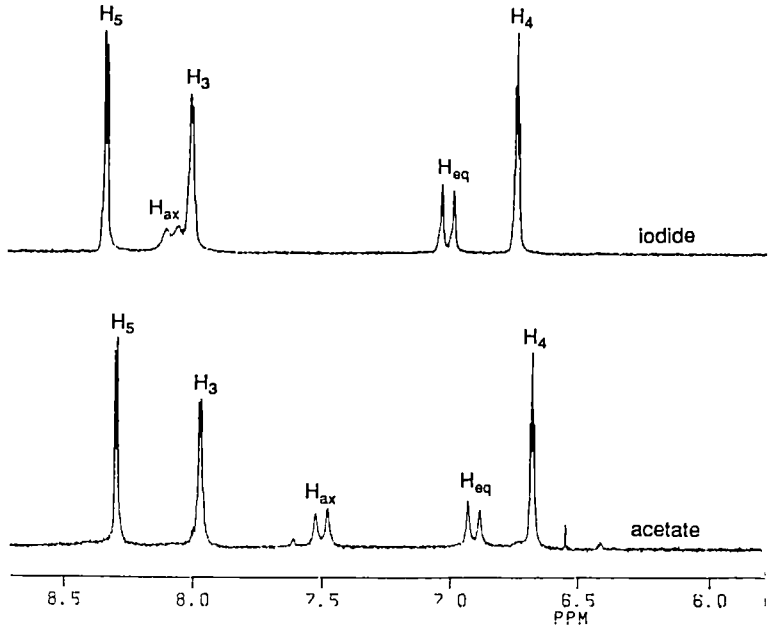


Figure 4.44 Aromatic resonances of $Me_3IPt(H_2Cpz_2)$ and $Me_3(OAc)Pt(H_2Cpz_2)$

$Me_2Pt(Ph(H)Cpz_2)$ reacts with excess MeI in acetone to give the neutral complex $Me_3IPt(Ph(H)Cpz_3)$ (p. 186). However, the reaction takes a different course if carried out in neat MeI.

$Me_2Pt(Ph(H)Cpz_2)$ "dissolves" in neat MeI and on standing a solid crystallizes out. This solid is not soluble in acetone, but enough complex slowly dissolves in $CDCl_3$ from which its ^1H NMR spectrum can be recorded (figure 4.45). Interestingly, only two MePt resonances are observed, both with $^2J(^1H-^{195}Pt)$ coupling constants consistent with a Pt(IV) species, with one methyl trans to N (1.84 ppm, $^2J(^1H-^{195}Pt)$ 72.12 Hz) and one methyl trans to I (0.80 ppm, $^2J(^1H-^{195}Pt)$ 74.73 Hz), although the coupling constant for the methyl trans to I is larger than normally found. The aromatic region of the spectrum integrates for 1 proton less than that expected for a simple $Me_3Pt(IV)$ complex, and 2D COSY spectra indicate that C5 of a pyrazolyl ring is deprotonated.

The H4 pyrazolyl proton of this ring displayed platinum satellites. This behaviour is consistent with both metallation and oxidative addition having occurred.

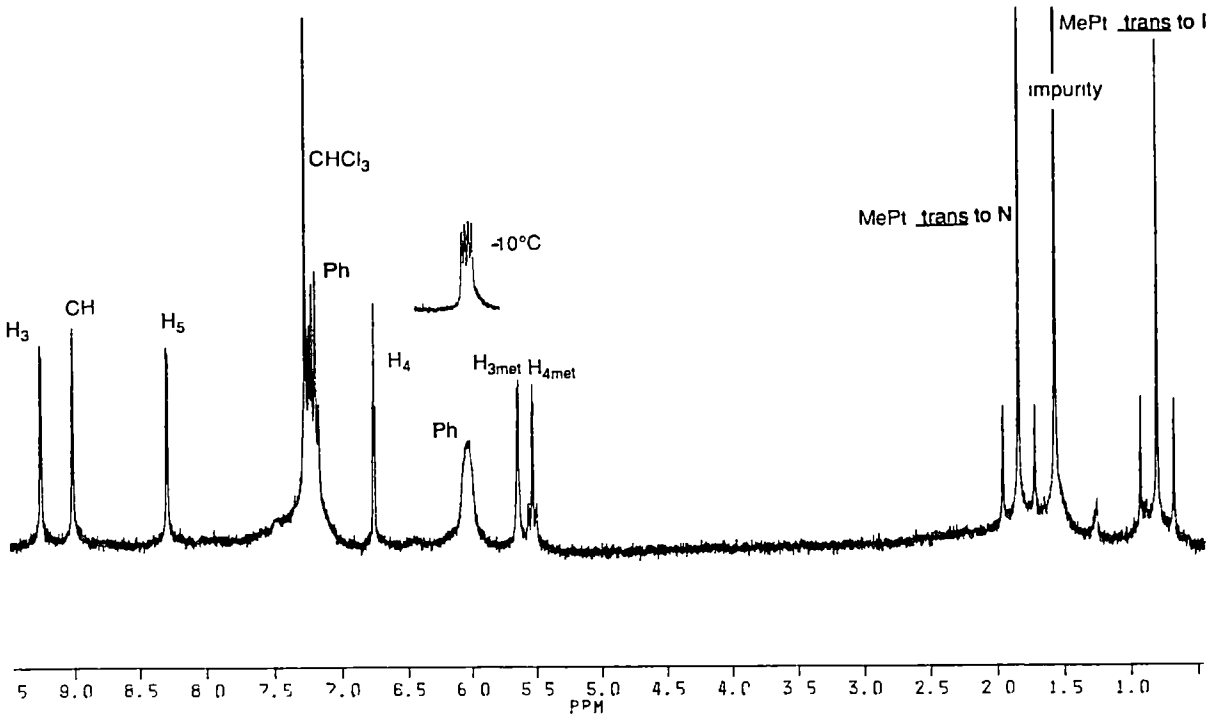


Figure 4.45 ^{1}H NMR Spectrum of the Product from $Me_2Pt(Ph(H)Cpz_2)$ + neat MeI. Inset NMR at $-10^{o}C$

To satisfy the coordination requirements of the platinum atom a dimeric iodo bridged structure is proposed in which all C-donors are fac and the $Ph(H)Cpz_2$ ligand is cis NC^{-}.

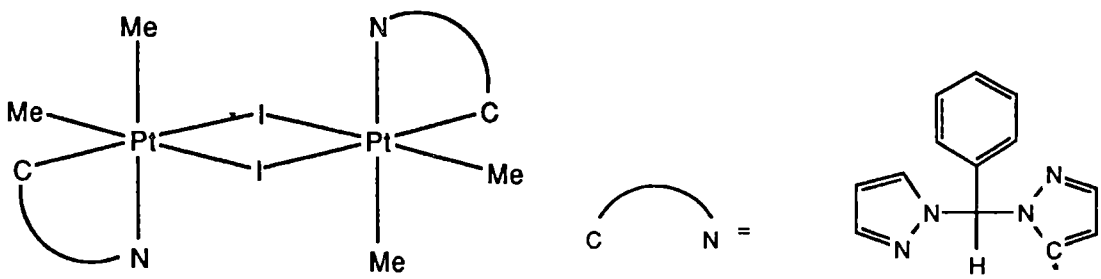


Figure 4.46

The metallated pyrazolyl ring H3 and H4 resonances are moved upfield ($H4_{met}$ 5.55 ppm, and $H3_{met}$ 5.62 ppm) in comparison with the free ligand (6.34 ppm). The broad phenyl resonance at 6.02 ppm resolves at $-10^{o}C$ into two doublets, each with different coupling constants (8.78 and 6.97 Hz respectively) and are thus not connected

protons. Molecular models show that the phenyl ring is most probably in an axial position with its 2 and 6 protons above the pz rings and thus in the shielding cones of these rings. The fact that the H5 resonance of the unmetallated ring is not moved well upfield is evidence that the phenyl group is not in an equatorial position.

(ii)

$Me_2Pt(Me(H)Cpz_2)$

$Me_2Pt(Me(H)Cpz_2)$ reacts rapidly (NMR) with excess MeI in a similar fashion to give a white microcrystalline product. The ^1H NMR spectrum (figure 4.47) shows MePt(IV) resonances in the ratio 2:1 and a single ligand environment.

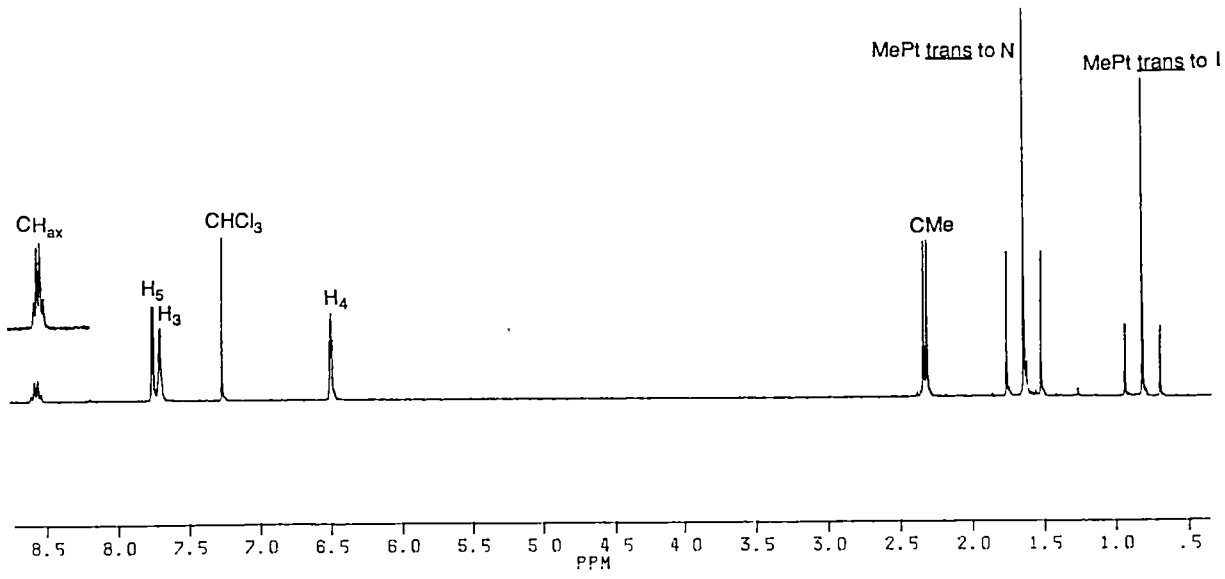


Figure 4.47 ^1H NMR Spectrum of $Me_3IPt(Me(H)Cpz_2)$.

The large downfield shift of the apical proton (1.25 ppm from the related Pt(II) complex) suggests that it is strongly deshielded and is thus assumed to be adjacent to the coordinated iodo ligand.

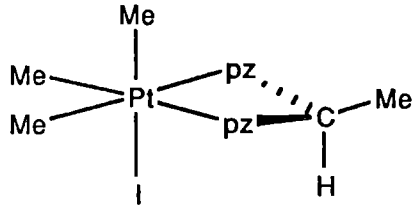


Figure 4.48

If an organohalide other than MeI is employed a mixture of products result.

Oxidative Addition of Benzylbromide

Benzylbromide adds readily to $Me_2Pt(Me(H)Cpz_2)$ to give mixtures of isomers, corresponding to cis and trans oxidative addition. Thus, the ^1H NMR spectrum (figure 4.49) of the white crystalline complex $Me_2(PhCH_2)BrPt(Me(H)Cpz_2)$, in D6 acetone, shows the presence of two apical ligand proton resonances in the ratio 1:1, and MePt resonances occur as the expected 'triplet' in the ratio 2:1:1 (1.55 ppm, $^2J(^1H-^{195}Pt)$ 71.91 Hz (6 protons), 1.53 ppm, $^2J(^1H-^{195}Pt)$ 72.87 Hz (3 protons), 0.91 ppm, $^2J(^1H-^{195}Pt)$ 73.53 Hz (3 protons), and are indicative of methyl trans to N,N and Br respectively.

The resonance at 1.55 ppm is assigned to the conformation which has both methyl groups in the plane of the platinum trans to N. The boat conformation with the apical proton in the axial position is preferred, as the related complex $Me_3IPt(Me(H)Cpz_2)$ was shown to exhibit this structure in solution at ambient temperature.

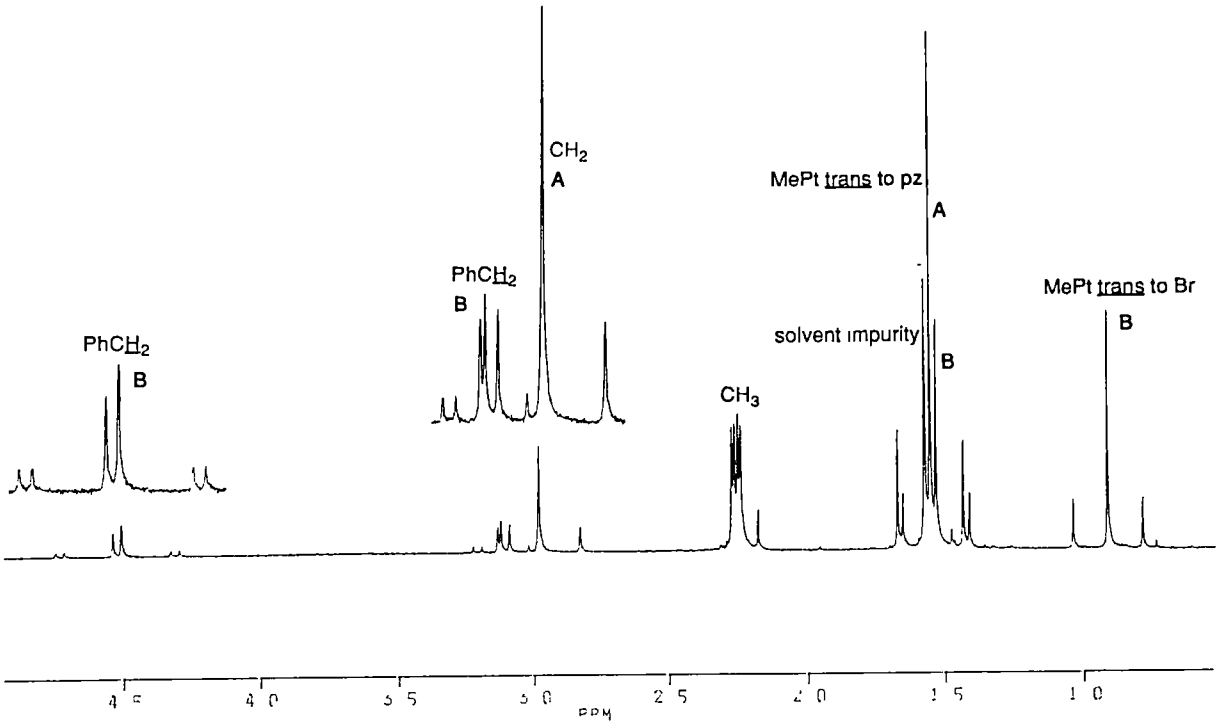


Figure 4.49 A ^{1}H NMR Spectrum of $Me_2(PhCH_2)BrPt(Me(H)Cpz_2)$ - Aliphatic Region

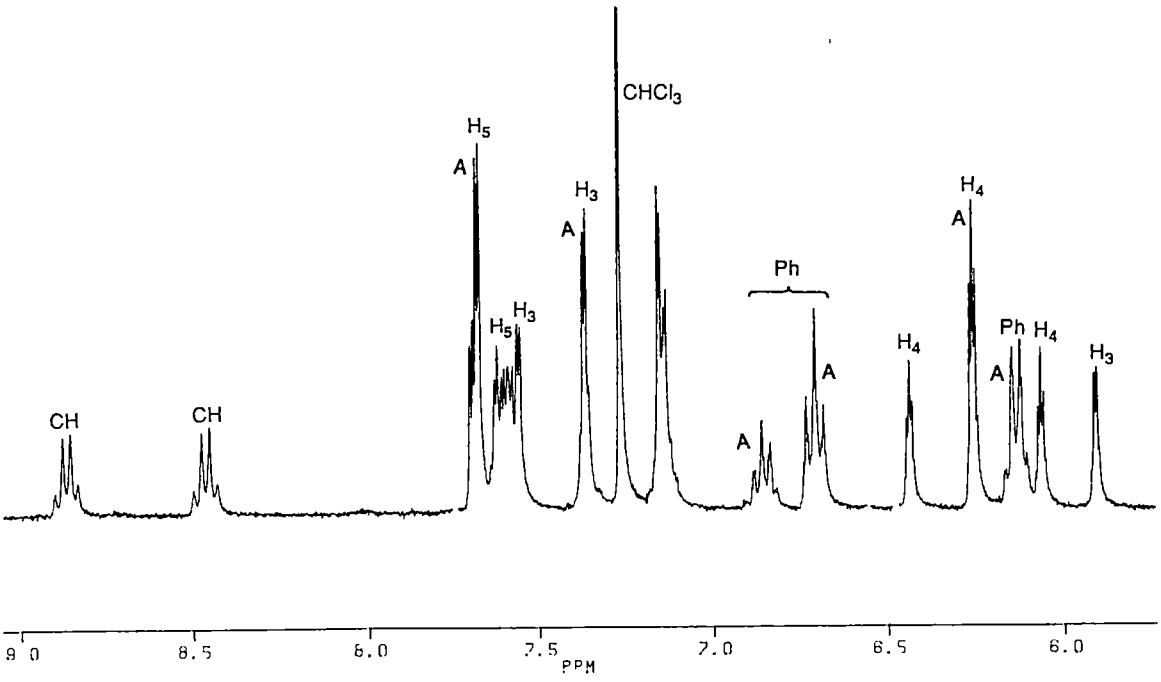


Figure 4.49 B ^{1}H NMR Spectrum of $Me_2(PhCH_2)BrPt(Me(H)Cpz_2)$ - Aromatic Region

The methylene resonances of the benzyl moiety (4.51 ppm, $^{2}J(^{1}H-^{195}Pt)$ 125.71 Hz, $^{2}J(^{1}H-^{1}H)$ 9.44 Hz 1H, 3.12 ppm, $^{2}J(^{1}H-^{195}Pt)$ 62.06 Hz, $^{2}J(^{1}H-^{1}H)$ 9.44 Hz 1H, 2.98 ppm, $^{2}J(^{1}H-^{195}Pt)$ 92.20 Hz 2H, suggest that the methylene groups within each conformer are in markedly different orientations. Examination of molecular models allow the probable orientations of each conformer to be estimated, with the symmetrical conformer being assigned structure (A).

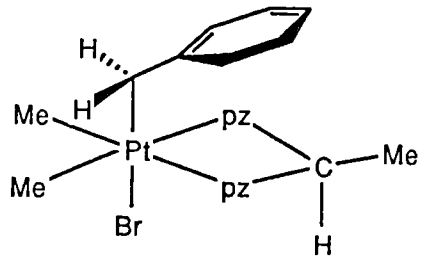


Figure 4.50 Conformer(A)

The unsymmetrical conformer (B) has the benzyl moiety in an orientation which strongly shields a H3 proton (5.91 ppm) to such an extent that this proton resonance is moved upfield of the normal H4 position. This orientation results in a methlyene proton being adjacent to the bromo ligand, and this is assigned to the downfield resonance at 4.51 ppm ($^{2}J(^{1}H-^{195}Pt)$ 125.71 Hz).

The phenyl resonances for conformer B are quite different than those of conformer (A) and may be due in part to ring shielding by a pyrazolyl ring and proximity to the halide ligand. The structure proposed for conformer (B) is shown below.

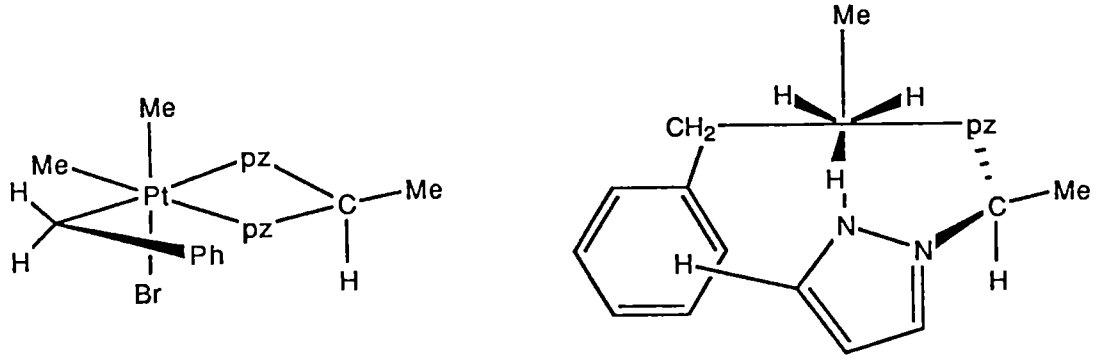


Figure 4.51 Conformer(B)

Assignment of either apical proton resonance to a particular conformation is difficult and uncertain, however, since by comparison with $Me_3IPt(Me(H)Cpz_2)$ whose apical proton appears at 8.52 ppm, it appears that the resonance at 8.44 ppm could be assigned to the more symmetrical structure, conformer (A). In conformer (B), the complex may be slightly more puckered to accommodate the benzyl group and thus the apical proton may be more affected by the adjacent halide ligand and as a consequence is moved downfield relative to that in conformer (A).

(iii)

$Me_2Pt(H_2C(mim)pz)$

The unsymmetrical complexes $Me_2Pt(H_2C(mim)pz)$ and $Me_2Pt(H_2C(py)pz)$ react rapidly with MeI in the same fashion as $Me_2Pt(Me(H)Cpz_2)$. The ^1H NMR spectrum of $Me_3IPt(H_2C(mim)pz)$ (figure 4.52) exhibits two bridgehead proton resonances, H_A (6.65 ppm)and H_B (5.45 ppm), consistent with an orientation identical to that proposed for $Me_3IPt(Me(H)Cpz_2)$ (figure 4.43)

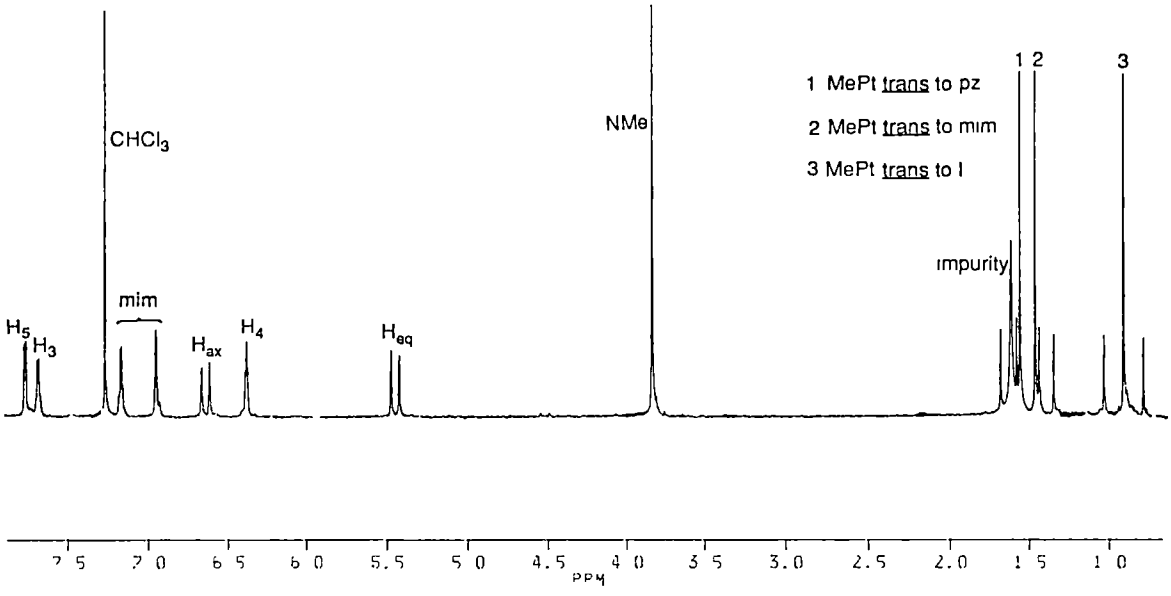


Figure 4.52 ^{1}H NMR Spectrum of $Me_3IPt(H_2C(mim)pz)$.

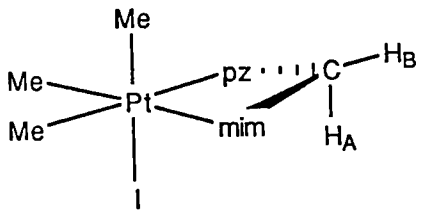


Figure 4.53

The more rapid oxidative addition, in comparison with $Me_2Pt(H_2Cpz_2)$, is expected owing to the higher donor ability of a N-methylimidazolyl ring compared with a pyrazolyl ring.

The complex $Me_3IPt(H_2C(py)pz)$ exhibits similar NMR features to that of $Me_3IPt(H_2C(mim)pz)$, except that the downfield bridgehead resonance for one proton, assigned as adjacent to the iodo group (figure 4.54) is somewhat broader than the upfield resonance.

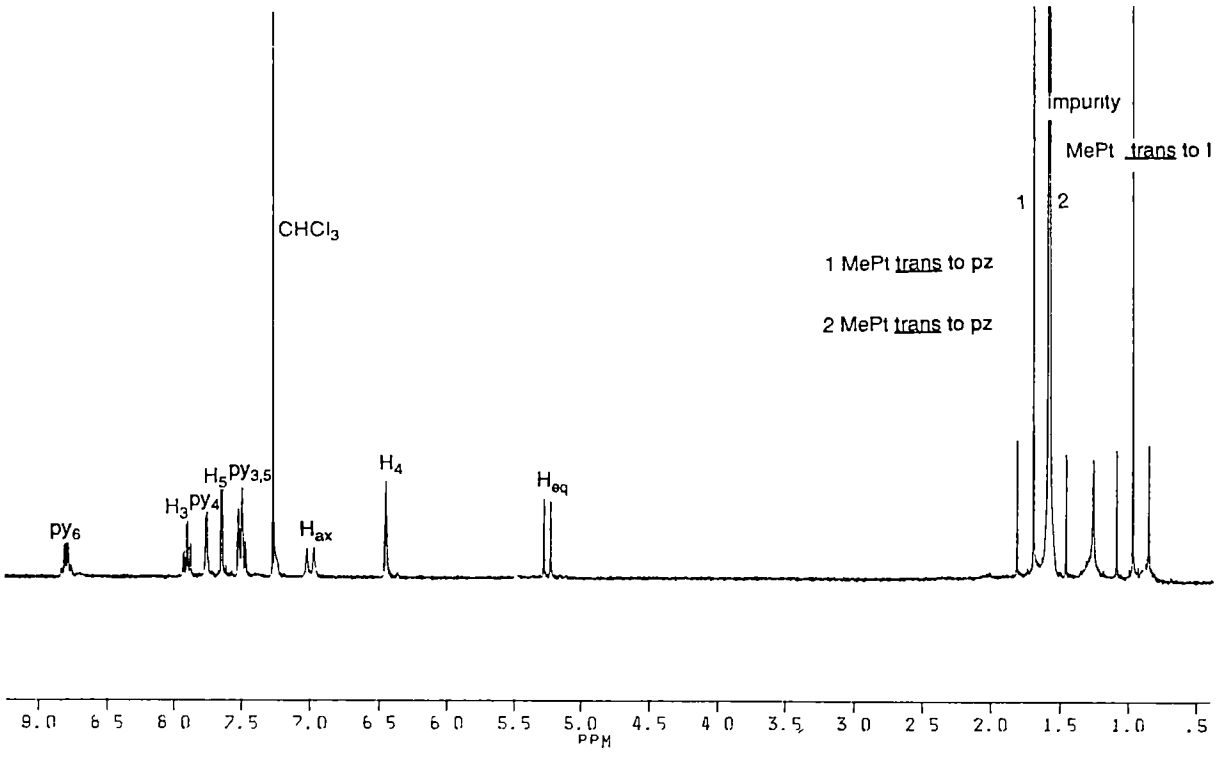


Figure 4.54 ^{1}H NMR Spectrum of $Me_3IPt(H_2C(py)pz)$.

On heating, the broadened apical proton resonance sharpens considerably, but still does not match the other apical resonance. If an acetate group is substituted for the iodide, the bridging protons exhibit similar doublets, with the axial proton resonance adjacent to acetate moved upfield by 0.6 ppm, and the equatorial proton resonance moved only 0.1 ppm upfield (figure 4.55), thus consistent with assignment of the downfield resonance to the proton adjacent to iodide.

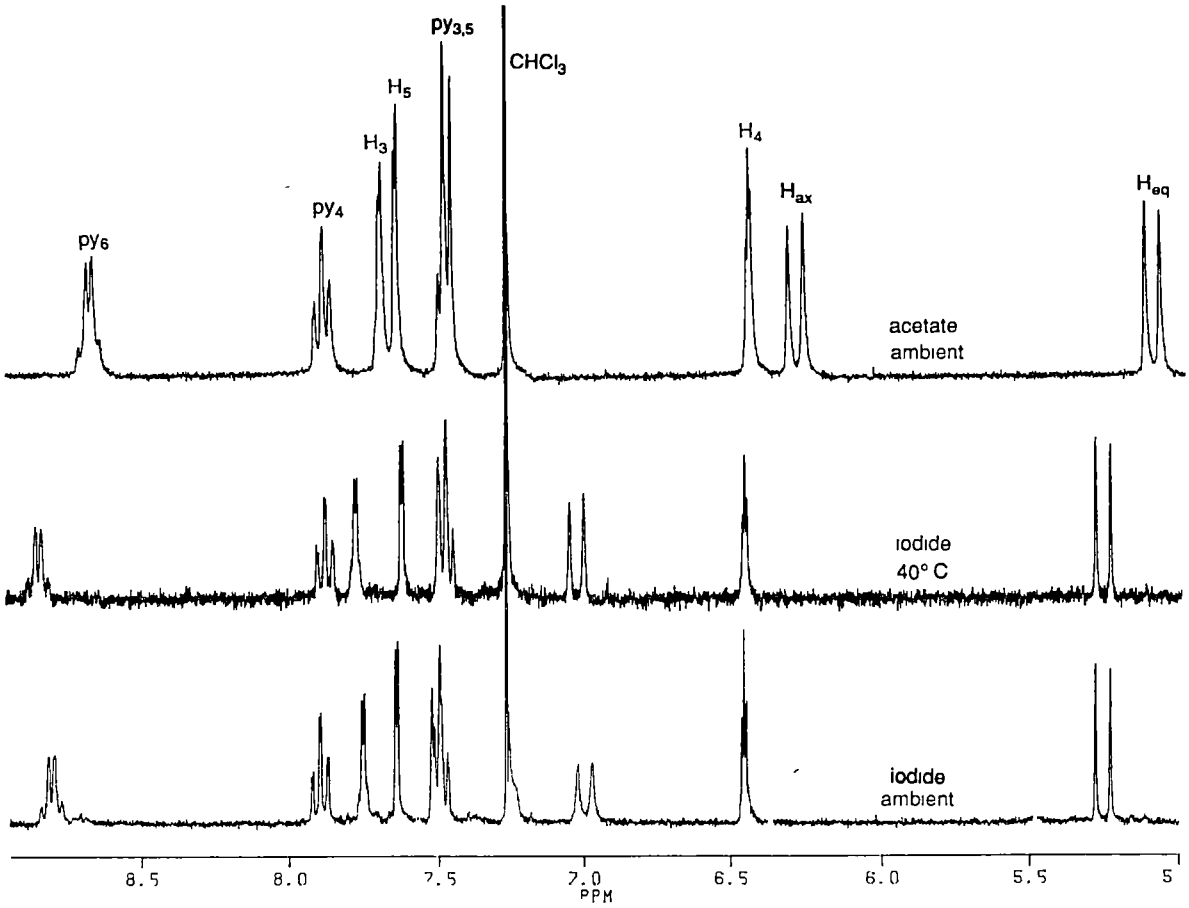


Figure 4.55 Comparison of the Aromatic Regions for the Complexes $Me_3IPt(H_2C(py)pz)$ at Ambient Temperature and 40°C, and $Me_3(OAc)Pt(H_2C(py)pz)$.

(iv)

$Me_3IPt(Me_2Cpz_2)$

If $Me_2Pt(Me_2Cpz_2)$ is dissolved in acetone, excess MeI added and the solution is allowed to stand overnight, then MeI removed (rotary evaporator) and hexane added until cloudiness, yellow microcrystals are deposited. The ^1H NMR spectrum of these crystals show the presence of MePt(IV) groups (1.72 ppm, $^2J(^1H-^{195}Pt)$ 77.34 Hz) but no ligand resonances are observed. If the reaction is repeated, excess MeI removed after 5 minutes reaction and hexane added, a white powder is obtained. The ^1H NMR of this powder in both $CDCl_3$ and D6 acetone show the presence of a Pt(IV) species, free ligand and a new MePt(IV) resonance. The ^1H NMR spectrum in $CDCl_3$ is shown (recorded 3 minutes

after dissolution). The resonances denoted by an asterisk correspond to the free ligand. Examination of the MePt region shows the presence of three separate MePt(IV) resonances.

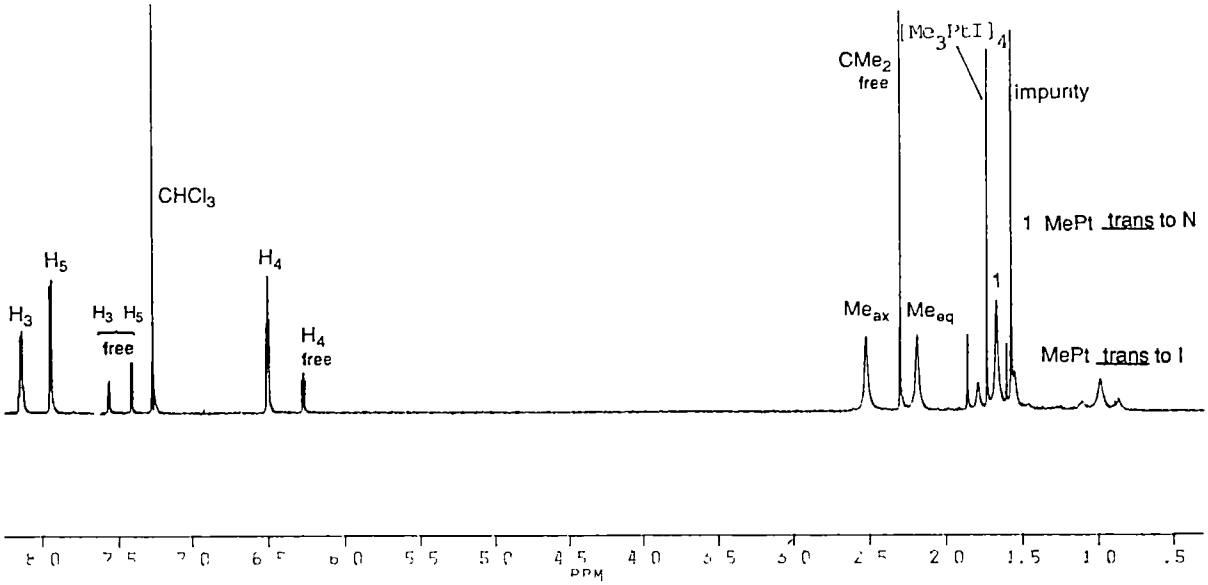


Figure 4.56 ^{1}H NMR Spectrum of $Me_3IPt(Me_2Cpz_2)$ 3 Minutes after Dissolution.

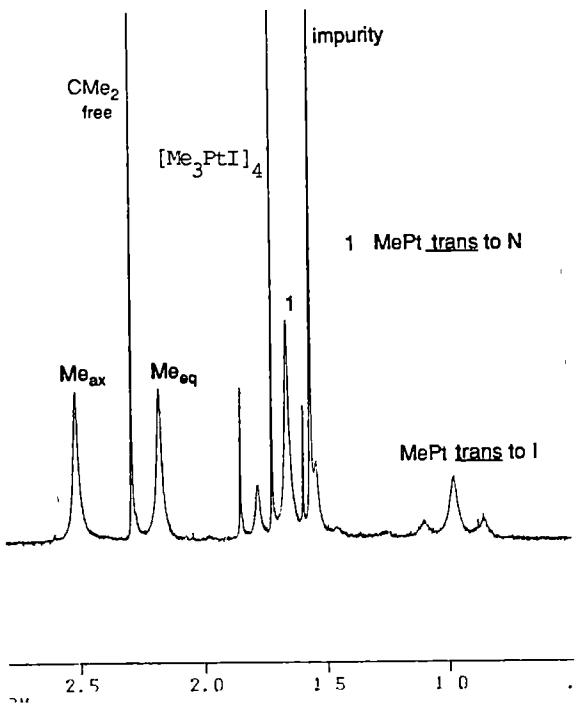


Figure 4.56B MePt Region of $Me_3IPt(Me_2Cpz_2)$.

The two broad resonances (1.66 ppm, $^{2}J(^{1}H-^{195}Pt)$ 72.83 Hz, 2H; 0.98 ppm, $^{2}J(^{1}H-^{195}Pt)$ 72.51 Hz, 1H) are consistent with methyl trans to N and methyl trans to I respectively, with the resonance at 1.72 ppm ($^{2}J(^{1}H-^{195}Pt)$ 77.34 ppm) unidentified.

If the ^{1}H NMR spectrum of this solution is recorded at successive time intervals, and eventually after strong warming (50°C, 20 minutes), spectral changes result which are consistent with decomposition of this complex and formation of a new MePt(IV) complex with equivalent methyl groups, the resonance of which is centred at 1.72 ppm (figure 4.57).

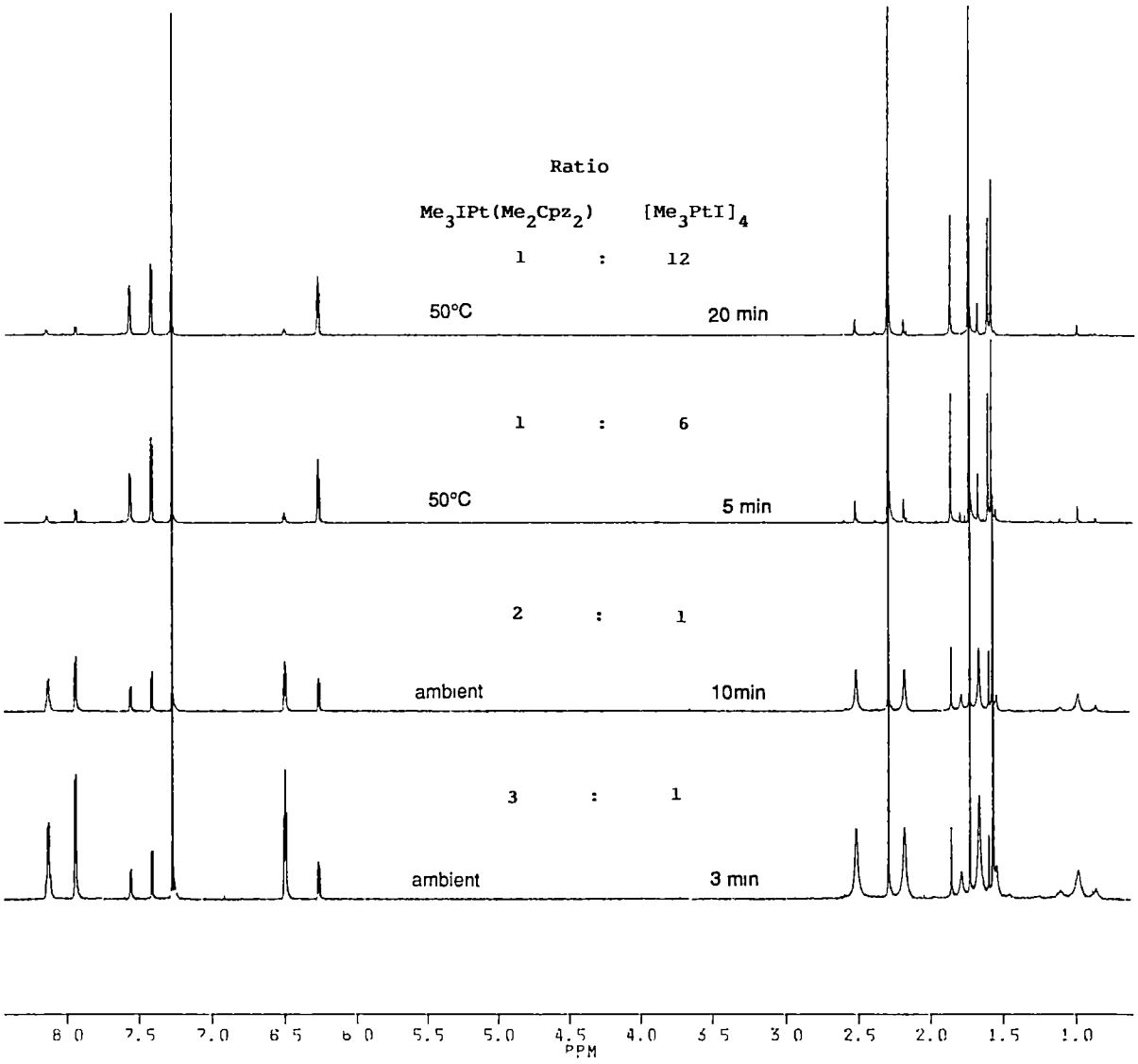


Figure 4.57 ^{1}H NMR Spectrum of $Me_3IPt(Me_2Cpz_2)$ after various time intervals and warming

These results suggest that oxidative addition of MeI to $Me_2Pt(Me_2Cpz_2)$ occurs to form the very crowded $Me_3IPt(Me_2Cpz_2)$ which undergoes decomposition in $CDCl_3$ solution. The relief of steric strain may be the major factor influencing the decomposition,

$$Me_3IPt(Me_2Cpz_2) \xrightarrow{CDCl_3} [Me_3PtI]_4 + Me_2Cpz_2 \qquad (14)$$

with the resonance at 1.72 ppm ($^2J(^1H-^{195}Pt)$ 77.34 Hz) due to $[Me_3PtI]_4$ (literature 1.73 ppm $^2J(^1H-^{195}Pt)$ 77.5 Hz, in $CDCl_3$).[21]

The conversion of $Me_3IPt(Me_2Cpz_2)$ into $[Me_3PtI]_4$ also occurs in D6 acetone, but less rapidly than in $CDCl_3$. The instability of $Me_3IPt(Me_2Cpz_2)$ in solution is in contrast to that displayed by $Me_2I_2Pt(Me_2Cpz_2)$ (made by in situ reaction of $[Me_2Pt(Et_2S)]_2/Me_2Cpz_2/I_2$) which is stable in solution. A single methyl ligand resonance is observed, which persists on cooling to -50^oC, and thus the methyl groups are in rapid equilibrium.

$Me_2Pt(Cpz_4)$ reacts rapidly with MeI to yield a $Me_3Pt(IV)$ complex. The ^1H NMR of the complex $Me_3IPt(Cpz_4)$ (figure 4.58) is interesting in that it exhibits two MePt resonances (trans to I 0.4 ppm, $^2J(^1H-^{195}Pt)$ 72.52 Hz, 6H; trans to N 1.60 ppm, $^2J(^1H-^{195}Pt)$ 73.83 Hz, 3H) thus indicating that the complex is neutral with the tridentate ligand acting in a chelating bidentate mode.

This chelating fashion causes uncoordinated pyrazolyl rings to be axial and equatorial, with the axial ring adjacent to either methyl or iodo; in keeping with previous assignments the latter is more probable.

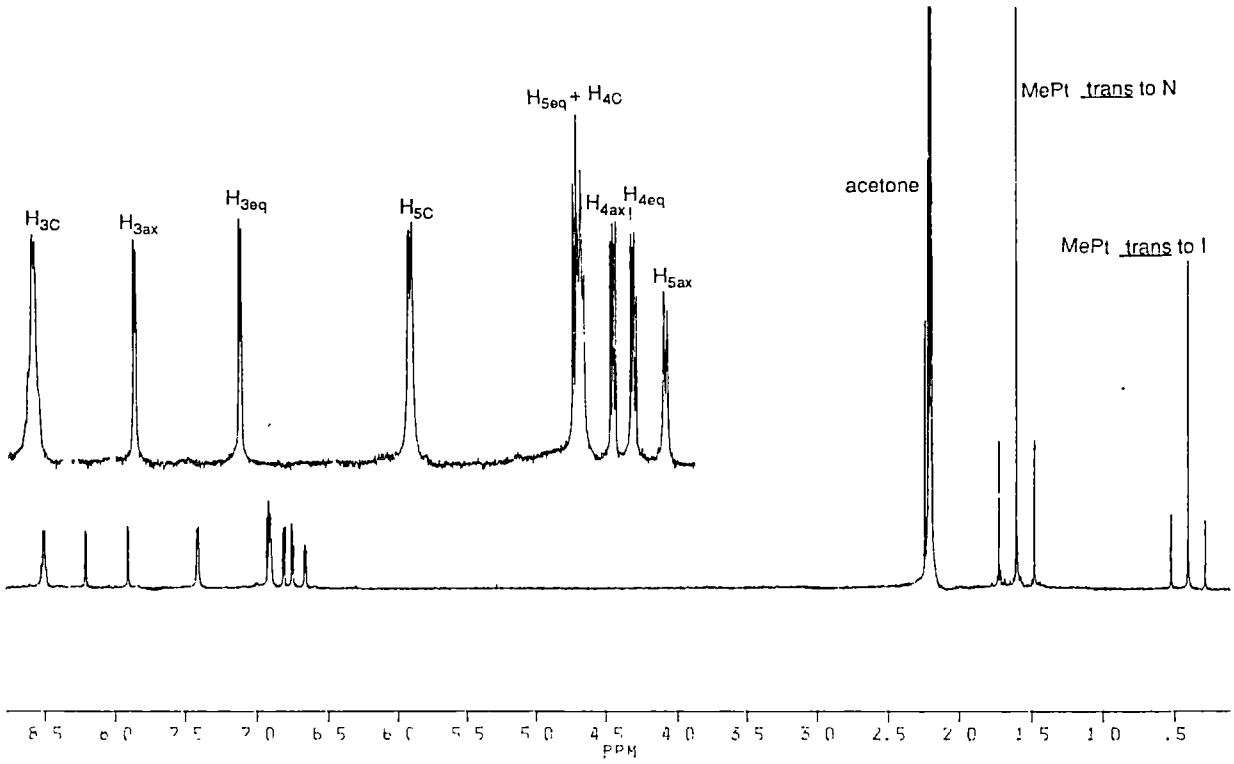


Figure 4.58 ^{1}H NMR Spectrum of $Me_3IPt(Cpz_4)$

Resonances H_C are assigned to the coordinated pyrazolyl rings (integration) with the H5 proton resonances moved upfield from the free ligand (7.72 ppm) due to shielding by the uncoordinated equatorial pyrazolyl ring. To accommodate the relatively large iodo ligand, the adjacent uncoordinated axial pyrazolyl ring is required to be 'face-on' to the iodo ligand and thus causing its H5 proton to be strongly shielded by a coordinated in-plane pyrazolyl ring, and the upfield H5 resonance at 6.65 ppm ($H5_{ax}$) is assigned to this proton. The equatorial pyrazolyl ring can have two orientations, either with its H5 proton up (N down) or the H5 proton down (N up). As the remaining H5 proton resonance is upfield of the coordinated H5 protons (which are known to be shielded) then it follows that this proton is also shielded and thus the latter orientation (N up) is assumed. Based on this assignment, the structure (figure 4.59) is proposed.

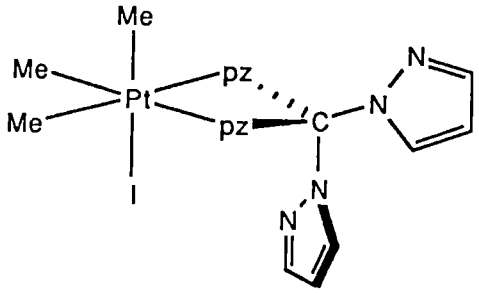


Figure 4.59

Heating $Me_3IPt(Cpz_4)$ in either $CDCl_3$ (55^oC, 30 minutes) or D6 acetone (50^oC, 30 minutes) did not affect the ^1H NMR spectrum and thus no conversion to an ionic species was observed, as would be expected since unfavourable steric interactions would be expected between the axially coordinated rings and the equatorial pyrazolyl ring.

If the reaction between $Me_2Pt(Cpz_4)$ and MeI is repeated in neat MeI a different complex is obtained. The ^1H NMR spectrum (figure 4.60) shows features consistent with metallation of a pyrazolyl ring.

The MePt region shows a singlet resonance (with platinum satellites) at 1.90 ppm ($^2J(^1H-^{195}Pt)$ 73.9 Hz) which integrates for 2 equivalent methyl groups. The aromatic region shows three distinct pyrazolyl environments, consistent with a C5 metallated pyrazolyl ring, two coordinated pyrazolyl rings and an uncoordinated equatorial pyrazolyl ring, as shown below. This ring causes the H5 proton belonging to the coordinated pyrazolyl rings to resonant well upfield of the H3 protons.

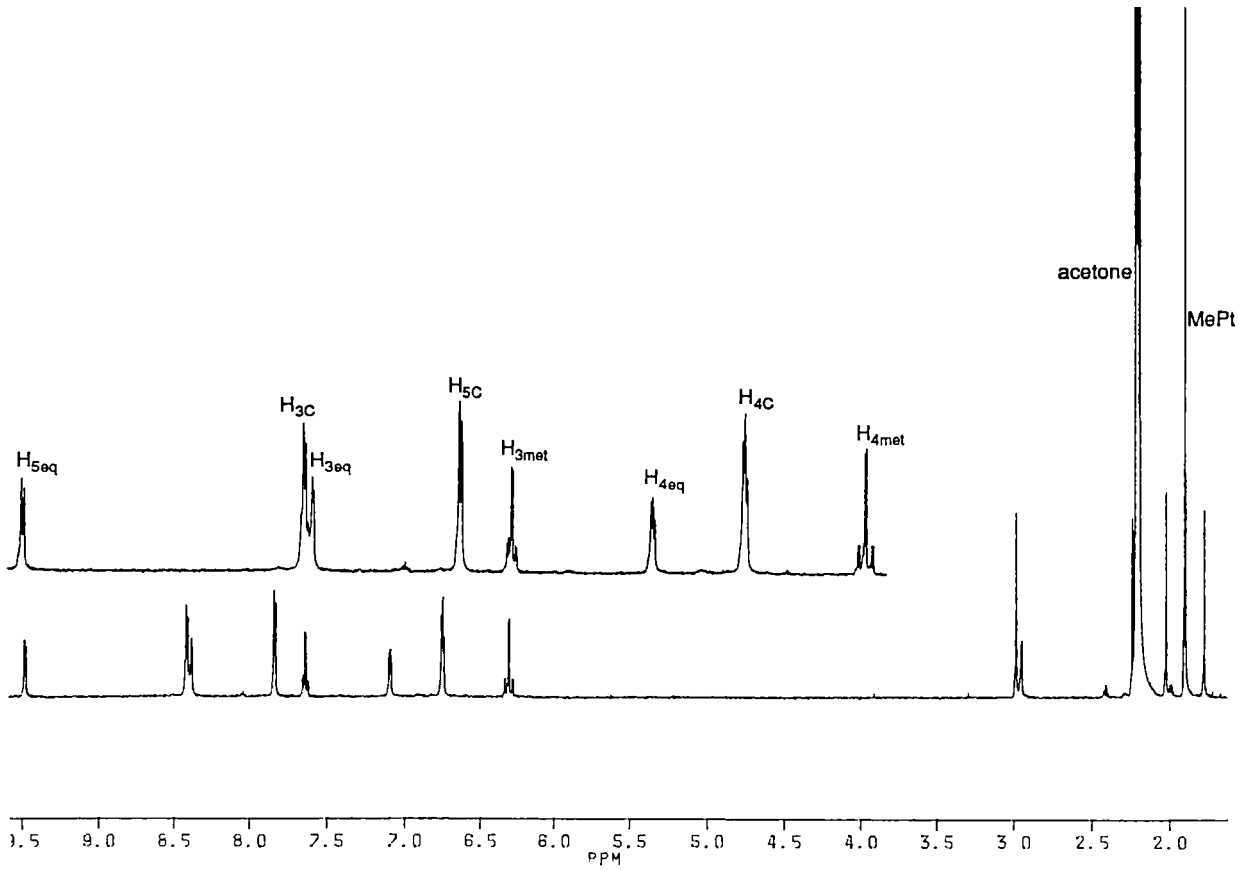


Figure 4.60 $Me_2IPt(Cpz_4)$ from $Me_2Pt(Cpz_4)$ + neat MeI

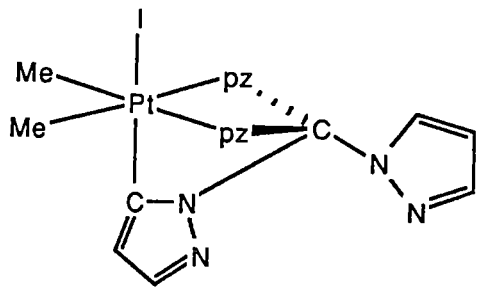


Figure 4.61

The ligand $H_2C{=}C(CH_2pz)_2$ reacts with $[Me_2Pt(Et_2S)]_2$ in refluxing acetone to produce a dark oil on removal of acetone. Although this oil did not give consistent ^1H NMR spectra, the complex is assumed to have the formula $Me_2Pt(H_2C{=}C(CH_2pz)_2)$ with the pyrazolyl rings of the ligand N coordinated. Molecular models indicate that interaction of the olefin group with platinum is feasible.

MeI reacts with '$Me_2Pt(H_2C{=}C(CH_2pz)_2)$' in acetone solution, from which a yellowish microcrystalline solid can be obtained by addition of hexane after removal of the excess MeI. A ^1H NMR spectrum (figure 4.62) shows the presence of three methyl resonances, in 1:1:1 ratio, with appropriate coupling constants for platinum(IV). The complex is non-conducting in acetone, and the iodo group is assumed to be coordinated to platinum with the alkene group uncoordinated.

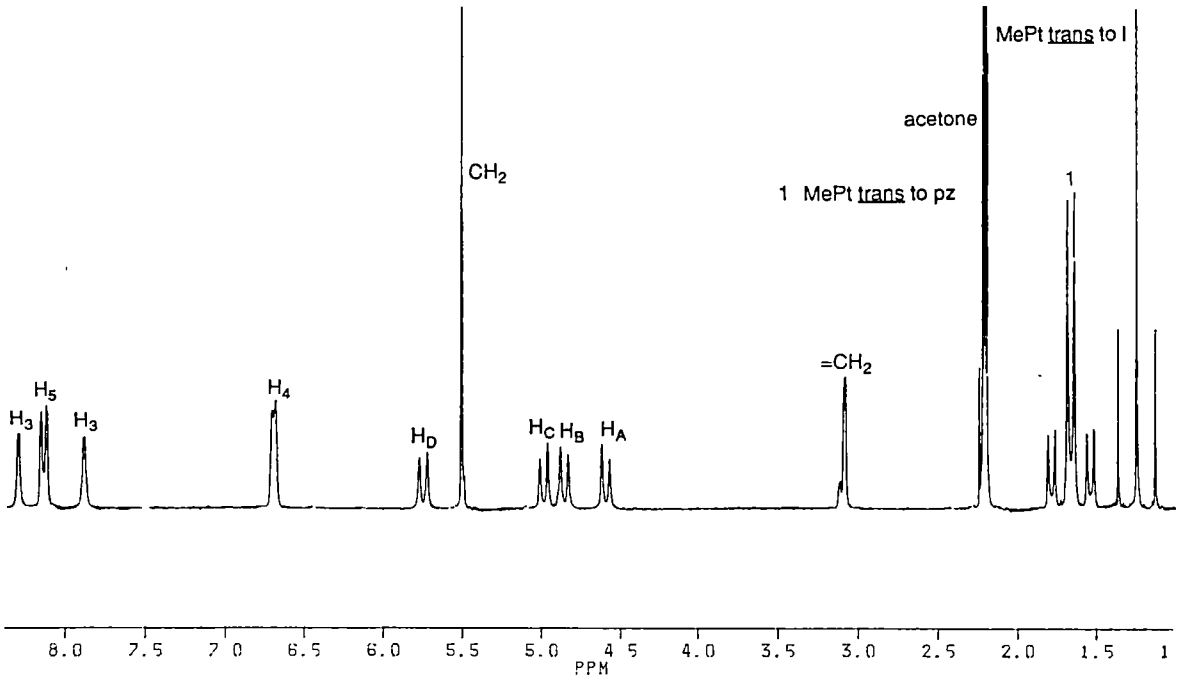


Figure 4.62 ^1H NMR Spectrum of $Me_3IPt(H_2C{=}C(CH_2pz)_2)$

The broadness of signals is assumed to be associated with motion of the alkene ligand.

Upon cooling to 0^oC, the spectrum becomes slightly sharper.

In addition to three MePt resonances (MePt at 1.24 ppm, $^2J(^1H-^{195}Pt)$ 69.69 Hz, trans to I), two pyrazolyl ring environments are observed, together with four methylene proton environments. A COSY spectrum shows connectivity between methylene protons A and C ($^2J(^1H-^1H)$ 14.80 Hz), and between B and D ($^2J(^1H-^1H)$ 14.86 Hz). The structure which most readily accounts for this spectrum requires the symmetrical ligand to be distorted with the pyrazolyl rings forming different dihedral angles with the platinum square plane, in order to

accommodate the 8 membered N,N chelate ring formed.

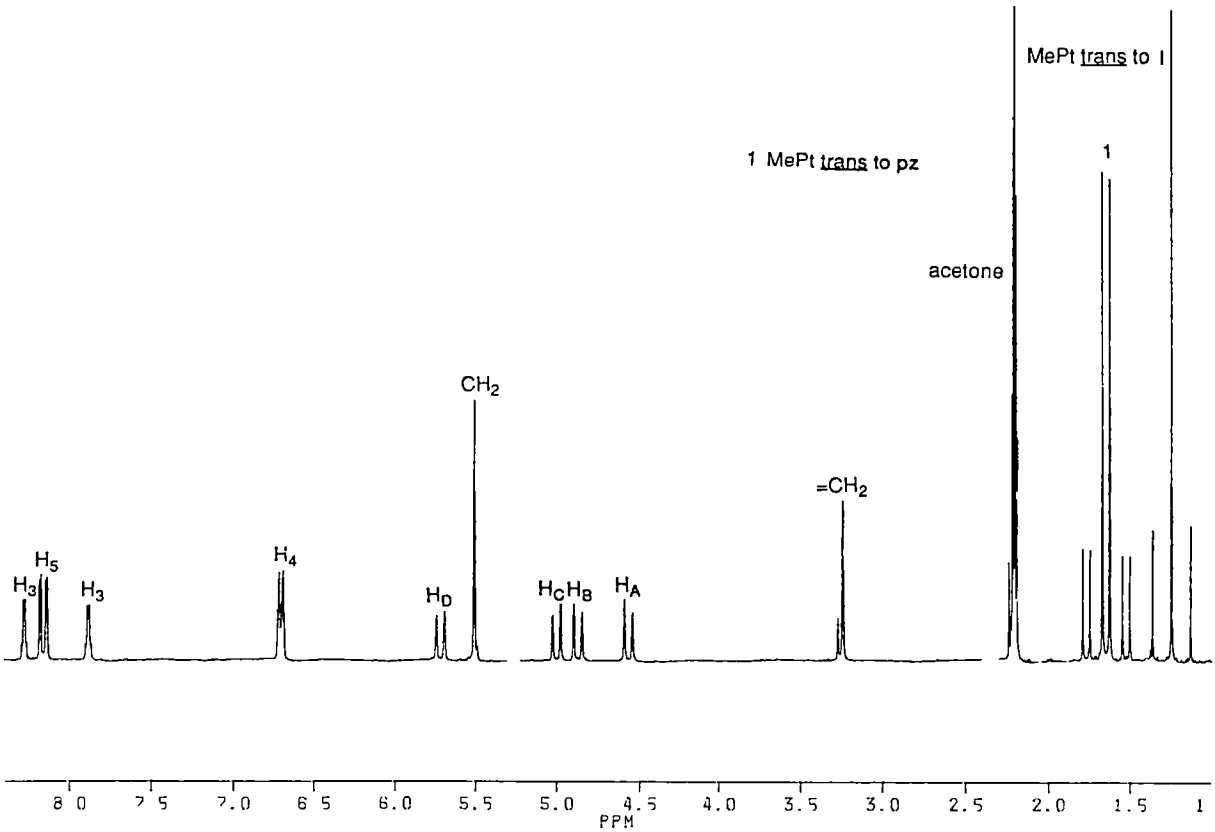


Figure 4.62 B 1H NMR Spectrum of $Me_3IPt(H_2C{=}C(CH_2pz)_2)$ at 0^oC

This orientation places a proton of one methylene group, assigned H_A, over a pyrazolyl ring and it is thus shielded, while a proton of the other methylene group, assigned H_D, is required to be in close proximity to the axial iodo group. The olefinic protons are well removed from the influence of the coordination centre, and exhibit coincident resonances at ~ 3.3 ppm.

$[Me_2Pt(Et_2S)]_2$ + L + MeI (L= bidentate ligand)

If a stoichiometric amount of $[Me_2Pt(Et_2S)]_2$ and ligand are dissolved in dry acetone, excess MeI (x5) added and the solution stirred for 10 minutes, excess MeI removed and hexane added dropwise, a white microcrystalline solid is deposited.

With bidentate ligands simple neutral $Me_3Pt(IV)$ complexes are formed. For example, with L = $H_2C(mim)pz$ the complex $Me_3IPt(H_2C(mim)pz)$ is formed which exhibits a ^1H NMR spectrum consistent with the structure shown in figure 4.53. In this complex all methyl groups are non-equivalent as they are <u>trans</u> to different ligands.

If the ligand $Ph(H)Cpz_2$ is used in the reaction in place of the less sterically demanding $H_2C(mim)pz$, an analogous $Me_3Pt(IV)$ complex, $Me_3IPt(Ph(H)Cpz_2)$, is formed, however this complex exhibits variable temperature NMR behaviour. At room temperature the ^1H NMR spectrum exhibits two MePt resonances in the ratio 2:1 (figure 4.63), with the upfield resonance (Me <u>trans</u> to I) being somewhat broadened.

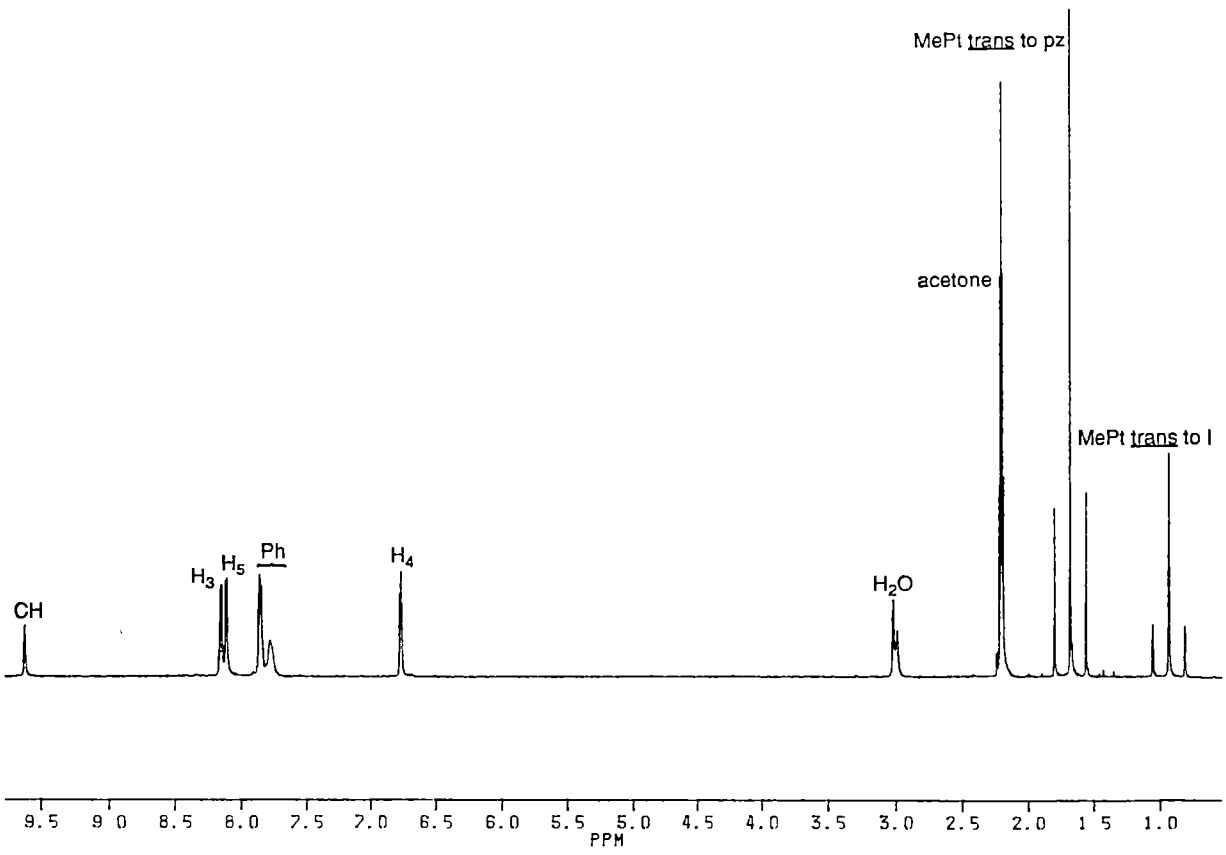
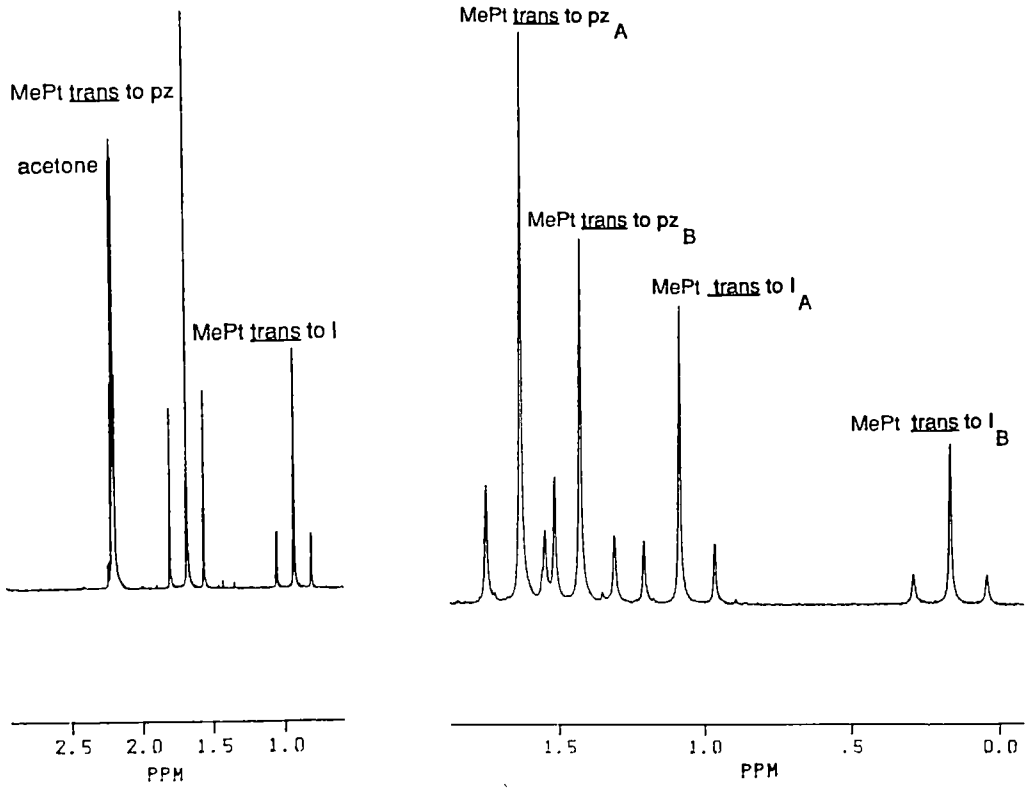


Figure 4.63 ^1H NMR Spectrum of $Me_3IPt(Ph(H)Cpz_2)$.

On cooling to -50^oC four MePt resonances are observed in the ratio 6:3:2:1 (figure 4.63B) suggesting a mixture of two isomers in

the ratio 3:1 (figure 4.64).

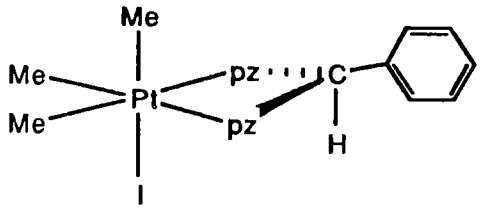


A) Ambient B) $-50^{o}C$

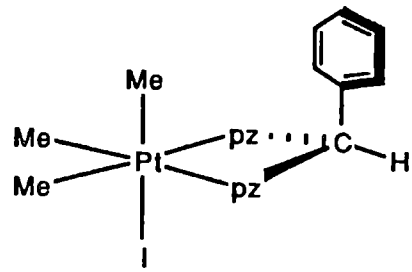
Figure 4.63 B MePt Region of $Me_3IPt(Ph(H)Cpz_2)$ at A) Ambient Temperature and B) $-50^{o}C$.

The minor isomer appears to contain the phenyl group in the axial position, adjacent and facial to a methyl group, causing strong shielding of this methyl group which is assigned to the MePt resonance (trans to I) at 0.19 ppm ($^{2}J(^{1}H-^{195}Pt)$ 74.04 Hz). The major isomer has MePt resonances at 1.09 ppm ($^{2}J(^{1}H-^{195}Pt)$ 72.63 Hz) (trans to I) and 1.65 ppm ($^{2}J(^{1}H-^{195}Pt)$ 71.89 Hz).

At this temperature the aromatic resonances are not well resolved and individual resonances cannot be assigned on the basis of coupling constant values. However, in conformer A the equatorial phenyl ring would shield both pyrazolyl H5 protons and these would be expected to occur well upfield in comparison to unshielded H5 protons.



Major Isomer (A)



Major Isomer (B)

Figure 4.64

Reaction of Me_2PtL Complexes with CD_3I

Oxidative addition reactions of CD_3I with Me_2PtL (L = bidentates, tridentate which do not metallate) complexes were carried out in order to determine whether the addition was specific or whether scrambling of alkyl ligands occurred.

Thus, CD_3I was added to D6 acetone solutions of the complexes in an NMR tube, and their ^1H NMR spectra recorded after approximately 2 minutes. The spectra obtained were identical to those from MeI addition, except that MePt resonances were of lower integration but retaining the same relative integration with each other, indicating that scrambling of Me and CD_3 groups has occurred.

Reaction of CD_3I with the Me_2PtL complex of the tridentate ligand $HC(thio)pz_2$, which does not metallate upon reaction with alkyl halide, also exhibits scrambling.

4.6 $Ph_2Pt(IV)$ Complexes

$Ph_2Pt(HCpz_3)$ reacts rapidly with a slight excess of MeI in acetone, and on dropwise addition of hexane a microcrystalline solid is deposited. The product forms a conducting solution in acetone (= 91 $^{-1}$ cm^2 $mole^{-1}$), and its ^1H NMR spectrum (figure 4.65) shows a single MePt resonance with $^2J(^1H-^{195}Pt)$ appropriate for platinum(IV) (73 Hz) trans to N.

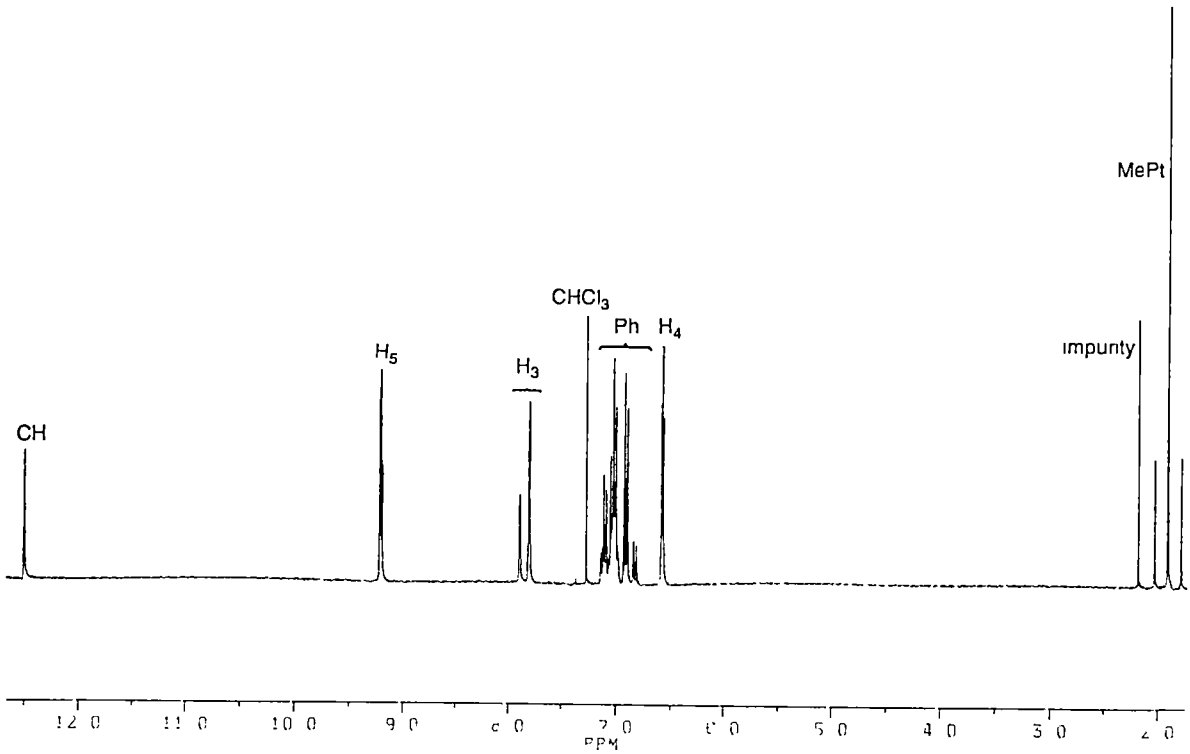


Figure 4.65 ^{1}H NMR Spectrum of $[Ph_2MePt(HCpz_3)]I$

The spectrum also exhibits inequivalent pyrazolyl ring resonances in the ratio 2:1, although the resonances of the H4 protons are coincident at 6.58 ppm. The furthest downfield H3 resonance (7.90 ppm) is assigned to the unique pyrazolyl ring , while the upfield H5 resonance (9.19 ppm) is also assigned to this ring (integration, COSY). The phenyl resonances are complicated, but, in comparison with the substrate $Ph_2Pt(HCpz_3)$, the order of phenyl ring resonances are reversed, with the 2,6-phenyl protons now furthest upfield.

The large downfield shift of the apical proton (12.5 ppm) compared with its position in the parent complex $Ph_2Pt(HCpz_3)$ (9.4 ppm), is consistent with the formulation as a cationic complex.

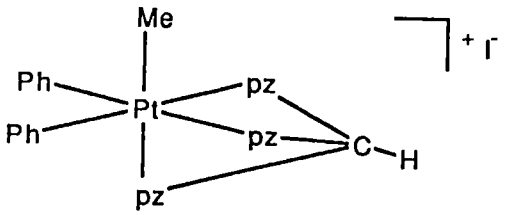


Figure 4.66

Unlike its $Me_2Pt(II)$ analogue $Me_2Pt(HCpz_3)$, $Ph_2Pt(HCpz_3)$ did not metallate on addition of MeI.

Ethyl iodide oxidatively adds to $Ph_2Pt(HCpz_3)$ in an analogous fashion to form $[Ph_2(Et)Pt(HCpz_3)]I$ ($\Lambda = 86\ \Omega^{-1}\ cm^2\ mole^{-1}$). The ^1H NMR spectrum in $CDCl_3$ (figure 4.67) (although soluble in acetone D6, part of the ethyl resonance is obscured) shows a 2:1 pyrazolyl environment for all protons, with the large downfield shift of the apical proton (12.5 ppm) again indicative of cation formation.

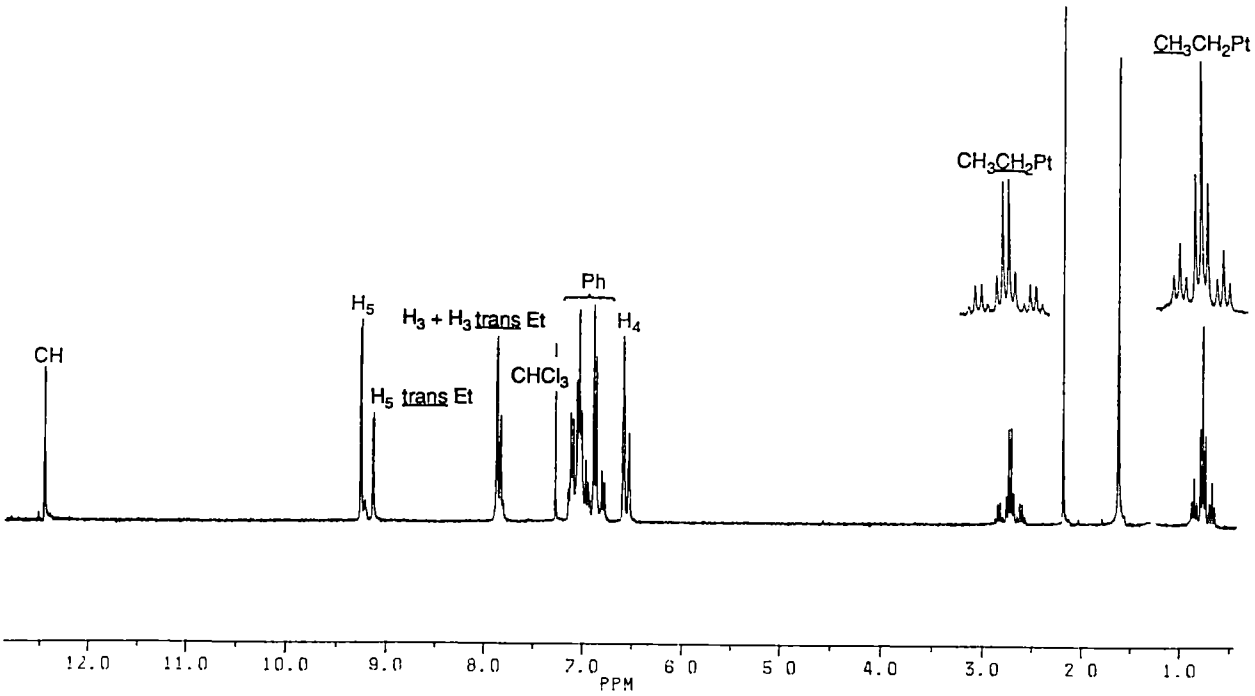


Figure 4.67 ^1H NMR Spectrum of $[Ph_2(Et)Pt(HCpz_3)]I$.

As in the product obtained by the oxidative addition of MeI to $Ph_2Pt(HCpz_3)$, the order of phenyl resonances is reversed on oxidation, with the 2,6-protons now occurring downfield from the 3,4,5 resonances. Iodoethane reacted readily with $Ph_2Pt(HCpz_3)$ in acetone over one hour to yield $[Ph_2(Et)Pt(HCpz_3)]I$, in contrast with $Me_2Pt(HCpz_3)$ for which reflux with EtI in acetone was required for completion of reaction. This difference in reactivity may be

associated with the insolubility of $Me_2Pt(HCpz_3)$ in acetone, since $Me_2Pt(bipy)$ reacts faster than $Ph_2Pt(bipy)$ with methyl iodide.[22]

$Ph_2Pt(HCpz_3)$ also reacts readily with propargyl bromide to yield a mixture of allenyl and alkynyl cationic complexes (Λ = 77 Ω^{-1} cm^2 $mole^{-1}$) (which could not be separated by fractional crystallization) with the ratio approximately 3:1 deduced from the ^1H NMR resonances of the allenyl and alkynyl protons.

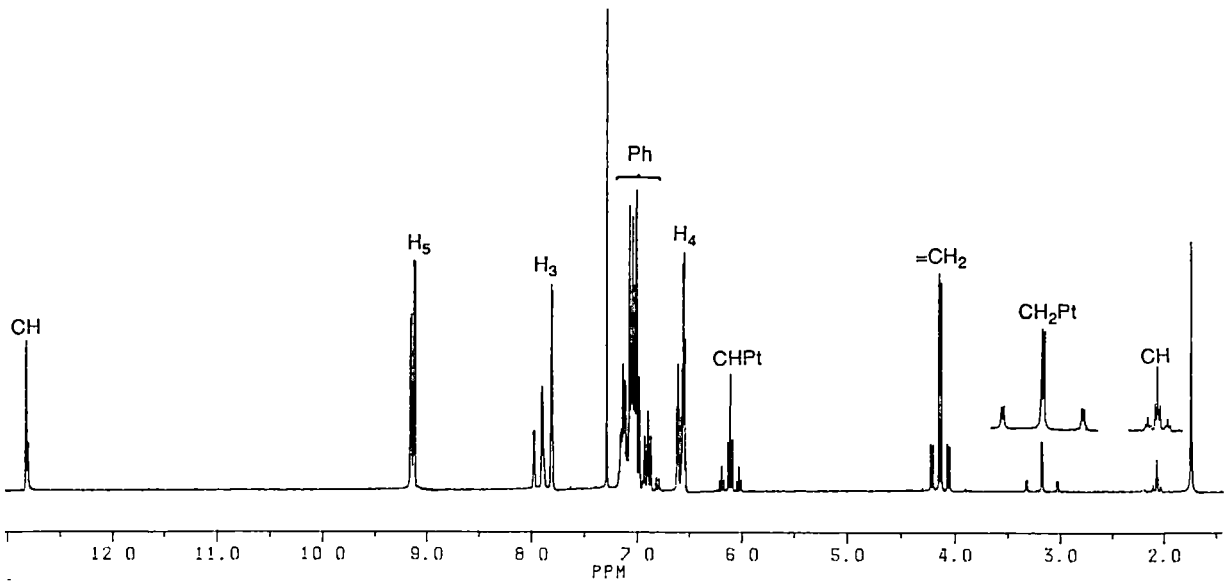


Figure 4.68 ^1H NMR Spectrum of the Product from $Ph_2Pt(HCpz_3)$ + Propargyl Bromide

Essentially the same features are observed in acetone D6, but the ratio of allenyl : alkynyl complexes is now approximately 5:1.

An infrared spectrum of a solid sample (KBr disc) exhibits absorptions characteristic of both allenyl and alkynyl groups.

$Ph_2Pt(HC(mim)pz_2)$ reacts rapidly with MeI in acetone, to form a microcrystalline solid on addition of hexane. The ^1H NMR spectrum (see experimental) in $CDCl_3$ (insoluble in acetone D6) shows a methyl resonance indicative of a platinum(IV) species (1.87 ppm, $^2J(^1H-^{195}Pt)$ 73.26 Hz), pyrazolyl resonances in 2:1 ratio and with a molar

conductivity of Λ = 78 Ω^{-1} cm^2 $mole^{-1}$, the structure below is proposed.

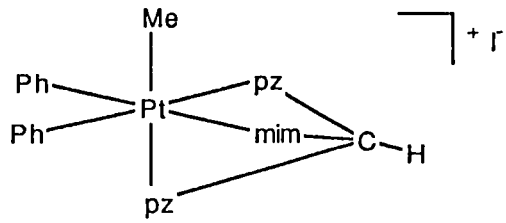


Figure 4.69

In contrast to this reaction, the complex $Ph_2Pt(HC(py)pz_2)$ gives a ^1H NMR spectrum which shows two MePt resonances (both trans to N) and two apical proton resonances in the ratio 1:2, along with a number of very complicated resonances in the aromatic region. These results indicate that a mixture of cationic isomers are formed with the methyl group trans to pyridine and pyrazolyl respectively.

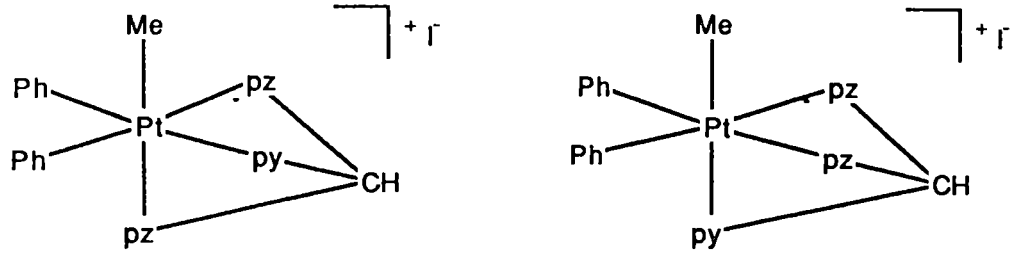
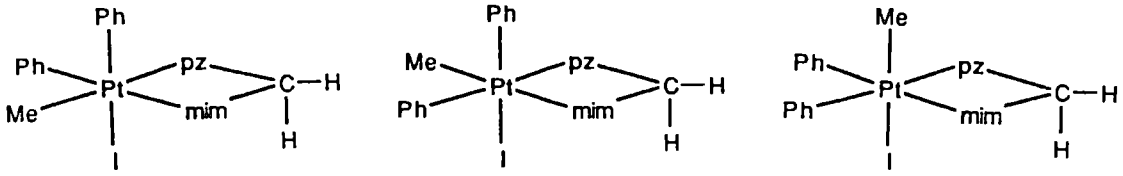


Figure 4.70

MeI also reacts with bidentate complexes of $Ph_2Pt(II)$, to yield products in which the organo groups have isomerized.

The ^1H NMR spectrum of $Ph_2MeIPt(H_2C(mim)pz)$ is very complicated and difficult to interpret. However, resonances in the aliphatic region enable probable structures to be assigned to the products of oxidative addition. Thus, MePt resonances in the ratio 2:2:1 are observed (trans to pz 2.27 ppm $^2J(^1H-^{195}Pt)$ 74.22 Hz, trans to mim 2.15 ppm $^2J(^1H-^{195}Pt)$ 71.33 Hz and trans to I 1.67 ppm $^2J(^1H-^{195}Pt)$ 70.2 Hz) together with NMe resonances in the same ratio (3.67 ppm, 3.65 ppm and 3.79 ppm) and three pairs of doublets are observed for

the apical protons. Isomerization has occurred to give a mixture of isomers with isomers A and B being present in approximately similar amounts, while isomer C is present in half this amount.



A B C

Figure 4.71

The apical ligand resonances are all similar, but the separation of the doublet pairs in isomer C is greater than in both isomer A or B (isomer A $J(^{1}H-^{1}H)$ 15.87 Hz, Δ 1.18 ppm; isomer B $J(^{1}H-^{1}H)$ 15.56 Hz, Δ 1.22 ppm; isomer C $J(^{1}H-^{1}H)$ 15.26 Hz, Δ 1.70 ppm).

$Ph_2Pt(H_2C(py)pz)$ reacts with MeI in a similar way to yield an isomeric mixture of products analogous to isomers A and B, but resonances due to the analogue of isomer C were not observed, and the ratio of isomers was 2:3 in favour of methyl trans to pyridine.

4.7 Conclusion

A large range of oxidative addition reactions of iodine and simple organohalides to $Me_2Pt(II)$ and $Ph_2Pt(II)$ complexes containing multidentate pyrazolyl based ligands has been described. The geometries of the resultant diorgano and triorganoplatinum(IV) complexes depends upon the mode of coordination of the ligand in the platinum(II) substrate, ligand denticity and in some cases the reaction conditions. Ligand geometries found include N_2, N_3, NC^- and N_2C^-.

In situ reactions between $Me_2Pt(II)$ substrate, ligand and electrophile yield neutral bidentate chelate complexes in the case of iodine, but triorgano platinum(IV) complexes in the case of RX with the complex being cationic when a tripod ligand is employed.

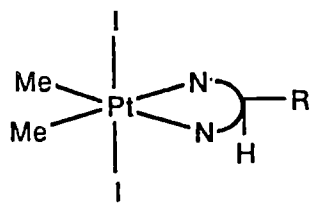
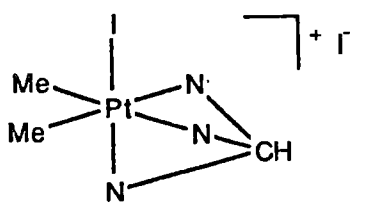
Reaction of simple preformed Me_2PtL (L = tridentate donor ligand, $HCpz_3$, $HC(mim)pz_2$) complexes with MeI causes a sequence of metallation and oxidative addition to occur resulting in the isolation of neutral N_2C^- complexes. This metallation reaction was also found to occur for the $Me_2Pt(II)$ complexes containing the ligands $Ph(H)Cpz_2$, and Cpz_4 if carried out in neat MeI but not in an acetone/MeI mixture, from which neutral monomeric bidentate Pt(IV) complexes were isolated. Substrates containing other bidentate ligands, eg. $H_2C(mim)pz$, resulted in the isolation of similar neutral complexes.

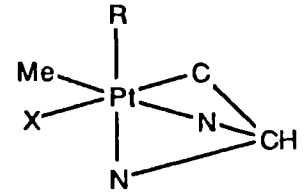
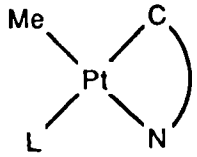
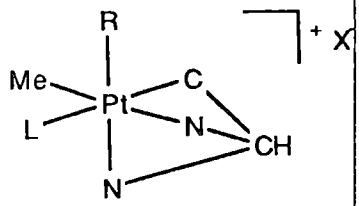
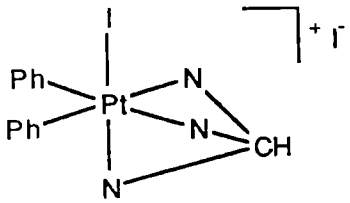
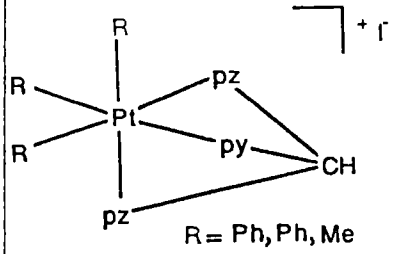
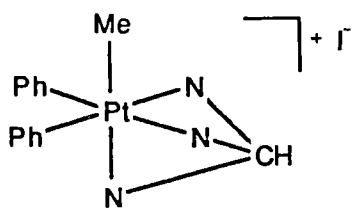
Reaction of complexes already containing a cyclometallated ligand resulted in the isolation of cationic N_2C^- products, except for the cyclometallated polymer $[MePt(HCpz_2(C_3N_2H_2)-C,N)]_n$ which gave neutral Pt(IV) species with the ligand in a N_2C^- coordination mode.

The different types of reactions for complexes containing tridentate ligands are summarised in Table 4-2.

Table 4-2

Products from Oxidative Addition of Iodine and Organohalides to Organoplatinum Complexes Containing Tridentate Ligands

Starting Material	Halide/Halogen	Product
$Me_2Pt(COD)/L$ L = $HCpz_3$ $HC(mim)pz_2$ $HC(py)pz_2$ $HC(thio)pz_2$	I_2	
	MeI	

$Me_2Pt(HCpz_3)$ $Me_2Pt(HC(mim)pz_2)$ $[MePt(HCpz_3)]_n$	MeI EtI $PhCH_2Br$	
 L = py, PPh_3 CN = Metallated $HCpz_3$ $HC(mim)pz_2$	MeI EtI $PhCH_2Br$ $CH_2{=}CHCH_2Br$	
$[Ph_2Pt(Et_2S)]_2/HCpz_3$	I_2	
$Ph_2Pt(HC(py)pz_2)$	MeI	
$Ph_2Pt(HCpz_3)$ $Ph_2Pt(HC(mim)pz_2)$	MeI EtI	

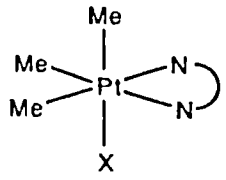
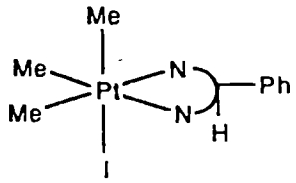
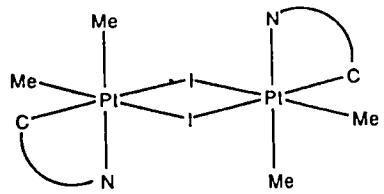
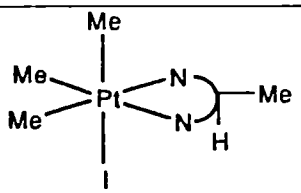
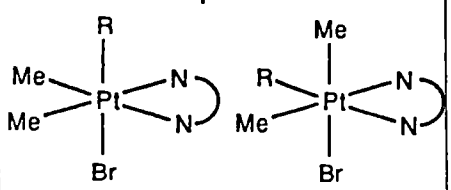
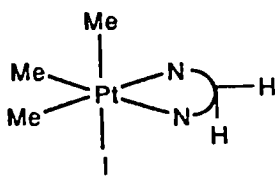
Thus, by carefully choosing the substrate and reaction conditions, complexes can be synthesized in which the ligand can be N_2 bidentate, N_3 tridentate or N_2C^- cyclometallated tripodal.

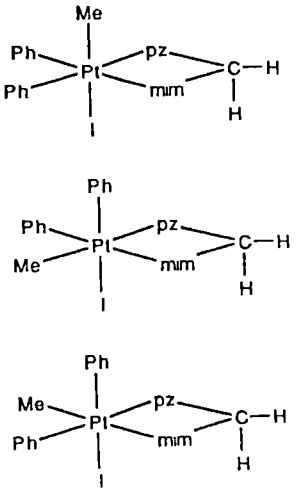
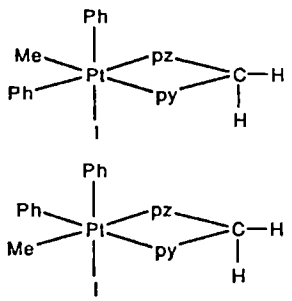
Oxidative addition to $Me_2Pt(II)$ complexes containing bidentate ligands resulted in complete scrambling of alkyl groups in the case of CD_3I addition, and mixtures of isomers in the case of $PhCH_2Br$.

General results from addition of RX to bidentate complexes are summarised in Table 4-3.

Table 4-3

Products from Oxidative Addition of Organohalides to Organoplatinum Complexes Containing Bidentate Ligands.

Complex	Electrophile	Product
$Me_2Pt(H_2Cpz_2)$	MeI	
$Me_2Pt(PhCH)(Cpz_2)$	MeI	
	neat MeI	
$Me_2Pt(Me(H)Cpz_2)$	MeI	
	$PhCH_2Br$	
$Me_2Pt(H_2C(py)pz)$ $Me_2Pt(H_2C(mim)pz$	MeI	

$Me_2Pt(Me_2Cpz_2)$	MeI	$[Me_3PtI]_4$
$Ph_2Pt(H_2C(mim)pz)$	MeI	
$Ph_2Pt(H_2C(py)pz)$	MeI	

Thus, oxidative addition reactions with bidentate ligands present in the complex give the expected triorganoplatinum(IV) product without cyclometallation except for the ligand $Ph(H)Cpz_2$ which forms a cyclometallated dimeric complex. Sterically crowded complexes, eg. $Me_2Pt(Me_2Cpz_2)$ were not stable in solution and decomposed to free ligand and $[Me_3PtI]_4$. Oxidative addition reactions of MeI with Ph_2Pt(bidentate) complexes yielded mixtures of products consistent with isomerization.

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CHAPTER 5

OXIDATIVE ADDITION to PRODUCE N_2C^- LIGAND COORDINATION

CHAPTER FIVE

PLATINUM(IV) N_2C^- TRIPODAL COMPLEXES

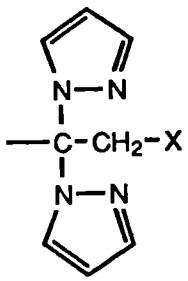
5.1 Introduction

Oxidative addition of simple organohalides, eg. MeI, to complexes containing a cyclometallated tridentate ligand has been shown to produce complexes in which this ligand acts in a N_2C^- tridentate mode (Chapter 4). As it is unusual for tridentate ligands to participate in the cyclometallation reaction, this route is not of general applicability for the formation of N_2C^- ligand coordination.

A new synthetic strategy was devised with a view to development of a simple, and more widely applicable, route to N_2C^- tridentate systems. In this approach bidentate nitrogen donor ligands containing carbon-halogen functional groups were synthesized, and the organohalide used in oxidative addition reactions with platinum(II) substrates, to obtain platinum(IV) N_2C^- complexes. Several new reagents were synthesized, with the reagents designed so that 5 or 6 membered $\overset{\frown}{N\text{-}Pt\text{-}N}$ and $\overset{\frown}{N\text{-}Pt\text{-}C}$ rings would be formed if oxidative addition were successful. This approach to Pt(IV) complexes was considered to be favourable because, if direct oxidative addition of the reagent does not occur, then coordination of the nitrogen donors may assist subsequent oxidative addition by bringing the C-X group near to platinum(II) in much the same way as coordination favours cyclometallation.

As with the investigations into cyclometallation, this approach was restricted to pyrazolyl rings as the N coordinating groups.

Use of molecular models suggested that two ligand skeletons were worthy of investigation:



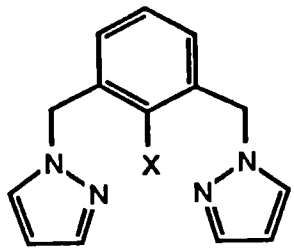


Figure 5.1

5.2 Ligand Syntheses

Ligands containing the $-Cpz_2-$ unit have previously been synthesized by a simple procedure developed by Peterson et al.,[1] involving condensation of bis(1-pyrazolyl)ketone with an appropriate ketone or aldehyde in the presence of anhydrous cobalt(II) chloride as a catalyst, eg.

$$pz_2C{=}O + (CH_3)_2C{=}O \xrightarrow{CoCl_2} (CH_3)_2Cpz_2 + CO_2 \qquad (1)$$

Although this reaction has been shown not to proceed with hexachloroacetone,[1] initial attempts with 1-chloroacetone were promising, and the reaction has been developed to give a high yield of the new reagent 1-chloro-2,2-bis(1-pyrazolyl)propane (88%).

$$(CH_3)\underset{\underset{O}{\|}}{C}CH_2Cl + pz_2C{=}O \xrightarrow{CoCl_2} CH_3Cpz_2CH_2Cl + CO_2 \qquad (2)$$

Other haloketones which react in a similar fashion include 1,3-dichloroacetone and 1,1-dichloroacetone, to yield 1,3-dichloro-2,2-bis(1-pyrazolyl)propane (equation (3)) and 1,1-dichloro-2,2-bis(1-pyrazolyl)propane (equation (4)) respectively.

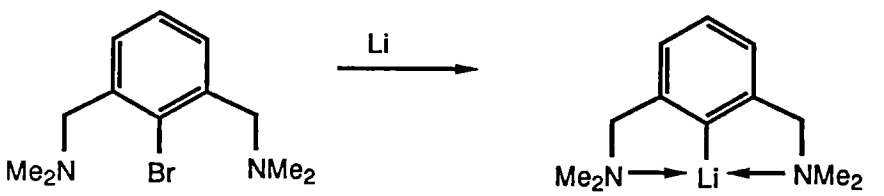
$$ClCH_2\underset{\underset{O}{\|}}{C}CH_2Cl + pz_2C{=}O \xrightarrow{CoCl_2} (ClCH_2)_2Cpz_2 + CO_2 \qquad (3)$$

$$CH_3\overset{\overset{O}{\|}}{C}CHCl_2 + pz_2C{=}O \xrightarrow{CoCl_2} CH_3Cpz_2CHCl_2 + CO_2 \qquad (4)$$

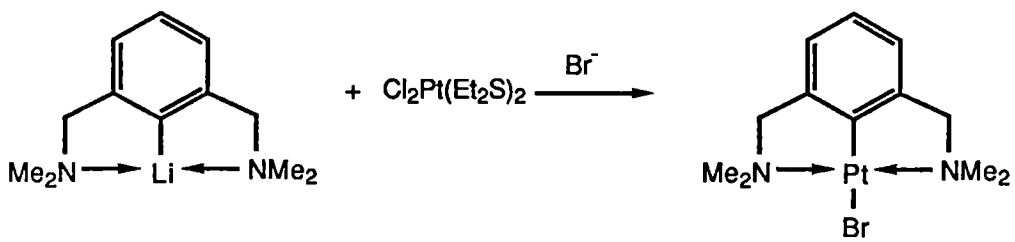
Reaction of 1-chloro-2-butanone with bis(1-pyrazolyl)ketone under various conditions resulted in the formation of black viscous oils from which the required ligand could not be isolated. Thus, by this procedure it does not seem possible to synthesize $-Cpz_2(CH_2)_nX$ ligands ($n > 2$) to potentially yield complexes containing 6 and 7 membered rings.

5.2.1 Skeletal Systems containing an Aromatic Ring

Three new arylhalide containing reagents have been synthesized, two designed as potential tripodal N_2C^- ligands and one designed as a pyrazolyl analogue of the well known planar N_2C^- system developed by van Koten et al.[2] (equations (5), (6))



(5)



(6)

Oxidative addition of MeI to the product from equation (6) does not produce a Pt(IV) complex with the ligand acting as a N_2C^- tridentate, but rather a Pt(II) complex containing a substituted arenonium ion.[3]

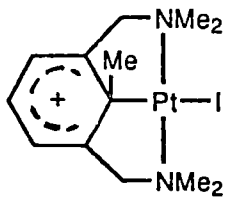
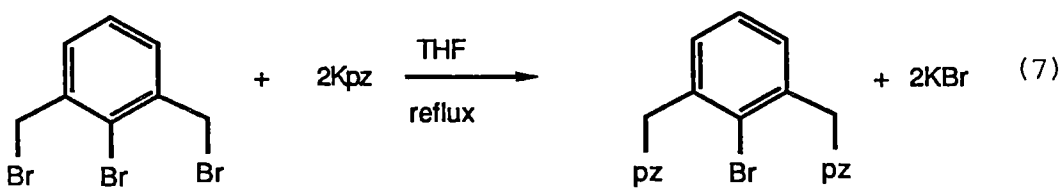


Figure 5.2

Platinum(IV) complexes of the ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ have been synthesized by oxidative addition of halogens to the complex $ClPt[C_6H_3(CH_2NMe_2)_2]$, resulting in isolation of the tetravalent complex $Cl_3Pt[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$ with the ligand acting in a tridentate mer configuration.[4]

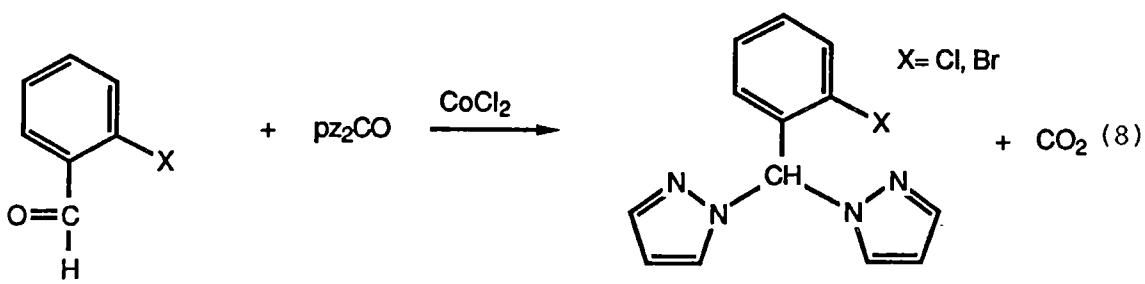
The reagent $2,6\text{-}(pzCH_2)_2C_6H_3Br$, synthesized by reaction of $2,6\text{-}(BrCH_2)_2C_6H_3Br$ with Kpz (equation (7)), exhibits a similar geometry to $2,6\text{-}(Me_2CH_2)_2C_6H_3Br$ and thus offers the possibility of forming a N_2C^- tridentate complex with dimethylplatinum(II).



(7)

In this instance, reaction with $Me_2Pt(II)$, if successful, would lead to formation of a complex containing two 6 membered chelate rings, in contrast to 5 membered rings for van Koten's ligand.

Two potential tripodal reagents were synthesized by Peterson's approach.



(8)

5.3 Platinum(IV) Complexes

5.3.1 Me_2PtLX

$Me_2Pt(IV)$ complexes of the above ligands were synthesized by reaction between $[Me_2Pt(Et_2S)]_2$ and ligand (1:2 mole ratio) in refluxing benzene, under a nitrogen atmosphere. Most of the complexes are microcrystalline and reasonably soluble in common organic solvents, thus allowing full characterization. Microanalyses and molecular weight determinations (see experimental) confirm that reaction occurs, and ^1H NMR spectra, (chemical shift and coupling constant) show the complexes to contain Pt(IV) rather than Pt(II) with the reagents as simple N,N-chelates.

$Me_2Pt(CH_2Cpz_2CH_3)Cl$

After 10 minutes reflux of a benzene solution containing $[Me_2Pt(Et_2S)]_2$ and $CH_3Cpz_2CH_2Cl$, a microcrystalline precipitate is deposited. The precipitate is soluble in warm acetone from which it can be recrystallized by ether diffusion. The ^1H NMR spectrum (figure 5.3) is best recorded in $CDCl_3$.

The single upfield Me_2Pt triplet (1.30 ppm, $^2J(^1H-^{195}Pt)$ 73.7 Hz) shows that the platinum bound methyl groups are equivalent, and thus must be in a cis arrangement. The chemical shift and coupling constant indicate that platinum is in oxidative state (IV), and the resonance at 2.38 ppm with ^{195}Pt satellites ($^2J(^1H-^{195}Pt)$ 51.4 Hz), is typical of a platinum bound methylene group. Other ligand resonances are in the expected positions, and are shifted downfield from the free ligand resonances. Of particular interest, the ligand methyl group at 2.45 ppm exhibits a $^4J(^1H-^{195}Pt)$ coupling of 5.8 Hz.

This evidence supports a structure (figure 5.4), in which the ligand is acting as a N_2C^- tripod forming 2 five membered ring chelate systems with the platinum atom.

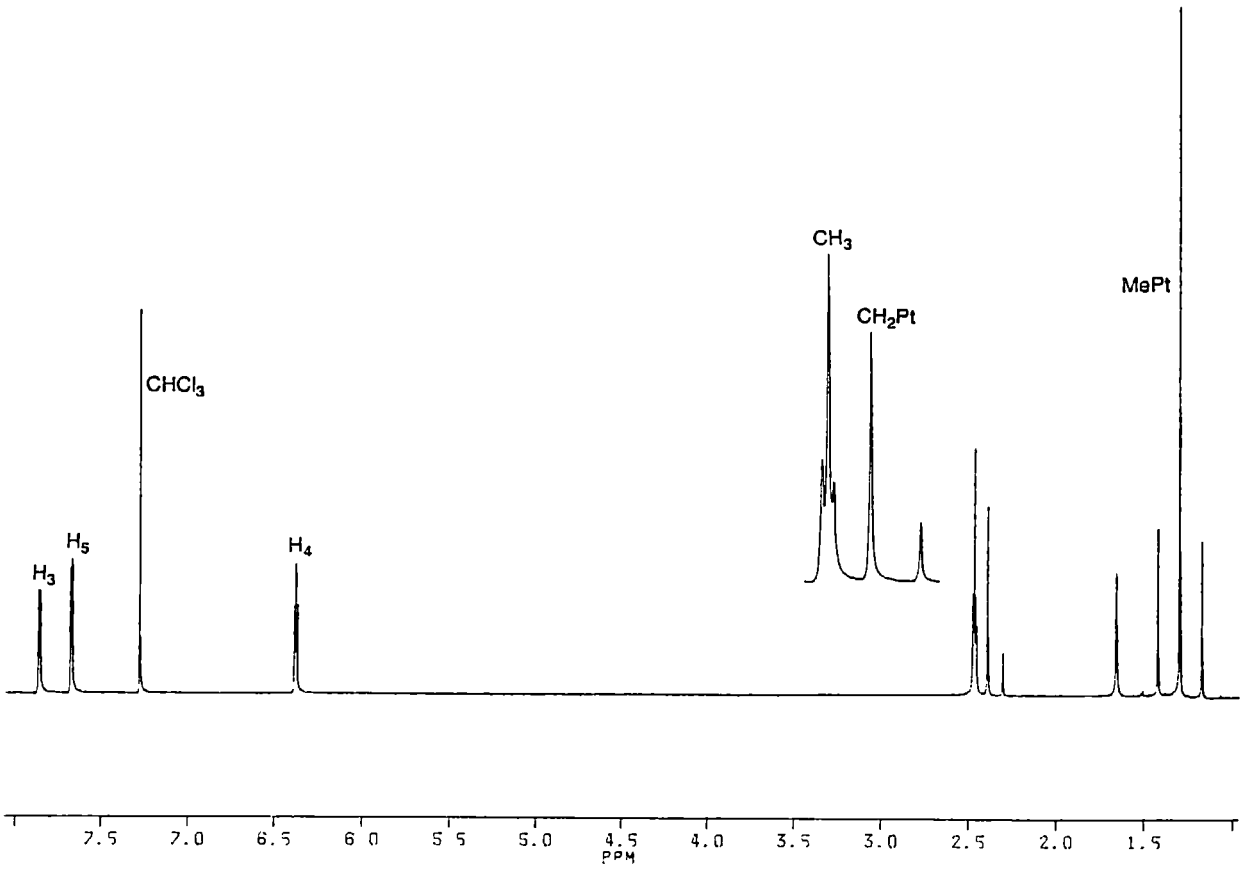


Figure 5.3 ^{1}H NMR Spectrum of $Me_2Pt(CH_2Cpz_2CH_3)Cl$ in $CDCl_3$

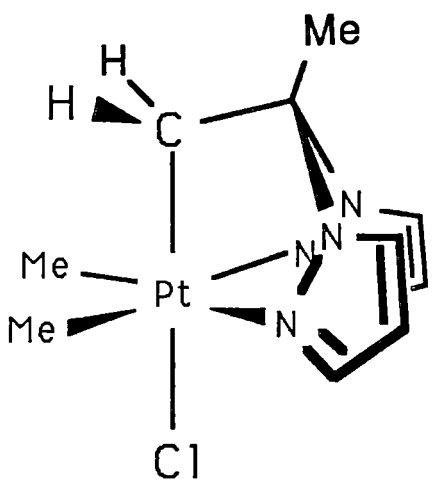


Figure 5.4 Proposed Structure of $Me_2Pt(CH_2Cpz_2Me)Cl$

The ^{13}C NMR spectrum of this complex (figure 5.5) supports the proposed structure, with two upfield platinum related resonances, MePt (-9.9 ppm) and CH_2Pt (32.5 ppm), exhibiting well defined $^1J(^{13}C-^{195}Pt)$ couplings of 693 Hz and 729 Hz respectively.

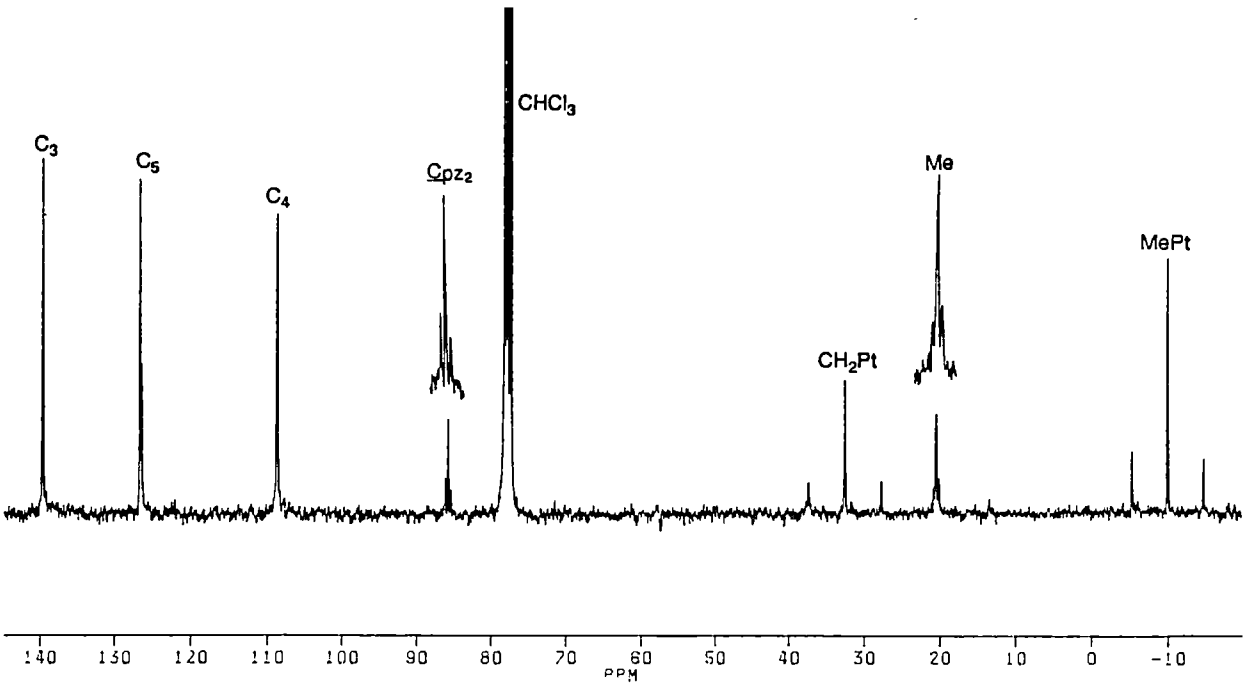


Figure 5.5 ^{13}C NMR Spectrum of $Me_2Pt(CH_2Cpz_2CH_3)Cl$.

$Me_2Pt(CH_2Cpz_2CH_2Cl)Cl$

Reaction of stoichiometric quantities of $[Me_2Pt(Et_2S)]_2$ and $(ClCH_2)_2Cpz_2$ (1:2) in warm benzene results in the isolation of a microcrystalline solid, the ^1H NMR spectrum (figure 5.6) of which suggests a structure (figure 5.7) analogous to that deduced for $Me_2Pt(CH_2Cpz_2CH_3)Cl$.

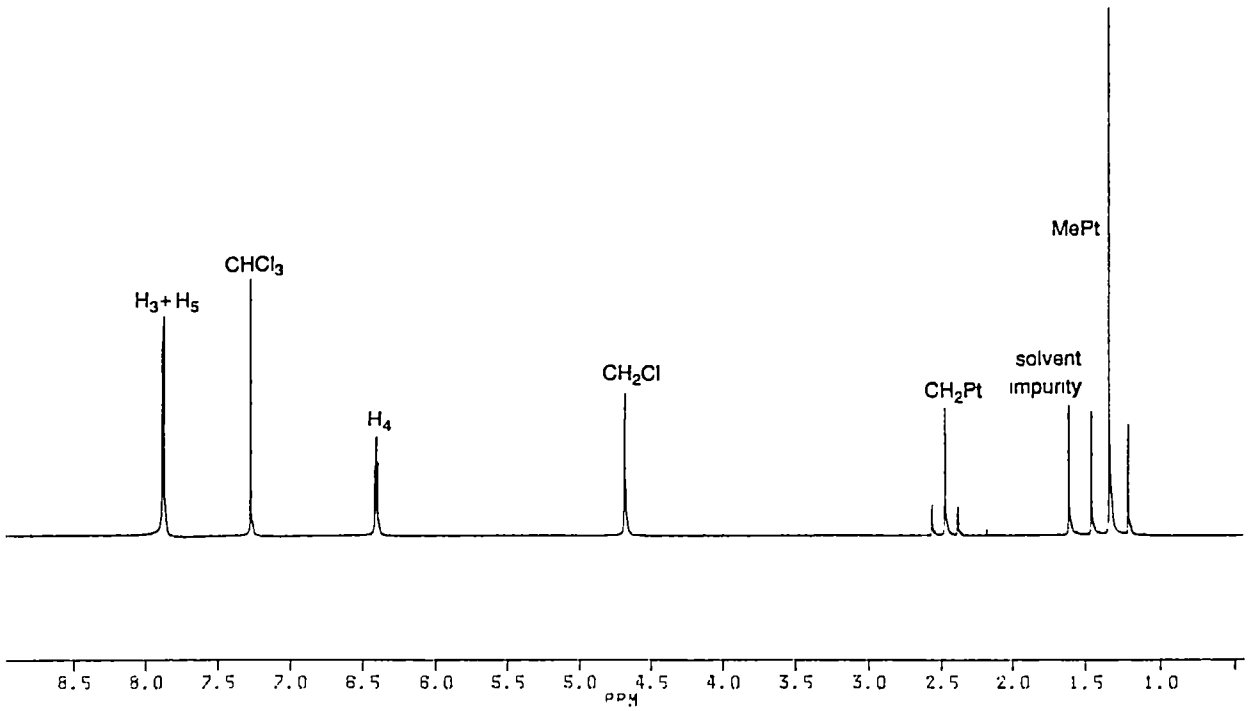


Figure 5.6 ^{1}H NMR Spectrum of $Me_2Pt(CH_2Cpz_2CH_2Cl)Cl$ in $CDCl_3$

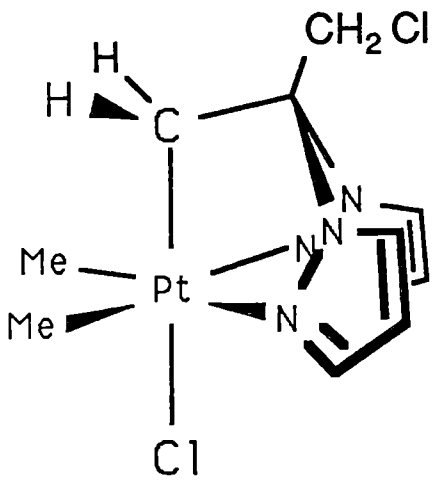


Figure 5.7

The $Me_2Pt(IV)$ resonance (1.33 ppm, $^{2}J(^{1}H-^{195}Pt)$ 75.4 Hz) and CH_2Pt resonance (2.46 ppm, $^{2}J(^{1}H-^{195}Pt)$ 54.3 Hz) are as expected, but, the bridging CH_2Cl unit exhibits a lower $^{4}J(^{1}H-^{195}Pt)$ coupling constant (2.9 Hz) in comparison to the methyl group in $Me_2Pt(CH_2Cpz_2CH_3)Cl$ (5.8 Hz), and the pyrazolyl H5 and H3 resonances are not separated by the same amount as in $Me_2Pt(CH_2Cpz_2CH_3)Cl$ (0.09

ppm c.f. 0.21 ppm respectively).

Both of these complexes would be expected to exhibit very similar ^{1}H NMR spectra as both contain a mirror plane through the apical portion of the ligand and bisecting the MePt bonds.

As these complexes appear to be the first example of complexes containing the N_2C^- unit in a tripodal orientation, except for the non-crystalline complexes of metallated $HCpz_3$ and related ligands (discussed in Chapter 4), x-ray diffraction studies were undertaken.[5] Crystals suitable for x-ray analysis were obtained by the slow vapour diffusion of ether into a saturated solution of the complex in acetone.

The two complexes have very similar structures, based on a distorted octahedral geometry for platinum(IV) with the N_2C^- ligands in a <u>fac</u> tripodal orientation (figure 5.8)

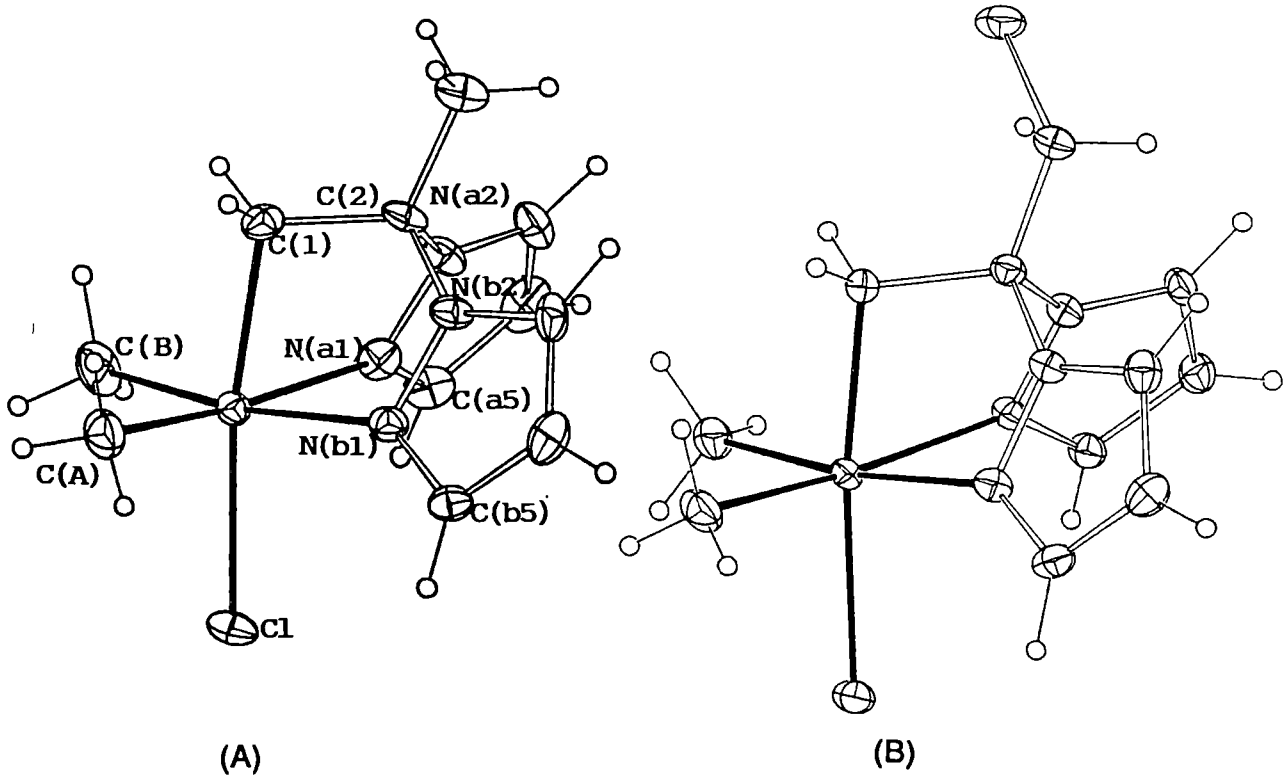


Figure 5.8 X-ray Crystallographic Structures

The main distortion from regular octahedral geometry results from the small bite angles of the tridentate, with C(1)-Pt-N and N-Pt-N angles of 78.5(2) - 82.5(4)^{o}. The chlorine atom is <u>trans</u> to the CH_2 group, and the three carbon atoms are in the expected <u>fac</u>-C_3Pt orientation.

The pyrazole rings are planar with maximum deviation from a mean plane observed for C(4) (0.015 Å) of ring B in $Me_2Pt(CH_2Cpz_2CH_3)Cl$, and the platinum atom is close to the projected planes of the rings (0.016 - 0.014 Å). In addition, the bite of the N_2C^- ligand results in smaller Pt-N(1)-N(2) angles (108.8(9) - 109.5(4)^{o}) than Pt-N-C(5) (143.4(8) - 144.6(5)^{o}), and a small value for Pt-C(1)-C(2) (101.4(6) - 102.2(4)^{o}). The MePt(IV) bond distances (2.05(1) and 2.00(1) Å for A, 2.043(7) and 2.035(9) Å for B) are within the expected bond length for a Pt-C (sp^3).

<u>$Me_2Pt(C(Cl)HCpz_2CH_3)Cl$</u>

Reaction between $[Me_2Pt(Et_2S)]_2$ and $MeCpz_2CHCl_2$ in acetone yields a clear solution after 5 minutes reflux. Prolonged reflux (15 minutes) causes no observable change. Cooling and addition of hexane until cloudiness causes a very fine crystalline solid to precipitate. The ^1H NMR spectrum of this complex, together with the proposed structure, are shown in figure 5.9.

The molecule, unlike the previous complexes, does not possess symmetry about the carbon bridging the platinum and pyrazolyl groups, and consequently two environments for MePt(IV) and the pyrazolyl groups are apparent in the ^1H NMR spectrum. Assignment of resonances to a particular pyrazolyl ring was not possible, although a COSY spectrum permitted assignment of protons within individual pyrazolyl rings.

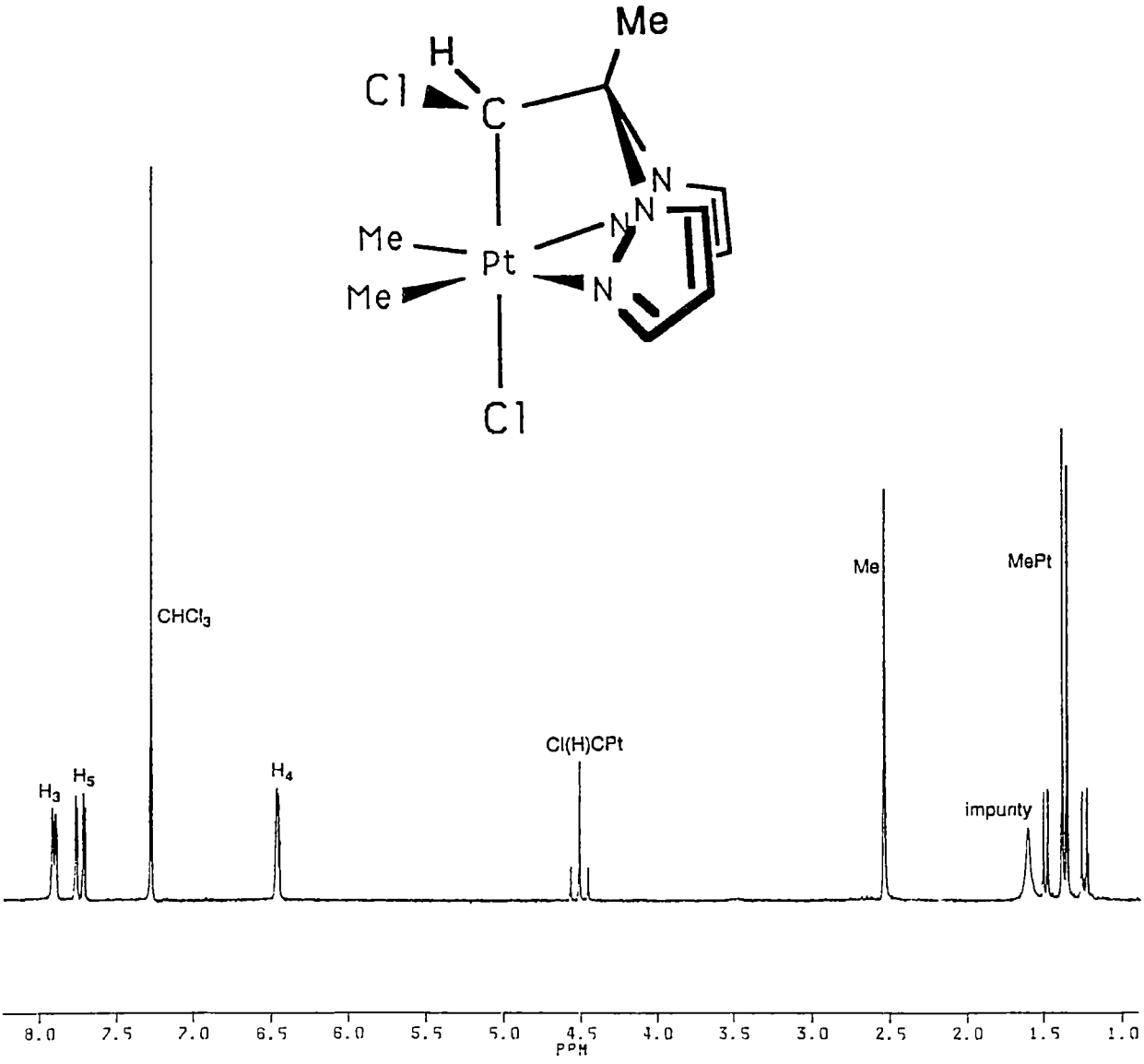


Figure 5.9 ^{1}H NMR Spectrum of $Me_2Pt(C(Cl)HCpz_2CH_3)Cl$ in $CDCl_3$ with proposed structure.

$Me_2Pt(2,6\text{-}(pzCH_2)_2C_6H_3)Br$

The product from the reaction of $[Me_2Pt(Et_2S)]_2$ and $2,6\text{-}(pzCH_2)_2C_6H_3Br$ is sufficiently soluble in $CDCl_3$ to allow its ^{1}H NMR spectrum to be recorded (figure 5.10).

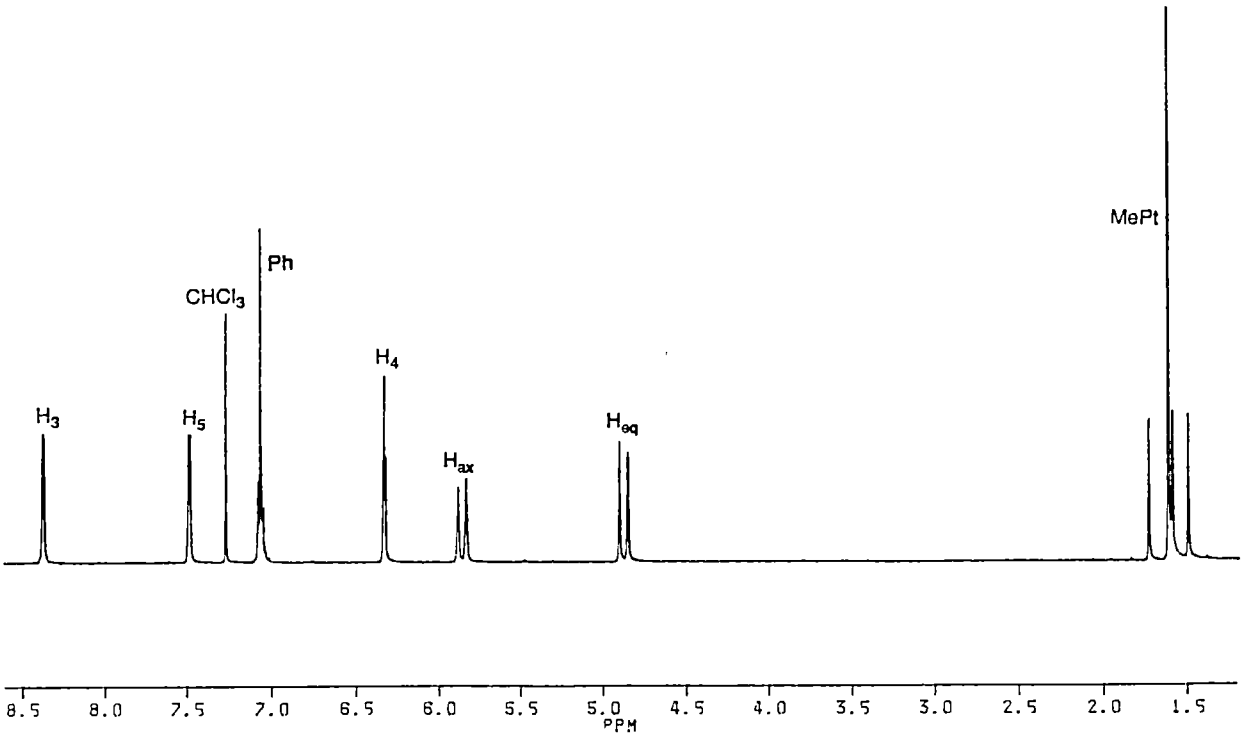


Figure 5.10 ^{1}H NMR Spectrum of $Me_2Pt(2,6\text{-}(pzCH_2)_2C_6H_3)Br$ in $CDCl_3$

The single MePt resonance (1.60 ppm, $^{2}J(^{1}H\text{-}^{195}Pt)$ 70.32 Hz), equivalent pyrazolyl environments, and equivalent methylene resonances illustrates that the complex is symmetric with a mirror plane bisecting the MePtMe bond angle. The high field methylene resonance (4.87 ppm) is assigned to the axial protons with the equatorial protons absorbing at 5.85 ppm. The H3 pyrazolyl ring protons (8.4 ppm) are moved downfield in comparison to the free ligand (7.58 ppm), and this is ascribed to them being adjacent to a bromo ligand.

The complex contains the ligand as a fac-N_2C^- tripod forming two six membered chelate rings with platinum (figure 5.11).

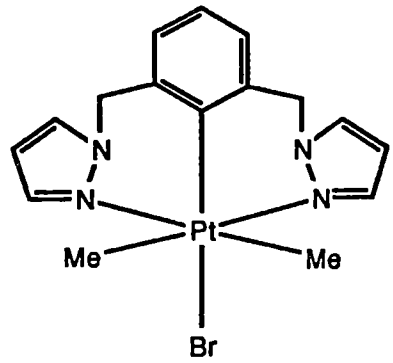
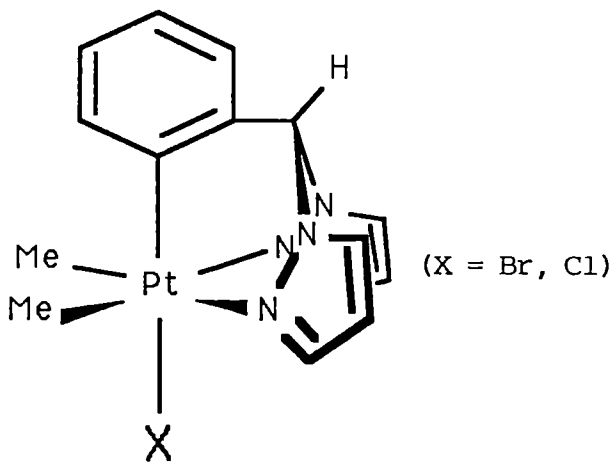


Figure 5.11

$Me_2Pt(C_6H_4(H)Cpz_2)X$ (X = Br, Cl)

The ligands $(2\text{-}XC_6H_4)(H)Cpz_2$ (X= Br, Cl) react with $[Me_2Pt(Et_2S)]_2$ in refluxing benzene to precipitate a white powder. This solid is extremely insoluble in all common organic solvents, although it does dissolve in an acetone - DMSO mixture to give a ^1H NMR spectrum (see experimental).

Although resonances are considerably broadened in the presence of DMSO, the spectrum does allow the essential features of the complex to be determined. Thus, from the chemical shift (1.13 ppm) and coupling constant ($^2J(^1H\text{-}^{195}Pt)$ 73.11 Hz) for the MePt resonance, it is apparent that oxidative addition has occurred and is consistent with a structure in which the ligand is acting as a <u>fac</u>-N_2C^- tridentate forming two six membered chelate rings.



(X = Br, Cl)

Figure 5.12

5.3.2 Reactions with Pyridine

If $Me_2Pt(CH_2Cpz_2Me)Cl$ is dissolved in pyridine and hexane added, a microcrystalline solid is obtained, which can be recrystallized from acetone by addition of hexane. After this treatment the following ^1H NMR spectrum (figure 5.13) is obtained.

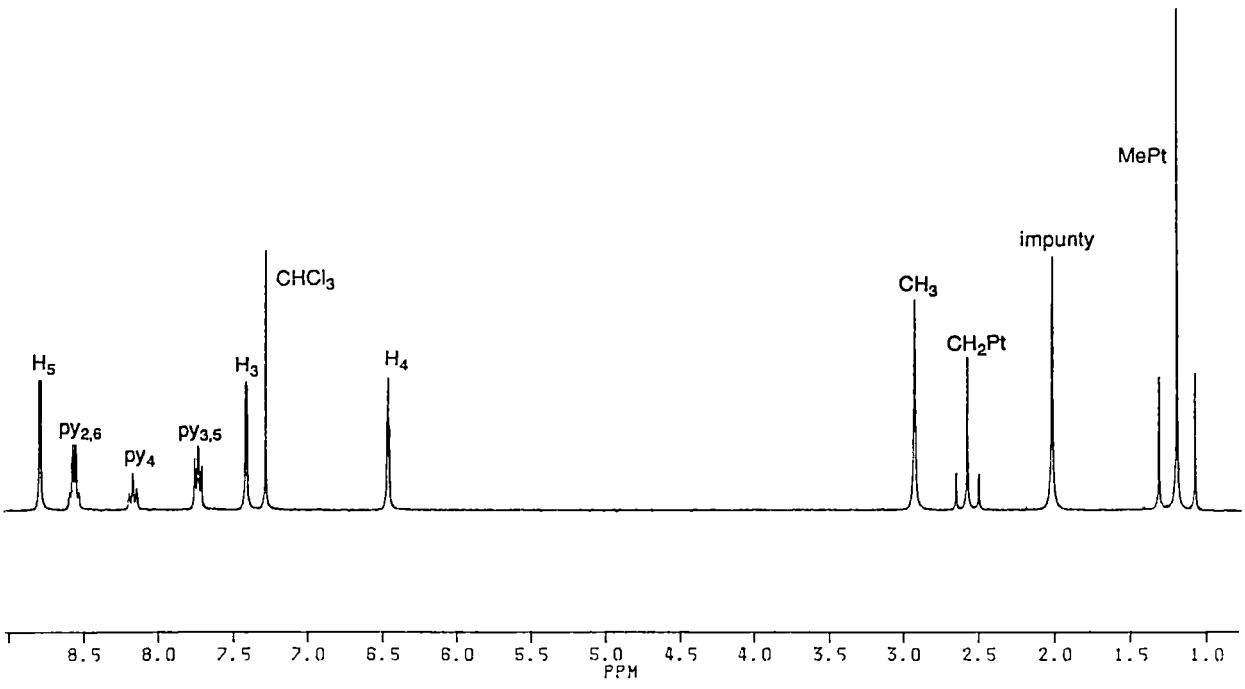


Figure 5.13 ^1H NMR Spectrum of $[Me_2Pt(CH_2Cpz_2CH_3)(py)]Cl$ in $CDCl_3$

In comparison with the parent complex, the H5 pyrazolyl resonance is moved downfield (~1 ppm) and the apical ligand methyl resonance also exhibits a downfield shift (~0.5 ppm). Changes in the chemical shift of these protons (pyrazolyl H5 and apical) are typical upon cationic formation (see Chapter 4).

Resonances for a single coordinated pyridine molecule are present together with appropriate ligand resonances. An infrared spectrum of this complex also exhibits a sharp absorption at 1600 cm^{-1}, consistent with the presence of coordinated pyridine. Conductivity measurements in acetone (Λ = 72 Ω^{-1} cm^2 $mole^{-1}$) confirm that the complex is ionic, and thus it can be assigned the structure shown in figure 5.14.

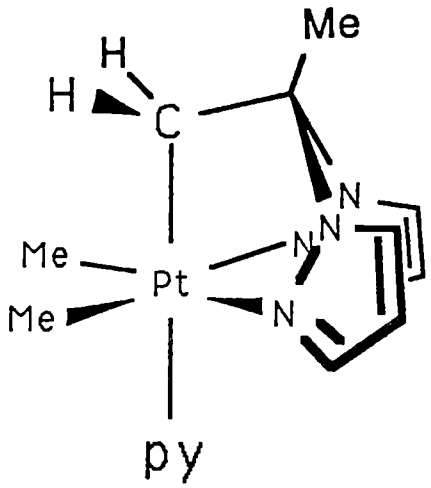


Figure 5.14

Other neutral complexes which react with pyridine to form cationic complexes include $Me_2Pt(CH_2Cpz_2CH_2Cl)Cl$ and $Me_2Pt(C(Cl)HCpz_2CH_3)Cl$.

In contrast, the complexes $Me_2Pt(2,6\text{-}(pzCH_2)_2C_6H_3)Br$ and $Me_2Pt(C_6H_5(H)Cpz_2)X$ (X = Br, Cl) do not react with pyridine to yield cationic complexes.

5.3.3 Ph_2PtLX

Two $Ph_2Pt(IV)$ complexes were synthesized in order to investigate if this experimental procedure is applicable to $Ph_2Pt(II)$ chemistry.

$Ph_2Pt(CH_2Cpz_2CH_3)Cl$

On refluxing $[Ph_2Pt(Et_2S)]_2$ with $CH_3Cpz_2CH_2Cl$ in the ratio 1:2 in benzene a white powder is deposited. This powder, although rather insoluble, can be recrystallized from a large volume of acetone by the addition of hexane until cloudiness develops. The ^1H NMR spectrum (figure 5.15) shows a $^2J(^1H\text{-}^{195}Pt)$ coupling for the ligand $-CH_2-$ protons, and thus oxidative addition has occurred to yield the platinum(IV) complex.

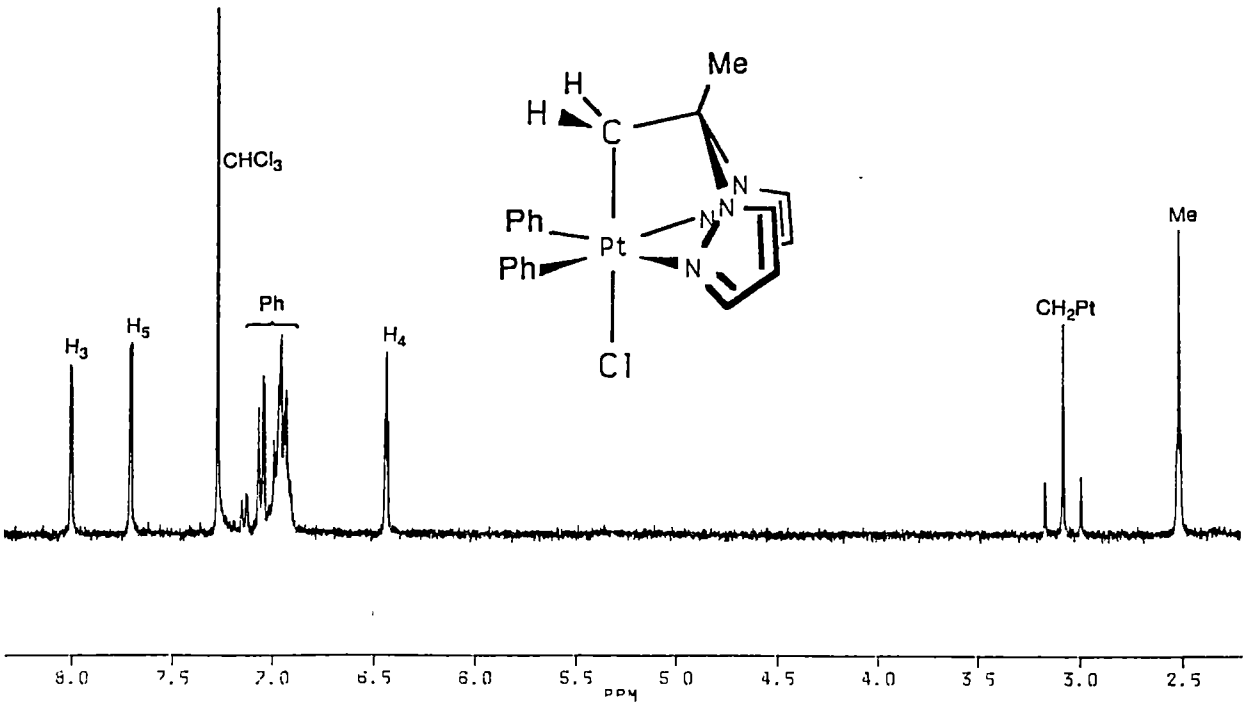


Figure 5.15 ^{1}H NMR Spectrum of $Ph_2Pt(CH_2Cpz_2CH_3)Cl$ in $CDCl_3$ with proposed structure

This complex reacts with pyridine to yield the cationic complex $[Ph_2Pt(CH_2Cpz_2Me)(py)]Cl$. $[Ph_2Pt(Et_2S]_2$ also reacts with 2,6-$(pzCH_2)_2C_6H_3Br$ to yield a platinum(IV) complex, although the aromatic portion of the ^{1}H NMR spectrum is complex and no attempt was made to interpret it.

5.4 Discussion

All of the ligands designed to contain bidentate N,N donors and an appropriately positioned halogen atom have been shown to react readily with $[Me_2Pt(Et_2S)]_2$ to yield neutral $Me_2Pt(IV)$ complexes with the ligand present as a fac N_2C^- tridentate.

Ligands containing an aliphatic skeletal system give rise to complexes possessing five membered chelate rings with small bite angles resulting in slight distortions from regular octahedral geometry.

The single $Ph_2Pt(IV)$ complex synthesized showed that this reaction path can occur readily for $Ph_2Pt(II)$, and the similarity of the ^1H NMR features suggests that the structure of the $Ph_2Pt(IV)$ complex is very similar to that of its $Me_2Pt(IV)$ analogue.

Ligands containing an aromatic (other than pyrazolyl) moiety give rise to complexes containing six-membered chelate rings, again, with the ligand adopting a <u>fac</u> N_2C^- tripod geometry. Molecular models show that there is less strain involved with these six-membered chelate rings, in comparison with the aliphatic skeletal system, and a less distorted octahedral geometry is expected. Unfortunately, attempts to grow crystals of these complexes suitable for x-ray diffraction studies were unsuccessful. Likewise, attempts to synthesize aliphatic ligand systems which would result in six-membered chelate N_2C^- rings was also unsuccessful.

The ease of this reaction suggests that it is facile, but whether reaction occurs via N,N-coordination of the ligand followed by rapid oxidative addition due to the proximity of the halogen atom, or via oxidative addition followed by N,N-coordination is difficult to assess. Under a range of experimental conditions only the hexa-coordinate complexes could be isolated.

The order of ease of oxidative addition of alkyl halides follows the halide series Cl < Br < I, and thus organobromides would be expected to oxidatively add more rapidly than organochlorides. The only complexes synthesized in which it was possible to compare the behaviour of chloro- and bromo- substituted ligands was $Me_2Pt(C_6H_4(H)Cpz_2)X$ (X= Cl, Br) with the ligands $2\text{-}XC_6H_4(H)Cpz_2$ (X = Cl, Br). In both instances reaction was rapid and this appears to be consistent with initial coordination, either N or N,N, followed by oxidative addition, with the oxidation being rapid due to the proximity of the halide to the platinum.

Reaction of $CH_3Cpz_2CH_2Cl$ with $Me_2Pd(II)$ resulted in the isolation of a microcrystalline solid, the ^1H NMR spectrum of which confirmed the ligand to be present and palladium to be in the divalent

oxidation state. Thus, N,N-coordination occurs, but not oxidative addition, although $Me_2Pd(II)$ does participate in oxidative addition reactions with organohalides to form stable isolable palladium(IV) complexes,[6] but generally the organohalide has to be very reactive.

This reaction pathway (coordination followed by oxidative addition) parallels that proposed for cyclometallation of $Me_2Pt(II)$ (Chapter 3), ie. initial simple coordination followed by oxidative addition of an appropriate C-H or C-X bond to platinum.

Cationic complexes of all the five-membered N_2C^- chelate ring systems are easily prepared by reacting the neutral complex with pyridine, with pyridine displacing the halide atom. Pyridine fails to replace the bromo ligand in $Me_2Pt(2,6\text{-}(pzCH_2)_2C_6H_3)Br$ and $Me_2Pt(C_6H_4(H)Cpz_2)Br$ even on prolonged heating of a pyridine solution of the complex.

This method of synthesis of N_2C^- tridentate systems offers the potential to be applicable to other organometallic systems which are favourable toward the oxidative addition reaction. The complexes formed are empirically analogous to cyclometallated systems except that they are in a different oxidation state.

5.5 Conclusion

Difunctionalized ligands containing N donor groups and an organohalide group react readily with $[R_2Pt(Et_2S)]_2$ (R = Me, Ph) to form $R_2Pt(IV)$ complexes containing the ligand in a $\underline{N_2C}^-$ tripodal tridentate orientation. Depending on the structure of the ligand five or six membered chelate rings result.

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CHAPTER 6

LIGAND SYNTHESES

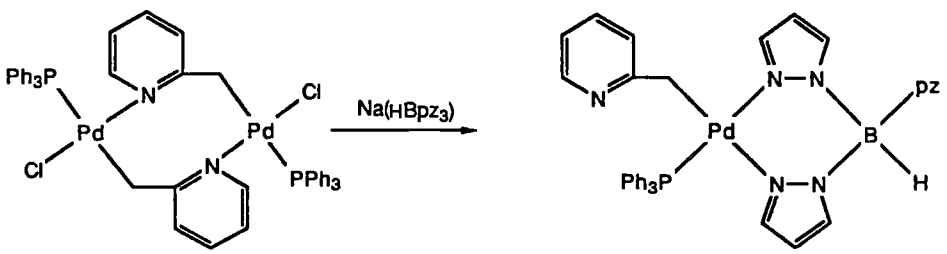
CHAPTER SIX

LIGAND SYNTHESES

6.1 Introduction

Since the first major reports of the complexing properties of pyrazole based ligands by Trofimenko,[1] numerous papers have appeared describing the preparation and characterisation of transition metal complexes of these ligands, and this literature has recently been reviewed by Trofimenko.[2] Pyrazole itself can act as both a monodentate ligand and, upon deprotonation, as an exo-bridging ligand, and may be readily incorporated in a variety of polydentate chelating ligands. Examples include the much studied poly-(1-pyrazolyl)borates and the isoelectronic, neutral, less well studied poly-(1-pyrazolyl)alkanes. Numerous complexes of a wide variety of metals have been prepared using these ligands. Some examples for palladium and platinum are illustrated in equations (1) - (4).[3-6]

$$Cl_2Pd(PhCN)_2 + H_2Cpz_2 \longrightarrow Cl_2Pd(H_2Cpz_2) + 2PhCN \qquad (1)$$



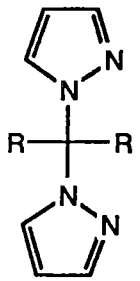
(2)

$$[Me_3PtI]_4 + K(HBpz_3) \longrightarrow Me_3Pt(HBpz_3) + KI \qquad (3)$$

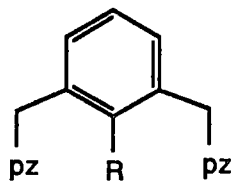
$$Me(Cl)Pt(COD) + AgPF_6 \xrightarrow{\text{acetone}} [MePt(COD)(acetone)]PF_6$$

$$[MePt(COD)(acetone)]PF_6 \xrightarrow{HCpz_3} [MePt(HCpz_3)]PF_6 \qquad (4)$$

All of the reagents containing donor groups utilized in this investigation were based on the poly(1-pyrazolyl)alkane series, and contained at least one pyrazole group linked through the pyrrolic (N1) nitrogen to a further donor system via a bridging saturated carbon atom(s), or a simple substituted aromatic ring, eg. figure



R = H, Me, Ph



R = H, Br

Figure 6.1

The aims of this work necessitated the use of known ligands and the preparation of new multidentate ligands. The unusual cyclometallation of $HCpz_3$ had been shown to proceed quite readily, and thus new pyrazolyl based polydentate ligands were designed to investigate this reaction further. Bidentate ligands containing at least one pyrazolyl group were synthesized to compare the behaviour towards cyclometallation of bidentate and tridentate ligands. Non-donor groups, both activated and unactivated toward metallation, were introduced into ligands containing the basic $-Cpz_2-$ unit in order to determine if they undergo metallation in preference to pyrazolyl rings. When it became apparent that metallated $HCpz_3$ could act as a N_2C^- tripodal tridentate ligand, following oxidation of Pt(II) complexes of cyclometallated $HCpz_3$, new ligands were designed to extend the range of compounds exhibiting this coordination mode, and to attempt to construct a more general synthetic route to this new class of intramolecular coordination compound.

The literature documents two potentially useful methods for the preparation of the types of pyrazole containing reagents required for this investigation.

6.2 Synthetic Methods

One important method is N-alkylation, involving nucleophilic displacement at saturated carbon, with pyrazole or pyrazolide anion serving as the nucleophile. The saturated carbon precursor is usually an acetal, ketal, or a suitably substituted organohalide. Trofimenko has successfully employed the acid catalyzed condensation of pyrazole with dialkoxyalkanes to prepare bis(1-pyrazolyl)alkane ligands.[1c]

$$2Hpz + Me_2C(OEt)_2 \underset{}{\overset{H^+}{\rightleftharpoons}} Me_2Cpz_2 + 2EtOH \qquad (5)$$

The ethanol produced in equation (5) is carefully distilled off as it is formed, to ensure completion of reaction.

Bis(1-pyrazolyl)alkanes are also accessible by the reaction of alkali metal pyrazolide with geminal dihaloalkanes.[1c] Both potassium and sodium readily react with pyrazole in dry THF to produce alkali metal pyrazolides,

$$M + Hpz \longrightarrow Mpz + {}^1/_2H_2 \qquad (6)$$
$$(M = K, Na)$$

which then react with a geminal dihaloalkane to produce the bis(1-pyrazolyl)alkane, eg.

$$2Mpz + CH_2I_2 \longrightarrow H_2Cpz_2 + 2MI \qquad (7)$$

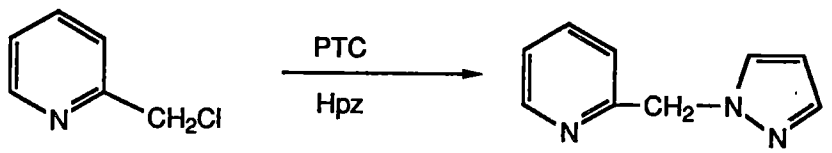
An analogous procedure, employing chloroform as the haloalkane, was first used by Huckel and Bretschneider to prepare tris(1-pyrazolyl)methane.[7] Trofimenko has also used this procedure with carbon tetrachloride to produce tetrakis(1-pyrazolyl)methane, although in very low yield.[1c]

A simpler, more efficient synthesis of these derivatives, which obviates the need for anhydrous conditions and the use of active

alkali metals, employs phase transfer catalysis (PTC)[8,9] techniques. A large range of substituted bis(1-pyrazolyl)methanes have been synthesized using the PTC procedure, eg. bis(1-pyrazolyl)methane in 90% yield.[9]

$$Hpz \xrightarrow[\text{tetrabutylammonium bromide}\\ \text{8hrs reflux/stirring}]{\text{40\% NaOH, xs } CH_2Cl_2} H_2Cpz_2 \qquad (8)$$

This method of incorporating pyrazole into a ligand system has been utilized to replace single reactive halogen atoms in many organohalide substrates,[10,11] eg.



(9)

$$HCCl_3 + 3,4,5\text{-}Me_3pz \xrightarrow{PTC} HC(3,4,5\text{-}Me_3pz)_3 \qquad (10)$$

The other major method reported, useful for the synthesis of ligands containing $-Cpz_2-$ units, involves a transition metal mediated condensation of bis(1-pyrazolyl)ketone with a carbonyl group of a suitable ketone or aldehyde. Bis(1-pyrazolyl)ketone is synthesized from sodium pyrazolide and phosgene,[12a,b]

$$2Napz + Cl_2C{=}O \longrightarrow pz_2C{=}O + 2NaCl \qquad (11)$$

and a more convenient synthesis for small amounts of this compound has been published by the same authors.[12c] We found that this reaction is just as effective in diethyl ether, if efficient stirring is employed, as in the recommended[12c] THF. Thus, Hpz (5g, 73.5 mmole), triethylamine (10.25 cm^3, 73.5 mmole) and diethyl ether (200 cm^3) were mixed by overhead mechanical stirring, under a nitrogen atmosphere, and phosgene (19 cm^3 of 1.93M in toluene) added in two portions. Stirring was continued for 15 minutes, the precipitate filtered, solvent removed under vacuum and hexane (10cm^3) added to assist in crystallization of the ketone. The ketone (5.66g, 95%) was

dried under vacuum and stored under a nitrogen atmosphere. The compound did not require further purification and was used as required.

The condensation between $pz_2C{=}O$ and the appropriate carbonyl substrate occurs in the presence of a catalytic quantity of anhydrous cobalt(II) chloride, eg.

$$pz_2C{=}O \quad + \quad (CH_3)_2C{=}O \xrightarrow{CoCl_2} Me_2Cpz_2 \quad + \quad CO_2 \qquad (12)$$

If more than a catalytic quantity of $CoCl_2$ is used then a cobalt complex of the ligand may be isolated. The ligand can be freed from this complex by hydrolysis.

The condensation reaction is sensitive to both electronic and steric substituent effects of the reacting carbonyl, and is ineffective in some instances.

6.3 Results and Discussion

6.3.1 Ligands Containing One Pyrazolyl Group

Although most of these compounds are bidentate ligands, they all contain one pyrazolyl group attached to a bridging carbon atom (Table 6-1)

Compounds 2-9 are new compounds, while the preparation of compound 1 was reported[10] during this work, although by the PTC procedure, and the 3,5-dimethylpyrazolyl analogue of compound 3 has been reported.[13]

Compounds 5 and 7 were isolated from the same reaction mixture, with compound 5 representing the intermediate to compound 7. Compound 6 was synthesized in the same way, but under conditions which maximized its yield.

Table 6-1

Ligands Containing a Single Pyrazolyl Group per Carbon Atom

	Compound	Preparation Method[a]	Yield(%)
1	$H_2C(py)pz$	B	90
2	$H_2C(mim)pz$	B	71
3	$1,3-(pzCH_2)_2C_6H_4$	B	82
4	$2,6-(pzCH_2)_2C_6H_3Br$	B	68
5	$pzCH_2CH_2Br$	C	52
6	$pzCH_2CH_2Cl$	C	73
7	$pzCH_2CH_2pz$	C	86
8	$pzCH_2CH_2CH_2pz$	C	92
9	$H_2C=C(CH_2pz)_2$	B	79

[a] B - potassium pyrazolide
C - phase transfer catalysis

These compounds encompass a varied array of possible coordination geometries for complexes. Compounds 1 and 2 would be expected to form 6 membered N,N-chelate rings upon coordination, while compounds 7, 8 and 9 could form 7 and 8 membered rings respectively. In addition, compound 8 could conceivably undergo metallation at the central CH_2 carbon, as the pyridine analogue of this ligand has been reported[14] to undergo C(2) metallation with palladium acetate to form a planar N_2C^- chelate.

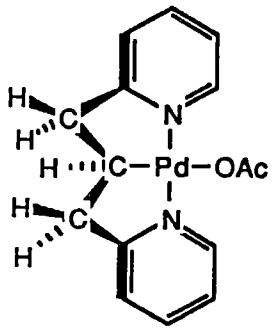
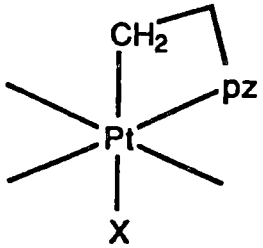
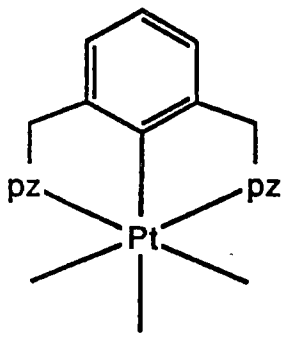


Figure 6.2

A similar cyclometallation is also considered possible for compound 3, with metallation on the central proton (2 position). Compounds 4-6 offer the possibility of direct oxidative addition, or coordination with subsequent oxidative addition, to form N_2C^- or NC^- chelates. In addition, molecular models indicate that N_2C- chelates derived from compounds 3 and 4 could potentially act as either planar or tripodal donors.



NC^-



N_2C^-

Figure 6.3

Molecular models show that compound 22 can coordinate in such an orientation that the alkene portion of the ligand is available for bonding to platinum.

6.3.2 Compounds Containing Two Pyrazolyl Groups

These compounds all contain two pyrazolyl groups attached to a bridging carbon atom (Table 6-2)

Table 6.2

Ligands Containing Two Pyrazolyl Groups per Carbon Atom

	Compound	Preparation Method[a]	Yield(%)
10	H_2Cpz_2	C	88
11	$Me(H)Cpz_2$	A	80
12	Me_2Cpz_2	D	93
13	$Ph(H)Cpz_2$	A,B	75
14	$Ph(MeO)(H)Cpz_2$	D	58
15	$(2\text{-}XC_6H_4)(H)Cpz_2$ (X = Cl, Br)	D	48
16	$HC(py)pz_2$	D	45
17	$HC(mim)pz_2$	D	49
18	$HC(thio)pz_2$	D	62
19	$1,3\text{-}(pz_2CH)_2C_6H_4$	B	74
20	$MeCpz_2CH_2Cl$	D	82
21	$ClCH_2Cpz_2CH_2Cl$	D	64
22	$CH_3Cpz_2CHCl_2$	D	41

[a] A - acid catalyzed condensation
B - potassium pyrazolide
C - phase transfer catalysis
D - cobalt chloride catalyzed condensation

Compounds 10-13 are known, but the preparative procedures reported here (see experimental) result in higher yields. Compound 17 has been reported while this work was in progress, as it was found to have application for stabilising high oxidation state organopalladium(IV) systems.[15]

Attempted preparation of some other potential new ligands failed. For example, N-methylimidazole is readily lithiated at the C(2) position and thus, in a compound of the type shown in figure 6.4, the C(2)-H bond may compete effectively with pyrazole rings for platination, and thus the ligand would be of interest for a comparison with $HCpz_3$.

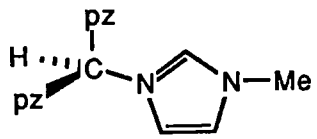


Figure 6.4

Attempted preparations of this compound via acid condensation failed.

$$(EtO)_2(H)C(im) + 2Hpz \xrightarrow{H^+} pz_2(H)C(im) \qquad (13)$$

Acid catalyzed condensation of pyrazole with bromoacetaldehdye dimethyl acetal to produce a bromo derivative analogous to compound 20 also failed, and resulted in isolation of a moisture sensitive compound.

$$(MeO)_2(H)CCH_2Br + 2Hpz \xrightarrow{H^+} HCpz_2CH_2Br \qquad (14)$$

Compounds 16 and 17 were prepared by an adaption of Peterson's cobalt(II) chloride catalyzed condensation reaction. The preparation of these compounds did not require the addition of cobalt(II) chloride, eg. in the preparation of $HC(py)pz_2$ (equation (15)) rapid reaction was found to occur on gentle warming of pyridine-2-aldehyde and bis(1-pyrazolyl)ketone.

$$pyCHO + pz_2C{=}O \xrightarrow{warm} HC(py)pz_2 + CO_2 \qquad (15)$$

The reaction was extremely exothermic and rapid and required careful cooling after it was initiated.

Potential coordination geometries obtainable from the compounds in Table 6-2 are varied. Complexes of compounds 10-14 all offer the potential for fluxional behaviour via axial-equatorial exchange of the non-bonding ligand bridgehead groups. Compounds 13 and 14 have substituents which could possibly compete with pyrazole rings under metallating conditions to form six membered planar CN^- systems. (Figure 6.5)

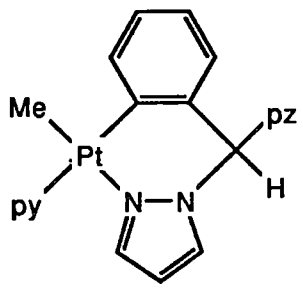
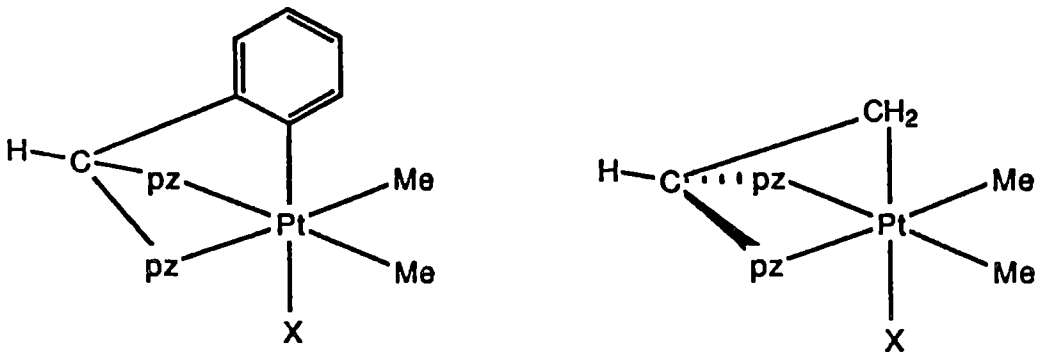


Figure 6.5

Likewise, compounds 16-18 contain groups which could result in N,N, N,N' or N,S planar coordination, with the added possibility of competition with pyrazole rings under metallating conditions to form $N\,C^-$, N',C^- or S,C^- coordination (N = pz; N' = mim, py).

The reagents 15 and 20-22 offer the possibility of forming 5 or 6 membered ring tripodal tridentate systems if both N,N coordination and oxidative addition result upon complexation with $Me_2Pt(II)$. eg.



(X = Br, Cl)

Figure 6.6

6.3.3 Ligands Containing Three or More Pyrazolyl Groups

Compounds utilized which contained three or more pyrazolyl groups per carbon atom are listed in Table 6-3.

Table 6-3

Ligands Containing 3 or more Pyrazolyl Groups per Carbon Atom

	Compound	Preparation Method[a]	Yield(%)
23	$HCpz_3$	B	40-45
24	$MeCpz_3$	E	78
25	Cpz_4	D	50

[a] B - potassium pyrazolide
D - cobalt chloride condensation
E - lithiation procedure

Compounds 23 and 25 are well known, and the new compound (24) was prepared by a lithiation procedure using $HCpz_3$ as a starting material.

In our hands the reported[7] preparation of $HCpz_3$ was erratic and irreproducible, but on modifying the reported procedure consistent yields of 40-45% were obtained (see experimental).

Coordination of Cpz_4 could result in the formation of dimeric platinum compounds, analogous to $Me_4Pt(bipym)$[18,19] (figure 6.7), but not planar, if all pyrazolyl groups participate in coordination.

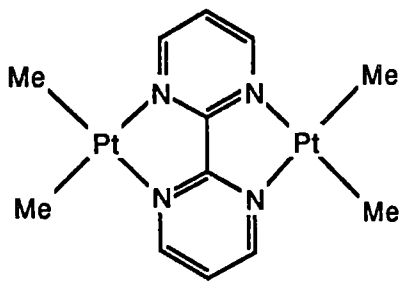


Figure 6.7

6.3.4 Reaction of Organolithium Reagents with Pyrazolyl Compounds Containing Acidic C-H Bonds

Metallation of N substituted pyrazoles with Bu^nLi yields a range of products after reaction with various electrophiles.[16] Thus, under kinetic control at -78^oC, 1-benzylpyrazole is lithiated at the bridging CH_2 group but at room temperature rearranges to yield the thermodynamically more stable 5-lithio-1-benzylpyrazole; 1-methylpyrazole gives mixtures of -and 5-lithiation.

Katritzky has recently reported the reaction of bis(1-pyrazolyl)methane with Bu^nLi and its subsequent reactions with various electrophilic reagents to yield a single major product,[17] eg. bis(1-pyrazolyl)methane on treatment with Bu^nLi at ambient temperature and subsequent reaction with MeI gave 1,1'-bis(1-pyrazolyl)ethane.

$$H_2Cpz_2 \xrightarrow{Bu^nLi} LiHCpz_2 \xrightarrow{MeI} Me(H)Cpz_2 \qquad (16)$$

However, if carbonyl electrophiles, eg. CH_3COCl, were used under the same conditions, pyrazolyl ring 5-lithiated products were isolated.

$$H_2Cpz_2 \xrightarrow{Bu^nLi} LiHCpz_2 \xrightarrow{CH_3COCl} \text{(5-acetyl-1-(pz)methylpyrazole)} \qquad (17)$$

The lithiation of pyrazolylalkanes was also independently discovered and investigated in our laboratory. Thus, $HCpz_3$ reacts with Bu^nLi in anhydrous ether at 0^oC to produce a white solid, presumably $LiCpz_3$, which on addition of THF (until the solid dissolves) and excess MeI produces $MeCpz_3$ in 78% yield.

$$HCpz_3 \xrightarrow[\text{ether}]{Bu^nLi} LiCpz_3 \xrightarrow[\text{THF}]{MeI} MeCpz_3 \qquad (18)$$

By the same procedure, $Me(H)Cpz_2$ and H_2Cpz_2 gave Me_2Cpz_2 and $Me(H)Cpz_2$ respectively.

This method was investigated as a possible route to haloheterocyclic compounds, eg. $CH_3Cpz_2(CH_2)_nX$. Thus, $Me(H)Cpz_3/Bu^nLi$ was reacted with 1,2-dibromoethane in the expectation that $CH_3Cpz_2CH_2CH_2Br$ may be formed. On all occasions, under various conditions (temperature control, reverse addition, excess of halide), the solution darkened on reaction with $BrCH_2CH_2Br$ and the dimeric compound $CH_3Cpz_2CH_2CH_2Cpz_2CH_3$ was isolated in low yield. Trofimenko[1c] has reported the preparation of similar compounds via an acid catalyzed condensation procedure. If H_2Cpz_2 was used as the substrate, a mixture of products, including the dimeric compound $HCpz_2CH_2CH_2Cpz_2H$ and products from ring lithiation, were isolated in low yield. The lithiation procedure does not appear to be suited to the preparation of these types of compound.

6.4 Conclusion

A wide range of multidentate pyrazolyl containing ligands have been synthesized by a variety of methods. Some of these ligands are obtained in high yield by simple and convenient preparative procedures. These ligands offer the possibility of a range of coordination modes, from simple bidentate N,N coordination to N_2C^- tripodal tridentate coordination. The platinum(II) and platinum(IV) chemistry of these reagents, given in Chapters 2-5, indicate that they may be of general use in a range of applications in coordination and organometallic chemistry.

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CHAPTER 7

EXPERIMENTAL

CHAPTER SEVEN

EXPERIMENTAL

General

7.1 Physical and Analytical Measurements

1. Microanalyses

Elemental analyses for C, H, P, Cl, Br and I were performed by the Australian Microanalytical Service Laboratories, Melbourne or the Canadian Microanalytical Service Ltd., Vancouver.

2. Melting Points

Melting points are reported for complexes which melted without decomposition at less than 200^{o}C and were determined with a Reichart Thermo apparatus and stereomicroscope, and are uncorrected.

3. Molecular Weights

Molecular weights were determined using a Knauer vapour pressure osmometer for ca. 1 - 3 x 10^{-2} M solutions in chloroform at 37^{o}C.

4. Conductivities

Conductivities were measured using a Philips PW 9504/00 conductivity meter with a Griffin George conductivity cell. Solution concentrations were ca. 10^{-3} in acetone at 25^{o}C.

5. Spectroscopic Measurements

(i) Where reported infrared (IR) spectra were recorded using a Hitachi 270-30 infrared spectrophotometer, as nujol mulls or neat

liquids between KBr plates.

(ii) Mass spectra (ms) were obtained using a Vacuum General Micromass 7070F spectrometer operating at 70 eV.

(iii) Nuclear Magnetic Resonance spectra (^{1}H, ^{13}C, ^{31}P) were recorded using a Bruker AM 300 spectrometer and are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shift values are referenced to internal tetramethyl silane (TMS, 0 ppm) in $CDCl_3$ solvent, or the central acetone resonance (2.2 ppm) of the acetone quintet in D6 acetone.

^{1}H NMR spectra are tabulated as H_n, denoting a pyrazolyl bound proton, eg. H_4, while protons belonging to other groups are denoted by their nominated abbreviations, eg. Ph_4, $py_{2,6}$.

6. Thermogravimetric Analysis

Thermogravimetric measurements (T.G.A.) were carried out using a Rigaku-Denki Differential Scanning Calorimeter (Thermoflex 8085).

7.2 Solvents and Reagents

All general purpose reagents and solvents were distilled prior to use, but not dried unless stated otherwise. For preparations which required more specialized solvent and reagent purification, the methods used were similar to those recommended by Perrin et al.[1] and Vogel[2].

Solvents

Acetone: Dried over $CaSO_4$, filtered and fractionated.

Acetic Acid (glacial): Refluxed and fractionally distilled from acetic anhydride and potassium permanganate.

Benzene: Washed with conc. H_2SO_4, H_2O, 2M NaOH, refluxed and distilled from P_2O_5, then stored over sodium wire.

Chloroform: Washed several times with H_2O, dried over $CaCl_2$, filtered and distilled from P_2O_5.

Dichloromethane: Dried over $CaCl_2$, filtered and distilled from P_2O_5.

Diethyl Ether (Ether): Pre-dried over $CaCl_2$, 4Å molecular sieves, followed by reflux and distillation from sodium/benzophenone and stored over sodium wire.

Ethanol: Absolute ethanol was refluxed with magnesium ethoxide for 1 hour, distilled and stored over 4Å molecular sieves.

Hexane: Dried over $CaCl_2$, distilled from sodium/benzophenone and stored over sodium wire.

Methanol: Fractionally distilled, refluxed over magnesium methoxide for 3 hours, distilled and stored over 4Å molecular sieves.

Pyridine: Refluxed with solid KOH for 3 hours, fractionally distilled and stored over 4Å molecular sieves.

Tetrahydrofuran (THF): Pre-dried over solid KOH followed by reflux and distillation from sodium/benzophenone and stored over sodium wire.

Toluene: Refluxed and distilled from sodium and stored over sodium wire.

Reagents

Organic Reagents

Acetyl Chloride: Refluxed with PCl_5 for several hours then distilled. Redistilled from one-tenth volume of quinoline.

Acetaldehyde: Shaken with $NaHCO_3$, dried over $CaSO_4$ and fractionally distilled under nitrogen.

Allyl Bromide: Washed with $NaHCO_3$, H_2O, dried with $MgSO_4$ and fractionally distilled.

Benzaldehyde: Washed with aq. Na_2CO_3 solution, saturated Na_2SO_3, H_2O, dried over $CaCl_2$ then distilled at reduced pressure.

Benzyl Bromide: Washed with conc. H_2SO_4, H_2O, 2M NaOH and H_2O. Dried over $MgSO_4$, fractionally distilled under reduced pressure in the dark and stored over 4Å molecular sieves.

Bromobenzene: Pre-dried over $CaCl_2$, refluxed and distilled from calcium turnings and stored over 4Å molecular sieves.

1-Bromobutane: Washed with conc. H_2SO_4, H_2O, 2M NaOH and H_2O. Dried over $CaCl_2$, P_2O_5 then distilled.

Chloroacetone: Dissolved in H_2O, shaken with small amounts of ether, extracted with a large volume of ether and distilled at reduced pressure

1,2-Dibromoethane: Washed with conc. H_2SO_4, H_2O, Na_2CO_3, H_2O, dried over $CaCl_2$ then fractionally distilled.

2,6-Dimethylpyridine (2,6-lutidine): Dried over solid KOH decanted and fractionally distilled.

Iodoethane: Washed with dilute aq. $NaHSO_3$, H_2O, dried over $CaCl_2$, distilled in the dark and stored over 4Å molecular sieves.

Iodomethane: As for iodoethane.

N-Methylimidazole: Distilled under reduced pressure and stored over 4 Å molecular sieves.

4-Methylpyridine (γ-picoline): As for lutidine.

Propargyl Bromide: As for allyl bromide.

Pyridine-2-aldehyde: Fractionally distilled under reduced pressure.

Triethylamine: Dried over $CaCl_2$, distilled from P_2O_5 and stored over 4Å molecular sieves.

Organolithium Reagents

Some preparative procedures required the use of pyrophoric organolithium reagents, eg. MeLi, PhLi and Bu^nLi. When required for use these reagents were transferred by either gas tight syringe (less than 10 cm^3) or flexible polyethylene tubing into a burette under a nitrogen atmosphere. Transfer by polyethylene tubing is more advantageous than by metal cannula as it is flexible, allows visible transfer, and is easily cleared, cleaned and dried.

The concentration of organolithium reagents was determined by titration with 1,3-diphenyltosylhydrazone in THF.[3]

When mentioned in the text, organolithium reagents were prepared by the following procedures.

(i) Lithium and Iodomethane:[4]

To a stirred suspension of finely cut lithium wire (0.70g, 100 mmole) in anhydrous ether (50 cm^3) at 0^oC (ice) and under an atmosphere of dry nitrogen, was added MeI (3.2 cm^3, 51 mmole) in ether (10 cm^3) at such a rate that the surface of the lithium chips appeared as metallic silver. At the completion of the addition the solution was titrated and used immediately. Yields were consistently in the 40 - 50% range.

(ii) Halide-free MeLi:[5]

The preparation of methyllithium using methyl iodide results in the formation of ether soluble lithium iodide. Halide free methyllithium can be prepared using chloromethane since LiCl is insoluble in ether. It is critical for the success of this

preparation[6] that the lithium contain a small percentage of sodium (~ 1%), and be of correct particle size. Lithium particles of an appropriate size can be prepared by vigorous mechanical stirring of molten lithium (1% Na) in dry paraffin oil (~ 220^{o}C) under an atmosphere of argon. An easily manageable quantity was found to be approximately 7g (1 mole) of lithium in 350 - 400 cm^{3} of paraffin. As the oil is slowly cooled, with stirring, lithium shot of an appropriate particle size forms. When the temperature falls to approximately 80^{o}C, excess oil is siphoned off, and the lithium shot washed with several portions of dry hexane (3 x 50 cm^{3}) and dry ether (3 x 20 cm^{3}). Lithium produced in this manner was suitable for the preparation of methyl lithium by reaction with chloromethane as described by House et al.,[5] and resulted in yields similar to those reported by House.

Halide free MeLi was stored at -20^{o}C, but required weekly titration as the concentration slowly decreased on storage.

Phenyllithium,[7] PhLi

To a stirred suspension of finely cut lithium wire (1.0g, 144 mmole) in anhydrous ether (50 cm^{3}) under an atmosphere of dry nitrogen was added a small portion (1 cm^{3}) of bromobenzene to initiate reaction. Once reaction had begun the remainder of the bromobenzene (6.58 cm^{3}, 62.5 mmole) in ether (10 cm^{3}) was added at such a rate as to maintain the reaction. At the completion of the addition the mixture was refluxed for 2 hours. This procedure reliably resulted in a near quantitative reaction yield, and titration was not required. Phenyllithium was prepared as required and was not stored.

n-Butyllithium, Bu^{n}Li[4,7]

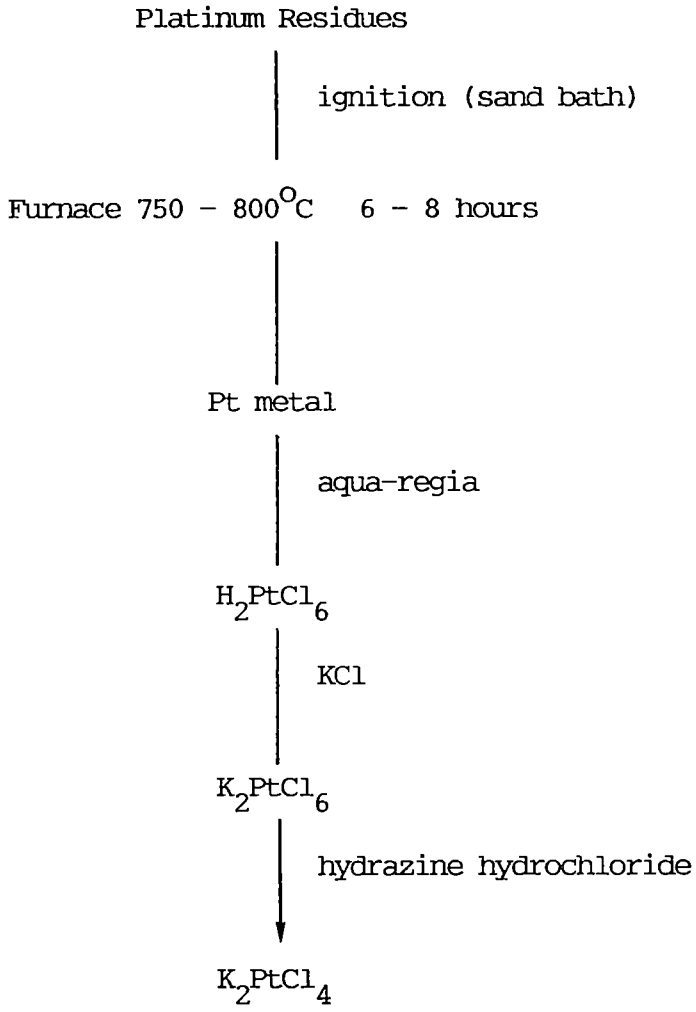
To a stirred suspension of finely cut lithium wire (5.3g, 0.75 mmole) in anhydrous ether (200 cm^{3}) under an atmosphere of dry nitrgoen was added a small amount of neat 1-bromobutane (0.5 cm^{3}) to initiate reaction. When reaction had begun the mixture was cooled to

approximately $-10^{o}C$ and the remainder of the 1-bromobutane (39.5 cm^3) in ether (20 cm^3) added dropwise at such a rate that the reaction solution temperature never rose above about $-5^{o}C$ (35 - 40 minutes). At the completion of the addition the mixture was stirred at room temperature for 0.5 hour, and stored at $-20^{o}C$. Titration of this solution indicated a $Bu^{n}Li$ concentration of approximately 1M (70%).

Platinum Recovery[8] - Platinum was recovered according to scheme 7.1.

All platinum containing residues were combined and evaporated to the lowest possible volume on a steam bath. The semi-solid residue was transferred to a small crucible, placed on a sand bath and gradually heated over 8 hours to maximum. Solid residues, such as filter papers, were carefully burnt and the ashes combined with the residue from the solution recovery. The combined residues containing platinum, inorganic salts and organic compounds were placed in a furnace and heated to 750 - $800^{o}C$ for 8 hours. On completion of firing the crucible was slowly cooled to room temperature, and the contents washed several times with hot water (x5) and dilute hydrochloric acid solution (x5) to remove inorganic salts. The remaining solid, predominantly platinum metal, was dissolved in hot aqua-regia by the addition of small portions of aqua-regia to the residue, and the resulting solution taken to near dryness on a steam bath. Conc. hydrochloric acid was added (20 cm^3) and the mixture evaporated to near dryness. This procedure was repeated 3 times in order to remove all oxides of nitrogen. The final hydrochloric acid solution, containing "H_2PtCl_6", was diluted with an equal volume of distilled water, filtered, and an excess of KCl added to precipitate yellow K_2PtCl_6. After filtration and drying, K_2PtCl_6 was reduced to K_2PtCl_4 in hot aqueous solution by the addition of a stoichiometric quantity of solid hydrazine hydrochloride or hydrazine sulphate. Addition of the solid reductant is regulated to avoid the reaction becoming too vigorous. The resulting red solution, containing K_2PtCl_4, and some metallic platinum, was filtered and the volume reduced (water bath) to yield, on cooling, crystalline K_2PtCl_4.

Potassium tetrachloroplatinate, K_2PtCl_4, was then used to synthesize either $Cl_2Pt(COD)$ or $Cl_2Pt(EtS)_2$ as required.



Scheme 7.1

7.3 Experimental for Chapter Two

Cl_2PtL (L = $HCpz_3$, H_2Cpz_2, $Me(H)Cpz_2$, Me_2Cpz_2, Cpz_4)

K_2PtCl_4 (0.1g, 2.4 mmole) was dissolved in H_2O (5 cm^3), filtered, and added to an acetone solution (5 cm^3) of ligand (2.4 mmole). The mixture (red in colour) was allowed to stand for 6 - 8 hours during which time the red colour discharged and a microcrystalline yellow solid deposited. Alternatively, the mixture was refluxed and a yellow powder precipitated over 0.5 hour. All complexes with the exception of $Cl_2Pt(Me_2Cpz_2)$ were insoluble in common organic solvents.

Yields, microanalyses (where applicable), melting points and far infrared spectral data are given below. Calculated microanalysis values (%) are given in parentheses.

$Cl_2Pt(HCpz_3)$: 97%;
Microanalysis: C 24.94 (25.00), H 2.20 (2.10), N 17.30 (17.50), Cl 15.30 (14.76)
I.R. (KBr disc): υ ($PtCl_2$) 342,358 cm^{-1}.

$Cl_2Pt(H_2Cpz_2)$: This complex has been reported.[9]
94%;
I.R. (KBr disc): υ ($PtCl_2$) 338, 345 cm^{-1}.

$Cl_2Pt(Me(H)Cpz_2)$: 94%;
Microanalysis: C 22.61 (22.40), H 2.52 (2.41), N 13.00 (13.07), Cl 16.94 (16.53)
I.R. (KBr disc): υ ($PtCl_2$) 332, 338, 348 cm^{-1}.

$Cl_2Pt(Cpz_4)$: 92%;
Microanalysis: C 28.04 (28.58), H 2.02 (2.21), N 19.50 (20.51), Cl 12.80 (12.98)
I.R. (KBr disc): υ ($PtCl_2$) 335, 350 cm^{-1}.

$\underline{Cl_2Pt(COD)}$:

Prepared by the procedure of Whitesides et al.[10]

$\underline{Me_2Pt(COD)}$:

Prepared by the procedure of Clark and Manzer.[11]

$\underline{Cl_2Pt(NBD) \text{ and } Me_2Pt(NBD)}$:

Prepared by the procedure of Appleton et al.[12]

$\underline{cis\text{-}Cl_2Pt(Et_2S)_2}$[13]:

K_2PtCl_4 (10g, 24.1 mmole) was dissolved in H_2O (120 cm^3) and Et_2S (10.4 cm^3) was added with stirring. Stirring was continued until the red colour had faded and a thick yellow precipitate formed. The suspension was stoppered and allowed to stand for 12 hours until the precipitate had dissolved. The resultant yellow solution was extracted with CH_2Cl_2 (2 x 30 cm^3), dried with $MgSO_4$, filtered, and allowed to evaporate to dryness. The yellow solid was crushed and vacuum dried at 50°C for 2 hours. Yield 10g, 94%

$\underline{[Me_2Pt(Et_2S)]_2}$[14]:

Dry crushed $\underline{cis}$-$Cl_2Pt(Et_2S)_2$ (6.8g, 15.25 mmole) was suspended in anhydrous ether (200 cm^3) with stirring at 0°C under a nitrogen atmosphere. Halide free MeLi (32.03 mmole) was added dropwise over 10 minutes, stirred at 0°C for 2 hours and carefully hydrolyzed (saturated NH_4Cl, 10 cm^3) until no solid was evident. The mixture was separated, the aqueous layer extracted with ether (3 x 20 cm^3), the combined ether extracts dried ($MgSO_4$), filtered and evaporated to near dryness on a rotary evaporator. Benzene (10 cm^3) was added and white crystalline $[Me_2Pt(Et_2S)]_2$ filtered off.

Yield: 3.8g, 80%

Molecular weight: 641 (630)

^{1}H NMR ($CDCl_3$):

MePt 0.49(t) $^2J(^1H-^{195}Pt)$ 86 Hz, 6H; $C\underline{H}_3CH_2$ 1.60(t) 3H; $CH_3C\underline{H}_2$ 3.05(q), 2H.

$\underline{Me_2Pt(HCpz_3)}$ from $\underline{Me_2Pt(COD)}$ and $\underline{Me_2Pt(NBD)}$

$Me_2Pt(COD)$ (0.5g, 1.50 mmole) and $HCpz_3$ (0.33g, 1.54 mmole) were dissolved in anhydrous benzene (20 cm^3) under an atmosphere of dry nitrogen and refluxed with stirring. Reflux was continued for 24 hours during which time a white solid precipitated. The solid was filtered, washed with ether, air dried and vacuum dried (60°C, 2 hours) to yield 0.38g, (58%) of $Me_2Pt(HCpz_3)$.

If toluene was substituted as the reaction solvent and the scheme in Chapter 2 followed, the yield was increased to 80% over 20 hours.

$Me_2Pt(NBD)$ was used in benzene in the above method to give a yield of 72%.

$\underline{Me_2Pt(L)}$ $\underline{(L = H_2Cpz_2, HCpz_3, Ph(H)Cpz_2)}$

$[Me_2Pt(Et_2S)]_2$ (0.10g, 0.16 mmole) was suspended in anhydrous benzene (20 cm^3), ligand (0.32 mmole) added and the mixture stirred and heated to reflux under a nitrogen atmosphere. Near reflux the $[Me_2Pt(Et_2S)]_2$ dissolved to yield a pale yellow solution from which a solid precipitated after a further 10 minutes heating. The solid was filtered, washed with ether, air dried and vacuum dried (60°C, 2 hours). All complexes were insoluble in common organic solvents.

$\underline{Me_2Pt(H_2Cpz_2)}$: 89%, white amorphous solid. This compound has been reported in 19% yield.[15]

$\underline{Me_2Pt(HCpz_3)}$: 93%, white amorphous solid.

$\underline{Me_2Pt(Ph(H)Cpz_2)}$: 90%, white amorphous solid.
Microanalysis: C 39.82 (39.96); H 4.28 (4.31); N 11.98 (12.47).

$\underline{Me_2Pt(L)\ (L = Me(H)Cpz_2, Me_2Cpz_2, H_2C(mim)pz, H_2C(py)pz, HC(mim)pz_2, HC(thio)pz_2, Cpz_4)}$

$[Me_2Pt(Et_2S)]_2$ (0.1g, 0.16 mmole) was dissolved in acetone (20 cm^3), ligand added (0.32 mmole) and the solution stirred and heated under a nitrogen atmosphere. After 10 minutes heating the solution (sometimes slightly yellow) was cooled, hexane (5 cm^3) added and the solution volume reduced on a rotary evaporator until the product began precipitating, the product was filtered, washed with ether, air dried and vacuum dried (50°C, 2 hours).

$\underline{Me_2Pt(Me(H)Cpz_2)}$: 88%, white crystalline solid;
Molecular Weight ($CHCl_3$): 388 (387)

^1H NMR (D6 acetone), ambient temperature:

MePt 0.80(t) $^2J(^1H-^{195}Pt)$ 89.7 Hz, 6H; C$\underline{Me}$ 2.64, 3H; H_4 6.57, 2H; CH 7.36, 1H; H_3 7.93, 2H; H_5 8.27, 2H;

All ligand resonances were broad.
^1H NMR (D6 acetone) -25°C:

$\underline{Conformer\ (B)}$: MePt 0.76(t) $^2J(^1H-^{195}Pt)$ 88.8 Hz; C$\underline{Me}$ 2.60(d) $^2J(^1H-^1H)$ 6.96 Hz; H_4 6.60(t); CH 7.28(q) $^2J(^1H-^1H)$ 6.92 Hz; H_3 7.90(d), $J_{(3,4)}$1.98 Hz; H_5 8.39(d) $J_{(4,5)}$2.73 Hz;

$\underline{Conformer\ (A)}$: MePt 0.78(t) $^2J(^1H-^{195}Pt)$ 89.2 Hz; C$\underline{Me}$ 2.74(d) $^2J(^1H-^1H)$ 6.63 Hz; H_4 6.60(t); CH 7.41(q) $^2J(^1H-^1H)$ 6.62 Hz; H_3 7.98(d) $J_{(3,4)}$2.07 Hz; H_5 8.27(d) $J_{(4,5)}$2.67 Hz.

$\underline{Me_2Pt(Me_2Cpz_2)}$: 82%, white crystalline solid.
Molecular Weight($CHCl_3$): 392 (401)

^1H NMR ($CDCl_3$), ambient temperature:

MePt 0.84(t) $^2J(^1H-^{195}Pt)$ 88.2 Hz, 6H; C$\underline{Me}_2$ 2.71(s,broad)

6H; H_4 6.35(t) 2H; H_5 7.76(d) $J_{(4,5)}$2.79 Hz, 2H; H_3 7.94(d) $J_{(3,4)}$ 2.10 Hz, 2H.

^1H NMR ($CDCl_3$), -20^oC:

MePt 0.82(t) $^2J(^1H-^{195}Pt)$ 87.4 Hz; $C\underline{Me}_2$ 2.46(s) axial, 3H, 2.96(s) equatorial, 3H; H_4 6.36(t); H_5 7.78(d) $J_{(4,5)}$2.79 Hz; H_3 7.91(d) $J_{(3,4)}$2.07 Hz.

$\underline{Me_2Pt(H_2C(mim)pz)}$: 91%, white crystalline solid.
Molecular Weight ($CHCl_3$): 372 (387)

^1H NMR (D6 acetone):

MePt <u>trans</u> to mim 0.69(t) $^2J(^1H-^{195}Pt)$ 87.0 Hz, 3H; MePt <u>trans</u> to pz 0.76(t) $^2J(^1H-^{195}Pt)$ 89.7 Hz, 3H; $N\underline{Me}$ 4.05(s) 3H; $C\underline{H}_2$ 5.65(s) 2H; H_4 6.50(t) 1H; H_{4mim} 7.25(d) $^3J(^1H-^{195}Pt)$ 12.62 Hz, $J_{(4,5)}$1.42 Hz 1H; H_{5mim} 7.30(d) $J_{(4,5)}$1.44 Hz, 1H; H_3 7.88(d) $J_{(3,4)}$2.18 Hz, 2H; H_5 8.17(d) $J_{(4,5)}$2.47 Hz, 2H.

$\underline{Me_2Pt(H_2C(py)pz)}$: 84%, pale yellow crystalline solid.
Molecular Weight ($CHCl_3$): 379 (384)

^1H NMR ($CDCl_3$), ambient temperature:

MePt <u>trans</u> to py, 0.86(t) $^2J(^1H-^{195}Pt)$ 85.6 Hz, 3H; MePt <u>trans</u> to pz, 0.91(t) $^2J(^1H-^{195}Pt)$ 86.2 Hz, 3H; $C\underline{H}_2$ 5.45(s, broad) 2H; H_4 6.35(t) 1H; py_5 7.33(m), 1H; py_3 7.35(d), 1H; H_5 7.63(d) $J_{(4,5)}$2.52 Hz, 1H; H_3 7.80(d) $J_{(3,5)}$2.21 Hz, 1H; py_4 7.89(t), 1H; py_6 9.02(m) 1H.

^1H NMR ($CDCl_3$), -40^oC:

MePt <u>trans</u> to py, 0.85(t) $^2J(^1H-^{195}Pt)$ 84.0 Hz, 3H; MePt <u>trans</u> to pz, 0.89(t) $^2J(^1H-^{195}Pt)$ 83.9 Hz, 3H; $C\underline{H}_2$ 5.12(d)

$^{2}J(^{1}H-^{1}H)$ 14.54 Hz, axial, 1H; 5.86(d) $^{2}J(^{1}H-^{1}H)$ 14.54 Hz, equatorial, 1H; H_4 6.42(s) 1H; py_5 7.42(t) 1H; py_3 7.47(d) 1H; H_5 7.74(s) 1H; H_3 7.81(s) 1H; py_4 7.98(t) 1H; py_6 8.97(d) 1H.

$Me_2Pt(HC(mim)pz_2)$ 86%, white amorphous powder.

^{1}H NMR (D6 acetone):

MePt trans to mim, 0.74(t) $^{2}J(^{1}H-^{195}Pt)$ 87.3 Hz, 3H; MePt trans to pz, 0.84(t) $^{2}J(^{1}H-^{195}Pt)$ 90 Hz, 3H; NMe 4.11(s) 3H; $H_{4(unco)}$ 6.41(t) 1H; $H_{4(coord)}$ 6.64(t) 1H; H_{4mim} + $H_{3(unco)}$ 7.50(m) 2H; H_{5mim} 7.63(d) $J_{(4,5)}$ 1.54 Hz, 1H; $H_{3(coord)}$ 8.09(d) $J_{(3,4)}$ 2.06 Hz, 1H; CH 8.37(s), 1H; $H_{5(coord)}$ 8.50(d) $J_{(4,5)}$ 2.70 Hz, $H_{5(unco)}$ 9.59(d) $J_{(4,5)}$ 2.56 Hz, 1H.

$Me_2Pt(HC(thio)pz_2)$:

Molecular Weight ($CHCl_3$): 438 (443)

^{1}H NMR (D6 acetone):

MePt 0.75(t) $^{2}J(^{1}H-^{195}Pt)$ 89.50 Hz, 6H; H_4 6.66(q) 2H; H_{4thio} 7.09(t) 1H; H_{3thio} 7.24(s,broad) 1H; H_{5thio} 7.63(d) 1H; H_3 8.07(d) $^{3}J(^{1}H-^{195}Pt)$ 9.29 Hz, $J_{(3,4)}$ 2.10 Hz, 2H; CH 8.65(s) 1H.

$Me_2Pt(Cpz_4)$: 91%, white crystalline solid.

Molecular Weight ($CDCl_3$): 497 (505)

^{1}H NMR Ambient (D6 acetone):

MePt 0.63(t) $^{2}J(^{1}H-^{195}Pt)$ 89.7 Hz, 6H; H_4 6.76(m) 4H; H_5 6.91(s, broad) 2H; H_5 7.44(dd, broad) 2H; H_3 8.04(s, broad) 2H; H_3 8.26(dd, broad) 2H.

^{1}H NMR (D6 acetone), -40^{o}C:

MePt 0.56(t) $^2J(^1H-^{195}Pt)$ 89.78 Hz, 3H; MePt 0.60(t) $^2J(^1H-^{195}Pt)$ 89.5 Hz, 3H; H_{5ax} 6.72(d) $J_{(4,5)}$ 2.73 Hz, 1H; H_{4C} 6.90(t) 1H; H_{5C}, 7.08(d) $J_{(4,5)}$ 2.63 Hz, 1H; H_{5C} 7.42(d) $J_{(4,5)}$ 2.99 Hz, 1H; H_{5eq} 7.65(d) $J_{(4,5)}$ 3.00 Hz, 1H; H_{3C}, 7.95(d) $J_{(3,4)}$ 1.15 Hz, 1H; H_{3eq} 8.22(t) $J_{(3,4)}$ 1.51 Hz, 1H; H_{3ax} 8.33(d) $J_{(3,4)}$ 1.53 Hz, 1H; H_{3C} 8.38(d) $J_{(3,4)}$ 1.84 Hz, 1H.

$[Ph_2Pt(Et_2S)]_2$[16]

Dry crushed cis-$Cl_2Pt(Et_2S)_2$ (4.00g, 8.97 mmole) was suspended in anhydrous ether (150 cm^3) with stirring at 0^{o}C under a dry nitrogen atmosphere. Phenyllithium (19.7 mmole) was added dropwise over 10 minutes and the mixture stirred for 2 hours. The off-white suspension was worked up as for $[Me_2Pt(Et_2S)]_2$ (p. 248). The solid was recrystallized from a benzene-ether mixture to yield the white product.

Yield: 2.95g, 75%

Molecular Weight($CHCl_3$): 856 (878)

^{1}H NMR($CDCl_3$):

CH_3CH_2 1.85(t), 6H; CH_3CH_2 2.50(q), 4H; Ph_4 6.79(m) 2H; $Ph_{3,5}$ 6.94(m) 4H; $Ph_{2,6}$ 7.32(m) $^3J(^1H-^{195}Pt)$ 71.9 Hz, 4H.

$Ph_2Pt(L)$ (L = H_2Cpz_2, $HCpz_3$, $Me(H)Cpz_2$, Me_2Cpz_2, $HC(py)pz_2$, $HC(mim)pz_2$, $HC(thio)pz_2$, $H_2C(py)pz$, $H_2C(mim)pz$)

$[Ph_2Pt(Et_2S)]_2$ (0.20g, 0.23 mmole) was suspended in anhydrous benzene (20 cm^3), ligand (0.46 mmole) added and the mixture heated and stirred under a nitrogen atmosphere. After 5-10 minutes heating the solution turned pale yellow and (in most cases) a white precipitate was deposited. In cases where precipitation did not occur, cooling and/or dropwise addition of hexane facilitated

precipitation. The solid was filtered, washed with ether, air dried and vacuum dried (50°C, 2 hours).

$Ph_2Pt(H_2Cpz_2)$: 92%.

^1H NMR ($CDCl_3$), ambient temperature:

CH_2 5.91(s, broad) 2H; H_4 6.21(t) 2H; $Ph_{3,4,5}$ 6.82-6.93(m, broad) 6H; H_3 7.33(dd) $J_{(3,4)}$2.22 Hz, 2H; H_5 7.39(dd) $J_{(4,5)}$2.67 Hz, 2H; $Ph_{2,6}$ 7.50(m) $^3J(^1H-^{195}Pt)$ 68.9 Hz, 4H.

^1H NMR ($CDCl_3$), -40°C:

CH_2 4.36(d) $^2J(^1H-^1H)$ 14.17 Hz, axial, 1H; 5.79(d) $^2J(^1H-^1H)$ 14.09 Hz, equatorial, 1H; H_4 6.15(t) 2H; $H_{3,4,5}$ 6.86-6.93(m) 6H; $H_{3,5}$ 7.22(s, broad) 2H; $Ph_{2,6}$ 7.56(m) 4H.

$Ph_2Pt(HCpz_3)$: 94%.

Microanalysis: C 47.10 (46.85); H 3.27 (3.57); N 14.87 (14.98).

^1H NMR (D6 acetone):

H_4 6.69(m) 3H; Ph_4 6.82(m) 2H; $Ph_{3,5}$ 6.84-6.94(m) 4H; $H_{3(coord)}$ + $Ph_{2,6}$ 7.50(m) $^3J(^1H-^{195}Pt)$ 73.5 Hz, 6H; $H_{3(unco)}$7.82(d) $J_{(3,4)}$1.73Hz, 1H; $H_{5(coord)}$8.61(dd) $J_{(4,5)}$3.03 Hz, 2H; $H_{5(unco)}$8.78(d) $J_{(4,5)}$2.57 Hz, 1H; CH 9.38(s), 1H.

$Ph_2Pt(Me(H)Cpz_2)$: 90%.

Molecular Weight ($CHCl_3$): 501 (511)

^1H NMR ($CDCl_3$), ambient temperature:

CMe 1.02(s,broad) 3H; H_4 6.23(t) 2H; $Ph_{3,4,5}$ 6.79(m, broad) 6H; $H_{3,5}$ + $Ph_{2,6}$ 7.49(m, broad) $^3J(^1H-^{195}Pt)$ 68.2 Hz, 8H; CH 7.97(s, broad), 1H.

^{1}H NMR ($CDCl_3$), -20°C:

$C\underline{CH}_3$ 0.75(d) $^2J(^1H-^1H)$ 6.51 Hz, 3H; H_4 6.26(t) 2H; $Ph_{3,4,5}$ 6.69-6.82(m) 6H; H_3 7.18(d) $J_{(3,4)}$1.92 Hz, 2H; H_5 7.38(d) $J_{(4,5)}$2.43Hz, 2H; $Ph_{2,6}$ 7.44(m) 4H; CH 8.01(q) $^2J(^1H-^1H)$ 6.65 Hz, 1H.

$\underline{Ph_2Pt(Me_2Cpz_2)}$: 92%.
Molecular Weight($CHCl_3$): 523 (525)

^{1}H NMR ($CDCl_3$), ambient temperature:

CMe 2.83(s, broad) 6H; H_4 6.27(t) 2H; Ph_4 6.85(m) 2H; $Ph_{3,5}$ 6.98(m) 4H; H_3 7.44(d) $J_{(3,4)}$2.13 Hz, 2H; $Ph_{2,6}$ 7.55(m) $^3J(^1H-^{195}Pt)$ 73.6 Hz, 4H; H_5 7.69(d) $J_{(4,5)}$2.82 Hz, 2H.

^{1}H NMR ($CDCl_3$), -30°C:

Me_{eq} 2.19(s) 3H; Me_{ax} 3.11(s) 3H; H_4 6.20(t) 2H; Ph_4 6.81(t) 2H; $Ph_{3,5}$ 6.94(t) 4H; H_3 7.37(d) $J_{(3,4)}$1.92 Hz, 2H; $Ph_{2,6}$ 7.48(m) $^3J(^1H-^{195}Pt)$ 69.03 Hz, 4H; H_5 7.63(d) $J_{(4,5)}$2.67 Hz, 2H.

$\underline{Ph_2Pt(HC(py)pz_2)}$: 84%.

^{1}H NMR ($CDCl_3$): the ^{1}H NMR spectrum is very complex and assignment has not been attempted, however the spectrum shows 4 separate H4 and 2 py_6 resonances consistent with a mixture of two conformers in approximately equal proportions.

H_4 6.34(m) 3H; H_4 6.68(t) 1H; 6.74-6.94(m, complex); 7.24(m), 7.26-7.67(m, complex); 7.85 (m); 7.91(m); py_6 8.68-8.69(dd) 2 signals, 2H; CH 9.04(s).

$Ph_2Pt(HC(mim)pz_2)$: 83%.

Molecular Weight ($CHCl_3$): 552 (577)

^1H NMR (D6 acetone):

NMe 4.15(s) 3H; $H_{4(coord)}$ 6.56(t) 1H; $H_{4(unco)}$ 6.66(t) 1H; Ph_4 + $H_{4(mim)}$ 6.80(m) 3H; $Ph_{3,5}$ 6.89-6.97(m) 4H; $H_{3(coord)}$ + $H_{5(mim)}$ 7.40(m) 2H; $Ph_{2,6}$ 7.50-7.63(m) 4H; $3H_{(unco)}$ 7.76(d) $J_{(3,4)}$ 1.75 Hz, 1H; $H_{5(coord)}$ 8.54(dd) $J_{(4,5)}$ 2.74 Hz, 1H; CH 8.56(s) 1H; $H_{5(coord)}$ 9.70(dd) $J_{(4,5)}$ 2.62 Hz, 1H.

$Ph_2Pt(HC(thio)pz_2)$: 88%.

Molecular Weight ($CHCl_3$): 567 (579)

^1H NMR (D6 acetone):

H_4 6.61(t) 2H; Ph_4 6.79(m) 2H; $Ph_{3,5}$ 6.88(m) 4H; $H_{3,4(thio)}$ 6.25(m) 2H; H_3 7.44(d) $J_{(3,4)}$ 2.14 Hz, 2H; $Ph_{2,6}$ 7.52(m) $^3J(^1H-^{195}Pt)$ 72.8 Hz, 4H; $H_{5(thio)}$ 7.86(dd) $J_{(4,5)}$ 4.9 Hz, 1H; H_5 8.52(dd) $J_{(4,5)}$ 2.70 Hz, 2H; CH 8.82(s) 1H.

$Ph_2Pt(H_2C(py)pz)$:

Molecular Weight ($CHCl_3$): 529 (508)

^1H NMR (D6 acetone), ambient temperature:

CH_2 6.06(s,broad) 2H; H_4 6.48(t) 1H; Ph_4 6.86(m, complex) 2H; $Ph_{3,5}$ 6.92(m,complex) 4H; 7.44-7.61 v. complex pattern containing py_5, H_5 and $Ph_{2,6}$ (2 distinct resonances) 6H; py_3 7.93(d) 1H; py_4 8.20(td) 1H; H_3 8.23(d) $J_{(3,4)}$ 1.76 Hz, 1H; py_6 (m) 1H.

^1H NMR (D6 acetone), -60^oC: apical protons resolved into broad doublets.

Heq 5.99(d) $^{2}J(^{1}H-^{1}H)$ 14.21 Hz, 1H; Hax 6.14(d) $^{2}J(^{1}H-^{1}H)$ 14.21 Hz, 1H.

$Ph_2Pt(H_2C(mim)pz)$:

Molecular Weight ($CHCl_3$): 532 (511)

^{1}H NMR ($CDCl_3$):

NMe 5.28(s) 3H; H_4 6.22(t) 1H; H_{5mim} 6.68(d) $J_{(4,5)}$ 1.48 Hz, 1H; H_{4mim} 6.71(d) $J_{(4,5)}$ 1.48 Hz, 1H; Ph_4 6.80(m) 2H; $Ph_{3,5}$ 6.87(m), 4H; H_3 7.43(d) $J_{(3,4)}$ 2.26 Hz, 1H; H_5 + $Ph_{2,6}$ 7.49(m), $^{3}J(^{1}H-^{195}Pt)$ 63.06 Hz, 5H.

7.4 Experimental for Chapter Three

$MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$

$Me_2Pt(HCpz_3)$ was suspended in dry pyridine (5-10 cm^3) under a nitrogen atmosphere and allowed to stand at ambient temperature until all of the solid had disappeared. Hexane was added dropwise until cloudiness developed, at which time crystallization occurred. The product was filtered, washed with ether (3 x 5 cm^3) and vacuum dried at 50°C (2 hours).

Yield: 80%

^1H NMR($CDCl_3$):

MePt 0.92(t) $^2J(^1H-^{195}Pt)$ 86.4 Hz, 3H; $H_{4(unco)}$ 6.24(t) 1H; $H_{4(coord + met)}$ $^3J_{(met)}(^1H-^{195}Pt)$ 24.43 Hz, 2H; $H_{3(coord)}$ 6.92(d) $J_{(3,4)}$2.13 Hz, 1H; $py_{3,5}$ 7.36(m) 2H; $H_{3(unco)}$7.58(d) $J_{(3,4)}$1.59 Hz, 1H; $H_{3(met)}$7.60(d) $J_{(3,4)}$1.68 Hz, 1H; $H_{5(unco)}$ + py_4 7.85(m) 2H; $H_{5(coord)}$8.10(d) $J_{(4,5)}$2.55 Hz, 1H; CH 8.38(s) 1H; $py_{2,6}$ 8.54(q) $^3J(^1H-^{195}Pt)$ 24.6 Hz, 2H.

$MePt(HCpz_2(C_3N_2H_2)-C,N)(mim)$

This complex was synthesized in an analogous manner to $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ using N-methylimidazole as solvent.

Yield: 76%

Microanalysis: C 35.73 (35.61); H 3.57 (3.59); N 22.06 (22.24)

^1H NMR($CDCl_3$):

MePt 0.88(t) $^2J(^1H-^{195}Pt)$ 86.20 Hz, 3H; NMe 3.73(s) 3H; H_4 6.20(t) 1H; $H_{4(coord + met)}$6.34(t) $^3J_{(met)}(^1H-^{195}Pt)$ 24.2 Hz, 2H; H_{5mim} 6.92(s) 1H; H_{4mim} 7.02(t) $^3J(^1H-^{195}Pt)$ 15.2 Hz, 1H; $H_{3(coord)}$7.13(d) $J_{(3,4)}$21.0 Hz, 1H; $H_{3(unco)}$7.53(d) $J_{(3,4)}$ 1.68 Hz, 1H; $H_{3(met)}$ + $H_{3(coord)}$7.58(m) 2H; $H_{5(unco)}$ 7.94(d) $J_{(4,5)}$2.70 Hz, 1H; CH 8.37(s) 1H.

MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(γ-picoline)

This complex was synthesized in an analogous manner to MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(py) using γ-picoline as solvent.
Yield: 82%
Microanalysis: C 40.28 (39.49); H 3.79 (3.70); N 18.78 (19.06)
^{1}H NMR ($CDCl_3$):

MePt 0.94(t) $^2J(^1H-^{195}Pt)$ 83.62 Hz, 3H; py_{Me} 2.41(s) 3H; $H_{4(unco)}$ 6.27(q) 1H; $H_{4(met)}$ + $H_{4(coord)}$ 6.37(m) $^3J_{(met)}(^1H-^{195}Pt)$ 24.02 Hz, 2H; $H_{3(coord)}$ 6.96(d) $J_{(3,4)}$ 2.13 Hz, 1H; $py_{3,5}$ 7.17(m) 2H; $H_{3(unco)}$ 7.61(d) $J_{(3,4)}$ 1.41 Hz, 1H; $H_{3(met)}$ 7.63(d) $J_{(3,4)}$ 1.68 Hz, 1H; $H_{5(unco)}$ 7.91(d) $J_{(4,5)}$ 2.31 Hz, 1H; $H_{5(coord)}$ 8.12(d) $J_{(4,5)}$ 2.70 Hz, 1H; H + $py_{2,6}$ 8.42(m) 3H.

[MePt(HCpz$_2$($C_3N_2H_2$)-C,N)]$_n$

Method 1

Crystalline MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(py) was refluxed in anhydrous benzene for 30 minutes during which time the crystalline solid dissolved and a white powder precipitated. The powder was collected by filtration and vacuum dried (2 hours, 50^{o}C).

Method 2

A suspension of MePt(HCpz$_2$($C_3N_2H_2$)-C,N)(py) was heated with stirring in acetone until a clear solution formed. Hexane was added to the hot solution to precipitate a white solid which was collected and vacuum dried (2 hours, 50^{o}C).
Yield: 96%
Microanalysis: C 31.85 (31.20); H 2.98 (2.86); N 20.16 (19.86)

$MePt(HCpz_2(C_3N_2H_2)-C,N)(CO)$

A suspension of $MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ was refluxed in acetone until a clear solution had formed, at which time heating was stopped and carbon monoxide was bubbled through the solution for 10 minutes. After cooling, hexane was added to precipitate a white solid, which was collected by filtration, washed with ether and vacuum dried.

Yield: 95%

Microanalysis: C 32.01(31.93); H 2.68 (2.68); N 18.48 (18.62)

I.R. (Nujol): υ(CO) 2074 cm^{-1} (strong)

^1H NMR ($CDCl_3$):

MePt 1.21(t) $^2J(^1H-^{195}Pt)$ 87.16 Hz, 3H; $H_{4(unco)}$6.21(t) 1H; $H_{4(met)}$6.53(t) $^3J(^1H-^{195}Pt)$ 14.96 Hz, 1H; $H_{4(coord)}$6.56(t) 1H; $H_{5(unco)}$7.26(d) 2.01 Hz, 1H; $H_{3(unco)}$7.54(s) 1H; $H_{3(met)}$7.66(t) $^4J(^1H-^{195}Pt)$ 9.09 Hz, 1H; $H_{3(coord)}$7.75(s) 1H; $H_{5(coord)}$8.16(d) $J_{(4,5)}$2.34 Hz, 1H; CH 8.38(s) 1H.

$MePt(HCpz_2(C_3N_2H_2)-C)(phosphine)$ (phosphine = $2PPh_3$, $2PPh_2Me$, $2PPhMe_2$, $2PPh_2Et$, $2PPh_2(CH_2Ph)$, PPh_2(o-tolyl), $PPh_2(PhOMe)$, $P(PhO)_3$, $PPh_2CH_2Ph_2P$, $PPh_2CH_2CH_2Ph_2P$)

$MePt(HCpz_2(C_3N_2H_2)-C,N)(py)$ (0.1g, 0.2 mmole) and phosphine (0.4 mmole) were heated with stirring in acetone (20 cm^3) under a nitrogen atmosphere. As the mixture neared reflux the suspension cleared, heating was stopped and the solution allowed to cool to ambient temperature with stirring. The solution was filtered, the volume reduced and hexane added dropwise until cloudiness developed and the solution was set aside to allow crystallization to occur. The crystalline product was collected and vacuum dried.

Alternatively, the reaction can be carried out entirely in neat pyridine starting with $Me_2Pt(HCpz_3)$ and adding the required amount of phosphine ligand after $Me_2Pt(HCpz_3)$ had "dissolved". However, it is

preferable to isolate the intermediate pyridine complex, where possible, as reactions carried out in neat pyridine have yielded mixtures of mono and bis(phosphine) complexes.

Generally the ^{1}H NMR spectra of these complexes were difficult to assign due to the large number of phosphine ligand resonances. Consequently, NMR characterization was by ^{31}P NMR spectroscopy and the MePt region of the ^{1}H NMR spectra only are reported.

$MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$

^{1}H NMR ($CDCl_3$):

MePt 0.11(tt) $^{2}J(^{1}H-^{195}Pt)$ 64.81 Hz.

^{31}P NMR ($CDCl_3$):

P *trans* to Me 20.5(td) $^{1}J(^{31}P-^{195}Pt)$ 1808 Hz, $^{2}J(^{31}P-^{31}P)$ 14.7 Hz; P *cis* to Me 22.9(td) $^{1}J(^{31}P-^{195}Pt)$ 2239 Hz, $^{2}J(^{31}P-^{31}P)$ 14.7 Hz.

$MePt(HCpz_2(C_3N_2H_2)-C)(PPh_2Me)_2$

Yield: 88%.

Microanalysis: C 53.52 (53.94); H 4.95 (4.65); N 10.30 (10.20); P 7.90 (7.52).

^{1}H NMR ($CDCl_3$):

MePt 0.18(tt) 0.18 $^{2}J(^{1}H-^{195}Pt)$ 62.86 Hz.

^{31}P NMR ($CDCl_3$):

P *trans* to Me 1.6(td) $^{1}J(^{31}P-^{195}Pt)$ 1718 Hz, $^{2}J(^{31}P-^{31}P)$ 16.1 Hz; P *cis* to Me 2.3(td) $^{1}J(^{31}P-^{195}Pt)$ 2262 Hz, $^{2}J(^{31}P-^{31}P)$ 16.1 Hz.

$MePt(HCpz_2(C_3N_2H_2)-C)(PPhMe_2)_2$

Yield: 81%

Microanalysis: C 46.24 (46.35); H 4.85 (4.89); N 11.90 (12.01); P 9.90 (9.85)

^{1}H NMR ($CDCl_3$):

MePt 0.25(tt) $^{2}J(^{1}H-^{195}Pt)$ 65.0 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me -14.3(td) $^{1}J(^{31}P-^{195}Pt)$ 1690 Hz, $^{2}J(^{31}P-^{31}P)$ 17.1 Hz; P cis to Me -15.0(td) $^{1}J(^{31}P-^{195}Pt)$ 2214 Hz, $^{2}J(^{31}P-^{31}P)$ 17.1 Hz.

$MePt(HCpz_2(C_3N_2H_2)-C)(PPh_2Et)_2$

Yield: 74%

Microanalysis: C 55.18 (54.96); H 5.50 (4.97); N 9.61 (9.91); P 7.70 (7.27)

^{1}H NMR ($CDCl_3$):

MePt 0.12(tt) $^{2}J(^{1}H-^{195}Pt)$ 64.35 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me 11.2(td) $^{1}J(^{31}P-^{195}Pt)$ 1752 Hz, $^{2}J(^{31}P-^{31}P)$ 15.6 Hz; P cis to Me 14.1(td) $^{1}J(^{31}P-^{195}Pt)$ 2264 Hz, $^{2}J(^{31}P-^{31}P)$ 15.6 Hz.

$MePt(HCpz_2(C_3N_2H_2)-C)(PPh_2(CH_2Ph))_2$

Yield: 76%.

Microanalysis: C 60.55 (60.30); H 4.85 (4.75); N 8.53 (8.61); P 6.80 (6.35)

^{1}H NMR ($CDCl_3$):

MePt 0.26(td) $^{2}J(^{1}H-^{195}Pt)$ 72.33 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me 12.8(td) $^{1}J(^{31}P-^{195}Pt)$ 1779 Hz, $^{2}J(^{31}P-^{31}P)$ 15.5 Hz; P cis to Me 12.6(td) $^{1}J(^{31}P-^{195}Pt)$ 2281 Hz, $^{2}J(^{31}P-^{31}P)$ 15.5 Hz.

$MePt(HCpz_2(C_3N_2H_2)-C,N)(PPh_2(o\text{-}tolyl))$

Yield: 70%

Microanalysis: C 52.49 (51.50); H 4.32 (4.18); N 12.36 (12.01); P 5.00 (4.43)

^{1}H NMR ($CDCl_3$):

MePt 0.31(td) $^{2}J(^{1}H-^{195}Pt)$ 77.50 Hz.

^{31}P NMR ($CDCl_3$):

P cis to Me 21.8 (t) $^{1}J(^{31}P-^{195}Pt)$ 2504 Hz.

MePt(HCpz$_2$(C$_3$N$_2$H$_2$)-C,N)(PPh$_2$PhOMe)

Yield: 68%.

Microanalysis: C 51.10 (50.34); H 4.15 (4.08); N 11.55 (11.75); P 3.70 (4.33)

^{1}H NMR ($CDCl_3$):

MePt 0.65(td) $^{2}J(^{1}H-^{195}Pt)$ 83.37 Hz.

^{31}P NMR ($CDCl_3$):

P cis to Me 20.7(t) $^{1}J(^{31}P-^{195}Pt)$ 2599 Hz.

MePt(HCpz$_2$(C$_3$N$_2$H$_2$)-C,N)(P(OPh)$_3$)$_2$

Yield: 88%.

Microanalysis: C 53.55 (54.07); H 4.07 (4.06); N 7.92 (8.05); P 6.10 (5.93)

^{1}H NMR ($CDCl_3$):

MePt 0.28(tt) $^{2}J(^{1}H-^{195}Pt)$ 67.14 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me 111.7(td) $^{1}J(^{31}P-^{195}Pt)$ 2863 Hz, $^{2}J(^{31}P-^{31}P)$ 33 Hz; P cis to Me 106.5(td) $^{1}J(^{31}P-^{195}Pt)$ 3820 Hz, $^{2}J(^{31}P-^{31}P)$ 33 Hz.

MePt(HCpz$_2$(C$_3$N$_2$H$_2$)-C)(PPh$_2$CH$_2$Ph$_2$P)

Yield: 75%.

Microanalysis: C 53.70 (53.53); H 4.41 (4.24); N 10.55 (10.40); P 7.30 (7.67)

^{1}H NMR ($CDCl_3$):

MePt 0.86(tt) $^{2}J(^{1}H-^{195}Pt)$ 70.20 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me -40.0(td) $^{1}J(^{31}P-^{195}Pt)$ 1291 Hz, $^{2}J(^{31}P-^{31}P)$ 20.7 Hz; P cis to Me -43.6(td) $^{1}J(^{31}P-^{195}Pt)$ 1959 Hz, $^{2}J(^{31}P-^{31}P)$ 20.7 Hz.

MePt(HCpz$_2$($C_3N_2H_2$)-C)($PPh_2CH_2CH_2Ph_2P$)

Yield: 72%

Microanalysis: C 53.85 (54.08); H 4.37 (4.42); N 10.21 (10.23); P 7.70 (7.54)

^{1}H NMR ($CDCl_3$):

MePt 0.48(tt) $^{2}J(^{1}H-^{195}Pt)$ 67.14 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me 40.9(t) $^{1}J(^{31}P-^{195}Pt)$ 1663 Hz; P cis to Me 44.0(t) $^{1}J(^{31}P-^{195}Pt)$ 2228 Hz.

MePt(HCpz($C_3N_2H_2$)-C,)(PPh_3)$_2$

In the preparation of the following three complexes the initial metallation reactions were carried out in neat pyridine, phosphine ligand in an equivalent volume of acetone added and the phosphine complexes isolated, as the intermediate pyridine complexes were difficult to isolate in a pure form.

Yield: 58%.

Microanalysis: C 59.52 (59.93); H 4.37 (4.57); N 6.12 (6.36); P 6.80 (7.02)

^{1}H NMR ($CDCl_3$):

MePt 0.09(tt) $^{2}J(^{1}H-^{195}Pt)$ 64.26 Hz.

^{31}P NMR ($CDCl_3$):

P trans to Me 23.5(td) $^{1}J(^{31}P-^{195}Pt)$ 1804 Hz, $^{2}J(^{31}P-^{31}P)$ 14.0 Hz; P cis to Me 19.8(td) $^{1}J(^{31}P-^{195}Pt)$ 2219 Hz, $^{2}J(^{31}P-^{31}P)$ 14.0 Hz.

MePt(Ph(H)Cpz($C_3N_2H_2$)-C,N)(PPh_3)

Yield: 63%

Microanalysis: C 55.24 (55.24); H 4.32 (4.20); N 7.91 (8.01);

^{1}H NMR ($CDCl_3$):

MePt 0.24(tt) $^{2}J(^{1}H-^{195}Pt)$ 86.91 Hz.

^{31}P NMR ($CDCl_3$):

P cis to Me 20.1(t) $^{1}J(^{31}P-^{195}Pt)$ 2560 Hz.

MePt(HC(mim)pz($C_3N_2H_2$)-C,N_{mim})(PPh_3)

Yield: 79%

Microanalysis: C 51.4 (51.50); H 4.4 (4.18); N 12.3 (12.02)

^{1}H NMR ($CDCl_3$):

MePt 0.58(td) $^{2}J(^{1}H-^{195}Pt)$ 82.48 Hz.

^{31}P NMR ($CDCl_3$):

P cis to Me 25.1(t) $^{1}J(^{31}P-^{195}Pt)$ 2552 Hz.

Pd(1,3-($pzCH_2$)$_2$$C_6H_3$)($CH_3COO$)

$Pd(oAc)_2$ (0.24g, 1.07 mmole) and 1,3-($pzCH_2$)$_2$$C_6H_3$ (0.26g, 1.09 mmole) were heated with stirring in glacial acetic acid (25 cm^3) under a nitrogen atmosphere. The suspension clarified on further heating to give a golden yellow solution which darkened to a purple colour as the acetic acid neared reflux. After twenty minutes at gentle reflux the solution lightened to a golden yellow colour and palladium reduction was not evident. Acetic acid was removed under vacuum at 70°C and the yellow oli recrystallized from CH_2Cl_2/hexane to yield a white crystalline solid.

Yield: 0.39g, 92%.

Microanalysis: C 47.40 (47.71); H 4.10 (4.00); N 12.30 (13.91)

^{1}H NMR ($CDCl_3$):

$Pd(CH_3COO)$ 1.94(s, broad) 3H; CH_2 5.3(s) 4H; H_4 6.32(t) 2H; $Ph_{3,4,5}$ 6.98(m) 3H; H_5 7.64(d) $J_{(4,5)}$2.25 Hz, 2H; H_3 7.90(d) $J_{(3,4)}$1.77 Hz, 2H.

^{13}C NMR ($CDCl_3$):

$\underline{CH}_3COO$ 25(s, broad); CH_2 58.4(s); C_4 106.6(s); Ph_4 124.5(s); $Ph_{3,5}$ 125.9(s); C_5 130.9(s); $Ph_{2,6}$ 136.3(s); Ph_1 139.9(s); C_3 142.4(s); $CH_3\underline{COO}$ 178(s).

7.5 Experimental for Chapter Four

Me_2PtI_2L (L = $HCpz_3$, $HC(thio)pz_2$, $HC(mim)pz_2$, $HC(py)pz_2$)

$Me_2Pt(COD)$ (0.1g, 0.30 mmole) and ligand (0.30 mmole) were dissolved in acetone (10 cm^3), and iodine (0.08g, 0.32 mmole) dissolved in acetone (2 cm^3) was added dropwise with stirring until the characteristic iodine colour persisted. The solution was taken to dryness (rotary evaporator) and excess iodine extracted from the residue with warm hexane (3 x 20 cm^3). The residue was dissolved in acetone (10 cm^3) and hexane added dropwise until cloudiness developed. Microcrystalline solids precipitated on standing, these were filtered, air dried and vacuum dried (50°C, 2 hours).

The same products were obtained if $[Me_2Pt(Et_2S)]_2$ was used in place of $Me_2Pt(COD)$.

$Me_2I_2Pt(HCpz_3)$: 95%, orange crystalline solid, m.pt. isomerizes 140°C, decomposes 225°C

Microanalysis: C 20.46 (20.78); H 2.22 (2.32); N 12.07 (12.18); I 36.60 (36.59)

Molecular Weight ($CHCl_3$): 669 (693)

^1H NMR ($CDCl_3$):

MePt 2.67(t) $^2J(^1H-^{195}Pt)$ 75.3 Hz, 6H; $H_{4(coord)}$ 6.46(t) 2H; $H_{4(unco)}$ 6.63(t) 1H; $H_{5(coord)}$ 7.57(d) $J_{(4,5)}$ 2.40 Hz, 2H; $H_{5(unco)}$ 7.99(d) $J_{(4,5)}$ 2.82 Hz, 1H; $H_{3(coord + unco)}$ 8.07(m) 3H; CH 10.12(s) 1H.

^1H NMR (D6 acetone):

MePt 2.72(t) $^2J(^1H-^{195}Pt)$ 75.41 Hz, 6H; $H_{4(coord)}$ 6.82(t) 2H; $H_{4(unco)}$ 6.90(t) 1H; $H_{5(coord)}$ 7.82(d) $J_{(3,4)}$ 1.66 Hz, 1H; $H_{3(coord)}$ 8.35(d) $^3J(^1H-^{195}Pt)$ 9.52 Hz, $J_{(3,4)}$ 2.23 Hz, 2H; $H_{5(unco)}$ 8.50(d) $J_{(4,5)}$ 2.60Hz, 1H; CH 9.93(s) 1H.

$Me_2I_2Pt(HC(mim)pz_2)$: 76%, yellow microcrystalline solid. Isomerizes at ~180°C

Molecular Weight ($CHCl_3$): 682 (707)

^1H NMR (D6 acetone):

MePt trans to mim 2.55(t) $^2J(^1H-^{195}Pt)$ 73.4 Hz, 3H; MePt trans to pz 2.68(t) $^2J(^1H-^{195}Pt)$ 76.1 Hz, 3H; NMe 4.06(s) 3H; $H_{4(unco)}$6.93(m) 1H; $H_{4(coord)}$6.88(m) 1H; $H_{4(mim)}$7.62(d) $^3J(^1H-^{195}Pt)$ 9.44 Hz, $J_{(4,5)}$1.63 Hz, 1H; $H_{3,5(unco)}$7.66(m) 2H; $H_{5(mim)}$7.74(d) $J_{(4,5)}$1.60 Hz, 1H; $H_{3(coord)}$8.32(d) $^3J(^1H-^{195}Pt)$ 9.82 Hz, $J_{(3,4)}$2.33 Hz, 1H; $H_{5(coord)}$8.60(dd) $J_{(4,5)}$2.76 Hz, 1H; CH 8.71 1H.

^1H NMR ($CDCl_3$):

Isomer A: MePt trans to mim 2.49(t) $^2J(^1H-^{195}Pt)$ 72.18 Hz; MePt 2.69(t) $^2J(^1H-^{195}Pt)$ 75.13 Hz; NMe 3.59(s); H_{4ax}6.29(q); H_4 6.59(t); H_{5mim}7.15(d) $J_{(4,5)}$1.54 Hz; H_{4mim}7.53(td) $^3J(^1H-^{195}Pt)$ 9.58 Hz, $J_{(4,5)}$1.56 Hz; H_{3ax}7.58(d) $J_{(3,4)}$1.73 Hz; H_{5ax}8.00(d) $J_{(4,5)}$2.52 Hz; H_5 7.97(d)$J_{(4,5)}$2.74 Hz; CH 8.04(s); H_3 8.11(d) $J_{(3,4)}$2.28 Hz.

Isomer B: MePt 2.61(t) $^2J(^1H-^{195}Pt)$ 75.93 Hz; NMe 3.90(s); H_4 6.42(q); H_{5mim}7.12(d) $J_{(4,5)}$1.17 Hz; H_{4mim}7.39(d) $J_{(4,5)}$1.17 Hz; H_5 7.96(d) $J_{(4,5)}$2.76 Hz; H_3 8.07(d) $J_{(3,4)}$2.37 Hz; CH 9.48(s).

$Me_2I_2Pt(HC(py)pz_2)$: 79%, orange crystalline solid. Isomerizes at ~190°C.

Molecular Weight ($CHCl_3$): 688 (704)

^1H NMR ($CDCl_3$):

Isomer A: MePt trans to py 2.60(t) $^2J(^1H-^{195}Pt)$ 72.89 Hz;

MePt 2.75(t) $^{2}J(^{1}H-^{195}Pt)$ 74.32 Hz; H_3, H_4 6.4 or 6.6; pz + py 7.4-8.5 complicated overlapping resonances; py_6 9.26(q) $^{3}J(^{1}H-^{195}Pt)$ 20.65 Hz; CH 9.61(s).

Isomer B: MePt 2.70(t) $^{2}J(^{1}H-^{195}Pt)$ 75.06 Hz; H_3, H_4 6.4 or 6.6; pz + py 7.4-8.5 complicated overlapping resonances; py_6 9.01(d); CH 9.31(s).

$Me_2I_2Pt(HC(thio)pz_2)$: 94%, black microcrystalline solid.
Molecular Weight ($CHCl_3$): 700 (708)
^{1}H NMR ($CDCl_3$):

MePt 2.64(t) $^{2}J(^{1}H-^{195}Pt)$ 74.8 Hz, 6H; H_4 6.45(t) $^{4}J(^{1}H-^{195}Pt)$ 7.54 Hz, 2H; $H_{4(thio)}$ 7.36(dd) 1H; H_5 7.68(d) $J_{(4,5)}$ 2.55 Hz, 2H; $H_{3,5(thio)}$ 7.72-7.79(m) 2H; H_3 8.09(d) $^{3}J(^{1}H-^{195}Pt)$ 9.32 Hz, $J_{(3,4)}$ 2.26 Hz, 2H; CH 9.36(s) 1H.

$[Ph_2IPt(HCpz_3)]I$ 79%

Molecular Weight ($CHCl_3$): 627 (622)
Conductivity (acetone): 87 Ω^{-1} cm^2 $mole^{-1}$
^{1}H NMR ($CDCl_3$):

H_3 6.65(q) 3H; Ph 7.0-7.20(m) 10H; H_3 trans to I 7.77(d) $J_{(3,4)}$ 2.35 Hz, 1H; H_3 8.17(d) $J_{(3,4)}$ 2.37 Hz, 2H; H_5 9.07(d) $J_{(4,5)}$ 2.70 Hz, 2H; H_5 trans to I 9.29(d) $J_{(4,5)}$ 2.49 Hz, 1H; CH 11.7(s) 1H.

$Me_2I_2Pt(L)$ + Heat (L = $HCpz_3$, $HC(mim)pz_2$, $HC(py)pz_2$).

Finely crushed Me_2I_2PtL (50mg) was heated on a microscope cover slip until a colour change was observed, or decomposition occurred.

[$Me_2IPt(HCpz_3)$]I: yellow crystalline solid. Isomerization occurred at 140-150°C

^1H NMR ($CDCl_3$):

MePt trans to Me 1.95(t) $^2J(^1H-^{195}Pt)$ 70.5 Hz, 6H; H_4 6.47(t) , 2H; H_4 trans to I 6.60(t), 1H; H_3 trans to I 7.95(d) $J_{(3,4)}$2.46 Hz, 1H; H_3 trans to Me 8.03(d) $J_{(3,4)}$2.37 Hz, 2H; H_5 trans to Me 9.04(dd) $J_{(4,5)}$2.73 Hz, 2H; H_5 trans to I 9.29(dd) $J_{(4,5)}$2.94 Hz, 1H; CH 12.57(s) 1H.

[$Me_2IPt(HC(mim)pz_2)$]I: yellow crystalline solid. Isomerization occurred at ~180°C.

^1H NMR ($CDCl_3$):

Isomer A: MePt 1.93(t) $^2J(^1H-^{195}Pt)$ 71.25 Hz; NMe 4.41(s); H_4 6.49(m); H_{5mim}7.07(d) $J_{(4,5)}$1.59 Hz; H_{4mim}7.18(m); H_3 8.00(d) $J_{(3,4)}$2.16 Hz; H_5 9.34(d) $J_{(4,5)}$2.73 Hz; CH 11.20 or 11.25(s).

Isomer B: MePt trans to mim 1.78(t) $^2J(^1H-^{195}Pt)$ 68.34 Hz; MePt 1.94(t) $^2J(^1H-^{195}Pt)$ 70.78 Hz; NMe 4.50(s); H_4 6.49(m); H_4 trans to I 6.60(m); H_3 trans to I 7.17(m); H_{5mim}7.49(d) $J_{(4,5)}$1.46 Hz; H_3 7.96(d) $J_{(3,4)}$2.31 Hz; H_5 9.24(d) $J_{(4,5)}$2.70Hz; H_5 trans to I 9.60(d) $J_{(4,5)}$2.88 Hz; CH 11.20 or 11.25(s).

$Me_2(R)XPtL$ (L = $HCpz_3$, $MeCpz_3$, $HC(mim)pz_2$; RX = MeI, propargyl bromide)

$[Me_2Pt(Et_2S)]_2$ (0.1g, 0.16 mmole) and ligand (0.32 mmole) were dissolved in acetone (10 cm^3) and excess RX (x5) added. The solution (stoppered flask) was stirred for 10 minutes, excess RX removed

(rotary evaporator), acetone added if required and hexane added dropwise until cloudiness developed. The products precipitated as white or slightly yellow solids.

[$Me_3Pt(HCpz_3)$]I: 92%,
Conductivity: 76 Ω^{-1} cm^2 $mole^{-1}$

^1H NMR ($CDCl_3$):

MePt 1.14(t) $^2J(^1H-^{195}Pt)$ 72.24 Hz, 9H; H_4 6.55(t) 3H; H_3 7.72(d) $J_{(3,4)}$2.34 Hz, 3H; H_5 9.08(dd) $J_{(4,5)}$2.76 Hz, 2H; CH 12.23(s) 1H.

[$Me_3Pt(MeCpz_3)$]I: 79%.
Conductivity: 68 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt 1.07(t) $^2J(^1H-^{195}Pt)$ 71.53 Hz, 9H; MeC 4.06(s) 3H; H_4 6.63(q) 3H; H_3 7.75(q) $^3J(^1H-^{195}Pt)$ 8.66Hz, $J_{(3,4)}$2.23 Hz, 3H; H_5 8.85(d) $J_{(4,5)}$2.99 Hz, 3H.

$Me_3IPt(H_2C(mim)pz)$: 89%.

^1H NMR ($CDCl_3$):

MePt 0.99(t) $^2J(^1H-^{195}Pt)$ 72.70 Hz, 3H; MePt *trans* to mim 1.51(t) $^2J(^1H-^{195}Pt)$ 70.31 Hz, 3H; MePt *trans* to pz 1.61(t) $^2J(^1H-^{195}Pt)$ 73.44 Hz, 3H; H_{eq} 5.39(d) $^2J(^1H-^1H)$ 15.45 Hz, 1H; H_4 6.38(t) 1H; H_{ax} 6.63(d) $^2J(^1H-^1H)$ 15.45 Hz, 1H; H_{5mim} 6.95(d) $J_{(4,5)}$1.55Hz, 1H; H_{4mim} 7.17(d) $^3J(^1H-^{195}Pt)$ 6.87 Hz, $J_{(4,5)}$ 1.56 Hz, 1H; H_3 7.69(d) $J_{(3,4)}$2.56 Hz, 1H; H_5 7.72(d) $J_{(4,5)}$2.76 Hz, 1H.

[Me_2(propargyl)$Pt(HCpz_3)$]Br: 92%, white crystalline solid. Isomeric mixture
Conductivity: 70 Ω^{-1} cm^2 $mole^{-1}$

^{1}H NMR ($CDCl_3$):

(alknynl): MePt 1.28(t) $^2J(^1H-^{195}Pt)$ 71.24 Hz, $\underline{C}H$ 2.19(t) $^4J(^1H-^{195}Pt)$ 19.79 Hz, $J(^1H-^1H)$ 2.82 Hz; $\underline{CH}_2$ 2.51(t) $^2J(^1H-^{195}Pt)$ 97.00 Hz, $J(^1H-^1H)$ 2.83 Hz;

(allenyl): MePt 1.31(t) $^2J(^1H-^{195}Pt)$ 71.55 Hz, $=\underline{CH}_2$ 4.29(t) $^4J(^1H-^{195}Pt)$ 46.90 Hz, $J(^1H-^1H)$ 6.35 Hz; $=\underline{CH}$ 5.57(t) $^2J(^1H-^{195}Pt)$85.29 Hz, $J(^1H-^1H)$ 6.35 Hz; H_4 6.51-6.57(m); H_3 7.79(m); H_5 9.01(m); CH 12.55(s)

$\underline{Me_2I_2Pt(py)_2}$ from $\underline{Me_2I_2Pt(L)}$ ($\underline{L = HCpz_3, HC(mim)pz_2, HC(thio)pz_2, HC(py)pz_2}$)

Me_2I_2PtL (50mg) was dissolved in dry pyridine (5 cm^3) and allowed to stand for 10 minutes. Hexane was added dropwise until cloudiness whereupon a yellow microcrystalline solid precipitated. In all cases the same product was isolated.

^{1}H NMR ($CDCl_3$):

MePt 2.51(t) $^2J(^1H-^{195}Pt)$ 72.5 Hz, 6H; $(py)_{3,5}$7.37(t) 4H; py_4 7.84(t) 2H; $py_{2,6}$ 9.08(m) 4H.

$\underline{Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)}$

$Me_2Pt(HCpz_3)$ (0.15g, 0.34 mmole) was suspended in dry acetone (10 cm^3) with stirring and excess MeI (100 l, x5) added. The flask was stoppered, wrapped with Alfoil and the suspension stirred for 3 hours, by which time a yellow solution resulted. Excess MeI was removed and hexane added to precipitate a white solid. The product was filtered, air dried and vacuum dried (60^{o}C, 2 hours).

Yield: 0.17g, 89%.

Microanalysis: C 29.44 (28.90), H 3.45 (3.4), N 13.87 (13.48), I 20.46 (20.36). Calculated for 0.1 acetone solvate.

^{1}H NMR (D6 Acetone):

MePt 1.87(t) $^{2}J(^{1}H-^{195}Pt)$ 74.1 Hz, 6H; $H_{4(met)}$ 6.18(t) $^{3}J(^{1}H-^{195}Pt)$ 14.02 Hz, $^{3}J(^{1}H-^{1}H)$ 1.87 Hz, 1H; H_4 6.76(t) 2H; $H_{3(met)}$ 7.54(t) $^{4}J(^{1}H-^{195}Pt)$ 10.80 Hz, $^{3}J(^{1}H-^{1}H)$ 1.87 Hz, 1H; H_5 8.33(d) $J_{(4,5)}$ 2.16 Hz, 2H; H_3 8.63(d) $J_{(3,4)}$ 2.64 Hz, 2H; CH 9.47(s), 1H.

^{13}C NMR (D6 Acetone):

MePt -8.74(t) $J(^{13}C-^{195}Pt)$ 617.26 Hz; CH 81.80(s); $C_{4(met)}$ 107.31(t) $^{2}J(^{13}C-^{195}Pt)$ 84.60 Hz; C_4 109.40(s); C_5 133.37(s); $C_{5(met)}$ 134.16(s); $C_{3(met)}$ 141.38(t) $^{3}J(^{13}C-^{195}Pt)$ 63.70 Hz; C_3 144.55(s).

Me(Et)IPt($HCpz_2(C_3N_2H_2)$-C,N,N)

$Me_2Pt(HCpz_3)$ (0.1g, 0.23 mmole) was suspended in acetone (20 cm^3), excess EtI (100 ul) added and the suspension refluxed until solution was complete, by which time the acetone had changed to a pale yellow colour. The volume was reduced and excess hexane added to precipitate a white solid, which was filtered, air dried and vacuum dried (50°C, 2 hours).

Yield: 0.11g, 81%.

^{1}H NMR ($CDCl_3$):

CH_3CH_2 0.90(m) $^{3}J(^{1}H-^{195}Pt)$ 49.7 Hz, 3H; MePt 1.74(t) $^{2}J(^{1}H-^{195}Pt)$ 75.0 Hz, 3H; CH_3CH_2 2.46(dd) $^{2}J(^{1}H-^{195}Pt)$ 55.5 Hz, $^{2}J(^{1}H-^{1}H)$ 7.58 Hz, 1H; CH_3CH_2 3.09(dd) $^{2}J(^{1}H-^{195}Pt)$ 91.55 Hz, $^{2}J(^{1}H-^{1}H)$ 7.65 Hz, 1H; $H_{4(met)}$ 6.18(t) $^{3}J(^{1}H-^{195}Pt)$ 14.00 Hz, $^{3}J(^{1}H-^{1}H)$ 1.0 Hz, 1H; H_4 6.42(m), 2H; $H_{3(met)}$ 7.47(t) $^{4}J(^{1}H-^{195}Pt)$ 11.00 Hz, $^{3}J(^{1}H-^{1}H)$ 0.98 Hz, 1H; H_5 7.98(d), $J_{(4,5)}$ 2.62 Hz, 2H; H_3 8.09(d) $J_{(3,4)}$ 1.53 Hz, 1H; H_3 8.23(d) $J_{(3,4)}$ 1.53 Hz, 1H; CH 8.63(s) 1H.

^{13}C NMR ($CDCl_3$ + DMSO):

$\underline{CH_3}CH_2$ -7.68 $J(^{13}C-^{195}Pt)$ 637.8 Hz; MePt 5.92 $J(^{13}C-^{195}Pt)$ 600.7 Hz; $CH_3\underline{CH_2}$ 17.68 $^2J(^{13}C-^{195}Pt)$ 30.5 Hz; CH 78.83(s), $C_{4(met)}$ 105.14(t) $^2J(^{13}C-^{195}Pt)$ 82.5 Hz; C_4 106.99(s); C_5 130.99(s); $C_{5(met)}$132.10(s); $C_{3(met)}$139.32(t) $^3J(^{13}C-^{195}Pt)$ 65.05 Hz, C_3 142.03(s), 143.58(s).

$\underline{Me(PhCH_2)BrPt(HCpz_2(C_3N_2H_2)-C,N,N)}$

Prepared by an analogous procedure to $Me_2IPt(H_2Cpz_2(C_3N_2H_2)$-C,N,N) substituting $PhCH_2Br$ for MeI.

Yield: 93%.

Molecular Weight ($CHCl_3$): 612 (594)

^1H NMR (D6 acetone):

MePt 1.80(t) $^2J(^1H-^{195}Pt)$ 73.8 Hz, 3H; $Ph\underline{CH_2}$ 4.05(d) $^2J(^1H-^{195}Pt)$ 69.77 Hz, $^2J(^1H-^1H)$ 8.79 Hz, 1H; 4.21(d) $^2J(^1H-^{195}Pt)$ 107.31 Hz, $^2J(^1H-^1H)$ 8.78 Hz, 1H; H_4 <u>trans</u> to Me 6.27(t) 1H; $H_{4(met)}$6.57(d) $^3J(^1H-^{195}Pt)$ 12.33 Hz, $^2J(^1H-^1H)$ 1.50 Hz, 1H; H_3 <u>trans</u> to Me 6.64(d) $J_{(3,4)}$1.70 Hz, 1H; H_4 <u>trans</u> to benzyl 6.71(t) 1H; Ph 7.03-7.27(m) 5H; $H_{3(met)}$7.65(d) $^4J(^1H-^{195}Pt)$ 9.05 Hz, $J_{(3,4)}$1.37 Hz, 1H; H_3 <u>trans</u> to benzyl 8.13(d) $J_{(3,4)}$2.04 Hz, 1H; H_5 <u>trans</u> to Me 8.39(d) $J_{(4,5)}$2.54 Hz, 1H; H_5 <u>trans</u> to benzyl 8.57(d) $J_{(4,5)}$2.60 Hz, 1H; CH 9.38(s) 1H.

$\underline{[Me_2IPt(HCpz_2(C_3N_2H_2)-C,N,N)]\ from\ [MePt(HCpz_2(C_3N_2H_2)-C,N)]_n + MeI}$

$[MePt(HCpz_2(C_3N_2H_2)-C,N)]_n$ (0.1g, 0.23 mmole) was suspended in acetone (10 cm^3) and MeI (100 ul) added, the flask stoppered, and stirring continued until solution had occurred. The solution was filtered, excess hexane added and the precipitate collected by filtration and vacuum dried (50°C, 2 hours).

Yield: 0.122g, 94%.

^{1}H NMR (D6 acetone):

MePt 1.51(t) $^2J(^1H-^{195}Pt)$ 69.2 Hz, 6H; $H_{4(met)}$ 6.09(d) $^3J(^1H-^{195}Pt)$ 14.34 Hz, $J(^1H-^1H)$ 1.70 Hz, 1H; H_4 6.47(t) 2H; H_3 7.32(d) $J_{(3,4)}$ 1.65 Hz, 2H; $H_{3(met)}$ 7.43(d) $^4J(^1H-^{195}Pt)$ 10.71 Hz, $J(^1H-^1H)$ 1.71Hz, 1H; $py_{3,5}$ 7.69(t) 2H; py_4 8.19(t) 1H; $py_{2,6}$ 8.35(m) 2H; H_5 9.61(d) $J_{(4,5)}$ 2.36 Hz, 2H; CH 10.45(s) 1H.

This compound is identical to that formed by reaction of $Me_2Pt(HCpz_3)$ with MeI (p. 272)

[$Me_2Pt(HCpz_2(C_3N_2H_2)$-C,N,N)(py)]I

$Me_2IPt(HCpz_2(C_3N_2H_2)$-C,N,N) (50mg) was dissolved in pyridine (5 cm^3) and hexane added to precipitate a microcrystalline white solid which was collected, filtered and vacuum dried (60^oC, 2 hours).
Yield: 54mg, 95%.
Conductivity (acetone); 89 Ω^{-1} cm^2 $mole^{-1}$

^{1}H NMR (acetone):

MePt 1.51(t) $^2J(^1H-^{195}Pt)$ 69.2 Hz, 6H; $H_{4(met)}$ 6.09(d) $^3J(^1H-^{195}Pt)$ 14.34 Hz, $J(^1H-^1H)$ 1.70 Hz, 1H; H_4 6.47(t) 2H; H_3 7.32(d) $J_{(3,4)}$ 1.65 Hz, 2H; $H_{3(met)}$ 7.43(d) $^4J(^1H-^{195}Pt)$ 10.71 Hz, $J(^1H-^1H)$ 1.71Hz, 1H; $py_{3,5}$ 7.69(t) 2H; py_4 8.19(t) 1H; $py_{2,6}$ 8.35(m) 2H; H_5 9.61(d) $J_{(4,5)}$ 2.36 Hz, 2H; CH 10.45(s) 1H.

[Me(R)Pt($HCpz_2(C_3N_2H_2)$-C,N,N)(py)]X (RX = MeI, allylBr, $PhCH_2Br$, propargyl bromide)

MePt($HCpz_2(C_3N_2H_2)$-C,N)(py) (0.1g, mmole) was suspended in dry acetone (10 cm^3), excess RX (100 l) added and the suspension stirred

until no solid was evident. Hexane was added until the solution became cloudy whereupon a white microcrystalline solid precipitated.

[$Me_2Pt(HCpz_2(C_3N_2H_2)$-C,N,N)(py)]I 95%.

Microanalysis: C 32.98 (33.25), H 3.44(3.66), N 14.61 (14.87)
(calculated for 0.5 acetone solvate; (C=O) 1724 cm^{-1})

Molecular Weight ($CHCl_3$): 643 (652)

Conductivity: 89 Ω^{-1} cm^2 $mole^{-1}$

^1H NMR ($CDCl_3$):

MePt 1.51(t) $^2J(^1H-^{195}Pt)$ 69.2 Hz, 6H; $H_{4(met)}$ 6.09(d) $^3J(^1H-^{195}Pt)$ 14.34 Hz, $J(^1H-^1H)$ 1.70 Hz, 1H; H_4 6.47(t) 2H; H_3 7.32(d) $J_{(3,4)}$ 1.65 Hz, 2H; $H_{3(met)}$ 7.43(d) $^4J(^1H-^{195}Pt)$ 10.71 Hz, $J(^1H-^1H)$ 1.71 Hz, 1H; $py_{3,5}$ 7.69(t) 2H; py_4 8.91(t) 1H; $py_{2,6}$ 8.35(m) 2H; H_5 9.61(d) $J_{(4,5)}$ 2.36 Hz, 2H; CH 10.45(s) 1H.

[$Me(PhCH_2)Pt(HCpz_2(C_3N_2H_2)$-C,N,N)(py)]Br 88%.

Microanalysis: C 41.15 (41.02), H 3.60 (3.59), N 14.33 (14.56), Br 11.93 (11.86)

Conductivity (Acetone): 65 Ω^{-1} cm^2 $mole^{-1}$

^1H NMR ($CDCl_3$):

MePt 1.56(t) $^2J(^1H-^{195}Pt)$ 69.73 Hz, 3H; CH_2 3.40(td) $^2J(^1H-^{195}Pt)$ 94.05 Hz, $J(^1H-^1H)$ 9.80 Hz, 1H; 4.18(td) $^2J(^1H-^{195}Pt)$ 78.87 Hz, $J(^1H-^1H)$ 9.80 Hz, 1H; H_3 5.54(d) $J_{(3,4)}$ 2.31 Hz, 1H; H_4 6.03(t) 1H; H_4, + $H_{4(met)}$ 6.39(m) $^3J(^1H-^{195}Pt)$ 14.21 Hz, 2H; $Ph_{2,6}$ 6.50(m) 2H; $Ph_{3,5}$ 6.86(t) 2H; Ph_4 7.03(m) 1H; H_3, 7.12(d) $J_{(3,4)}$ 2.10 Hz, 1H; $H_{3(met)}$ 7.55(d) $^4J(^1H-^{195}Pt)$ 10.50 Hz, 1H; $py_{3,5}$ 7.73(t) 2H; py_4 8.27(t) 1H; $py_{2,6}$ 8.41(m) $^3J(^1H-^{195}Pt)$ 22.21 Hz, 2H; H_5 9.48(d) $J_{(4,5)}$ 2.70 Hz, 1H; H_5, 9.53(d) $J_{(4,5)}$ 2.61 Hz, 1H; CH 10.78(s) 1H.

[Me(allyl)Pt(HCpz$_2$($C_3N_2H_2$)-C,N,N)(py)]Br 91%.

Microanalysis: C 36.71 (36.60), H 3.57 (3.56), N 15.60 (15.73), Br 12.94 (12.82)

Molecular Weight ($CHCl_3$): 622 (631)

Conductivity: 84 Ω^{-1} cm^2 $mole^{-1}$

^1H NMR ($CDCl_3$):

MePt 1.51(t) $^2J(^1H-^{195}Pt)$ 69.63 Hz, 3H; $\underline{CH}_2$ 2.96(dd) $^2J(^1H-^{195}Pt)$ 91.54 Hz, $J(^1H-^1H)$ 9.90 Hz, 1H; 3.37(dd) $^2J(^1H-^{195}Pt)$ 88.24 Hz, $J(^1H-^1H)$ 9.94 Hz, 1H; $=\underline{CH}_2$ 5.06(m) 2H; $=\underline{CH}$ 5.62(m) 1H; $H_{4(met)}$ 6.19(t) $^3J(^1H-^{195}Pt)$ 11.76 Hz, $J(^1H-^1H)$ 1.59 Hz, 1H; H_4 6.41(t) 1H; 6.46(t) 1H; H_3 7.20(d) $J_{(3,4)}$ 1.59 Hz, 1H; 7.41(t) $J_{(3,4)}$ 1.83 Hz, 1H; $H_{3(met)}$ 7.47(t) $^4J(^1H-^{195}Pt)$ 8.70 Hz, $J(^1H-^1H)$ 1.64 Hz, 1H; $py_{3,5}$ 7.70(t) 2H; py_4 8.21(t) 1H; $py_{2,6}$ 8.36(m) $^3J(^1H-^{195}Pt)$ 22.03 Hz, 2H; H_5 9.59(d) $J_{(4,5)}$ 2.68 Hz, 1H; 9.66(d) $J_{(4,5)}$ 2.65 Hz, 1H; CH 10.81(s) 1H.

[Me(allene)Pt(HCpz$_2$($C_3N_2H_2$)-C,N,N)(py)]Br 84%

Molecular Weight ($CHCl_3$): 549 (540)

Conductivity (Acetone): 70 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt 1.67(t) $^2J(^1H-^{195}Pt)$ 69.06 Hz, 3H; $=CH_2$ 4.45(m) $J(^1H-^{195}Pt)$ 45.05 Hz, $J(^1H-^1H)$ 6.3 Hz, 2H; =CH 5.89(tt) $^2J(^1H-^{195}Pt)$ 67.11 Hz, $^4J(^1H-^{195}Pt)$ 6.3 Hz, 1H; $H_{4(met)}$ 6.17(td) $^3J(^1H-^{195}Pt)$ 13.78 Hz, $^3J(^1H-^1H)$ 1.71 Hz, 1H; H_4 6.47(m) 2H; H_3 7.36(d) $J_{(3,4)}$ 2.10 Hz, 1H; $H_{3(met)}$ + H_3 7.44(m) 2H; $py_{3,5}$ 7.68(m) 2H; py_4 8.20(t) 1H; $py_{2,6}$ 8.38(m) 2H; H_5 9.58(d)

$J_{(4,5)}$2.70 Hz, 1H; H_5 9.68(d) $J_{(4,5)}$2.70 Hz, 1H; CH 10.88(s) 1H.

[Me($pzCH_2CH_2$)Pt($HCpz_2(C_3N_2H_2)$-C,N)(py)]Br 84%

($pzCH_2CH_2$)Br (0.04g, 0.23 mmole) was added to a suspension of MePt($HCpz_2(C_3N_2H_2)$-C,N)(py) (0.1g, 0.2 mmole) in acetone (20 cm^3) and the mixture refluxed for 30 minutes. After cooling (ambient) the volume was reduced to half and hexane added until cloudiness developed. Overnight small crystals deposited, which were insoluble in common organic solvents.

Yield: 0.12g, 89%.

^1H NMR ($CDCl_3$):

MePt 1.42(t) $^2J(^1H-^{195}Pt)$ 70.23 Hz, 3H; CH_2 2.88(m) 2H; CH_2 4.47(m) 2H; $H_{4(met)}$ trans to pz + H_4 trans to Me 6.17(m) 2H; H_4 trans to CH_2 6.49(t) 1H; H_4 trans to $pz_{(met)}$ 6.62(t) 1H; H_3 trans to CH_3 6.95(d) $J_{(3,4)}$2.10 Hz, 1H; $H_{3(met)}$+ H_3 trans to $pz_{(met)}$ 7.42(m) 2H; H_3 trans to CH_2 7.77(d) $J_{(3,4)}$1.98 Hz, 1H; H_5 trans to $pz_{(met)}$ 8.10(d) $J_{(4,5)}$2.40 Hz, 1H; H_5 trans to Me 9.40(d) $J_{(4,5)}$2.40 Hz, 1H; H_5 trans to CH_2 9.55(d) $J_{(4,5)}$2.73 Hz, 1H; CH 10.77(s) 1H.

[$Me_2Pt(HCpz_2(C_3N_2H_2)$-C,N,N)(L)]I (L= PPh_3, PPh_2(o-tolyl))

MePt($HCpz_2(C_3N_2H_2)$-C,N)(py) (0.1g, 0.2 mmole) and phosphine ligand (0.2 mmole) were warmed and stirred in acetone, (10 cm^3) under a nitrogen atmosphere, until no solid was evident (10 minutes). The clear solution was cooled to ambient temperature, excess MeI (x5) added and the solution stirred for 30 minutes. Excess MeI and some acetone were removed (rotary evaporator) and hexane added until solids began to precipitate. These were filtered and vacuum dried (2 hours) at 50°C.

[$Me_2Pt(HCpz_2(C_3N_2H_2)$-C,N,N)(PPh_3)]I

Yield: 92%

Microanalysis: C 43.76 (43.54); H 3.77 (3.65); N 10.45 (10.12); P 4.00 (3.74); I 15.20 (15.33)

Molecular Weight ($CHCl_3$): 794 (827)

Conductivity (Acetone): 95 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt 1.45(td) $J(^1H-^{195}Pt)$ 70.66 Hz, $J(^1H-^{31}P)$ 7.06 Hz, 6H; H_4 + $H_{4(met)}$ 6.13(m) 3H; H_3 6.56(d) $J_{(3,4)}$ 2.08 Hz, 2H; $Ph_{3,5}$ 7.12(m) 6H; Ph_4 7.58(td) 3H; H_5 9.54(d) $J_{(4,5)}$ 2.73 Hz, 2H; CH 10.58(s) 1H.

^{31}P NMR ($CDCl_3$):

P <u>trans</u> to $pz_{(met)}$ -6.89(t) $^1J(^{31}P-^{195}Pt)$ 1491 Hz.

[$Me_2Pt(HCpz_2(C_3N_2H2)$-C,N,N)$(PPh_2$(o-tolyl)]I

Yield: 79%.

Molecular Weight ($CHCl_3$): 832 (841)

Conductivity (acetone): 102 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt 1.55(td) $^2J(^1H-^{195}Pt)$ 69.63 Hz, $^2J(^{31}P-^{195}Pt)$ 6.90 Hz, 6H; $CH_{3(tolyl)}$ 1.67(s) 3H; H_4 + $H_{4(met)}$ 6.12(m) 3H; H3 6.36(d) $J_{(3,4)}$ 1.80 Hz, 2H; Ph 7.24-7.39(m) 8H; $H_{3(met)}$ + Ph 7.44-7.55(m) 7H; H_5 9.58(d) $J_{(4,5)}$ 2.70 Hz, 2H; CH 10.54(s) 1H.

^{31}P NMR ($CDCl_3$):

P <u>cis</u> to Me -11.6(t) $J(^{31}P-^{195}Pt)$ 1533 Hz.

[$Me_2Pt(HC(mim)pz(C_3N_2H_2)$-C,N,N)(py)]I

$Me_2Pt(HC(mim)pz_2)$ (0.2g, 0.44 mmole) was added to dry pyridine (5 cm^3) under a nitrogen atmosphere. The solid dissolved almost immediately with bubble evolution and the solution turned a yellow colour. Excess hexane was added which caused a white solid to precipitate. The precipitate was filtered and washed well with hexane

(5 x 5 cm^3) and ether (5 x 5 cm^3) to remove all traces of pyridine. The damp solid was dissolved in acetone (10 cm^3), MeI (x5) added and the mixture stirred for 30 minutes, after which time it was filtered and excess hexane added to precipitate a white solid. The solid was vacuum dried for 2 hours at 50°C.

Yield: 0.18g, 64%.

Molecular Weight ($CHCl_3$): 649 (657)

Conductivity (Acetone): 78 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt trans to mim 1.36(t) $^2J(^1H-^{195}Pt)$ 67.77 Hz, 3H; MePt trans to pz 1.46(t) $^2J(^1H-^{195}Pt)$ 69.27 Hz, 3H; NMe 4.37(s) 3H; $H_{4(met)}$ 6.08(t) $^3J(^1H-^{195}Pt)$ 14.00 Hz, 1H; H_4 6.46(t) 1H; H_3 6.71(d) $J_{(3,4)}$ 1.53 Hz, 1H; H_{5mim} 7.18(d) $J_{(4,5)}$ 1.47 Hz, 1H; H_{4mim} 7.27(broad,s) 1H; $H_{3(met)}$ 7.42(t) $^4J(^1H-^{195}Pt)$ 10.41 Hz, 1H; $py_{3,5}$ 7.68(t) 2H; py_4 8.15(t) 1H; $py_{2,6}$ 8.56(m) $^3J(^1H-^{195}Pt)$ 21.19 Hz, 2H; CH 8.60(s) 1H; H_5 9.18(d) $J_{(4,5)}$ 2.58 Hz, 2H.

[$Me_2Pt(HC(mim)pz(C_3N_2H_2)$-C,N,N)($PPh_3$)]I

$MePt(HCpz_2(C_3N_2H_2)$-C,N)(PPh_3) (0.1g, 0.14 mmole) was dissolved in acetone (10 cm^3), excess MeI added (x5) and the solution stirred for 30 minutes. Excess MeI was removed and hexane added dropwise until crystallization began.

Yield: 0.11g, 96%

Microanalysis: C 51.50 (51.40); H4.18 (4.40); N 12.02 (12.30)

Molecular Weight ($CHCl_3$): 813 (841)

Conductivity (Acetone): 91 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt trans to mim 1.30(td) $^2J(^1H-^{195}Pt)$ 68.41 Hz, $J(^{31}P-^{195}Pt)$ 7.02 Hz, 3H; MePt trans to pz 1.38(td) $^2J(^1H-^{195}Pt)$ 71.02 Hz, $J(^{31}P-^{195}Pt)$ 7.02 Hz, 3H; NMe 4.43(s) 3H;

H_{4mim}5.92(d) $J_{(3,4)}$1.58 Hz, 1H; H_4 + H_{4met}6.12(m) 2H; H_3 6.48(d) $J_{(3,4)}$2.18 Hz, 1H; H_{5mim}6.76(d) $J_{(4,5)}$ 1.58 Hz, 1H; $Ph_{3,5}$ 7.23(td) 6H; H_{3met}7.38(td) $^4J(^1H-^{195}Pt)$ 9.32 Hz, 1H; $Ph_{2,6}$ 7.49(m) 6H; Ph_4 7.56(m) 3H; CH 8.66(s) 1H; H_5 9.44(d) $J_{(4,5)}$2.67 Hz, 1H.

^{31}P NMR ($CDCl_3$):

P <u>trans</u> to pz_{met} -11.80(t) $J(^{31}P-^{195}Pt)$ 1503 Hz.

<u>$Me_3IPt(H_2Cpz_2)$</u>

<u>Method A</u>: $Me_2Pt(H_2Cpz_2)$ was suspended in $CHCl_3$ and excess MeI added. The solution was stirred for 8 hours after which a pale yellow solution with suspended white solids resulted. This was filtered and hexane added to the filtrate to precipitate a white solid.
Yield: 42%.

<u>Method B</u>: Excess MeI (x5) was added to a stoichiometric mixture (1:2) of $[Me_2Pt(Et_2S)]_2$ and H_2Cpz_2 in acetone. The solution was stirred for 10 minutes, excess MeI removed and hexane added until crystallization began. The crystalline precipitate was filtered and vacuum dried.
Yield: 91%
Molecular Weight ($CHCl_3$): 498 (515)

^1H NMR (D6 Acetone):

MePt 0.96(t) $^2J(^1H-^{195}Pt)$ 71.64 Hz, 3H; MePt 1.69(t) $^2J(^1H-^{195}Pt)$ 73.15 Hz, 6H; H_4 6.72(q) 2H; H_{eq} 7.00(d) $J(^1H-^1H)$ 13.92 Hz, 1H; H_3 8.00(d) $J_{(3,4)}$2.27 Hz, 2H; H_{ax} 8.05 (d,broad) $J(^1H-^1H)$ 16.1 Hz, 1H; H_5 8.33(d) $J_{(4,5)}$2.58 Hz, 2H.

$Me_3(OAc)Pt(H_2Cpz_2)$

$Me_3IPt(H_2Cpz_2)$ (80mg, 0.16 mmole) was suspended in acetone (10 cm^3), AgOAc (28mg, 0.17 mmole) added and the mixture stirred for 30 minutes. The flocculent AgI precipitate was filtered, the filtrate reduced to approximately 5 cm^3 and hexane added dropwise until crystallization began.

Yield: 60mg, 87%

Molecular Weight ($CHCl_3$): 429 (447)

^1H NMR (D6 acetone):

MePt trans to OAc 0.67(t,broad) $^2J(^1H-^{195}Pt)$ 73.42 Hz, 3H; MePt 1.39(t) $^2J(^1H-^{195}Pt)$ 72.05 Hz, 6H; H_4 6.67(t) 2H; H_{eq} 6.90(d) $^2J(^1H-^1H)$ 14.05 Hz, 1H; H_{ax} 7.47(d) $^2J(^1H-^1H)$ 14.08 Hz, 1H; H_3 7.96(d) $J_{(3,4)}$2.39 Hz, 2H; H_5 8.29(d) $J_{(4,5)}$2.46 Hz, 2H.

$[Me_2Pt(Ph(H)Cpz_2(C_3N_2H_2)-C,N)\mu I]_2$

$Me_2Pt(Ph(H)Cpz_2)$ (80mg) was suspended in neat MeI (2 cm^3) and allowed to stand at ambient temperature. After 5 minutes the suspension had dissolved and formed a clear solution. On further standing a white solid precipitated. This was filtered, washed with ether (3x5 cm^3) and vacuum dried at 40°C.

Yield: 81%

Microanalysis: C 31.32 (31.40); H 2.98 (3.10); N 9.74 (9.70)

^1H NMR ($CDCl_3$) ambient temperature:

MePt trans to I 0.80(t) $^2J(^1H-^{195}Pt)$ 74.55 Hz, 3H; MePt trans to N 1.84(t) $^2J(^1H-^{195}Pt)$ 72.30 Hz, 3H; $H_{4(met)}$5.53(t) $^3J(^1H-^{195}Pt)$ 16.16 Hz, 1H; $H_{3(met)}$5.65(d) $J_{(3,4)}$2.22 Hz, 1H; Ph 6.02(s, v.broad) 2H; H_4 6.76(t) 1H; Ph 7.16-7.21(m) 3H; H_5 8.29(d) $J_{(4,5)}$2.13 Hz, 1H; CH 9.01(s) 1H; H_3 9.25(d) $J_{(3,4)}$2.00 Hz, 1H.

^{1}H NMR ($CDCl_3$) -10°C:

MePt trans to I 0.76(t) $^2J(^1H-^{195}Pt)$ 73.36 Hz, 3H; MePt trans to N 1.82(t) $^2J(^1H-^{195}Pt)$ 72.63 Hz, 3H; $H_{4(met)}$ 5.52(t) $^3J(^1H-^{195}Pt)$ 16.8 Hz, 1H; $H_{3(met)}$ 5.62(s, broad) 1H; $Ph_{2,6}$ 6.04(dd) 2H; H_4 6.79(t) 1H; $Ph_{3,4,5}$ 7.22(m) 3H; H_5 8.31(d) $J_{(4,5)}$ 2.22 Hz, 1H; CH 8.96(s) 1H; H_3 9.25(d) $J_{(3,4)}$ 2.02 Hz, 1H.

$Me_3IPt(Me(H)Cpz_2)$

MeI (100 µl) was added to an acetone solution (10 cm^3) of $Me_2Pt(Me(H)Cpz_2)$ (0.1g, 0.26 mmole) and the mixture stirred for 10 minutes. Hexane was added dropwise until cloudiness developed whereupon needle-like crystals deposited over 30 minutes. These were collected, washed with ether and vacuum dried (50°C) for 2 hours.
Yield: 89%.
Molecular Weight ($CHCl_3$): 513 (529)
^{1}H NMR ($CDCl_3$):

MePt trans to I 0.81(t) $^2J(^1H-^{195}Pt)$ 71.97 Hz, 3H; MePt 1.62(t) $^2J(^1H-^{195}Pt)$ 72.33 Hz, 6H; CMe 2.31(d) $^2J(^1H-^1H)$ 6.81 Hz, 3H; H_4 6.44(q) $^3J(^1H-^{195}Pt)$ 8.76 Hz, $J_{(3,4)}$ 2.25 Hz, 2H; H_5 7.75(d) $J_{(4,5)}$ 2.73 Hz, 2H; CH 8.58(q) $^2J(^1H-^1H)$ 6.81 Hz, 1H.

$Me_2(PhCH_2)BrPt(Me(H)Cpz_2)$

An analogous procedure to that used above was followed, substituting $PhCH_2Br$ for MeI.
Yield: 89%
Molecular Weight ($CHCl_3$): 538 (556)
^{1}H NMR ($CDCl_3$):

Conformer A: MePt trans to N 1.55(t) $^2J(^1H-^{195}Pt)$ 71.91 Hz,

6H; CH_3 2.26(d) $^3J(^1H-^{195}Pt)$ 6.82 Hz, 3H; CH_2 2.98(t) $^2J(^1H-^{195}Pt)$ 92.20 Hz, 2H; $Ph_{2,6}$ 6.12(q) 2H; H_4 6.26(t) 2H; $Ph_{3,5}$ 6.73(m) 2H; Ph_4 6.86(m) 1H; H_3 7.37(d) $J_{(3,4)}$2.42 Hz, 2H; H_5 7.68(d) $J_{(4,5)}$2.70 Hz, 2H; CH 8.47 or 8.86(q) 1H.

Conformer B: MePt trans to Br 0.91(t) $^2J(^1H-^{195}Pt)$ 73.53 Hz, 3H; MePt trans to N 1.53(t) $^2J(^1H-^{195}Pt)$ 72.88 Hz, 3H; CH_3 2.26(d) $^3J(^1H-^1H)$ 6.82 Hz, 3H; CH_2 A 3.12(t, d) $^2J(^1H-^{195}Pt)$ 61.95 Hz, $^2J(^1H-^1H)$ 9.44 Hz, 1H; B 4.51(t, d) $^2J(^1H-^{195}Pt)$ 125.84 Hz, $^2J(^1H-^1H)$ 9.44 Hz, 1H; pz ring trans to MePt H_3 5.91(d) $J_{(3,4)}$2.09 Hz, 1H; H_4 6.06(q) 1H; H_5 7.58(d) $J_{(4,5)}$2.52 Hz, 1H; pz ring trans to benzyl H_4 6.44(t) 1H; H_3 7.60(d) $J_{(3,4)}$1.89 Hz, 1H; H_5 7.69(d) $J_{(4,5)}$2.70 Hz, 1H; CH 8.47 or 8.86(q) 1H.

$Me_3IPt(H_2C(mim)pz)$

Made by an analogous procedure to $Me_3IPt(Me(H)Cpz_2)$.

Yield: 89%

Molecular Weight($CHCl_3$): 526 (529)

^1H NMR ($CDCl_3$):

MePt trans to I 0.91(t) $^2J(^1H-^{195}Pt)$ 73.50 Hz, 3H; MePt trans to mim 1.46(t) $^2J(^1H-^{195}Pt)$ 70.00 Hz, 3H; MePt trans to pz 1.56(t) $^2J(^1H-^{195}Pt)$ 72.86 Hz, 3H; NMe 3.82(s) 3H; H_{eq} 5.45(d) $^2J(^1H-^1H)$ 15.45 Hz, 1H; H_4 6.38(t) 1H; H_{ax} 6.64(d) $^2J(^1H-^1H)$ 15.43 Hz, 1H; H_{5mim} 6.95(d) $J_{(4,5)}$1.55 Hz, 1H; H_{4mim} 7.17(q) $^3J(^1H-^{195}Pt)$ 6.87 Hz, $J_{(4,5)}$1.46 Hz, 1H; H_3 7.69(d) $J_{(3,4)}$2.26 Hz, 1H; H_5 7.72(d) $J_{(4,5)}$2.46 Hz, 1H.

$Me_3IPt(H_2C(py)pz)$

Made by the same synthetic route as $Me_3IPt(Me(H)Cpz_2)$.

Yield: 88%

Molecular Weight($CHCl_3$): 515 (526)

^1H NMR ($CDCl_3$):

MePt *trans* to I 0.96(t) $^2J(^1H-^{195}Pt)$ 71.63 Hz, 3H; MePt *trans* to py 1.57(t) $^2J(^1H-^{195}Pt)$ 70.91 Hz, 3H; MePt *trans* to pz 1.69(t) $^2J(^1H-^{195}Pt)$ 70.80 Hz, 3H; H_{eq} 5.25(d) $^2J(^1H-^1H)$ 15.07 Hz, 1H; H_4 6.45(t) 1H; H_{ax} 7.01(d, broad) $^2J(^1H-^1H)$ 15.07 Hz, 1H; $py_{3,5}$ 7.51(m) 2H; H_5 7.64(d) $J_{(4,5)}$2.4 Hz, 1H; H_3 7.75(d) $J_{(3,4)}$ 2.35 Hz, 1H; py_4 7.91(t) 1H; py_6 8.80(q) 1H.

$Me_3(OAc)Pt(H_2C(py)pz)$

$Me_3IPt(H_2C(py)pz)$ (0.1g), 0.19 mmole) was dissolved in acetone (10 cm^3), solid Ag(OAc) (0.032g, 0.19 mmole) added and the mixture stirred for 30 minutes, filtered and hexane added to the filtrate to precipitate a microcrystalline solid.

Yield: 0.09g, 79%.

Molecular Weight ($CHCl_3$): 442 (458).

^1H NMR ($CDCl_3$):

Me *trans* to I 0.68(t) Me *trans* to py 1.19(t) $^2J(^1H-^{195}Pt)$ 68.94 Hz, 3H; Me *trans* to pz 1.29(t) $^2J(^1H-^{195}Pt)$ 69.32 Hz, 3H; OAc 1.92(s) 3H; CH_{eq} 5.75(d) $^2J(^1H-^1H)$ 14.62 Hz, 1H; CH_{ax} 6.29(d) $^2J(^1H-^1H)$ 14.62 Hz, 1H; H_3 6.43(t) 1H; $py_{3,5}$ 7.47(m) 2H; H_5 7.63(d) $J_{(4,5)}$2.52 Hz, 1H; H_3 7.69(d) $J_{(3,4)}$2.45 Hz, 1H; py_4 7.88(t) 1H; py_6 8.66(q) 1H.

$Me_3IPt(Me_2Cpz_2)$

Method A: MeI (100 μl) was added to a solution of $Me_2Pt(Me_2Cpz_2)$ (100mg, 0.25 mmole) in acetone (10 cm^3) and the mixture stirred for 5 minutes. Excess MeI and some acetone were removed under vacuum and hexane added to precipitate a white powder.

Yield: 112mg, 83%.

^1H NMR ($CDCl_3$): Recorded after 3 minutes dissolution.

MePt trans to I 0.98(t,broad) $^2J(^1H-^{195}Pt)$ 71.00 Hz; MePt trans to N 1.66(t,broad) $^2J(^1H-^{195}Pt)$ 72.54 Hz; MePt ($[Me_3PtI]_4$) 1.72(t) $^2J(^1H-^{195}Pt)$ 77.34 Hz; CMe 2.18 (s,broad); CMe_2 2.29(s); CMe 2.51(s,broad); $H_{4(free)}$ 6.27(t); H_{4C} 6.49 (t); $H_{5(free)}$ 7.40(d,d) $J_{(4,5)}$ 2.45 Hz; $H_{3(free)}$ 7.56(d) $J_{(3,4)}$ 1.82 Hz; H_{5C} 7.95(d) $J_{(4,5)}$ 2.75 Hz; H_{3C} 8.13(d) $J_{(3,4)}$ 2.20 Hz.

Method B: The reaction in A (above) was repeated except that it was allowed to continue overnight (12 hours). The product, yellow microcrystals, were isolated in the same manner.

Yield: 72%

M.pt.: Decomposes ~200°C.

^1H NMR ($CDCl_3$): MePt 1.72(t) $^2J(^1H-^{195}Pt)$ 77.34 Hz.

$Me_3IPt(Cpz_4)$

Made by an analogous method to $Me_3IPt(Me(H)Cpz_2)$.

Yield: 76%

Molecular Weight ($CHCl_3$): 641 (647)

^1H NMR (D6 acetone):

MePt trans to I 0.40(t) $^2J(^1H-^{195}Pt)$ 72.52 Hz, 3H; MePt trans to N 1.60(t) $^2J(^1H-^{195}Pt)$ 73.83 Hz, 6H; H_{5ax} 6.66(d) $J_{(4,5)}$ 2.67 Hz, 1H; H_{4eq} 6.75(q) 1H; H_{4ax} 6.81(q) 1H; H_{4C} + H_{5eq} 6.92(m) 3H; H_{5C} 7.41(d) $J_{(4,5)}$ 2.76 Hz, 2H; H_{3eq} 7.90(d) $J_{(3,4)}$ 1.75 Hz, 1H; H_{3ax} 8.20(d) $J_{(3,4)}$ 1.76 Hz, 1H; H_{3C} 8.50(d) $J_{(3,4)}$ 1.80 Hz, 2H.

$Me_2IPt(HCpz_3(C_3N_2H_2)-C,N,N)$

$Me_3IPt(Cpz_4)$ was added to neat MeI and dissolved over 15 minutes. After 1 hour acetone was added, MeI removed (rotary evaporator) and hexane added until cloudiness developed and the solution was then set aside. Microcrystals formed overnight.

Yield: 65%

^1H NMR (D6 acetone):

MePt 1.90(t) $^2J(^1H-^{195}Pt)$ 73.86 Hz, 6H; $H_{4(met)}$ 6.30(t,d) $^3J(^1H-^{195}Pt)$ 15.88 Hz, 1H; H_{4C} 6.75(q) 2H; H_{4eq} 7.09(q) 1H; $H_{3(met)}$ 7.63(t, d) $^4J(^1H-^{195}Pt)$ 9.78 Hz, 1H; H_{5C} 7.83(d) $J_{(4,5)}$ 2.67 Hz, 2H; H_{3eq} 8.38(d) $J_{(3,4)}$ 1.55 Hz, 1H; H_{3C} 8.41(d) $J_{(3,4)}$ 1.45 Hz, 2H; H_{5eq} 9.47(d) $J_{(4,5)}$ 2.79 Hz, 1H.

$Me_3IPt(H_2C=C(CH_2pz))$

$[Me_2Pt(Et_2S)]_2$ (0.15g, 0.24 mmole) and $H_2C=C(CH_2pz)_2$ (0.092g, 0.49 mmole) were refluxed in acetone (20 cm^3) for 15 minutes during which the solution turned a yellow colour. The solution was cooled (ambient), excess MeI (x5) added and the solution stirred for 30 minutes. Excess MeI was removed and hexane added until cloudiness developed. Microcrystals deposited overnight.

Yield: 0.15g, 58%

Molecular Weight ($CHCl_3$): 523 (555)

^1H NMR (D6 acetone) ambient temperature:

MePt <u>trans</u> to I 1.24(t) $^2J(^1H-^{195}Pt)$ 69.67 Hz, 3H; MePt <u>trans</u> to N 1.70(t, d) $^2J(^1H-^{195}Pt)$ 73.58 Hz, 6H; CH_2, <u>A</u> 4.59(d) $^2J(^1H-^1H)$ 14.31 Hz, 1H; <u>B</u> 4.85(d) $^2J(^1H-^1H)$ 14.68 Hz, 1H; <u>C</u> 4.98(d) $^2J(^1H-^1H)$ 14.35 Hz, 1H; <u>D</u> 5.75(d) $^2J(^1H-^1H)$ 14.68 Hz, 1H; $=CH_2$ 5.49(s) 2H; H_4 6.68(s, broad) 2H; H_3 7.88(s, broad) 1H; H_5 8.12(s, broad) 2H; H_3 8.29(s, broad) 1H.

^{1}H NMR (D6 acetone) 0°C:

MePt trans to I 1.24(t) $^2J(^1H-^{195}Pt)$ 69.69 Hz, 3H; MePt trans to N 1.64(t, d) $^2J(^1H-^{195}Pt)$ 73.42 Hz, 6H; CH_2 A 4.56(d) $^2J(^1H-^1H)$ 14.57 Hz, 1H; B 4.87(d) $^2J(^1H-^1H)$ 14.87 Hz, 1H; C 5.00(d) $^2J(^1H-^1H)$ 14.57 Hz, 1H; D 5.71(d) $^2J(^1H-^1H)$ 14.62 Hz, 1H; $=CH_2$ 5.50(s) 2H; H_4 6.71(m) 2H; H_3 7.88(d) $J_{(3,4)}$2.36 Hz, 1H; H_5 8.13(d) $J_{(4,5)}$2.49 Hz, 1H; H_5 8.17(d) $J_{(4,5)}$2.51 Hz, 1H; H_3 8.27(d) $J_{(3,4)}$2.44 Hz, 1H.

$Me_3IPt(Ph(H)Cpz_2)$:

Stoichiometric quantities of $[Me_2Pt(Et_2S)]_2$ and $Ph(H)Cpz_2$ (1:2) were dissolved in acetone and excess MeI added. After 10 minutes stirring excess MeI was removed and hexane added to precipitate a microcrystalline product.

Yield: 88%.

Molecular Weight ($CHCl_3$): 568 (591)

^{1}H NMR (D6 acetone), ambient temperature:

MePt trans to I 0.93(t) $^2J(^1H-^{195}Pt)$ 72.50 Hz, 3H; MePt trans to pz 1.68(t) $^2J(^1H-^{195}Pt)$ 72.79 Hz, 6H; H_3 6.76(t) 2H; Ph 7.78(s,broad) 2H; Ph 7.85(m) 3H; H_5 8.10(d) $J_{(4,5)}$2.68 Hz, 2H; H_3 8.15(d) $J_{(3,5)}$2.20 Hz, 2H; CH 9.62(s,broad) 1H.

^{1}H NMR (D6 acetone), -40°C: mixture of conformers - aromatic region not assigned.

Isomer A: MePt trans to I 1.09(t) $^2J(^1H-^{195}Pt)$ 72.63 Hz; MePt trans to pz 1.65(t) $^2J(^1H-^{195}Pt)$ 71.89 Hz.

Isomer B: MePt trans to I 0.19(t) $^2J(^1H-^{195}Pt)$ 74.04 Hz; MePt trans to pz 1.44(t) $^2J(^1H-^{195}Pt)$ 73.06 Hz.

Reactions with CD_3I

10mg of sample was dissolved in D6 acetone in a NMR tube and CD_3I in D6 acetone (usually 10 ul of a 0.24M solution) added in one portion, and the ^1H NMR spectrum recorded after approximately 3 minutes.

This reaction was carried out with $Me_2Pt(H_2C(mim)pz)$, $Me_2Pt(H_2C(py)pz)$ and $Me_2Pt(Me(H)Cpz_2)$, to produce $Me_2(CD_3)I$ $Pt(H_2C(mim)pz)$, $Me_2(CD_3)IPt(H_2C(mim)pz)$ and $Me_2(CD_3)IPt(Me(H)Cpz_2)$ respectively.

In all cases spectra of the complexes showed MePt resonances consistent with Me trans to I and N, and thus complete scrambling (integration values) occurred. The spectra were identical to the related MeI oxidative addition complexes.

$[Ph_2MePt(HCpz_3)]I$

$Ph_2Pt(HCpz_3)$ was dissolved in acetone, RX added and the mixture stirred for 15 minutes, excess RX removed and hexane added until cloudiness.

Molecular Weight ($CHCl_3$): 726 (705).

Conductivity (acetone): 91 Ω^{-1} cm^2 $mole^{-1}$.

^1H NMR ($CDCl_3$):

MePt 1.90(t) $^2J(^1H-^{195}Pt)$ 72.93 Hz, 3H; H_4 6.58(q) 3H; $Ph_{2,6}$ 6.99(m) 4H; $Ph_{3,5}$ 7.03(m) 4H; Ph_4 7.08(m) 2H; H_3 7.79(d) $J_{(3,4)}$ 2.25 Hz, 2H; H_3 trans to Me 7.88(d) $J_{(3,4)}$ 2.16 Hz, 1H; H_5 trans to Me 9.19(s, near coincident with H_5 trans to Ph) 1H; H_5 9.21(d) $J_{(4,5)}$ 2.76 Hz, 2H; CH 12.49(s) 1H;

$[Ph_2EtPt(HCpz_3)]I$

Molecular Weight ($CHCl_3$): 730 (719)

Conductivity: 86 Ω^{-1} cm^2 $mole^{-1}$.

^{1}H NMR ($CDCl_3$):

$\underline{CH_3}CH_2Pt$ 0.78(tt) $^3J(^1H-^{195}Pt)$ 52.22 Hz, $^3J(^1H-^1H)$ 14.71 Hz, 3H; CH_2Pt 2.73(tq) $^2J(^1H-^{195}Pt)$ 67.23 Hz, $^3J(^1H-^1H)$ 14.71 Hz, 2H; H_4 trans to Et 6.52(t) 1H; H_4 6.58(t) 2H; Ph 6.77-7.20(m) 10H; H_3 trans to Et 7.82(d) $J_{(3,4)}$1.71 Hz, 1H; H_3 7.86(d) $J_{(3,4)}$1.80 Hz, 2H; H_5 trans to Et 9.12(d) $J_{(4,5)}$2.70 Hz, 1H; H_5 9.25(d) $J_{(4,5)}$2.70 Hz, 2H; CH 12.44(s) 1H.

$\underline{[Ph_2(propargyl)Pt(HCpz_3)]I}$

Mixture of isomers (allenyl/alknynl)

Conductivity (acetone): 77 Ω^{-1} cm^2 $mole^{-1}$.

^{1}H NMR ($CDCl_3$) 3:1 allenyl:alknynl

CH 2.04(tt) $^4J(^1H-^{195}Pt)$ 21.76 Hz; H_3 $^4J(^1H-^{195}Pt)$ 2.79 Hz; CH_2Pt 3.14(td) $^2J(^1H-^{195}Pt)$ 88.60 Hz, $^4J(^1H-^1H)$ 2.79Hz; $=CH_2$ 4.11(td) $^4J(^1H-^{195}Pt)$ 46.97 Hz, $^4J(^1H-^1H)$ 6.18 Hz; CHPt 6.08(tt) $^2J(^1H-^{195}Pt)$49.46 Hz; H_4 6.53(q), 6.58(t); Ph 6.95-7.10(m); H3 7.78(d) $J_{(3,4)}$2.19 Hz,; H_5 9.09(d) $J_{(4,5)}$2.76 Hz; CH 12.76(s)

$\underline{[Ph_2MePt(HC(mim)pz_2)]I}$

Molecular Weight ($CHCl_3$): 701 (719)

Conductivity (acetone): 78 Ω^{-1} cm^2 $mole^{-1}$.

^{1}H NMR ($CDCl_3$):

MePt 1.87(t) $^2J(^1H-^{195}Pt)$ 73.53 Hz, 3H; NMe 4.45(s) 3H; H_3 6.48(q) 2H; Ph + H_{4mim} 6.95-7.08(m) 11H; H_{5mim} 7.30(d) $J_{(4,5)}$1.50 Hz, 1H; H_3 7.60(d) $J_{(3,4)}$2.40 Hz, 1H; H_3 7.78(d) $J_{(3,4)}$2.10 Hz, 1H; H_5 6.48(m) 2H; CH 11.04(s) 1H.

7.6 Experimental for Chapter Five

R_2PtLX Complexes

All R_2PtLX (R = Me, Ph) complexes were synthesized by the same general procedure using $[Me_2Pt(Et_2S)]_2$ or $[Ph_2Pt(Et_2S)]_2$ as platinum substrate, and the preparation of $Me_2Pt(CH_2Cpz_2CH_3)Cl$ is given as an example.

$Me_2Pt(CH_2Cpz_2CH_3)Cl$

$[Me_2Pt(Et_2S)]_2$ (0.15g, 0.24 mmole) and $CH_3Cpz_2CH_2Cl$ (0.11g, 0.52 mmole) were stirred and heated in benzene (20 cm^3) solution under a nitrogen atmosphere. After 10 minutes heating a white microcrystalline precipitate was suddenly deposited, which was filtered hot, washed with warm benzene (2 x 2 cm^3) and dry ether (2 x 5 cm^3) and air dried. The complex was readily recrystallized from a low volume of acetone by ether diffusion.

Yield: 0.17g, 74% (recrystallized).

Microanalysis: C 30.62 (30.31), H 3.90 (3.93), N 13.04 (12.86), Cl 8.30 (8.13)

Molecular weight ($CHCl_3$): 429 (435)

^1H NMR ($CDCl_3$):

MePt 1.30(t) $^2J(^1H-^{195}Pt)$ 73.70 Hz, 6H; CH_2Pt 2.38(t) $^2J(^1H-^{195}Pt)$ 51.48 Hz, 2H; CH_3 2.45(t) $^4J(^1H-^{195}Pt)$ 5.83 Hz, 3H; H_4 6.37(t) 2H; H_5 7.65(d) $J_{4,5}$ 2.61 Hz, 2H; H_3 7.86 (d) $J_{3,4}$ 1.98 Hz, 2H.

^{13}C NMR ($CDCl_3$):

MePt -9.95(t) $^1J(^{13}C-^{195}Pt)$ 693.4 Hz; CH_3 20.6(t) $^3J(^{13}C-^{195}Pt)$ 51.9 Hz; CH_2Pt 32.4(t) $^1J(^{13}C-^{195}Pt)$ 729.4 Hz; Cpz_2 85.66(t) $^2J(^{13}C-^{195}Pt)$ 51.9 Hz; C_4 108.7(s); C_5 126.7(s); C_3 139.7(s)

$\underline{Me_2Pt(CH_2Cpz_2CH_2Cl)Cl}$

Yield: 78%.

Recrystallized from acetone by ether diffusion.

Microanalysis: C 28.22 (28.09), H 3.22 (3.43), N 11.78 (11.92), Cl 15.10 (15.08)

Molecular weight ($CHCl_3$): 459 (470)

^1H NMR ($CDCl_3$):

MePt 1.33(t) $^2J(^1H-^{195}Pt)$ 73.58 Hz, 6H; CH_2Pt 2.46(t) $^2J(^1H-^{195}Pt)$ 54.29 Hz, 2H; CH_2Cl 4.65(t) $^2J(^1H-^{195}Pt)$ 2.89 Hz, 2H; H_4 6.42(t) 2H; H_5 7.85(d) $J_{4,5}$ 2.64 Hz, 2H; H_3 7.89(d) $J_{3,4}$ 2.04 Hz, 2H.

^{13}C NMR ($CDCl_3$):

MePt -9.57(t) $^1J(^{13}C-^{195}Pt)$ 689.33 Hz; CH_2Pt 28.85(t) $^1J(^{13}C-^{195}Pt)$ 730.62 Hz; CH_2Cl 42.31(t) $^3J(^{13}C-^{195}Pt)$ 60.30 Hz; $\underline{Cpz}_2$ 87.84(t) $^1J(^{13}C-^{195}Pt)$ 51.88 Hz; C_4 109.19(s); C_5 127.50(s); C_3 139.61(s).

$\underline{Me_2Pt(C(Cl)HCpz_2CH_3)Cl}$

This complex was not deposited from hot benzene solution but required addition of hexane and cooling. The complex was recrystallized from acetone by the dropwise addition of hexane.

Yield: 74%.

Molecular Weight ($CHCl_3$): 464 (470)

^1H NMR ($CDCl_3$):

MePt 1.36(t) $^2J(^1H-^{195}Pt)$ 75.30 Hz, 3H; 1.39(t) $^2J(^1H-^{195}Pt)$ 73.83 Hz, 3H; CH_3 2.55(s) 3H; HCPt 4.53(t) $^2J(^1H-^{195}Pt)$ 34.54 Hz, 1H; H_4 6.47(m) 2H; H_5 7.73(d) $J_{4,5}$ 2.70 Hz, 1H; 7.78(d) $J_{4,5}$ 2.73 Hz, 1H; H_3 7.90(d) $J_{3,4}$ 1.92 Hz, 1H; 7.92(d) $J_{3,4}$ 1.98 Hz, 1H.

^{13}C NMR ($CDCl_3$):

MePt 9.6(t) $^{1}J(^{13}C-^{195}Pt)$ 685.3 Hz, CH_2Pt (t) $^{1}J(^{13}C-^{195}Pt)$ 730.2 Hz; CH_3 (t) $^{3}J(^{13}C-^{195}Pt)$ 60.1 Hz; Cpz_2 (t) $^{2}J(^{13}C-^{195}Pt)$ 51.9 Hz; C_4 109.2(s); C_5 127.5(s); C_3 139.8 (s).

$Me_2Pt(2,6-(pzCH_2)_2C_6H_3)Br$

Yield: 92%, white microcrystalline.

Molecular Weight ($CHCl_3$): 528 (542)

^{1}H NMR($CDCl_3$):

MePt 1.60(t) $^{2}J(^{1}H-^{195}Pt)$ 70.32 Hz, 6H; CH_2(axial) 4.87(d) $^{2}J(^{1}H-^{1}H)$14.85 Hz, 2H; CH_2(equatorial) 5.85(d) $^{2}J(^{1}H-^{1}H)$14.75 Hz, 2H; H_4 6.33(t) 2H; Ph 7.05(m) 3H; H_5 7.48(d) $J_{4,5}$ 2.10 Hz, 2H; H_3 8.37(d) $J_{3,4}$ 1.42 Hz, 2H.

^{13}C NMR($CDCl_3$):

MePt -8.31(t) $J(^{13}C-^{195}Pt)$ 649.9 Hz; CH_2 59.22(t) $^{1}J(^{13}C-^{195}Pt)$ 30.50 Hz; H_4 107.30(s); $Ph_{2,6}$ 125.12(s); $Ph_{3,5}$ 129.59(t) $^{3}J(^{13}C-^{195}Pt)$45.66 Hz; H_5 131.76(s); Ph_1-Pt 133.22(s), Ph_4 137.35(s); H_3 141.67(s).

$Me_2Pt(C_6H_4(H)Cpz_2)Br$

Yield: 88%, white powder.

^{1}H NMR(acetone + 3 drops DMSO):

MePt 1.69(t) $^{2}J(^{1}H-^{195}Pt)$ 73.74 Hz, 6H; H_4 6.66(t), 2H; Ph_4 7.24(m) 1H; $Ph_{3,5}$ 7.39(m) 2H; Ph_6 7.59(m) 1H; H_3 8.10(d) $J_{3,4}$ 2.12 Hz, 2H; CH 8.42(s) 1H; H_5 8.48(d) $J_{4,5}$ 2.68 Hz, 2H.

$Me_2Pt(C_6H_4(H)(pz_2)Cl$

Yield: 90%, white powder, insoluble in common NMR solvents.

$Ph_2Pt(CH_2Cpz_2CH_3)Cl$

Yield: 92%, white amorphous powder which could be recrystallized from a large volume of hot acetone by cooling and dropwise addition of hexane.

^1H NMR($CDCl_3$):

CH_3 2.51(t) $^4J(^1H-^{195}Pt)$ 5.82 Hz, 3H; CH_2Pt 3.08(t) $^2J(^1H-^{195}Pt)$ 47.15 Hz, 2H; H_4 6.43(t) 2H; $Ph_{3,4,5}$ 6.96(m) 6H; $Ph_{2,6}$ 7.03(dt) $^3J(^1H-^{195}Pt)$ 48.80 Hz, 4H; H_5 7.69(d) $J_{(4,5)}$ 2.73 Hz, 2H; H_3 7.99(d) $J_{(3,4)}$ 2.04 Hz, 2H.

Reaction of R_2PtLX with pyridine

The complex (50mg) was dissolved in pyridine (5 cm^3) and the stoppered flask allowed to stand for 30 minutes, at which time hexane was added until cloudiness developed and crystallization began. The product was filtered, washed with ether, air dried and vacuum dried at 50°C (2 hours).

$[Me_2Pt(CH_2Cpz_2CH_3)(py))Cl$

Yield: 92%, clear microcrystalline.

Molecular Weight ($CHCl_3$): 496 (513)

Conductivity (acetone): 72 $^{-1}$ cm^2 $mole^{-1}$.

^1H NMR($CDCl_3$):

MePt 1.18(t) $^2J(^1H-^{195}Pt)$ 70.95 Hz, 6H; CH_2Pt 2.57(t) $^2J(^1H-^{195}Pt)$ 44.90 Hz, 2H; CH_3 2.92(s) 3H; H_4 6.46(t) 2H; H_3 7.41(d) $J_{(3,4)}$ 1.98 Hz, 2H; $py_{3,5}$ 7.73(t) 2H; py_4 8.16(t) 1H; py_6 8.57(m) $^3J(^1H-^{195}Pt)$ 18.52 Hz, 2H; H_5 8.79(d) $J_{(4,5)}$ 2.70 Hz, 2H.

7.6 Experimental for Chapter Six

The synthesis of some ligands required the preparation of known compounds as starting materials. These are listed below, and changes in procedures are fully described.

1. Chloromethylpyridine: made by the chlorination of 2-picoline as reported by Mathes and Schuly.[17]

2. 1,3-bis(bromomethyl)benzene: prepared by the free radical bromination of m-xylene using N-bromosuccinimide as reported by Wenner.[18]

3. 2-thiophene carboxaldehyde: prepared by the method of Weston and Michaels.[19]

4. N-methyl-2-imidazole carboxaldehyde: prepared by a modification of the reported method.[20]

Bu^nLi (140 cm^3 of 1.2M) was added dropwise to a stirred solution of N-methylimidazole (13.4 cm^3, 0.168 mole) in ether (20 cm^3) at -80^oC under a nitrogen atmosphere. After all of the Bu^nLi had been added the lithio-reagent was allowed to slowly warm to 0^oC. The lithio-reagent was re-cooled to -80^oC and added dropwise at this temperature to a well-stirred solution of DMF (25 cm^3, excess) and ether (30 cm^3) also at -80^oC. When the addition was complete the white suspension was allowed to warm to room temperature and left, with stirring, for 6 hours, after which time HCl (5M, 100 cm^3) was added and the acidified aqueous layer separated, the organic layer was washed with small portions of 5M HCl (2 x 20 cm^3). The combined acid extracts were made slightly alkaline with solid sodium bicarbonate, extracted twice with $CHCl_3$ (40 cm^3), and the combined extracts dried over $MgSO_4$. After removal of solvent and vacuum distillation a clear oil was obtained ($60-65^oC$/1mm Hg) which crystallized on standing.
Yield: 12.8g (69%)

5. 2-(chloromethyl)-1-methylimidazole hydrochloride ($mimCH_2Cl.HCl$): was prepared by a similar method to that described by Jones.[21]

6. 2-bromo-1,3-bis(bromomethyl)benzene: prepared by the free radical bromination of 2-bromo-m-xylene, as described by Vogtle.[22] 2-bromo-m-xylene was prepared by the method of Newman and Wise.[23]

7. 1,3-bis(dibromomethyl)benzene: prepared by the bromination of m-xylene using bromine as described by Snell and Weissberger.[24]

General Preparative Methods

A. Acid Catalyzed Condensation

The acetal or ketal (50 mmole), pyrazole (100 mmole) and p-toluene sulphonic acid (200 mg) were heated with stirring under a nitrogen atmosphere in a distillation apparatus. Heating was continued until either the theoretical amount of alcohol was distilled from the mixture or distillation ceased. The product was sublimed and recrystallized from a minimum volume of hot hexane.

Compounds made by this procedure included compounds 11 and 13.

B. Potassium Pyrazolide

(i) Pyrazole (8.7g, 128 mmole) was added to a stirred suspension of finely cut potassium (5g, 128 mmole) in anhydrous THF (150 cm^3) under a nitrogen atmosphere. After the initial rapid evolution of hydrogen the mixture was heated to reflux with continued stirring. Reflux was continued until beads of molten potassium were no longer evident. The thick white suspension was cooled and used immediately.

(ii) Typically, the appropriate halide was added (neat) in one portion to a suspension of potassium pyrazolide with stirring under a nitrogen atmosphere at room temperature. The resultant mixture was refluxed for a sufficient length of time, cooled, filtered and the filtrate stripped on a rotary evaporator. The residue was purified as reported.

Compounds synthesised by this method included compounds 1-4, 9, 13, 19 and 23.

C. Phase Transfer Catalysis (PTC)

Pyrazole (7g, 102.9 mmole), tetrabutylammonium bisulphate (0.4g), 40% sodium hydroxide solution (30 cm^3) and benzene (50 cm^3) were vigorously stirred under a nitrogen atmosphere. The appropriate quantity of halide substrate was added and the mixture vigorously refluxed for the appropriate length of time (generally 8 hours). In some preparations the halide substrate was used in place of benzene as the organic phase. After cooling, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 20 cm^3). The combined organic extracts was dried ($MgSO_4$), taken to low volume on a rotary evaporator and purified as reported.

Compounds made by this procedure include compounds 5-8 and 10.

D Cobalt(II)Chloride Condensation

(i) Bis-(1-pyrazolyl)ketone

Pyrazole (5g, 73.5 mmole), triethylamine (10.25 cm^3, 73.5 mmole) and anhydrous diethyl ether (200 cm^3) were mixed by overhead mechanical stirring under a nitrogen atmosphere, and phosgene (19 cm^3 of 1.93 M in toluene) was added in two portions. Stirring was continued for 15 minutes, the precipitate filtered at the pump, solvent removed under vacuum, and hexane (10 cm^3) added to assist in crystallization of the ketone. The solid ketone (5.65g, 95%) was dried under vacuum and stored under a nitrogen atmosphere. Generally this material was made as required and used immediately.

(ii) $CoCl_2$ Condensation

To a side arm flask flushed with nitrogen was added bis(1-pyrazolyl)ketone (1g, 6.17 mmole), the appropriate ketone or aldehyde (6.17 mmole) and a catalytic quantity of anhydrous cobalt(II) chloride

(10mg). If reaction did not occur immediately as evidenced by lack of CO_2 bubbles, the mixture was gently warmed until bubbling was observed. The mixture was allowed to stand until the reaction had subsided, water (5 cm^3) added and the mixture extracted with CH_2Cl_2 (2 x 20 cm^3). The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and CH_2Cl_2 removed under vacuum. The product was purified as reported below.

Compounds prepared by this procedure include compounds 12, 14-18, 20-22 and 25.

E. Lithiation Procedure

The lithiation of tris(1-pyrazolyl)methane is given as a typical example.

$HCpz_3$ (1g, 4.67 mmole) was dissolved in anhydrous ether (20 cm^3) under a nitrogen atmosphere and cooled to 0°C. Bu^nLi (5 cm^3, 0.94 M in ether) was added dropwise with stirring to produce a thick white solid ($LiCpz_3$). After 10 minutes stirring sufficient anhydrous THF (4-6 cm^3) was added to dissolve the lithio salt and produce a light yellow solution, to which an excess (x 3) of MeI was added. Stirring was continued for 2 hours, water (2 cm^3) added and the volume reduced under vacuum. The residue was extracted with CH_2Cl_2 (2 x 15 cm^3), the extracts dried ($MgSO_4$), CH_2Cl_2 removed and the product recrystallized from hot hexane (20 cm^3) to yield a white solid.
Yield: 78%.

1. $H_2C(py)pz$

Method	:	B
Starting Material	:	Chloromethylpyridine (9.2g, 72.2 mmole)
Halide : pyrazolide	:	1 : 1
Reflux Time	:	5 hours
Purification	:	Vacuum distillation, 76-78°C/0.1 mm Hg
Yield	:	10.2g, 90%, viscous oil
Mass Spectrum	:	m/e(%I): 159(M^+, 100), 92 (56), 81 (54), 65(46)

^{1}H NMR (D6 acetone)

pz resonances: CH_2 5.60(s) 2H; H_4 6.43(t) 1H; H_3 7.62(d) $J_{(3,4)}$1.50 Hz, 1H; H_5 7.91(d) $J_{(4,5)}$2.25 Hz, H.

py resonances: H_3 7.10(d) $J_{(3,4)}$7.75 Hz, 1H; H_5 7.42(m) 1H; H_4 7.88(td) $J_{(4,5)}$~$J_{(3,4)}$7.74 Hz,1H; H_6 8.64(d) $J_{(5,6)}$4.4 Hz, 1H.

^{1}H NMR ($CDCl_3$)

pz resonances: CH_2 5.46(s) 2H; H_4 6.32(t) 1H; H_3 7.47(d) $J_{(3,4)}$2.10 Hz, 1H; H_5 7.54(d) $J_{(4,5)}$2.34 Hz, 1H;

py resonances: H_3 6.98(d) $J_{(3,4)}$7.68 Hz, 1H; H_5 7.21(m) 1H; H_4 7.59(ddd) $J_{(4,5)}$~$J_{(3,4)}$7.52 Hz, 1H; H_6 8.56(d) $J_{(5,6)}$4.2 Hz, 1H.

2. $H_2C(mim)pz$

Method	:	B
Starting Material	:	2-(chloromethyl)-1-methylimidazole hydrochloride (5g, 30 mmole)
Halide : Pyrazolide	:	1 : 2
Reflux Time	:	5 hours
Purification	:	Sublimation, m.pt 77-79^{o}C
Yield	:	3.44g, 71%
Microanalysis	:	C 59.07 (59.24), H 5.94 (6.21), N 34.25 (34.55),
Mass Spectrum	:	m/e(%I): 162(M^+, 30), 95 (100), 81 (15), 54 (30)

^{1}H NMR (acetone D6)

pz resonances: CH_2 5.40(s) 2H; H_4 6.24(t) 1H; H_3 7.42(d) $J_{(3,4)}$1.29 Hz, 1H; H_5 7.59(d) $J_{(4,5)}$2.10 Hz, 1H.

mim resonances: NMe 3.72(s) 3H; $H_{5(4)}$ 6.85(d) $J_{(4,5)}$ 1.09Hz, 1H; $H_{4(5)}$ 7.02(d) $J_{(4,5)}$ 1.14 Hz, 1H.

3. $1,3\text{-}(pzCH_2)_2C_6H_4$

Method	:	B
Starting Material	:	1,3-bis(bromomethyl)benzene (4g, 15.2 mmole)
Halide : Pyrazolide	:	1 : 2
Reflux Time	:	6 hours
Purification	:	Recrystallization hot hexane/charcoal, m.pt 36°C
Yield	:	2.96g, 82%
Microanalysis	:	C 70.50 (70.56), H 5.78 (5.92), N 23.62 (23.52)
Mass Spectrum	:	m/e(%I): 237(M^+, 15), 170 (100), 143 (10), 103 (12)

^1H NMR ($CDCl_3$):

CH_2 5.29(s) 4H; H_4 6.28(t) 2H; Ph_1 7.04(s,broad) 1H; $Ph_{3,5}$ 7.10(dd) J 7.72 Hz, 2H; Ph_4 7.30(d) $J_{(4,5)}$ 7.74 Hz, 1H; H_5 7.37(d) $J_{(4,5)}$ 2.28 Hz, 1H; H_3 7.54(d) $J_{(3,4)}$ 1.77 Hz, 1H.

4. $2,6\text{-}(pzCH_2)_2C_6H_3Br$

Method	:	B
Starting Material	:	2,6-bis(bromomethyl)bromobenzene (4.5g, 13.1 mmole)
Halide : Pyrazolide	:	1 : 2
Reflux Time	:	8 hours
Purification	:	Recrystallization hot hexane/charcoal, m.pt 95°C.
Yield	:	2.83g, 68%
Mass Spectrum	:	m/e(%I): 317(M^+, 2), 237 (100), 169 (50).

^1H NMR ($CDCl_3$):

CH_2 5.46(s) 4H; H_4 6.32(t) 2H; $Ph_{3,5}$ 6.77(d) $^2J(^1H\text{-}^1H)$ 7.72

Hz, 2H; Ph_4 7.21(t), $^2J(^1H-^1H)$ 7.71 Hz, 1H; H_5 7.47(d) $J_{(4,5)}$2.32 Hz, 2H; H_3 7.58(d) $J_{(3,4)}$1.79 Hz, 2H.

5. $pzCH_2\underline{CH_2}Br$

Method : C
Starting Material : 1,2-dibromoethane (halide and organic phase)
Reflux Time : 1 hour
Purification : Vacuum distillation 64-66°C/0.5 mm Hg
Yield : 52% (based on pyrazole), viscous oil
Mass Spectrum : m/e(%I): 175(M^+, 5), 174 (60), 176 (60), 95 (100), 81 (100), 68 (100)

^1H NMR ($CDCl_3$):

$pz\underline{CH_2}$ 3.73(t) $^2J(H-^1H)$ 12.71 Hz, 2H; $\underline{CH_2}Br$ 4.51(t) $^2J(^1H-^1H)$ 12.71 Hz, 2H; H_4 6.26(t) 1H; H_5 7.47(d) $J_{(4,5)}$2.11 Hz, 1H; H_3 7.56 (d) $J_{(3,4)}$1.56 Hz, 1H.

6. $pzCH_2\underline{CH_2}Cl$

Method : C
Starting Material : 1,2-dichloroethane (halide and organic phase)
Reflux Time : 1 hour
Purification : Vacuum distillation 46-49°C/0.5 mm Hg
Yield : 73% (based on pyrazole), viscous oil
Mass Spectrum : m/e(%I): 130(M^+, 20), 95 (16), 81 (100), 68 (70)

^1H NMR ($CDCl_3$):

$pz\underline{CH_2}$ 3.86(t) $^2J(^1H-^1H)$ 12.01 Hz, 2H; $\underline{CH_2}Cl$ 4.44(t)$^2J(^1H-^1H)$ 12.04 Hz, 2H; H_4 6.27(t) 1H; H_5 7.48(d) $J_{(4,5)}$2.28 Hz, 1H; H_3 7.58(d) $J_{(3,4)}$ 1.38 Hz, 1H.

7. $pzCH_2CH_2pz$

Method : C
Starting Material : 1,2-dibromoethane (4.4 cm^3, 51 mmole)
Reflux Time : 12 hours
Purification : Vacuum distillation 76-78°C/0.5 mm Hg
Yield : 7.17g, 86%, viscous oil
Mass Spectrum : m/e(%I): 162(M^+, 16), 94 (100), 81 (100), 68 (100)

^1H NMR ($CDCl_3$):

CH2 4.53(s) 4H; H4 6.26(t) 2H; H_5 6.92(dd) $J_{(4,5)}$2.79 Hz, 2H; H_3 7.56(dd) $J_{(3,4)}$1.50 Hz, 2H.

8. $pzCH_2CH_2CH_2pz$

Method : C
Starting Material : 1,3-dibromopropane (5 cm3, 49.25 mmole)
Reflux Time : 12 hours
Purification : Vacuum distillation 92-94°C/0.5 mm Hg
Yield : 7.90g, 92%, viscous oil

^1H NMR ($CDCl_3$):

CH_2 2.45(q) 2H; CH_2 4.10(t) 4H; H_4 6.23(t) 2H; H_3 7.38(d) $J_{(3,4)}$1.90 Hz, 2H; H_5 7.52(d) $J_{(4,5)}$2.20 Hz, 2H.

9. H_2Cpz_2

Method : C
Starting Material : CH_2Cl_2 (halide and organic phase)
Reflux Time : 8 hours
Purification : Recrystallization from hot hexane/charcoal
Yield : 88%

^1H NMR (acetone D6):

H_4 6.27(dd) $J_{(4,5)}$2.37 Hz, 2H; CH 6.41(s) 2H; H_3 7.47(d) $J_{(3,4)}$1.78 Hz, 2H; H_5 7.85(dd), $J_{(4,5)}$2.40 Hz, 2H.

10. $Me(H)Cpz_2$

Method : A
Starting Material : acetaldehyde diethyl acetal
Purification : Sublimation, m.pt 53°C.
Yield : 80% (based on pyrazole)

^1H NMR (acetone D6):

CMe 2.13(d) $^3J(^1H-^1H)$ 6.84 Hz, 3H; H_4 6.25(dd) $J_{(4,5)}$2.35 Hz, 2H; CH 6.76(q) $^3J(^1H-^1H)$ 6.84 Hz, 1H; H_5 7.80(dd) $J_{(4,5)}$2.40, 2H.

^1H NMR ($CDCl_3$):

CH_3 2.17(d) $^3J(^1H-^1H)$ 6.8 Hz, 3H; H_4 6.25(t) 2H; CH 6.61(q) $^3J(^1H-^1H)$ 6.8 Hz, 1H; H_3 7.54(d) $J_{(3,4)}$2.0 Hz, 2H; H_5 7.57(d) $J_{(4,5)}$2.4 Hz, 2H.

11. Me_2Cpz_2

Method : D
Starting Material : Acetone (5 cm^3, excess)
Reaction Time : 5 minutes
Purification : Recrystallization from hot hexane/charcoal,
Yield : 93%

^1H NMR (acetone D6):

CMe 2.26(s) 6H; H_4 6.24(dd) $J_{(4,5)}$2.57 Hz, 2H; H_3 7.47(s) , 2H; H_5 7.58(dd) $J_{(4,5)}$2.57 Hz, 2H.

^1H NMR ($CDCl_3$):

CH_3 2.80(s), 6H; H_4 6.30(t) 2H; H_5 7.43(d) $J_{(4,5)}$2.5 Hz, 2H; H_3 7.60(d) $J_{(3,4)}$1.80 Hz, 2H.

12. $Ph(H)Cpz_2$

Method : A
Starting Material : Benzaldehyde dimethyl acetal
Purification : Vacuum sublimation, m.pt 60°C.
Yield : 75% (based on pyrazole)

^1H NMR ($CDCl_3$):

H_4 6.40(t) 2H; Ph 7.33(m) 5H; H_5 7.59(d) $J_{(4,5)}$2.40 Hz, 2H; H_3 7.63(d) $J_{(3,4)}$1.8 Hz, 2H;

13. $Ph(MeO)HCpz_2$

Method : D
Starting Material : 3-methoxybenzaldehyde (0.85g, 6.2 mmole)
Reaction Time : 2 hours with warming
Purification : Recrystallization from minimum volume of hot hexane, m.pt 49°C.
Yield : 0.91g, 58%

^1H NMR ($CDCl_3$):

OMe 3.74(s), 3H; H_4 6.33(t) 2H; Ph_2 6.56(s, broad) 1H; Ph_6 6.62(dd) J 7.68 Hz, 1H; Ph_4 6.91(dd) J 8.25 Hz, 1H; Ph_5 7.28(t) 1H; H_5 7.52(d) $J_{(4,5)}$2.16 Hz, 2H; H_3 7.60(d) $J_{(3,4)}$1.14 Hz, 2H; CH 7.71(s) 1H.

14. $(2\text{-}XC_6H_4)(H)Cpz_2$; X = Br, Cl

Method : D
Starting Material : 2 halobenzaldehyde (6.2 mmole)
Reaction Time : 2 hours with warming
Purification : Recrystallization from hot hexane/charcoal,
m.pt (X = Br) 73°C
m.pt (X = Cl) 62-63°C
Yield : 48%

X = Br

Mass Spectrum : m/e(%I): 258(M^+, 2), 223 (82), 191 (54), 156 (100), 101 (12)

^{1}H NMR ($CDCl_3$):

H_4 6.35(q) 2H; Ph_5 6.82(dd) J 7.56 Hz, 1H; Ph_4 7.30(m) 2H; H_5 7.37(d) $J_{(4,5)}$2.37 Hz, 2H; Ph_3 7.62(dd) J 7.80 Hz, 1H; H_3 7.66(d) $J_{(3,4)}$1.44 Hz, 2H; CH 7.90(s)

X = Cl

Microanalysis : C 60.12 (60.35); H 4.30 (4.28); N 21.51 (21.66)

Mass Spectrum : m/e(%I): 304 (60) 303(M^+, 12), 302 (60), 223 (80), 191 (50), 111 (100), 101 (20)

^{1}H NMR ($CDCl_3$):

H_4 6.34(t) 2H; Ph_3 6.84(dd) 1H; H_5 7.30(td) 1H; Ph_4 7.35(td) 1H; H_5 7.39(d) $J_{(4,5)}$2.42 Hz, 1H; Ph_6 7.43(td) 1H; H_3 7.65(d) $J_{(3,4)}$1.69 Hz, 1H; CH 7.98(s) 1H.

15. HC(py)pz_2

Method : D

Starting Material : 2-pyridinecarboxyaldehyde (0.60 cm^3, 6.3 mmole)

Reaction Time : 5 minutes with cooling. This reaction proceeds without the addition of $CoCl_2$ catalyst also.

Purification : Recrystallization from hot hexane/charcoal, m.pt 55^oC

Yield : 0.62g, 45%

Microanalysis : C 64.24 (63.98), H 4.82 (4.92), N 31.42 (31.10)

Mass Spectrum : m/e(%): 225(M^+, 15), 158 (100), 147(68), 131 (35)

^{1}H NMR (D6 acetone):

pz resonances: H_4 6.36(dd) $J_{(4,5)}$2.36 Hz, 2H; H_3 7.57(d) $J_{(3,4)}$1.73 Hz, 2H; H_5 7.85(m) 2H; CH 7.88(s) 1H.

py resonances: H_3 7.15(d) $J_{(3,4)}$7.92 Hz, 1H; H_5 7.42(ddd) $J_{(4,5)}$7.59 Hz, $J_{(3,4)}$4.81 Hz, 1H; H_4 7.85(m) 1H; H_6 8.61 (ddd) $J_{(5,6)}$4.83, $J_{(4,6)}$1.80 Hz, 1H.

^{1}H NMR ($CDCl_3$):

H_4 6.35(q) 2H; py_3 7.02(d) 1H; H_5 + H_3 7.65(t) 4H; py_4 + CH 7.74(m) 2H; py_6 8.66(m) 1H.

16. $HC(mim)pz_2$

Method	:	D
Starting Material	:	N-methyl-2-imidazole carbaldehyde (0.68g, 6.2 mmole)
Reaction Time	:	5 minutes with cooling. This reaction proceeds in the absence of $CoCl_2$ catalyst.
Purification	:	Recrystallization from hot hexane/charcoal, m.pt 104-106°C
Yield	:	0.70g, 49%

^{1}H NMR (acetone D6)

pz resonances: H_4 6.33(dd) 2H; H_3 7.52(s) 2H; H_5 7.93(d) $J_{(4,5)}$2.56 Hz, 2H; CH 8.00(s), H.

mim resonances: NMe 3.56(s) 3H; $H_{5(4)}$ 6.95(d) $J_{(4,5)}$1.11 Hz, 1H; $H_{4(5)}$ 7.16(d) $J_{(4,5)}$1.08 Hz, 1H.

17. $HC(thio)pz_2$

Method	:	D
Starting Material	:	2-thiophenecarboxaldehyde (0.58 cm^3, 6.2 mmole)
Reaction Time	:	2 hours with warming
Purification	:	Recrystallization from hot hexane, m.pt 87°C
Mass Spectrum	:	m/e(%I): 230(M^+, 5), 214 (8), 163 (100), 91 (2)

^{1}H NMR (D6 acetone):

H_4 6.47(t) 2H; $thio_{(3,4)}$ 7.22(m, complex) 2H; H_3 7.71(d) $J_{(3,4)}$1.52 Hz, 2H; $thio_5$ 7.72(dd) J 5.08 Hz, 1H; H_5 8.05(d) $J_{(4,5)}$2.43 Hz, 2H; CH 8.31(s) 1H.

18. 1,3-$(pz_2CH)_2C_6H_4$

Method	:	B
Starting Material	:	2,6-bis(dibromomethyl)benzene (5g, 11.86 mmole)
Reaction Time	:	12 hours
Purification	:	Recrystallization from hot hexane/charcoal, m.pt 126^{o}C
Yield	:	3.25g, 74%

^{1}H NMR ($CDCl_3$):

H_4 6.31(s) 4H; Ph_2 6.59(s) 1H; $Ph_{4,6}$ 7.04(d) J(^{1}H-^{1}H) 7.82 Hz, 2H; Ph_5 7.38(t) 1H; H_3 7.51(d) $J_{(3,4)}$1.68 Hz, 4H; H_5 7.72(d) $J_{(4,5)}$2.52 Hz, 4H.

19. $MeCpz_2CH_2Cl$

Method	:	D
Starting Material	:	1-chloroacetone (1.70 cm^3, 21.6 mmole)
Reaction Time	:	15 minutes with warming
Purification	:	Recrystallization from hot hexane/charcoal, m.pt 60-62^{o}C
Yield	:	3.73g, 82%
Microanalysis	:	C 51.50 (51.31);H 5.52 (5.26); N 26.88 (26.60); Cl 16.2 (16.83)
Mass Spectrum	:	m/e(%I): 210(M^+, 20), 175 (22), 161 (50), 143 (100), 107 (38)

^{1}H NMR ($CDCl_3$):

CH_3 2.38(s) 3H; CH_2 4.56(s) 2H; H_4 6.30(t) 2H; H_5 7.36(d)

$J_{(4,5)}$2.59 Hz, 2H; H_3 7.61(d) $J_{(3,4)}$1.56 Hz, 2H.

20. $ClCH_2Cpz_2CH_2Cl$

Method	:	D
Starting Material	:	1,3-dichloroacetone (1.5g, 11.81 mmole)
Reaction Time	:	30 minutes with warming
Purification	:	Recrystallization from hot hexane/charcoal, m.pt 127°C
Yield	:	1.85g, 64%
Microanalysis	:	C 44.33 (44.10); H 4.07 (4.11); N 23.12 (22.86); Cl 28.80 (28.92)
Mass Spectrum	:	m/e(%I): 246 (15), 245 (M^+, 2), 244 (24), 195 (100), 177 (65), 176 (60), 141 (70) 106 (82)

^1H NMR ($CDCl_3$):

CH_2 4.78(s) 4H; H_4 6.34(t) 2H; H_5 7.52(d) $J_{(4,5)}$2.63 Hz, 2H; H_3 7.61(d) $J_{(3,4)}$1.67 Hz, 2H.

21. $CH_3Cpz_2CHCl_2$

Method	:	D
Starting Material	:	1,1-dichloroacetone (1.5g, 11.81 mmole)
Reaction Time	:	5 hours with warming
Purification	:	Recrystallization from minimum volume of hot hexane/charcoal, m.pt 83°C
Yield	:	1.19g, 41%
Microanalysis	:	C 44.80 (44.10); H 4.89 (4.12), N 22.25 (22.86)
Mass Spectrum	:	m/e(%I): 244 (20); 245 (M^+, 2); 244 (35); 209 (36); 177 (35); 161 (100); 141 (22); 109 (25)

^1H NMR ($CDCl_3$):

CH_3 2.29(s) 3H; $CHCl_2$ 2.62(s) 1H; H_4 6.26(t) 1H; H_4

6.37(t) 1H; H_5 7.40(d) $J_{(4,5)}$2.46 Hz, 1H; H_3 7.55(d) $J_{(3,4)}$1.62 Hz, 1H; H_3 7.63(d) $J_{(3,4)}$1.68 Hz, 1H; H_5 7.81(d) $J_{(4,5)}$2.58 Hz, 1H.

22. $H_2C=C(CH_2pz)_2$

Method	:	B
Starting Material	:	3 chloro-2-chloromethyl-1-propene
Reaction Time	:	4 hours
Purification	:	Vacuum distillation, viscous oil
Yield	:	79%
Mass Spectrum	:	m/e(%I): 188 (M^+,2), 121 (100), 81 (52)

^1H NMR (D6 acetone):

CH_2 4.64(t) 4H; $=CH_2$ 5.13(t) 2H; H_4 6.28(t) 2H; H_5 7.35(d) $J_{(4,5)}$2.32 Hz, 2H; H_3 7.55(d) $J_{(3,4)}$1.65 Hz, 2H.

23. $HCpz_3$

Method: B.

This compound was made by an adaption of the original procedure as reported by Huckel and Bretschneider.[25].

To a stirred suspension of potassium pyrazolide (30g pyrazole and 17.25g K) in THF (400 cm^3) under a nitrogen atmosphere at ambient temperature was added distilled chloroform (11.76 cm^3, 147 mmole) in one portion. After 30 minutes stirring the suspension was slowly heated to gentle reflux and left for 8 hours during which time the mixture turned a tan colour. The mixture was filtered hot, the precipitate of KCl washed with $CHCl_3$ (3 x 30 cm^3) and the combined organic extracts reduced to a minimum volume under vacuum. Zone sublimation of the resultant semi-solid residue gave a yellow solid which was continually extracted with hot hexane. on reduction of volume and cooling, tris-(1-pyrazolyl)methane crystallized out.
Yield: 13.53g, 43%

^{1}H NMR (acetone D6):

H_4 6.41(dd) $J_{(4,5)}$2.56Hz, 3H; H_3 7.63(d) $J_{(3,4)}$1.53 Hz, 3H; H_5 7.87(d) $J_{(4,5)}$2.51 Hz, 3H; CH 8.74(s) 1H.

^{1}H NMR ($CDCl_3$):

H_4 6.25(t) 3H; H_5 7.51(d) $J_{(4,5)}$2.51 Hz, 3H; H_3 7.62(d) $J_{(3,5)}$1.89 Hz, 3H; CH 8.37(s) 1H.

24. $MeCpz_3$

Method: Described on p. 234.

Purification : Zone sublimation followed by crystallization from hot hexane, m.pt. 77°C

Yield : 78%

Microanalysis : C 57.77 (57.78), H 5.22 (5.30), N 37.12 (36.82)

^{1}H NMR (D6 acetone):

CMe 2.93(s) 3H; H_4 6.39(dd) $J_{(4,5)}$2.53 Hz, 3H; H_5 6.94(dd) $J_{(4,5)}$2.69 Hz, 3H; H_3 7.67(d) $J_{(3,4)}$1.68 Hz, 3H.

25. Cpz_4

Method : D

Starting Material : Bis-(1-pyrazolyl)methane (3g, 18.5 mmole)

Reaction Time : 8 hours at 190°C (bomb)

Purification : Recrystallization from hot hexane/charcoal, m.pt

Yield : 1.30g, 50%

^{1}H NMR (acetone D6):

H_4 6.45(dd) $J_{(4,5)}$2.73 Hz, 4H; H_5 7.58(dd) $J_{(4,5)}$2.69 Hz, 4H; H_3 7.70(dd) $J_{(3,4)}$1.71 Hz, 4H.

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APPENDIX 1.

T.G.A. $MePt(HCpz_2(C_3N_2H_2)-C)(PPh_3)_2$ p. 106

Weight Loss 1: 0.48mg, acetone solvate.

Weight complex:	9.59 mg	Weight acetone:	0.48mg
mmoles complex:	1.013×10^{-2}	mmoles acetone:	1.041×10^{-2}

Weight Loss 2: 0.17mg, 124-131^{o}C, methane gas.

Weight complex:	9.42mg	Weight methane:	0.17mg
mmoles complex:	1.012×10^{-2}	mmoles methane:	1.062×10^{-2}

Weight Loss 3: 2.64 mg, 160-200^{o}C, PPh_3.

Weight complex:	6.78mg,	Weight PPh_3:	2.64mg
mmoles complex:	1.013×10^{-2}	mmoles PPh_3:	1.008×10^{-2}

PUBLICATIONS

1. Intramolecular Coordination involving Tripodal N_2C^- Ligands.
A.J. Canty and R.T. Honeyman,
Inorg. Chimica. Acta., **114** (1986) L39.

Intramolecular Coordination involving Tripodal 'N_2C^-' Ligands, including Structural Analysis of Complexes formed by Oxidative Addition of Chlorobis-(1-pyrazolyl)propanes to Dimethylplatinum(II)

ALLAN J. CANTY, R. THOMAS HONEYMAN

Chemistry Department, University of Tasmania, Hobart, Tas. 7001, Australia

BRIAN W. SKELTON and ALLAN H. WHITE

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

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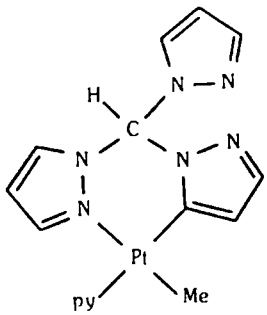
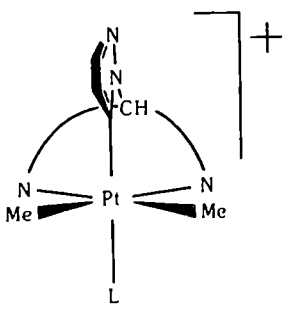
Dimethyl[tris(1-pyrazolyl)methane]platinum(II), $Me_2Pt(HCpz_3)$, undergoes a cyclometallation reaction in warm pyridine to form $MePt(HCpz_2(pzH_{-1}))(py)$ involving presence of the ligand as a bidentate 'NC$^-$' donor, characterized by spectroscopic [1, 2] and X-ray structural analysis [2]. As this represents a new binding mode of tris(1-pyrazolyl)methane we have sought derivatives involving the metallated ligand as a tridentate 'N_2C^-' organometallic analogue of 'N_3' tris(1-pyrazolyl)methane and 'N_3^-' tris(1-pyrazolyl)borate, e.g. as in $[Me_3Pt(HCpz_3)][PF_6]$ [3] and $MePt(HBpz_3)(CF_3C_2CF_3)$ [4], and as a tripodal analogue of planar intramolecular 'N_2C^-' coordination systems, e.g. as in $Cl_3Pt[C_6H_3(CH_2NMe_2)_2\text{-}o,o']$ [5].



$MePt(HCpz_2(pzH_{-1}))(py)$



$[Me_2Pt(HCpz_2(pzH_{-1}))(L)]^+$

(L = py, PPh_3)

We report here the synthesis of organoplatinum(IV) cations involving metallated tris(1-pyrazolyl)methane, $[Me_2Pt(HCpz_2(pzH_{-1}))(L)]^+$ (L = py, PPh_3), and related complexes with intramolecular coordination by pyrazole groups, prior to investigation of their reactivity and further development of the organometallic chemistry of these ligands.

Platinum(II) derivatives of metallated tris(1-pyrazolyl)methane were oxidized to Pt(IV) derivatives via oxidative addition of iodomethane, since diorganoplatinum(II) complexes may be readily oxidized in this manner, e.g. $Me_2Pt(2,2'$-bipyridyl) [6–9], and characteristic octahedral geometry for Pt(IV) is expected to ensure 'N_2C^-' coordination. Thus, $MePt(HCpz_2(pzH_{-1}))(py)$ reacts with a 4–5 fold excess of iodomethane in acetone under nitrogen at ambient temperature in darkness (12 h) to form a pale yellow solution, from which, after removal of excess iodomethane and some acetone followed by addition of petroleum–ether, colourless crystals were isolated. The complex has infrared and ^1H NMR spectra (in $CDCl_3$ at 300 MHz) consistent with the formulation* $[Me_2Pt(HCpz_2(pzH_{-1}))(py)]I \cdot 0.5Me_2CO$, e.g. $\nu(C{=}O)$ for solvate at 1704 cm^{-1}, appropriate relative intensities in NMR spectra, a single $Me_2Pt(IV)$ resonance at 1.51 ppm from Me_4Si with $^2J(^1H{-}^{195}Pt)$ 69.2 Hz, a single methine resonance at 10.45 ppm, and $^3J(^{ortho}H{-}^{195}Pt)$ 20.5 Hz for the pyridine group. A similar procedure, but with prior addition of a molar equivalent of triphenylphosphine, gave $[Me_2Pt(HCpz_2(pzH_{-1}))(PPh_3)]I$, which exhibited a similar NMR spectrum, e.g. δ [Me_2-Pt(IV)] 1.45 with $^2J(^1H{-}^{195}Pt)$ 70.6 Hz and $^3J(^1H{-}^{31}P)$ 7.0 Hz. The PPh_3 complex is sufficiently soluble for measurement of conductance in acetone, giving a molar conductance of 100 ohm^{-1} cm^2 mol^{-1}, appropriate [10] for a 1:1 electrolyte.

As the complexes did not give crystals suitable for X-ray structural analysis, related pyrazole donor Pt(IV) complexes involving 'N_2C^-' coordination were sought via oxidative addition reactions of a Pt(II) substrate with haloalkane reagents containing two pyrazole groups. The new reagents 1-chloro-2,2-bis-(1-pyrazolyl)propane ($ClCH_2Cpz_2CH_3$) and 1,3-dichloro-2,2-bis(1-pyrazolyl)propane [$(ClCH_2)_2Cpz_2$] were obtained in high yield by condensation reactions as shown, using anhydrous cobalt(II) chloride as catalyst in the manner described [11] for related bis(1-pyrazolyl)alkanes.

$$pz_2C{=}O + (ClCH_2)(XCH_2)C{=}O \longrightarrow ClCH_2Cpz_2CH_2X + CO_2$$

(X = H, Cl)

The complex $[Me_2Pt(SEt_2)]_2$ was chosen as a substrate because the diethylsulfide ligands are readily displaced by nitrogen donors and the complex undergoes facile oxidative addition reactions [6]. If nitro-

*All complexes have satisfactory microanalyses (C, H, N, P, halogen).

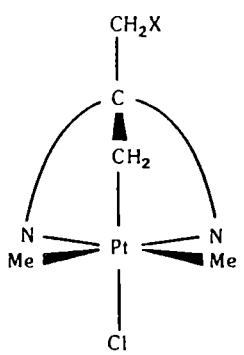
0020-1693/86/$3.50

TABLE I. Crystal Data for Complexes $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

Complex	X = H	X = Cl
Formula	$C_{11}H_{17}ClN_4Pt$	$C_{11}H_{16}Cl_2N_4Pt$
M	435.8	470.3
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	14.206(8)	8.407(2)
b (Å)	10.888(6)	13.836(6)
c (Å)	8.959(5)	113.139(4)
β (deg)		110.16(2)
V (Å^3)	1386(1)	1434.6(8)
D_{calc} (g cm^{-3})	2.09	2.17
Z	4	4
$F(000)$	824	888
μ_{Mo} (cm^{-1})	99	97
Crystal dimensions (mm)	0.18 × 0.16 × 0.48	0.15 × 0.40 × 0.10
$A^*_{min,max}$	4.0, 6.3	2.3, 3.4
$2\theta_{max}$ (deg)	60	60
Number of unique data	2248	4213
Number of data with $I > 3\sigma(I)$	1818	2912
R	0.032	0.032
R'	0.029 (preferred chirality)	0.033

gen donor complexes such as '$Me_2Pt(ClCH_2Cpz_2CH_2X)$' form, subsequent oxidative addition is expected in view of the proximity of chlorine atom(s) and platinum.

On heating $[Me_2Pt(SET_2)]_2$ with $ClCH_2Cpz_2CH_2X$ in benzene under nitrogen for 15 min a colourless crystalline precipitate formed, and was collected from the hot solution by filtration, washed with benzene and diethyl ether, and recrystallized by exposure of an acetone solution to diethyl ether vapour in a closed container. The complexes were characterized as $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$ by microanalysis, osmometric molecular weight determinations in chloroform at 37 °C [found 421 (X = H), 449 (Cl); calc. 435 (H), 470 (Cl)], conductance measurements (non-electrolytes in acetone), NMR spectra and X-ray structural analysis. Thus, in addition to pyrazole resonances, NMR spectra exhibit $Me_2Pt(IV)$ resonances at δ 1.30 (X = H), 1.33 (X = Cl), with $^2J(^1H-^{195}Pt)$ 73.7 Hz (H), 73.6 Hz (Cl); $PtCH_2$ resonances at δ 2.38 (H), 2.46 (Cl) with $^2J(^1H-^{195}Pt)$ 51.4 Hz (H), 54.3 Hz (Cl); and CH_2X resonances at δ 2.45 (H), 4.65 (Cl) with $J(^1H-^{195}Pt)$ 5.8 Hz (H) and 2.9 Hz (Cl).



$Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

(X = H, Cl)

Single crystal X-ray diffraction studies were undertaken for both complexes using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with Mo Kα radiation (Table I)*. Full matrix least-squares refinements, after analytical absorption corrections, involved anisotropic thermal parameters for the non-hydrogen atoms with hydrogen atoms included with calculated (x, y, z, U_{iso}) and constrained, with reflection weights $w = 1/\sigma^2(F)$ and $\sigma^2(I) = \sigma^2_{diff}(I) + 0.00012\sigma^4_{diff}(I)$. Neutral complex scattering factors were used [12]; computation used the XTAL 83 program system [13] implemented by Dr S. R. Hall on a Perkin–Elmer 3240 computer. Details of the coordination geometry for platinum are given in Table II, and the structure of $Me_2(Cl)Pt(CH_2Cpz_2CH_3)$ is illustrated in Fig. 1.

The complexes have very similar structures, based on distorted octahedral geometry for Pt(IV), with the 'N_2C^-' ligands confirmed as tripodal (*facial*) tridentates. The main distortion from regular octahedral geometry results from the small bite angles of the tridentate, with C(1)–Pt–N and N–Pt–N angles 78.5(2)–82.5(4)°. The chlorine atom is

*Further information is available, see Supplementary Material.

TABLE II. Bond Distances (Å) and Angles (°) for Platinum in $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

Atoms	X = H	X = Cl	Atoms	X = H	X = Cl
Distances					
Pt–C(1)	2.06(1)	2.030(6)	Pt–Cl	2.421(3)	2.443(2)
Pt–C(A)	2.05(1)	2.043(7)	Pt–N(a1)	2.129(8)	2.166(4)
Pt–C(B)	2.00(1)	2.035(9)	Pt–N(1b)	2.145(7)	2.163(6)
Angles					
C(A)–Pt–C(B)	89.2(5)	88.1(3)	C(B)–Pt–Cl	91.3(3)	90.8(2)
C(1)–Pt–C(A)	93.8(5)	94.3(3)	N(a1)–Pt–N(b1)	82.5(4)	81.4(2)
C(1)–Pt–C(B)	94.7(4)	93.6(3)	N(a1)–Pt–Cl	94.5(3)	96.6(1)
C(1)–Pt–N(a1)	78.7(4)	78.5(2)	N(b1)–Pt–Cl	95.9(2)	96.4(1)
C(1)–Pt–N(b1)	77.9(3)	79.1(2)	C(1)–Pt–Cl	171.2(3)	173.6(2)
C(A)–Pt–N(b1)	93.6(4)	93.7(3)	C(A)–Pt–N(a1)	172.1(4)	171.9(2)
C(A)–Pt–Cl	92.8(4)	90.4(2)	C(B)–Pt–N(b1)	172.1(4)	172.5(2)
C(B)–Pt–N(a1)	93.8(5)	95.9(2)			
Pt–C(1)–C(2)	101.4(6)	102.2(4)	Pt–N(a1)–C(a5)	143.4(8)	143.4(4)
Pt–N(a1)–N(a2)	108.8(6)	108.8(9)	Pt–N(b1)–C(b5)	144.3(7)	144.6(5)
Pt–N(b1)–N(b2)	109.1(5)	109.5(4)			

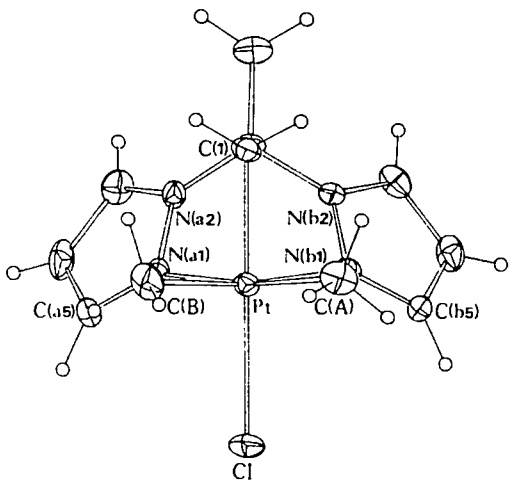


Fig. 1. Projection of $Me_2(Cl)Pt(CH_2Cpz_2CH_3)$ with selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

trans to the CH_2 group, and the three carbon atoms are in a *facial* 'C_3Pt' orientation.

Although metallated tris(1-pyrazolyl)methane acts as a tripodal, 'N_2C^-' ligand with Pt(IV), the new chloro-bis(1-pyrazolyl)propane reagents may be of more general interest as sources of tripodal 'N_2C^-' coordination because they are readily synthesized and the presence of halogen should allow the synthesis of derivatives for a wider range of metal species, e.g. $R_2Sn(IV)$ [14], Pd(II) and Pt(II) [15], Pt(IV) [5], and Ni(II) [16] recently studied with the planar 'N_2C^-' ligand $[C_6H_3(CH_2NMe_2)_2\text{-}o,o']^-$.

Supplementary Material

The atomic coordinates, ligand geometries, least squares planes for pyrazole rings, thermal parameters, and diagrams of both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this Letter.

Acknowledgements

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