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Leo Ernest Manzer

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SYNTHESIS, REACTIVITY AND SPECTROSCOPIC STUDIES OF ORGANOPLATINUM COMPLEXES

by

Leo Ernest Manzer
Department of Chemistry

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ABSTRACT

Cationic methylplatinum(II) nitrile complexes of the type trans-$[PtMeL_2(N{\equiv}C\text{-}R)](X)$ have been prepared by the reaction of trans-$PtMeClL_2$ (where L = PMe_2Ph or $AsMe_3$) with an aryl nitrile and AgX (X = BF_4, PF_6). Use of pentafluorobenzonitrile and 2,3,5,6-tetrafluoroterephthalonitrile in alcohol has led to the preparation of a series of imino ether complexes. A mechanism for imino ether formation, involving nucleophilic attack by an alcohol at a π-bonded nitrile, is proposed and the course of the reaction is shown to be dependent not only on the alcohol but also on the size of the anion used.

A variety of cationic platinum(II) isocyanide complexes of the types trans-$[PtXL_2(C{\equiv}N\text{-}R)]Z$ and trans-$[Pt(C{\equiv}N\text{-}R)_2L_2]Z_2$ (where L = PMe_2Ph, $PMePh_2$; X = Cl, I, Me; Z = PF_6^-, BF_4^-, SbF_6^-, BPh_4^-) have been prepared. The proton nmr spectra of the methylplatinum cations are temperature dependent due to rapid intermolecular exchange of the phosphines. $[Pt(C{\equiv}NEt)_2L_2](PF_6)_2$ reacts slowly with protic nucleophiles to give carbene complexes, whose mode of formation and stereochemistry are discussed.

Improved syntheses for $PtR_2(COD)$ (where R = Me, Ph, CH_2Ph, CH_2SiMe_3, I, and COD = 1,5-cyclooctadiene) and PtRCl(COD) are described. Oxidative addition and displacement reactions of these complexes have yielded new organoplatinum(II) and organoplatinum(IV) compounds. Several cations have also been prepared. Trifluoromethyl iodide reacted with $PtMe_2(COD)$ to give $Pt(CF_3)_2(COD)$. Displacement reactions and oxidative addition reactions of the $Pt-CF_3$ compounds are discussed.

A number of five coordinate complexes of platinum(II) of the type $PtMe[R_nBpz_{4-n}](un)$, (where R_nBpz_{4-n} is a tridentate polypyrazolylborate ligand, and un = acetylene, allene, olefin, and CO) have been prepared. Double resonance nmr studies have allowed definite assignment of all 3-H, 4-H, and 5-H protons. The acetylenes, allenes and olefins are constrained within the trigonal plane and are stereochemically rigid. The carbonyl complex is stereochemically non-rigid, in solution, at room temperature.

^{13}C nmr data for a series of σ-bonded organoplatinum complexes are reported. Correlations between $^{1}\underline{J}(Pt-C)$ and $^{2}\underline{J}(Pt-C-H)$ and factors governing the coupling constant between ^{195}Pt and sp^3, sp^2, sp hybridized carbons are discussed. Variations in the chemical shifts of sp^3, sp^2 and sp hybridized carbons are related to the known chemistry of these compounds.

Cations of the type $[PtMe_2(PMe_2Ph)_2L_2]^{+2}$ and $[PtMe_2(PMe_2Ph)_2LI]^+$ have been prepared, where L is a neutral ligand such as phosphite, nitrile, isocyanide, carbene, etc. The coupling constant $^2\underline{J}(Pt(IV)-C-H)$ is used to establish an NMR *trans*-influence series. The reactions of the dimethylplatinum(IV) cations with 1-butyn-4-ol and pentafluorobenzonitrile are compared with those of the corresponding methylplatinum(II) compounds.

A series of platinum(IV) cations of the type *fac*-$[PtMe_3Q_2L]^+$, where Q = PMe_2Ph, NC_5H_5, $AsMe_3$ or p-CN-C_6H_4-Me and L is a neutral ligand, have been prepared, although in some cases the preparative reactions led to elimination of ethane and formation of *trans*-$[PtMeQ_2L]^+$. Factors governing the stability of the platinum(IV) cations are discussed. Deuteration studies have shown that the Pt-CD_3 bond is more resistant to cleavage than the Pt-CH_3 bond, and that substitution reactions occur *via* a dissociative mechanism. The Raman spectra of the trimethylplatinum(IV) complexes have also been examined.

Complexes of the type *trans*-$[Pt(CF_3)Q_2L]^+X^-$ and $Pt(CF_3)ZQ_2$ have been prepared, where Q = PMe_2Ph, L is a neutral ligand and Z is an anionic ligand. $^2\underline{J}(Pt-CF_3)$ for these complexes varies linearly with $^2\underline{J}(Pt-CH_3)$ for the corresponding methylplatinum complexes except where L requires synergic σ-π bonding. These results suggest that the Pt-CF_3 bond does not depend to any great extent on π-back bonding for its stability. The *trans*-influence of the trifluoromethyl group is discussed, and some reactions of the trifluoromethylplatinum complexes are compared with those of the corresponding methylplatinum compounds.

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CHAPTER I

GENERAL INTRODUCTION

In recent years there has been a considerable increase in interest in the field of organometallic chemistry, especially in the area of homogeneous catalysis by transition metal complexes [1].

A number of transition metal-assisted catalytic cycles have been discovered, probably the best understood cycle being the hydrogenation of olefins by Wilkinson's catalyst [2], $RhClL_3$ (where L is a tertiary phosphine or arsine). This cycle is outlined in Figure I-1.

Step (1) represents the oxidative addition of hydrogen to a square planar Rh(1) complex to give an 18-electron Rh(III) dihydride. Step (2), Lewis base dissociation, is followed by olefin coordination in step (3). Insertion in step (4) gives an unstable hydrido-alkyl which is an 18-electron Rh(III) complex. Phosphine association in step (5) gives an 18-electron hydrido-alkyl which produces an alkane by reductive elimination and regenerates $RhClL_3$.

There are several key steps in the catalytic cycle; (i) oxidative addition-reductive elimination; (ii) ligand dissociation and association; (iii) coordination and activation of the C=C bond; (iv) addition

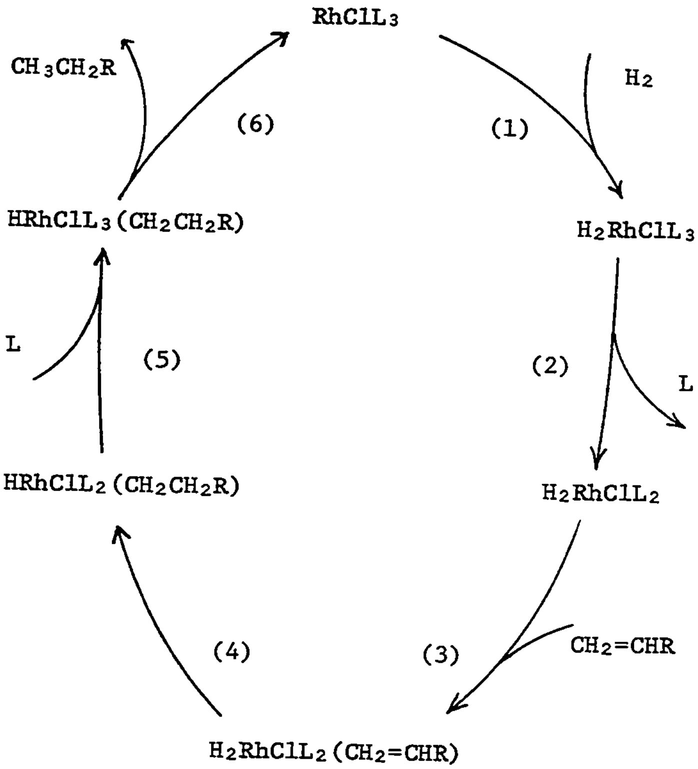


Figure I-1

Hydrogenation of an Olefin by $RhClL_3$

of H^- across the C=C bond.

In order to fully understand a catalytic reaction, and ultimately to design the most efficient catalyst, each step in the cycle must be completely understood. At present oxidative addition [3,4] and ligand exchange reactions [5] have been extensively investigated. However, little is known about (a) the mechanism of reductive elimination, (b) the factors which govern the activation of an unsaturated organic molecule towards electrophilic or nucleophilic attack by transition metal complexes, (c) the actual insertion mechanism, and (d) the role played by the other ligands on the metal atom. An understanding of the bonding properties of a particular ligand towards a metal atom catalyst is clearly an important factor in understanding a catalytic cycle. By altering the electronic and steric properties of a ligand the course of a reaction may be completely changed. Throughout this thesis the bonding properties of a variety of ligands will be qualitatively assessed and classified according to their relative trans-influence [6]. Therefore, it seems appropriate to define the term and to briefly outline the main techniques that are available for measuring this trans "bond-weakening" effect.

The trans-influence of a ligand in a metal complex was defined in 1966 by Pidcock, Richards and Venanzi [7,8] as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of that complex". The term has gained wide (though not unanimous) acceptance among Inorganic Chemists since it conveniently and unambiguously distinguishes this "bond-weakening" effect of a ligand from its trans-effect [9], which is "that effect of a coordinated group A upon the rate of substitution reactions of the group opposite to A". The trans-effect of a ligand thus describes a kinetic phenomenon and is a partial description of the transition state in a substitution reaction; it may or may not be related to its trans-influence in the equilibrium state of a complex.

The trans-influence may be measured by a variety of techniques such as x-ray crystallography, infrared, Raman, nuclear magnetic resonance, nuclear quadrupole resonance and photoelectron spectroscopy. A recent review [6] has summarized the information that may be obtained about the trans-influence using each of these techniques. In this thesis we shall be concerned mainly with the use of nuclear magnetic resonance spectroscopy to assess the relative trans-influences of various ligands.

Organoplatinum complexes are particularly useful for such a study since one of the isotopes of platinum has a nuclear spin of ½ and is present in 33.8% natural abundance. Thus, it is possible to measure the coupling constant between ^{195}Pt and other nuclei in the complex which also possess a nuclear spin such as ^{31}P, ^{13}C, ^{1}H and ^{19}F and to see what effect, if any, a particular ligand will have on this measured coupling constant.

The coupling constant between two directly-bound nuclei is believed to be dominated by the Fermi contact term [10,11] and in particular the amount of s-electron density in the hybrid orbitals used by the two nuclei in the bond. Therefore as the s-character in the bond increases so does the one-bond coupling constant.

The nmr trans-influence for organoplatinum complexes (as measured by nmr spin-spin coupling constants) is believed to arise from a rehybridization of the Pt σ-orbitals in response to changes in the orbitals of the ligand used in bonding [7,12]. Thus, within a series of square planar platinum-hydride cations[13] trans-$[PtHL(PEt_3)_2]^+$, as the trans-influence of the ligand L increases, the Pt-L bond gains in platinum 's' and 'd' character and loses 'p' character. Conversely the bond trans to L, namely the Pt-H bond, gains in 'p' character and loses 's' and 'd' character. Therefore, by varying L, and measuring $^1J(Pt-H)$ it is possible to arrange a series of ligands according to their trans-influence.

The research in this thesis is directed towards obtaining a better understanding of many of the basic steps which occur in Figure I-1, although the work is not directly related to the above or any other catalytic cycle. A number of nitrile and isocyanide complexes of platinum(II) have been prepared and the reactions of the coordinated ligands with alcohols have been investigated; the results are described in Chapters II and III. In Chapter IV a variety of dimethylplatinum(IV) cations have been prepared and an NMR trans-influence for a series of neutral ligands has been determined. The reactivity of these platinum(IV) cations towards pentafluorobenzonitrile and terminal acetylenes is discussed and compared with the analogous reactions of methylplatinum(II) cations. The stability of a series of trimethylplatinum(IV) cations, with respect to reductive elimination, is discussed in Chapter V and related to the *trans*-influence of the surrounding ligands, as measured in the previous chapter. In Chapter VI the two-bond coupling constants, ^2J(Pt-C-H) and ^2J(Pt-C-F), for a variety of Pt-CH_3 and Pt-CF_3 complexes are compared. Factors governing the two-bond coupling constants are also discussed. The reactions of trifluoromethylplatinum(II) cations with perfluoroarylnitriles and acetylenes are compared with the reactions of analogous methyl-platinum(II) cations. The syntheses of a number of new organoplatinum compounds are described in Chapter VII. In the following chapter the preparation and structures of a variety of five-coordinate acetylene, allene and olefin complexes of platinum(II) containing a tridentate polypyrazolylborate ligand are discussed. High resolution nmr spectroscopy and homonuclear double resonance experiments have permitted the assignment of all the 3-H, 4-H and 5-H protons on the pyrazolyl rings. ^{13}C nmr data for a number of σ-bonded organoplatinum complexes are presented in Chapter IX and the relationships between the ^{13}C nmr parameters, *trans*-influences and ligand reactivities are discussed.

CHAPTER II

CATIONIC METHYLPLATINUM(II) NITRILE AND IMINO-ETHER COMPLEXES

a) Introduction

In recent years there has been a considerable amount of interest in the reactions of unsaturated organic molecules with transition metal complexes.

Clark and Puddephatt [15,16] have examined the reactions of tetrafluoroethylene and hexafluorobut-2-yne with methylplatinum(II) complexes of the type trans-$PtMeClQ_2$ and cis-$PtMe_2Q_2$ (where Q = tertiary phosphine or arsine) and have found that insertion of the methyl group into the C-C unsaturated bond occurred, apparently by rearrangement of intermediate π-complexes the stability of which governed the rate of insertion.

Coordinated isocyanides have been found to be susceptible to nucleophilic attack by alcohols and amines [17-21] leading to the formation of a variety of neutral palladium(II) and platinum(II) carbene complexes.

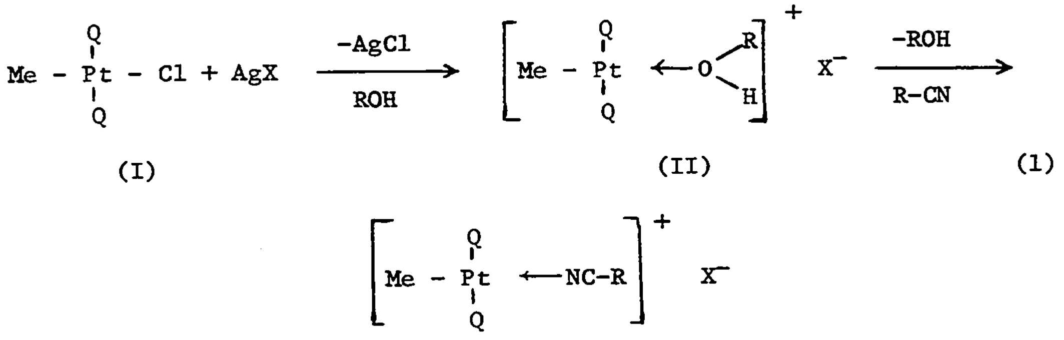
Methylplatinum(II) cations are very reactive towards terminal acetylenes [22,23] in alcohols leading to the formation of alkoxy-carbene complexes of the type trans-$[PtMeQ_2(:C(OR)CH_2R')](PF_6)$. Similar reactions involving various disubstituted acetylenes led to the preparation of methylplatinum(II) acetylene cations.[24]

Therefore it was of interest to examine the reactions of methylplatinum(II) cations with other unsaturated organic molecules such as isocyanides [25,26] and nitriles [22,28] in alcohol to see if the C≡N bond would be activated towards nucleophilic attack. In this chapter the reactions of organic nitriles with methylplatinum(II) cations are discussed.

b) Results and Discussion

(i) Preparation and Spectroscopic Data for Mononitrile Complexes.

The chloride in *trans*-$PtMeClQ_2$ (where Q = PMe_2Ph and $AsMe_3$)(I) is labile due to the high *trans*-influence [6] of the methyl group, and the addition of a silver salt of a non-coordinating anion such as AgX (X = BF_4^-, PF_6^-, SbF_6^-, NO_3^-) gives an immediate precipitate of silver chloride with the formation of an intermediate alcohol complex (II) [14]. The silver chloride may be removed by centrifugation and the alcohol displaced by a nitrile to give *trans*-$[PtMeQ_2(N{\equiv}C{-}R)]^+X^-$(III) (equation 1). The compounds so obtained are described in Table II-1.



$$\mathrm{Me-\underset{Q}{\overset{Q}{Pt}}-Cl + AgX \xrightarrow[ROH]{-AgCl} \left[Me-\underset{Q}{\overset{Q}{Pt}} \leftarrow O{<}^{R}_{H}\right]^{+} X^{-} \xrightarrow[R-CN]{-ROH}} \qquad (1)$$

(I) (II) (1)

$$\mathrm{\left[Me-\underset{Q}{\overset{Q}{Pt}} \leftarrow NC-R\right]^{+} X^{-}}$$

(III)

Table II-1

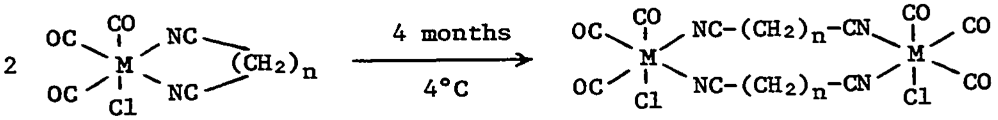
Analytical and Physical Data for Cationic Methylplatinum(II)–Nitrile and –Imino Ether Complexes

Compound[a]	Analyses, %				Decomp temp,[b] °C	Recrystn solvents	Color
	Carbon		Hydrogen				
	Calcd	Found	Calcd	Found			
$[PtCH_3A_2(NCC_6F_5)](PF_6)$	21.37	21.47	2.72	2.60	156–176	$CHCl_3$–n-C_5H_{12}	White
$[PtCH_3Q_2(NCC_6F_5)](BF_4)$	37.62	37.54	3.28	3.43	>115	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3A_2(o\text{-}NCC_6F_2H_3)](PF_6)$	22.59	22.73	3.25	3.16	140–148	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3A_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	52.83	52.53	5.47	5.32	90–93	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3Q_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	63.78	63.31	5.69	5.57	118–120	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3Q_2(m\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	63.78	63.10	5.69	5.49	95–110	CH_3COCH_3–$(C_2H_5)_2O$	White
$[PtCH_3Q_2(p\text{-}NCC_6H_4OCH_3)](PF_6)$	39.27	39.30	4.23	4.13	107–112	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3Q_2(p\text{-}NCC_6H_4NO_2)](PF_6)$	36.98	36.43	3.75	3.48	121–125	CH_2Cl_2–$(C_2H_5)_2O$	Pale yellow
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_5)](BF_4)$	37.59	37.93	3.66	3.67	129–132	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3Q_2(NCC_6H_4CN)PtCH_3Q_2](PF_6)_2$	36.20	36.36	3.91	3.65	226–228	Hot CH_3OH	White
$[PtCH_3Q_2(NCC_6H_4CN)PtCH_3Q_2](BF_4)_2$	39.58	39.73	4.27	4.32	205–207	CH_2Cl_2–$(C_2H_5)_2O$	White
$[PtCH_3A_2(NCC_6F_4CN)PtCH_3A_2](PF_6)_2$	19.00	19.19	3.05	3.12	178–194	CH_2Cl_2–$(C_2H_5)_2O$	Yellow
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](PF_6)_2$	34.50	34.42	3.45	3.45	178–186	CH_2Cl_2–n-C_5H_{12}	Yellow
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](SbF_6)_2$	30.68	30.72	3.06	2.97	206–207	CH_2Cl_2–$(C_2H_5)_2O$	Yellow
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](BF_4)_2$	37.46	37.22	3.74	3.68	>184	CH_2Cl_2–$(C_2H_5)_2O$	Yellow
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3Q_2](PF_6)_2$	34.52	34.35	3.64	3.60	100–102	CH_2Cl_2–n-C_6H_{14}	Yellow
$[PtCH_3A_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3A_2](PF_6)_2$	19.40	19.08	3.27	3.27	181–185	CH_2Cl_2–$C_2H_5)_2O$	Yellow
$[PtCH_3Q_2(NH{=}C(OC_2H_5)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	37.95	37.80	4.05	4.03	196–199	Hot C_2H_5OH	White
$[PtCH_3Q_2(NH{=}C(OC_3H_7)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	38.42	38.46	4.15	4.07	129–133	CH_2Cl_2–$(C_2H_5)_2O$	Pale yellow
$[PtCH_3Q_2(NH{=}C(O_2C_3H_7)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	37.99	38.03	4.11	4.02	>155	CH_2Cl_2–$(C_2H_5)_2O$	Pale yellow
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](BF_4)_2$	37.46	37.22	3.74	3.68	207–208	Hot CH_3OH	White
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](NO_3)_2$	39.80	39.64	4.40	4.37	134–136	CH_2Cl_2–$(C_2H_5)_2O$	White

[a] $Q = P(CH_3)_2(C_6H_5)$; $A = As(CH_3)_3$. [b] Melting points are corrected.

In general, the complexes were difficult to crystallize, possibly due to their fairly high solubility in polar solvents and the weak coordinating power of the nitrile. However, the solubility could be decreased by changing the anion in the order BF_4^- > NO_3^- > SbF_6^- > PF_6^- >> BPh_4^-. Care must be taken however, when using sodium tetraphenylborate since it acts as a good phenylating agent when a weakly coordinating ligand is present [14]. In several instances, when sodium tetraphenylborate was added to a solution of trans-$[PtMeQ_2(NC\text{-}R)]^+X^-$ ($X = BF_4^-$, PF_6^-) in methanol white crystalline cis-$PtPh_2Q_2$ was obtained. The reaction probably proceeds by way of nucleophilic attack by a phenyl ring to give an intermediate π-bonded complex [29] which then gives directly the insoluble diphenyl complex.

The CN triple bond possesses two sites for coordination, namely the nitrogen lone pair and the π-electrons. Nitriles are usually σ-bonded through nitrogen [30], this being accompanied by an increase of ca 70-110 cm^{-1} in $\nu(C{\equiv}N)$. However, examples of π-bonding are known. In the series[31,32] $M(CO)_3(NC\text{-}(CH_2)_n\text{-}CN)Cl$ (M = Re,Mn; n = 1,2,3) the dinitrile was initially postulated as bonding in a chelating fashion and because of the short carbon chain the nitrile groups were forced to π-bond, this being shown spectroscopically by a decrease in $\nu(C{\equiv}N)$ of about 150-200 cm^{-1}. Recently an attempted synthesis of these compounds led to products of the same empirical formula but in which the nitrile was bonded through nitrogen and bridging two metal atoms.[33] A reinvestigation [34] showed that the π-bonded dinitriles were the kinetically controlled products and after standing at 4°C for four months rearranged to the dimeric species (equation 2).



(2)

For the complexes prepared in this present study the absorption band due to $\nu(C\equiv N)$ was very weak in the infrared spectrum and in many cases was completely absent; however the band was very strong and sharp in the Raman spectrum. The Raman data are listed in Table II-2. Positive values for $\Delta\nu(C\equiv N)$ indicate that the nitrile is σ-bonded through nitrogen; the increase in $\nu(C\equiv N)$ being primarily due to an increase in the CN force constant upon coordination [35]. The platinum-methyl stretching vibration appears as a strong and polarizable [24] (0.75P) band in the Raman in the region 575-545 cm^{-1}, yet is weak in the infrared.

The methyl groups in *trans*-$[PtMeQ_2(NC{-}R)]^+X^-$ show the expected patterns in the proton n.m.r. spectra (data given in Table II-3). The methyl groups in Q, where Q = PMe_2Ph give a 1:2:1 triplet due to strong phosphorus-phosphorus coupling [36] between the two *trans* ^{31}P nuclei, with triplet satellites of one-quarter intensity due to coupling with ^{195}Pt (I = ½, natural abundance 33.8%). The platinum-methyl group appears as a triplet due to coupling with the two equivalent ^{31}P nuclei, with platinum satellites of one-quarter intensity. When Q = $AsMe_3$ the methyl absorptions appear as singlets flanked by platinum satellites.

As mentioned in Chapter I the two-bond coupling constant $^2J(Pt{-}C{-}H)$ (Table II-3) may be used to measure the relative NMR *trans*-influence [6] of a ligand trans to the methyl group, i.e. the

Table II-2

RAMAN DATA[a] (CM^{-1}) FOR CATIONIC METHYLPLATINUM(II)-NITRILE AND -IMINO ETHER COMPLEXES

Compound	ν(C≡N)	$\Delta\nu$(C≡N)[b]	ν(C=N)	ν(N—H)	ν(PtC—H$_3$)
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_5)](BF_4)$	...	...	1667	3251	551
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](BF_4)_2$	...	...	1671	3350, 3250	576
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](NO_3)_2$	...	...	1675	3263	558
$[PtCH_3Q_2(\pi\text{-}NCC_6F_4C(OC_2H_5){=}NH)PtCH_3Q_2](BF_4)_2$	2141	−113	1667	3271	554
$[PtCH_3Q_2(NH{=}C(OC_3H_7)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	2282	28	1663	3340	551
$[PtCH_3Q_2(NH{=}C(OCH_2CH_2OCH_3)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	2283	29	1668	3260	563
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	2281	27	1663	3315	552
$[PtCH_3A_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3A_2](PF_6)_2$	2274	20	1662	3311	554
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](PF_6)_2$	2292	38	...	...	556
$[PtCH_3A_2(NCC_6F_4CN)PtCH_3A_2](PF_6)_2$	2272	18	...	...	554
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](BF_4)_2$	2283	29	...	...	551
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](SbF_6)_2$	2291	37	...	...	554
$[PtCH_3Q_2(NCC_6H_4CN)PtCH_3Q_2](PF_6)_2$	2264	28	...	...	567
$[PtCH_3Q_2(NCC_6H_4CN)PtCH_3Q_2](BF_4)_2$	2265	29	...	...	566
$[PtCH_3Q_2(NCC_6F_5)](BF_4)$	2276	27	...	...	549
$[PtCH_3A_2(NCC_6F_5)](PF_6)$	2274	29	...	...	556
$[PtCH_3Q_2(p\text{-}NCC_6H_4OCH_3)](PF_6)$	2270	57	...	...	572
$[PtCH_3A_2(o\text{-}NCC_6F_2H_3)](PF_6)$	2275	26	...	...	567
$[PtCH_3Q_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	2256	24	...	...	570
$[PtCH_3A_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	2254	22	...	...	570
$[PtCH_3Q_2(p\text{-}NCC_6H_4NO_2)](PF_6)$	2230	2	...	...	570
$[PtCH_3Q_2(m\text{-}NCC_6H_4CH_3)](PF_6)$	2258	22	...	...	569

[a] Values are accurate to ±2 cm^{-1}. [b] ν(C≡N)(complex) − ν(C≡N)(free ligand).

Table II-3

^{1}H NMR[a] DATA FOR CATIONIC METHYLPLATINUM(II)-NITRILE AND -IMINO ETHER COMPLEXES

Compound[c]	Phosphine or arsine methyls δ(CH$_3$)	Phosphine or arsine methyls J(P–H)[b]	Phosphine or arsine methyls J(Pt–H)	Platinum methyls δ(CH$_3$)	Platinum methyls J(P–H)	Platinum methyls J(Pt–H)	Other resonances
$[PtCH_3Q_2(m\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	−1.86	7.4	32.8	−0.61	7.8	80.4	δ(CH$_3$) −2.63
$[PtCH_3A_2(NCC_6F_5)](PF_6)$	−1.58	...	23.4	−0.61	...	79.7	
$[PtCH_3Q_2(NCC_6F_5)](BF_4)$	−1.92	7.1	30.0	−0.51	8.0	80.4	
$[PtCH_3A_2(o\text{-}NCC_6F\ H_4)](PF_6)$	−1.60	...	23.6	−0.53	...	77.6	
$[PtCH_3A_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	−1.28	...	23.6	−0.52	...	76.0	δ(CH$_3$) −2.28
$[PtCH_3Q_2(p\text{-}NCC_6H_4CH_3)][B(C_6H_5)_4]$	−1.86	7.0	32.2	−0.61	7.8	80.2	δ(CH$_3$) −2.46
$[PtCH_3Q_2(p\text{-}NCC_6H_4OCH_3)](PF_6)$	−1.89	7.0	32.0	−0.46	7.7	80.0	δ(OCH$_3$) −3.86
$[PtCH_3Q_2(p\text{-}NCC_6H_4NO_2)](PF_6)$	−1.92	7.2	32.6	−0.55	7.8	80.4	
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_5)](BF_4)$	−1.75	6.8	30.6	−0.31	7.6	76.4	δ(NH) −9.18, δ(OCH$_3$) −3.94
$[PtCH_3Q_2(p\text{-}NCC_6H_4CN)PtCH_3Q_2](PF_6)_2$[d]							
$[PtCH_3Q_2(p\text{-}NCC_6H_4CN)PtCH_3Q_2](BF_4)_2$	−1.89	7.2	32.4	−0.55	7.8	80.4	
$[PtCH_3A_2(NCC_6F_4CN)PtCH_3A_2](PF_6)_2$	−1.57	...	23.8	−0.61	...	80.8	
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](PF_6)_2$	−1.89	7.2	33.4	−0.48	7.9	80.4	
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](SbF_6)_2$	−1.92	7.0	31.5	−0.26	8.1	81.6	
$[PtCH_3Q_2(NCC_6F_4CN)PtCH_3Q_2](BF_4)_2$	−1.94	7.3	31.2	−0.66	8.0	80.6	
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3Q_2](PF_6)_2$	−1.91	7.2	31.2	−0.48	7.6	80.4	
	−1.76	7.2	31.2	−0.31	7.6	77.6	δ(NH) −8.81, δ(OCH$_3$) −3.84
$[PtCH_3A_2(NH{=}C(OCH_3)C_6F_4CN)PtCH_3Q_2](PF_6)_2$	−1.53	...	23.2	−0.56	...	80.0	δ(NH) −9.05, δ(OCH$_3$) −4.14
	−1.38	...	20.0	−0.40	...	78.0	
$[PtCH_3Q_2(p\text{-}NCC_6F_4C(OC_2H_5){=}NH)PtCH_3Q_2](BF_4)_2$	−1.76	6.6	30.0	−0.27	7.6	75.4	δ(NH) −9.01, δ(OCH$_2$) −4.13 δ(CH$_3$) −1.27, J(H–H) 7.2
$[PtCH_3Q_2(NH{=}C(OC_3H_7)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	−1.92	7.0	30.4	−0.49	7.7	80.4	δ(NH) −9.25, δ(OCH$_2$) −4.15 t
	−1.77	7.0	30.8	−0.31	7.6	76.8	δ(CH$_3''$) −0.94 t, J(H–H$'$) 7.0, J(H$'$–H$''$) 7.1
$[PtCH_3Q_2(NH{=}C(O_2C_3H_7)C_6F_4CN)PtCH_3Q_2](BF_4)_2$	−1.78	6.8	30.4	−0.50	7.7	80.4	δ(NH) −9.07
	−1.78	6.8	30.4	−0.21	7.6	75.6	
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](BF_4)_2$	−1.77	7.0	30.8	−0.28	7.6	75.8	δ(NH) −9.18, δ(OCH$_3$) −3.94
$[PtCH_3Q_2(NH{=}C(OCH_3)C_6F_4C(OCH_3){=}NH)PtCH_3Q_2](NO_3)_2$	−1.79	6.8	31.0	−0.25	7.7	76.8	δ(NH) −9.13, δ(OCH$_3$) −3.84

[a] Chemical shifts (δ) in ppm relative to TMS using dichloromethane as internal standard. [b] ^2J(P–H) + ^4J(P–H) is quoted: R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964). [c] A = As(CH$_3$)$_3$, Q = P(CH$_3$)$_2$(C$_6$H$_5$). [d] Insoluble.

larger the coupling constant, the weaker the trans-influence of the ligand [14]. The relatively large coupling constant of ~80 Hz for a nitrile trans to the platinum methyl group suggests that the nitrile is in fact a ligand of fairly weak trans-influence. This is also reflected by the high frequency of the platinum-methyl stretching vibration at ~560 cm^{-1}. These values may be compared with those of a ligand of high trans-influence e.g. carbene complexes [23], with $^{2}J(Pt-C-H) \approx 48$ Hz and $\nu(Pt-Me) \approx 518\ cm^{-1}$ (although this absorption is almost certainly not due to a pure Pt-Me mode).

There is a marked decrease in $\Delta\nu(C{\equiv}N)$ as the Hammett substituent constant (ρ),[37] which may be used as a measure of the inductive effect of an aromatic substituent, increases (Table II-4).

Thus, as the electron withdrawing ability of the para substituent increases so does the Hammett constant, yet the value for $\Delta\nu(C{\equiv}N)$ decreases. Consequently, drainage of electron density from the CN triple bond back into the aromatic π-system as a result of an electronegative para-substituent lowers the C≡N π^{*} antibonding orbitals and facilitates back-donation of platinum d electrons into these π^{*} orbitals. As a result, the C≡N bond order is decreased and the Raman absorption occurs at a lower frequency, although $\Delta\nu(C{\equiv}N)$ is still positive. In contrast, in a series of complexes [38-40] of the type $Ru(NH_3)_5(NCR)^{2+}$, $\Delta\nu(C{\equiv}N)$ is negative as a result of unusually strong back-donation into nitrile π^{*} orbitals. In the present case, also, there is essentially no change in $^{2}J(Pt-C-H)$ on varying the para substituent, indicating little effect on the σ-donor ability of the nitrile. On the other hand, a very strong electron-withdrawing

Table II-4

A Comparison of the Hammett Substituent Constant and $\Delta\nu(C{\equiv}N)$ for Some Methylplatinum(II) Nitrile Cations

Substituent	$\Delta\nu(C{\equiv}N)$	ρ
p-OCH_3	57	-0.268
p-CH_3	24	-0.170
m-CH_3	22	-0.069
p-NO_2	2	+0.778

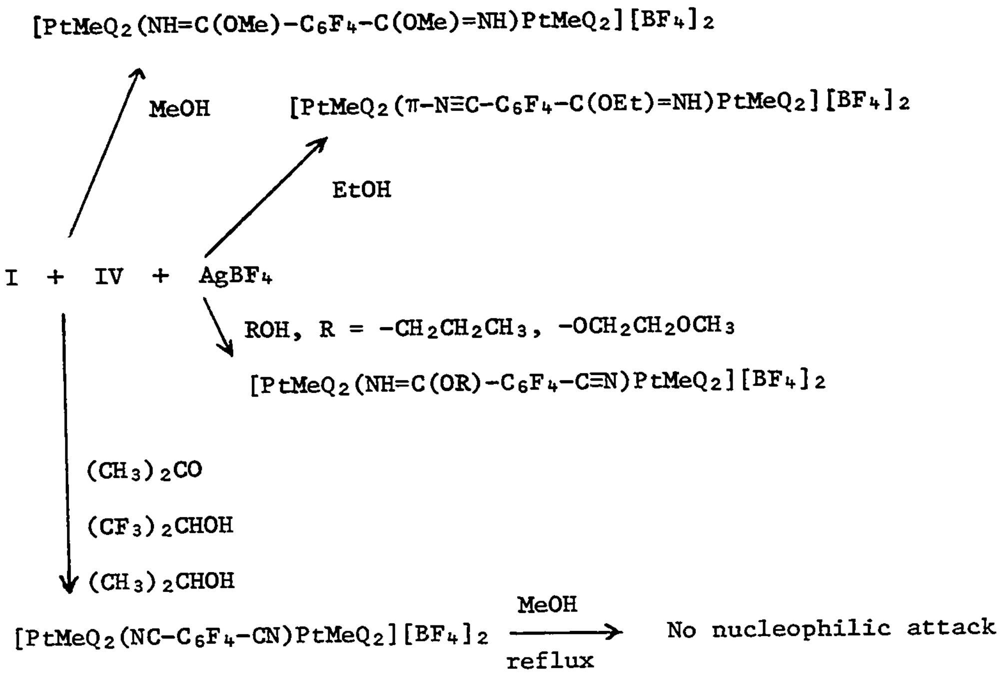
group such as a perfluoronitrile might well change the relative energies of all the orbitals sufficiently to allow π bonding through the CN triple bond, although one cannot predict a priori whether end bonding or sideways bonding of the nitrile would be preferred.

Attempts to prepare cationic methylplatinum(II) nitrile complexes with perfluoroalkyl nitriles, such as CF_3CN, C_2F_5CN and C_3F_7CN led to viscous oils that could not be crystallized. However, examination of the ^1H n.m.r. spectra indicated that the phosphines had a cis configuration and the ^{19}F n.m.r. showed that complete dealkylation had occurred with loss of the perfluoroalkyl group. The infrared spectra revealed the presence of C=N and N-H stretching vibrations, however a structure could not be assigned on the basis of the spectroscopic and analytical results.

(ii) Preparation of Dinitrile and Imino Ether Complexes

Trans-$PtMeClQ_2$ (where Q = PMe_2Ph) with pentafluorobenzonitrile and silver hexafluorophosphate in methanol at 25°C gave trans-$[PtMeQ_2(NC\text{-}C_6F_5)]^+PF_6^-$ in which the nitrile is bonded through nitrogen as shown by an increase in $\nu(C{\equiv}N)$ to 2276 cm^{-1}. However, a reaction in methanol using silver tetrafluoroborate gave the imino ether complex trans-$[PtMeQ_2(NH{=}C(OMe)C_6F_5)]^+BF_4^-$, showing no $\nu(C{\equiv}N)$, but $\nu(C{=}N)$ at 1667 cm^{-1} and $\nu(N\text{-}H)$ at 3251 cm^{-1}.

Using 2,3,5,6-tetrafluoroterephthalonitrile(IV) and silver tetrafluoroborate in methanol, a variety of products was obtained as shown in the following reaction scheme, depending on the alcohol.



All the imino ether complexes show strong sharp ν(C=N) Raman and infrared absorptions in the region 1675-1660 cm^{-1}. Absorption in the infrared due to ν(N-H) appears as a weak peak at 3400-3200 cm^{-1}. The proton n.m.r. spectra of the coordinated imino ether complexes show N-H resonances as broadened singlets at δ(N-H) *ca* -9.20 ppm. Platinum-methyl resonances, where δ(CH$_3$) is in the region -0.70 to -0.20 ppm show ^2J(Pt-C-H) of about 80 Hz when the methyl is trans to a σ-bonded nitrile and about 75 Hz when the methyl is trans to an imino ether, indicating a higher *trans*-influence for the coordinated imino ether.

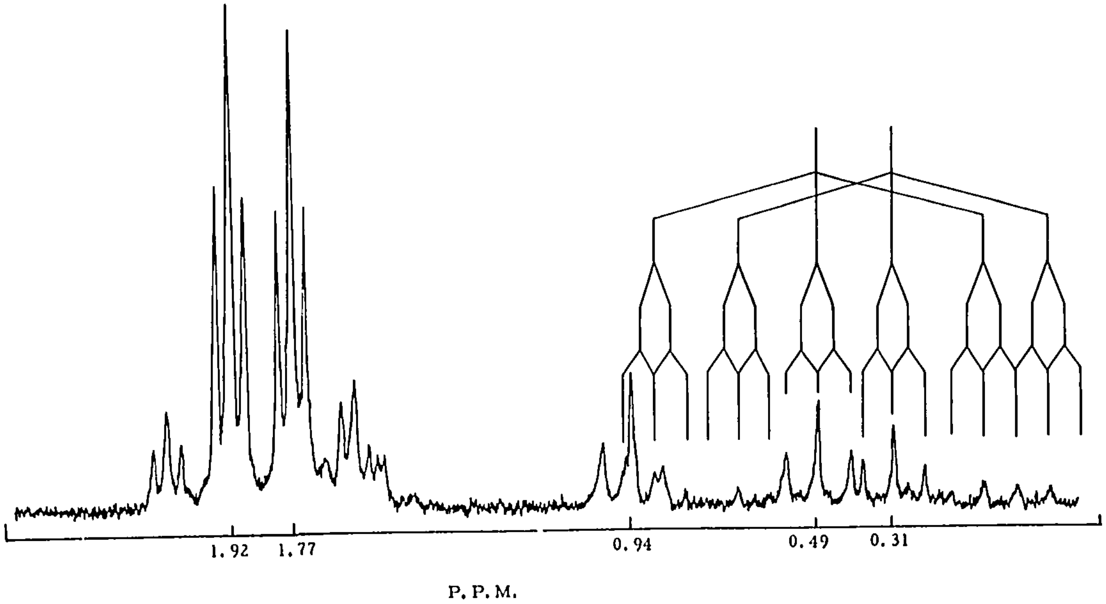
In the reaction with ethanol, the product contains an imino ether group, as shown by ν(C=N) at 1667 cm^{-1} in the Raman spectrum, as well as a π-bonded nitrile. This is revealed spectroscopically by a shift to lower frequency of the ν(C≡N) Raman absorption by 113 cm^{-1} to 2141

cm^{-1}. Products from reactions in n-propanol and β-methoxyethanol contain one σ-bonded nitrile, in which ν(C≡N) is shifted to slightly higher frequency, and one imino ether. As a result the two $PtMe(PMe_2Ph)_2$ groups are not equivalent, as can easily be seen in Figure II-1. The protons of the $-OCH_2CH_2CH_3$ group give the expected pattern; a triplet centered at -4.15δ for the α protons; a multiplet at *ca* -1.65δ for the β protons, and a triplet at -0.94δ for the γ protons.

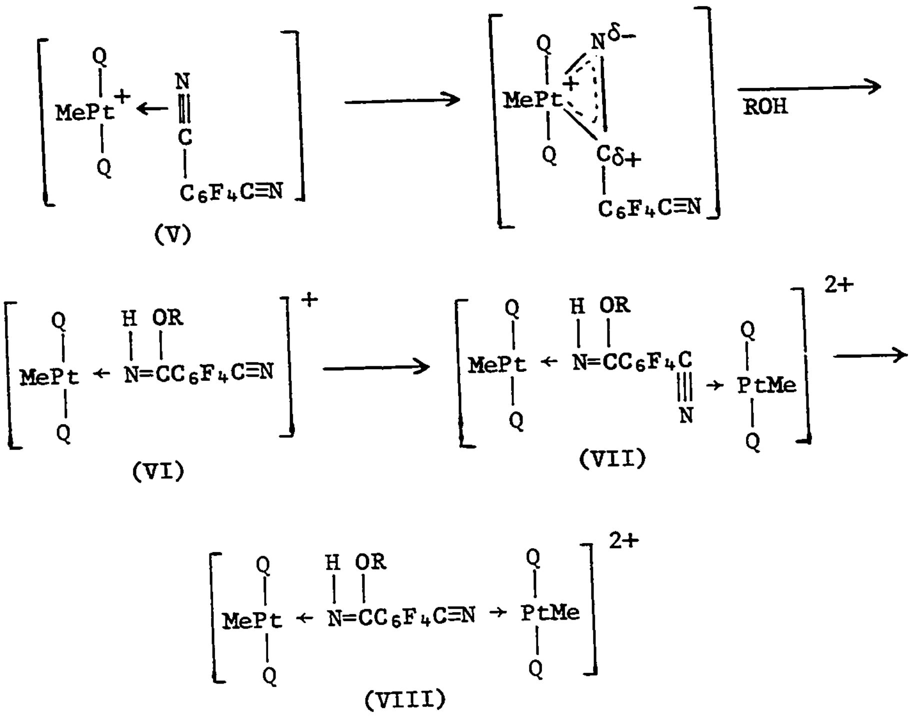
Reactions in acetone, *iso*propanol and hexafluoro*iso*propanol give only the σ-bonded dinitrile complexes.

Clark and Chisholm [42] have extensively examined the reactions of acetylenes with methylplatinum cations of the type described here. After a careful investigation of the many diverse and interesting reactions that occur a model was proposed to explain these reactions[41,42]. This "Carbonium Ion Model" may be used to explain the reactions of coordinated π-bonded perfluoroarylnitriles with alcohols to give imino-ether complexes and the mechanistic scheme is shown below.

Figure II-1

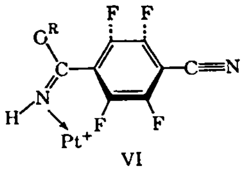


The ^1H nmr spectra of the phosphine-methyl and platinum-methyl resonances of *trans*-$[PtCH_3\{P(CH_3)_2(C_6H_5)\}(NH{=}C(OC_3H_7)C_6F_4C{\equiv}N)PtCH_3\{P(CH_3)_2(C_6H_5)\}_2](BF_4)_2$ at 100 MHz on a 250-Hz sweep width. Spectra recorded on a CH_2Cl_2 solution at 31°.

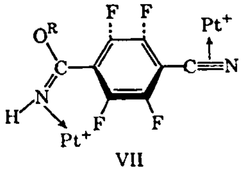


Initial π-bond formation (V) is apparently essential for nucleophilic attack, since refluxing the coordinated σ-bonded dinitrile complex in methanol for six hours did not lead to imino ether formation. This mechanism is also consistent with characterization of the π-bonded function in the ethanol product (VII). The apparent decrease in the reactivity of the second nitrile group of the ligand for different alcohols in the order $\mathrm{MeOH} > \mathrm{EtOH} > \mathrm{Pr^{n}OH} > (\mathrm{CF_3})_2\mathrm{CHOH}$, $\mathrm{Pr^{i}OH}$ may be due largely to steric requirements of the $-\mathrm{OR}$ and $-\mathrm{C_6F_4}-$ groups assuming cis addition of the alcohol to the coordinated nitrile. Once nucleophilic attack has occurred at the first nitrile group (VI), the carbon-nitrogen orbitals are rehybridized from $sp \rightarrow sp^2$. Steric interaction between the -OR group and the ortho-fluorines twist the

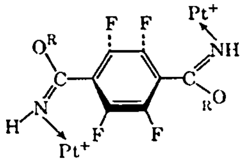
C=N bond out of the plane of the ring so that the -NH and -OR groups are now perpendicular to the phenyl ring. As a result the nitrogen lone pair is directed below the ring with the platinum coordinated in this position (VI).



VI



VII



IX

Subsequent π-bonding of the CN triple bond (VII) is governed by the size of R. For R=CH_3 attack can occur but this leads to a rather crowded molecule (IX). For R=CH_2CH_3 (IX) would be very crowded so the reaction stops at (VII) and for R=$-CH_2CH_2CH_3$, $-OCH_2CH_2OCH_3$ there appears to be even greater crowding in (VII). Hence σ-bonding to platinum is preferred (VIII) where there is little steric interaction.

The course of the reaction is also anion dependent; the reactions with pentafluorobenzonitrile described above illustrate this. A similar anion dependence was also found using 2,3,5,6-tetrafluoroterephthalonitrile and these reactions are outlined below.

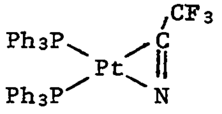
$$\begin{tikzcd}
{[PtMeQ_2(NH=C(OMe)-C_6F_4-C(OMe)=NH)PtMeQ_2]X_2} & \\
{I + IV} \arrow[u, "\begin{array}{l}AgX,\ X=BF_4^-,\ NO_3^-\\ MeOH\end{array}"'] \arrow[r, "{AgPF_6,\ MeOH}"'] \arrow[d, "\begin{array}{l}1.\ AgPF_6,\ EtOH\\ 2.\ AgSbF_6,\ MeOH\end{array}"'] & {[PtMeQ_2(NH=C(OMe)-C_6F_4-C{\equiv}N)PtMeQ_2][PF_6]_2} \\
{[PtMeQ_2(N{\equiv}C-C_6F_4-C{\equiv}N)PtMeQ_2]X_2 \quad X=PF_6^-,\ SbF_6^-} &
\end{tikzcd}$$

Silver nitrate with (I) and (IV) in methanol gave attack at both nitriles as was found in the reactions using silver tetrafluoroborate. However, silver hexafluorophosphate with (I) and (IV) in methanol gave attack at only one nitrile, the second being σ-bonded to platinum. Reactions using silver hexafluorophosphate in ethanol or a higher alcohol, and silver hexafluoroantimonate in methanol gave only the σ-bonded dinitriles. Since the same products were obtained using trimethylarsine the course of the reaction appears to depend on the size of the anion used.

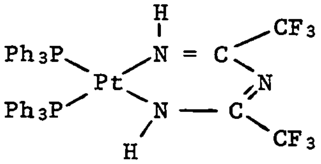
Several years ago Rouschias and Wilkinson [43] investigated nucleophilic addition reactions to the coordinated nitrile in some rhenium(IV) complexes. Thus $ReCl_4(NCMe)_2$ reacted rapidly in the cold with primary aromatic amines ($ArNH_2$) to give the N-substituted amidine complexes $ReCl_4(NH=C(NHAr)Me)_2$. A similar reaction occurred with methanol and ethanol to give the imino-ether complexes. The infrared spectra of these complexes are similar to the spectra of the platinum complexes in this chapter. It is interesting that they were able to obtain imino-ethers by reacting the coordinated N-bonded nitrile with an alcohol while we observed no reaction between a coordinated N-bonded nitrile and alcohols. This may suggest that the rhenium complexes react via a different mechanism, viz, direct attack of the alcohol at the coordinated nitrile carbon rather than attack at a π-bonded intermediate.

(iii) Attempted Polymerization and Insertion Reactions

Various transition metals [44,45] have been found to catalyse the trimerization of benzonitrile to triphenyltriazine. Kemmett et al[46] found that reactions of excess trifluoroacetonitrile with tetrakis(triphenylphosphine)platinum(0) in benzene led to oxidative addition reactions and isolated products in varying degrees of polymerization (X, XI).



(X)



(XI)

Unlike the reactions of acetylenes [15,16] with (I), which do lead to polymerization and insertion products, the perfluoroalkyl- and aryl- nitriles do not react with (I) even under vigorous conditions in the absence of silver salts.

c) Experimental

All reactions were carried out under nitrogen and 'spectro' grade solvents were used without further purification.

Infrared spectra were recorded on Beckman IR10 and IR7 spectrophotometers as 2% by weight KBr discs or on a Perkin Elmer 621 spectrometer as a nujol suspension between KBr plates.

Raman spectra were run on a Spex 1400 spectrometer (McMaster University, Hamilton, Ontario, Canada) using a He-Ne (6328Å) laser and a Cary 82 spectrometer using the 5145Å line of an argon laser. The numbers reported are accurate to ±2 cm^{-1}.

^1H nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer at 100 MHz using either dichloromethane, chloroform or tetramethylsilane as internal lock. All chemical shifts are reported in parts per million downfield from TMS. ^{19}F nmr spectra were recorded on the HA-100 spectrometer at 94.1 MHz using "Freon-II" ($CFCl_3$) as internal reference-lock signal. ^{19}F chemical shifts are reported in parts per million upfield from $CFCl_3$.

Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory Inc., Woodside, N.Y., and Chemalytics Inc., Tempe, Arizona.

Since many of the complexes were prepared by similar methods only a few representative examples will be described in each chapter.

Physical and analytical data for the new complexes described in this chapter are given in Table II-1.

(i) Preparation of cis-$PtCl_2(AsMe_3)_2$ [47]

To a magnetically stirred solution of K_2PtCl_4 (2.0 g.; 4.81 mmoles) in 50 ml. of water was added a solution of 1.20 ml. of $AsMe_3$ in 10 ml. of ethanol under nitrogen. An orange precipitate formed immediately and the solution was stirred for 12 hours to give a pale yellow solution. The solvents were removed under vacuum to give pale yellow crystals which were extracted with methylene dichloride and precipitated with pentane. Yield was 2.0 g. (82%).

(ii) Preparation of cis-$PtMe_2(AsMe_3)_2$ [15,47]

cis-$PtCl_2(AsMe_3)_2$ (1.91 g.) was suspended in 50 ml. of diethyl ether under nitrogen. The solution was stirred and 5 ml. of a 2.16M solution of methyllithium in ether was added dropwise from a syringe. The solution turned pale yellow and after one hour the excess methyllithium was hydrolysed with a saturated aqueous ammonium chloride solution. The ether layer was decanted and the aqueous layer was extracted with two 50 ml. portions of ether. The ether layer was dried over anhydrous magnesium sulphate and a small amount of activated charcoal was added. The solution was filtered and the ether was removed on a rotary evaporator to give white crystals of $PtMe_2(AsMe_3)_2$. Yield was 1.8 g. (90%).

(iii) Preparation of trans-$PtMeCl(AsMe_3)_2$ [48]

To a solution of cis-$PtMe_2(AsMe_3)_2$ (5.44 g.) in 100 ml. of diethyl ether was added acetyl chloride (0.77 ml.). The solution was allowed to stand for 15 minutes and white crystals of $PtMe_2(COMe)(AsMe_3)_2Cl$ deposited. The solution was cooled for several hours at

0°C and the ether was decanted. The yield of the Pt(IV) complex was 6.35 g. The crystals were suspended in 50 ml. of methanol, refluxed for one hour and the solvent was removed on a rotary evaporator to give white crystals which were filtered and washed with ether. Yield was 5.27 g. (94% based on $PtMe_2(AsMe_3)_2$)

(iv) Preparation of cis-$PtCl_2(PMe_2Ph)_2$

To a solution of K_2PtCl_4 (4.0g.) in 50 ml. of water was added 2.60 g. of PMe_2Ph under nitrogen. A beige precipitate formed immediately and the solution was stirred for two hours. The solid was filtered, washed with 50 ml. of ethanol and 50 ml. of diethyl ether, then air dried. The solid was placed in the bottom of a 500 ml. erlenmeyer flask and just covered with β-methoxyethanol. The flask was placed in a water bath and swirled constantly until all of the solid dissolved. The flask was then cooled at 0°C for four hours and large white crystals deposited. They were filtered and washed with diethyl ether. Yield was 5.0 g. (96%)

(v) Preparation of cis-$PtMe_2(PMe_2Ph)_2$ [49,50]

To a solution of 5.0 g. of $PtCl_2(PMe_2Ph)_2$ in 75 ml. of diethyl ether was added 15 ml. of a 2.16M solution of methyllithium in ether. The solution turned pale yellow and after stirring for one hour the excess methyllithium was hydrolysed with an ice-cold saturated aqueous ammonium chloride solution and worked up as in (ii). Yield was 4.1 g. (89%)

(vi) Preparation of trans-$PtMeCl(PMe_2Ph)_2$ [49]

To a solution of 4.1 g. of cis-$PtMe_2(PMe_2Ph)_2$ in 20 ml. of ether was added (0.60 ml.) of acetyl chloride. After several minutes white crystals deposited so the solution was cooled at 0°C for four hours and the ether decanted. The solid was refluxed in 50 ml. of methanol for one hour and the solution was cooled for three hours at 0°C to give large white crystals which were filtered and washed with ether. Yield was 4.02 g. (94%)

(vii) Preparation of Mononitrile Complexes

To a suspension of trans-$PtMeCl(AsMe_3)_2$ (0.125 g.) in 10 ml. of methanol was added $AgPF_6$ (0.065 g.) in 2 ml. of methanol. A flocculent precipitate of silver chloride formed immediately. The solution was stirred for 10 minutes and the silver chloride was removed by centrifugation to give a clear solution. A solution of p-$NC\text{-}C_6H_4\text{-}CH_3$ (0.030 g.) in 2 ml. of methanol was added and the mixture was stirred for 10 minutes. The methanol was then removed on a rotary evaporator to give a clear colourless oil which did not crystallize from dichloromethane/ether. Consequently the oil was taken up in 10 ml. of methanol, and the solution of sodium tetraphenylborate (0.089 g.) in 2 ml. of methanol was added slowly to give a white precipitate which was filtered off, washed with methanol and ether, then recrystallized from dichloromethane/ether to give white crystals. Yield was 65%.

(viii) Preparation of Dinitrile Complexes

To a solution of trans-$PtMeCl(PMe_2Ph)_2$ (0.230 g.) in 10 ml. of acetone was added $AgBF_4$ (0.086 g.) in 2 ml. of acetone. After

10 minutes the silver chloride was removed and 2,3,5,6-tetrafluoroterephthalonitrile (0.0441 g.) in 2 ml. of acetone was added to give a bright yellow solution. Subsequent removal of the acetone yielded a clear, yellow oil which was taken up in the minimum amount of dichloromethane. The slow addition of ether yielded yellow needles which were filtered off, washed with ether and dried under high vacuum. Yield was 87%.

(ix) Preparation of Imino Ether Complexes

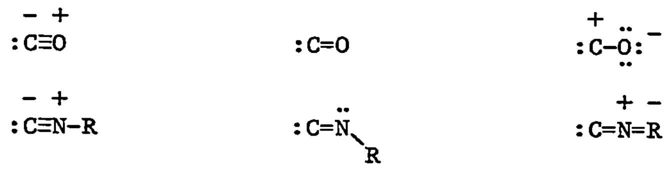
To a suspension of trans-$PtMeCl(PMe_2Ph)_2$ (0.205 g.) in n-propanol was added $AgBF_4$ (0.077 g.). Silver chloride slowly precipitated and the solution was stirred for 15 minutes to allow complete removal of the chloride and coagulation of the silver chloride which was then removed by centrifugation to give a clear solution. 2,3,5,6-Tetrafluoroterephthalonitrile (0.039 g.) was added and the solution stirred for two hours to give a dirty brown precipitate which was filtered off and washed with ether. The precipitate was then dissolved in about 2 ml. of dichloromethane and filtered through a small 1" florisil column to remove any organic tars, colloidal silver or platinum. A clear, pale yellow solution was eluted with dichloromethane and subsequent addition of diethyl ether yielded pale yellow needles. Yield was 84%.

CHAPTER III

CATIONIC PLATINUM(II) ISOCYANIDE AND CARBENE COMPLEXES

a) Introduction

Isocyanides are among the few substances with a lone pair of electrons on the carbon atom. Their structure is isoelectronic with carbon monoxide and can be considered as a hybrid of the three resonance forms I, II, III.

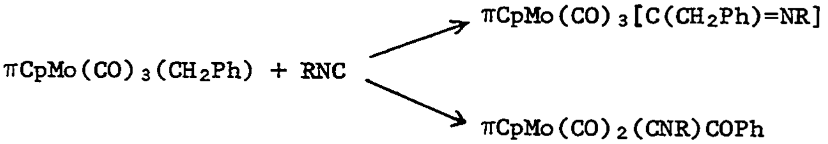


I II III

The presence of the lone pair of electrons on the terminal carbon atom enables isocyanides to act as carbon ligands in coordination compounds [51,52] and to behave as Lewis bases similar to carbon monoxide and phosphines. Although a large number of isocyanide coordination compounds have been prepared, only in the last few years have inorganic chemists examined the reactions of coordinated isocyanides.

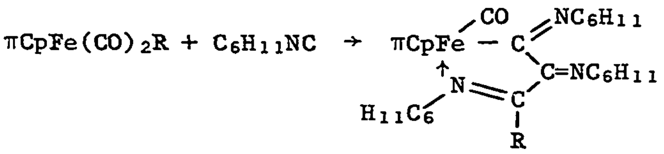
Many simple molecules such as carbon monoxide, sulphur dioxide and olefins are known to insert into metal-carbon σ-bonds [53] and among these the insertion of carbon monoxide is the best studied and most firmly established. Similar insertion reactions might be expected for isocyanides but they have received less attention than those of carbon monoxide.

Isocyanides react with complexes of the type $\pi CpMo(CO)_3R$ to afford either the carbonyl or isocyanide insertion products[54,55] depending on the nature of the isocyanide and R. The reaction of π-$CpMo(CO)_3Me$ with cyclohexyl-isocyanide gave the carbonyl insertion product π-$CpMo(CO)_2(CNR)COMe$. However, the benzyl complex $\pi CpMo(CO)_3(CH_2Ph)$ reacted with cyclohexyl isocyanide to give both the acyl and imino complexes (reaction 1).



$$\pi CpMo(CO)_3(CH_2Ph) + RNC \begin{array}{l} \nearrow \pi CpMo(CO)_3[C(CH_2Ph){=}NR] \\ \searrow \pi CpMo(CO)_2(CNR)COPh \end{array} \qquad (1)$$

Similar insertion reactions are also known for iron,[56,57] nickel,[58,59] palladium[60,61] and platinum[62,63]. A multiple insertion of isocyanide into an Fe-C bond has been reported[57] to give the tris-imino complex (equation 2).



(2)

Cationic isocyanide complexes also react with alkyllithium and Grignard reagents. For example, Treichel and Stenson[64] found that the reaction of pentafluorophenyllithium with coordinated methyl isocyanide gave pentafluorophenylimino derivatives (equation 3).

$$[\pi CpFe(CO)_2(CNMe)]^+ \xrightarrow[LiC_6F_5]{} \pi CpFe(CO)_2[C(C_6F_5){=}NMe] \qquad (3)$$

In 1969 while investigating the reactions of coordinated isocyanides in complexes of the type cis-$PtX_2(PR_3)(CNR)$ (X=Cl,Br,I) Chatt et al [17] found that alcohols added across the C≡N bond to give alkoxy-carbene complexes (equation 4). The proposed mechanism involved activation of

$$PtCl_2(PEt_3)(NCPh) + EtOH \rightarrow Cl_2Pt(PEt_3)[C(OEt)NHPh] \qquad (4)$$

the nitrogen towards electrophilic attack by a proton.[18] Several publications [19-21, 25,26,65-74] followed describing the additions of amines and alcohols across the C≡N bond in a variety of palladium, platinum, rhodium, mercury, iron and gold complexes to give alkoxy and amino carbenes.

Due to the wide variety of reactions that coordinated isocyanides undergo, we decided to investigate the reactions of platinum(II) cations with isocyanides.

b) Results and Discussion

(i) Preparation of the Complexes

Three types of cationic platinum(II) isocyanide complexes have been prepared, using aliphatic and aromatic isocyanides as well as different phosphines, in order to examine the extent to which the electron density on platinum may affect the bonding and the reactivity of the coordinated ligand. Physical and spectroscopic data are listed in Tables III-1 and III-2.

Type I $[PtMeQ_2(CN\text{-}R)]^+X^-$

These cations were prepared in a similar manner to the nitrile cations described in Chapter II. The chloride in trans-$PtMeClQ_2$ (Q = PMe_2Ph or $PMePh_2$) was removed in methanol by the addition of a

Table III-1

PHYSICAL AND RAMAN (cm^{-1}) DATA[a] FOR PLATINUM–ISOCYANIDE COMPLEXES

Compound[b]	Calcd % C	Found % C	Calcd % H	Found % H	Dec pt,[e] °C	Recrystn solvent	$\nu(N\equiv C)$	$\Delta\nu(N\equiv C)$[c]
$PtCH_3ClQ_2(CNC_6H_4OCH_3)$[d]	45.84	45.32	4.92	4.92	78–79	$CH_2Cl_2-(C_2H_5)_2O$	2181	56
$[PtCH_3Q_2(CNC_6H_4OCH_3)](PF_6)$	39.27	39.65	4.23	4.26	129–130	$CH_2Cl_2-(C_2H_5)_2O$	2193	68
$[PtCH_3Q_2(CNC_6H_4NO_2)][B(C_6H_5)_4]$	60.45	60.23	5.18	4.90	68–71	$CH_2Cl_2-CH_3OH$	2178	62
$[PtCH_3Q_2(CNC_6H_4CH_3)][B(C_6H_5)_4]$	63.78	63.75	5.68	5.87	129–132	$CH_2Cl_2-CH_3OH$	2178	53
$[PtCH_3Q_2(CNC_6H_4CH_3)](BF_4)$	43.50	43.73	4.67	4.49	91–94	$CH_2Cl_2-(C_2H_5)_2O$	2192	67
$[PtCH_3L_2(CNC_6H_5)][B(C_6H_5)_4]$	67.44	67.20	5.27	4.87	149–151	$CH_2Cl_2-(C_2H_5)_2O$	2183	66
$[PtCH_3Q_2(CNC_6H_5)](SbF_6)$	34.93	35.16	3.66	3.44	148–149	$CH_2Cl_2-(C_2H_5)_2O$	2187	80
$[PtCH_3Q_2(CNCH_3)](SbF_6)$	29.90	30.27	3.70	3.57	118–120	$CH_2Cl_2-(C_2H_5)_2O$	2242	72
$[PtCH_3L_2(CNCH_3)](SbF_6)$	39.25	39.02	3.64	3.58	120–123	$CH_3OH-(C_2H_5)_2O$	2267	97
$[PtCH_3L_2(CNC_6H_4CH_3)](SbF_6)$	43.63	43.67	3.77	3.53	184–185	$CH_2Cl_2-(C_2H_5)_2O$	2189	64
$[PtCH_3L_2(CNC_6H_4OCH_3)](SbF_6)$	42.96	42.92	3.70	3.64	143–145	Hot CH_3OH	2193	68
$[PtCH_3Q_2(CNCH_2CH_3)](SbF_6)$	30.90	30.84	3.91	3.80	83–85	$CH_2Cl_2-(C_2H_5)_2O$	2234	83
$Pt(CH_3)_2Q(CNC_6H_4OCH_3)$	43.55	43.30	4.87	4.76	95–96	$(C_2H_5)_2O-n-C_5H_{12}$	2149	24
$PtCH_3ClQ(CNC_6H_4OCH_3)$	39.50	39.53	4.10	4.05	130–133	$CH_2Cl_2-n-C_5H_{12}$	2186	61
$[PtCH_3Q(CNC_6H_4OCH_3)(CNC_6H_4CH_3)](PF_6)$	40.38	40.53	3.80	3.63	160–164	$CH_2Cl_2-(C_2H_5)_2O$	2217, 2240	92, 115
$[PtClQ_2(CNC_6H_4CH_3)](PF_6)$	37.49	37.85	3.80	3.84	225–226	$CH_3OH-(C_2H_5)_2O$	2250	125
$[PtClQ_2(CNC_6H_4OCH_3)](PF_6)$	36.72	36.73	3.72	3.43	233–235	$CH_2Cl_2-(C_2H_5)_2O$	2237	112
$[PtClL_2(CNC_6H_4CH_3)](PF_6)$	45.82	46.06	3.73	3.65	239–240	$CH_2Cl_2-(C_2H_5)_2O$	2243	118
$[PtClQ_2(CNCH_2CH_3)](PF_6)$	32.00	32.08	3.74	3.71	114–115	$CH_3OH-(C_2H_5)_2O$	2267	116
$[PtIQ_2(CNCH_2CH_3)](PF_6)$	27.89	27.85	3.33	3.30	116–117	$CH_3OH-(C_2H_5)_2O$	2251	100
$[PtQ_2(CNCH_2CH_3)_2](PF_6)_2$	30.32	30.25	3.70	3.70	275–278	CH_3OH	2294	143
$[PtL_2(CNCH_2CH_3)_2](BF_4)_2$	43.81	43.66	4.14	3.98	206–207	$CH_2Cl_2-(C_2H_5)_2O$	2283	132
$[PtQ_2(CNCH_2CH_3)\{C(NHC_2H_5)(NHC_6H_5)\}](PF_6)_2$	34.86	34.71	4.08	4.13	143–146	$CH_3OH-(C_2H_5)_2O$	. . .	. . .
$[PtQ_2(CNCH_2CH_3)\{C(NHC_2H_5)(NHC_6H_4CH_3)\}](PF_6)_2$	35.59	35.70	4.22	3.97	151–155	$CH_3OH-(C_2H_5)_2O$	. . .	. . .
$[PtQ_2(CNCH_2CH_3)\{C(NHC_2H_5)(OC_2H_5)\}](PF_6)_2$	31.42	31.36	4.06	4.05	>165	$CH_2Cl_2-(C_2H_5)_2O$	. . .	. . .
$[PtQ_2(CNCH_2CH_3)\{C(NHC_2H_5)(SCH_2C_6H_5)\}](PF_6)_2$	34.84	34.99	4.05	3.75	>198	$CH_3OH-(C_2H_5)_2O$	. . .	. . .

[a] Values are accurate to $\pm 2\ cm^{-1}$. [b] $Q = P(CH_3)_2C_6H_5$; $L = P(CH_3)(C_6H_5)_2$; all compounds are white except the *p*-nitrophenyl isocyanide complex which is orange. [c] $\nu(N\equiv C)$(complex)–$\nu(N\equiv C)$(free ligand). [d] Chloride analysis: calcd, 5.41%; found, 5.73%. [e] Decomposition points are corrected.

Table III-2

^{1}H NUCLEAR MAGNETIC RESONANCE DATA^a FOR PLATINUM-ISOCYANIDE COMPLEXES

Compound^d	Probe^b temp, °C	Phosphine methyls			Platinum methyls			Isocyanide resonances
		δ(CH$_3$)	J(P-H)^c	J(Pt-H)	δ(CH$_3$)	J(P-H)	J(Pt-H)	
$PtCH_3ClQ_2(CNC_6H_4OCH_3)$	−30	−2.01	7.2	33.0	−0.35	8.0	62.0	δ(OCH$_3$) −3.99
$[PtCH_3Q_2(CNC_6H_4OCH_3)](PF_6)$	−30	−1.99	7.2	33.0	−0.39	8.0	62.0	δ(OCH$_3$) −3.75
$[PtCH_3Q_2(CNC_6H_4NO_2)][B(C_6H_5)_4]$	31	−1.90	7.4	32.8	−0.69	8.5	61.8	
$[PtCH_3Q_2(CNC_6H_4CH_3)][B(C_6H_5)_4]$	31	−2.03	7.2	32.6	−0.63	8.1	61.8	δ(CH$_3$) −2.49
$[PtCH_3Q_2(CNC_6H_4CH_3)](BF_4)$	0	−2.04	7.5	33.0	−0.43	7.9	63.4	δ(CH$_3$) −2.37
$[PtCH_3L_2(CNC_6H_5)][B(C_6H_5)_4]$	31	−2.27	7.0	34.5	−0.44	8.1	62.4	
$[PtCH_3Q_2(CNC_6H_5)](SbF_6)$	0	−2.04	7.2	33.3	−0.45	8.4	63.0	
$[PtCH_3Q_2(CNCH_3)](SbF_6)$	0	−1.94	7.4	33.3	−0.25	8.2	63.8	δ(CH$_3$) −3.05^e
$[PtCH_3L_2(CNCH_3)](SbF_6)$	−50	−2.26	7.0	34.5	−0.40	7.7	62.5	δ(CH$_3$) −3.02
$[PtCH_3L_2(CNC_6H_4CH_3)](SbF_6)$	31	−2.36	7.2	34.5	−0.45	8.1	62.0	δ(CH$_3$) −2.33
$[PtCH_3L_2(CNC_6H_4OCH_3)](SbF_6)$	−65	−2.36	7.2	34.0	−0.45	8.0	62.0	δ(OCH$_3$) −3.82
$[PtCH_3Q_2(CNCH_2CH_3)](SbF_6)$	−20	−1.93	7.4	33.2	−0.24	8.1	63.6	δ(CH$_2$) −3.38, δ(CH$_3$) −1.15^f
$Pt(CH_3)_2Q(CNC_6H_4OCH_3)$	31	−2.32	8.4	21.2	−0.71	7.4	62.8	δ(OCH$_3$) −3.82
					−0.39	9.4	68.0	
$PtCH_3ClQ(CNC_6H_4OCH_3)$	31	−2.01	11.2	49.6	−0.58	4.8	56.6	δ(OCH$_3$) −3.84
$[PtCH_3Q(CNC_6H_4OCH_3)(CNC_6H_4CH_3)](PF_6)$	31	−1.73	16.0	52.0	−0.50	6.0	62.5	δ(OCH$_3$) −3.42, δ(CH$_3$) −1.93
$[PtClQ_2(CNC_6H_4CH_3)](PF_6)$	31	−2.10	8.0	29.6	...	...	...	δ(CH$_3$) −1.88
$[PtClQ_2(CNC_6H_4OCH_3)](PF_6)$	31	−2.00	8.8	28.8	...	...	...	δ(OCH$_3$) −3.40
$[PtL_2(CNCH_2CH_3)_2](BF_4)_2$	−30	−2.64	7.5	31.6	...	...	...	δ(CH$_3$) −0.79, δ(CH$_2$) −3.33
$[PtClQ_2(CNCH_2CH_3)](PF_6)$	31	−2.03	7.2	25.2	...	...	...	δ(CH$_3$) −0.93, δ(CH$_2$) −3.74
$[PtIQ_2(CNCH_2CH_3)](PF_6)$	31	−2.26	7.2	25.6	...	...	...	δ(CH$_3$) −0.98, δ(CH$_2$) −3.09

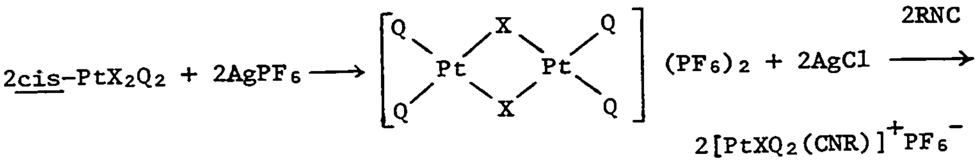
[a] Chemical shifts (δ) in ppm using dichloromethane as internal standard. $[PtClL_2(CNC_6H_4CH_3)](PF_6)$ and $[PtQ_2(CNCH_2CH_3)_2](PF_6)_2$ are insoluble. Coupling constants (J) in hertz. [b] Temperature at which ^{31}P–^{1}H coupling was clearly resolved. [c] ^2J(P-H) + ^4J(P-H) is quoted. [d] L = $P(CH_3)(C_6H_5)_2$; Q = $P(CH_3)_2C_6H_5$. [e] J(Pt-H) = 12.8, J(P-H) = 1.3 [f] J(H-H′) = 7.5.

silver salt such as $AgPF_6$ or $AgSbF_6$ to give the alcohol cation $[PtMeQ_2(MeOH)]^+X^-$. The addition of an isocyanide readily displaces the alcohol and subsequent removal of the solvent gives a clear oil which may be dissolved in a suitable solvent and induced to crystallize by the addition of diethyl ether or pentane. The complexes were generally quite easy to crystallize using PF_6^- or SbF_6^- as the anion. However, in several instances where crystallization was difficult, exchange of the anion could be achieved by the addition of an alcoholic solution of sodium tetraphenylborate to give a crystalline product.

The addition of a one molar equivalent of p-methoxyphenyl isocyanide to trans-$PtMeCl(PMe_2Ph)_2$ in benzene gave an immediate white precipitate of $PtMeCl(CN{-}C_6H_4{-}OCH_3)(PMe_2Ph)_2$. The complex was soluble in hot benzene and may be five coordinate in the solid state. However, in a polar solvent such as chloroform or dichloromethane it is dissociated presumably to $[PtMe(PMe_2Ph)_2(CN{-}C_6H_4{-}OCH_3)]^+Cl^-$ since the proton nmr spectrum in CH_2Cl_2 is identical with that of the analogous PF_6^- salt in solution.

Type II $[PtXQ_2(CN{-}R)]^+PF_6^-$ (X = Cl,I)

Complexes of this type were prepared by cleavage of the cationic halogen-bridged dimers in methanol (equation 5).



(5)

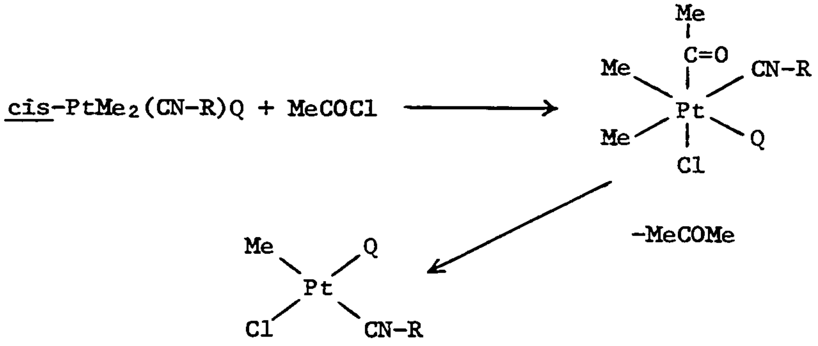
The reaction proceeded smoothly with precipitation of the isocyanide complexes from the methanol solutions. These complexes were generally much less soluble than the corresponding methylplatinum(II) compounds. As for most reactions involving cleavage of the bridged dimer [75], the phosphines occupy a trans configuration as shown from the nmr data.

Type III $[PtQ_2(CNR)_2]X_2$

The addition of 2 molar equivalents of an isocyanide to cis-$PtCl_2Q_2$ in methanol gave an immediate, clear and colourless solution, and the subsequent addition of an aqueous solution of Na^+X^- where $X = BF_4^-$ or PF_6^- gave an immediate precipitate of the dipositive cation (equation 6).

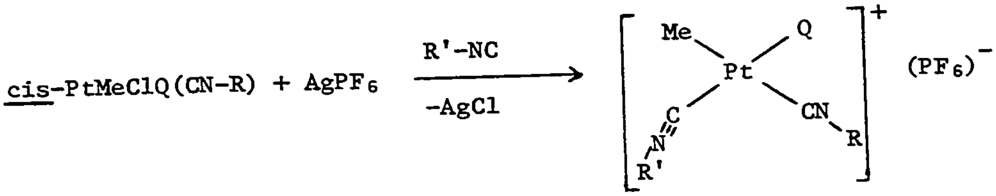
$$Cl_2PtQ_2 + 2RNC \rightarrow [PtQ_2(CNR)_2]Cl_2 \xrightarrow{2NaX} [PtQ_2(CNR)_2]X_2 \qquad (6)$$

The addition of a one molar equivalent of isocyanide to a benzene solution of cis-$PtMe_2Q_2$, Q = PMe_2Ph, readily displaced one phosphine to give cis-$PtMe_2(CN\text{-}R)Q$. Such a displacement has previously been observed by Treichel and Hess [62]. The addition of a molar equivalent of acetyl chloride to this complex gave cis-$PtMe_2ClQ(CN\text{-}R)$ (equation 7).



(7)

The reaction probably proceeded by an oxidative addition reaction to give an unstable platinum(IV) complex, followed by the elimination of acetone. The configuration of the final complex can easily be determined from nmr coupling constants. The platinum-methyl resonance appears as a doublet, due to coupling with the ^{31}P nucleus with ^{3}J(P-Pt-C-H) = 4.8 Hz indicating a *cis*-phosphine, with platinum satellites of one quarter intensity (^{2}J(Pt-C-H) = 56.6 Hz, indicative of a methyl group *trans* to an isocyanide). The phosphine methyl resonance appears as a doublet with platinum satellites showing ^{3}J(Pt-P-C-H) = 49.6 HZ indicating that the phosphine is *trans* to a weak σ-donor such as chloride[49]. This compound may readily be converted to a cationic methylplatinum(II) bis(isocyanide) complex (equation 8).



(8)

(ii) Raman and NMR Spectroscopic Data

The infrared and Raman spectra of the isocyanide complexes show very strong and sharp N≡C stretching vibrations in the region 2300-2100 cm^{-1}. The values of $\Delta\nu$(N≡C) (= ν(N≡C) complex - ν(N≡C) free ligand) are positive and 20-150 cm^{-1} in magnitude, indicating an increase in bond order on coordination. For a series of cationic methylplatinum(II) arylnitrile complexes (chapter II) a correlation was observed between the increase on coordination of the nitrile stretching frequency and the electronegativity of the para-substituent. There does not appear to be any obvious correlation in the analogous isocyanide complexes as $\Delta\nu$(N≡C) decreases in the order CN-Et > CN-Ph > CN-Me > CN-C_6H_4-OCH_3 > CN-C_6H_4-CH_3. However, there is a noticeable increase in $\Delta\nu$(N≡C) in the order type III > type II > type I and this will be discussed later.

The platinum-methyl stretching vibration appears as a strong and polarizable band in the Raman spectrum [24] yet is very weak in the infrared. The values of $\nu(Pt\text{-}CH_3)$ are in the region ~540 cm^{-1}, and since coupling to other vibrational modes is possible it is unlikely to be a pure mode.

The proton nmr spectra for many of the methylplatinum(II) isocyanide cations are particularly interesting in that they are temperature dependent. For example, Figure III-1 shows the variable temperature nmr spectra of trans-$[PtMe(CNEt)(PMe_2Ph)_2](SbF_6)$. The platinum methyl resonance at 0.24 δ appears as a sharp singlet at room temperature and is flanked by ^{195}Pt satellites. As the temperature is lowered the resonance broadens and at -10°C splits into a triplet due to coupling with the two phosphine ^{31}P nuclei. The phosphine methyl resonance appears only as a singlet at room temperature and as the temperature is lowered coupling due to ^{195}Pt appears and at even lower temperatures further splitting due to coupling with the ^{31}P nuclei occurs. Since the magnitude of the coupling constant to the platinum methyl group, $^2J(Pt\text{-}C\text{-}H)$, is temperature independent, the methyl group must be trans to ethyl isocyanide over the observed temperature range. The loss of phosphorus coupling must be due to intermolecular exchange of phosphines. This is further substantiated by the loss of platinum coupling to the phosphine methyl groups. The observed temperature dependence of the nmr spectra of the methylplatinum isocyanide cations is consistent with exchange of the two phosphines cis to the platinum methyl group. Since the publication of this work [26] there have been

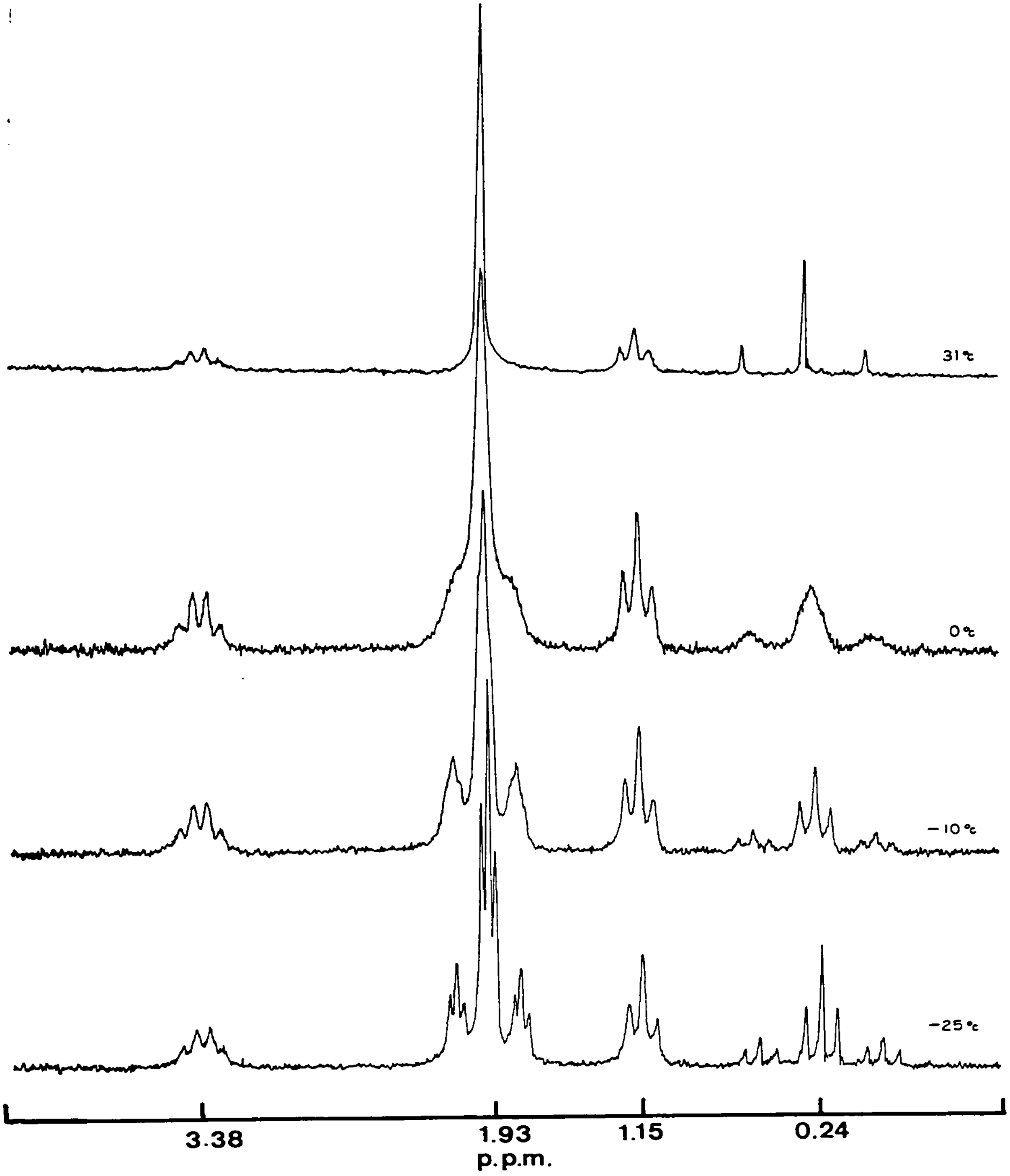


Figure III-1 Variable temperature nmr spectra of $[PtMe(PMe_2Ph)_2(CNEt)](SbF_6)$

several reports [76-78] of phosphine exchange in hydrido platinum phosphine cations of the type trans-$[PtH(PR_3)_3]^+$. For the cation where PR_3 = $PMePh_2$ the hydride resonance, at room temperature appears as a doublet with platinum satellites and in the limiting low temperature spectrum the hydride resonance gives the expected pattern, i.e. a doublet of triplets with ^{195}Pt satellites of one-fourth intensity. These observed spectra are consistent only with exchange of the two mutually trans phosphines.

Assuming that the coupling constant $^2J(Pt\text{-}C\text{-}H)$ is governed by the Fermi Contact term, an nmr trans-influence series (Table III-3) has been established [14] for the series of complexes trans-$[PtMe(PMe_2Ph)_2L]^+$ where L is a neutral ligand. From the values of $^2J(Pt\text{-}C\text{-}H)$ given in Table III-3 it is clear that carbon monoxide and isocyanides have very similar trans-influences, i.e. there is an equivalent amount of Pt(6s) character in the Pt-CO and Pt-CNR bonds. Attempts are constantly being made to separate the relative σ and π bonding components of various ligands and it is fairly well established [52,81,82] that isocyanides are very weak π-acceptors relative to carbon monoxide. For example, Cotton and Zingales [81] prepared a series of complexes $(RNC)_nMo(CO)_{6-n}$ and from infrared studies of $\nu(C\equiv O)$ and $\nu(C\equiv N)$ concluded that the isocyanides were weaker π-acceptors than carbon monoxide. This may well be the reason why phosphine exchange is observed in $[PtMe(CNR)(PMe_2Ph)_2]^+$ but not for the analogous carbonyl cation. The carbonyl cation is more electrophilic and hence the basic phosphine ligands are bound more tightly to the platinum. However, no phosphine exchange was observed for the carbene cations $[PtMe(PMe_2Ph)_2(carbene)]^+$ although exchange

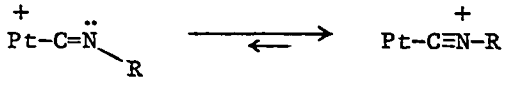
Table III-3

An NMR *Trans*-Influence Series for Pt(II) Cations of the type $[PtMe(PMe_2Ph)_2L]^+$

L	^2J(Pt-C-H) in Hz	^3J(Pt-P-C-H) in Hz	Reference
$:\overline{CCH_2CH_2CH_2O}$	51	34	23
$SbPh_3$	55	29	14
PMe_2Ph	57	30	14
PPh_3	58	30	14
CO	63	33	14
EtNC	63.6	33.2	26
$AsPh_3$	67	29	14
NC_5H_5	74	32	14
$CH_2{=}CH_2$	74.2	29.5	79
$NH{=}C(OMe)C_6F_5$	76.4	30.6	28
$MeC{\equiv}CMe$	77	29	24
MeCN	80	32	14
Me_2CO	88	32.4	81
MeOH	88	32.4	81

a. *Trans*-influence of L decreases down the series $:\overline{CCH_2CH_2CH_2O} \rightarrow$ MeOH.

might have been expected since carbenes are better σ-donors than isocyanides. Therefore we believe that isocyanides are very effective in reducing the effective positive charge on platinum due to the following resonance forms:



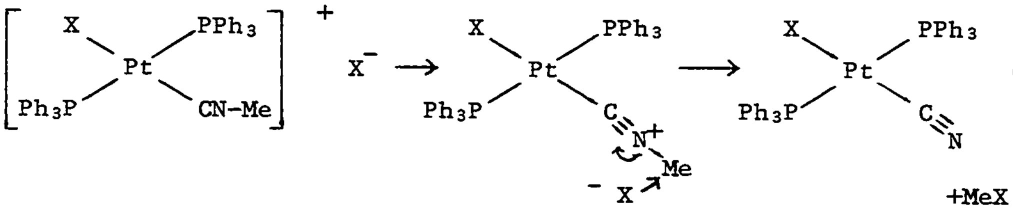
II I

X-ray crystal structures on several neutral platinum(II) isocyanide complexes [83-87] have shown that the C-N-C bond angle is not linear, i.e. *cis*-$PtCl_2(CNPh)(PEt_3)$ where the C-N-C bond angle is 165.5°. For the isocyanide cations in this work, a more linear C-N-C bond angle would be expected due to a greater delocalization of the nitrogen lone pair electrons into the p_z orbital of the electron deficient isocyanide carbon.

A similar argument [81] was used to explain the fact that more than one infrared active CN stretching band was found for the complexes $(RNC)_6Cr$ and $(RNC)_4Ni$. If the C-N-C bond angle was 180° the molecules would have effective O_h and T_d symmetries in the $(>CNC)_6Cr$ and $(>CNC)_4Ni$ portions of the molecule. Since $\nu(C\equiv N)$ was lowered relative to the free ligand it was concluded that there was a bending of the C-N-C group due to a significant contribution from II, thus lowering the symmetry of the molecules.

Therefore, in general, the greater the positive charge on the platinum, the greater is the delocalization and the greater is the value of $\Delta\nu(N\equiv C)$. This is clearly shown by the fact that $\Delta\nu(N\equiv C)$ increases in the order type III > type II > type I. In the type I complexes, the methyl group is a good electron donating group and this tends to reduce the positive nuclear charge whereas in type II complexes the chloride is electronegative, thus increasing the positive charge resulting in a greater delocalization of the nitrogen lone pair and a greater increase in $\nu(N\equiv C)$. Type III compounds exhibit very large positive values for $\Delta\nu(N\equiv C)$ (~140 cm^{-1}) as would be expected due to the dipositive charge on the cation.

Treichel and Hess[88] reported a mechanism for the dealkylation of cationic methyl isocyanide complexes involving a five coordinate intermediate. We believe that the mechanism may involve some concentration of the positive charge on nitrogen, followed by elimination of methyl halide (equation 9).



(9)

A similar mechanism may also be proposed for the well-known preparation of alkyl isocyanides by alkylation of the nitrogen lone pair in the metal cyanide complexes[52,90] (equation 10).

$$\text{M-C}\equiv\text{N} + \text{RX} \rightarrow \overset{+}{[\text{M-C}\equiv\text{N-R}]}\text{X}^- \xrightarrow[\Delta]{} \text{M}^+\text{X}^- + \text{R-NC} \qquad (10)$$

(iii) Preparation and Spectroscopic Studies of Carbene Complexes

The addition of alcohols and amines to coordinated isocyanides requires much more vigorous conditions for carbene formation than do the reactions involving mono-substituted acetylenes. Methoxy- and ethoxy-carbene complexes [23] are obtained instantaneously by the addition of R-C≡C-H to a solution of trans-$PtMeClQ_2$ (Q = tertiary phosphine or arsine) and silver hexafluorophosphate in the appropriate alcohol. In contrast neutral arylamino (alkoxy) carbene platinum complexes [18] are obtained only by refluxing the appropriate isocyanide complex in alcohol for long periods of time. Reactions with amines usually proceed smoothly at room temperature within a few hours.

As the positive charge on the platinum increases, so does the degree of difficulty in obtaining carbene complexes. Richards and coworkers [65] have prepared several carbene complexes derived from isocyanide complexes analogous to our type II (equation 11).

$$[PtX(CNR)(PEt_3)_2]^+ClO_4^- + QH \rightarrow [PtX(C(NHR)Q)(PEt_3)_2]^+ClO_4^- \qquad (11)$$

$$(Q = PhNh,\ EtNH,\ EtO;\ X = Cl,\ Br;\ R = Ph^-,\ Me^-)$$

The complexes were more difficult to obtain than the neutral carbene complexes and the ethoxy carbene was not obtained pure but only as a mixture with the parent isocyanide complex.

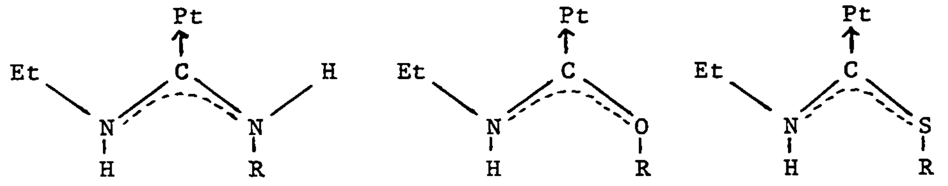
Attempts to prepare cationic methylplatinum(II) carbene complexes by refluxing the appropriate isocyanide complexes in alcohols and amines for long periods of time were unsuccessful since the methylplatinum compounds are not stable under these vigorous conditions. However, we have found that type III isocyanide complexes are particularly suitable for carbene formation since they are very stable under prolonged reflux conditions (equation 12).

$$[Pt(CNEt)_2(PMe_2Ph)_2](PF_6)_2 + RH \rightarrow [Pt\{C(NHEt)R\}(CNEt)(PMe_2Ph)_2](PF_6)_2 \tag{12}$$

$$(R = p\text{-}NHC_6H_4Me;\ -NHPh;\ -OEt;\ -SCH_2Ph)$$

The resulting carbene complexes are very soluble in polar solvents and can easily be separated from the unreacted, sparingly soluble bis(isocyanide) complex by fractional crystallization. The ease of preparation decreases in the order RNH_2 > RSH >> ROH, and the ethoxy (amino) carbene was obtained only in 40% yield after refluxing the parent isocyanide complex in ethanol for ten days.

The phosphine methyl resonances in the nmr appear as 1:2:1 triplets, indicative of mutually trans phosphines, flanked by platinum satellites of one quarter intensity with $^3J(Pt\text{-}P\text{-}C\text{-}H) \approx 32$ Hz. Elucidation of the stereochemistry comes from the ^1H nuclear magnetic resonance spectra in the phosphine methyl region. Four sets of overlapping triplets are observed (Figure III-2) indicating four inequivalent phosphine methyls caused by the absence of a plane of symmetry along the C-Pt-C axis and restricted rotation of the carbene about the Pt-C bond. The nmr spectra also indicate the presence of only one isomer in solution and the most likely structures are shown below, resulting from a 1,2-cis-addition of the nucleophile across the CN triple bond.



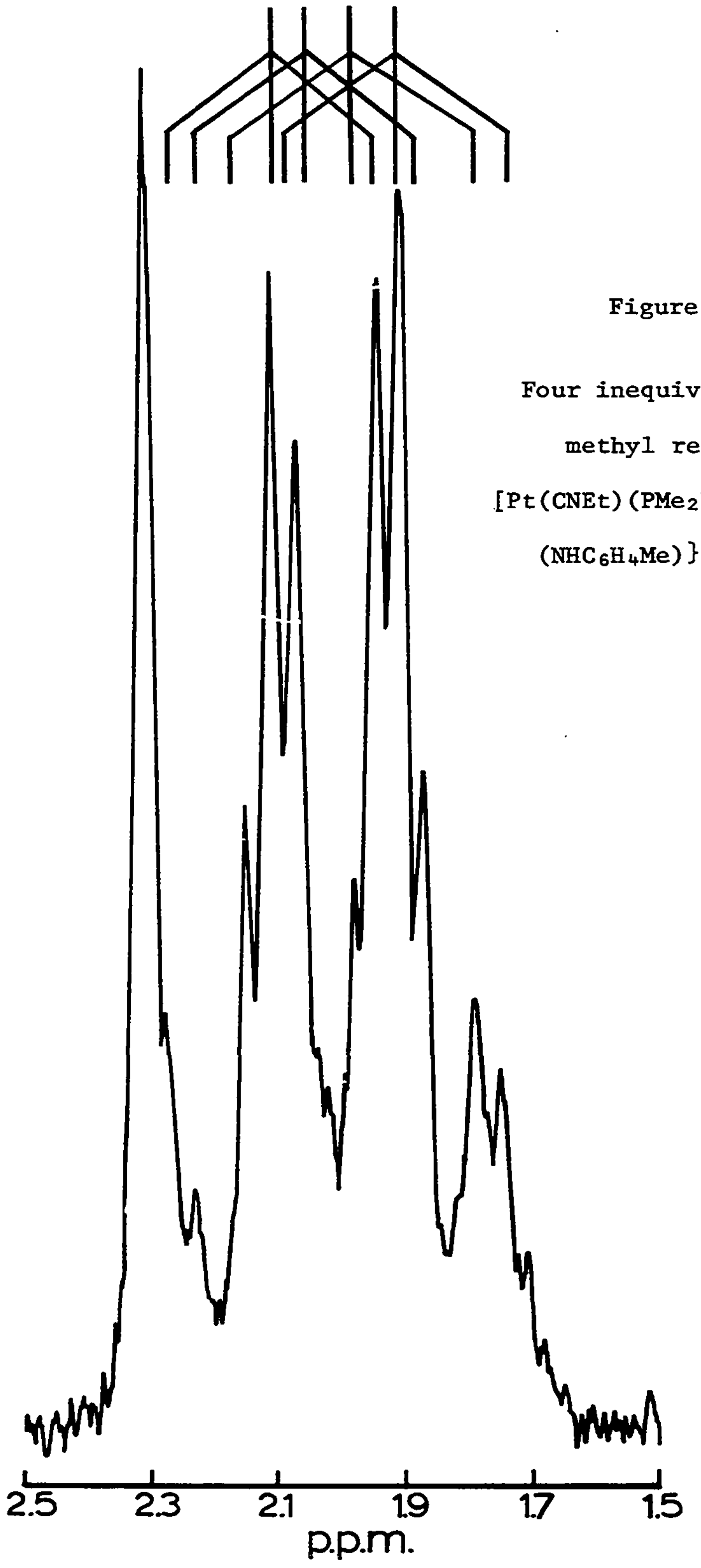


Figure III-2

Four inequivalent phosphine-methyl resonances of $[Pt(CNEt)(PMe_2Ph)_2\{:C(NHEt)-(NHC_6H_4Me)\}](PF_6)_2$

The X-ray structure by Richards et al[17] indeed shows that such cis-addition may occur and that the carbene plane is perpendicular to the plane of the complex. It is difficult to predict, a priori, whether this is the most stable configuration. In the completely planar structure extensive π-bonding involving the carbene carbon $2p_z$ and platinum $5d_{xz}$ orbitals is possible, although there must also be considerable steric interaction between the carbene and the phosphines. That the structure with the carbene perpendicular to the plane of the complex has been observed, in which the carbene carbon $2p_z$ orbital is competing with the phosphines for in-plane π-bonding with the Pt $5d_{xy}$ orbitals, suggests that π-bonding possibilities are less important than steric requirements.

Since an increase in the isocyanide stretching frequency, $\Delta\nu(N{\equiv}C)$, reflects the total positive charge on platinum, the carbene is shown to be a stronger σ-donor than the parent isocyanide (Table III-4). A comparison of ^2J(Pt-C-H) for the complexes trans-$[PtMeL(PMe_2Ph)_2]^+$, where L = methyl(methoxy) carbene[23] and ethyl isocyanide, gives values of 51 and 63 Hz respectively, indicating that indeed the carbene has a higher trans-influence than the isocyanide. In the methoxy(amino) carbene complex cis-$PtCl_2(CNR)\{C(OCH_3)NHR\}$ (R = p-tolyl, cyclohexyl) a higher trans-influence for the carbene than the isocyanide has been suggested on the basis of a lower ν(Pt-Cl) stretching frequency than that found in the parent isocyanide complex[66] cis-$Pt(CNR)_2Cl_2$.

Table III-4

INFRARED[a] AND ^{1}H NMR DATA[b] FOR CARBENE COMPLEXES

Complex	Phosphine–methyls			Ethyl resonances		ν(N–H)	ν(N≡C)	$\Delta\nu$(N≡C)[c]
	$\delta(CH_3)$	J(P–H)	J(Pt–H)	$\delta(CH_3)$	$\delta(CH_2)$			
$[(Et{-}NC)_2Pt(PMe_2Ph)_2](PF_6)_2$	insoluble					–	2294	143
$[(Ft{-}NC)Pt(PMe_2Ph)_2(C\substack{\diagup O{-}Et \\ \diagdown NH{-}Et})](PF_6)_2$	2.10 2.11 2.14 2.15	6.0 6.0 6.4 6.4	32.5 32.5 31.6 31.6	1.01 1.09 1.11	3.05 3.63	3382	2271	120
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\substack{\diagup NH{-}C_6H_5 \\ \diagdown NH{-}Et})](PF_6)_2$	1.99 2.00 2.16 2.17	8.2 8.0 8.0 8.0	32.4 31.6 32.8 32.8	1.14 1.22	3.51 3.64	3341 3389	2265	114
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\substack{\diagup NH{-}C_6H_4{-}CH_3 \\ \diagdown NH{-}Et})](PF_6)_2$[d]	1.91 1.94 2.07 2.11	6.9 6.9 7.6 7.6	32.4 32.4 31.6 31.6	1.12 1.14	3.42 3.57	3346 3393	2264	113
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\substack{\diagup SCH_2{-}C_6H_5 \\ \diagdown NH{-}Et})](PF_6)_2$	2.03[e]	8.0	31.2	1.19 1.23	3.52 3.58	3342	2257	106

[a] Accurate to ± 2 cm^{-1}. [b] Spectra recorded using dichloromethane as solvent and internal standard. Chemical shifts in ppm and coupling constants in Hz. [c] ν(N≡C) (complex) – ν(N≡C) (free ligand). [d] $\delta(CH_3)$ = 2.31. [e] Other resonances were complex and could not be interpreted.

(iv) Mechanism of Carbene Formation

Chatt _et al_ [18] suggested that the nitrogen might be activated towards electrophilic attack by a proton but clearly, since amines react much faster than alcohols the rate determining step must involve nucleophilic attack at the electron-deficient isocyanide carbon of the complex. Crociani _et al_ [90] have recently published a kinetic study on the reactions of various para-substituted phenyl isocyanide palladium complexes with para-substituted aromatic amines. The rate of carbene formation increased with electron withdrawing substituents on the isocyanide and electron donating substituents on the amine supporting the suggestion [25] that the mechanism involves attack of the amine on the carbon atom of the isocyanide linked to the central metal. Similar conclusions were reached for several palladium(II) carbene complexes [91].

c) Experimental

p-Tolylisocyanide, p-nitrophenylisocyanide, and phenylisocyanide were prepared by the phosgene method [92]; p-methoxyphenyl isocyanide by the method of Hertler and Corey [93], and methyl and ethyl isocyanide by the method of Casanova, Schuster and Werner [94].

Many of the complexes were prepared by similar methods so only representative examples are described.

(i) Preparation of $[PtMe(PMe_2Ph)_2(CN-C_6H_4-OCH_3)]^+(PF_6)^-$

To a suspension of _trans_-$PtMeCl(PMe_2Ph)_2$ (0.194 g.) in 10 ml. of methanol was added silver hexafluorophosphate (0.094 g.). A flocculent precipitate of silver chloride formed immediately and the solution was magnetically stirred for 10 minutes to allow complete removal of the chloride and coagulation of the silver chloride. The silver chloride was removed by centrifugation to give a clear, colourless solution. p-Methoxyphenyl isocyanide (0.049 g.) was slowly added and a white precipitate formed immediately. The mixture was stirred for 10 minutes and filtered, then washed with methanol and ether. The product was recrystallized from hot methanol to give white needles. Yield was 85%.

(ii) Preparation of $PtMeCl(PMe_2Ph)_2(CN-C_6H_4-OCH_3)$

To a solution of trans-$PtMeCl(PMe_2Ph)_2$ (0.157 g.) in 10 ml. of benzene was added p-methoxyphenyl isocyanide (0.040 g.). An oily precipitate formed immediately and the solution was stirred for 15 minutes. The white solid was filtered, washed with benzene and ether, and then recrystallized from hot benzene to give white crystals. Yield was 53%.

(iii) Preparation of cis-$PtMe_2(CN-C_6H_4-OCH_3)(PMe_2Ph)$

A solution of cis-$PtMe_2(PMe_2Ph)_2$ (0.146 g.) and p-methoxyphenyl isocyanide (0.039 g.) in 10 ml. of benzene was stirred for three hours. A strong smell of phosphine was detected. The benzene was then removed under reduced pressure to give a yellow oil which was taken up in 2 ml. of diethyl ether and passed through a short florisil column. Addition of pentane to the ether solution yielded large white needles. Yield was 93%.

(iv) Preparation of cis-$PtMeCl(CN-C_6H_4-OCH_3)(PMe_2Ph)$

cis-$PtMe_2(CN-C_6H_4OCH_3)(PMe_2Ph)$ (0.111 g.) was dissolved in 3 ml. of diethyl ether and acetyl chloride (0.017 g.) was added. The flask was cooled at -10°C for 12 hours and white crystals separated. The ether was removed under reduced pressure and the white crystals were recrystallized from dichloromethane and ether. Yield was 48%.

(v) Preparation of $[PtCl(CN-C_6H_4-CH_3)(PMe_2Ph)_2]^+(PF_6)^-$

To a suspension of cis-$PtCl_2(PMe_2Ph)_2$ (0.208 g.) in 10 ml. of methanol was added $AgPF_6$ (0.095 g.) in 2 ml. of methanol. The mixture was stirred for 10 minutes and the silver chloride was removed by centrifugation to give a pale yellow solution. p-Tolyl isocyanide (0.044 g.) was added and the solution turned colourless and a white precipitate formed. The volume of the solvent was reduced and the solid was filtered, washed with ether and recrystallized from hot methanol. Yield was 73%.

(vi) Preparation of $[Pt(CNEt)_2(PMePh_2)_2](BF_4)_2$

Ethyl isocyanide (0.029 g.) was added to a suspension of cis-$Cl_2Pt(PMePh_2)_2$ (0.176 g.). The resulting clear, colourless solution was stirred for 10 minutes and $NaBF_4$ (0.058 g.) in methanol was added. A slight precipitate formed and the methanol was removed under reduced pressure. The complex was extracted with 10 ml. of dichloromethane. The solution was filtered and ether then added dropwise to give white crystals. Yield was 96%.

(vii) Preparation of $[Pt(CNEt)\{C(NHEt)(NHPh)\}(PMe_2Ph)_2](PF_6)_2$

A suspension of $[Pt(CNEt)_2(PMe_2Ph)_2](PF_6)_2$ (0.350 g.) in 10 ml. of tetrahydrofuran and 2 ml. of aniline was refluxed for 24 hours to give a clear solution. The solvents were removed under vacuum to give a clear yellow oil which was dissolved in dichloromethane and chromatographed through a short florisil column. The dichlorcmethane was removed on a rotary evaporator and the clear colourless oil was dissolved in methanol. Diethyl ether was added until the solution became slightly cloudy, then the flask was placed in a refrigerator at -10°C for two days to yield white crystals. Yield was 36%.

(viii) Preparation of $[Pt(CNEt)\{C(NHEt)(OEt)\}(PMe_2Ph)_2](PF_6)_2$

A suspension of $[Pt(CNEt)_2(PMe_2Ph)_2](PF_6)_2$ (0.400 g.) was refluxed in ethanol for ten days to give a dirty yellow solution. The methanol was removed under vacuum and the resulting oil chromatographed as above with dichloromethane. The solvent was removed on a rotary evaporator and the oil was dissolved in methanol. The addition of diethylether and subsequent cooling at -10°C yielded off-white crystals. Yield was 40%.

CHAPTER IV

DIMETHYLPLATINUM(IV) CATIONS: CHEMICAL REACTIVITY AND AN NMR TRANS-INFLUENCE SERIES

a) Introduction

Trimethylplatinum(IV) iodide was the first organoplatinum complex to be prepared [95] and most of the chemistry of organoplatinum(IV) has evolved from this compound [96]. Dimethylplatinum(IV) complexes have received much less attention due more to difficulty in their preparation rather than to any inherent instability [97].

While investigating the nature of the Pt-CF_3 bond in a series of CF_3-Pt(II) and CF_3-Pt(IV) complexes (Chapter VI) it was discovered that the iodide trans- to CF_3 was quite labile to the extent that we were able to prepare several platinum(IV) cations including a carbene complex [98]. Consequently, the apparent stability of these platinum(IV) cations prompted us to extend our investigations to the synthesis of other organoplatinum(IV) cations.

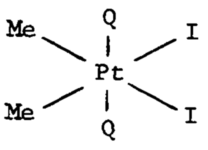
We have recently been interested in the reactivity of unsaturated systems with methylplatinum(II) cations so it was also of interest to examine the reactivity of these ligands when present in organoplatinum (IV) cations. On oxidation from Pt(II) to Pt(IV), two electrons are removed from the metal resulting in a contraction of the metal orbitals and it is these orbitals that are used for π-back donation into ligand π^* orbitals. Therefore, any complexes with unsaturated ligands, that rely on M $d\pi \rightarrow L\pi^*$ bonding would be expected to be less stable for Pt(IV) compared with Pt(II).

In this chapter we report the synthesis of a wide variety of dimethylplatinum(IV) cations and the reactions of these cations with acetylenes and pentafluorobenzonitrile. The relationship between $^2\underline{J}(^{195}Pt\text{-}CH_3)$ and the nmr trans-influence of a neutral ligand trans to the methyl group in such dimethylplatinum(IV) cations is also discussed.

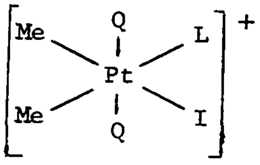
b) Results and Discussion

(i) Preparation of the Complexes

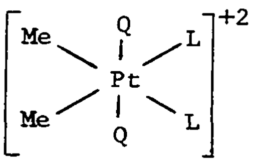
One or both of the iodine atoms in dimethylbis(dimethylphenylphosphine)platinum(IV) diiodide(I) may be removed by addition of the silver salt of a non-coordinating anion in the presence of a neutral ligand to give two types of cations (configurations II and III).



I



II

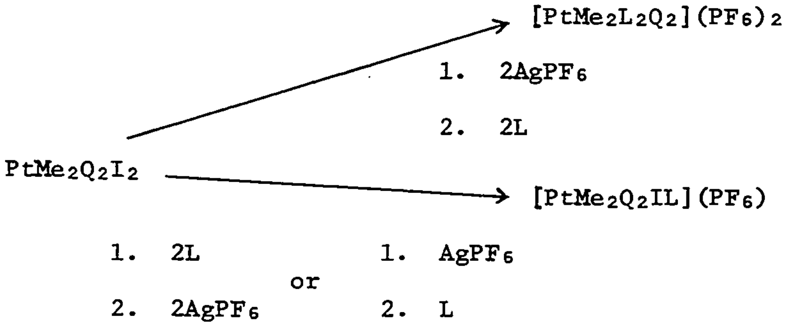


III

Q = PMe_2Ph

The dipositive cations (III) are prepared by the addition of two molar equivalents of silver hexafluorophosphate to an acetone solution of (I). Removal of the silver iodide gives a clear, colourless solution, presumably containing the cation (III) (L = acetone). The addition of two molar equivalents of a neutral ligand readily displaces acetone and the desired dipositive cations are obtained. Physical properties and recrystallization solvents are listed in Table IV-1.

The monopositive cations may be prepared in two ways. The addition of one molar equivalent of silver hexafluorophosphate to (I) in acetone followed by an equivalent amount of ligand (L) leads to the isolation of (II) in good yields. In an attempt to prepare the dipositive cations (III) by the addition of two molar equivalents of silver hexafluorophosphate to an acetone solution containing (I) <u>and</u> the ligand (L) <u>only</u> the monopositive cations (II) were isolated (Scheme 1), even though both iodine atoms can be readily removed in the absence of L.



Scheme 1

Table IV-1

ANALYTICAL, PHYSICAL, AND RAMAN DATA FOR DIMETHYLPLATINUM(IV) CATIONS[a]

Complex	Analysis, % calcd (% found)		Mp, °C	Recrystallizn solvents	Raman data, cm^{-1}		
	Carbon	Hydrogen			ν_{Pt-CH_3}	Other	$\Delta\nu_{N\equiv C}$[c]
$[PtMe_2Q_2(NCC_6H_4OCH_3)_2](PF_6)_2$	38.61 (38.17)	4.00 (4.32)	150-153	CH_2Cl_2-CH_3OH-$(C_2H_5)_2O$	561	$\nu_{C\equiv N}$ 2261	48
$[PtMe_2Q_2(phen)](PF_6)_2$	36.41 (36.89)	3.67 (3.58)	309-311	CH_3COCH_3-CH_2Cl_2	560, 551		
$[PtMe_2Q_2(NH{=}C(OCH_3)C_6F_5)_2](PF_6)_2$	32.63 (32.58)	2.90 (3.15)	111-115	CH_3OH-$(C_2H_5)_2O$	586, 555	$\nu_{C=N}$ 1663	
$[PtMe_2Q_2\{S_2CN(C_2H_5)_2\}](PF_6)$	34.91 (34.97)	4.78 (5.22)	174-176	CH_2Cl_2-$(C_2H_5)_2O$	*b*		
$[PtMe_2Q_2(terpy)](PF_6)_2$	38.68 (38.47)	3.81 (3.61)	242-248	CH_3COCH_3-CH_2Cl_2	553, 532, 523		
$[PtMe_2Q_2(bipy)](PF_6)_2$	35.49 (35.50)	3.83 (3.98)	304-306	CH_3COCH_3-CH_2Cl_2	562, 548		
$[PtMe_2Q_2(py)_2](PF_6)_2$	35.42 (35.37)	4.03 (3.72)	208-211	CH_3OH	540		
$[PtMe_2Q_2(diphos)](SbF_6)_2$	38.21 (38.01)	3.79 (3.61)	229-233	CH_2Cl_2-$(C_2H_5)_2O$	536, 517		
$[PtMe_2Q_2\{P(OMe)_3\}_2](PF_6)_2$	27.78 (27.71)	4.46 (4.32)	210-214	CH_3COCH_3-$(C_2H_5)_2O$	523		
$[PtMe_2Q_2(CNCH_3)_2](PF_6)_2$	30.25 (30.27)	3.92 (3.79)	162-166	CH_2Cl_2-CH_3OH-$(C_2H_5)_2O$	546, 535	$\nu_{N\equiv C}$ 2278	108
$[PtMe_2Q_2(CNC_6H_4CH_3)_2](PF_6)_2$	39.83 (39.59)	4.13 (4.09)	211-213	CH_3COCH_3-$(C_2H_5)_2O$	539	$\nu_{N\equiv C}$ 2227	111, 102
$[PtMe_2Q_2(CNC_6H_4OCH_3)_2](PF_6)_2$	38.61 (38.71)	4.00 (3.73)	209-211	CH_3COCH_3-$(C_2H_5)_2O$	540	$\nu_{N\equiv C}$ 2232, 2217	107, 92
$[PtMe_2Q_2(diars)](PF_6)_2$	31.21 (31.13)	4.17 (3.90)	211-214	CH_3COCH_3-$(C_2H_5)_2O$	513		
$[PtMe_2Q_2I(NC_5H_5)](PF_6)$	32.41 (32.29)	3.90 (3.94)	134-135	CH_3OH	555, 531		
$[PtMe_2Q_2I(CNC_6H_4OCH_3)][B(C_6H_5)_4]$	55.57 (56.23)	5.13 (5.39)	161-162	$CHCl_3$-$(C_2H_5)_2O$	544, 513	$\nu_{N\equiv C}$ 2216	91
$[PtMe_2Q_2I(CNC_6H_4CH_3)][B(C_6H_5)_4]$	56.40 (56.71)	5.21 (5.13)	168-169	CH_2Cl_2-CH_3OH-$(C_2H_5)_2O$	541, 518	$\nu_{N\equiv C}$ 2203	78
$[PtMe_2Q_2I(P(CH_3)_2C_6H_5)][B(C_6H_5)_4]$	55.31 (55.26)	5.48 (5.39)	158-159	CH_2Cl_2-CH_3OH	525, 503		
$[PtMe_2Q_2I(CNC_2H_5)](PF_6)$	30.45 (30.55)	4.02 (3.75)	148-149	CH_2Cl_2-$(C_2H_5)_2O$	546, 519	$\nu_{N\equiv C}$ 2243	92
$[PtMe_2Q_2(CNC_2H_5)_2](PF_6)_2$	31.97 (31.94)	4.25 (3.96)	178-179	CH_2Cl_2-$(C_2H_5)_2O$	550, 527	$\nu_{N\equiv C}$ 2246	95
$[PtMe_2Q_2\{B(pz)_4\}](PF_6)$	39.00 (38.75)	4.32 (4.19)	245-247	CH_2Cl_2-$(C_2H_5)_2O$	568, 559		

This is not expected nor can it easily be explained since methylplatinum(II) cations [14] are readily obtained by the use of a silver salt and a neutral ligand regardless of the order of addition. Presumably the equilibrium, (equation 1)

$$Ag^+ + L \rightleftarrows AgL^+ \qquad (1)$$

lies sufficiently far to the right to prevent removal of the second iodine atom, which would be expected to be more difficult than removal of the first iodide.

The acetone complex(III) (L = acetone) readily reacts with anionic bidentate ligands such as dialkyldithiocarbamates or tetrapyrazolylborates to form monopositive cations (configuration III with L = chelate).

The complexes are air-stable crystalline solids and melt without effervescence unlike trimethylplatinum(IV) complexes [99,100] which melt with effervescence and loss of ethane. They are readily soluble in acetone and moderately soluble in dichloromethane or chloroform.

(ii) NMR Spectra

The phosphine methyl resonances of complexes with configurations II and III (Tables IV-2, IV-3) appear as 1:2:1 triplets indicative of strong $^{31}P-^{31}P$ coupling of mutually <u>trans</u> phosphines [36] with coupling to ^{195}Pt giving rise to satellites of one-quarter total intensity. In several instances the absence of a plane of symmetry containing the P-Pt-P axis gives rise to inequivalent phosphine methyls and two sets of overlapping triplets are observed.

The platinum methyl resonances appear as 1:2:1 triplets due to coupling with two equivalent ^{31}P nuclei together with platinum satellites of one-quarter intensity. The magnitude of $^2\underline{J}(^{195}Pt-C-^1H)$

Table IV-2

NMR DATA FOR DIMETHYLPLATINUM(IV) CATIONS $[PtMe_2Q_2L_2]^{2+}$

Complex[c]	Phosphine methyls			Platinum methyls			Other resonances
	δ_{CH_3}[a]	J_{P-H}[b]	J_{Pt-H}	δ_{CH_3}	J_{P-H}	J_{Pt-H}	
$[PtMe_2Q_2(NCC_6H_4OCH_3)_2](PF_6)_2$	2.17	8.1	20.2	1.18	6.5	70.2	δ_{OCH_3} 3.81
$[PtMe_2Q_2(phen)](PF_6)_2$	1.64	8.0	21.0	1.43	6.3	65.5	
$[PtMe_2Q_2(NH{=}C(OCH_3)C_6F_5)_2](PF_6)_2$	1.92	7.0	18.2	0.71	6.6	65.2	δ_{OCH_3} 3.97, δ_{NH} 8.80
$[PtMe_2Q_2\{S_2CN(C_2H_5)_2\}](PF_6)$	1.82	7.6	20.6	0.63	6.1	64.8	δ_{CH_3} 0.99, δ_{CH_2} 3.26, $J_{H-H} = 7$
$[PtMe_2Q_2(terpy)](PF_6)_2$	1.69	8.2	19.1	0.06	6.2	64.6	
	1.65	8.2	20.0				
$[PtMe_2Q_2(bipy)][PF_6]_2$	1.61	8.1	21.0	1.31	6.3	64.4	
$[PtMe_2Q_2\{B(pz)_4\}](PF_6)$	1.40	7.6	18.8	1.00	6.4	64.2	
$[PtMe_2Q_2(py)_2](PF_6)_2$	1.72	7.6	20.2	1.24	6.5	60.8	
$[PtMe_2Q_2(diphos)](SbF_6)_2$	1.50	10.0 d	31.0	0.43	6.5 t 8.1 d	60.6	
$[PtMe_2Q_2\{P(OCH_3)_3\}_2](PF_6)_2$	2.16	7.6	19.8	0.26	6.7	60.0	δ_{OCH_3} 4.09, $J_{P-OCH_3} = 11$
$[PtMe_2Q_2(CNCH_3)_2](PF_6)_2$	2.19	7.8	21.6	0.61	6.7	58.2	δ_{CH_3} 3.38, $J_{Pt-H} = 8.3$
$[PtMe_2Q_2(CNC_2H_5)_2](PF_6)_2$	2.22	7.6	20.4	0.78	6.8	58.2	δ_{CH_3} 1.28, δ_{CH_2} 3.79
$[PtMe_2Q_2(CNC_6H_4CH_3)_2](PF_6)_2$	2.32	8.0	21.2	0.90	6.6	58.0	δ_{CH_3} 2.26
$[PtMe_2Q_2(CNC_6H_4OCH_3)_2](PF_6)_2$	2.29	8.0	21.6	0.87	6.7	57.8	δ_{OCH_3} 3.71
$[PtMe_2Q_2(diars)](PF_6)_2$	1.99	7.4	21.6	1.34	7.5	56.0	δ_{AsCH_3} 1.34
	1.97	7.2	21.7				$J_{Pt-H} = 7.0$

[a] Chemical shifts are reported in ppm downfield from TMS using dichloromethane as solvent. [b] $^2J_{P-H} + {^4J_{P-H}}$ is quoted

[c] Q = $P(CH_3)_2(C_6H_5)$, phen = o-phenanthroline, terpy = 2,2′,6′,2″-terpyridine, bipy = 2,2′-bipyridyl, py = pyridine, diphos = 1,2-bis(diphenylphosphino)ethane, diars = o-phenylenebis(dimethylarsine), Me = CH_3, d = doublet, t = triplet.

Table IV-3

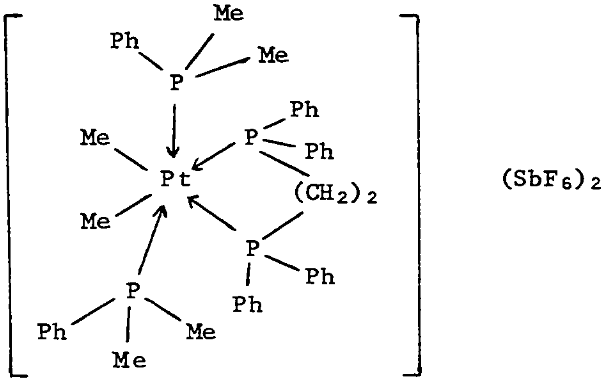
NMR DATA FOR DIMETHYLPLATINUM(IV) CATIONS $[PtMe_2Q_2IL]^+$

Ligand (L)	Phosphine methyls			Methyl trans to I			Methyl trans to L			Other resonances
	δ_{CH_3}	J_{P-H}	J_{Pt-H}	J_{CH_3}	J_{P-H}	J_{Pt-H}	δ_{CH_3}	J_{P-H}	J_{Pt-H}	
NC_5H_5	2.14	7.6	18.8	1.27	6.2	64.2	1.49	5.5	61.6	
	2.02	7.6	21.2							
$CNC_6H_4OCH_3$	2.32	8.0	18.8	0.88	5.6	64.9	0.88	6.0	58.3	δ_{OCH_3} 3.65
	2.01	8.2	20.6							
$CNC_6H_4CH_3$	2.43	7.3	20.0	1.02	5.5	62.5	1.09	7.1	57.0	δ_{CH_3} 2.46
	1.99	7.9	21.0							
$P(CH_3)_2C_6H_5$	2.08	6.5	18.4	0.95	5.3 t	62.6	1.18	6.8	50.5	
	1.98	7.6	19.5		8.1 d					
	1.64 d	9.6	15.6							
$:\overline{CCH_2CH_2CH_2O}$	2.39	6.3	16.0	1.41	5.57	64.5	0.75	7.5	47.0	
	1.87	6.4	16.8							
CNC_2H_5	2.44	7.4	20.2	0.89	5.5	64.4	0.95	5.5	58.0	δ_{CH_3} 1.06
	2.11	7.8	21.0							δ_{CH_2} 3.40

is dependent on the nature of the ligand trans to the methyl group.

The ^1H nmr spectra of $[PtMe_2Q_2(diphos)](SbF_6)_2$ (diphos = 1,2-bis-(diphenylphosphino)ethane) is particularly interesting (Figure IV-1). The platinum methyl resonances (C) appear as a doublet of triplets. The triplet pattern must arise from coupling to two equivalent ^{31}P nuclei thus confirming the mutually trans configuration of the two dimethylphenylphosphines (configuration III). The fact that this resonance is split into a doublet indicates that coupling to the trans ^{31}P nucleus of the chelating diphosphine is much greater than coupling to the cis phosphorus.

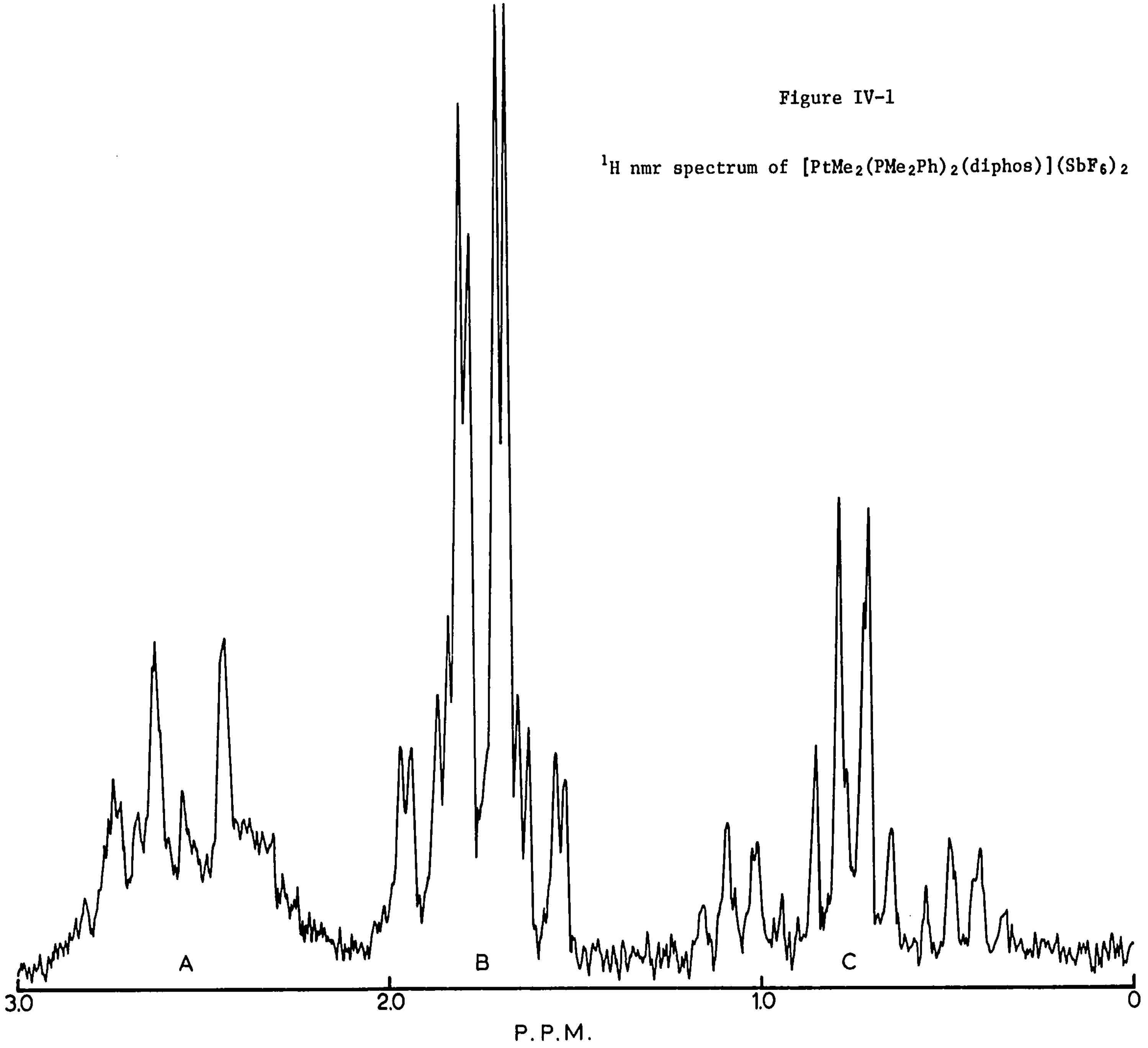
The phosphine-methyl resonance (B) appears only as two overlapping doublets with platinum satellites. Such a pattern is usually associated with cis-phosphines where the P-M-P bond angle is close to 90° and $^{31}P-^{31}P$ coupling is small. However, little is known of the magnitude of $^2J(^{31}P-^{31}P)$ when the angle P-M-P is between 180° (virtual coupling) and 90°. Since the phosphine methyl resonance appears only as a doublet the P-M-P bond angle in this complex must be less than 180° as a result of steric interaction with the chelating diphosphine(V).



(V)

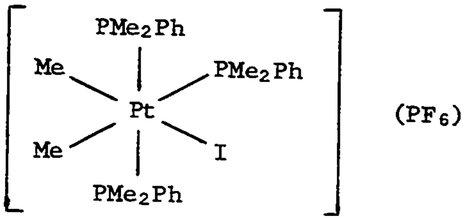
Figure IV-1

^1H nmr spectrum of $[PtMe_2(PMe_2Ph)_2(diphos)](SbF_6)_2$



Values of ^{3}J(Pt-H) for Pt(IV) complexes are generally about 20 Hz (Table IV-2), however for the diphos complex this value is 31 Hz. The coupling constant is dependent on the hybridization of phosphorus as well as the bond angles H-C-P and C-P-Pt which might all be affected by steric crowding and the molecular distortion from 180°.

The proton nmr spectrum of the cation (VI) $[PtMe_2Q_2I](PF_6)$, is also interesting (Figure IV-2).

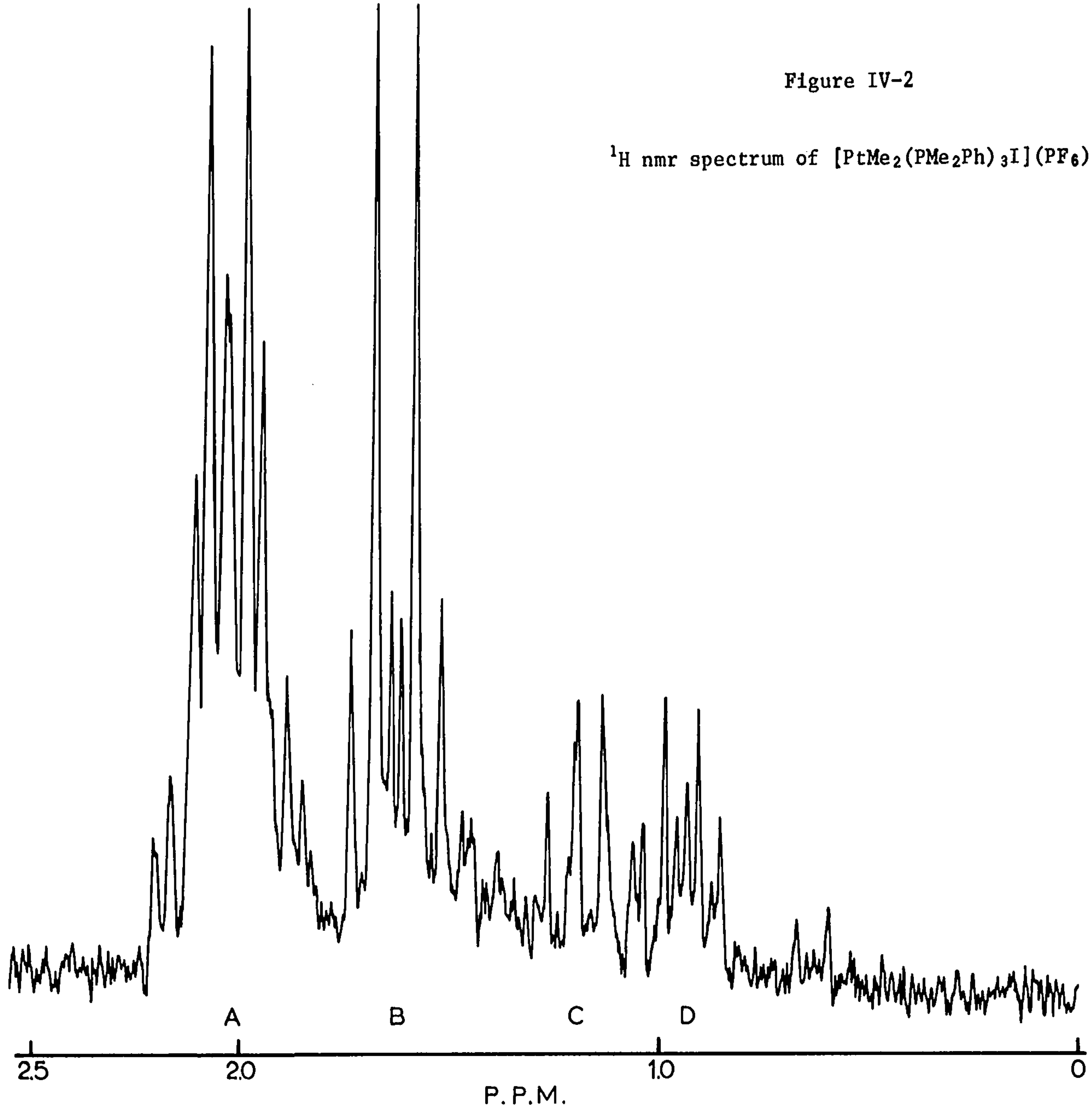


(VI)

The resonances of the two mutually *trans* phosphines (A) appear as two overlapping 1:2:1 triplets due to the lack of a plane of symmetry containing the P-Pt-P bonds and thus the P-Pt-P angle must be close to 180° with little of the distortion observed with the diphos complex. The platinum methyl group *trans* to the phosphine (C) gives a 1:3:3:1 quartet due to an overlapping doublet of triplets with *trans* ^{3}J(P-H) equal to *cis* ^{3}J(P-H). It is interesting that *cis* ^{3}J(P-H) is greater than *trans* ^{3}J(P-H) for the platinum methyl resonance of the complex[14] *trans* $[PtMeQ_3]^+$ whereas *cis* ^{2}J(P-H) is less than *trans* ^{2}J(P-H) for the hydride resonance[101] of *trans* $[PtH(PEt_3)_3]^+$. The platinum-methyl resonance for the methyl group *trans* to iodide (D) appears as an overlapping doublet of triplets.

Figure IV-2

^{1}H nmr spectrum of $[PtMe_2(PMe_2Ph)_3I](PF_6)$



(iii) The NMR Trans-Influence for Pt(IV) Cations

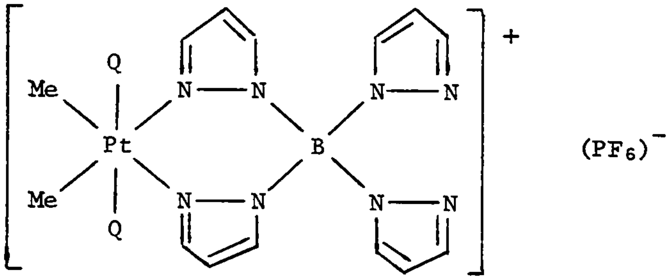
As discussed briefly in the previous chapters, changes in the two bond coupling constant $^2\underline{J}$(Pt-C-H) for a series of methylplatinum(II) cations have been used to establish a trans-influence series. In a similar manner it is possible to establish an NMR trans-influence series by measuring $^2\underline{J}$(Pt-C-H) for the platinum(IV) complexes of configurations II and III and this series is given below in order of decreasing trans-influence: (abbreviations are listed at the bottom of Table IV-2)

$:\overline{C-CH_2CH_2CH_2O} > PMe_2Ph >$ diars $> p\text{-}CNC_6H_4OMe \geq p\text{-}CNC_6H_4Me \gtrsim CNMe \approx CNEt > P(OMe)_3 >$ diphos $> NC_5H_5 > Bpz_4^- >$ bipy $\gtrsim$ terpy $> S_2CNEt_2^- > NH{=}C(OMe)C_6F_5 >$ phen $> p\text{-}NCC_6H_4OMe$

Attempts to prepare cations of configuration III, with L = triphenylarsine, phosphine, or stibine were unsuccessful and only very low yields of the methylplatinum(II) cations [14], $[PtMeQ_2L]^+$, were obtained. The reason for the instability of these platinum(IV) complexes is probably steric.

Carbon monoxide is high in the NMR trans-influence series for platinum(II) complexes (Table III-3), however this has been attributed to a synergic σ-π bonding mechanism [11], viz, strong π-bonding resulting in a strong Pt-CO σ-bond. Attempts to prepare $[PtMe_2Q_2(CO)_2]^{+2}$ by bubbling carbon monoxide through a solution of $[PtMe_2Q_2(CH_3COCH_3)_2]^{+2}$ in acetone yielded only a small amount of the corresponding methylplatinum(II) cation $[PtMeQ_2(CO)]^+$. The 5d orbitals of Pt(IV) would not be expected to be as effective for π-backbonding as those of Pt(II), and as a result the Pt(IV)-CO bond would be very weak and reduction occurs, although the mechanism of this reduction remains obscure. A similar argument may also account for the instability of the complexes with triphenyl phosphine, arsine, and stibine although the major reason is probably steric. Attempts to prepare the complex $[PtMe_2Q_2I(AsPh_3)]^+$ by the addition of a molar equivalent of $AsPh_3$ to a solution of $AgPF_6$ and $PtMe_2Q_2I_2$ were unsuccessful. However, the platinum(II) cation $[PtMeQ_2(AsPh_3)]^+$ was obtained in good yield presumably due to the instability of the platinum(IV) cation and the ease by which methyl iodide is eliminated.

Trofimenko [102,103] has recently reviewed the coordination chemistry of polypyrazolylborates $[R_nB(pz)_{4-n}]^-$. The tetrapyrazolylborate ion reacts with III, L = acetone, to give the cation VIII.



(VIII)

Attempts to prepare the bridged species $[(PtMe_2Q_2)_2\{B(pz)_4\}](PF_6)_3$ were unsuccessful and only the cation VIII was isolated. The pyrazolylborate ion lies between pyridine and bipyridyl in the NMR trans-influence series and thus is typical of other nitrogen heterocycles.

For a related series of complexes of Pt(II) and Pt(IV) the ratio ${}^2\underline{J}$(Pt(IV)-H)/${}^2\underline{J}$(Pt(II)-H) would be expected to be 0.67 [7] if the platinum 6s character was distributed equally over all bonds. This may be illustrated by the two complexes $[Pt(en)_2]Cl_2$ [104] and $[Pt(en)_3]Cl_4$ [105] (en = NH_2-CH_2-CH_2-NH_2) where the ratio is 0.66. A comparison between ${}^2\underline{J}$(Pt(IV)-CH_3) and ${}^2\underline{J}$(Pt(II)-CH_3) for the complexes prepared here (Figure IV-3) indicates that this ratio is approximately 0.88. These results suggest that on oxidation from Pt(II) to Pt(IV) the Pt-CH_3 bond retains 80-90% of the Pt(6s) character.

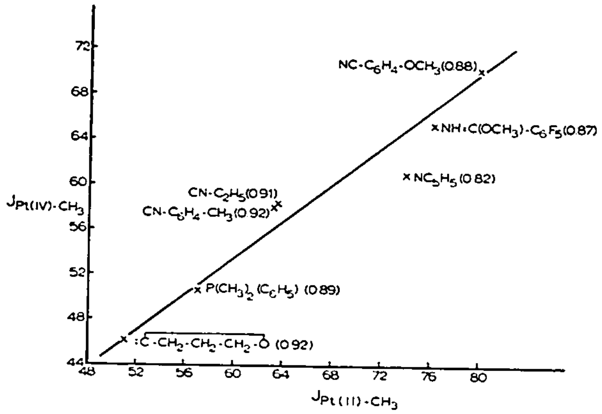
One interesting feature is that the methylplatinum(IV) bond requires more platinum 6s orbital contribution as the ligand trans to the methyl group rises in the NMR trans-influence series. Consider the cation $[PtMe_2Q_2I(CN\text{-}C_6H_4\text{-}CH_3)]^+$ where the ratio ${}^2\underline{J}$(Pt(IV)-CH_3) /${}^2\underline{J}$(Pt(II)-CH_3) is 0.92 for the methyl trans to isocyanide and 0.77 trans to iodide. Since the isocyanide is high in the NMR trans-influence series the methyl group trans to it requires more "s" character which is presumably obtained from the methyl trans to iodide.

The ratio of the coupling constants between the phosphine methyl protons and platinum for Pt(IV) and Pt(II) complexes is nearly theoretical at about 0.68.

(iv) Raman and Infrared Spectroscopic Data

All of the complexes show characteristic absorptions due to PMe_2Ph [106]. The presence of the octahedral PF_6^- ion is easily detected due to ν_3 (f_{1u}) at 850 cm^{-1} and ν_4 (f_{1u}) at 565 cm^{-1}, both of which appear as intense bands in the infrared spectra [107], and ν_1 (a_{1g}), is

Figure IV-3



—A plot of $^2J_{Pt(IV)-CH_3}$ *vs.* $^2J_{Pt(II)-CH_3}$ for a variety of cations. The number in parentheses after the ligand gives the value of $^2J_{Pt(IV)-CH_3}/^2J_{Pt(II)-CH_3}$.

observed in the Raman spectrum [108] at 741 cm^{-1}. The most intense peak in the Raman spectra occurs in the region 500-600 cm^{-1} and this has been assigned to the platinum-methyl stretching [109] vibration although it is unlikely to be a pure mode.

In the Raman spectra, two platinum methyl stretching vibrations are expected for each configuration although the symmetries of each would be different. Complexes with configuration III belong to the C_{2v} point group and thus two bands of A_1 and B_1 or B_2 symmetry are predicted from group theory and those with configuration II have lower symmetry (Cs) and two A_1 bands are predicted. In most cases the expected two bands are observed (Table IV-1).

The N≡C stretching vibration for the isocyanide complexes appears as a very sharp and strong absorption in both the infrared and Raman spectra. For the series of platinum(II) isocyanide complexes discussed in the previous chapter it was shown that $\Delta\nu$(N≡C) increased as the electron density on the metal decreased. From Table IV-4 it may be seen that $\Delta\nu$(N≡C) for the platinum(IV) complexes lies between the methyl- and trifluoromethylplatinum(II) cations. Thus it would appear that the electron density on platinum(IV) is similar to platinum(II) for these isocyanide cations. One must be careful when considering metals in different oxidation states; however, since the platinum isocyanide bond is very similar (from nmr data) for Pt(II) and Pt(IV) we feel these considerations are valid.

The platinum electron density does not appear to be related entirely to the formal oxidation state but to some extent on the ligands surrounding the metal. Recent x-ray photoelectron studies [110]

Table IV-4

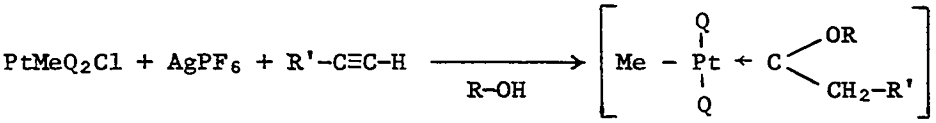
A Comparison of the Isocyanide Stretching Vibration for Some Organoplatinum Ethylisocyanide Cations

Cation	ν(N≡C)	Δν(N≡C)	Ref.
trans-$[Pt(CNEt)_2Q_2]^{+2}$	2294	143	26
trans-$[PtCl(CNEt)Q_2]^{+1}$	2267	116	26
trans-$[Pt(CNEt)Q_2(C\begin{smallmatrix}NHC_6H_4Me\\NHEt\end{smallmatrix})]^{+2}$	2264	113	26
trans-$[Pt(CF_3)Q_2(CNEt)]^{+1}$	2256	105	11
trans-$[Pt(CH_3)_2Q_2(CNEt)_2]^{+2}$	2246	95	
trans-$[Pt(CH_3)_2Q_2I(CNEt)]^{+1}$	2243	92	
trans-$[Pt(CH_3)Q_2(CNEt)]^{+1}$	2234	83	26

on some platinum complexes suggest that the electron density on a dimethyl platinum(II) complex is similar to platinum metal and in fact greater than several platinum acetylene complexes which are formally in a zero-valent oxidation state.

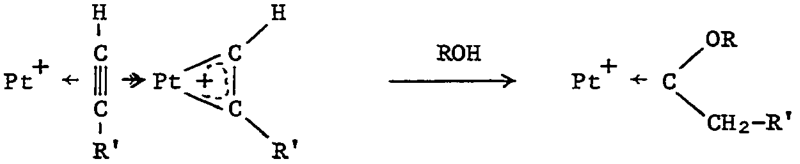
(v) Ligand Reactivities

Methylplatinum(II) cations react with monosubstituted acetylenes in alcohol to give carbene complexes[23] (equation 2).



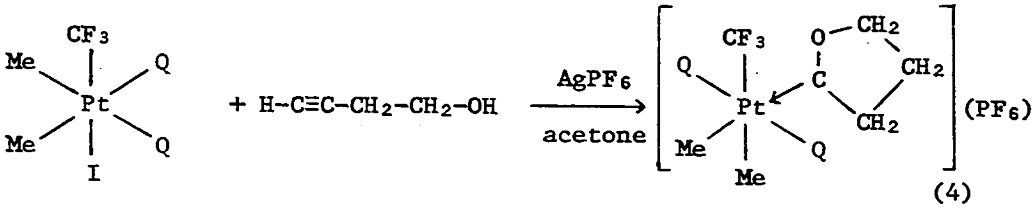
(2)

The reaction is believed to proceed via a π-bonded acetylene, delocalization of the positive charge from platinum onto the acetylene activating it towards nucleophilic attack by the alcohol[41,42] (equation 3).



(3)

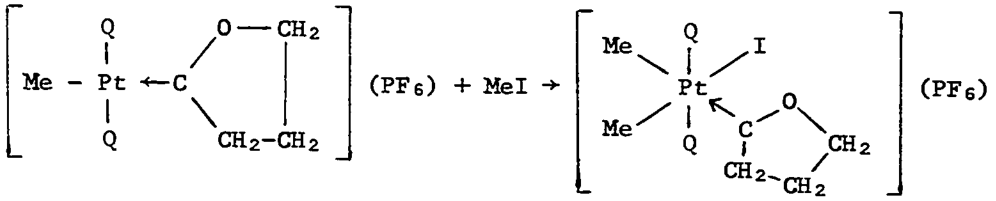
The carbenoid structures have been confirmed by x-ray crystallographic studies[111]. Attempts to isolate dimethylplatinum(IV) carbene complexes by this method were unsuccessful. Reaction of $PtMe_2Q_2I_2$ with silver hexafluorophosphate and acetylenes in methanol led only to extensive polymerization and no platinum complex could be isolated. In contrast[98] $PtMe_2(CF_3)Q_2I$ reacts with 1-butyn-4-ol and $AgPF_6$ to give a platinum(IV) carbene (equation 4).



(4)

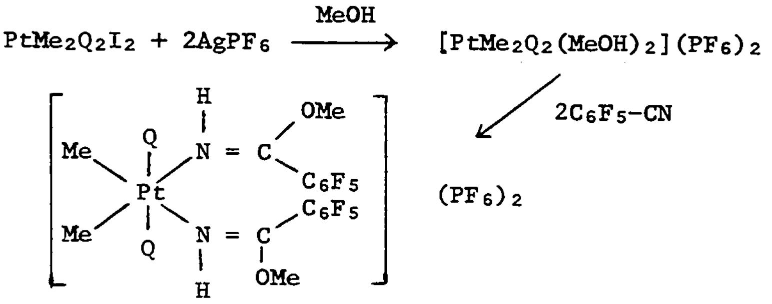
The activated π-bonded acetylene must rearrange prior to attack by the alcohol. Since polymerization occurs with the dimethylplatinum(IV) cations there must be a weak association with the acetylene, but apparently carbene formation is still not the preferred reaction route.

Cationic methylplatinum(II) complexes are oxidized by methyl iodide [48] and by this method a dimethylplatinum(IV) carbene cation has been prepared. The configuration was confirmed by nmr spectroscopy. (equation 5)



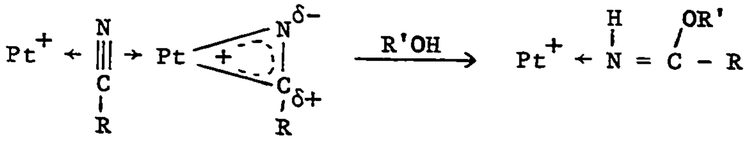
(5)

Perfluoroarylnitriles react with methylplatinum(II) cations in alcohol to give imino ether complexes (Chapter II). Similarly with platinum(IV) a bis-imino ether complex (configuration III) may be obtained (equation 6).



(6)

Reactions with alcohols to give imino ether complexes occur more readily for trifluoromethylplatinum(II) cations than for the corresponding methylplatinum cations (Chapter VI). These reactions were shown to proceed <u>via</u> a π-bonded nitrile followed by nucleophilic attack by the alcohol (equation 7).



(7)

Since the π-bonded nitrile is higher in the NMR <u>trans</u>-influence series for platinum(II) than N-bonded nitrile (Chapter II), the decreased electron density on the platinum in the trifluoromethyl complexes causes the preference for the π-bonded nitrile to be greater than for the methyl complexes. Since the electron density on the platinum atom in the dimethylplatinum(IV) cation is closer to that of the CF_3-Pt(II) cation than the CH_3-Pt(II) cation the reactivity towards imino ether formation should be similar to the CF_3-Pt(II) case. This is indeed supported by the formation of the bis-imino ether complex.

It has been shown that dimethylplatinum(IV) cations are quite stable with respect to reductive elimination and react very readily with C_6F_5CN to give imino ether complexes. In the next chapter the syntheses of trimethylplatinum(IV) cations are described and the relative ease with which these cations reduce to Pt(II) by elimination of ethane is discussed.

c) Experimental

Diiododimethylbis(dimethylphenylphosphine)platinum(IV) was prepared by the method of Ruddick and Shaw [49] with minor modifications. trans-$PtMeIQ_2$ was dissolved in methyl iodide and set aside for six hours. The methyl iodide was removed on a rotary evaporator to give, quantitatively, pure $PtMe_2I_2Q_2$ (characterized by melting point and nmr spectroscopy).

(i) Preparation of $[PtMe_2Q_2(NH{=}C(OMe){-}C_6F_5)_2](PF_6)_2$

$AgPF_6$ (0.123 g., 0.488 mmoles) was added to a magnetically stirred suspension of $PtMe_2I_2Q_2$ (0.184 g., 0.244 mmoles) in methanol. Silver iodide slowly precipitated over approximately a five minute period and was then removed by centrifugation to give a clear colourless solution. Pentafluorobenzonitrile (0.095 g., 0.488 mmoles) was added and after five minutes the solvent was removed to give white crystals which were recrystallized from methanol/ether to give the bis(imino ether) complex (0.100 g., 0.088 mmoles).

(ii) Preparation of $[PtMe_2Q_2(NC_5H_5)_2](PF_6)_2$

To a magnetically stirred solution of $PtMe_2I_2Q_2$ (0.180 g., 0.239 mmoles) in 10 ml. of acetone was added $AgPF_6$ (0.121 g., 0.478 mmoles). After five minutes the silver iodide was removed by centrifugation to give a clear colourless solution. Pyridine (0.045 g., 0.478 mmoles) was added and the solvent removed on a rotary evaporator to give a clear colourless oil. Methanol (2 ml.) was added and the flask was warmed on a water bath, causing the oil to crystallize. The flask was cooled and the white crystals were filtered off and washed with ether. Yield was 0.187 g., 0.197 mmoles (83%).

(iii) Preparation of $[PtMe_2Q_2(S_2CNEt_2)](PF_6)$

$AgPF_6$ (0.122 g., 0.482 mmoles) was added to a solution of $PtMe_2I_2Q_2$ (0.183 g., 0.243 mmoles) in acetone. The AgI was removed by centrifugation and sodium diethyldithiocarbamate (0.055 g., 0.243 mmoles) was added to give a yellow solution. The acetone was removed and the yellow solid was extracted from the $NaPF_6$ with dichloromethane. The addition of diethylether yielded pale yellow crystals which were filtered off and washed with ether. Yield was 0.142 g., 0.163 mmoles (67%).

(iv) Preparation of $[PtMe_2Q_2(CN\text{-}C_6H_4\text{-}OCH_3)I][BPh_4]$

To a solution of $PtMe_2I_2Q_2$ (0.211 g., 0.28 mmoles) in acetone was added p-$CH_3O\text{-}C_6H_4\text{-}NC$ (0.075 g., 0.56 mmoles). The solution was stirred for ten minutes and $AgPF_6$ (0.121 g., 0.56 mmoles) was added. The dirty yellow precipitate of AgI was removed by centrifugation. The solvent was removed to give an oil that could not be crystallized so $Na^+BPh_4^-$ (0.195 g., 0.56 mmoles) in methanol (5 ml.) was added. The solvent was removed and the complex extracted with dichloromethane and passed through a short florisil column to remove traces of colloidal silver. The complex was eluted with dichloromethane. The volume was reduced and the addition of diethyl ether yielded white crystals (0.160 g., 0.142 mmoles, 53%) which were filtered off and washed with ether.

A better yield of the iodoplatinum cations may be obtained by method (i) using a one molar equivalent of ligand and silver salt.

CHAPTER V

TRIMETHYLPLATINUM(IV) COMPLEXES AND REDUCTIVE ELIMINATION REACTIONS

a) Introduction

Many neutral, anionic and cationic platinum(IV) complexes [96] have been prepared from the first organoplatinum(IV) compound, trimethylplatinum(IV) iodide [95]. In contrast to the methyl-platinum(II) bond, which is readily cleaved [113], the methyl-platinum(IV) bond in the complexes $[PtMe_3X]_4$ is quite stable and may be cleaved only under vigorous conditions [97]. However, complexes of the type $PtMe_3L_2I$, where L = phosphine or arsine, have been found to pyrolyse [114] smoothly at temperatures > 100°C with loss of ethane.

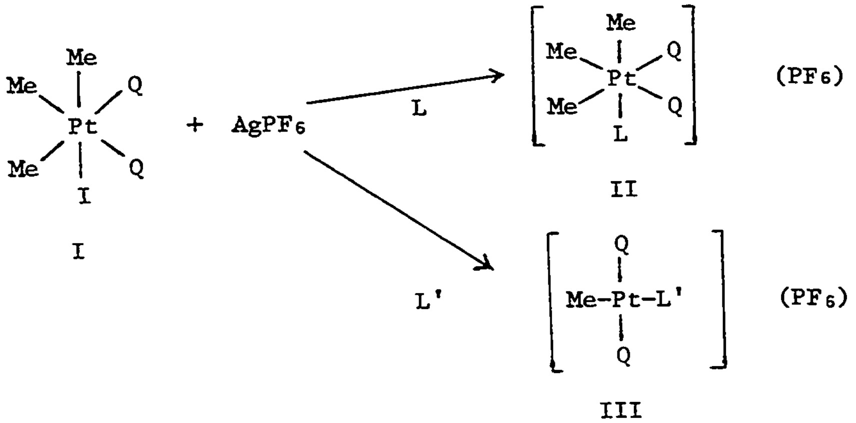
In the previous chapter we discussed the preparation and reactivity of a wide variety of cationic dimethylplatinum(IV) complexes [115] of the type $[PtMe_2Q_2L_2]^{+2}$ or $[PtMe_2Q_2LI]^{+}$, where Q is dimethylphenylphosphine and L is a neutral or anionic ligand. These complexes were found to be quite stable; reduction occurred only when L was a large and bulky ligand such as triphenylphosphine, -arsine and -stibine, or when the platinum-ligand bond required much Pt $d\pi \rightarrow L\pi^*$ back bonding for its stability (i.e. CO).

In this chapter the preparation and stability, with respect to reductive elimination, of the complexes *fac*-$[PtMe_3Q_2L]^+$, where $Q = PMe_2Ph$, CNC_6H_4Me, $AsMe_3$, or NC_5H_5, and L is a variety of neutral ligands are discussed. The oxidative addition of CD_3I to *cis*-$PtMe_2Q_2$ ($Q = PMe_2Ph$ and $AsMe_3$) and the stereochemistry of the CD_3-Pt(IV) compounds are also discussed.

b) Results and Discussion

(i) Preparation of the Complexes

The iodide in *fac*-$PtMe_3Q_2I$, I, where Q is dimethylphenylphosphine, may be removed easily in solution, as silver iodide, by the addition of AgX where X is a non-coordinating anion, e.g. $AgPF_6$. In the presence of a neutral ligand L, a variety of platinum(IV) cations, II, are obtained while for L', reductive elimination occurs to give the corresponding methylplatinum(II) cations, III, as shown in reaction (1).



(1)

L = NC_5H_5, PMe_2Ph, $P(OMe)_3$,	L' = MeCOMe, MeOH, NC-CH=CH_2,
CN-C_6H_4-Me, CN-C_6H_4-OMe,	NC-C_6H_4-OMe, $SbPh_3$, $AsPh_3$,
CN-Me, CN-Et, $SbMe_3$	PPh_3, HC≡C-CH_2-CH_2-OH

Thus, addition of silver hexafluorophosphate to a solution of I in acetone or methanol readily causes discolouration with effervescence. However, if the solution contains a ligand L, the iodide is removed cleanly. In the absence of a silver salt no displacement of iodide by L occurs; a solution of p-tolylisocyanide and I in dichloromethane showed no evidence of reaction after one week.

The trimethylplatinum(IV) cations, II, give stable salts (usually as the hexafluorophosphate) which melt sharply with effervescence. Analytical, physical and Raman data for the complexes are given in Table V-1.

(ii) NMR Spectra

The phosphine methyl resonances of the Pt(IV) complexes, II, appear as doublets due to coupling with the ^{31}P nucleus and are flanked by ^{195}Pt satellites of one fourth intensity. Such a pattern is associated with cis-phosphines [36] where $^2J(^{31}P-^{31}P)$ is small. For many of the complexes two overlapping doublets are observed (Figure V-1) due to non-equivalent phosphine methyls P(MeMe'Ph), the non-equivalence being attributable to restricted rotation of the phosphine about the Pt←P bond.

Two distinct resonances may be assigned to the platinum-methyl groups. The resonance for the two methyl groups trans to phosphine appears as a complicated pattern (Figure V-1,B) quite typical of the

Table V-1 Analytical, Physical and Raman Data for Trimethylplatinum(IV) Complexes

Complex[a]	Analyses Calculated (Found)		Melting Point[b]	Recrystallization[c]	Raman Data (cm^{-1})			
	Carbon	Hydrogen	°C	Solvents	$\nu(Pt\text{-}CH_3)$	$\nu(N{\equiv}C)$	$\Delta\nu(N{\equiv}C)$	Other
$[Pt(CH_3)_3Q_2(NC_5H_5)](PF_6)$	38.92 (39.01)	4.90 (4.69)	99-100	A	569,561,524			
$[Pt(CH_3)_3Q_3](PF_6)$	40.56 (40.50)	5.29 (5.27)	155-156	A	530,525,510			
$[Pt(CH_3)_3Q_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$	57.56 (57.55)	6.30 (6.09)	141-142	B	515			
$[Pt(CH_3)_3Q_2\{Sb(CH_3)_3\}](PF_6)$	31.89 (32.05)	4.87 (4.65)	135-136	C	539,523,516			$\nu(Sb\text{-}CH_3)$=531
$[Pt(CH_3)_3Q_2(CN\text{-}C_6H_4CH_3)](PF_6)$	41.65 (41.68)	4.92 (4.79)	180-182	A	541,521,511	2210	85	
$[Pt(CH_3)_3Q_2(CNC_6H_4OCH_3)](PF_6)$	40.81 (40.78)	4.82 (4.81)	171-172	A	544,520,512	2210	85	
$[Pt(CH_3)_3Q_2(CNCH_3)][B(C_6H_5)_4]$	61.65 (61.89)	6.25 (6.48)	144-146	D	548,522,514	2243	73	
$[Pt(CH_3)_3Q_2(CNC_2H_5)](PF_6)$	36.88 (36.90)	5.06 (4.73)	103-108	A	546	2260	109	
$[Pt(CH_3)_3A_2(NC\text{-}C_6F_5)](PF_6)$	23.49 (23.40)	3.33 (2.95)	125-128	A	540,531	2280		
$[Pt(CH_3)_3A_2\{P(CH_3)_2C_6H_5\}](PF_6)$	26.75 (26.42)	5.02 (4.72)	145-150	A	e			
$[Pt(CH_3)_3A_2(\overline{C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O})](PF_6)$	f		90- 92	A	e			
$[Pt(CH_3)_3(CNC_6H_4CH_3)_3](PF_6)$	44.02 (43.92)	4.11 (3.90)	170-173	A	555	2236,2211	111,86	
$[Pt(CH_3)_3(CNC_6H_4CH_3)_2\{P(CH_3)_2C_6H_5\}](PF_6)$	42.80 (42.65)	4.52 (4.39)	161-162	A	551,542,520	2220,2207	95,82	
$[Pt(CH_3)_3(NC_5H_5)_2\{P(CH_3)_2C_6H_5\}](PF_6)$	37.01 (36.90)	4.44 (4.34)	108-110	E	580,572,538			
$Pt(CH_3)_3A_2I$	17.81 (17.67)	4.45 (4.31)	177-180	E	546,532			$\nu(As\text{-}CH_3)$=591
$Pt(CH_3)_3Q_2I$	d			E	544,531,521			
$Pt(CH_3)_2(CD_3)A_2I$	d			E	547,533,507			$\nu(As\text{-}CH_3)$=591
$Pt(CH_3)_2(CD_3)Q_2I$	d			E	532,520,502			
$Pt(CH_3)_3(CNC_6H_4CH_3)_2I$	37.94 (37.95)	3.85 (3.60)	143-146	E	563,536	2208,2198	83,73	

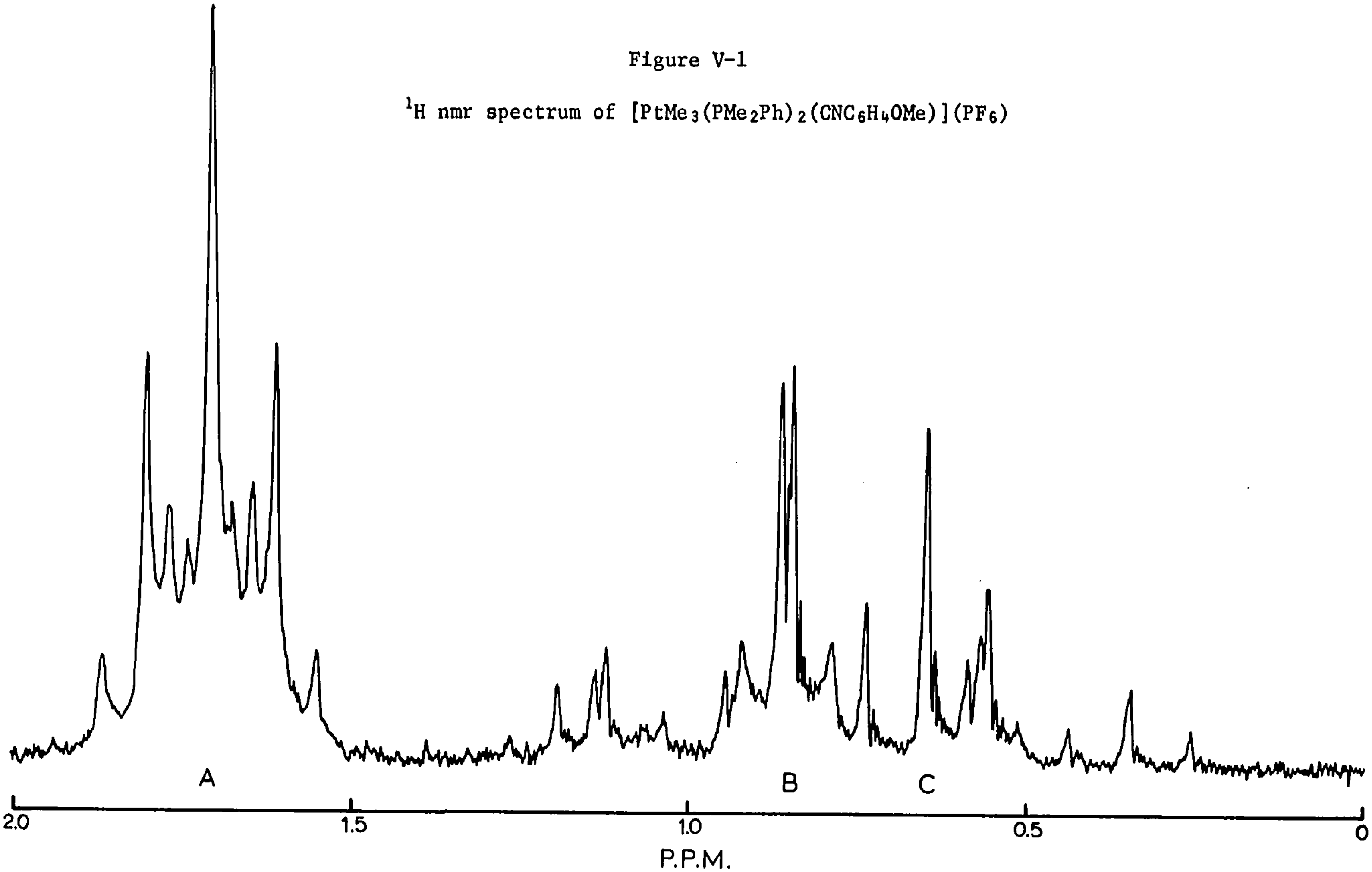
a. Q = $P(CH_3)_2C_6H_5$, A = $As(CH_3)_3$; all complexes are colourless. b. Melting points are uncorrected

c. A = $CH_2Cl_2/(C_2H_5)_2O$, B = CH_3OH, C = $CHCl_3/(C_2H_5)_2O$, D = $(CH_3OH)/(C_2H_5)_2O$, E = CH_2Cl_2/ n-C_5H_{12}

d. not analysed. e. decomposed in the laser beam. f. not analysed due to instability.

Figure V-1

^1H nmr spectrum of $[PtMe_3(PMe_2Ph)_2(CNC_6H_4OMe)](PF_6)$



A part of $A_3A_3'XX'$ spectrum. A recent spectral analysis [116] of cis-$PtMe_2(PMe_2Ph)_2$ showed that trans-$^3J(^{31}P-^1H)$ is only slightly greater than cis-$^3J(^{31}P-^1H)$ and that the coupling constants have opposite signs.

The platinum-methyl group trans to L appears as a triplet (Figure V-1,C) due to equal coupling with the two cis phosphines and is accompanied by ^{195}Pt satellites. Each platinum-methyl resonance in the spectrum $[PtMe_3(PMe_2Ph)_2\{P(OMe)_3\}]^+$ is further split into a doublet by the ^{31}P nucleus of trimethylphosphite.

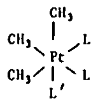
The NMR spectrum of the complex $[PtMe_3(PMe_2Ph)_3](PF_6)$ shows a very complicated resonance in the platinum methyl region (Figure V-2) due to an $A_3A_3'A_3''XX'X''$ spin system.

^1H NMR data for the trimethyl platinum(IV) complexes are given in Table V-2.

(iii) Stability vs. Reductive Elimination

In the previous chapter an NMR trans-influence series for Pt(IV) was established (Table V-3) and from equation 1 it may be seen that stable platinum(IV) cations (II, with Q = PMe_2Ph) are obtained only for ligands L with a trans-influence equal to or greater than that of pyridine. The pyridine complex, although quite stable in the solid state, slowly decomposes in solution to give trans-$[PtMeQ_2(NC_5H_5)](PF_6)$ while the complex $[PtMe_3Q_3](PF_6)$ is stable for weeks in acetone solution. It is tempting to postulate that reduction will occur if any one of the three ligands has a relatively low trans-influence; yet the complexes $[PtMe_3(OH_2)_3]^+$ [117] and $[PtMe_3(NC_5H_5)_3]^+$ [118] are quite stable and exhibit no tendency towards reductive decomposition. Since the reason for this resistance to reduction is not obvious the importance

Table V-2 ^1H NMR Data[c] for Trimethylplatinum(IV) Complexes



Complex[a]	Phosphine Methyls			Methyls Trans to L			Methyl Trans to L′			Other Resonances
	$\delta(CH_3)$	$J(P\text{-}H)$	$J(Pt\text{-}H)$	$\delta(CH_3)$	$J(P\text{-}H)$	$J(Pt\text{-}H)$	$\delta(CH_3)$	$J(P\text{-}H)$	$J(Pt\text{-}H)$	
$[Pt(CH_3)_3Q_2(NC_5H_5)](PF_6)$	1.54	8.5	14.0	0.94	b	53.0	0.65	8.5	68.0	
	1.49	9.0	14.0							
$[Pt(CH_3)_3Q_2(CNC_2H_5)](PF_6)$	1.70	9.8	15.8	0.71	b	53.6	0.52	9.2	61.2	$\delta(CH_3)=1.35$, $\delta(CH_2)=3.72$
	1.60	10.0	16.0							
$[Pt(CH_3)_3Q_2(CNC_6H_4OCH_3)](PF_6)$	1.66	9.6	15.8	0.84	b	54.4	0.68	9.1	61.2	$\delta(OCH_3)=3.90$
	1.63	9.9	16.0							
$[Pt(CH_3)_3Q_2(CNCH_3)][B(C_6H_5)_4]$	1.65	9.4	15.6	0.85	b	55.6	0.64	8.9	60.8	$\delta(CH_3)=2.73$
	1.54	9.4	15.6							
$[Pt(CH_3)_3Q_2(CNC_6H_4CH_3)](PF_6)$	1.77	9.6	15.6	0.87	b	55.0	0.66	9.0	60.0	$\delta(CH_3)=2.49$
	1.68	9.4	15.6							
$[Pt(CH_3)_3Q_2\{Sb(CH_3)_3\}](PF_6)$	1.87	8.8	15.2	0.75	b	54.4	1.02	8.2	60.0	$\delta(CH_3)=0.98$
	1.81	8.7	14.6							
$[Pt(CH_3)_3Q_3](PF_6)$	1.98	8.5	14.0	0.58	b	54.5	0.58		54.5	
$[Pt(CH_3)_3Q_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$	1.69	9.4	15.0	0.69	8.4^d	54.2	0.42	9.5	53.8	$\delta(OCH_3)=3.78$, $J(P\text{-}H)=10.8$
								8.8^d		
$[Pt(CH_3)_3A_2(NC\text{-}C_6F_5)](PF_6)$				1.02	-	59.4	0.84	-	77.4	$\delta(As\text{-}CH_3)=1.50$, $J(Pt\text{-}H)=7.0$
$[Pt(CH_3)_3A_2\{P(CH_3)_2C_6H_5\}](PF_6)$	1.88	8.0^d	14.6	0.78	-	60.2	0.79	8.2^d	60.8	$\delta(As\text{-}CH_3)=1.49, 1.32$ $J(Pt\text{-}H)=6.8$
$[Pt(CH_3)_3A_2(:\overline{CCH_2CH_2CH_2O})](PF_6)$				0.83	-	61.8	0.20	-	49.0	$\delta(OCH_2)=3.35^t$, $\delta(OCCH_2)=2.10^q$, $\delta(CCH_2)=1.56^t$
										$\delta(As\text{-}CH_3)=1.38$, $J(Pt\text{-}H)=7.0$
$[Pt(CH_3)_3(CNC_6H_4CH_3)_3](PF_6)$				1.16	-	63.6	1.16		63.6	$\delta(CH_3)=2.48$
$[Pt(CH_3)_3(CNC_6H_4CH_3)_2\{P(CH_3)_2C_6H_5\}](PF_6)$	1.98	10.0^d	16.2	0.79	8.8^d	62.8	1.02	6.8^d	55.6	$\delta(CH_3)=2.40$
$[Pt(CH_3)_3(NC_5H_5)_2\{P(CH_3)_2C_6H_5\}](PF_6)$	1.63	8.6^d	13.6	1.02	8.4^d	67.2	0.95	7.2^d	54.5	
$Pt(CH_3)_3A_2I$				1.23	-	63.6	0.91		72.8	$\delta(As\text{-}CH_3)=1.44$, $J(Pt\text{-}H)=7.0$
$Pt(CH_3)_3(CNC_6H_4CH_3)_2I$				1.34		64.0	1.44		73.3	$\delta(CH_3)=2.44$

a. $Q = P(CH_3)_2C_6H_5$, $A = As(CH_3)_3$; b. Coupling cannot be directly obtained; c. d - doublet, t - triplet, q - quintet

Figure V-2

Platinum-methyl resonances in the NMR spectrum of _fac_-[PtMe$_3$(PMe$_2$Ph)$_3$](PF$_6$)

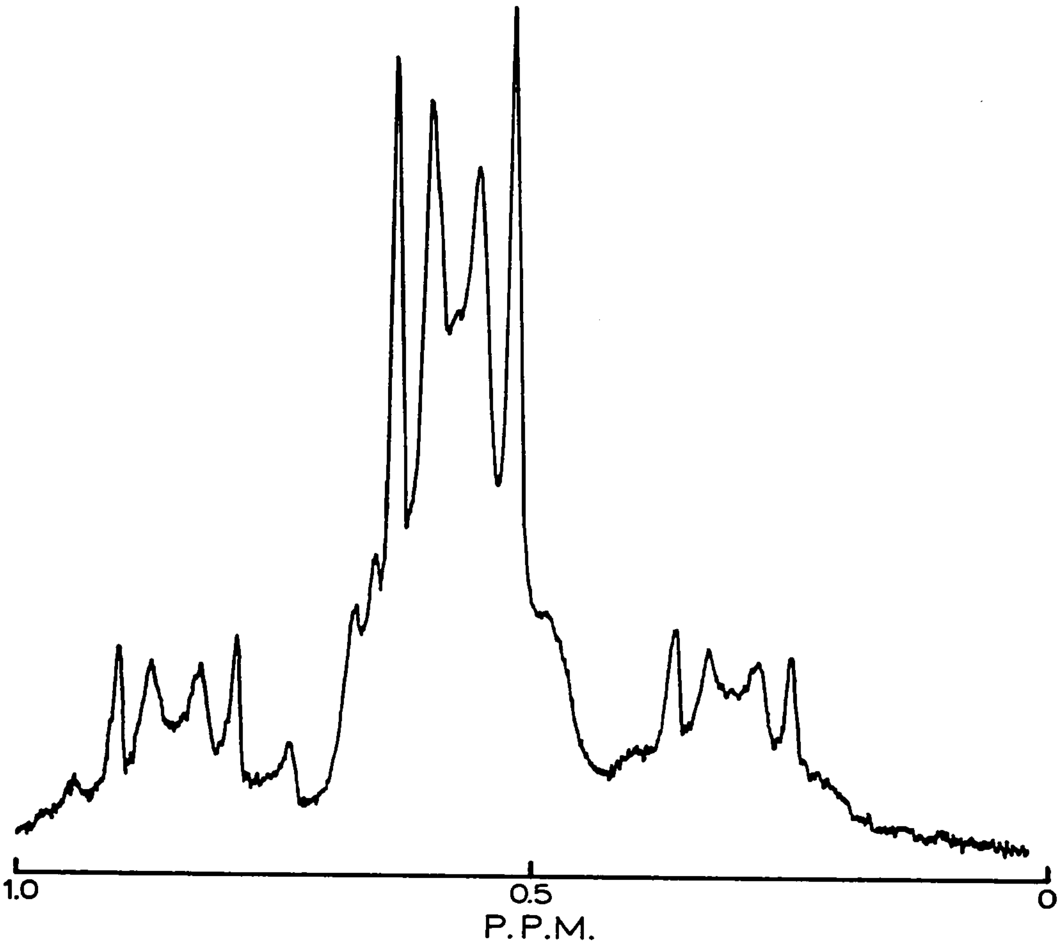


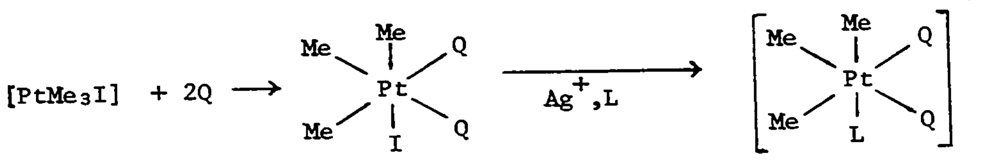
Table V-3

An NMR <u>Trans</u>-Influence Series for Complexes $[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2\text{L}_2]^{+2}$ and $[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2\text{LI}]^{+}$

<u>L</u>	$^2J(\text{Pt-H})$
$\text{NC-C}_6\text{H}_4\text{-OMe}$	70.2
1,10-phenanthroline	65.5
$\text{NH=C(OMe)-C}_6\text{F}_5$	65.2
NC_5H_5	60.8
P(OMe)_3	60.0
CN-Me	58.2
CN-Et	58.2
$\text{CN-C}_6\text{H}_4\text{-Me}$	58.0
$\text{CN-C}_6\text{H}_4\text{-OMe}$	57.0
PMe_2Ph	50.5
$:\overline{\text{C-CH}_2\text{CH}_2\text{CH}_2\text{O}}$	47.0

of the ligand Q in determining the stability of the cations was investigated.

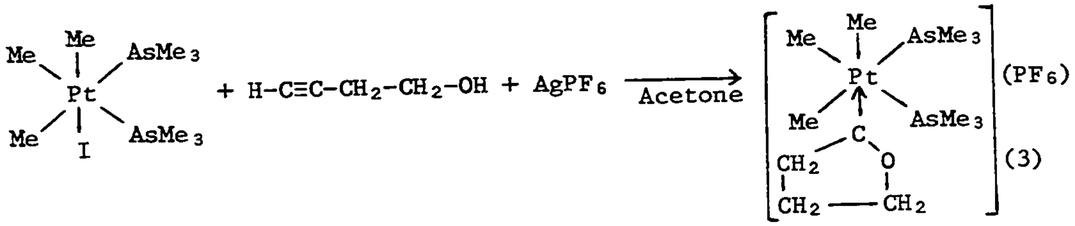
Trimethylplatinum(IV) iodide reacts smoothly with two molar equivalents of isocyanide, pyridine, or trimethylarsine as shown in equation (2).



IV V (2)

Q = $AsMe_3$, CNC_6H_4Me, NC_5H_5

For each of the compounds, IV, an attempt was made to prepare trimethylplatinum(IV) cations, V, with ligands L of high and low <u>trans</u>-influence. With Q = CNC_6H_4Me the cations, V, were stable for L having a <u>high</u> <u>trans</u>-influence while reduction occurred for L = nitrile, a ligand of <u>low</u> <u>trans</u>-influence. With trimethylarsine and pyridine as ligands all platinum(IV) cations were stable and exhibited no tendency to reduce. The apparent stability of the trimethylarsine cations, V, (Q = $AsMe_3$) with ligands L of high and low <u>trans</u>-influence suggested that it might be possible to prepare a stable Pt(IV) carbene cation by the use of the acetylene 1-butyn-4-ol (equation 3).



VI (3)

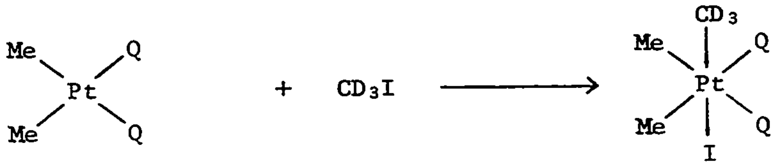
The NMR spectrum of the carbene cation, VI, supports the cyclic structure of the carbene, viz, the α-alkoxy ($O-CH_2-$) and α-carbene ($C-CH_2-$) protons appear as triplets at 3.35 and 1.56 δ respectively and the β-alkoxy protons ($O-C-CH_2$) appear as a quintet at 2.10 δ.

The series of cations, V, L = PMe_2Ph and Q = $CN-C_6H_4-Me$, $AsMe_3$ and NC_5H_5 also provide interesting NMR spectroscopic data. For the isocyanide and pyridine cations cis-$^3J(^1H-C-Pt-^{31}P)$ is slightly greater than trans-$^3J(^1H-C-Pt-^{31}P)$ (Table V-2) while for the arsine cation there is no apparent coupling cis-$^3J(H-P)$ yet there is a substantial trans-coupling, $^3J(H-C-Pt-^{31}P)$ = 8.2 Hz. The NMR spectrum of $[PtMe_3(AsMe_3)_2(PMe_2Ph)]^+$ also shows two resonances which may be attributed to the arsine methyls. The separation between these two peaks is field dependent (17.5 Hz at 100 MHz and 10.5 Hz at 60 MHz) and is thus not due to coupling with phosphorus but asymmetry of the arsines. This must arise from restricted rotation of the phosphine and a preferred orientation of the phenyl group near one of the arsines.

The following conclusions may be drawn regarding the stability of trimethylplatinum(IV) cations. Trimethylplatinum(IV) cations will reduce to Pt(II) by elimination of ethane provided that two conditions are met: (i) two of the three methyl groups must be trans to ligands of high trans-influence, e.g. $[PtMe_3(PMe_2Ph)_2(NC_5H_5)]^+$ reduces to $[PtMe(PMe_2Ph)_2NC_5H_5]^+$ whereas $[PtMe_3(PMe_2Ph)(NC_5H_5)_2]^+$ is quite stable; (ii) the three platinum methyl groups must not be chemically equivalent, e.g. $[PtMe_3(PMe_2Ph)_3]^+$ and $[PtMe_3(MeOH)_3]^+$ are quite stable whereas $[PtMe_3(PMe_2Ph)_2(MeOH)]^+$ reduces immediately to Pt(II). These results suggest that it is the two equivalent methyl groups trans to the ligands

Q of high trans-influence that are labilized and couple to form ethane during the reductive elimination reaction. An attempt to prove this was made by isotopically labelling one of the platinum-methyl groups. Unfortunately the results are inconclusive, in that while they indicate a preference for Pt-CH_3 rather than Pt-CD_3 cleavage, they cannot readily be related to the relative trans-influence of the ligands Q and L.

Thus, iodomethane-d_3 oxidizes cis-$PtMe_2Q_2$, where Q = PMe_2Ph or $AsMe_3$, giving exclusively trans-addition (equation 4).

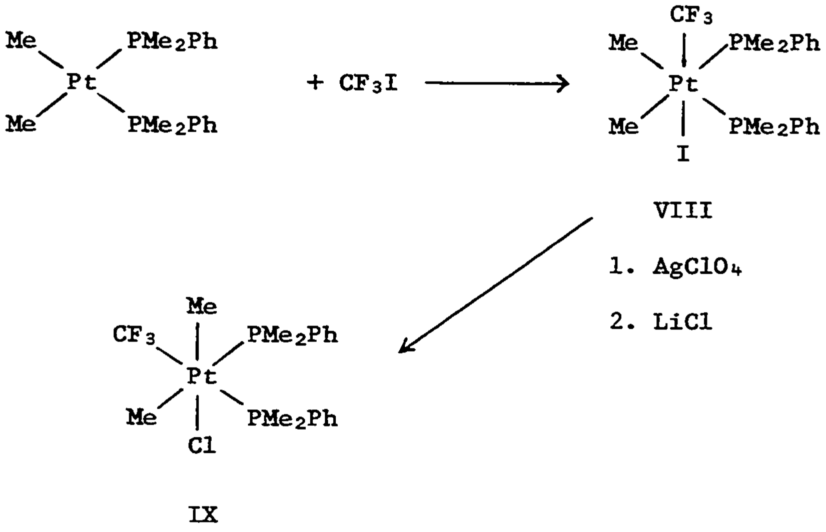


(4)

VII

A similar stereospecific oxidative addition is also observed in the addition of bromomethane to trans-Ir(CO)Cl$(PPh_3)_2$ and is believed to entail an SN2 type attack involving an unsymmetrical transition state [4].

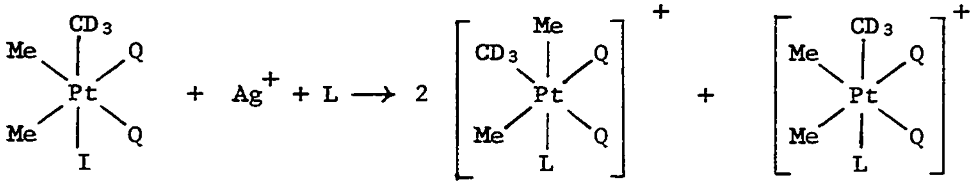
It has recently been shown [48] that oxidative addition reactions of Pt(II) usually give trans-addition although these products may not necessarily be the most thermodynamically stable. For example, the addition of CF_3I to cis-$PtMe_2(PMe_2Ph)_2$ gave VIII (equation 5).



(5)

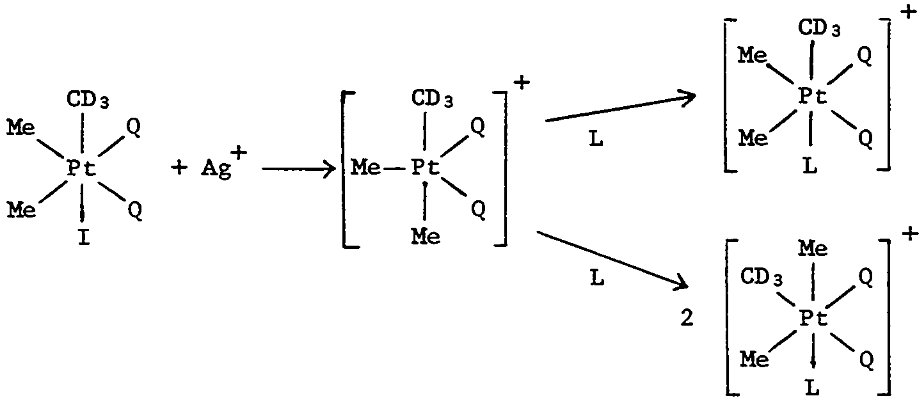
Removal of the iodide from VIII with silver perchlorate followed by the addition of lithium chloride to the solution gave mainly IX. Presumably the isomerization activation energy was lowered by the removal of iodide ion and formation of the cationic intermediate.

The NMR spectra of the stable Pt(IV) cations $[PtMe_2(CD_3)Q_2L]^+$, (where Q = PMe_2Ph and L = $CN-C_6H_4-Me$, NC_5H_5 or $P(OMe)_3$; and Q = $AsMe_3$ with L = $NC-C_6F_5$) show the presence in solution of two geometrical isomers in the ratio of 2:1 as shown in equation 6.



(6)

Many octahedral substitution reactions proceed by a dissociative pathway [53,119-121] involving a five coordinate intermediate and this is probably the reason for the scrambling of the methyl groups during the preparation of the Pt(IV) cations (equation 7).



(7)

Since the isotopic scrambling occurs much quicker than the rate of reduction it is not possible to observe reductive elimination from a stereospecifically labelled Pt(IV)-cation. After reduction the ratio of Pt(II)-CH_3 to Pt(II)-CD_3 should be 2:1 regardless of the trans-influences of the other three ligands. However, the addition of $AgPF_6$ and p-NC-C_6H_4OMe to an acetone solution $PtMe_2(CD_3)(PMe_2Ph)_2I$ gave a mixture of Pt(II) cations containing 55% Pt-CH_3 and 45% Pt(II)-CD_3. At this time we are unable to explain why the Pt-CD_3 bond is more resistant to cleavage than the Pt-CH_3 bond.

Pyrolysis of $PtMe_3(PMe_2Ph)_2I$ at 165°C proceeds very smoothly with concomitant loss of ethane [114]. A similar pyrolysis of VII gave a mixture of 54% trans-$PtMe(PMe_2Ph)_2I$ and CD_3-CH_3 and 46% trans-$Pt(CD_3)(PMe_2Ph)_2I$ and CH_3-CH_3. The relative proportions of each Pt(II) complex were determined by integration of the platinum-methyl-h_3 resonance against the phosphine methyl resonances and are estimated to be accurate to ±5%. The percentages of Pt(II)-CH_3 and Pt(II)-CD_3 are very close to the values obtained by reduction of the platinum(IV) cations suggesting that the mechanisms of reductive elimination are similar. Since the solids melt before effervescence occurs we believe that isomerization probably takes place before reductive elimination and again the greater amount of $Pt(II)-CD_3$ (46%) supports the observation that the $Pt-CD_3$ bond is more resistant to cleavage than the $Pt-CH_3$ bond.

(iv) Infrared and Raman Spectroscopic Data

The platinum-methyl stretching vibration appears as a very strong, sharp band in the Raman spectrum and is very weak in the infrared spectrum. Clegg and Hall [122] have examined the vibrational spectra for the trimethyl cations $[PtMe_3L_3]^+$, where L = OH_2 or NH_3. For such cations of C_{3v} symmetry, two platinum-methyl vibrations are expected, an A_1 and E mode. Since most of the present cations contain large and bulky phosphines the symmetry of the molecule is reduced to C_s, thus splitting the degenerate E mode in C_{3v} symmetry into an A' and A" mode. Thus three Raman active bands are expected in the 500-600 cm^{-1} region ascribable to the $Pt-CH_3$ stretching vibrations and in most cases (Table V-1) three are observed.

The solid state Raman spectra of $PtMe_3(PMe_2Ph)_2I$ and $PtMe_2(CD_3)(PMe_2Ph)_2I$ show three very strong peaks at 544, 531 and 521, and 532, 520 and 502 cm^{-1} respectively (Figure V-3). On deuteration the high frequency band is lowered in frequency by a factor of $(15/18)^{1/2}$ indicating that the platinum-methyl group trans to I moves as a unit [123] and is not coupled to any extent to other vibrations. Therefore, within a series of trimethyl platinum(IV) cations the high frequency platinum-methyl stretching vibration should decrease as the NMR trans-influence of the ligand L increases. Although the series is limited the trend

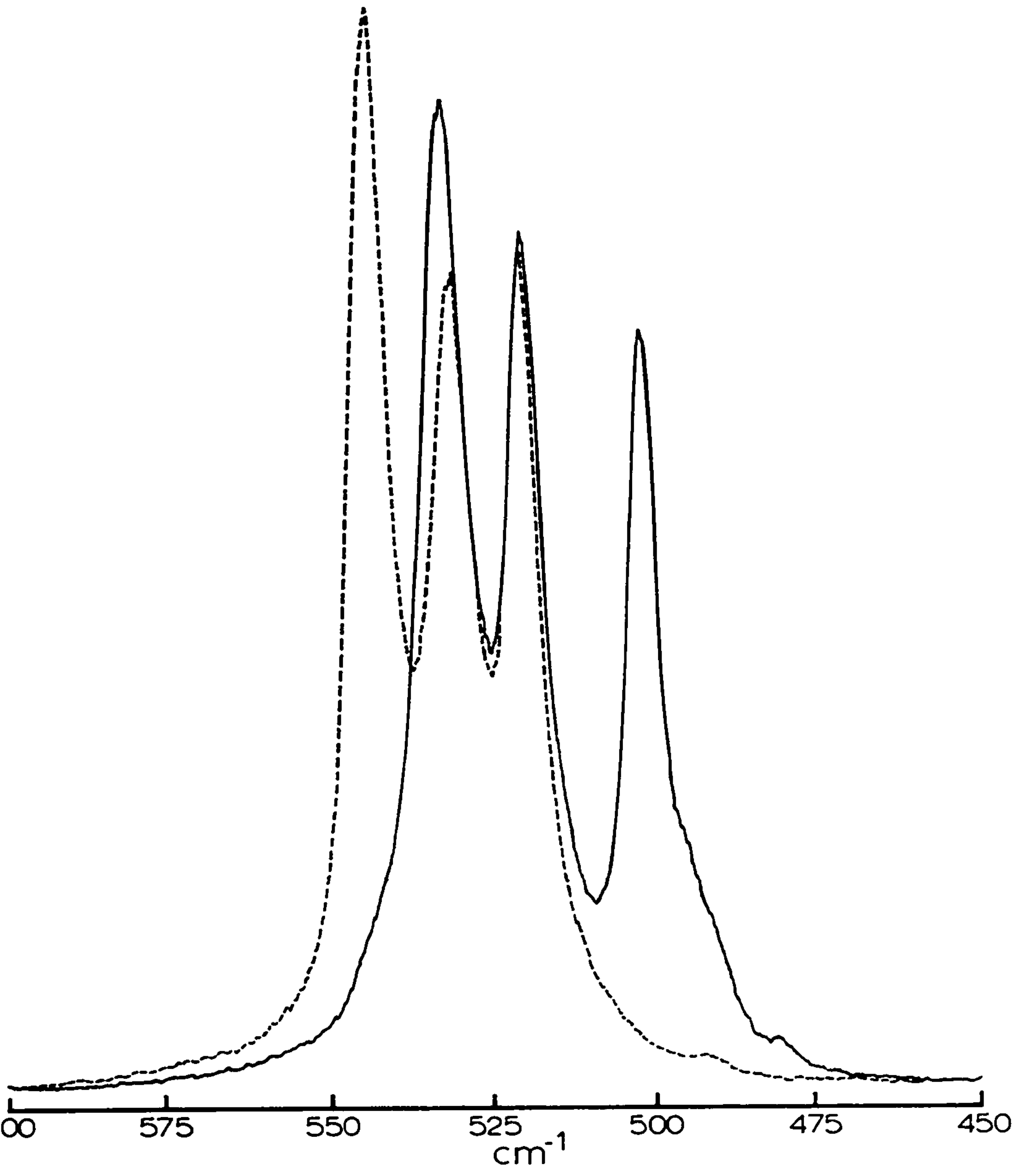


Figure V-3

Raman spectra of $PtMe_2(CD_3)(PMe_2Ph)_2I$ (——)

and $PtMe_3(PMe_2Ph)_2I$ (---)

does hold as shown in Table V-4 for the cations $[PtMe_3(PMe_2Ph)_2L]^+$.

c) Conclusions

A variety of trimethylplatinum(IV) cations have been prepared and reductive elimination reactions of these cations have been studied. Several conditions have been postulated that must be met before reductive elimination occurs. Prior to this work all trimethylplatinum (IV) cations had contained ligands of low trans-influence and hence were quite stable towards reductive elimination. Therefore it is quite clear that the ligands on platinum must be carefully chosen when examining reactions of trimethylplatinum(IV) cations.

d) Experimental

Iodotrimethylbis(dimethylphenylphosphine) platinum(IV) was prepared by the method of Ruddick and Shaw [49] with minor modifications. cis-$PtMe_2Q_2$ (Q = dimethylphenylphosphine) was dissolved in methyl iodide. The solution became quite warm and white crystals of $PtMe_3Q_2I$ precipitated from solution. The flask was allowed to cool, the ether was decanted and the crystals were washed with diethyl ether. The yield was quantitative and the product was obtained spectroscopically pure.

$PtMe_3I$ was prepared by the method of Hall and Clegg [124].

(i) Preparation of $PtMe_2(CD_3)Q_2I$

As above only the CD_3I was distilled, under vacuum into a flask containing $PtMe_2Q_2$ at liquid nitrogen temperature. The flask was allowed to warm up to room temperature at which time the $PtMe_2(CD_3)Q_2I$ crystallized from solution. The excess CD_3I was distilled into an

Table V-4

A Comparison of $^2\underline{J}$(Pt-C-H) and ν(Pt-Me) for the Cations <u>fac</u>-$[PtMe_3(PMe_2Ph)_2L]^+$

<u>L</u>	$^2\underline{J}$(Pt-C-H)	ν(Pt-Me)
NC_5H_5	68.0	569
CNEt	61.2	546
CNC_6H_4Me	60.0	541
$SbMe_3$	60.0	539
PMe_2Ph	54.5	530

ampoule and sealed under vacuum.

(ii) Preparation of $PtMe_3(CN\text{-}C_6H_4\text{-}Me)_2I$

To a benzene solution of $PtMe_3I$ (0.173 g., 0.470 mmoles) was added p-CNC_6H_4Me (0.110 g., 0.940 mmoles). The solution was stirred for 10 minutes and the volume of the benzene was reduced. The addition of diethyl ether yielded pale yellow crystals of $PtMe_3(CN\text{-}C_6H_4\text{-}Me)_2I$ (0.260 g., 0.434 mmoles).

(iii) Preparation of $PtMe_3(AsMe_3)_2I$

cis-$PtMe_2(AsMe_3)_2$ was dissolved in methyl iodide and the solution became bright yellow. After 10 minutes the methyl iodide was removed on a rotary evaporator to give a yellow solid which was recrystallized from dichloromethane and pentane. The yield was quantitative.

(iv) Preparation of $[PtMe_3Q_2(NC_5H_5)](PF_6)$

Pyridine (0.027 g., 0.342 mmoles) was added to a solution of $PtMe_3Q_2I$ (0.215 g., 0.336 mmoles) in 10 ml. of acetone. $AgPF_6$ (0.084 g., 0.336 mmoles) in 2 ml. of acetone was added dropwise and AgI precipitated immediately from solution. The solution was stirred for 10 minutes and the AgI removed by centrifugation to give a clear colourless solution. The acetone was removed on a rotary evaporator and the oil was taken up in 2 ml. of dichloromethane. Ether was added and the flask was placed in a refrigerator at 0°C for 30 minutes to give white needles of $[PtMe_3Q_2(NC_5H_5)](PF_6)$ (0.231 g., 0.312 mmoles). The crystals were filtered, washed with ether and recrystallized from dichloromethane and ether.

(v) Preparation of [$PtMe_3Q_3$](PF_6)

To a solution of $PtMe_3Q_2I$ (0.495 g., 0.780 mmoles) in 30 ml. of acetone was added PMe_2Ph (0.106 g., 0.790 mmoles). $AgPF_6$ (0.195 g., 0.780 mmoles) was added, silver iodide precipitated immediately from solution and was removed by centrifugation to give a dark-coloured solution. The acetone was removed on a rotary evaporator and the black oil was taken up in dichloromethane and passed through a 3" florisil column, eluting with dichloromethane, to remove colloidal silver and platinum. A clear colourless solution was obtained. The volume of solvent was reduced, diethyl ether was added until the solution became cloudy and the flask was cooled at 0°C for two hours to give white needles. The crystals (0.460 g., 0.575 mmoles) were filtered, washed with ether and recrystallized from dichloromethane and diethyl ether.

(vi) Preparation of [$PtMe_3Q_2\{P(OMe)_3\}$][BPh_4]

The complex was prepared by method (v) except that a crystalline product could not be obtained with PF_6^- as the anion. Consequently the oil was dissolved in a small volume of methanol and an equivalent amount of Na(BPh_4) was added. The white precipitate which formed immediately was filtered and washed with methanol then recrystallized from methanol to give white needles. Yield was 75%.

(vii) Attempted preparation of [$PtMe_3Q_2(CO)$](PF_6)

Carbon monoxide was bubbled through a solution of $PtMe_3Q_2I$ (0.130 g., 0.202 mmoles) and an equivalent amount of $AgPF_6$ was added. The precipitated silver iodide was removed by centrifugation to give a clear colourless solution. The acetone was removed and the oil dissolved in methanol. $NaBPh_4$ (0.070 g., 0.202 mmoles) was added and a white precipitate of $[PtMeQ_2(CO)][BPh_4]$ (0.082 g., 0.10 mmoles) formed. The solid was filtered and recrystallized from dichloromethane and ether.

(viii) Preparation of $[PtMe_3(CN{-}C_6H_4{-}Me)_3](PF_6)$

To a solution of $PtMe_3(CN{-}C_6H_4{-}Me)_2I$ (0.144 g., 0.240 mmoles) in acetone was added a molar equivalent of $AgPF_6$ (0.061 g.). Silver iodide precipitated rapidly and was removed by centrifugation to give a colourless solution; $p{-}CN{-}C_6H_4{-}Me$ (0.028 g., 0.240 mmoles) was added, the solvent removed on a rotary evaporator and the oil was dissolved in dichloromethane. The addition of diethyl ether gave white crystals of $[PtMe_3(CN{-}C_6H_4{-}Me)_3](PF_6)$ (0.147 g., 0.200 mmoles).

(ix) Preparation of $[PtMe_3(AsMe_3)_2(:\overline{C{-}CH_2CH_2CH_2O})](PF_6)$

$AgPF_6$ (0.079 g., 0.312 mmoles) was added to a solution of $PtMe_3(AsMe_3)_2I$ (0.190 g., 0.312 mmoles) in 10 ml. acetone. The AgI was removed by centrifugation to give a clear colourless solution. 1-Butyn-4-ol (0.312 mmoles) was added, the solution stirred for 10 minutes and the solvent was removed on a rotary evaporator to give a white solid that was recrystallized from dichloromethane and ether to give white needles. Yield was 85%. The crystals slowly darkened and decomposed over a period of a few hours even when stored under nitrogen.

(x) Pyrolysis of $PtMe_2(CD_3)Q_2I$

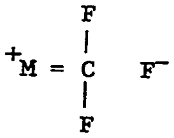
0.100 g. of $PtMe_2(CD_3)Q_2I$ was placed in the bottom of a 25 ml. round-bottom flask. The flask was evacuated and the bottom was placed in the preheated oil bath at 165°C. Effervescence immediately occurred leaving a white solid. The evolved gases were analyzed by mass spectrometry and infrared spectroscopy. The solid residue was then recrystallized from methanol to give white needles. The NMR was recorded and the platinum-methyl peak was integrated against the phosphine methyls.

CHAPTER VI

TRIFLUOROMETHYLPLATINUM COMPLEXES AND THE NATURE OF THE Pt-CF_3 BOND

a) Introduction

Perfluoroalkyl groups are of interest in organometallic chemistry because of the great stability of their complexes with transition metals compared with the corresponding alkyl-metal compounds. It has been suggested [125-127] that this stability is due at least in part to π-backbonding between filled d-orbitals on the metal atom and σ^*-orbitals of the perfluoroalkyl group, or, in valence-bond terms, hyperconjugation of the type



$$^{+}M = \overset{\displaystyle F}{\underset{\displaystyle F}{C}} \quad F^{-}$$

Evidence from infrared spectra [128] and short metal-carbon bond lengths combined with large M-C-F angles in crystal structures of fluoroalkyl complexes [129,130] seem to support this postulate. However, an alternative explanation for the infrared data has been given [131], and Graham's interpretation of carbonyl force constants [132] suggests that π-backbonding is not important. Consequently, this whole question must be considered an open one, especially in the current period of reaction against an earlier over-indulgence in invoking π-backbonding in inorganic chemistry generally. It is worth noting that evidence has been mounting against the concept of fluorine hyperconjugation in organic compounds [133].

In the previous chapters variations of $^2\underline{J}(Pt-CH_3)$ with trans-ligands for methylplatinum(II) and methylplatinum(IV) compounds have been discussed. It seemed that a study of $^2\underline{J}(Pt-CF_3)$ for a variety of trifluoromethylplatinum complexes might provide information on factors affecting coupling constants involving ^{195}Pt as well as some insight into the nature of the Pt-CF_3 bond. Several reactions of trifluoromethylplatinum cations with acetylenes and pentafluorobenzonitrile are described and compared with the analogous reactions for methylplatinum(II) cations described in Chapter II. Throughout this chapter Q will be used to represent PMe_2Ph; L, a neutral ligand and Z will be used to represent an anionic ligand. This research was carried out with Dr. T.G. Appleton who prepared most of the neutral compounds and these will be included along with the cations for completeness.

b) Results and Discussion

A list of the trifluoromethylplatinum complexes prepared, together with analytical data, is given in Table VI-1. Data for a few methylplatinum complexes not previously prepared are given in Table VI-2.

All the Pt(II) complexes have the trans-configuration about platinum, since the phosphine-methyl resonances appeared as triplets[49,134] with triplet 'satellites' from coupling to ^{195}Pt. NMR spectroscopic

Table VI-1

ANALYTICAL DATA FOR TRIFLUOROMETHYLPLATINUM COMPLEXES

Complex[a]	Analyses, % C Calcd	C Found	H Calcd	H Found	F Calcd	F Found	Mp,[b] °C	Recrystn solv
$[Pt(CF_3)Q_2(NCCH{=}CH_2)][PF_6]$	32.5	32.7	3.4	3.6			118–119	CH_2Cl_2–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2(p\text{-}NCC_6H_4OCH_3)][PF_6]$	36.7	36.7	3.6	3.3			133–136	CH_2Cl_2–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2\{NH{=}C(OCH_3)C_6F_5\}][PF_6]$	33.0	32.8	2.9	2.5			134–135	CH_2Cl_2–$(C_2H_5)_2O$
$[\{Pt(CF_3)Q_2\}_2\{p\text{-}(NH{=}C(OCH_3))_2C_6F_4\}][PF_6]_2$	33.1	32.9	3.2	3.3			132–134	CH_2Cl_2–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2(NC_5H_5)][PF_6]$	34.6	34.8	3.6	3.8			171–173	CH_2Cl_2–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2(CO)][PF_6]$	30.3	30.7	3.1	3.3	24.0	23.2	137	$CHCl_3$–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2(CNC_2H_5)][PF_6]$	32.4	32.6	3.7	3.6			118–120	CH_3OH
$[Pt(CF_3)Q_2(p\text{-}CNC_6H_4OCH_3)][PF_6]$	36.7	36.6	3.6	3.4			155–156	CH_2Cl_2–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2\{As(C_6H_5)_3\}][PF_6]$	42.7	42.6	3.8	3.6			100–102	C_2H_5OH
$[Pt(CF_3)Q_2\{P(C_6H_5)_3\}][PF_6]$	44.3	44.4	3.9	3.9			138–140	CH_3OH
$[Pt(CF_3)Q_3][PF_6]$	36.5	36.9	4.0	4.2			100–102	$(CH_3)_2CO$–n-C_5H_{12}–$(C_2H_5)_2O$
$[Pt(CF_3)Q_2\{Sb(C_6H_5)_3\}][PF_6]$[c]	40.5	40.7	3.6	3.6			105–106	CH_3OH
$Pt(ONO_2)(CF_3)Q_2$	33.9	33.8	3.7	3.6	9.5	9.2	141	CH_3OH
$PtBr(CF_3)Q_2$	32.9	32.8	3.6	3.5	9.2	9.1	134	CH_3OH
$PtCl(CF_3)Q_2$	35.5	35.6	3.9	3.9	9.9	10.3	127–128	CH_3OH
$Pt(NCO)(CF_3)Q_2$	37.1	37.2	3.8	3.6	9.8	9.6	118–120	CH_3OH
$Pt(NCS)(CF_3)Q_2$	36.1	36.1	3.7	3.5	9.5	9.2	141–143	CH_3OH
$Pt(N_3)(CF_3)Q_2$	35.1	35.2	3.8	3.9	9.8	10.2	113	CH_3OH
$Pt(NO_2)(CF_3)Q_2$	34.8	35.0	3.8	4.0	9.7	10.0	126–127	CH_3OH
$Pt(CN)(CF_3)Q_2$	38.2	38.3	3.9	3.9	10.1	10.3	127–129	$(C_2H_5)_2O$–C_6H_{14}

[a] All complexes trans. Colorless unless otherwise stated. $Q = P(CH_3)_2(C_6H_5)$. [b] Uncorrected. [c] Pale yellow.

Table VI-2

METHYLPLATINUM COMPLEXES

Complex[a]	δ_{Pt-CH_3}[b]	$^2J_{Pt-CH_3}$, Hz	$^2J_{P-H}$, Hz	δ_{P-CH_3}[b]	$^3J_{Pt-P-CH_3}$, Hz	$^4J + {}^2J_{P-H}$, Hz	Analyses, % C Calcd	Analyses, % C Found	Analyses, % H Calcd	Analyses, % H Found	Mp (uncor), °C
$Pt(ONO_2)(CH_3)Q_2$	−0.18	86.0	7.1	−1.71	29.5	6.8	37.2	37.6	4.6	4.9	70-72
$Pt(NCO)(CH_3)Q_2$	−0.11	78.0	7.0	−1.78	30.0	6.8	40.9	40.9	4.8	4.7	89-92
$Pt(NCS)(CH_3)Q_2$	+0.02	78.5	7.2	−1.81	31.0	6.8	39.7	39.6	4.6	4.6	107-109
$Pt(NO_2)(CH_3)Q_2$	−0.04	71.3	7.7	−1.72	32.3	6.8	38.4	38.4	4.7	4.8	123-125
$Pt(CN)(CH_3)Q_2$[c]	+0.03	61.0	7.4	−2.06	32.6	8.0	42.1	42.3	4.9	4.8	98-99

[a] All complexes trans and colorless. Q = $P(CH_3)_2(C_6H_5)$. Spectra in CH_2Cl_2. [b] Ppm upfield from TMS. [c] Rapid phosphine exchange at room temperature. Spectrum run at low temperature.

data are tabulated in Table VI-3. In a few cases the hexafluorophosphate salts were insufficiently soluble for NMR spectra to be obtained, so the more soluble tetrafluoroborate salts were used. For some complexes, as indicated in Table VI-3, the dimethylphenylphosphine ligands exchanged rapidly at room temperature, so the solution was cooled until all coupling constants could be measured. Complete NMR data for the platinum(IV) compounds may be found in reference 48.

The ^{19}F spectra of the Pt(II) complexes are, in general, similar to the spectrum of trans-$PtI(CF_3)Q_2$ previously reported [135], consisting of a central triplet (from coupling to the two equivalent ^{31}P nuclei of the phosphine ligands), with triplet 'satellites' from coupling with ^{195}Pt. When L is a phosphine in complexes trans-$Pt(CF_3)Q_2L^+$, each peak is further split into a doublet by coupling with the trans ^{31}P nucleus.

Infrared C-F stretching frequencies are listed in Table VI-3. For complexes trans-$Pt(R)ZQ_2$ with Z = NCS, NCO, and NO_2, linkage isomerism is possible. The very similar values of $^2J(Pt-CH_3)$ for the complexes $Pt(NCS)(CH_3)Q_2$ and $Pt(NCO)(CH_3)Q_2$ (and of $^2J(Pt-CF_3)$ for the corresponding trifluoromethyl complexes) strongly suggest that these ligands are N-bonded. The N-C stretching frequencies (Table VI-4) are consistent with this assignment [136]. The relation between $^1J(Pt-H)$, $^2J(Pt-CH_3)$, and $^2J(Pt-CF_3)$ (Figures VI-1 - VI-3) in the complexes trans-$Pt(R)(NO_2)(PR'_3)_2$ (R = H, CH_3, CF_3) indicates that the bonding mode of the nitrite ligand is the same in these three complexes. Because the hydride resonance in the complex trans-$Pt(H)(NO_2)(PEt_3)_2$ showed no sign of coupling with the ^{14}N nucleus or broadening caused

Table VI-3

SPECTROSCOPIC DATA FOR TRIFLUOROMETHYLPLATINUM COMPLEXES

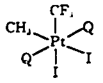
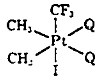
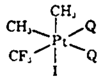
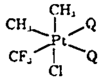
No.	Complex	$\delta_{\mathrm{CF_3}}$	$^2J_{\mathrm{Pt-CF_3}}$, Hz	$^3J_{\mathrm{P-F}}$, Hz	$\delta_{\mathrm{P-CH_3}}$	$^3J_{\mathrm{Pt-P-CH_3}}$, Hz	$^4J + {}^2J_{\mathrm{P-H}}$, Hz	$^2J_{\mathrm{Pt-CH_3}}$, Hz	Other peaks in spectra	$\nu_{\mathrm{C-F}}$ (sym), cm^{-1}	$\nu_{\mathrm{C-F}}$ (deg), cm^{-1}
1	$[\mathrm{Pt(CF_3)Q_2(acetone)}][\mathrm{PF_6}]$	11.20	858					88			
2	$[\mathrm{Pt(CF_3)Q_2(NCCH{=}CH_2)}][\mathrm{PF_6}]$	15.22	780	20.0	2.01	30.8	7.6	80		1107 s	1000 sh 1011 1025 sh
3	$[\mathrm{Pt(CF_3)Q_2(\mathit{p}\text{-}NCC_6H_4OCH_3)}][\mathrm{PF_6}]$	14.71	778	20.0	2.06	30.0	8.4	80	$\delta_{\mathrm{OCH_3}}$ 3.93	1105 s	1026 b
4	$[\mathrm{Pt(CF_3)Q_2\{NH{=}C(OCH_3)C_6F_5\}}][\mathrm{PF_6}]$	13.68	724	19.0	1.93	29.2	7.2	76.4	$\delta_{\mathrm{OCH_3}}$ 3.88	1104 s	1004 b 1027 sh
5	$[\{\mathrm{Pt(CF_3)Q_2}\}_2\{\mathit{p}\text{-}\mathrm{(NH{=}C(OCH_3))_2\text{-}C_6F_4}\}][\mathrm{PF_6}]_2$	13.19	721	20.0	1.98 1.82	30.8 31.6	7.8 7.4	74.5	$\delta_{\mathrm{OCH_3}}$ 3.63 δ_{NH} 8.67	1104 s	999 b 1017 b
6	$[\mathrm{Pt(CF_3)Q_2(NC_5H_5)}][\mathrm{PF_6}]$	13.81	702	18.2	1.78	30.4	7.2	74.0		1074 sh 1101 s	1001 b 1016 b
7	$[\mathrm{Pt(CF_3)Q_2(CO)}][\mathrm{PF_6}]$	22.28	656	19.0	2.25	32.0	9.0	63.0		1117 s	1053 b
8	$[\mathrm{Pt(CF_3)Q_2(CNC_2H_5)}][\mathrm{PF_6}]$	20.24	620	17.5	2.03	31.4	7.6	63.5	$\delta_{\mathrm{CH_2}}$ 3.27 $\delta_{\mathrm{CH_3}}$ 0.98 $J_{\mathrm{CH_2-CH_3}}$ = 7.0 Hz	1109 s	1008 b 1027 sh
9	$[\mathrm{Pt(CF_3)Q_2(\mathit{p}\text{-}CNC_6H_4OCH_3)}][\mathrm{PF_6}]$	20.18	620	17.0	2.13	31.6	8.0	63.5	$\delta_{\mathrm{OCH_3}}$ 3.84	1107 s	1017 b 1033 sh
10	$[\mathrm{Pt(CF_3)Q_2\{As(C_6H_5)_3\}}][\mathrm{BF_4}]$	14.36	662	19.8	1.64	27.2	7.2	67.0		1093 s	1000 b 1022 b
11	$[\mathrm{Pt(CF_3)Q_2\{P(C_6H_5)_3\}}][\mathrm{BF_4}]$	15.40	566	57.0	1.53	30.4	7.2	60.0		1093 s	
12	$[\mathrm{Pt(CF_3)Q_3}][\mathrm{PF_6}]$	15.75	550	56.0 17.0	1.80 0.91	28.0 19.0	8.0 9.8	57.0		1097 s	995 sh 1010 b 1032 b
13	$[\mathrm{Pt(CF_3)Q_2\{Sb(C_6H_5)_3\}}][\mathrm{BF_4}]$	14.64	708	20.3	1.86	28.8	7.2	55.0		1072 sh 1089 s	1000 b 1018 b
14	$[\mathrm{Pt(CF_3)Q_2\{\overline{CH_2CH_2O\ddot{C}CH_2}\}}][\mathrm{PF_6}]$	19.97	482					51.0		1077 w 1107 s	972 b 1002 sh 1013 b 1041 w
15	$[\mathrm{Pt(CF_3)Q_2\{C(CH_3)(OCH_3)\}}][\mathrm{PF_6}]$	19.85	468					51.0			
16	$\mathrm{Pt(ONO_2)(CF_3)Q_2}$	11.20	795	20.0	1.78	30.0	7.7	86.0		1101 s	992 b 1022 b
17	$\mathrm{PtI(CF_3)Q_2}$	11.95	754					81.0		1084 s	982 b 1015 b
18	$\mathrm{PtBr(CF_3)Q_2}$	10.79	763	20.1	1.90	29.4	7.5	83.0		1090 s	986 b 1015 b
19	$\mathrm{PtCl(CF_3)Q_2}$	10.52	757	19.3	1.83	29.6	7.7	82.0		1091 s	981 b 1010 b
20	$\mathrm{Pt(NCO)(CF_3)Q_2}$	11.81	714	18.8	1.81	30.5	7.7	78.0		1098 s	988 b 1008 b
21	$\mathrm{Pt(NCS)(CF_3)Q_2}$	13.00	721	19.5	1.84	30.5	7.7	78.5		1100 s	997 b 1012 b
22	$\mathrm{Pt(N_3)(CF_3)Q_2}$	11.60	710	17.8	1.86	30.2	7.4	78.6		1097	1001 b
23	$\mathrm{Pt(NO_2)(CF_3)Q_2}$	15.04	644	18.5	1.77	32.4	7.8	71.3		1103	1001 b 1016 b
24	$\mathrm{Pt(CN)(CF_3)Q_2}$	17.6	565	16.0	2.02	32.6	7.8	61.0		1102 s	982 b 1007 b
25		17.0	505					67.0			
26		19.3	517					70.0		1075 sh 1085 s 1105 sh	1007 b 1055 sh
27		22.62	419					56.0		1084	
28		29.45	411					56.0		1092 s 1110 sh	1017 b 1016 b

Table VI-4

SOME CHARACTERISTIC LIGAND VIBRATIONAL BANDS

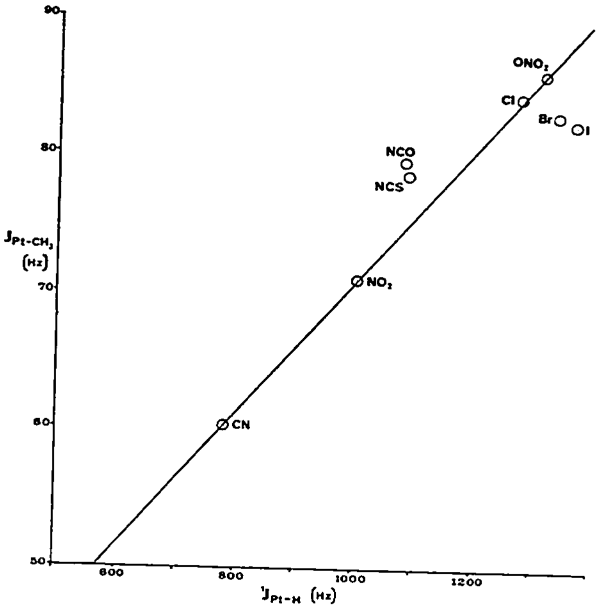
Complex[a]	Band[b]	R = CH_3		R = CF_3	
		ν, cm^{-1}	$\Delta\nu$,[c] cm^{-1}	ν, cm^{-1}	$\Delta\nu$,[c] cm^{-1}
$[Pt(R)Q_2(NCC_6H_4OCH_3)][PF_6]$	$\nu_{C\equiv N}$(R)	2270	57	2283	70
$[Pt(R)Q_2(CNC_2H_5)][PF_6]$[e]	$\nu_{N\equiv C}$(R)	2234	83	2256	105
$[Pt(R)Q_2(p\text{-}CNC_6H_4OCH_3)][PF_6]$	$\nu_{N\equiv C}$(R)	2193	68	2223	98
$[Pt(R)Q_2(CO)][PF_6]$[d]	$\nu_{C\equiv O}$(ir)	2095	−48	2140	−3
$Pt(NCO)(R)Q_2$	$\nu_{N\equiv C}$(ir)	2240	75	2245	80
$Pt(NCS)(R)Q_2$	$\nu_{N\equiv C}$(ir)	2120	79	2108	67
$Pt(CN)(R)Q_2$	$\nu_{C\equiv N}$(R)	2111	30	2134	53
		2118	37	2143	62

[a] Q = PMe_2Ph; [b] IR = infrared, R = Raman;

[c] $\Delta\nu = \nu_{complex} - \nu_{free\ ligand}$; [d] reference 14

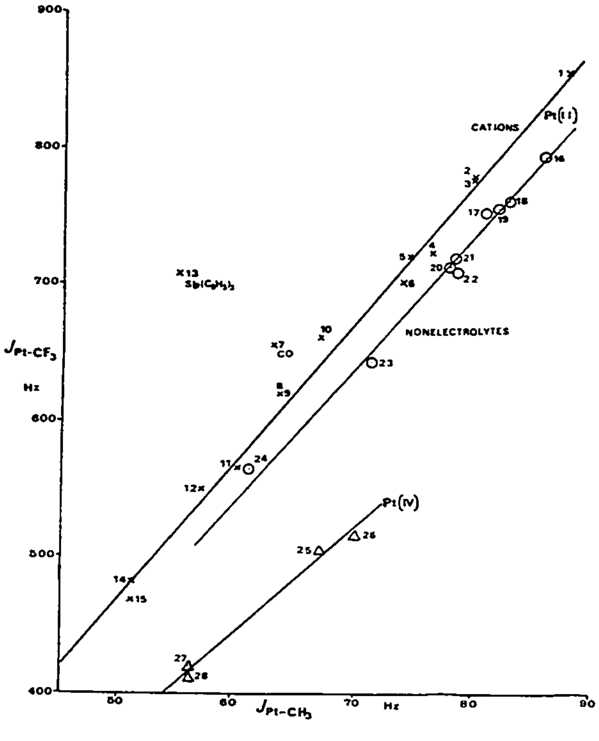
[e] R = Cl, $\Delta\nu(C\equiv N) = 116\ cm^{-1}$; R = I, $\Delta\nu(C\equiv N) = 100\ cm^{-1}$

Figure VI-1



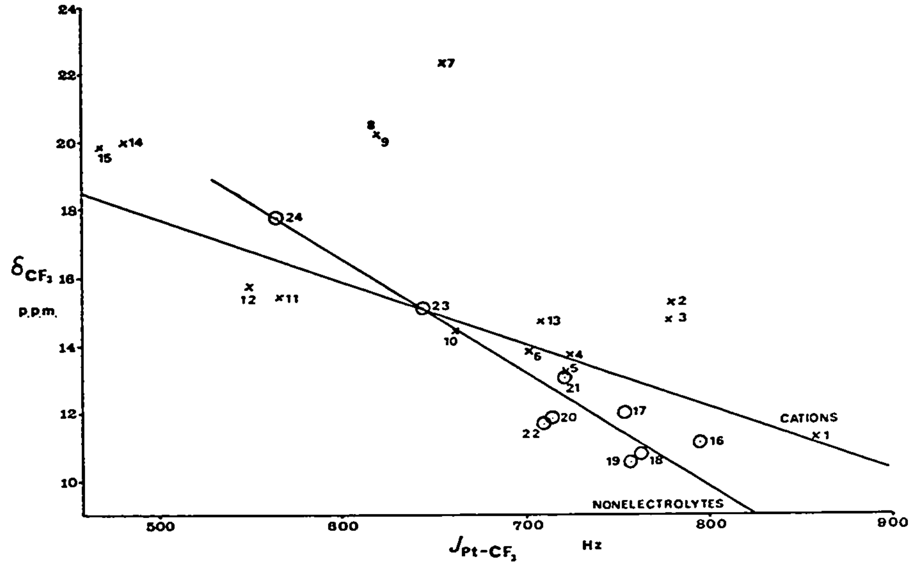
$^2\underline{J}(Pt-CH_3)$ plotted against $^1\underline{J}(Pt-H)$ for corresponding complexes $Pt(CH_3)Z(PEt_3)_2$ and $Pt(H)Z(PEt_3)_2$. Data from ref 10 and 137.

Figure VI-2



$^2\underline{J}(Pt-CF_3)$ plotted against $^2\underline{J}(Pt-CH_3)$ for $Pt(R)ZQ_2$, $Pt(R)Q_2L^+$, and Pt(IV) complexes (R = CF_3, CH_3). Numbers from Table VI-3.

Figure VI-3



^{19}F chemical shift plotted against $^{2}\underline{J}(Pt-CF_3)$ for the complexes $Pt(CF_3)ZQ_2$ and $Pt(CF_3)Q_2L^+$. Numbers from Table VI-3.

by its quadrupole (as observed for N-bound NCS and NCO) Powell and Shaw[137] suggested that in benzene solution the nitrite is O-bonded. This reversed the earlier assignment[138] for the solid complex based on infrared spectra. Powell and Shaw also noted that τ_H was rather high for an N-bound species. The lack of interaction between the hydride proton and the ^{14}N nucleus seems, however, to be very flimsy evidence on which to assign the configuration, since the quadrupole relaxation time is very dependent on the electric field gradient at the ^{14}N nucleus, which is related to molecular symmetry[139,140] clearly different for N-bound nitrite from N-bound thiocyanate.

Arguments for N-bound nitrite are:

(A) Trans-$Pt(H)(NO_2)(PEt_3)_2$ appears to be N-bound in the solid state[138].

(B) Platinum prefers nitrogen donors in general to oxygen donors. No O-bound platinum-nitrite complexes are known.

(C) As measured by coupling constants for trans-$Pt(R)(NO_2)(PR'_3)_2$ the trans-influence of nitrite is greater than for the nitrogen donors N_3, NCS, and NCO. If the nitrite were O-bound, its trans-influence would be expected to be lower, perhaps comparable to nitrate.

Allen and Pidcock[10] and Atkins et al[141] appear to consider nitrite as N-bound in the complexes they studied, although they do not discuss this question.

In Figure VI-2, $^2J(Pt-CF_3)$ for the trifluoromethyl complexes is plotted against $^2J(Pt-CH_3)$ for the corresponding methyl complexes. Except for the points representing L = $SbPh_3$ and CO, the cationic complexes $Pt(R)Q_2L^+$ give a straight line. The points corresponding to the non-electrolytes $Pt(R)ZQ_2$ lie on a slightly different line, while the Pt(IV) complexes give a line with a slope [$^2\underline{J}$(Pt-CF_3)/$^2\underline{J}$(Pt-CH_3)] much less than for Pt(II) complexes. All three lines may be extrapolated back to the origin.

In Figure VI-3, the chemical shifts of the trifluoromethyl groups are plotted against $^2\underline{J}$(Pt-CF_3). For the non-electrolyte complexes, there is clearly a general trend for the chemical shift to decrease as the coupling constant increases. For the cations, most points appear to follow a similar trend, but the chemical shifts for L = CO, RNC, and RCN appear to be 'anomalously' high.

(i) $^2\underline{J}$(Pt-CF_3) Compared With $^2\underline{J}$(Pt-CH_3)

As mentioned briefly in Chapter I, most discussions of $^1\underline{J}$(Pt-H) in platinum hydride complexes have assumed that the coupling constant is dominated by the Fermi Contact term [13,141] shown below.

$$^1\underline{J}(\text{Pt-H}) \propto \gamma_{Pt}\, \gamma_H\, \alpha^2{}_{Pt}\, \alpha^2{}_H\, [\psi_{Pt(6s)}(0)]^2\, [\psi_{H(1s)}(0)]^2 \Delta E^{-1} \qquad (1)$$

γ_i is the gyromagnetic ratio for the nucleus i.

$\alpha^2{}_i$ is the s-character of the hybrid orbital used by i.

$[\psi_{i(ns)}(0)]^2$ is the ns electron density at the nucleus i.

ΔE is the singlet-triplet excitation energy between the σ-bonding and antibonding orbitals for the Pt-H bond.

Since the equation applies to a covalent bond, any decrease in covalency will cause $^1\underline{J}$(Pt-H) to decrease. An analogous equation has been used in considering $^1\underline{J}$(^{195}Pt-^{31}P) [7,10].

For $^2\underline{J}$(Pt-CH_3) in methylplatinum complexes, the situation is theoretically more complex, but a treatment based on that of Smith [142] assuming only Fermi Contact contribution to coupling, would predict a relationship of the type

$$^{2}\underline{J}(\mathrm{Pt{-}CH_3}) \propto \gamma_{Pt}\,\gamma_{H}\,\alpha^{2}_{Pt}\,\alpha^{2}_{H}\,f(C)[\psi_{Pt(6s)}(0)]^{2}\,[\psi_{H(1s)}(0)]^{2}\,\Delta E^{-1} \qquad (2)$$

where most of the symbols have the same significance as before, and f(C) is a function of the electronic factors that control transmission of the coupling through the carbon atom. At least to a first approximation, $^{2}\underline{J}$(Pt-CH$_3$) for the complexes trans-Pt(CH$_3$)Z(PEt$_3$)$_2$ varies linearly with $^{1}\underline{J}$(Pt-H) in the corresponding complexes trans-Pt(H)Z(PEt$_3$)$_2$ as Z is changed (Figure VI-1). This indicates that $^{2}\underline{J}$(Pt-CH$_3$) is indeed governed by the same factors as $^{1}\underline{J}$(Pt-H). Furthermore, the ratio (1):(2) remains approximately constant as the ligand Z varies, so that changes in f(C) within the methylplatinum series cannot be very important. All other variable factors in (1) and (2) must also change proportionally in the two series.

In treatments of $^{1}\underline{J}$(Pt-H) [13,141], $^{1}\underline{J}$(Pt-P) [7,10] and $^{2}\underline{J}$(Pt-CH$_3$) [10], it is usually considered that within a series of complexes the only factors likely to vary significantly are α^{2}_{Pt}, $[\psi_{Pt(6s)}(0)]^{2}$, and ΔE. If changes in $[\psi_{Pt(6s)}(0)]^{2}$ were dominant, the 'cis-influence' of a ligand would be comparable to its trans-influence (measured by NMR coupling constants). That this is not so is quite clear, for example, from the large difference between the values of $^{1}\underline{J}$(Pt-P) for the phosphorus nuclei in cis-PtCl(CH$_3$)(PEt$_3$)$_2$ [10].

Most authors [7,10,13] have assumed that the variation in α^{2}_{Pt}, perhaps combined with a change in covalency, predominates. The presence of a very strong σ-donor trans- to the bond in question will cause a rehybridization of the Pt atom, and α^{2}_{Pt} will decrease, or the bond could become less covalent (i.e. more ionic) which would also decrease the coupling. It is difficult to separate these two effects within a series of Pt(II) complexes, but a comparison of coupling constants for analogous Pt(II) and Pt(IV) complexes suggests that α^2_{Pt} is the dominant factor [7] (discussed later). Atkins et al [141] have suggested on the basis of a relationship between $^1J(Pt-H)$ and the position of the trans-ligand in the spectrochemical series that changes in ΔE cannot be ignored when 'gross changes' are made in the nature of this ligand. However, the position of a ligand in the spectrochemical series is not altogether unrelated to its position in the trans-influence series if the latter is based mainly on a σ-donor bond strength. A ligand which is a good σ-donor and forms strong covalent bonds will be high in both series. Except for the halogens, where changes in trans-influence (measured by coupling constants) are relatively small, the two series are almost parallel.

Since coupling involving the ^{19}F nucleus is rather more complicated in general than that involving ^1H (e.g. 'through space' contributions are often important), the dependence of $^2J(Pt-CF_3)$ on L or Z in the complexes trans-$Pt(CF_3)Q_2L^+$ and $Pt(CF_3)ZQ_2$ could conceivably be much more complicated than that of $^2J(Pt-CH_3)$. However, if the points representing L = CO and $SbPh_3$ are ignored, a good straight line may be drawn through the points representing cations (Figure VI-2) (i.e. $^2J(Pt-CF_3)/^2J(Pt-CH_3)$ is constant). This immediately indicates that:

(A) Factors influencing $^2J(Pt-CF_3)$ in trifluoromethyl complexes parallel those for $^2J(Pt-CH_3)$, and an equation analogous to (2) determines the coupling. Further, since $^2J(Pt-CF_3)/^2J(Pt-CH_3)$ is constant,

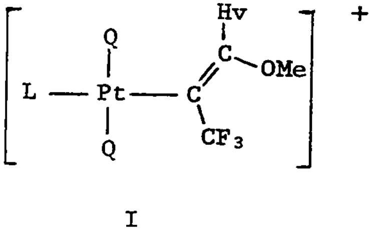
$$\frac{\{\alpha^2_{Pt}\alpha^2_{F}f(C)\ [\psi_{Pt(6s)}(0)]^2[\psi_{F(2s)}(0)]^2\ \Delta E^{-1}\}_{CF_3}}{\{\alpha^2_{Pt}\alpha^2_{H}f(C)\ [\psi_{Pt(6s)}(0)]^2[\psi_{H(1s)}(0)]^2\ \Delta E^{-1}\}_{CH_3}} = \text{constant} \qquad (3)$$

In particular, if variation in α^2_{Pt} is the main factor,

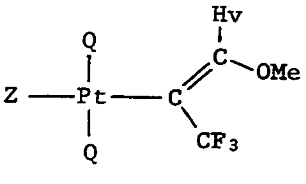
$$\frac{(\alpha^2_{Pt})_{CF_3}}{(\alpha^2_{Pt})_{CH_3}} = (\text{constant})^1 \qquad (4)$$

(B) The Pt-CF_3 bond is not very dependent on synergic σ-π bonding for its strength. As L becomes a weaker σ-donor (towards the upper right of Figure VI-2) the total electron density on the Pt atom will decrease significantly, the filled d_{xz} and d_{yz} orbitals will contract, and the availability of electrons for π-backbonding would decrease. A synergic bonding mechanism would depend on the availability of such electrons, and the line in Figure VI-2 would be expected to curve downwards at the upper right of the graph or upwards at the lower left (since the methyl group is incapable of π-backbonding). There is no sign of such curvature. Furthermore, a similar argument would predict, if Pt-CF_3 π-bonding were important, that $^2\underline{J}$(Pt-CF_3)/$^2\underline{J}$(Pt-CH_3) would be much larger for the complexes Pt(R)ZQ_2 than for the relatively electron-deficient cations Pt(R)Q_2L^+. In fact, the slope of the line representing non-electrolyte complexes is slightly less than that for the cations.

For L = CO and $SbPh_3$, $^2\underline{J}$(Pt-CF_3) is greater than would be expected from the value of $^2\underline{J}$(Pt-CH_3). Unless the coupling mechanism for these compounds is different from that for other ligands, this implies that the Pt-L bond is considerably weaker in the trifluoromethyl complex than it is in the methyl complex. For L = CO, a rationalization can be given. It is well-accepted that the carbonyl ligand bonds to transition metals by synergic σ-π bonding [143]. When the Pt-atom is bonded to the relatively electronegative trifluoromethyl group, its electron density will be considerably less than it is in the methylplatinum complex, reducing the availability of electrons for π-backbonding to the carbonyl group. Consequently, because of the σ-π synergism, the Pt-CO σ-bond becomes weaker. The C-O stretching frequencies (Table VI-4) are consistent with a considerable reduction in platinum-carbonyl π-bonding for the trifluoromethyl complex. The deviation from the line in Figure VI-2 is much greater for the triphenylstibine complex. It has been suggested, on the basis of a variety of experimental data [144-146] that π-backbonding is more important relative to the ligand-metal σ-bond for stibines than for arsines or phosphines. Cheeseman *et al* [147] have found that stibines exert a higher *trans*-effect than arsines and phosphines. It is therefore tempting to postulate that triphenyl stibine also bonds by a synergic σ-π mechanism and that there is considerable Pt-Sb double bond character for the methylplatinum cation. In order to clarify this point a series of vinylplatinum(II) complexes I, II were prepared[148]



I



II

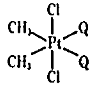
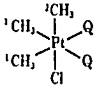
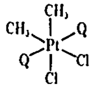
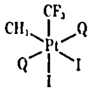
and the coupling constants $^{3}J(Pt\text{-}CF_3)$ and $^{3}J(Pt\text{-}Hv)$ were plotted against $^{2}J(Pt\text{-}CH_3)$ for the analogous methylplatinum complexes. The point representing L = $SbPh_3$ still deviated from the line whilst for L = CO and MeC≡CMe (which are generally regarded as utilizing a synergic bonding mechanism) there was no discrepancy. Thus it seems unlikely that the deviation in Figure VI-2 for L = $SbPh_3$ is entirely attributable to synergism but rather that for some unknown reason the value of $^{2}J(Pt\text{-}CH_3)$ is anomalous for the triphenylstibine complex.

These results imply that the Pt-L σ-bond for the other ligands under consideration is not appreciably affected by any Pt-L π-bonding. That is, the ligands studied, other than CO do not utilize synergic σ-π bonding in these complexes. Olefinic and acetylenic ligands which must utilize a σ-π synergic bonding mechanism do not form stable trifluoromethyl platinum(II) cations. It would be expected however, that these compounds would also give values of $(^{2}J(Pt\text{-}CF_3)/^{2}J(Pt\text{-}CH_3))$ which would deviate from the line in Figure VI-2.

The slope $(^{2}J(Pt\text{-}CF_3)/^{2}J(Pt\text{-}CH_3))$ of the line representing Pt(IV) complexes is significantly smaller than that for the Pt(II) complexes. From Table VI-5, it is clear that this is because the methyl-platinum coupling constants are 'anomalously' high for Pt(IV) complexes. As pointed out by Allen and Pidcock [7], on oxidation from square planar Pt(II) to octahedral Pt(IV), the s-orbital originally used in forming four hybrid orbitals must now be shared by six, so that $\alpha^2{}_{Pt(IV)}/\alpha^2{}_{Pt(II)}$ would be 0.67, and if coupling depends mainly on $\alpha^2{}_{Pt}$, the ratio $^{2}J_{Pt(IV)}/^{2}J_{Pt(II)}$ for a given nucleus coupled to Pt should approximate to this value. This argument is strictly applicable only when all

Table VI-5

COUPLING CONSTANTS INVOLVING ^{195}Pt

Pt(II) complex	Pt(II) coupling, Hz	Pt(IV) complex	Pt(IV) coupling, Hz	$J_{Pt(IV)}/J_{Pt(II)}$
$[Pt(en)_2]Cl_2$	41.0 ($^3J_{Pt-N-CH_2}$)	*trans*-$[Pt(en)_2Cl_2]Cl_2$	26.0, 27.0 ($^3J_{Pt-N-CH_2}$)	0.64
		$[Pt(en)_3]Cl_4$		0.66
trans-$PtCl[P(n\text{-}Bu)_3]_2$	2380 ($^1J_{Pt-P}$)	*trans*-$PtCl_4[P(n\text{-}Bu)_3]_2$	1462 ($^1J_{Pt-P}$)	0.615
cis-$PtCl_2[P(n\text{-}Bu)_3]_2$	3508 ($^1J_{Pt-P}$)	*cis*-$PtCl_4[P(n\text{-}Bu)_3]_2$	2070 ($^1J_{Pt-P}$)	0.590
cis-$Pt(CH_3)_2Q_2$	19 ($^3J_{Pt-P-CH_3}$) 67 ($^2J_{Pt-CH_3}$)		10.5 ($^3J_{Pt-P-CH_3}$) 57 ($^2J_{Pt-CH_3}$)	0.55 0.85
			56 ($^2J_{Pt-{}^1CH_3}$)	0.84
trans-$PtCl(CH_3)Q_2$	85 ($^2J_{Pt-CH_3}$) 29.5 ($^3J_{Pt-P-CH_3}$)		68 ($^2J_{Pt-CH_3}$) 17.6 ($^3J_{Pt-P-CH_3}$)	0.80 0.60
trans-$PtI(CH_3)Q_2$	80 ($^2J_{Pt-CH_3}$)		65 ($^2J_{Pt-CH_3}$)	0.81
trans-$PtI(CF_3)Q_2$	753 ($^2J_{Pt-CF_3}$)		505 ($^2J_{Pt-CF_3}$)	0.67

the ligands attached to platinum are the same, or similar in their demand for Pt(6s) orbital participation (e.g. the ethylenediamine complexes in Table VI-5, for which nearly theoretical values are obtained). The situation is less clear-cut when ligands of different types are bound to Pt, but $^2\underline{J}_{Pt(IV)}/^2\underline{J}_{Pt(II)}$ might be expected to approach 0.67 under the following conditions:

(A) The coupling constant must be dominated by α^2_{Pt}. All other factors in (2) and analogous equations must remain almost constant on oxidation.

(B) The trans-ligand remains the same.

(C) The ligand in question is as demanding of Pt(6s) orbital contribution to its bond with Pt(IV) relative to the other ligands as it is for Pt(II).

Condition (B) is fulfilled for all the complexes in Table VI-5. The rather low values of the ratios $^2\underline{J}_{Pt(IV)}/^2\underline{J}_{Pt(II)}$ involving phosphines[7] may reflect the crudity of the arguments above. Alternatively, the bond from 'soft' phosphines to relatively 'hard' Pt(IV) may be appreciably weaker than to 'soft' Pt(II), so that condition (C) is not quite fulfilled.

Almost certainly, the high values of $^2\underline{J}_{Pt(IV)-CH_3}/^2\underline{J}_{Pt(II)-CH_3}$ (~0.8) reflect a greater demand by the methyl group for Pt(6s) participation in its bonding to Pt(IV) (relative to other ligands) than with Pt(II) (i.e. condition (C) is not fulfilled). This is probably associated with the comparative stability of the Pt(IV)-CH_3 bond, which, for example, is cleaved much less readily than the Pt(II)-CH_3 bond. The Pt-CH_3 bonds in the complexes cis-$Pt(CH_3)_2(PR_3)_2$

and trans-$PtCl(CH_3)(PR_3)_2$ are readily cleaved by HCl and halogens [113], while very severe conditions (e.g. refluxing Br_2 in the presence of HBr) [97] are required to cleave the methyl-platinum bonds in the complexes $[PtX(CH_3)_3]_4$, where no 'stabilizing ligands' [113] are present. The ratios $^2J(Pt(IV)-CF_3)/^2J(Pt(II)-CF_3)$ are almost 'theoretical' (Table VI-5), indicating that condition (C) holds for the trifluoromethyl group.

(ii) ^{19}F Chemical Shifts

Pitcher, Buckingham, and Stone [149] explain the downfield chemical shifts of α-fluorine atoms in perfluoralkyl transition metal complexes in terms of paramagnetic screening resulting from overlap between filled F-p-orbitals and metal d-orbitals. If the ligand L or Z is a strong σ-donor,

(A) The electron density on Pt will increase, causing expansion of the d-orbitals, resulting in a downfield chemical shift.

(B) The electronegativity of the group bound to $-CF_3$ would decrease, causing an upfield chemical shift.

(C) The ligand probably has a high trans-influence (low $Pt-CF_3$ coupling), tending to increase the Pt-C bond length, decreasing the orbital overlap, and causing an upfield chemical shift.

(D) The ligand is probably high in the spectrochemical series, so that the excitation energy at the Pt atom will be high, and the fluorine resonance will shift upfield.

The trends displayed in Figure VI-3 (chemical shift upfield increasing with decreasing $^2J(Pt-CF_3)$) suggest that (B), (C) and (D) outweigh (A) within a series.

The relatively high chemical shifts for the trifluoromethyl group in the complexes $Pt(CF_3)Q_2L^+$ where L = CO, RNC and RCN probably reflect the effect of anisotropic magnetic fields generated by the triple bonds in these ligands. For these same ligands the phosphine-methyl resonances are further downfield than for other L (Table VI-3). Similar effects have been observed in some platinum hydride complexes [76]. Although some of the anionic ligands, Z, in the non-electrolyte complexes contain multiple bonds, there appears to be no pronounced anisotropic effect here (even for Z = CN, where the phosphine-methyl resonance does occur well downfield).

(iii) Vibrational Spectra of the Trifluoromethyl Groups

Cotton and Wing [128] observed two bands in the region 1000-1100 cm^{-1} in the infrared spectrum of the complex $CF_3Mn(CO)_5$ attributable to C-F stretching. On the basis of band shapes in the spectrum of the gaseous complex, the higher frequency band (1063 cm^{-1}) was assigned to symmetric C-F stretching and the lower frequency band (1045 cm^{-1}) to the degenerate stretching modes. This order was the reverse of that found for the molecules CF_3X, where X = Cl, Br, I, and for non-transition-metal complexes, such as $Hg(CF_3)_2$ [150]. Johnson [131], in his discussion of the CF_3 stretching vibrations of a number of trifluoromethyl complexes, follows Cotton's assignment, and notes that for some complexes the lower (degenerate) band is split, presumably as a result of low molecular symmetry.

With the trifluoromethyl platinum complexes discussed in this chapter, a moderately sharp, strong band was always observed near 1100 cm^{-1}, and at least one broad band (often split into two or three resolvable peaks) near 1000 cm^{-1} (Table VI-3). The splitting of this lower-frequency band again supports its assignment as corresponding to the degenerate modes.

In the complexes trans-$PtZ(CF_3)Q_2$ and $Pt(CF_3)Q_2L^+$, both bands are sensitive to changes in Z or L. However, the splitting of the lower-frequency band, with its components varying considerably in relative intensities, makes frequency comparisons between complexes difficult, and the following discussion will deal mainly with the higher-frequency (symmetric stretching) band.

It is clear from Table VI-3 that the frequency of this band within the series of complexes $Pt(CF_3)Q_2L^+$ is not very sensitive to changes in electron density on Pt caused by varying L. Thus, for the weak σ-donor, acrylonitrile, the frequency is 1107 cm^{-1}, while for the strong σ-donors ethyl isocyanide and the cyclic carbene the frequencies are 1109 and 1107 cm^{-1} respectively. The band frequency, however, falls well below 1100 cm^{-1} for the phosphine, arsine, and stibine complexes, the order being $PMe_2Ph > PPh_3 > AsPh_3 > SbPh_3$. One would be tempted to correlate this order with π-acceptor capacity of L, except that when L = CO (certainly a π-acceptor) [143] this frequency becomes very high (1117 cm^{-1}, highest frequency for all the complexes examined; in this case the degenerate stretching frequency, 1053 cm^{-1} is also very high). A more valid correlation is with the mass of L. The ligands for which the frequency is lowest are the heaviest in the series, while carbonyl, for which it is highest, is the lightest ligand. Of course, more is involved than the mass of the ligand as a whole. The mass of the donor atom is probably most important, followed by the weights of directly-bound groups. Technically, the complex $[Pt(CF_3)Q_2\{\underline{p}-(NH=C(OMe))-C_6F_4-(C(OMe)=NH)\}Pt(CF_3)Q_2](PF_6)_2$ has the heaviest ligand (taken as a whole), since it can be considered to contain another Pt atom. However, the heavy part of the ligand is removed from the metal by several bonds, and the C-F stretching frequency is similar to that for other N-donors.

Similar comments apply to the non-electrolyte complexes $PtZ(CF_3)Q_2$. Electron density on Pt, as affected by changes in Z, has little effect within the series, since the frequency differs by only 1 cm^{-1} between Z = nitrate (a weak donor) and Z = cyanide (a strong donor). Once again, there appears to be a correlation between ligand mass and the frequency. Lowest frequencies are obtained when Z is a halogen, and decrease in the order $Cl > Br > I$. For the other Z (donor-atom N, C, or O) the frequency is within 3 cm^{-1} of 1100 cm^{-1}.

Cotton[128] considers π-backbonding from filled metal d-orbitals to the trifluoromethyl group to be chiefly responsible for the low C-F stretching frequencies in trifluoromethyl-transition metal complexes. It would be predicted from this that, as electron density on Pt decreased, with consequent reduction of the availability of suitable d-electrons, these frequencies would increase. Conclusions from coupling constants (discussed above) suggest, however, that

Pt-CF_3 π-backbonding is not important for Pt(II) complexes. Johnson [131] predicts that as the electron-pair affinity of the metal increases (i.e. electron density of Pt decreases) ν_{C-F} should increase. There does seem to be a general trend for the frequencies in the cationic complexes to be slightly higher than in the non-electrolytes (with similar masses of ligand donor-atoms). This would be consistent with either theory, but the effect of ligand mass on the frequency is much greater than this 'electronegativity' effect.

Both theories would predict higher frequencies for Pt(IV) complexes than for Pt(II). The frequencies are actually somewhat lower. Once again, it appears that this frequency shift is caused by a ligand mass effect. The total mass of ligands coordinated to Pt is greater in general for Pt(IV) than Pt(II), since Pt(IV) complexes contain two additional ligands. This hypothesis is supported by the frequencies observed in the complexes $PtZ(CF_3)(CH_3)_2Q_2$, Z = I, Cl (27,28 in Table VI-3). The frequency for the chloro complex (1092 cm^{-1}) is considerably higher than for the iodo complex (1084 cm^{-1}). For the other isomer of the iodo complex (26) the frequency is 1085 cm^{-1} so that the frequency is not very dependent on the particular ligand trans- to the trifluoromethyl group (iodide in the complex (26), phosphine in the complex (27)).

The dependence of ν_{C-F} (sym) on the mass of the ligands, coordinated to Pt presumably occurs via coupling between the C-F stretching modes and ν_{Pt-C}, which, in turn, must be sensitive to the mass of metal plus ligands. Such vibrational coupling may help to explain the absence, in both Raman and infrared spectra, of any reasonably intense band assignable to Pt-C stretching in these complexes, although corresponding methylplatinum complexes show moderately intense $\nu_{\mathrm{Pt-C}}$ bands in their Raman spectra [23,26,28]. The only band present in (some) trifluoromethylplatinum complexes not present in corresponding methylplatinum complexes in the region 200-600 cm^{-1} was a very weak band in the vicinity of 300 cm^{-1}, which may have some Pt-C stretching character.

The C-F stretching bands were very weak in the Raman spectra.

(iv) <u>Trans</u>-Influence of the Trifluoromethyl Group

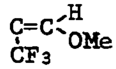
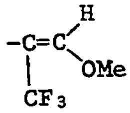
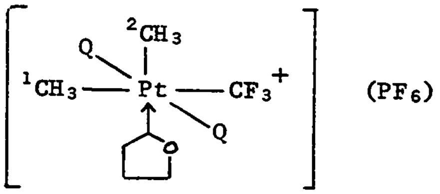
If $^{3}\underline{J}(\mathrm{Pt{-}P{-}CH_3})$ depends mainly on α^{2}_{Pt} in the Pt-P bond, the values of this coupling constant for the phosphine trans to Z or R in the complexes $\mathrm{PtZQ_3}^{+}$ and $\mathrm{PtRQ_3}^{+}$ (where R is a σ-bonded alkyl or aryl group) can be used to determine the *trans*-influence of R, Z. A few such coupling constants are listed in Table VI-6. The *trans*-influence order deduced from these values, is Ph > $\mathrm{CH_3}$ > $\mathrm{CF_3}$ >  $\underset{\mathrm{CF_3}}{\mathrm{C}}{=}\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{OMe}}$ >> Cl. The trifluoromethyl group is almost as high in this series as the methyl group, (i.e. has almost the same effect on Pt hybridization) which would not be expected on the basis of a comparison between the electronegativities of the two groups. Despite the smaller degree of charge transfer to Pt, the trifluoromethyl group must form very strong covalent bonds with platinum, with much s-character. This conclusion is consistent with the recent observation of a very low value of $^{2}\underline{J}(\mathrm{Pt{-}\ CH_3})$ in the complex [42]

Table VI-6

$^{3}J(Pt\text{-}P\text{-}CH_3)$ in Complexes $[PtR(PMe_2Ph)_3](PF_6)$

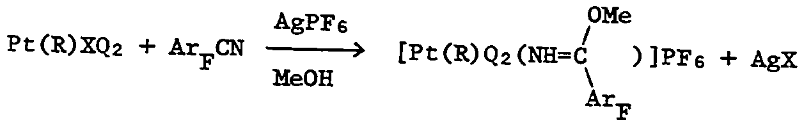
R	$^{3}J(Pt\text{-}P\text{-}CH_3)$ (*cis* to R)	$^{3}J(Pt\text{-}P\text{-}CH_3)$ (*trans* to R)	Reference
$-Cl$	23.5	40.0	14
	30.0 29.2	20.6	148
$-CF_3$	28.0	19.0	
$-CH_3$	30.0	18.5	14
$-C_6H_5$	32.6	17.6	148



(v) Comparisons Between Reactions and Properties of Trifluoromethyl- and Methyl-platinum Complexes

Because the trifluoromethyl group is comparable both sterically and in its effect on Pt hybridization to the methyl group, the chief difference between the moieties 'CH_3PtQ_2' and 'CF_3PtQ_2' will be the electron density on the Pt atom, since the more electronegative trifluoromethyl group will transfer less negative charge to the metal ion. The effect of this on the synergically bonding carbonyl ligand has already been discussed. Olefins and acetylenes also use synergic σ-π bonding in their transition metal complexes, and would be expected to form less stable complexes with the trifluoromethylplatinum group than with the methylplatinum group. Indeed, no simple complexes of the type $Pt(CF_3)Q_2$ (unsaturated hydrocarbon)$^+$, analogous to the known methylplatinum complexes [24] have been sufficiently stable to be isolated. However, the complexes <u>trans</u>-$Pt(CF_3)Q_2(HC{\equiv}CH)^+$ and $Pt(CF_3)Q_2(HC{\equiv}C\text{-}CH_2CH_2OH)^+$ must exist at least fleetingly in solution, since they are intermediates in the formation of the carbene complexes [23,42] <u>trans</u>-$Pt(CF_3)Q_2\{:C(Me)(OMe)\}^+$ and <u>trans</u>-$Pt(CF_3)Q_2\{:\overline{C(CH_2)_3O}\}^+$ respectively.

It was also of interest to see what effect the relatively positive Pt atom in the trifluoromethyl complexes would have on the reactions of alcohols with perfluoroarylnitriles (Chapter II). The reaction shown below occurs more readily when R = CF_3 than when R = CH_3.



$$\mathrm{Pt(R)XQ_2} + \mathrm{Ar_FCN} \xrightarrow[\mathrm{MeOH}]{\mathrm{AgPF_6}} [\mathrm{Pt(R)Q_2(NH{=}}\overset{\mathrm{OMe}}{\underset{\mathrm{Ar_F}}{\mathrm{C}}}\ )]\mathrm{PF_6} + \mathrm{AgX}$$

(X = Cl,I, Ar_F is a perfluoroaryl group)

The reaction mechanism is believed to proceed via a π-bonded nitrile, delocalization of positive charge from the metal onto the C≡N bond thus activating it towards nucleophilic attack by the alcohol.

It was suggested (Chapter II) from nmr coupling constants that the π-bonded perfluoroarylnitrile had a higher nmr trans-influence than the N-bonded nitrile. Therefore the decreased electron density on platinum in the trifluoromethyl complexes may well cause a preference for a π-rather than a σ-bonded nitrile relative to the methylplatinum complexes. Also the greater positive charge on the CF_3-Pt complex may well be delocalized onto the C≡N bond making it more susceptible to nucleophilic attack by the alcohol.

The low electron density on Pt in trifluoromethyl complexes is also reflected in the Raman spectra of the coordinated nitriles and isocyanides. The frequencies of the ν(C≡N) bands for various complexes are given in Table VI-4, together with the values of Δν(CN). For the isocyanides, Δν(CN) decreases with increasing negative charge on the Pt atom [26]. As expected, Δν(CN) is greater for the complexes

$Pt(CF_3)Q_2(CN\text{-}R)^+$ than for $Pt(CH_3)Q_2(CN\text{-}R)^+$. $\Delta\nu(CN)$ for $Pt(CF_3)Q_2(CN\text{-}Et)^+$ is between the values for $PtClQ_2(CN\text{-}Et)^+$ and $PtIQ_2(CN\text{-}Et)^+$, consistent with an electronegativity for the trifluoromethyl group between the two halides.

The characteristic $\nu(CN)$ bands for coordinated nitriles and cyanide (where $\nu(CN)$ occurs as a doublet in the solid-state Raman spectrum) all occur at higher frequencies in trifluoromethyl complexes than in methylplatinum compounds, reflecting greater ligand-metal charge transfer and/or less π-interaction between Pt and the ligand in the trifluoromethylplatinum complexes. Only with cyanate (NCO) and thiocyanate (NCS) is the $\nu(N\equiv C)$ frequency lower in the trifluoromethyl complex. Here the C—O or C-S bond can acquire some double-bond character at the expense of N-C triplet-bond character [136].

The high value of $\nu(CO)$ in the complex $Pt(CF_3)Q_2(CO)^+$ has already been mentioned.

c) Experimental

Trans-$PtI(CF_3)Q_2$ was prepared as previously described [135], and served as the starting-material for the preparation of all other trifluoromethylplatinum(II) complexes.

(i) Non-electrolyte Complexes

The complexes trans-$Pt(CF_3)ZQ_2$ were prepared by a general method for Z = Br,Cl,NCS,NCO,N_3, and NO_2, which may be illustrated by the preparation of the nitrite complex.

0.323 g. $PtI(CF_3)Q_2$ (0.48 mmoles) dissolved in boiling methanol was treated with a solution of 0.104 g. $AgBF_4$ (0.54 mmoles) in methanol. Yellow silver iodide precipitated immediately. The colourless solution was filtered from this precipitate, and excess solid sodium nitrite was added. The solution was evaporated to dryness. The solid residue was extracted with dichloromethane, the solution was filtered, passed down a short florisil column (to remove traces of silver salts) and evaporated to dryness. The resultant solid was recrystallized from methanol to give colourless crystals (first crop 0.111 g.).

A different procedure was used for Z = NO_3 and CN.

Z = NO_3: To a solution of 0.142 g. $PtI(CF_3)Q_2$ in acetone was added excess ground silver nitrate. The suspension was warmed. Small quantities of silver nitrate were added until the particles no longer became coated with silver iodide (yellow). The suspended AgI and $AgNO_3$ were filtered off, and the solution was evaporated to dryness. The resultant solid was recrystallized from methanol to give colourless crystals (first crop 0.092 g.).

Z = CN: Great care was required in the preparation of trans-$Pt(CN)(CF_3)Q_2$, apparently because of the ability of cyanide to displace the phosphine ligands to yield complexes of the type $Na[Pt(CN)_2(CF_3)Q]$. The odour of phosphine was always noticed above the solution during the preparation. To a solution of 0.469 g. $PtI(CF_3)Q_2$ (0.70 mmoles) in boiling methanol was added a solution containing 0.2 g. $AgPF_6$ (0.79 mmoles). Silver iodide was filtered off, and to the filtrate was added a solution of 0.04 g. sodium cyanide in methanol. The solution was evaporated to dryness to give an oil which was extracted with dichloromethane. When the filtered solution was evaporated, an oil was obtained which could not be crystallized. This oil was redissolved in dichloromethane and the solution was passed down a long florisil column. Evaporation of the eluted solution gave a white solid which was recrystallized from ether-hexane (0.099 g.).

The complexes trans-$Pt(CH_3)ZQ_2$ which have not previously been prepared (Table VI-2) were prepared by methods analogous to those used for the corresponding trifluoromethyl complexes, starting with trans-$PtCl(CH_3)Q_2$. For Z = NO_2, NCS, and NCO the product was recrystallized from dichloromethane-hexane. For Z = NO_3, crystallization occurred only with difficulty, and the complex could not be satisfactorily recrystallized from any solvent. Again, care was required for Z = CN. The oil obtained from evaporating a dichloromethane solution slowly crystallized under diethyl ether. For Z = N_3, a pure complex could not be obtained.

(ii) Cationic Complexes

The preparation of the complexes trans-$[Pt(CF_3)Q_2L][PF_6]$ is illustrated by that of the p-NC-C_6H_4-OMe complex: To a suspension of trans-$PtI(CF_3)Q_2$ (0.171 g., 0.256 mmoles) in 10 ml. methanol was added $AgPF_6$ (0.065 g., 0.258 mmoles). Silver iodide was removed by centrifugation to give a colourless solution. p-NC-C_6H_4-OMe (0.034 g., 0.255 mmoles) in 2 ml. methanol was added. Solvent was removed on a rotary evaporator to give a pale yellow oil. This was dissolved in 2 ml. dichloromethane and diethyl ether was slowly added. White needles of trans-$[Pt(CF_3)Q_2(\underline{p}\text{-}NC\text{-}C_6H_4\text{-}OMe)][PF_6]$ precipitated (0.140 g.).

The imino-ether complex, $[Pt(CF_3)Q_2NH{=}C(OMe)\text{-}C_6F_4\text{-}C(OMe){=}NH\text{-}Pt(CF_3)Q_2][PF_6]_2$ was prepared by the following procedure. To a suspension of $PtI(CF_3)Q_2$ (0.176 g., 0.264 mmoles) in methanol was added $AgPF_6$ (0.067 g., 0.264 mmoles) in 2 ml. methanol. Silver iodide was removed by centrifugation and $\underline{p}\text{-}NC\text{-}C_6F_4\text{-}CN$ was added (0.026 g., 0.013 mmoles). The solution was stirred for 10 minutes. The volume of methanol was reduced to give a white precipitate which was filtered off, washed with ether, then pentane. The product was recrystallized from dichloromethane/ether (0.124 g.).

The preparation of $[Pt(CF_3)Q_2\{NH{=}C(OMe)\text{-}C_6F_5\}][PF_6]$ was similar, except that the molar ratio of $PtI(CF_3)Q_2$/nitrile was halved. The preparations of the complexes with L = acetone or a carbene have been previously described [42].

CHAPTER VII

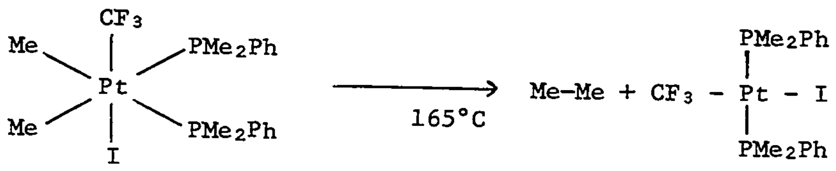
REACTIONS OF (π-1,5-CYCLOOCTADIENE)ORGANOPLATINUM(II) COMPOUNDS AND THE SYNTHESIS OF PERFLUOROALKYLPLATINUM COMPLEXES

a) Introduction

Although a large number of organoplatinum compounds have been prepared, most have contained phosphines or arsines as stabilizing ligands [49,50]. Similar complexes with other ligands such as isocyanides and amines have not been prepared, presumably because a competitive reaction occurs during the attempted synthesis, involving interaction of the organolithium or Grignard reagent with the ligand itself. In this chapter is described a convenient preparative route to several types of organoplatinum compounds.

Since the preparation of tetrameric trimethylplatinum(IV) iodide in 1909 [95,96] only two other similar platinum(IV) compounds have been prepared, and only then with some difficulty. Thus, $[PtMe_2Br_2]_x$ was prepared [97] from $[PtMe_3I]_4$ after refluxing for eight hours in bromine and concentrated hydrobromic acid, while triethylplatinum(IV) chloride [154] was prepared in 30% yield by the reaction of diethylmercury with platinum tetrachloride. In this chapter is described a very convenient preparation of $[PtMe_2X_2]_2$ and $[PtMe_3I]_4$ as well as the synthesis of four similar new Pt(IV) compounds. Several reactions of these compounds are discussed as well as the mechanism of their formation from Pt(II) compounds.

The synthesis of perfluoroalkyl metal complexes pose interesting synthetic challenges to organometallic chemists particularly since short chain perfluoroalkyl lithium or Grignard compounds are not suitable synthetic reagents [151]. Many platinum(IV) perfluoroalkyl compounds have been prepared by conventional oxidative addition reactions [21,135] and the pyrolysis of some of these compounds has led to the synthesis of CF_3-platinum(II) compounds containing phosphines or arsines (equation 1).



(1)

We now present a general route [152,153] to a variety of bis-trifluoromethyl platinum(II) and platinum(IV) compounds.

b) Results and Discussion

(i) Syntheses of $PtR_2(COD)$, and $PtRCl(COD)$

Attempts to prepare $Pt(COD)I_2$ from K_2PtCl_6 according to the method published by Doyle [155] have been unsuccessful. A better method, outlined in the Experimental section, is rather time-consuming (2 days) but gives pure $Pt(COD)Cl_2$ in good yield; metathetical replacement of the chloride with iodine then proceeds quantitatively. The dimethyl [155], diethyl [155], and diphenyl [155] and bis-trimethylsilylmethyl [156] complexes have been prepared previously; however, our procedures gave improved yields. The dibenzyl complex is new and was isolated as stable white crystals.

Platinum(II)-carbon bonds are very susceptible to attack by mineral acids [49,50]; conversion to a platinum(II) halide occurs readily on the addition of a molar equivalent of HCl in ether. However, such reactions are difficult to control due to problems of standardizing the ether solution and maintaining its concentration. The addition *in situ* of the appropriate amount of acetyl chloride to a dichloromethane-methanol solution greatly simplifies this hydrohalogenation reaction, and facilitates the generation of the milligram amounts of HCl necessary for the small scale syntheses in good yield of the complexes PtRCl(COD), where R = Me, Ph, CH_2Ph.

The ^1H nmr spectra of these complexes (Table VII-1) show resonances typical of the organo group as well as two distinct resonances for the olefinic hydrogens. The high field peak shows a significant coupling to ^{195}Pt ($J(Pt\text{-}H) \approx 75\text{-}80$ Hz) and is assigned to the olefinic group *trans* to chloride while the other resonance with $J(Pt\text{-}H) \approx 40$ Hz is assigned to the group *trans* to R. The methylene resonances were complex and no attempt was made to extract platinum coupling constants from the spectra.

(ii) Displacement Reactions

The cyclooctadiene in $PtMe_2(COD)$ is strongly bonded to platinum due to the presence of the strongly electron-donating methyl groups which enlarge the Pt 5d orbitals allowing greater overlap with

Table VII-1 ^1H NMR Data[a] for Organoplatinum(II) 1,5-Cyclooctadiene Complexes

Complex	Cyclooctadiene Resonances			Other Resonances
	$\delta_{(CH)}$	$J_{(Pt-H)}$	$\delta_{(CH_2)}$	
$Pt(CH_3)_2(COD)$	4.65	40	2.15	$\delta_{(Pt-CH_3)}0.58$, $^2J_{(Pt-H)}83.4$
$Pt(C_6H_5)I(COD)$	5.80	33	2.41	
	4.72	74		
$Pt(CH_3)Cl(COD)$	5.52	35	2.37	$\delta_{(Pt-CH_3)}0.89$, $^2J_{(Pt-H)}72.0$
	4.50	78	2.30	
$Pt(C_6H_5)Cl(COD)$	5.82	33	2.48	
	4.63	77		
$Pt(CH_2C_6H_5)_2(COD)$	4.59	41	1.75	$\delta_{(Pt-CH_2)}3.28$, $^2J_{(Pt-H)}114$
$Pt(CH_2C_6H_5)Cl(COD)$	5.59	36	2.30	$\delta_{(Pt-CH_2)}3.13$, $^2J_{(Pt-H)}102$
	4.31	74		
$Pt(CH_2C_6H_5)I(COD)$	5.54	35	1.50	$\delta_{(Pt-CH_2)}3.90$, $^2J_{(Pt-H)}105$
	3.21	73		
$Pt\{CH_2Si(CH_3)_3]I(COD)$	5.37	39	1.60	$\delta_{(Pt-CH_2)}1.72$, $^2J_{(Pt-H)}78$
	4.29	71		$\delta_{(SiCH_3)}0.44$
$Pt(C_2H_5)_2(COD)$	4.76	38	1.90	$\delta_{(PtCH_2)}1.87$, $^2J_{(Pt-H)}92.2$, $\delta_{(Pt-C-CH_3)}1.52$, $^3J_{(Pt-H)}80.5$

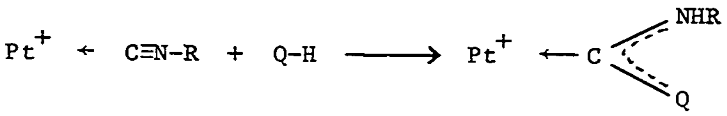
a) Spectra were recorded on $CHCl_3$ solutions, chemical shifts are in ppm downfield from TMS and coupling constants are given in hertz., COD = 1,5-cyclooctadiene.

the olefinic π^* orbitals and synergistically strengthening the Pt-(COD) bond. Consequently, displacement of COD is difficult and high temperatures are required for ligands of low trans-influence. However for ligands of high trans-influence the reaction is usually complete within one hour. A number of phosphine, arsine and stibine complexes have been prepared by Kistner et al [144], and we have extended these displacement reactions as shown in equation (2). ^1H nmr data for the new complexes are given in Table VII-2.

$$PtMe_2(COD) + 2L \xrightarrow[\substack{\sim 80°C \\ 1\ hour}]{} \underline{cis}\text{-}PtMe_2L_2 + COD \qquad (2)$$

$L = pCNC_6H_4Me$, CNEt, $AsMe_3$, bipy [157], $Ph_2PC{\equiv}CPPh_2$, $Me_2NCH_2CH_2NMe_2$, $P(p\text{-}C_6H_4Me)_3$

Of particular interest are the two isocyanide complexes. Organometallic isocyanide complexes are susceptible to reaction at the C≡N bond by organolithium compounds [57], and hence these two platinum-isocyanide complexes may not be prepared by the action of lithio or Grignard reagents on the Pt(II) dihalide-isocyanide complexes. In Chapter II the reactivity of isocyanide complexes towards various protic nucleophiles to give "carbene" complexes (equation 3) was discussed.



$$Pt^+ \leftarrow C{\equiv}N\text{-}R + Q\text{-}H \longrightarrow Pt^+ \leftarrow C{\Large\langle}\begin{smallmatrix}NHR\\ Q\end{smallmatrix} \qquad (3)$$

$Q = R'NH-$, $R'O-$, $R'S-$

It was suggested that nucleophilic attack at the isocyanide was facilitated by increasing the electron density on platinum (reflected by lowering $\Delta\nu(N\equiv C)$). The Raman $N\equiv C$ stretching frequency in cis-$PtMe_2(CNC_6H_4Me)_2$ is 2139 cm^{-1}, an increase on coordination of only 14 cm^{-1} over that of the free isocyanide. Although this compound should thus be a prime candidate for carbene formation, there was no tendency for the complex to react with aniline derivatives bearing electron-donating para-substituents [90]. Carbene formation is usually thermodynamically favourable (the reactions being exothermic [80]) since the carbenes are excellent σ-donors [23] and thus increase the electron density on the metal. We have recently examined [48], kinetically, oxidative addition reactions of $PtMe_2(CNC_6H_4Me)_2$ and the low activation energies indicate that the platinum atom in this compound is already very electron rich. If the electron density on platinum is a critical factor, the fact that carbene formation from $PtMe_2(CNC_6H_4Me)_2$ does not occur is therefore understandable. This may also be the reason that no zerovalent transition metal carbenes, derived from isocyanides, (where $\Delta\nu(N\equiv C)$ is negative) have been synthesized. Interestingly, cis-$PtMe_2(CNC_6H_4Me)_2$ reacted readily with a molar equivalent of hydrogen chloride to give the cis isomer of $PtMeCl(CNC_6H_4Me)_2$, even though most complexes of the type $PtMeClL_2$ are trans [49] (c.f. cis-$PtMeCl(CNC_6H_5Me)(PMe_2Ph)$ [26]. $PtPh_2(COD)$ also reacted with two moles of isocyanide to displace 1,5-cyclooctadiene, giving cis-$PtPh_2(CNC_6H_4Me)_2$.

Although the 1,5-cyclooctadiene in PtMeCl(COD) is strongly bonded, refluxing with bipyridyl in dichloromethane for thirty minutes gave PtMeCl(bipy) in nearly quantitative yields. The chloride was removed in the presence of a neutral ligand by $AgPF_6$, exemplified by the reaction with p-anisonitrile (equation 4).

$$\underline{\text{cis}}\text{-PtMeCl(bipy)} + AgPF_6 + pNC\text{-}C_6H_4OMe \xrightarrow[\text{-AgCl}]{\text{Acetone}} \qquad (4)$$

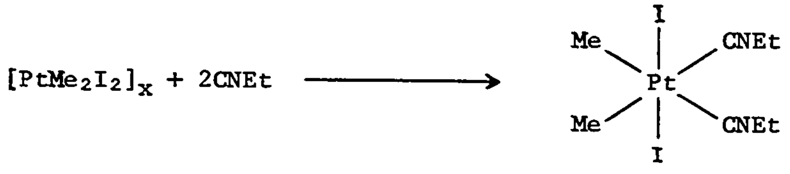
$$\underline{\text{cis}}\text{-[PtMe(bipy)(NCC}_6\text{H}_4\text{OMe)]}^+PF_6^-$$

Similarly, as a result of the lability of the chloride in PtRCl(COD) (R = Me, Ph, CH_2Ph), other series of cationic complexes may be prepared. The cyclooctadiene is readily displaced from these cations by neutral [158] and anionic ligands (e.g. see Chapter VIII).

(iii) Reactions of PtR_2(COD)

To date, there have been no reports of stable olefin and acetylene complexes of Pt(IV), although they have been suggested as reaction intermediates [42,99,115]. In an attempt to prepare $PtMe_3$(COD)I by the addition of methyl iodide to $PtMe_2$(COD), we found that oxidative addition occurred; however, cyclooctadiene was displaced to give $[PtMe_3I]_4$. The relative ease of oxidation of $PtMe_2$(COD) with the elimination of cyclooctadiene prompted us to investigate this reaction as a possible source for a variety of new organoplatinum(IV) compounds.

$PtMe_2$(COD) reacted immediately with bromine or iodine in dichloromethane or ether to give $[PtMe_2X_2]_x$ in nearly quantitative yields. The compounds precipitate from solution as powders which are insoluble in organic solvents. They were characterized by elemental analysis and reaction with ethyl isocyanide as shown in equation 5.



(5)

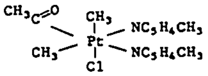
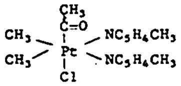
I

The nmr spectrum of I (Table VII-2) is unusual in that the ethyl protons of the isocyanide are coupled to the ^{14}N nucleus (I = 1, 99.635% natural abundance) splitting each peak into a 1:1:1 "triplet". In most ethyl isocyanide complexes [26,99,115] the ethyl resonances are broadened as a result of a relaxation process associated with the interaction of the ^{14}N quadrupole with the large electric field gradients within the molecule [159]. However in the present case, as for the free isocyanide the electric field gradients surrounding the ^{14}N nucleus must be small and the quadrupolar relaxation is diminished. The measured ^{14}N-^{1}H couplings (Table VII-2) are interesting since the β-coupling is larger than the α-coupling.

Acetyl chloride reacted with $PtMe_2(COD)$ to give the acyl compound $[PtMe_2(COMe)Cl]_x$ which is probably tetrameric as are all other such platinum complexes [160]. The reaction of two molar equivalents of γ-picoline with $[PtMe_2(COMe)Cl]_x$ gave a product with empirical formula $PtMe_2(COMe)(\gamma\text{-pic})_2Cl$. The nmr spectrum in chloroform (Table VII-2) showed the presence of three methyl groups of equal intensity and only two acyl peaks in the ratio of 2:1. These results and the various Pt-H coupling constants are consistent with the presence of two isomers in the ratio of 2:1, as predicted for the cleavage of a cubane type structure with bridging chlorides (equation 6).

Table VII-2

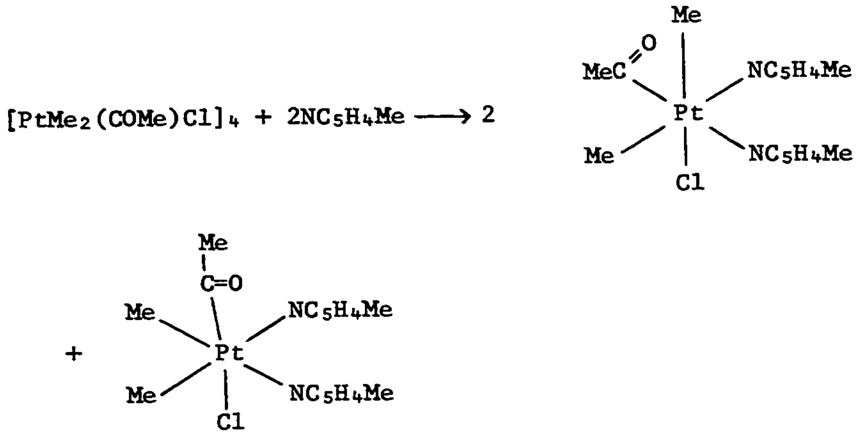
^{1}H NMR Data[a] for Organoplatinum Complexes

Complex	δ(Pt-CH$_3$)	^{2}J(Pt-CH$_3$)	Other Resonances and Coupling Constants
Pt(CH$_3$)$_2$(CNC$_6$H$_4$CH$_3$)$_2$	0.74	74.6	δ(CH$_3$)2.34
Pt(CH$_3$)$_2${P(p-C$_6$H$_4$CH$_3$)$_3$}$_2$	0.30	69.0	δ(CH$_3$)2.32
[Pt(CH$_3$)$_2$]$_2$(DPPA)$_2$	0.49	74.0	
Pt(CH$_3$)$_2$(CNC$_2$H$_5$)$_2$	0.30	75.0	δ(CH$_3$)1.31,δ(CH$_2$')3.45,J(H-H')7.0
Pt(CH$_3$)$_2${(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$}	0.19	86.0	δ(NCH$_3$)2.59,^{3}J(Pt-H)22.7,δ(NCH$_2$)2.57,^{3}J(Pt-H)12.2
Pt(CH$_3$)Cl(CNC$_6$H$_4$CH$_3$)$_2$	0.91	61.4	δ(CH$_3$)2.39
Pt(CH$_3$)Cl(bipy)	1.09	79.4	
[Pt(CH$_3$)(bipy)(NCC$_6$H$_4$OCH$_3$)](PF$_6$)	1.06	80.4	δ(OCH$_3$)2.57
Pt(CH$_3$)$_2$(CNC$_2$H$_5$)$_2$Br$_2$	1.66	64.8	δ(CH$_3$)1.48 ^{3}J(^{1}H-^{14}N)2.8 δ(CH'$_2$)3.89 ^{2}J(^{1}H-^{14}N)1.0 } J(H-H')7.2
Pt(CH$_3$)$_2$(COCH$_3$)Cl	1.66	85.4	δ(COCH$_3$)2.43,^{3}J(Pt-H)15.6
	1.21[b] 1.41[c]	74.2 71.0	δ(COCH$_3$)2.43,^{3}J(Pt-H)8.0 δ(CH$_3$)2.42
	1.32	72.0	δ(COCH$_3$)2.17,^{3}J(Pt-H)16.0 δ(CH$_3$)2.42
Pt(CH$_3$)(C$_2$H$_5$)$_2$I	1.54	81.4	δ(Pt-CH$_2$)2.33,^{2}J(Pt-CH)78.8 δ(Pt-C-CH$_3$)0.87,^{3}J(PtCCH$_3$)81.9 } J(H-H')7.6
[Pt(CH$_3$)(C$_2$H$_5$)$_2$(NC$_5$H$_5$)$_3$](ClO$_4$)	1.23	71.8	δ(PtCH$_2$)2.01,^{2}J(Pt-CH$_2$)79.4 δ(Pt-C-CH$_3$)0.58,^{3}J(Pt-C-CH$_3$)57.0 }J(H-H')7.6
Pt(C$_2$H$_5$)$_2$(4-NC$_5$H$_4$CH$_3$)$_2$I$_2$			δ(PtCH$_2'$)4.21,^{2}J(Pt-CH$_2$)87.0,J(H-H')7.6 δ(Pt-CCH$_3$)1.25,^{3}J(PtCCH$_3$)29.2,δ(4-CH$_3$)1.64

a. Spectra were recorded in CH$_2$Cl$_2$ or CHCl$_3$ solutions. Chemical shifts are in ppm downfield from Si(CH$_3$)$_4$ and coupling constants are given in hertz;bipy = α,α'-bipyridine;DPPA= 1,2-bis(diphenylphosphino)acetylene.

b. <u>trans</u> to chloride

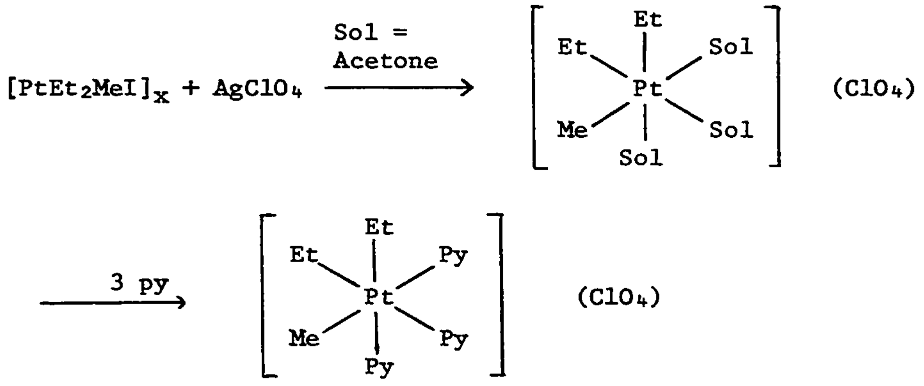
c. <u>trans</u>- to 4-methylpyridine.



(6)

No reaction occurred between $PtMe_2(COD)$ and ethyl iodide or benzoyl chloride.

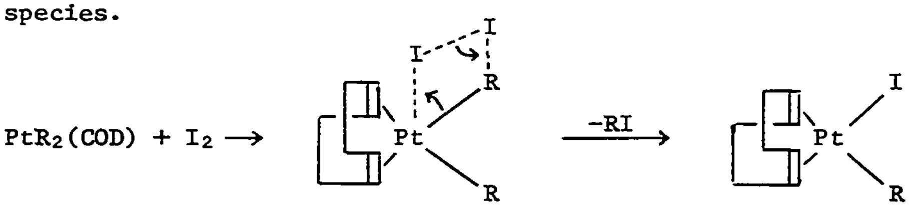
$PtEt_2(COD)$ reacted readily with methyl iodide and iodine to give the two new platinum(IV) compounds $[PtEt_2MeI]_x$ and $[PtEt_2I_2]_x$ (where x is probably four). The addition of two molar equivalents of γ-picoline to $[PtEt_2I_2]_x$ gave golden crystals of $PtEt_2(\gamma\text{-pic})_2I_2$. Similarly, $[PtEt_2MeI]_x$ reacted with pyridine to give white crystals of $PtEt_2Me(NC_5H_5)_2I$; however, the nmr spectrum was exceedingly complicated as might be expected for a mixture of isomers. For $[PtEt_3I]_4$ the values of $^2\underline{J}(Pt\text{-}CH_2)$ and $^3\underline{J}(Pt\text{-}CH_3)$ are opposite in sign, as observed for other ethyl-metal complexes [161,162]. Similarly, for $[PtEt_2MeI]$, irradiation of the low field ^{195}Pt satellite of the CH_2 group caused the high field satellite of the CH_3 peak to collapse, indicating opposite signs for these two platinum coupling constants. The iodide in $[PtEt_2MeI]_x$ may be removed by the addition of a silver salt of a non-coordinating anion, e.g. $AgClO_4$, in acetone or methanol to give a stable solvent cation.



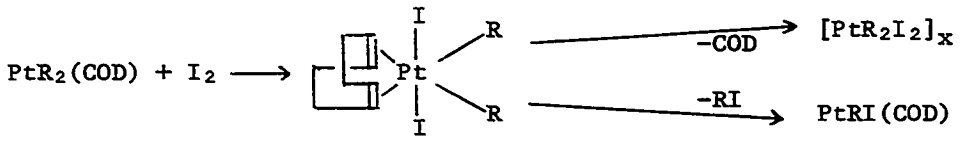
(7)

The addition of 3 molar equivalents of ligand (e.g. pyridine) caused the ready displacement of the solvent molecules to form the white crystalline tris (ligand) salt (equation 7).

Methyl iodide does not react with $PtR_2(COD)$ (R = CH_2Ph, CH_2SiMe_3). Iodine, however, reacted with $Pt(CH_2Ph)_2(COD)$ to give a mixture of $[Pt(CH_2Ph)_2I_2]_x$ and $Pt(CH_2Ph)I(COD)$ and with $Pt(CH_2SiMe_3)_2(COD)$ to give only $Pt(CH_2SiMe_3)I(COD)$. Two reaction pathways (shown in equations 8 and 9) are possible for the formation of the PtRI(COD) species.



(8)



(9)

Equation (8) involves a concerted bond scission mechanism with elimination of alkyl iodide. Equation (9) involves initial oxidation of Pt(II) to Pt(IV) to give an intermediate Pt(IV) olefin compound which may then reductively eliminate to give PtRI(COD) or displace 1,5-cyclooctadiene to give Pt(IV) polymers. Although we have no direct evidence at this time to support either mechanism, equation (9) is favoured since it offers a possible route to the two products obtained from the reaction of $Pt(CH_2Ph)_2(COD)$ with iodine.

(iv) Perfluoroalkylplatinum Complexes - Oxidative Addition and Displacement Reactions

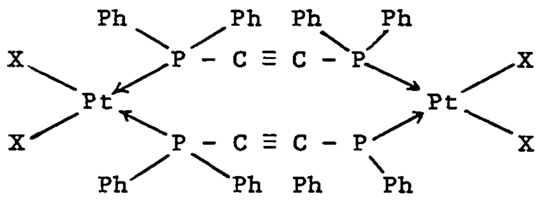
During the past several years organometallic chemists have been interested in synthesizing fluorocarbon transition metal complexes because of the greater stability of these compounds compared to their hydrocarbon analogues. Several methods have been developed[163] for the preparation of such compounds: (1) the reaction of metal carbonyl anions with perfluoroacyl halides followed by decarbonylation; (2) nucleophilic substitution of fluoride with metal carbonyl groups by reactions of fluorinated olefins or aromatic compounds with metal carbonyl anions; (3) addition of fluoroolefins, fluorinated alkynes or perfluoroalkyl iodides to appropriate transition metal systems, particularly those in low oxidation states; (4) reactions of metal halide derivatives with fluoroalkyl or fluoroaryl derivatives of electropositive metals such as lithium or magnesium; (5) reactions of transition metal halide compounds with silver fluorocarbon derivatives [164]. We have now found a very convenient method for the preparation of a variety of bis(perfluoroalkyl)platinum compounds.

In an attempt to prepare $[PtMe_2(CF_3)I]_4$ by the oxidative addition of trifluoromethyl iodide to $PtMe_2COD$ the major product of the reaction was found to be $Pt(CF_3)_2COD$ with some $[PtMe_3I]_4$. There are two possible reaction pathways as in the reaction of iodine with Pt(II)-COD compounds, i.e. (i) a concerted mechanism involving scission of the Pt-Me bond by CF_3I giving MeI and (ii) an oxidative addition mechanism involving formation of $PtMe_2(CF_3)(COD)I$, elimination of MeI to give $PtMe(CF_3)(COD)$ and a further oxidative addition-reductive elimination reaction. The latter reaction would be expected to proceed very slowly since Pt(II)-CF_3 complexes are fairly electrophilic and hence oxidized only with strong oxidizing agents such as iodine [48]. The concerted mechanism is favoured although it is possible that this bond scission may involve radicals. The formation of $[PtMe_3I]_4$ presumably results from the addition of some of the generated methyl iodide to $PtMe_2COD$.

The 1,5-cyclooctadiene in $Pt(CF_3)_2(COD)$ is more labile than in $PtMe_2(COD)$ due to (a) the high <u>trans</u>-influence of the CF_3 group and (b) the greater electronegativity of CF_3, which contracts the Pt5d orbitals and synergistically weakens the Pt-COD bond. Therefore a variety of ligands readily displace COD from $Pt(CF_3)_2(COD)$ forming a series of complexes $Pt(CF_3)_2L_2$ (L = CNEt, PMe_2Ph, $AsMe_3$, bipy, 4-NC_5H_4-Me, $SbPh_3$, $AsPh_3$, $Ph_2PC{\equiv}CPPh_2$, and $Me_2NCH_2CH_2NMe_2$. Although many more compounds could readily be obtained, we have only prepared a few with ligands covering a range of trans-influence to emphasize the versatility of the reaction. The products are stable crystalline solids, soluble in polar solvents.

The values of $^2J(Pt-CF_3)$ for these complexes (Table VII-3) are dependent on the platinum hybridization (Chapter VI), specifically on the amount of Pt 6s character in the Pt-CF_3 bond. Therefore the ligands L, may be arranged in an order of increasing trans-influence as follows: 4-NC_5H_4-Me < $SbPh_3$ < $Me_2NCH_2CH_2NMe_2$ < 1,5-cyclooctadiene < bipy < $AsPh_3$ < CNEt < $AsMe_3$ < PMe_2Ph. The phosphine methyl resonances of $Pt(CF_3)_2(PMe_2Ph)_2$ appear as doublets, flanked by ^{195}Pt satellites, confirming the cis-stereochemistry.

The acetylenic phosphine $Ph_2P-C{\equiv}C-PPh_2$(DPPA) readily displaces COD from PtX_2(COD), X = Me, CF_3, to form the binuclear complexes II.



II

Carty and Efraty [165] have prepared a number of transition metal DPPA complexes and have examined the acetylenic C≡C stretching frequency in the solid state Raman spectra. The low value of $\nu(C{\equiv}C)$ in the free ligand was attributed to a lowering of the C≡C bond order

Table VII-3 ^{19}F and ^{1}H NMR Data[a] for Trifluoromethylplatinum Complexes

Complex[b]	$\delta(Pt\text{-}CF_3)$	$^2J(Pt\text{-}CF_3)$	Other Resonances and Couplings
$Pt(CF_3)_2(NC_5H_4CH_3)_2$	24.80	793	$\delta(CH_3)2.66, \delta(\alpha\text{-}H)8.56^3, J(PtH)20.4, \delta(\beta\text{-}H)7.28$
$Pt(CF_3)_2\{Sb(C_6H_5)_3\}_2$	11.09	791	
$Pt(CF_3)_2\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}$	24.60	752	$\delta(NCH_3)2.81, ^3J(Pt\text{-}H)24.1, \delta(NCH_2)2.70^3, J(PtH)15.0$
$Pt(CF_3)_2(\pi\text{-}1,5\text{-}C_8H_{12})$	29.73	736	$\delta(CH)5.75, J(PtH)42, \delta(CH_2)2.59$
$Pt(CF_3)_2(bipy)$	23.90	741	
$Pt(CF_3)_2\{As(C_6H_5)_3\}_2$	29.01	731	
$Pt(CF_3)_2(CNC_2H_5)_2$	24.20	719	$\delta(CH_3)1.50, ^5J(Pt\text{-}H)2.3, \delta(CH_2)3.77$
$Pt(CF_3)_2\{As(CH_3)_3\}_2$	19.61	713	$\delta(AsCH_3)1.51, ^3J(Pt\text{-}H)13.0$
$Pt(CF_3)_2\{P(CH_3)_2(C_6H_5)\}_2$	21.60	627	$\delta(PCH_3)1.56, ^3J(PtH)21.0, ^2J(PH)9.6, ^3J(PF)72.$
$Pt(CF_3)_2\{P(CH_3)_2(C_6H_5)\}_2I_2$	10.41^t	289	$\delta(PCH_3)2.55, ^3J(Pt\text{-}H)18.7, ^2J(PH)4.0, ^3J(PF)8.4$
$Pt(CF_3)_2(CNC_2H_5)_2I_2$	11.61	452	$\delta(CH_3)1.59, \delta(CH_2)4.15.$
$Pt(CF_3)_2(bipy)I_2$	10.21	441	
$[Pt(CF_3)_2]_2(DPPA)_2$	c		

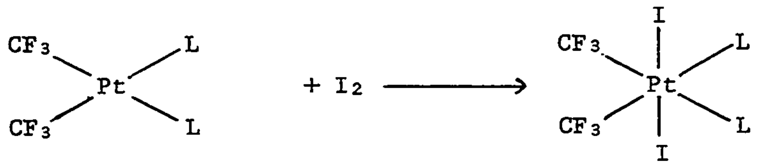
a. Spectra were recorded in CH_2Cl_2 or $CHCl_3$ polutions. ^{19}F chemical shifts are in ppm upfield from $CFCl_3$ and ^{1}H chemical shifts are in ppm downfield from $Si(CH_3)_4$. t = triplet.

b. bipy = α,α'-bipyridine, DPPA = 1,2 bis(diphenylphosphine)acetylene.

c. complex too insoluble for NMR measurements.

resulting from a drift of π-electron density from the carbon pπ-orbitals to phosphorus dπ-orbitals. It was suggested that back-bonding Mdπ > Pdπ would decrease the π-electron drift from the carbon 2pπ-orbitals to phosphorus dπ-orbitals, causing $\nu(C{\equiv}C)$ to move to higher frequency. Consequently the more positive $\Delta\nu(C{\equiv}C)$ becomes, the greater is the $M \rightarrow P$ π-bonding. The values of $\Delta\nu(C{\equiv}C)$ for the complexes II, X = Cl [165], CF_3, Me are 39, 34, 27 cm^{-1} respectively. If the explanation of Pdπ-Cpπ bonding is correct, these results infer that there is a greater positive charge on phosphorus for the methyl platinum complex than for the chloro analogue.

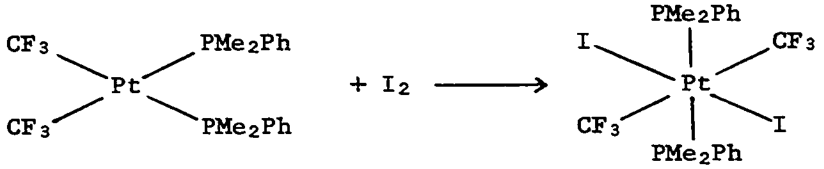
The oxidative addition of iodine to $Pt(CF_3)_2L_2$ (L = CNEt, bipy, PMe_2Ph) was also studied. For the isocyanide and bipyridyl complexes the iodine gave exclusively the trans-addition product. (equation 10)



(10)

L = CNEt, bipy

However, the addition of iodine to $Pt(CF_3)_2(PMe_2Ph)_2$ gave a brown crystalline solid whose ^{19}F nmr showed a triplet pattern with platinum satellites, $^2J(Pt\text{-}F)$ = 289, consistent with trans-CF_3 groups [48]. The phosphine methyl resonances appear as "virtually" coupled triplets [36], confirming the stereochemistry shown in equation (11).



(11)

The phosphine complex $Pt(CF_3)_2(PMe_2Ph)_2$ did not react with tetracyanoethylene [166] or hexafluorobut-2-yne, unlike the analogous methyl platinum complex [15,16].

The triphenylstibine complex cis-$Pt(CF_3)_2(SbPh_3)_2$ was not oxidized with iodine.

The reaction between C_2F_5I and cis-$PtEt_2(COD)$ proceeded smoothly giving mainly $Pt(C_2F_5)_2(COD)$ and some $[PtMe_3I]_4$. The perfluoroethyl compound could not be isolated pure, however the cyclooctadiene was displaced by excess triphenylphosphine to give $Pt(C_2F_5)_2(PPh_3)_2$. Similar reactions with perfluoroisopropyl iodide and n-perfluoropropyl iodide and $PtMe_2COD$ gave a mixture of products of which none could be isolated in pure form.

c) Conclusions

From our present and previous studies of methyl and trifluoromethyl platinum complexes, we can now arrive at several generalizations as follows:

(i) Both CH_3 and CF_3 have a high trans-influence [11] (i.e. defined as a trans bond-weakening effect) [6].

(ii) Both CH_3 and CF_3 contain a large amount of Pt(6s) orbital contributions in the Pt-C bond as shown from NMR coupling constants [11].

(iii) Pt-CF_3 complexes are much more thermally stable than analogous Pt-CH_3 complexes.

(iv) Pt-CF_3 complexes are much less nucleophilic than Pt-CH_3 complexes, as shown by (a) oxidative addition reactions; trans-Pt(CH_3)I(PMe_2Ph)$_2$ is oxidized by CF_3I to give Pt(CH_3)(CF_3)I_2(PMe_2Ph)$_2$[135] whereas trans-Pt(CF_3)I(PMe_2Ph)$_2$ is not oxidized by CH_3I or CF_3I [48]; (b) reactions with dilute mineral acids; $PtMe_2$(COD) reacts instantaneously with HCl whereas Pt(CF_3)$_2$(COD) is stable to HCl; (c) reactions with olefins or acetylenes bearing electron withdrawing substituents, cis-Pt(CF_3)$_2$(PMe_2Ph)$_2$ does not react with CF_3-C≡C-CF_3 whereas $PtMe_2$(PMe_2Ph)$_2$ is very reactive [166]; (d) reactions of CH_3-Pt^+ and CF_3-Pt^+ cations with unsaturated organic molecules [11].

(v) There appears to be no significant π-back bonding from platinum to either the CF_3 or CH_3 group and the Pt-R bond is very covalent (R = CF_3, CH_3) [11].

d) Experimental

Analytical and physical data for new platinum complexes are given in Tables VII-4 and VII-5. A few of the compounds have been previously prepared, however the following methods gave much better yields. All reactions were performed with 'spectro-analyzed' solvents without purification except that the diethylether used in the Grignard or lithium reactions was dried over lithium aluminum hydride and distilled under nitrogen.

Table VII-4

Physical and Analytical Data for New Platinum Complexes

COMPLEX[a]	Analysis % Calc.(Found)		Colour	Melting Point[b]	Recrystallization
	Carbon	Hydrogen		(°C)	Solvents
$Pt(CH_3)_2(CNC_6H_4CH_3)_2$	47.05(46.87)	4.39(4.10)	White	82-84	CH_2Cl_2-nC_5H_{12}
$Pt(CH_3)_2\{P(p\text{-}C_6H_4CH_3)_3\}_2$	63.43(63.33)	5.81(5.59)	White	230-240[d]	CH_2Cl_2-nC_5H_{12}
$[Pt(CH_3)_2]_2(DPPA)_2$	54.33(53.93)	4.23(4.10)	White	264-266	CH_2Cl_2-nC_5H_{12}
$Pt(CH_3)_2(CNC_2H_5)_2$	28.66(28.84)	4.81(4.89)	White	39-41	$(C_2H_5)_2O$-nC_5H_{12}
$Pt(CH_3)_2\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}$	28.15(28.03)	6.50(6.21)	White	>143[d]	CH_2Cl_2-$(C_2H_5)_2O$
$Pt(C_6H_5)_2(CNC_6H_4CH_3)_2$	57.50(57.47)	4.12(4.07)	Yellow	>130[d]	CH_2Cl_2-nC_5H_{12}
$Pt(CH_3)Cl(COD)$	30.55(30.45)	4.27(4.30)	White	166-167	CH_3OH
$Pt(CH_3)Cl(CNC_6H_4CH_3)_2$	42.55(42.40)	3.57(3.59)	White	>120[d]	CH_2Cl_2-nC_5H_{12}
$Pt(C_6H_5)Cl(COD)$	40.44(40.66)	4.12(4.23)	White	166-168	CH_2Cl_2-nC_5H_{12}
$Pt(CH_2C_6H_5)_2(COD)$	54.42(54.01)	5.40(5.23)	White	112-115	CH_2Cl_2-nC_5H_{12}
$Pt(CH_2C_6H_5)Cl(COD)$	41.92(41.83)	4.46(4.36)	White	136-138	CH_3OH-$(C_2H_5)_2O$
$Pt(CH_3)Cl(bipy)$	33.72(33.61)	2.83(2.73)	Yellow	248-252	CH_2Cl_2-$(C_2H_5)_2O$
$Pt(CH_3)Cl(phen)$	35.18(35.01)	2.50(2.52)	Yellow	310-320	$(CH_3)_2CO$-$(C_2H_5)_2O$
$[Pt(CH_3)(bipy)(NCC_6H_4OCH_3)](PF_6)$	35.41(35.25)	2.81(2.91)	Yellow	232-233	$(CH_3)_2CO$-$(C_2H_5)_2O$
$Pt(C_6H_5)I(COD)$	33.15(32.94)	3.38(3.43)	Yellow	125-130	CH_2Cl_2-$(C_2H_5)_2O$
$Pt(CH_3)_2(CNC_2H_5)_2Br_2$	19.41(19.09)	3.26(3.17)	Yellow	70-73	CH_2Cl_2-nC_5H_{12}
$Pt(CH_3)_2(COCH_3)Cl$[c]	15.80(16.00)	2.46(2.92)	White	>130[d]	CH_2Cl_2-nC_5H_{12}
$Pt(CH_3)_2(COCH_3)(4\text{-}NC_5H_4CH_3)_2Cl$	40.04(39.78)	4.83(4.66)	White	137-138	$(C_2H_5)_2O$-nC_5H_{12}
$Pt(C_2H_5)_2I_2$[d]	9.48(9.46)	1.99(1.68)	Brown	--	----
$Pt(C_2H_5)_2(4\text{-}NC_5H_4CH_3)_2I_2$	27.72(27.49)	3.49(3.37)	Gold	>150[d]	CH_3OH
$Pt(C_2H_5)_2(CH_3)I$[e]	15.20(15.36)	3.32(3.28)	White	>200[d]	$CHCl_3$-$(CH_3)_2CO$
$Pt(C_2H_5)_2(CH_3)(NC_5H_5)_2I$	32.56(32.73)	4.19(4.20)	White	130-132	CH_3OH-nC_5H_{12}
$[Pt(C_2H_5)_2(CH_3)(NC_5H_5)_3](ClO_4)$	39.71(39.80)	4.66(4.67)	White	143-145	CH_3OH-$(C_2H_5)_2O$
$Pt(CH_2C_6H_5)I(COD)$	34.60(34.47)	3.65(3.63)	Yellow	>120[d]	$(C_2H_5)_2O$-nC_5H_{12}
$Pt(CH_2C_6H_5)_2I_2$[f]	26.64(26.31)	2.24(2.04)	Brown	--	----
$Pt\{CH_2Si(CH_3)_3\}(COD)I$	27.86(27.97)	4.48(4.29)	White	51-53	CH_3OH

a) DPPA = 1,2-bis(diphenylphosphine)acetylene, COD - 1,5-cyclooctadiene, bipy = α, α'-bipyridine, phen = 1,10-phenanthroline.

b) melting points are uncorrected, d = decomposes.

c) chloride analysis 11.68(12.06)

d) iodide analysis 50.06(49.83)

e) iodide analysis 32.12(32.01)

f) iodide analysis 40.20(39.84)

Table VII-5 Analytical and Physical Data for Perfluoroalkylplatinum Complexes

Complex[b]	Colour	Analyses % Calc.(Found)			Melting Point[a]	Recrystallization[c]
		Carbon	Hydrogen	Fluorine	(°C)	Solvents
$Pt(CF_3)_2\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}$	white	21.38(21.33)	3.59(3.68)	25.40(25.44)	> 200[d]	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2(NC_5H_4CH_3)_2$	white	32.38(32.26)	2.72(2.59)	21.95(21.64)	250-252	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2\{Sb(C_6H_5)_3\}_2$	white	43.92(44.18)	2.91(3.17)	10.97(10.95)	150-151	$(CH_3)_2CO$-n C_5H_{12}
$Pt(CF_3)_2(\pi$-$1,5C_8H_{12})$	white	27.22(27.11)	2.74(2.70)	27.06(27.27)	179-181	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2$(bipy)	yellow	29.46(29.17)	1.65(1.54)	23.30(23.26)	303-305	DMF-$(C_2H_5)_2O$
$Pt(CF_3)_2\{As(C_6H_5)_3\}_2$	white	48.27(48.09	3.20(3.46)	12.06(11.67)	245-250	CH_2Cl_2-$(C_2H_5)_2O$
$Pt(CF_3)_2(CNC_2H_5)_2$	white	17.37(17.24)	1.82(1.74)	20.61(20.38)	130-132	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2\{P(CH_3)_2(C_6H_5)\}_2$	white	35.47(35.56)	3.64(3.68)	18.71(18.88)	188-190	CH_2Cl_2-$(C_2H_5)_2O$
$Pt(CF_3)\{P(CH_3)_2(C_6H_5)\}_2I_2$	brown	25.04(24.85)	2.57(2.46)	13.21(12.91)	128-130	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2(CNC_2H_5)_2I_2$	brown	11.91(12.01)	1.25(1.21)	14.13(14.21)	145-150	CH_2Cl_2-n C_5H_{12}
$Pt(CF_3)_2$(bipy)I_2	red	19.40(19.28)	1.08(1.12)	15.36(15.13)	> 105[d]	DMF-$(C_2H_5)_2O$
$[Pt(CF_3)_2]_2$(DPPA)$_2$	white	46.25(46.47)	2.77(2.93)	15.69(15.53)	274-276	$(CH_3)_2CO$-$(C_2H_5)_2O$
$[Pt(C_2F_5)_2\{P(C_6H_5)_3\}_2]$	white	50.16(50.25)	3.16(3.55)	19.84(19.14)	235-237	CH_2Cl_2-$(C_2H_5)_2O$

a. Melting points are uncorrected, d = decomposed

b. bipy: α,α'-bipyridine, DPPA = 1,2 bis(diphenylphosphino)acetylene

c. DMF = dimethylformamide

(i) Preparation of Pt(COD)I_2

To a solution of K_2PtCl_4 (10 g.) in 160 ml. of distilled water was added 110 ml. of n-propanol, 20 ml. of 1,5-cyclooctadiene and 0.150 g. of $SnCl_2$. The mixture was magnetically stirred for two days (or until the solution was nearly colourless), during which time a white precipitate formed. The mixture was filtered, washed with distilled water (100 ml.) and 20 ml. of ethanol, then air-dried. The yield of $PtCl_2$(COD) was usually better than 8.8 g. (98%). The dichloride was readily converted to the diiodide in 98% yield by the addition of a slight excess of NaI (7 g. NaI for 8.2 g. $PtCl_2$(COD)) to a suspension of $PtCl_2$(COD) in acetone. The solution immediately turned yellow and the acetone was removed by rotary evaporation. The residue was collected on a frit and washed three times with 50 ml. portions of distilled water and air-dried.

(ii) Preparation of $PtMe_2$(COD)

To an ice-cold solution of PtI_2(COD) (11.8 g.) in 100 ml. of diethylether under nitrogen was added an excess of methyl-lithium (30 ml. of a 1.95 M solution in ether). The solution was stirred for two hours and hydrolyzed at 0°C with an ice-cold saturated aqueous solution of ammonium chloride. The ether layer was separated and the aqueous layer extracted with three 50 ml. portions of diethyl ether. The ether fractions were dried over anhydrous magnesium sulphate containing a small amount of activated charcoal. The solution was filtered and the ether removed by rotary evaporation to give white crystals of $PtMe_2$(COD) (6.05 g. 87%).

(iii) Preparation of $PtEt_2(COD)$

An ethylmagnesium iodide solution was prepared from 1.0 g. of Mg and 6.24 g. of ethyliodide (3.2 ml.) in 100 ml. of dried ether. This solution was filtered under nitrogen and cooled to 0°C, then $PtI_2(COD)$ (5.0 g.) was added. The solution was stirred at 0°C for three hours, hydrolyzed and dried as in (ii). The ether was removed to give a pale yellow oil, which solidified on cooling to 0°C. The yield of $PtEt_2(COD)$ (mp 25-30°C) was 79% (2.55 g.).

(iv) Preparation of $Pt(CH_2Ph)_2(COD)$

An ether solution of the benzyl Grignard, prepared from magnesium (1.0 g.) and 6.84 g. $PhCH_2Br$ in 100 ml. of dried ether, was filtered and $PtI_2(COD)$ (5.0 g.) was added. The solution was stirred for 4 hours at room temperature and worked up as in (ii). The yield was 3.55 g. (82%).

(v) Preparation of $[PtMe_2I_2]_x$

To a solution of $PtMe_2(COD)$ (0.682 g.) in 50 ml. of dichloromethane was added a solution of iodine (0.52 g.) in dichloromethane. There was an immediate orange-red precipitate; the solution was stirred for one hour, filtered and washed with ether and pentane. Yield 0.875 g. (91%). The dibromide was prepared similarly using bromine.

(vi) Preparation of $PtMe_2(CNEt)_2Br_2$

To a suspension of $[PtMe_2Br_2]_x$ (0.150 g.) in 8 ml. of dichloromethane was added 0.055 ml. of ethylisocyanide. The mixture was stirred for 20 hours to give a clear yellow solution which was passed through a 1" florisil column, eluting with dichloromethane. The volume was reduced and the addition of pentane caused the formation of yellow needle-shaped crystals. Yield 0.139 g. (68%).

(vii) Preparation of $PtMeEt_2I$

$PtEt_2(COD)$ (0.402 g.) was dissolved in 5 ml. of iodomethane. After two hours large crystals formed. After 10 hours the iodomethane was removed by rotary evaporation. The white solid was dissolved in chloroform and acetone was added to give white needles. The solution was cooled for several hours, filtered and the crystals were washed with pentane. The yield was 0.360 g. (82%).

(viii) Preparation of $[PtMeEt_2(NC_5H_5)_3](ClO_4)$

To a solution of $PtMeEt_2I$ (0.158 g.) and pyridine (0.100 ml.) in 5 ml. of dichloromethane was added a solution of $AgClO_4$ (0.084 g.) in 5 ml. of acetone. Silver iodide precipitated immediately and after the mixture had been stirred for 10 minutes, the precipitate was removed by centrifugation. The solvent was removed by rotary evaporation to give a clear colourless oil, which was dissolved in 2 ml. of methanol. Ether was added and the solution was cooled to 0°C. Scratching the flask initiated the crystallization of white needles which were filtered and washed with ether. Yield 0.178 g. (74%).

(ix) Preparation of $PtMe_2(COMe)Cl$

$PtMe_2(COD)$ (0.844 g.) was dissolved in the minimum amount of diethylether and a molar equivalent of acetylchloride (0.20 ml.) was added. After 12 hours white crystals had deposited; the solution was cooled at 0°C for several hours and the ether was decanted. Yield 0.650 g. (84%).

(x) Preparation of $PtMe_2(COMe)(4\text{-}NC_5H_4CH_3)_2Cl$

$PtMe_2(COMe)Cl$ (0.070 g.) was dissolved in 2 ml. of chloroform and 4-methylpyridine (0.043 g.) was added and the solution became warm. The solvent was removed to give a clear oil that was crystallized from ether and pentane. Yield 0.084 g. (75%).

(xi) Reaction of $Pt(CH_2Ph)_2(COD)$ with Iodine

To a solution of $Pt(CH_2Ph)_2(COD)$ (0.680 g.) in ether was added a solution of iodine (0.366 g.) in ether. The solution became red and over a period of one hour a brown powder precipitated. It was filtered and identified as $Pt(CH_2Ph)_2I_2$ (yield 48% based on $Pt(CH_2Ph)_2(COD)$). The yellow filtrate was reduced in volume and pentane was added; after cooling yellow needles of $Pt(CH_2Ph)I(COD)$ separated (45% yield). They were filtered, washed with pentane and air-dried.

(xii) Preparation of $[PtEt_2I_2]_x$

To an ice-cold solution of $PtEt_2(COD)$ (0.412 g.) in ether was added a molar equivalent of iodine (0.290 g.) in ether. A brown powder separated immediately and after stirring for 10 minutes the solution was filtered and the brown powder was washed with ether and pentane. Yield 0.380 g. (75%).

(xiii) Preparation of $PtMe_2(p\text{-}CNC_6H_4Me)_2$

$PtMe_2(COD)$ (0.252 g.) was dissolved in 5 ml. of acetone and p-tolylisocyanide (0.177 g.) was added. The solution was stirred for three hours and the solvent removed by rotary evaporation to give dirty yellow crystals which were washed with pentane to remove cyclooctadiene and free isocyanide. The crystals were dissolved in 2 ml. of dichloromethane and passed through a 1" florisil column, eluting with CH_2Cl_2. The volume was reduced and the addition of pentane induced crystallization. The flask was cooled for 2 hours and the white crystals were filtered and washed with pentane. Yield 0.267 g. (77%).

(xiv) Preparation of $PtMe_2(Me_2NCH_2CH_2NMe_2)$

$PtMe_2(COD)$ (0.40 g.) was dissolved in 2 ml. of N,N,N',N'-tetramethylethylenediamine and the solution was heated to 100°C for 1 hour. The excess amine was removed under vacuum to give an oil which was taken up in dichloromethane. The addition of diethyl ether, and subsequent cooling gave white crystals which were filtered and washed with ether. Yield 0.375 g. (91%).

(xv) Preparation of $Pt(CF_3)_2(COD)$

$PtMe_2(COD)$ (2.80 g.) was placed in a 10 ml. thick-walled Carius tube and dissolved in 3 ml. of dichloromethane. The solution was frozen and degassed twice using conventional freeze-thaw vacuum techniques. Trifluoromethyliodide (20 mmoles, slightly greater than 2 molar equivalents) was condensed into the tube and the Carius tube was sealed. The solution was allowed to warm up to ambient temperature and was shaken for four days during which time several large crystals deposited from solution. The tube was then opened, the solution filtered to give 0.40 g. of $PtMe_3I$. The filtrate was passed through a short florisil column, eluting with dichloromethane, to give a pale yellow solution. The volume was reduced and pentane added to give white crystals. After cooling for 2 hours the crystals were filtered and washed with pentane. Yield 2.25 g. (61%).

(xvi) Preparation of $Pt(CF_3)_2(PMe_2Ph)_2$

To a solution of $Pt(CF_3)_2(COD)$ (0.381 g.) in 5 ml. of dichloromethane was added PMe_2Ph (0.238 g.). The solution was stirred for 2 hours and the solvent was removed by rotary evaporation to give a white solid that was recrystallized from dichloromethane and pentane. Yield 0.480 g. (92%).

(xvii) Preparation of $Pt(CF_3)_2(bipy)$

Bipyridine (0.083 g.) was added to an acetone solution of $Pt(CF_3)_2(COD)$ (0.234 g.). The solution turned yellow and after 15 minutes the solvent was removed to give a yellow solid. Recrystallization from dimethylformamide and ether yielded 0.200 g. (77%).

(xviii) Preparation of $Pt(CF_3)_2(PMe_2Ph)_2I_2$

Iodine (0.024 g.) was added to a solution of $Pt(CF_3)_2(PMe_2Ph)_2$ in dichloromethane (1 ml.). There was an immediate colour change and the addition of pentane gave brown needles. Yield 0.066 g. (82%).

(xix) Preparation of PtMeCl(COD)

$PtMe_2(COD)$ (2.84 g.) was dissolved in 30 ml. of dichloromethane and 20 ml. of methanol. Acetyl chloride (0.58 g., 0.61 ml.) was added dropwise and effervescence was immediately observed. The solution was stirred for 10 minutes after all of the acetyl chloride had been added and the volume of the solution was reduced to about 5 ml. giving white crystals. After cooling for two hours the solution was filtered and the crystals were washed with pentane. Yield 2.70 g. (97%).

(xx) Preparation of $PtMeCl(p\text{-}CNC_6H_4Me)_2$

Acetyl chloride (0.036 ml.) was added to a solution of $PtMe_2(CNC_6H_4Me)_2$ (0.235 g.) in 2 ml. of dichloromethane and 2 ml. of methanol. After effervescence had ceased, the volume of the solution was reduced and ether was added to give white crystals. After cooling at 0°C the solution was filtered and the crystals were washed with pentane. Yield 0.214 g. (88%).

(xxi) Preparation of PtMeCl(bipy)

PtMeCl(COD) (0.215 g.) was dissolved in 5 ml. of dichloromethane and bipyridine (0.061 g.) was added. The solution was refluxed for 30 minutes and cooled to give yellow needles. Ether was added and the solution was cooled for several hours at 0°C and filtered. Yield 0.240 g. (98%).

(xxii) Preparation of [PtMe(bipy)(NC-C_6H_4OMe)](PF_6)

$AgPF_6$ (0.120 g.) in 2 ml. of acetone was added to a solution of PtMeCl(bipy) (0.185 g.) and p-methoxybenzonitrile (0.063 g.) in 5 ml. of acetone. AgCl slowly precipitated and after one hour was removed by centrifugation to give a pale yellow solution. The volume was reduced and ether was added to give pale yellow needles. After cooling at 0°C for 2 hours the crystals were filtered and washed with ether. Yield 0.160 g. (53%). Yield was 80%.

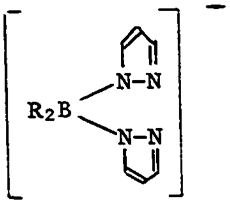
CHAPTER VIII

FIVE COORDINATE ACETYLENE, ALLENE, AND OLEFIN COMPLEXES OF PLATINUM(II) CONTAINING A TRIDENTATE POLYPYRAZOLYLBORATE LIGAND

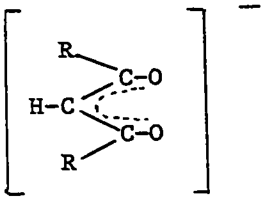
a) Introduction

Several years ago Trofimenko discovered a new class of ligands [167], the polypyrazolylborate ions $[R_nB_{4-n}]^-$. Subsequent work [102,103] has shown that these ligands have unusually strong coordinating powers which are a consequence of favourable electronic and geometric factors. For example, a stable dinitrogen complex of platinum(IV), $PtMe_3(N_2)[H_2Bpz_2]$, has been prepared [203] presumably as a consequence of the excellent ligand properties of this pyrazolylborate ion.

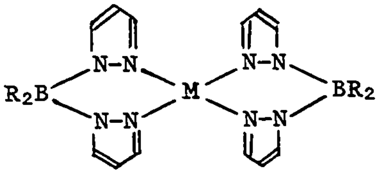
The dipyrazolylborate ion, I, is quite similar to the β-diketonate ion, II, in that both are anionic and bidentate. A number of bidentate bis-chelate complexes, III, have been prepared [168], however unlike the β-diketonate complexes, the dipyrazolylborate complexes are monomeric. The Ni and Cu chelates are square planar, while chelates of Mn, Fe, Co and Zn are tetrahedral.



I



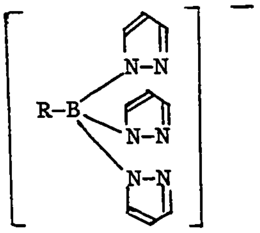
II



III

$M = Ni^{+2}, Cu^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}$

When one of the R groups is 1-pyrazolyl, it too can coordinate to a transition metal and the resulting ion, IV, is the first known example of a uninegative-tridentate ligand of C_{3v} symmetry. The tridentate poly(1-pyrazolyl)borate ligands form a number of compounds [102,103] which may be regarded as analogues of the corresponding cyclopentadienyl compounds although the polypyrazolyl borate complexes are usually much more stable to air and heat.

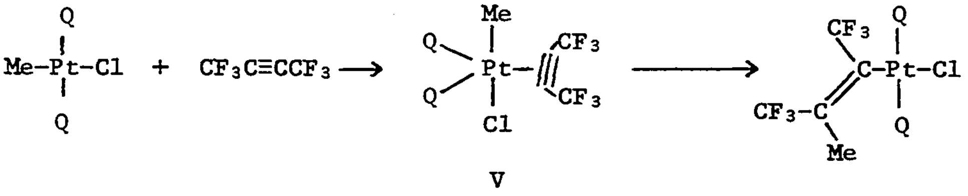


IV

For example $[HBpz_3]Cu(CO)$ [169] is very air and heat stable while the analogous cyclopentadienyl complex [170] $(\pi\text{-}C_5H_5)Cu(CO)$ is thermally unstable and air sensitive.

Five coordinate complexes of platinum(II) are somewhat of a rarity [89,148,171-175], so it occurred to us that the unusually strong chelating ability of the $[R\ Bpz_3]^-$ ion might well stabilize five coordinate complexes of platinum(II). We were particularly interested in the formation of five coordinate platinum(II) olefin and acetylene complexes since they have been proposed as intermediates in the transition metal catalyzed polymerization and hydrogenation of olefins and acetylenes [1,15,16,176-181].

Clark and Puddephatt [16,181] were able to isolate a number of five coordinate olefin and acetylene complexes of platinum(II), V, and proposed that such complexes were intermediates in the insertion of the platinum methyl group into the C-C unsaturated bond [16]. (equation 1)



(1)

Q = phosphine, arsine or stibine

A single crystal x-ray structural determination [182] of V, ($Q = AsMe_3$) has confirmed the trigonal bipyramidal structure with the acetylene bonded in the trigonal plane. The complexes, unfortunately, were stable in solution only in the presence of excess olefin or acetylene.

We have now been successful preparing a number of five coordinate complexes [183] and in this chapter present the syntheses and nuclear magnetic resonance studies of these compounds.

b) Results and Discussion

(i) Preparation of the Complexes

In the previous chapter we discussed the preparation of PtMeCl(COD) and indicated that the 1,5-cyclooctadiene was very tightly bonded to platinum. However, the removal of the chloride ion in acetone by silver hexafluorophosphate with the formation of the cationic complex $[PtMe(COD)(acetone)](PF_6)$, considerably weakens the Pt-COD bonds. Consequently, the addition of an acetone solution of $K[HBpz_3]$ to the acetone solution containing the methyl-platinum cation results in the displacement of 1,5-cyclooctadiene and the formation of an insoluble beige precipitate. The reaction is usually accompanied by some reduction of platinum to the metallic state. The exact nature of the precipitate is not known. Due to its insolubility we were unable to purify the compound so that good analytical data could not be obtained. The compound is unlikely to be monomeric because of its low solubility and on the basis of its derivatives we have assigned it the empirical formula $PtMe[HBpz_3]$. The structure is likely to be polymeric with two pyrazolyl borate rings coordinated in a bidentate manner to one platinum atom with the third pyrazolyl ring bridging to fill the fourth coordination site of a second platinum atom.

Although the polymer is insoluble in dichloromethane, it readily dissolves in the presence of various acetylenes, olefins and allenes; the extent of the reaction may be monitored by dissolution of the polymer. Since the dichloromethane solutions were always coloured, due to contamination by platinum metal, it was always necessary to pass the solutions through a short florisil column to remove this contaminant. The complexes were then isolated in reasonable yields and were stable both in solution and in the air. ^{1}H nmr data for the complexes are given in Table VIII-1 and physical, analytical and infrared data are given in Table VIII-2.

(ii) Five Coordinate Acetylene Complexes

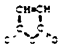
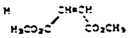
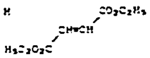
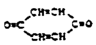
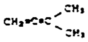
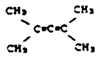
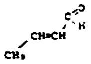
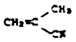
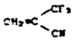
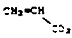
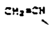
PtMe[HBpz$_3$] was readily cleaved by $CF_3C\equiv CCF_3$, $MeO_2CC\equiv CCO_2Me$ and $PhC\equiv CMe$ giving stable 1:1 adducts. With dimethylacetylene a complex was obtained but it was stable only in the presence of excess acetylene; upon removal of excess $MeC\equiv CMe$ the original polymer was recovered.

The hexafluorobut-2-yne and dimethylacetylene-dicarboxylate complexes showed only one resonance in the nmr spectra which could be assigned to the acetylene indicating either that there was a plane of symmetry through the $C\equiv C$ bond or that the acetylene was rotating. The nmr spectra to −100°C were temperature independent. The platinum-methyl resonances appeared as singlets, flanked by ^{195}Pt satellites with $^2J(Pt\text{-}H) \approx 68$ Hz. The pyrazolyl ring proton resonances were observed in the region 6-8 ppm downfield from tetramethylsilane. The 4-H protons (VI) are easily assigned since they

Table VIII-1

NMR Data^a for Five Coordinate Platinum(II) Complexes of the type $[RBpz_3]Pt(CH_3)un$

where $RBpz_3$ = polypyrazolylborate and un = olefin, acetylene, or allene

R	Olefin or Acetylene	Platinum Methyl		Pyrazole Ring^d	3-H		4-H			5-H	Other Resonances and Couplings
		δ($Pt-CH_3$)	^2J(Pt-H)		δ	J(Pt-H)	δ	JH-H	J(Pt-H)	δ	
pz	$CF_3C{\equiv}CCF_3$	1.13	66.8	eq.	7.82	10.5	6.28	2.5	9.5	7.70	δ(CF_3) 56.70; J(Pt-F) 66.6
				ax.	7.31	7.0	6.17	2.0	3.0	8.00	
				free^b	7.98		6.62	2.0		8.03	
pz	$(CH_3)O_2CC{\equiv}CCO_2(CH_3)$	1.04	67.6	eq.	7.88	10.5	6.40	2.0	8.0	7.66	δ(OCH_3) 3.85
				ax.	7.36	6.0	6.25	1.5	4.5	7.84	
				free^b	7.90		6.72	1.5		7.99	
pz	$CH_3C{\equiv}CC_6H_5$	0.52	75.4	eq.	7.81	6.5	6.31	2.0	6.5	6.96	δ(CH_3) 2.10; J(Pt-H) 46.0
				ax.	7.19	7.0	6.17	2.0	3.0	6.90	
				free^b	7.82		6.30	2.0		7.34	
H	$CF_3C{\equiv}CCF_3$	1.06	67.4	eq.	7.22	7.0	6.26	2.5	10.0	7.76	δ(CF_3) 67.40; J(Pt-F) 65.0
				ax.	7.74	8.8	6.11	2.1	3.5	7.65	
h	$CH_3O_2CC{\equiv}CCO_2CH_3$	1.02	67.9	eq.	7.80	9.0	6.23	2.2	10.0	7.73	δ(OCH_3) 3.84
				ax.	7.28	7.0	6.08	2.2	3.0	7.61	
H	$CH_3C{\equiv}CC_6H_5$	0.67	62.8	eq.	7.74	7.0	6.24	2.0	7.5	7.72	δ(CH_3) 2.29; J(Pt-H) 62.6
				eq.	7.88	8.0	6.21	2.0	7.5		
				ax.	7.07		5.94	2.1	3.3	7.60	
H		0.95	65.6	eq.	7.02	8.0	6.29	2.0	10.0	7.76	δ(CH) 4.13; J(Pt-H) 80.6
				ax.	7.08	5.5	6.27	2.0	4.5	7.74	
H	 $H_3CO_2C{-}CH{=}CH{-}CO_2CH_3$	0.97	67.3	eq.	7.76	9.0	6.26	2.0	9.0	7.73	δ(CH) 3.76; J(Pt-H) 81.7
				ax.	7.10	5.5	6.19	2.0	4.5	7.68	δ(OCH_3) 3.80
H	 $H_5C_2O_2C{-}CH{=}CH{-}CO_2C_2H_5$	0.95	66.0	eq.	7.73	8.0	6.26	2.0	9.0	7.75	δ(CH_3) 0.89, 1.30
				eq.	7.50	8.5	6.21	2.5	10.0	7.71	δ(CH_2) 3.88, 4.21} J(H-H) 7.0
				ax.	7.87	4.5	6.09	2.5	4.5	7.61	
H		0.90	67.0	eq.	7.51	8.0	6.24	2.0	10.4	7.72	δ(CH) 4.41; J(Pt-H) 81.4
				ax.	7.10	5.5	6.21	2.0	4.0	7.69	δ(CH) 6.54
H	 $CH_2{=}C{=}C(CH_3)_2$	0.60	68.0	eq.	7.77	7.0	6.19	2.0	8.0	7.68	δ(C-CH_3) 1.78; J(Pt-H) 11.5
				eq.			6.18	2.0	8.0	7.67	δ(C-CH_3) 2.08; J(Pt-H) <1.0
				ax.	7.00	7.5	6.05	2.2	4.5	7.62	
H	 $(CH_3)_2C{=}C{=}C(CH_3)_2$	0.70	72.0		7.60		6.02	2.0		7.34	δ(CH_3) 1.07; J(Pt-H) 70.0
					7.60		6.10	2.0		7.65	δ(CH_3) 1.26; J(Pt-H) 52.5
					7.72		6.22	2.0		7.68	δ(CH_3) 1.82; J(Pt-H) 8.5
											δ(CH_3) 2.03; J(Pt-H) 2.5
H	 $CH_3{-}CH{=}CH{-}CHO$	0.93	67.0		c			c		c	δ(CHO) 9.52; J(Pt-H) 2.0;J(H-H)5.0
		0.92	67.0								δ(CH_3) 1.36;J(Pt-H) 46.0;J(H-H)6.0
											δ(CH_3) 1.35;J(Pt-H) 37.5;J(H-H)6.5
H	 $CH_2{=}C(CH_3)CN$	1.02	66.0		c			c		c	δ(CH_3) 1.57; J(Pt-H) 44.0
		0.77	67.0								δ(CH_3) 1.47; J(Pt-H) 55.9
											δ(CH) =2.5 (m)
H	 $CH_2{=}C(CF_3)CN$	1.02	66.5		c			c		c	J(H-F) = 3.0; δ(CH) =2.9
		1.18	64.5								δ(CF_3) 57.90; J(H-F) = 1.4, 3.0
											J(Pt-F) = 66.0
H	 $CH_2{=}CH{-}CO_2CH_3$	0.82	66.0		c			c		c	δ(OCH_3) 3.46, 3.04
		0.68	66.0								
H	 $CH_2{=}CH{-}CN$	1.00	64.0		c			c		c	
		0.71	64.0								

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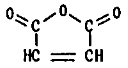
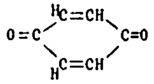
a. Chemical shifts are reported in p.p.m. downfield from TMS and coupling constants are in hertz.
b. 3-H and 5-H protons may be interchanged.
c. Resonances were complex due to the presence of two isomers.
d. eq. = equatorial, ax. = axial, free = uncoordinated pyrazolyl ring.

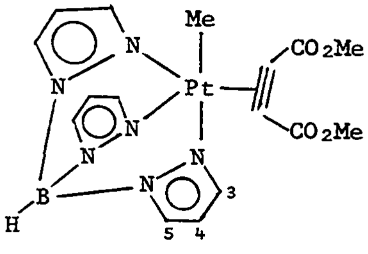
Table VIII-2

Analytical, Physical and Infrared Data for Five Coordinate Complexes of $PtMe[RBpz_3](un)$

R	un	Analyses % Calculated (% Found) Carbon	Hydrogen	Nitrogen	Melting Point(°C)	Recrystallization Solvents	Infrared Data [a] (cm^{-1})
pz	$CF_3\text{-}C\equiv CCF_3$	31.37 (31.37)	2.32 (2.24)	17.20 (17.41)	154-156	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(C\equiv C)$ 1861, 1833
pz	$(C_6H_5)C\equiv C(C_6H_5)$	48.62 (48.29)	3.78 (3.67)	16.80 (16.71)	209-211	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(C\equiv C)$ 1816
pz	$(CH_3)O_2CC\equiv CCO_2(CH_3)$	36.17 (36.87)	3.36 (3.25)	17.75 (17.51)	150-152	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(C\equiv C)$ 1829; $\nu(CO)$ 1715
pz	$(C_6H_5)C\equiv CCH_3$	43.68 (43.58)	3.83 (3.85)	18.51 (18.39)	148-150	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(C\equiv C)$ 2031
H	$CF_3C\equiv CCF_3$	28.73 (28.77)	2.24 (2.03)	14.36 (14.45)	216-217	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2495; $\nu(C\equiv C)$ 1858, 1828
H	$(CH_3)O_2CC\equiv CCO_2(CH_3)$	33.99 (33.97)	3.39 (3.21)	14.87 (14.96)	209-210	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2517; $\nu(C\equiv C)$ 1823; $\nu(CO)$ 1707, 1694
H	$(C_6H_5)C\equiv C(CH_3)$	42.32 (42.68)	3.93 (3.82)	15.59 (15.63)	139-141	CH_3OH	$\nu(B\text{-}H)$ 2465; $\nu(C\equiv C)$ 1857
H		32.22 (31.95)	2.90 (2.71)	16.11 (15.53)	236-238	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2489; $\nu(CO)$ 1827, 1760
H	*cis*-$(CH_3)O_2CHC{=}CHCO_2(CH_3)$	33.87 (33.87)	3.73 (3.55)	14.82 (14.81)	202-204	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2482; $\nu(CO)$ 1753(sh), 1744(s), 1726(sh)
H	*trans*-$(C_2H_5)O_2CCH{=}CHCO_2(C_2H_5)$	36.31 (36.30)	4.23 (4.10)	14.12 (14.34)	136-137	$CH_2Cl_2\text{-}n\text{-}C_2H_{12}$	$\nu(B\text{-}H)$ 2494; $\nu(CO)$ 1713, 1696
H		36.17 (35.98)	3.23 (3.06)	15.82 (15.82)	>220	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2487; $\nu(CO)$ 1653(b)
H	$CH_2{=}CHCO_2(CH_3)$	33.01 (33.30)	3.76 (3.70)	16.50 (16.70)	168-169	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2492; $\nu(CO)$ 1719
H	$CH_2{=}CHCN$	32.78 (33.22)	3.39 (3.66)	20.59 (19.97)	103-105	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2489; $\nu(C\equiv N)$ 2223
H	*trans*-$(CH_3)CH{=}CH(CHO)$	34.08 (34.66)	3.88 (3.96)	17.04 (16.71)	135-140	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2480; $\nu(C{=}O)$ 1680
H	$CH_2{=}C(CF_3)(CN)$	30.90 (30.93)	2.78 (2.76)	18.02 (17.99)	150-153	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2494; $\nu(C\equiv N)$ 2235
H	$CH_2{=}C(CH_3)(CN)$	34.29 (34.48)	3.70 (3.82)	20.00 (20.00)	>180	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2487; $\nu(C\equiv N)$ 2216
H	$(CH_3)_2C{=}C{=}C(CH_3)_2$	39.31 (39.71)	4.85 (4.85)	16.18 (15.71)	101-103	$(C_2H_5)_2O\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2472; $\nu(C{=}C{=}C)$ ~1720(b)
H	$(CH_3)_2C{=}C{=}CH_2$	36.67 (36.93)	4.31 (4.07)	17.11 (17.10)	191-192	$CH_2Cl_2\text{-}n\text{-}C_5H_{12}$	$\nu(B\text{-}H)$ 2483; $\nu(C{=}C{=}C)$ ~1730(b)

[a] s = strong, sh = shoulder, b = broad.

appear as triplets due to coupling with the 3-H and 5-H protons and they usually appear upfield of the 3-H and 5-H protons. Prior to the present work definite assignment of the 3-H and 5-H protons had not been possible; however by making use of the presence of the ^{195}Pt nuclear spin and homonuclear double resonance nmr techniques [186] we have been able to assign these protons. The proton nmr spectrum of $PtMe[HBpz_3](MeO_2CC{\equiv}CCO_2Me)$ in the pyrazolyl region is shown in Figure VIII-1a. The two triplet resonances (labelled B_1 and B_2) appear in the ratio of 2:1 and each resonance shows $^{195}Pt-^{1}H$ coupling indicating that the hydrotris(1-pyrazolyl)borate ligand is tridentate. The coupling constant $^{4}\underline{J}(Pt-H)$ is greater to the resonance at B_1 than B_2 indicating that the single pyrazolyl ring is trans to the group of highest trans-influence [6], i.e. Me^-, and structure VI is assigned. Therefore we can assign the resonance labelled B_1 to the



VI

two equivalent equatorial 4-H protons and resonance B_2 to the single axial 4-H proton. Irradiation of B_1 (Figure VIII-1b) caused two resonances, labelled A_1 and C_1, to collapse into singlets which indicated that the 4-H equatorial protons were spin-spin coupled to protons A_1 and C_1. Both the A_1 and C_1 proton resonances are coupled

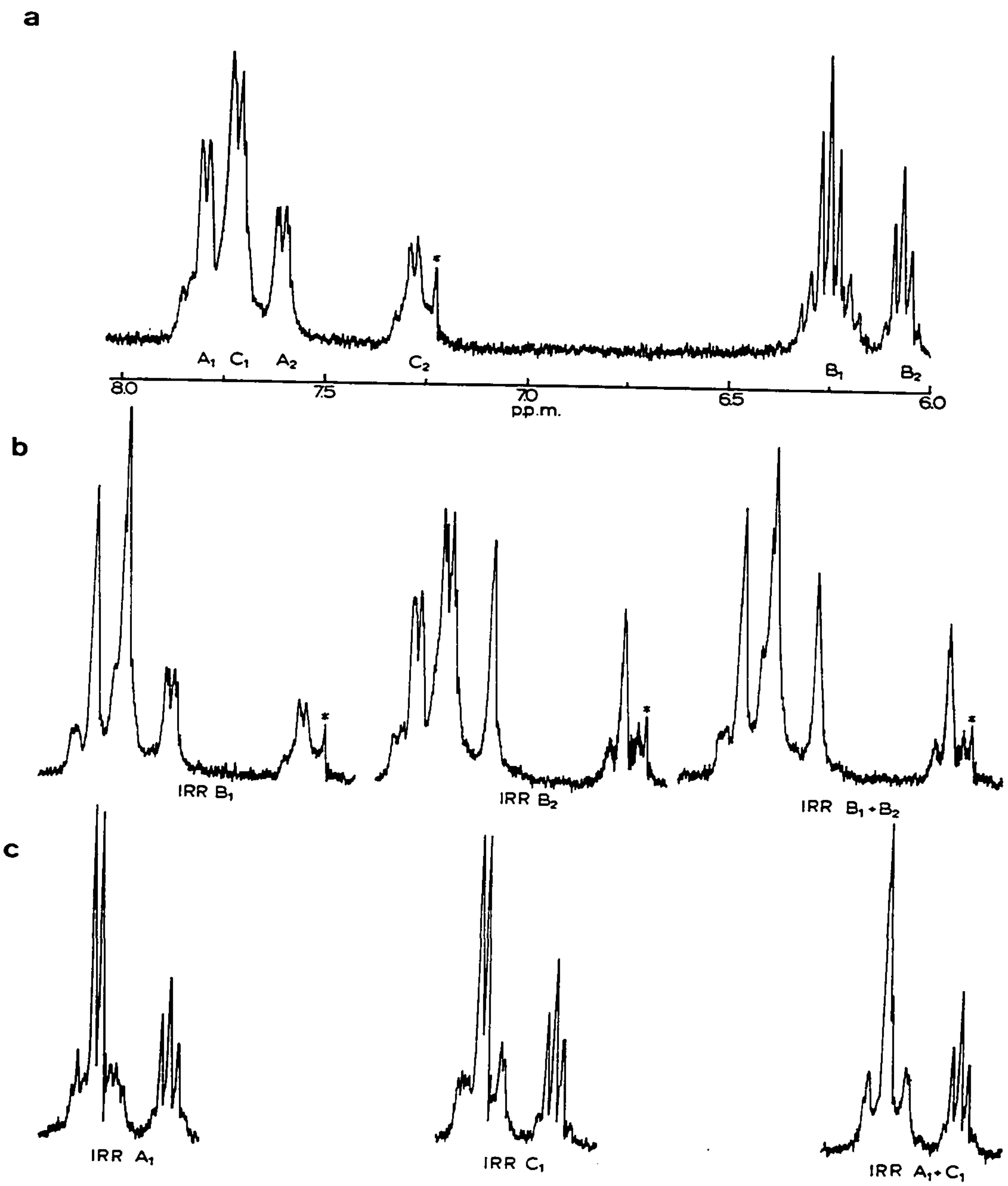


Figure VIII-1

^{1}H nmr spectrum of PtMe[HBpz$_3$](MeO$_2$CC≡CCO$_2$Me) showing the pyrazolyl ring protons during a double resonance experiment.

to ^{195}Pt with coupling constants of 9 and 2 Hz respectively. Therefore we can assign A_1 to the resonance of the equatorial 3-H protons and C_1 to the equatorial 5-H protons. Similarly, by irradiating at B_2 the resonances labelled A_2 and C_2 collapsed. There is a negligible coupling between ^{195}Pt and the proton labelled A_2 and a coupling of 7.0 Hz between ^{195}Pt and proton C_2. Resonances A_2 and C_2 are therefore assigned to the axial 5-H and 3-H protons. By simultaneous irradiation at B_1 and B_2 the complete 4-H decoupled spectrum may be obtained. In Figure VIII-1c is shown the effect of irradiating A_1 and C_1 on the two equatorial 4-H protons, B_1. By decoupling A_1 (3-H equatorial protons) the resonance at B_1 is reduced to a doublet with complex ^{195}Pt satellites as expected for an ABX spectrum (X = ^{195}Pt), and similarly by irradiating at C_1 (5-H equatorial protons) the 4-H equatorial protons give an A'BX spectrum. By simultaneously irradiating at A_1 and C_1, the resonance due to the 4-H equatorial proton is reduced to a simple BX pattern and $^4\underline{J}$(Pt-H) may easily be obtained. Similarly, by irradiation of peaks A_2 and C_2 the coupling constant $^4\underline{J}$(Pt-H) to the axial 4-H proton was obtained.

The proton nmr spectrum of the methylphenylacetylene complex showed the presence of a single platinum methyl resonance and one acetylene methyl resonance with $\underline{J}$(Pt-H) = 62.6 Hz. The nmr spectrum in the region 6-8 δ was very complicated but by careful double resonance experiments three resonances could be assigned to the 3-H, 4-H, and 5-H protons respectively on the pyrazolyl rings. The inequivalence of the two equatorial pyrazolyl rings must indicate that the acetylene is not rotating and is constrained within the trigonal plane.

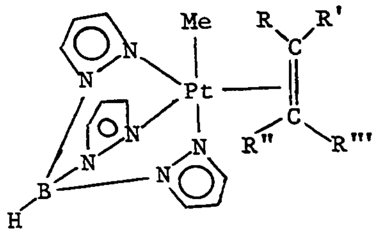
A number of tetrakis(1-pyrazolyl)borate complexes are known to be stereochemically non-rigid [186,187] so it was of interest to prepare a few complexes analogous to VI using the $[Bpz_4]^-$ ion.

$PtMe[Bpz_4]$ was prepared in a similar manner to $PtMe[HBpz_3]$. It is insoluble in organic solvents and may also be polymeric. Hexafluorobut-2-yne, phenylmethylacetylene and dimethylacetylene dicarboxylate readily cleave $PtMe[Bpz_4]$ in dichloromethane giving crystalline 1:1 adducts. The proton nmr spectra of the hexafluorobut-2-yne and dimethylacetylene dicarboxylate complexes were consistent with a five coordinate structure. Three resonances in the pyrazolyl region of the nmr spectra in the ratio of 2:1:1 appeared as triplets and could thus be assigned to the 4-H protons. Only two of the three peaks showed coupling to ^{195}Pt, so the third peak was assigned to the free pyrazolyl ring. By a simple double resonance experiment it was possible to assign all of the 3-H and 5-H protons on the coordinated pyrazolyl rings. Irradiation of the 4-H proton on the uncoordinated ring collapsed two peaks into singlets, however due to the lack of ^{195}Pt coupling these peaks could not be unambiguously assigned to either the 3-H or 5-H protons.

The high temperature nmr spectra (to 90°C) did not show any evidence that the molecules exhibited fluxionality.

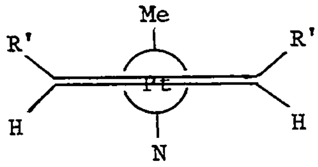
(iii) Five Coordinate Olefin Complexes

The polymer PtMe[HBpz$_3$] was readily cleaved by a variety of substituted olefins bearing at least one electron withdrawing-substituent to give the five coordinate complexes, VII.

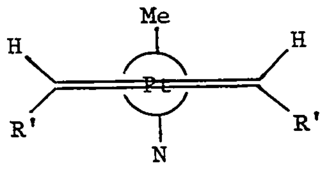


VII

With the two 1,2-cis-disubstituted ethylenes, dimethylmaleate and maleic anhydride, two isomers are possible, VIII, IX.



VIII



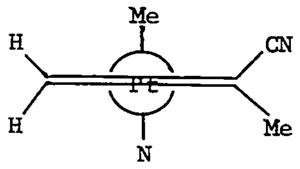
IX

Unlike the disubstituted acetylenes where the substituents are colinear with the coordinated triple bond, the olefinic substituents do not lie in the trigonal plane of the complex and may orient themselves either towards the platinum-methyl group, VIII, or towards the axial pyrazolyl ring, IX. The nmr spectra showed that for these two complexes only one isomer was present and the pyrazolyl proton resonances appeared in the ratio of 2:1, consistent with the proposed trigonal bipyramidal structure and constraint of the olefin within the trigonal plane.

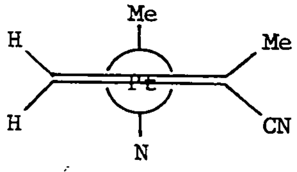
Reaction of PtMe[HBpz$_3$] with p-benzoquinone gave a bright yellow complex whose nmr spectrum showed the presence of just one isomer. Two resonances could be assigned to the olefin; the hydrogens of the uncoordinated double bond appeared at 6.54 δ while the hydrogens of the coordinated double bond were considerably more shielded, absorbing at 4.41 δ , and showing a large coupling constant to ^{195}Pt(*J*(Pt-H) = 81.7 Hz).

The situation becomes more complex with 1,1'-disubstituted, *trans*-disubstituted, and mono-substituted ethylenes.

The reaction between PtMe[HBpz$_3$] and methacrylonitrile (CH$_2$ = C(CN)Me) gave a solid whose nmr spectrum (Figure VIII-2) was consistent with the presence of two isomers, X, XI. Of course, two optical isomers of X, XI are also present but these are not detectable by nmr. The pyrazolyl region in the nmr is very complex since the equatorial rings are not equivalent and therefore 18 proton resonances are expected for the two isomers. No attempt was made to assign these resonances but, as usual, the 4-H proton resonances (Figure VIII-2,B) are to high field of the 3-H and 5-H protons (Figure VIII-2,A). The olefinic proton resonances appear as two overlapping ABX patterns in the nmr spectrum, centered near 2.8 δ



X

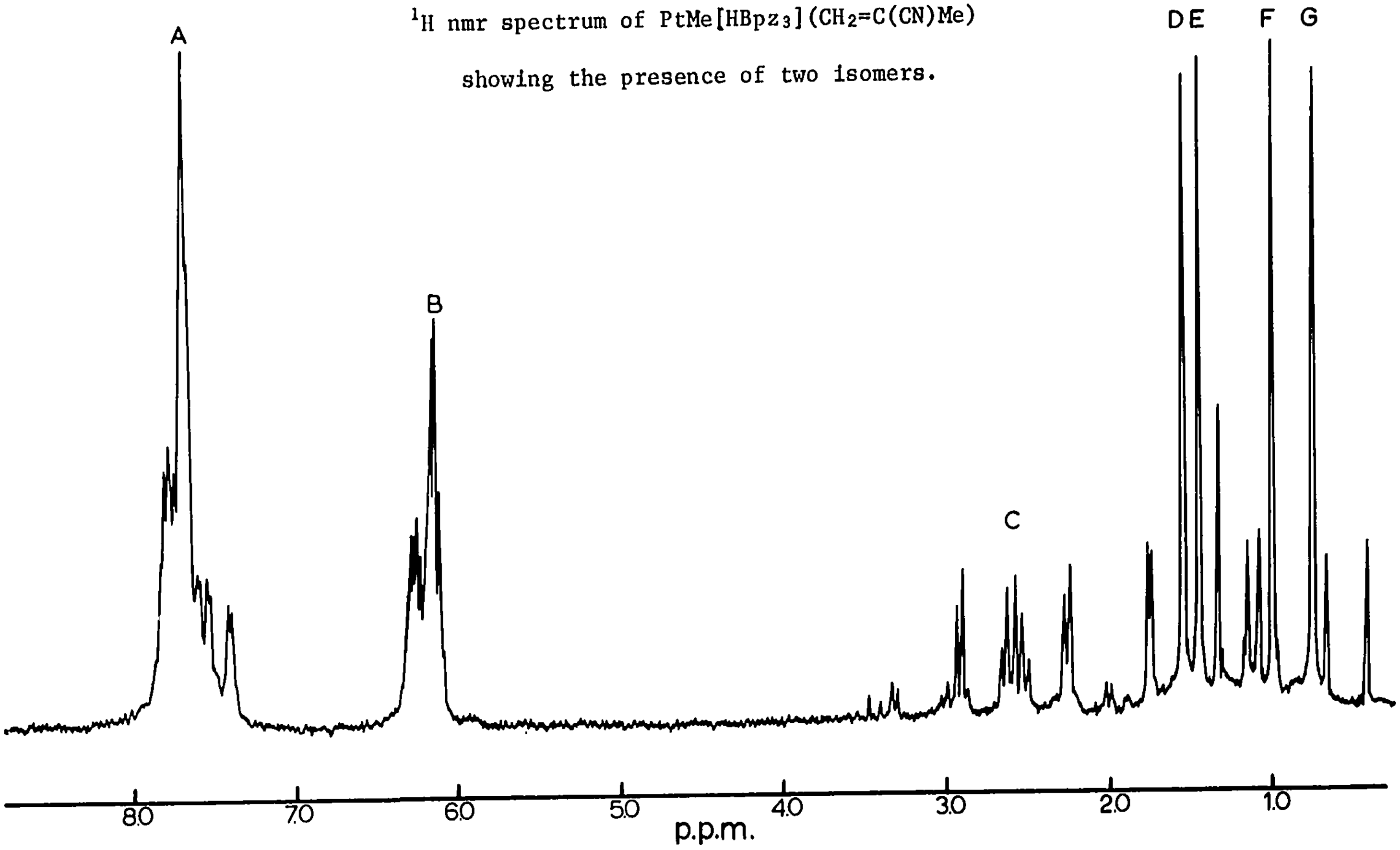


XI

Figure VIII-2

^1H nmr spectrum of $PtMe[HBpz_3](CH_2{=}C(CN)Me)$

showing the presence of two isomers.



(Figure VIII-2,C); however due to the complexity of the resonances no attempt was made to resolve the spectra. As expected for two isomers, two platinum-methyl (F,G) and two olefinic-methyl (D,E) resonances are observed. It is interesting that there is a difference in the two ^{195}Pt coupling constants to resonances at D and E (44.0, 55.9 Hz respectively).

PtMe[HBpz$_3$] is also cleaved by the CF$_3$ analogue of methacrylonitrile ($CH_2{=}C(CF_3)(CN)$) to give the expected two isomers. Two platinum-methyl resonances are observed at 1.18 and 1.02 ppm downfield from TMS and each is accompanied by ^{195}Pt satellites. The high field resonance, however, appears as a quartet which we attribute to a 'through-space' coupling [189] with the fluorine atoms on the olefin (J(H-F) = 3.0 Hz). The ^{19}F nmr spectrum shows a CF$_3$ resonance which appears as a doublet of quartets due to coupling with the platinum methyl protons and one of the terminal olefinic protons (J(H-F) = 3.0, 1.4 Hz respectively).

Trans-diethylfumarate ($EtO_2CCH{=}CHCO_2Et$) readily reacts with PtMe[HBpz$_3$] to give a white crystalline complex. From the proton nmr spectrum, only one geometrical isomer is present but since there is no plane of symmetry along the Pt-olefin axis all three pyrazolyl rings are inequivalent and nine resonances are observed (Figure VIII-3). The high field triplet with a small ^{195}Pt coupling constant (4.5 Hz) is assigned to the axial 4-H proton and the two overlapping triplets at 6.21, 6.26 δ with ^{195}Pt coupling constants of 10.0 and 9.0 Hz respectively are assigned to the two equatorial 4-H protons. All 3-H and 5-H protons were easily assigned by a simple homonuclear

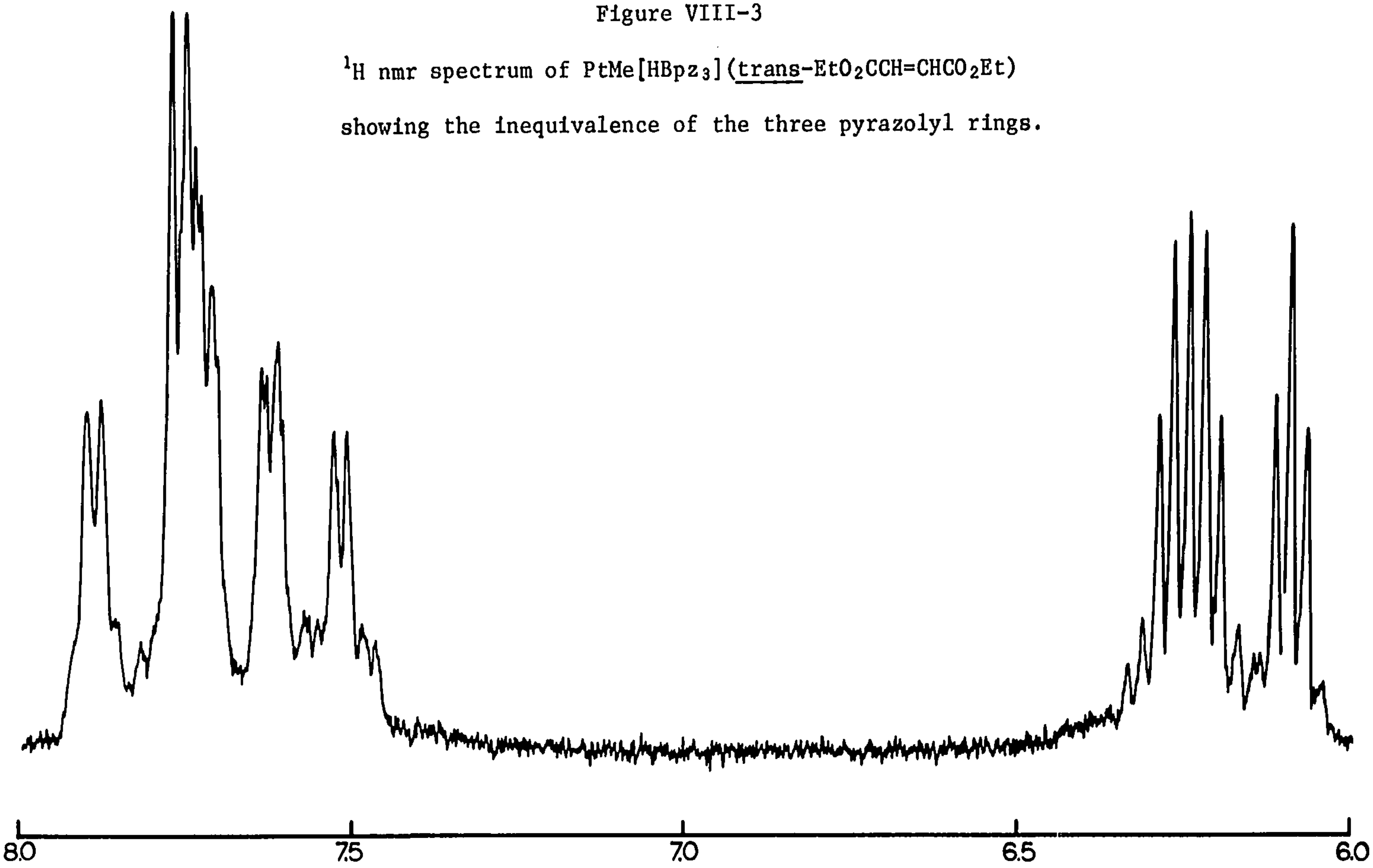
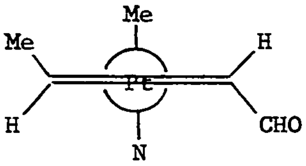


Figure VIII-3

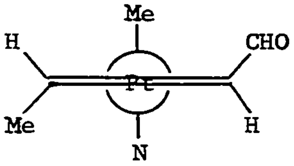
^{1}H nmr spectrum of PtMe[HBpz$_3$](trans-EtO$_2$CCH=CHCO$_2$Et) showing the inequivalence of the three pyrazolyl rings.

double resonance experiment, as illustrated in Figure VIII-1. The observation of three distinct pyrazolyl rings for the diethylfumarate complex, coupled with the fact that the two equatorial rings were equivalent for the cis-disubstituted olefins suggests that the olefins are not rotating (on the nmr time scale) and that the C=C bond is constrained within the trigonal plane.

Crotonaldehyde (trans-MeCH=CH(CHO)) reacts with PtMe[HBpz$_3$] to give a complex whose nmr spectrum shows the presence of the expected two geometric isomers XII, XIII, in the ratio of 1:1.



XII



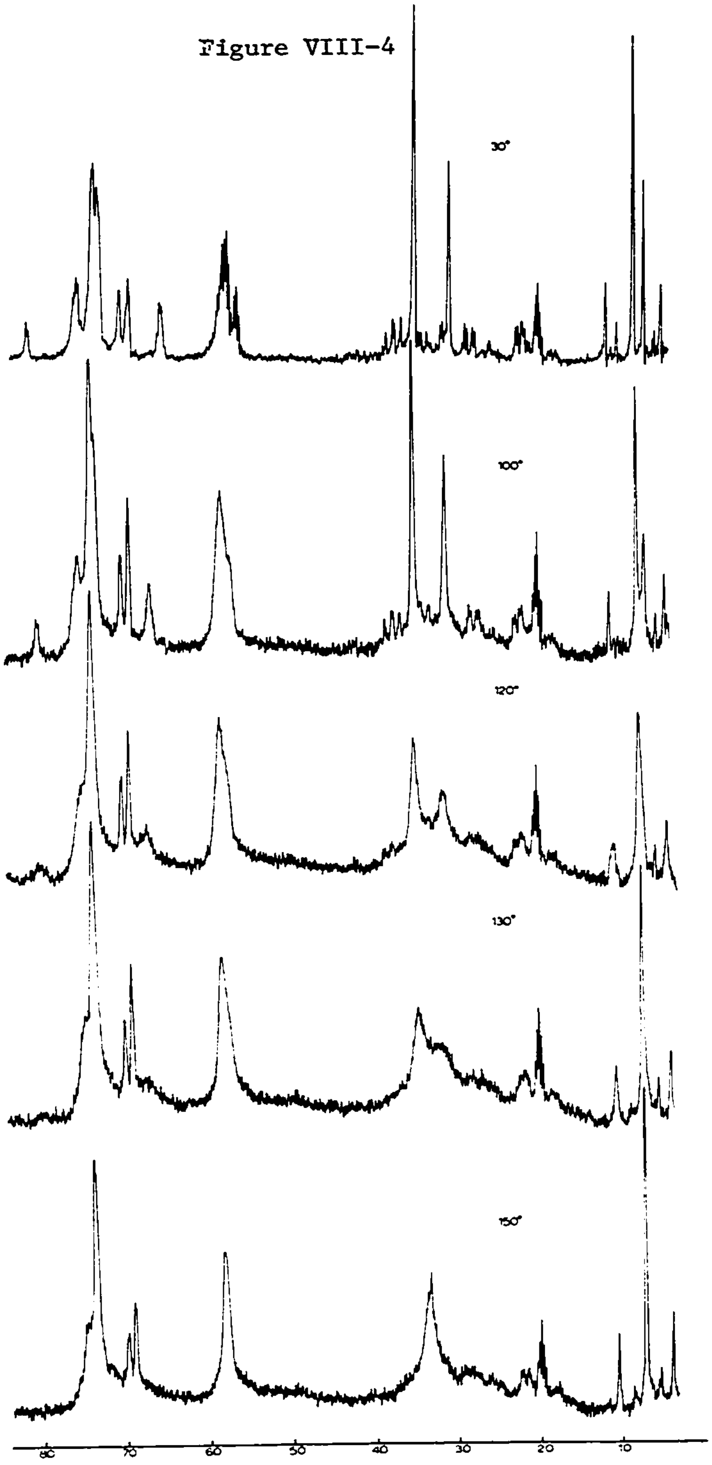
XIII

The aldehyde proton appears at 9.52 δ in the nmr spectrum as a doublet due to coupling with the vicinal olefinic hydrogen (^3J(H-H) = 5.0 Hz) and is flanked by satellites due to coupling with ^{195}Pt (J(Pt-H) = 2.0 Hz). Two platinum-methyl resonances were observed, each with a coupling constant to ^{195}Pt of 67.0 Hz. Two resonances may also be assigned to the olefinic-methyl groups, which appear as doublets due to coupling with the vicinal olefinic hydrogen (^{3}J(H-H) 6-7 Hz). As observed in complexes X, XI, the coupling constants, J(Pt-H), for the crotonaldehyde-methyl groups differ for the two isomers (37.5 and 46.0 Hz). No attempt was made to interpret the olefinic hydrogen resonances since they were exceedingly complicated.

For all of the olefin complexes where two geometric isomers were obtained, the two substituents on the olefin were of similar size. The observed 1:1 ratio of the two isomers was therefore that expected statistically. A molecular model of VII showed that there was little difference between the steric effect of the axial 3-H proton and that of the platinum-methyl protons. However, without an x-ray structural determination, it is not possible to say unambiguously that there is no difference in the steric effects. Therefore, we thought that a monosubstituted ethylene, $CH_2{=}C\genfrac{}{}{0pt}{}{H}{R}$, where R was much larger than H, might well be sensitive to small differences in the steric effects between the axial 3-H and PtMe groups. We have therefore prepared two complexes and examined their nmr spectra.

Acrylonitrile ($CH_2{=}CHCN$) reacted with $PtMe[HBpz_3]$ to give a 1:1 adduct whose nmr spectrum showed the presence, once again, of two isomers in the ratio of 1:1. For the corresponding methylacrylate complex in which R=COOMe and is larger, two geometric isomers were obtained in the ratio of 2:1. There existed the possibility that this ratio was not the most thermodynamically stable one and that some of one isomer may have been lost during the work up procedure. Accordingly, the high temperature (up to 150°) nmr spectra were examined in the hope of equilibrating the two isomers. (Figure VIII-4) The presence of the two isomers may be seen in the 30°C spectrum from the presence of two platinum-methyl resonances and two $-CO_2Me$ resonances (3-4 δ). As the temperature is raised, the first noticeable change is a coalescence of the pyrazolyl

Figure VIII-4



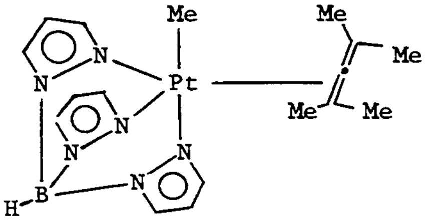
Variable temperature ^{1}H nmr spectra of PtMe[HBpz$_3$](CH$_2$=CHCO$_2$Me).

proton resonances which begin at 100°C and is nearly complete at 150°C. This fluxionality is probably due to a rotation of the three rings about the C_{3v} axis of the ligand [187]. At 100°C the two platinum-methyl resonances begin to merge. At 120°C the platinum-methyl peaks have coalesced and the OMe peaks are broadening. At 150°C only one olefinic-methyl group is observed due to rotation of the olefin, presumably about the Pt–olefin bond [202]. On cooling, the spectrum is identical to the 30°C spectrum in Figure VIII-4, which must indicate that the 2:1 ratio is the most favourable. This may well be a result of the large difference in the size of the CO_2Me and H substituents and the sensitivity of these substituents to a small difference in the steric effects of the axial 3-H proton and platinum methyl group.

(iv) Five Coordinate Allene Complexes

Since the olefin and acetylene complexes were so stable, it was of interest to examine the reactions of PtMe[$HBpz_3$] with 3,3'-dimethyl- and tetramethylallene since there have been very few allene complexes prepared for Pt(II) [190].

PtMe[$HBpz_3$] reacted in four hours with an excess of tetramethylallene to give XIV.



XIV

The nmr spectrum (Figure VIII-5) showed the expected five peaks above 2.5 δ which could be assigned to the four allene-methyl and platinum-methyl groups. The two methyl resonances with values of J(Pt-H) = 2.5, 8.5 Hz (A and B) are assigned to the methyl groups of the uncoordinated double bond and the peaks C, D are assigned to the methyl resonances of the coordinated double bond since they show substantial coupling constants to ^{195}Pt (52.5 and 70.0 Hz respectively). The high field resonance (E) is assigned to the platinum-methyl group. The high temperature nmr spectra of XIV (30-120°C) were examined and the allene was stereochemically rigid to 110°C; at which temperature decomposition occurred.

PtMe[HBpz$_3$] reacted with $CH_2{=}C{=}CMe_2$ to give a white crystalline complex. The nmr spectrum showed the presence of one platinum-methyl resonance and two allene methyl resonances with values of J(Pt-H) = 68.0, 11.5 and <1.0 Hz respectively. The allenic CH_2 resonances were buried beneath the methyl resonances. By comparing the coupling constants between ^{195}Pt and the Me groups with the values obtained for the tetramethylallene complex it is obvious that dimethylallene is coordinated through the $CH_2{=}C$ double bond. The reason for this is probably steric.

(v) Description of the Bonding in the Acetylene Complexes

To date acetylene complexes of platinum are known [191-193] only with the metal in a formally 0 or +2 oxidation state. The formally zero-valent complexes [194,195] are of the type PtL$_2$(acetylene) where L = phosphine, and the acetylene is bonded essentially in the

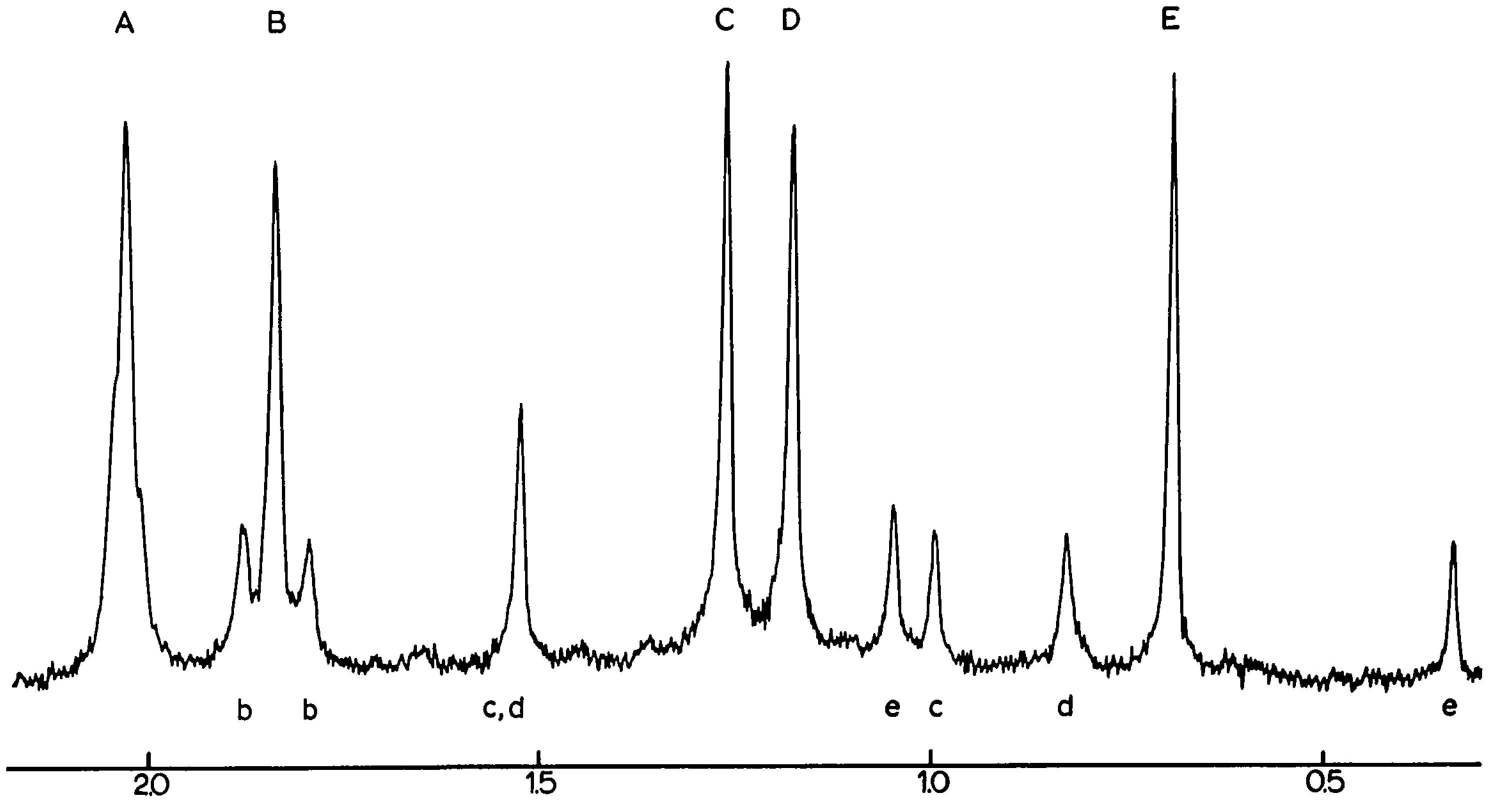
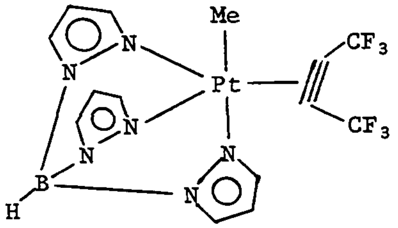


Figure VIII-5

^{1}H nmr spectrum of PtMe[HBpz$_3$](Me$_2$C=C=CMe$_2$) showing ^{195}Pt coupling to the four allene-methyl resonances (A-D) and the platinum-methyl resonance (E).

plane of the two phosphines [196]. On the other hand, the square planar platinum(II) acetylene complexes of the type Cl_2PtL(acetylene), where L is Cl^- or an amine, and trans-$[PtMe(PMe_2Ph)_2(RC{\equiv}CR')](PF_6)$ have the acetylene bonded perpendicular to the plane of the complex[197,198]. The only x-ray structure determination of a five coordinate trigonal bipyramidal platinum(II) complex was done by Payne et al [182] on $PtMe(AsMe_3)_2Cl(CF_3C{\equiv}CCF_3)$, V. The arsines and the two acetylene carbons are coplanar and the angular deviations from linearity of the hexafluorobut-2-yne are 30(4) and 45(4)°. It was suggested that the bonding between the platinum and the acetylene in V was similar to the bonding in trigonal platinum(0) complexes.

The stability of a metal acetylene complex is usually related to the amount of $Md\pi \rightarrow Lp\pi^*$ back bonding [199]. It is probably for this reason that the pyrazolylborate complex, XV, is more thermally stable than the arsine complex, V, ($Q = AsMe_3$).



XV

The acetylene is bonded in the trigonal plane, rather than perpendicular to it, presumably because greater π-back bonding is achieved between the in-plane Pt d_{xy} orbital and the acetylene π^* orbitals. Furthermore, the two anionic nitrogen donor ligands in the trigonal plane are likely to transfer more electron density to the platinum atom than the neutral arsine ligands in V. Consequently the acetylene is strongly bonded to platinum in the hydrotris(1-pyrazolyl)borate complex.

Preliminary experiments have indicated that the five coordinate platinum(II) acetylene complexes show no tendency towards insertion of the methyl group across the C≡C bond, as in equation (1), at high temperatures [15], under ultraviolet irradiation [200], or in the presence of free radical initiators [200].

(vi) Infrared Spectra of the Five Coordinate Complexes

All of the hydrotris(1-pyrazolyl)borate complexes show an intense, broad band in the infrared spectrum near 2500 cm^{-1} due to a B-H stretching vibration. No attempt was made to assign ν(C=C) for the olefin complexes since the infrared spectra below 1600 cm^{-1} were extremely complicated due to vibrations of the polypyrazolylborate. Infrared absorptions for the two allene complexes due to ν(C=C=C) were in the region 1750-1700 cm^{-1} and appeared as one or more [184] broad, weak peaks. Other vibrations such as ν(C=O) and ν(C≡N) were observed in the expected regions. An intense sharp absorption in the region 1800-1900 cm^{-1} for the acetylene complexes was assigned to ν(C≡C). The lowering of ν(C≡C) by approximately 400 cm^{-1} upon coordination is consistent with considerable π-back bonding from the metal into the acetylene π^* orbitals for both the tetrakis(1-pyrazolyl)borate and hydridotris(1-pyrazolyl)borate complexes. We are unable to explain the high value of ν(C≡C) observed in PtMe[Bpz_4](PhC≡CMe), which would suggest a weak Pt-acetylene bond.

(vii) A Five Coordinate Carbonyl Complex

PtMe[HBpz$_3$] readily dissolves in dichloromethane in the presence of carbon monoxide giving a white stable crystalline 1:1 adduct. In contrast to the nmr spectra of the acetylene, allene and olefin complexes, the pyrazolyl proton resonances of PtMe[HBpz$_3$](CO) are very simple. Three resonances in the ratio of 1:1:1 are observed at 7.67, 7.57 and 6.25 δ. The high field resonance appears as a triplet (J(H-H) = 2.0 Hz) with platinum satellites (J(Pt-H) = 5.0 Hz) and is thus assigned to the three 4-H protons. By a double resonance experiment the low field resonance is assigned to the three 3-H protons (J(Pt-H) = 9.0 Hz) and the peak at 7.57 δ is assigned to the three 5-H protons. Since all pyrazolyl ring protons are equivalent at room temperature and coupling to platinum-195 is observed, the fluxionality must be due to a rotation of the tridentate ligand about the C_{3v} axis of the ligand, analogous to the trigonal or Bailar twist [188] proposed for octahedral complexes. A "tumbling" or dissociative-associative exchange process would necessitate loss of ^{195}Pt coupling to the 3-H and 4-H protons. The limiting low temperature spectrum (~ -125°C) showed the presence of two resonances, due to the 4-H protons, in the ratio of 2:1. These results are consistent with a 5-coordinate trigonal-bipyramidal structure.

c) Experimental

PtMeCl(COD) was prepared by the procedure outlined in Chapter VII.

Potassium tetrakis(1-pyrazolyl)borate and potassium hydrotris-(1-pyrazolyl)borate were prepared by the method of Trofimenko [168,201] with minor modifications.

(i) Preparation of K[$HBpz_3$]

Pyrazole (10.8 g., 0.159 moles) and potassium borohydride (2.14 g., 0.040 moles) were placed in the bottom of a 250 ml. round bottom flask containing a magnetic stirring bar. A reflux condenser was fitted to the flask and the system was connected to a paraffin oil gas bubbler. The flask was placed in an oil bath on a magnetic stirrer and slowly heated. At 80°C the pyrazole melted and the KBH_4 dissolved slowly with evolution of hydrogen. At 100°C hydrogen evolution was vigorous. The temperature was slowly raised to 180°C with slow stirring. After about 4 hours hydrogen evolution had ceased so the hot solution was poured into 25 ml. of toluene. After 15 minutes white crystals separated. The solution was allowed to stand for two hours, filtered and washed with three 50 ml. portions of hot toluene, then the crystals were washed with 50 ml. of pentane and air dried. Yield was 6.80 g. (67%).

(ii) Preparation of PtMe[$HBpz_3$]

To a solution of PtMeCl(COD) (4.0 g., 1.13 mmoles) in 50 ml. of acetone was added $AgPF_6$ (2.88 g., 1.13 mmoles). The solution was

stirred for 15 minutes and the silver chloride was removed by centrifugation to give a clear colourless solution. A solution of K[HBpz$_3$] (2.75 g., 1.13 mmoles) in 20 ml. of acetone was added dropwise. The solution turned yellow then dark brown and after several minutes a precipitate formed. The solvent was removed on a rotary evaporator to give a gray-brown solid. The solid was washed with pentane, then three 50 ml. portions of distilled water, 50 ml. of absolute ethanol, 50 ml. of diethyl ether and air dried. The yield was 5.27 g., m.p. > 150°. Analyses, Calculated (Found):
C, 28.38(27.38); H, 3.10(3.11); N, 17.03(19.86).

(iii) Preparation of PtMe[HBpz$_3$](CF$_3$C≡CCF$_3$)

PtMe[HBpz$_3$] (0.390 g.) was placed in the bottom of a 20 ml. thick-walled Carius tube and 5 ml. of dichloromethane were added. Using standard high-vacuum techniques, a two-fold excess of hexafluorobut-2-yne was condensed into the tube and the tube was sealed. The Carius tube was shaken for two hours and the solid dissolved. The tube was opened and the solution was passed through a short 2" florisil column, eluting with dichloromethane to give a clear colourless solution. The solvent was reduced in volume to about 2 ml. and pentane was added to give white crystals. The flask was cooled at -14°C for 12 hours, then the solvent was decanted and the crystals were dried under vacuum. Yield was 80%.

(iv) Preparation of PtMe[HBpz$_3$](MeO$_2$CC≡CCO$_2$Me)

To a suspension of PtMe[HBpz$_3$] (0.360 g.) in dichloromethane was added 0.150 ml. of dimethylacetylene-dicarboxylate. The solution was stirred for 10 minutes to give a dirty yellow solution which was then chromatographed on a 1" florisil column, eluting with dichloromethane. The solvent volume was reduced and pentane was slowly added to give pale yellow crystals. The flask was cooled in ice for 6 hours, the solvent was decanted and the crystals were dried under vacuum. Yield was 78%.

(v) Preparation of PtMe[HBpz$_3$]($\overline{\mathrm{CH{=}CHCOOCO}}$)

A suspension of PtMe[HBpz$_3$] (0.300 g.) and maleic anhydride (0.070 g.) in dichloromethane was magnetically stirred for 15 minutes to give a clear solution. The solution was passed through a 1" florisil column, eluting with dichloromethane. The solvent volume was reduced and pentane was added to give white crystals. Yield was 84%.

(vi) Preparation of PtMe[HBpz$_3$]()

A solution of PtMe[HBpz$_3$] (0.200 g.) and p-benzoquinone (0.051 g.) in 5 ml. of dichloromethane was stirred for 30 minutes to give a bright yellow solution. After passing the solution through a short florisil column the solvent volume was reduced and pentane was added to give bright yellow crystals. The flask was cooled over night, the mother liquor was decanted and the crystals were dried under vacuum. Yield was 62%.

(vii) Preparation of PtMe[HBpz$_3$](CH_2=CH-CN)

Acrylonitrile (0.100 ml.) and PtMe[HBpz$_3$] (0.280 g.) were suspended in 5 ml. of dichloromethane and magnetically stirred for

20 minutes. The solution was chromatographed with dichloromethane to give a clear colourless solution. The solvent was removed to give an oil which was taken up in 2 ml. of diethyl ether. A serum cap was fitted to the top of the flask which was then cooled to -78°C in dry ice for 30 minutes. Pentane was added dropwise from a 1 ml. syringe to give a white precipitate. After an excess of pentane had been added the flask was kept at -78°C for one hour. The serum cap was then removed, the solvents were decanted and the white precipitate was dried under high vacuum. Yield was 65%.

(viii) Preparation of $PtMe[HBpz_3](Me_2C{=}C{=}CMe_2)$

To a suspension of $PtMe[HBpz_3]$ (0.310 g.) in 10 ml. of dichloromethane was added tetramethylallene (0.20 ml.). The solution was stirred for 4 hours and then passed through a 1" florisil column, eluting with dichloromethane. The solvent was removed and the oil was dissolved in 1 ml. of diethyl ether. Pentane (5 ml.) was added and the solvents were allowed to evaporate slowly in the air to give white crystals. Yield was 58%.

(ix) Preparation of $PtMe[HBpz_3](Me_2C{=}C{=}CH_2)$

A solution of $PtMe[HBpz_3]$ (0.300 g.) and 3,3'-dimethylallene (0.100 ml.) in 5 ml. of dichloromethane was stirred for 15 minutes to give a clear solution which was passed through a 1" florisil column. The solvent volume was reduced to about 1 ml. and pentane was added. The flask was cooled for 12 hours to give white crystals. The solvents were decanted and the complex was dried under vacuum. Yield was 83%.

(x) Preparation of PtMe[HBpz$_3$](CO)

Carbon monoxide was bubbled through a suspension of PtMe[HBpz$_3$] (0.262 g.) in 10 ml. of dichloromethane for 30 minutes. The solution was then passed through a short florisil column, eluting with dichloromethane to give a clear colourless solution. The solvent was removed and the oil was taken up in 1 ml. of diethyl ether. Pentane was added slowly to give white crystals. The flask was cooled for 12 hours and the complex was dried under vacuum. Yield was 78%. m.p. 92-94°. Analyses, Calculated (Found): C, 29.28(29.46); H, 2.90 (2.96); N, 18.63(18.76).

(xi) Preparation of PtMe[Bpz$_4$]

To a solution of PtMeCl(COD) (0.690 g.) in 10 ml. of tetrahydrofuran was added AgPF$_6$ (0.493 g.) in 1 ml. of THF. The solution was magnetically stirred for 10 minutes and the silver chloride was removed by centrifugation. K(Bpz$_4$) (0.620 g.) in 5 ml. of THF was added slowly. The solution turned yellow, then brown and a white solid precipitated. After 30 minutes the solution was filtered and the solid was washed with 50 ml. of distilled water, 50 ml. of absolute ethanol and 10 ml. of diethyl ether. Yield was 1.35 g. m.p. > 240°. Analyses, Calculated (Found): C, 31.93(33.48); H, 3.09(3.45).

(xii) Preparation of PtMe[Bpz$_4$](Ph-C≡C-Me)

To a suspension of PtMe[Bpz$_4$] (0.147 g.) in 5 ml. of dichloromethane was added 0.050 ml. of phenylmethylacetylene. After 30 minutes the solution was passed through a short florisil column with dichloromethane. The solvent was removed and the oil was dissolved in 1 ml. of diethyl ether and cooled to -78°C. Pentane was added slowly to give pale yellow crystals. The solvents were decanted and the crystals were dried under vacuum. Yield was 67%.

CHAPTER IX

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME σ-BONDED ORGANOPLATINUM COMPLEXES

a) Introduction

Carbon-13 nuclear magnetic resonance spectroscopy has been used quite extensively in recent years by organic chemists [204], however, applications to inorganic and organometallic chemistry have been limited due to the low carbon concentrations in many heavy transition metal complexes. Recent advances in Fourier transform techniques and the development of modern high resolution nuclear magnetic resonance spectrometers have now removed many of these difficulties so that ^{13}C nmr spectra may be run quite routinely, on many organometallic complexes, in short periods of time. There are many obvious advantages in obtaining ^{13}C nmr spectra, since one is observing large chemical shifts and spin-spin coupling constants associated with an atom that is directly bonded to the metal. More importantly, these parameters may be related to changes in hybridization and electron density so that the effect of coordination on the unsaturated carbon atoms of acetylenes [11,15,23,24,42,80,99,117,206], carbonyls [75,206], isocyanides [26], nitriles [28,99,117,205] and olefins [79] may be investigated.

Since many of these unsaturated organic ligands are activated towards nucleophilic attack on coordination to a metal, ^{13}C nmr spectroscopy may thus offer a unique method for studying these reactions.

Although there have been several reports in the literature of applications of ^{13}C nmr spectroscopy to organometallic chemistry [118], detailed studies of closely related series of complexes are lacking. In this chapter we shall examine a variety of closely related organoplatinum complexes containing sp, sp^2 and sp^3 hybridized carbon atoms. Platinum was chosen as the metal for two reasons; firstly, the nuclear spin of ^{195}Pt provides valuable information from $^{195}Pt-^{13}C$ coupling constants and secondly, many of these complexes undergo interesting chemical reactions. We shall discuss the coupling constants and chemical shifts of the σ-bonded carbon atoms and will try to relate these parameters to the known chemistry of the complexes.

b) Results and Discussion

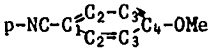
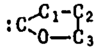
The ^{13}C nmr data (with random noise decoupling of the protons) are listed in Tables IX-1 to IX-5. Analytical and ^1H nmr data for the new complexes are given in the experimental. Throughout the chapter we shall use Q and A to represent PMe_2Ph and $AsMe_3$ respectively.

Four series of methylplatinum compounds have been examined:

(1) trans-square planar platinum(II) complexes of the type $[PtMeQ_2L](PF_6)$, $[PtMeA_2L](PF_6)$ and $PtMeQ_2Z$, where L is a neutral ligand such as a nitrile, acetylene, isocyanide, phosphine, carbene,

Table IX-1

^{13}C NMR Data [a] for Complexes *trans*-[PtMeL(PMe$_2$Ph)$_2$](PF$_6$)

L	Platinum Methyl			Phosphine Methyls			Other Resonances and Couplings
	δ(Pt-C)	^{2}J(P-C)	^{1}J(Pt-C)	δ(P-C)	^{1}J+^{3}J(P-C)	^{2}J(Pt-C)	
Me$_2$N-CHO	-27.8	5	698	11.0	36	36	δ(NMe)32.0,38.2; δ(CO)166.9
	-19.1	6	652	11.9	40	40	δ(CN)121.2, ^{2}J(PtNC)82
							δ(C$_1$)100.8, δ(C$_2$)135.6, δ(C$_3$)115.9, δ(C$_4$)165.2
							δ(OMe)56.3
Me-C≡C-Me	-4.2	6	632	11.4	36	36	δ(Me)8.1, J(Pt-C)14
							δ(≡C-)69.5, J(Pt-C)18
CH$_2$=CH$_2$	5.6	6	615	10.5	32	36	δ(=C-)84.4, J(Pt-C)50
CN-Me	-6.9	7	510	13.4	40	40	δ(Me)29.2
CO	0.0	6	509	13.6	40	40	δ(CO)177.6, ^{2}J(P-C)10, ^{1}J(Pt-C)986
PMe$_2$Ph	0.7	6	457	16.6	40	20	
				13.8	36	-	
	-10.1	6	396	12.1	40	40	δ(:C)299.0, ^{1}J(Pt-C)783
							δ(C$_1$)57.2, ^{2}J(Pt-C)90; δ(C$_2$)18.9, ^{3}J(Pt-C)15
							δ(C$_3$)87.9, ^{3}J(Pt-C)50

[a] Chemical shifts are reported in ppm (positive) downfield from SiMe$_4$ and coupling constants are given in hertz.

Table IX-2

^{13}C NMR Data [a] for Complexes trans-$[PtXL(AsMe_3)_2](PF_6)$

X	L	Platinum Methyl		Arsine Methyls		Other Resonances and Couplings
		δ(Pt-C)	^1J(Pt-C)	δ(As-Me)	^2J(Pt-C)	
Me	$p\text{-NC-}C_1{<}^{C_2-C_3}_{C_2=C_3}{>}C_4\text{-OMe}$	-26.9	613	8.1	48	δ(CN)121.2; ^2J(Pt-N-C)82 δ(C_1)99.5; δ(C_2)134.5; δ(C_3)115.2; δ(C_4)164.2 δ(OMe)55.6
Me	$NC\text{-}C_6F_5$	-25.5	616	8.3	48	
Me	CN-Me	-14.0	475	9.7	47	
Me	CO	-6.8	470	10.0	42	δ(CO)178.7; ^1J(Pt-C)1000
Me	$:C{<}^{OMe}_{Me}$	-15.9	360	9.5	50	δ(:C)321; ^1J(Pt-C)759 δ(Me)44.2; ^2J(Pt-C)86; δ(OMe)70.6; ^3J(Pt-C)67
Me	$:C{<}^{NH_2}_{Me}$	-18.6	380	8.8	53	δ(:C)255; ^1J(Pt-C)666 δ(Me)37.7; ^2J(Pt-C)58
Me	$:C{<}^{NHMe}_{Me}$	-17.6	381	9.1	51	δ(:C)247.3; ^1J(Pt-C)687 δ(Me)36.6; ^2J(Pt-C)50; δ(NMe)39.6; ^3J(Pt-C)60
Me	$:C{<}^{NMe_2}_{Me}$	-19.7	382	9.6	51	δ(:C)245.1; ^1J(Pt-C)694 δ(Me)31.9; ^2J(Pt-C)51 δ(NMe)41.1, 50.5; ^3J(Pt-C)20, 66
Cl	CO	-	-	10.0	33	δ(CO)159.3; ^1J(Pt-C)1747
Cl	$:C{<}^{OMe}_{Me}$	-	-	8.7	48	δ(:C)278.3 δ(Me)9.8; ^2J(Pt-C)78; δ(OMe)72.1; ^3J(Pt-C)95
Cl	$:C{<}^{NMe_2}_{Me}$	-	-	8.6	50	δ(:C)210.0; ^1J(Pt-C)1070 δ(Me)33.0; ^2J(Pt-C)80 δ(NMe)41.6, 51.9; ^3J(Pt-C)94, 40

[a] Coupling constants are reported in hertz and chemical shifts in ppm (positive) downfield from $SiMe_4$.

Table IX-3

^{13}C NMR Data [a] for Complexes trans-PtMeX(PMe$_2$Ph)$_2$

X	Platinum Methyl			Phosphine Methyl		
	δ(Pt-C)	^2J(P-C)	^1J(Pt-C)	δ(P-C)	$^1J+^3J$(P-C)	^2J(Pt-C)
-Cl	-18.7	6	673	12.0	38	38
-I	-7.4	6	664	15.2	38	38
-NCS	-22.8	6	632	12.3	36	36
-NO$_2$	-26.1	6	564	12.3	38	38
-CN [b]	-11.1	7	500	14.2	40	40

[a] Coupling constants are reported in hertz and chemical shifts in ppm (positive) downfield from SiMe$_4$.

[b] δ(C≡N) 138.5

Table IX-4

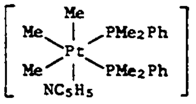
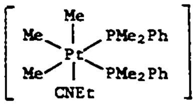
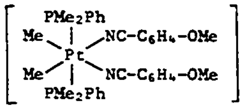
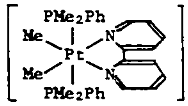
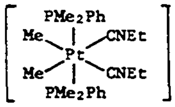
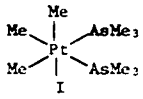
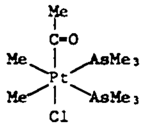
^{13}C NMR Data [a] for Complexes *cis*-$PtMe_2L_2$

L	δ(C)	*J*(Pt-C)	Assignment
1,5-C_8H_{12}	4.7	773	Pt-Me
	29.9	<3	-CH_2
	98.8	55	=CH
$AsMe_3$	-4.1	689	Pt-Me
	11.6	19	As-Me
$AsMe_2Ph$	-3.0	685	Pt-Me
	10.6	20	As-Me
p-CN-C_6H_4-Me	-5.7	590	Pt-Me
	21.2		Aromatic-Me
	147.7	932	C≡N-
PMe_2Ph	3.3	594	Pt-Me;^{2}*J*(P-C),9(cis),104(trans)
	15.1	28	P-Me;^{1}*J*(P-C),32

[a] Chemical shifts are reported in ppm downfield (positive) from $SiMe_4$ and coupling constants are given in hertz.

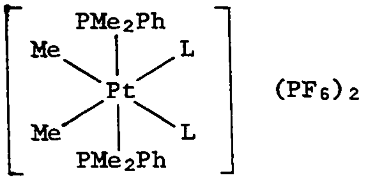
Table IX-5

^{13}C NMR Data [a] for Platinum(IV) Complexes

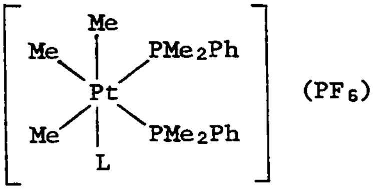
Compound	δ(C)	J(P-C)	J(Pt-C)	Assignment
 (PF_6)	-8.6	4	597	Me-trans to NC_5H_5
	12.1	4,108	522	Me-trans to PMe_2Ph
	9.8			Phosphine methyls
 (PF_6)	-4.3	8	514	Me-trans to CNEt
	0.5	6,108	460	Me-trans to PMe_2Ph
	13.9			Isocyanide-Me
	39.9			Isocyanide-CH_2-
 $(PF_6)_2$	-2.3	4	560	Me-trans to NCC_6H_4OMe
	8.8	20	20	Phosphine methyls
	56.4			Nitrile methoxy-carbon
	99.2,137			Aromatic nitrile carbons
	116,166.2			
 $(PF_6)_2$	4.3	4	528	Me trans to $N_2C_{10}H_8$
	6.1	20	22	Phosphine methyls
 $(PF_6)_2$	5.1	4	428	Me trans to CNEt
	10.6	22	20	Phosphine methyls
	13.0			Isocyanide-methyl
	40.9			Isocyanide-CH_2
	-0.8		620	Me trans to I
	2.0		556	Me trans to $AsMe_3$
	8.7		7	Arsine methyls
	3.4		583	Me trans to $AsMe_3$
	8.5		10	Arsine methyls
	36.3		221	Acyl methyl
	193.6		851	Acyl carbonyl

[a] Chemical shifts are reported in ppm downfield (positive) from $SiMe_4$ and coupling constants are given in hertz.

etc., and Z is an anionic ligand such as chloride, nitro, or cyanide;
(2) *cis*-square planar platinum(II) complexes of the type $PtMe_2L_2$ where L is a neutral ligand;
(3) octahedral dimethylplatinum(IV) cations, I, where L is a neutral ligand (Chapter IV);
(4) octahedral trimethylplatinum(IV) cations, II, where L is a neutral ligand (Chapter V).



I

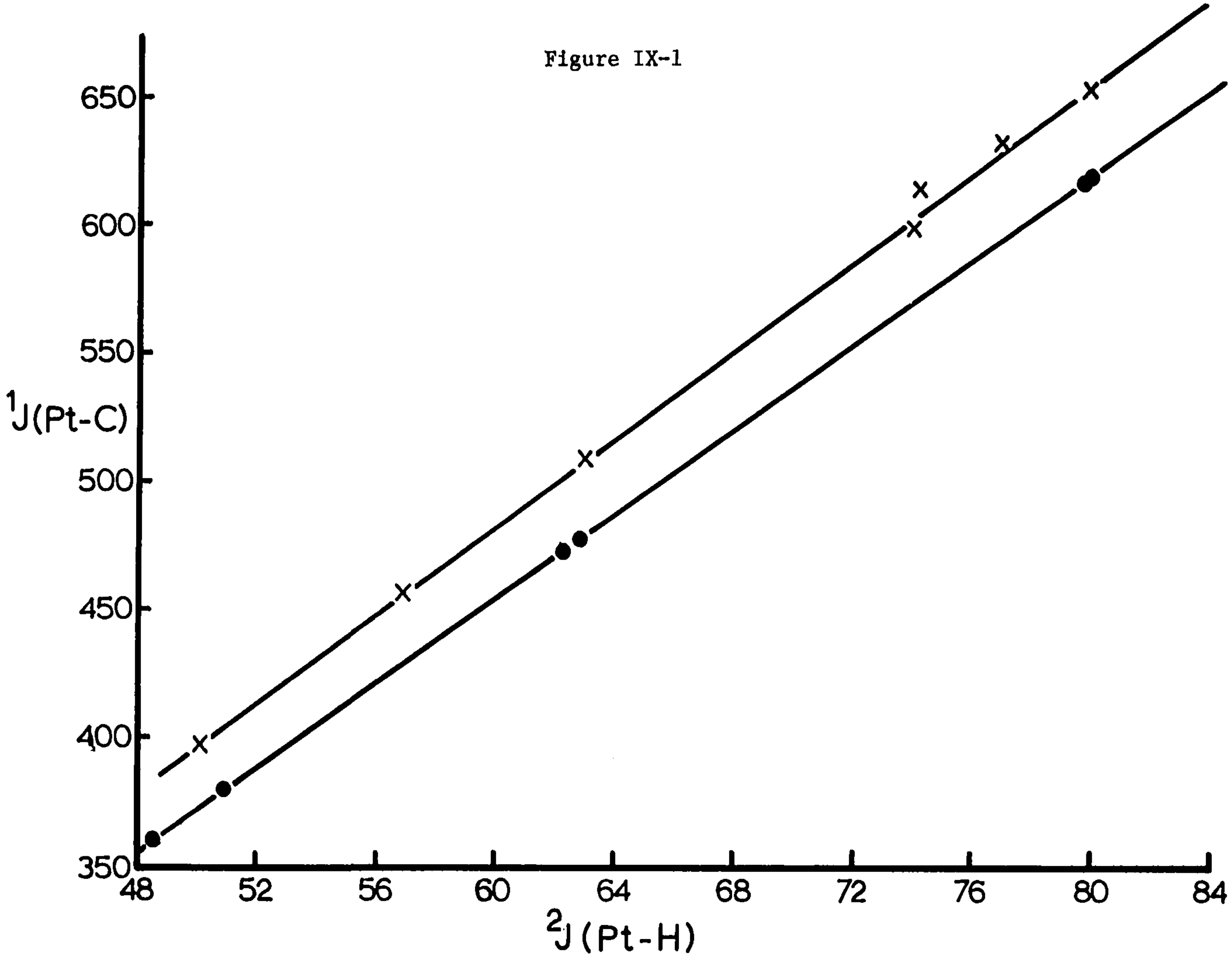


II

A wide range of complexes in series 1 have been examined; however, a limited number of compounds belonging to series (2)-(4) have been studied due to experimental problems in their synthesis, and to instability [99] (Chapter V). We have specifically chosen L and Z in the first series to cover a wide range of *trans*-influence so that a very large variation in coupling constants and chemical shifts would be observed.

In Figure IX-1, ^{1}J(Pt-C) is plotted against ^{2}J(Pt-C-H) for the cations of series (1) and in Figure IX-2 ^{1}J(Pt-C) is plotted against ^{2}J(Pt-C-H) for the neutral compounds of series (1). Linear relationships are also observed between ^{1}J(Pt-C) and ^{2}J(Pt-H) for the platinum methyl group trans to L in series (2-4) but these are not plotted due to the limited number of complexes available. A least squares

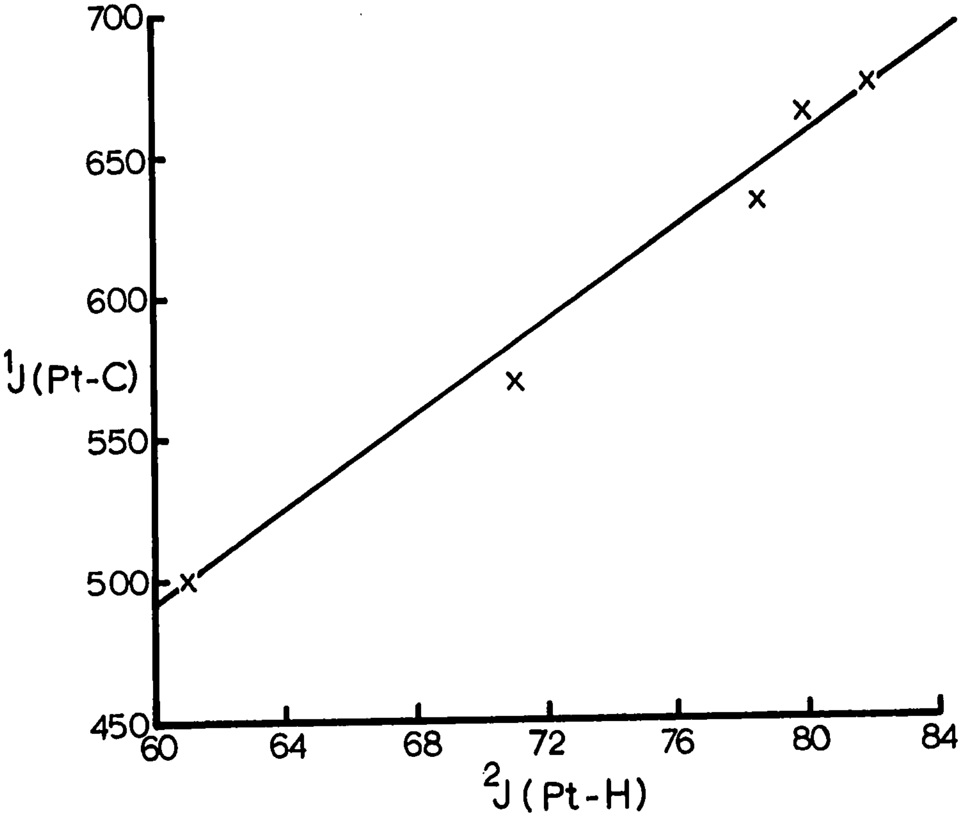
Figure IX-1



Plot of $^1\underline{J}$(Pt-C) vs. $^2\underline{J}$(Pt-H) for <u>trans</u>-$[PtMe(PMe_2Ph)_2L](PF_6)$(x) and <u>trans</u>-$[PtMe(AsMe_3)_2L](PF_6)$(●),

(L = neutral ligand, Tables IX-1, IX-2)

Figure IX-2



Plot of $^1\underline{J}$(Pt-C) vs. $^2\underline{J}$(Pt-H) for trans-PtMe$(PMe_2Ph)_2Z$

(Z = anionic ligand, Table IX-3)

approximation was applied to the data in Tables IX-1 to IX-5 to determine the linear relationship between $^{1}\underline{J}$(Pt-C) and $^{2}\underline{J}$(Pt-H) for each methyl group trans to L in series (1) to (4). These relationships are given in Table IX-6. Several observations may be drawn from these results. None of the lines pass through the origin; a negative intercept on the $^{1}\underline{J}$(Pt-C) axis is found for each series and the magnitude of this intercept appears to depend on stereochemistry rather than oxidation state. Similarly the slope of the line appears to depend more on stereochemistry than on oxidation state. For example the complexes of series (2), cis-$PtMe_2L_2$, have a similar slope and intercept to those for the complexes in series (3) and (4) and although the oxidation state of platinum differs, each complex in series (2), (3) and (4) has cis-methyl groups. The relationships between $^{1}\underline{J}$(Pt-C) and $^{2}\underline{J}$(Pt-H) are very similar for series (1a) and (1c) although one series is neutral and the other is cationic.

The phosphine-methyl resonances for the complexes of series (1) and (3) appear as 1:2:1 triplets, consistent with a trans-configuration of phosphines and strong ^{31}P-^{31}P coupling [36]. These resonances are flanked by ^{195}Pt satellites of one-fourth intensity. The phosphine-methyl resonances of series (2) and (4) appear as doublets, indicative of cis-phosphines and small ^{31}P-^{31}P coupling, and are accompanied by ^{195}Pt satellites. For the cations of series (4), the absence of a plane of symmetry in the P-Pt-P plane makes the phosphine-methyl carbons magnetically inequivalent and overlapping doublets are observed. These resonances are further complicated by the ^{195}Pt satellites since $^{2}\underline{J}$(Pt-C) is less than $^{1}\underline{J}$(P-C).

Table IX-6

The Relationships Between ^{1}J(Pt-C) and ^{2}J(Pt-H) for a Series of Methylplatinum Compounds

Series	Relationship of Coupling Constants
1. (a) *trans*-$[\mathrm{PtMe(PMe_2Ph)_2L}]^+$	^{1}J(Pt-C)=8.39 ^{2}J(Pt-H)-22.1
(b) *trans*-$[\mathrm{PtMe(AsMe_3)_2L}]^+$	^{1}J(Pt-C)=8.18 ^{2}J(Pt-H)-38.1
(c) *trans*-$\mathrm{PtMe(PMe_2Ph)_2Z}$	^{1}J(Pt-C)=8.44 ^{2}J(Pt-H)-23.0
2. *cis*-$\mathrm{PtMe_2L_2}$	^{1}J(Pt-C)=11.4 ^{2}J(Pt-H)-199.6
3. $[\mathrm{PtMe_2(PMe_2Ph)_2L_2}]^{+2}$	^{1}J(Pt-C)=11.1 ^{2}J(Pt-H)-205.4
4. *fac*-$[\mathrm{PtMe_3(PMe_2Ph)_2L}]^+$	^{1}J(Pt-C)=12.6 ^{2}J(Pt-H)-258.1

The platinum-methyl resonances of the phosphine complexes in series (1) and (3) and the methyl group trans to L in series (4) appear as triplets due to coupling of the methyl-carbon equally to the two ^{31}P nuclei and these resonances are flanked by ^{195}Pt satellites, the magnitude of which is dependent on the trans-ligand, L. The resonance of the two platinum-methyl carbons trans to phosphine in series (2) (L = PMe_2Ph) and series (4) appears as doublets of doublets, consistent with an AA'XX' spectrum with J(AX) >> J(AX') and J(X-X') small. Typically for cis-$PtMe_2(PMe_2Ph)_2$, trans-^2J(P-C) = 104 Hz and cis-^2J(P-C) = 9 Hz.

(i) Spin-Spin Coupling Constants

As mentioned in previous chapters, most discussions of one bond coupling constants, i.e., ^1J(Pt-P) and ^1J(Pt-H), have assumed that the coupling constant is dominated by the Fermi Contact term [7,141], and the appropriate form of that expression for the one bond $^{195}Pt-^{13}C$ coupling constant is given in equation (1) (the symbols were described in Chapter VI).

$$^1J(\text{Pt-C}) \propto \gamma_{Pt}\gamma_C\alpha^2{}_{Pt}\alpha^2{}_C\,[\psi_{Pt(6s)}(0)]^2[\psi_{C(2s)}(0)]^2/\Delta E \qquad (1)$$

In this section we shall discuss the relative importance of both $\alpha^2{}_{Pt}$ and $\alpha^2{}_C$ in determining the magnitude of this coupling constant [207].

A. $^{195}Pt-^{13}C(sp^3)$ Coupling Constants

In previous chapters the two bond coupling constant ^2J(Pt-H) for a variety of methyl-platinum complexes was used to establish an NMR trans-influence series. Variations in ^2J(Pt-C-H) were related specifically to $\alpha^2{}_{Pt}$ for closely related series of complexes [11]. It was assumed that $\alpha^2{}_C$ was constant and that the hydrogen nucleus was sensitive only to changes in the Pt(6s) orbital contribution to the Pt-Me bond. We are now able to test this assumption for the series $[PtMeA_2L](PF_6)$. The proton coupled ^{13}C nmr spectra [211] for the cations where L = NCC_6H_4OMe, CO, :C(OMe)Me gave equivalent values of $^1\underline{J}(^{13}C-^1H)$, equal to 128 Hz. (c.f. $^1\underline{J}(^{13}C-^1H)$ coupling constants in hydrocarbons [208], ~125 for sp^3, ~160 for sp^2 and ~250 Hz for sp hybridized carbons). Since the variations in $^1\underline{J}$(Pt-C) (380-616 Hz) and $^2\underline{J}$(Pt-C-H) (47-80 Hz) are large for the series of methyl-platinum cations while $^1\underline{J}(^{13}C-^1H)$ is constant, the assumption that $\alpha^2{}_C$ is constant appears to be valid. Since such good linear correlations exist between $^1\underline{J}$(Pt-C) and $^2\underline{J}$(Pt-H) it also appears that the use of the two bond coupling constant is quite valid for determining the NMR trans-influence of a ligand within closely related series of complexes. As mentioned briefly in Chapter I, variations in $\alpha^2{}_{Pt}$ are believed to result from a rehybridization of Pt σ-orbitals as the bonding properties of L are varied [10,209]. For example, if L is a weak σ-donor such as a nitrile it will not require much Pt "s" character in its bond to platinum. Consequently the Pt-C bond contains much Pt "s" and "d" character and a large coupling constant is observed. As the σ-donor strength of L increases, L will compete more effectively with the methyl group for Pt(6s) character. The increase in s-character in the Pt-L bond is thus obtained at the expense of the Pt-C bond and a lower value of $^1\underline{J}$(Pt-C) is observed.

Several two and three bond $^{195}Pt-^{13}C(sp^3)$ coupling constants are reported for a series of platinum(II) methyl(amino)carbene complexes[210] in Table IX-7. In the methyl(dimethylamino)carbene ligand ^{195}Pt coupling is greater to the methyl carbon *cis* to platinum than to the *trans*-carbon. Replacing -Me by -Cl as the *trans*-ligand in the complex causes large changes in the two and three bond coupling constants to the methyl carbons of the carbene. The changes are brought about by the large difference in s-demand of -Me and -Cl.

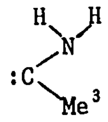
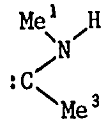
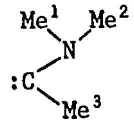
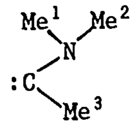
B. $^{195}Pt-^{13}C(sp^2)$ and $^{195}Pt-^{13}C(sp)$ Coupling Constants

The magnitude of $^1J(Pt-C)$ should also be dependent on α^2_C (equation 1), the amount of carbon 2s contribution to the Pt-C bond. That this is indeed the case is clearly evident from the data reported in Tables (IX-1) - (IX-3); values of $^1J(Pt-C)(sp^3)$ fall in the range 380-650 Hz, $^1J(Pt-C)(sp^2)$ in the range 660-1070 Hz and values of $^1J(Pt-C)(sp)$ are in the range 1000-1747 Hz. Therefore gross changes in $^1J(Pt-C)$ may result from changes in hybridization of the carbon atom directly bonded to platinum. The values of $^1J(Pt-C)(sp^2)$ and $^1J(Pt-C(sp)$ are also dependent on the nature of the *trans*-ligand and parallel the changes previously discussed for $^1J(Pt-C)(sp^3)$, e.g. for *trans*-$[PtR(C{\equiv}O)A_2]^+(PF_6)^-$, $^1J(Pt-CO)$ = 1000 and 1747 Hz for R = -Me and -Cl respectively.

^{13}C nuclear magnetic resonance spectroscopy provides a unique technique for studying the bonding in the carbene complexes *trans*-$[PtMeA_2(:C{<}^{X}_{Me})](PF_6)$, where X is a heteroatom substituent. $^1J(Pt-C)$ changes for both the platinum-methyl carbon and the carbene carbon as

Table IX-7

^{195}Pt-^{13}C(sp^3) Coupling Constants for Carbene Complexes trans-[PtX(AsMe$_3$)$_2$(carbene)](PF$_6$) [a]

X	Carbene	δC$_1$	^{3}J(Pt-C$_1$)	δC$_2$	^{3}J(Pt-C$_2$)	δC$_3$	^{2}J(Pt-C$_3$)
Me		-	-	-	-	37.7	58
Me		39.6	60	-	-	36.6	50
Me		50.5	66	41.1	20	31.9	51
Cl		41.6	94	51.9	40	33.0	80

[a] Coupling constants are reported in hertz and chemical shifts in ppm downfield (positive) from SiMe$_4$.

a function of the heteroatom and its substituents. $^1\underline{J}(Pt-C)(sp^2)$ for the carbene carbon decreases in the order X = OMe > NMe_2 > NHMe > NH_2 while $^1\underline{J}(Pt-C)(sp^3)$ for the platinum-methyl carbon increases in the order X = OMe < NMe_2 < NHMe < NH_2. These results suggest that the platinum-carbene bond and hence the trans-influence of the carbene are sensitive to the hybridization of the carbene carbon atom. Changing the heteroatom from oxygen to nitrogen results in an increase in p-character at the carbene carbon (see later discussion of carbene carbon chemical shifts) and consequently lowers the carbon 2s character (α^2_C), resulting in a lower $^1\underline{J}(Pt-C)(sp^2)$ coupling constant. This is probably the best example to date to support the concept of the trans-influence (measured by nmr coupling constants) defined by Allen and Pidcock [10] since (i) both trans-ligands are carbon atoms and can thus be observed by ^{13}C nmr and (ii) small changes in α^2_C at the carbene atom result in inverse changes in α^2_{Pt} in the trans-Pt-Me bond, as predicted by the rehybridization scheme.

Coupling to the acyl carbon in $PtMe_2(COMe)A_2Cl$ (Table IX-5, $^1\underline{J}(Pt-C)(sp^2)$ = 851 Hz) falls in the range observed for other sp^2 hybridized carbons [212].

Repeated efforts to observe the isocyanide carbon resonance in the cations $[PtMe(CNMe)A_2]^+$ and $[PtMe(CNMe)Q_2]^+$ failed, presumably due to a long relaxation time (T_1) and broadening caused by the ^{14}N quadrupole. Consequently a comparison of the two coupling constants $^1\underline{J}(Pt-C\equiv O)$ and $^1\underline{J}(Pt-C\equiv N)$, for analogous complexes, unfortunately, could not be made.

Coupling between ^{195}Pt and the nitrile carbon atom in the cations $[PtMe_2Q_2(N{\equiv}C{-}C_6H_4{-}OMe)_2]^{+2}$ and $[PtMeQ_2(N{\equiv}C{-}C_6H_4{-}OMe)]^{+}$ has been observed and the magnitude of this coupling constant is dependent on the oxidation state of platinum, i.e. 27 Hz and 82 Hz for the Pt(IV) and Pt(II) cations respectively.

(ii) ^{13}C Chemical Shifts

It is usual to approximate the total shielding (σ_N) for the carbon-13 nucleus by the sum of a diamagnetic screening term (σ_d), a term representing anisotropic contributions and non-localized effects (σ'), and a paramagnetic screening constant (σ_p), such that $\sigma_N = \sigma_d + \sigma' + \sigma_p$. Contributions from σ_d are generally considered to be small, and in the absence of large anisotropic effects the variations in carbon-13 chemical shifts are attributed to variations in the local paramagnetic screening constant [213-216] (equation 2),

$$\sigma_p = -\frac{e^2h^2}{2m^2c^2\Delta E} <r^{-3}>_{2p} \{Q_{AA} + \sum_{B\neq A} Q_{AB}\} \qquad (2)$$

where ΔE is an average excitation energy between the ground state and lowest lying paramagnetic state of the molecule, r_{2p} is the radius of the carbon 2p orbital, and the Q terms contain elements of the charge density and bond-order matrix. Both the factor $<r^{-3}>_{2p}$ and the term Q_{AA} depend primarily on the local electron density on the carbon atom. As the total electronic charge on atom A increases, the orbitals expand and $<r^{-3}>_{2p}$ decreases. The terms involving Q_{AB} with $B\neq A$ are of considerable importance. Physically they arise because the external magnetic field acting on atom B mixes in certain excited electronic states of the molecule and thereby induces a current flow on atom A; however, this Q_{AB} term occurs only if there is both σ and π bonding between A and B [216].

The general shift sequence from low to high field is for sp^2, sp and sp^3 hybridization; sp^2 and sp carbons are to low field of sp^3 carbons because ΔE is smaller and Q_{AB} is larger, resulting in a larger σ_p and a downfield shift.

^{13}C chemical shifts are well understood for simple organic molecules but the problem is much more complicated for large molecules, especially when carbon is bonded to a transition metal atom with large d orbitals.

A. sp^3-Carbon Chemical Shifts

The platinum-methyl carbon chemical shifts for all of the complexes in series (1) (Tables IX-1 to IX-3) are from 0 to 28 ppm upfield from tetramethylsilane and in this respect are similar to the high field hydride chemical shifts observed for analogous platinum-hydride complexes [76] $[PtHLQ_2]$ (where L = neutral or anionic ligand).

Buckingham and Stevens [217,218] proposed a theory in 1964 whereby the large upfield hydride shifts observed for square planar platinum(II) hydride complexes were attributed to a paramagnetic contribution arising from partially filled Pt 5d orbitals, while small variations in the hydride shift, as the other ligands on platinum were varied, were related to changes in the Pt-H bond length (R) (i.e. $\sigma_p \alpha - {}^1/R$). Powell et al [219] have recently suggested that the chemical shifts of sp^2 and sp^3 hybridized carbons bonded to transition metals are governed by a non-bonding shielding parameter associated with partially filled metal d orbitals, similar to the concepts of Buckingham and Stevens. There appear to be two obvious contradictions to this model. Firstly, Powell stated that the small upfield shift of the coordinated ethylene carbons in the silver(I) ethylene cation [220], $Ag-C_2H_4^+$, was due to the filled d orbitals of the d^{10}-Ag complex. However, we have recently examined a series of olefin and acetylene complexes [221] of d^8-platinum(II) and d^{10}-platinum(0) and observed the largest upfield shift of the ethylene carbons when coordinated to Pt(0) - a d^{10} metal with filled d orbitals. These results appear to contradict the model proposed by Powell. Secondly, if the platinum-methyl carbon chemical shift was related to the Pt-C bond length [218], an increase in the trans-influence of the trans-ligand would increase R, giving a smaller negative σ_p and an upfield shift. That this is not the case is clearly shown from the shifts reported in Tables IX-1 to IX-3. The random scattering of Pt-C shifts with the trans-influence of L or Z suggests that the factors governing carbon-13 shifts are more complex in origin than those governing hydride shifts. This may result from a screening by the hydrogens bonded to carbon or from a contribution from the carbon 2p orbital as predicted by Pople [214,216].

B. sp^2-Carbon Chemical Shifts

The carbon-13 resonance of the acyl carbon in $PtMe_2(COMe)A_2Cl$ is at 193.6 ppm downfield from TMS, which is typical of organic ketones and aldehydes [212] but is upfield from other metal acyls such as $\pi CpFe(CO)_2(COMe)$ 254.4 ppm [222] and $\pi CpFe(CO)_2(COPh)$ 255.5 ppm [223].

The bonding between carbenoid ligands ($:C\genfrac{}{}{0pt}{}{R}{R'}$) and transition metals poses an interesting problem to organometallic chemists [73,74]. It was initially considered that π-back donation from filled metal d orbitals into the electron deficient carbene carbon $2p_z$ orbital was necessary to stabilize these complexes. However the recent synthesis of metal-carbene complexes with the metal in a high oxidation state (e.g. Pt(IV) [24,99,117,224], Ir(III) [205,225], Rh(III) [226]) suggests that such π-back bonding is not entirely necessary [205] although for the very electron rich zero-valent metal complexes some $Md\pi \rightarrow Cp_z$ π-bonding is likely.

The low field resonance of the central carbene carbon in the :C(OMe)Me moiety (321 ppm downfield from $SiMe_4$) is consistent with considerable positive charge on the central carbon (c.f. $-C\genfrac{}{}{0pt}{}{O}{Me}$, 194 ppm in the acyl complex). This deshielding is comparable to that found for tertiary alkyl carbonium ion carbons [227] (320-334 ppm) and hence we have suggested that carbene complexes may be considered as metal stabilized carbonium ions [207]. Substitution of the methoxy group in the complex $[PtMeA_2(:C(OMe)Me)](PF_6)$ by $-NH_2$, NHMe, and NMe_2 causes substantial upfield shifts in the carbene carbon resonance (Table IX-2). This increase in shielding may well result from the stabilization achieved by π-donation from nitrogen into the carbene carbon $2p_z$ orbital which will decrease $\langle r^{-3}\rangle_{2p}$ and result in a smaller negative σ_p (equation 2) and an upfield shift.

Connor et al [228] have recently examined a series of carbene complexes of the type $(CO)_5Cr(:CXY)$, where X = -OR, -NRR' and Y is an organic group. Their results suggested that the carbene carbon is more strongly influenced by the heteroatom X than by the organic group Y, and that stabilization of the carbene by Y is a result of an inductive rather than a π-bonding effect.

It is interesting to compare the carbene-carbon chemical shifts for analogous carbenes in the complexes $Cr(CO)_5(:C(OMe)Me)$ [228] and $[PtMe(AsMe_3)(:C(OMe)Me)](PF_6)$ (362 and 321 ppm downfield from $SiMe_4$ respectively). The carbene in the chromium complex is deshielded relative to the platinum complex and this difference may indicate the presence of some π-back bonding for the electron rich zerovalent complex. Overlap of the filled metal d orbitals with the carbene carbon $2p_z$ orbital is likely to decrease ΔE and increase Q_{M-C}, both of which will result in a larger σ_p and a downfield shift for the chromium complex relative to the platinum(II) complex.

C. sp-Carbon Chemical Shifts

A very large number of organometallic complexes contain carbon monoxide as a ligand. Before the development of ^{13}C nmr techniques, vibrational spectroscopy and x-ray crystallography were the only tools at the disposal of chemists to examine the structure and bonding of these compounds. However, recently ^{13}C nuclear magnetic resonance spectroscopy has been shown to be a most informative spectroscopic technique for studying metal carbonyls [229,230].

A carbonyl ^{13}C nmr resonance is usually difficult to obtain not only because of the absence of an Overhauser effect but because of a long T_1 relaxation time associated with the carbonyl carbon. The presence of paramagnetic metal ions in solution substantially reduces

T_1 relaxation times [231-233], however a chemical shift (contact shift) usually results [231-236]. Gansow et al [237] have found that the addition of tris(acetylacetonato)chromium(III) greatly reduces T_1 relaxation times of carbonyl carbons in organometallic compounds without causing chemical shifts. Fortunately, we were able to observe the carbonyl-carbon resonance in our complexes without the use of Cr(acac)$_3$; however the intensity of the ^{195}Pt satellites could be greatly enhanced by the addition of several mg. of the Cr(III) compound.

The ^{13}C chemical shift of the carbonyl-carbon in trans-[PtMeA$_2$CO](PF$_6$) is at 178.7 ppm downfield from SiMe$_4$, and it is in fact slightly shielded relative to free carbon monoxide. The carbonyl carbon in trans-[PtClA$_2$(CO)](PF$_6$) absorbs much further upfield (159.3 ppm) than any previously reported metal carbonyl complex (most metal carbonyls absorb from 200-230 ppm downfield from TMS). In metal complexes where π-back bonding from the metal into the anti-bonding π^* orbitals is possible the carbonyl resonance occurs at low field, presumably as a result of an increase in Q_{M-C} and a decrease in ΔE (equation 2). However, for the electrophilic platinum carbonyl cations in this work (ν(CO) >2100 cm^{-1}), where there is likely to be little π-back bonding, the high field resonance may be a consequence mainly of σ-donation of the carbonyl pair of electrons into a Pt 'spd' hybrid orbital.

Gansow et al [238] have recently examined the ^{13}C nmr spectra for a variety of neutral iron complexes of the type πCpFe(CO)$_2$Z (where Z is an anionic ligand) and found that an upfield shift of the carbonyl carbon resonance occurred as the electron-withdrawing ability of Z increased. These results are consistent with ours (i.e. replacing Me^- by Cl^- causes an upfield shift).

Although ^{13}C nmr spectroscopy appears to be very sensitive to changes in electron density on carbonyl carbons in electrophilic metal carbonyl complexes, the reason for the large upfield shifts is not known at this time.

c) Experimental

The carbon-13 nuclear magnetic resonance spectra were obtained by Professor J.B. Stothers on a Varian XL-100-15 system operating in the Fourier transform mode. The spectra were obtained at 25.2 MHz using saturated CD_2Cl_2, $CDCl_3$, CD_3COCD_3 solutions (25-30% w.v.).

(i) Preparation of $[PtMeA_2(NCC_6H_4OMe)](PF_6)$

To a magnetically stirred solution of p-NCC_6H_4OMe (0.227 g., 1.71 mmoles) and trans-$PtMeA_2Cl$ (0.826 g., 1.71 mmoles) in 20 ml. of acetone was added $AgPF_6$ (0.431 g., 1.71 mmoles). The solution was stirred for 10 minutes and the silver chloride was removed by centrifugation to give a colourless solution. The solvent was removed on a rotary evaporator and the oil was taken up in 5 ml. of chloroform. Ether was added dropwise to give large colourless crystals which were filtered and washed with ether. Yield was 1.06 g., 1.45 mmoles. m.p. 178-181°C. Analyses, Calculated for $PtAs_2F_6NOPC_{15}H_{28}$: C, 24.74; H, 3.87. Found C, 25.00; H, 3.59. ^1H nmr in $CDCl_3$ with chemical shifts in ppm downfield from TMS: δ(Pt Me) 0.50; ^2J(Pt-H) = 79.5; δ(AsMe) 1.57; ^3J(Pt-H) = 22; δ(OMe) 3.90.

(ii) Preparation of [PtMeA_2(CNMe)](PF_6)

To a solution of trans-PtMeA_2Cl (0.540 g., 1.11 mmoles) in 20 ml. of acetone was added methylisocyanide (0.057 ml., 1.11 mmoles) followed by the addition of KPF_6 (0.205 g., 1.11 mmoles). The solution was stirred for 30 minutes and the solvent was removed by rotary evaporation. The complex was extracted from the KCl with dichloromethane and filtered. Ether was added and the flask was cooled to 0°C for four hours to give white needles. Yield was 0.611 g., 0.966 mmoles. Analyses, Calculated for $PtAs_2NPF_6C_9H_{24}$: C, 16.99; H, 3.80. Found: C, 17.19; H, 3.67. Nmr in $CDCl_3$: δ(PtMe) 0.36; ^2J(Pt-H) 62.8; δ(AsMe) 1.62; ^3J(Pt-H) 23.6; δ(NMe) 3.39; ^4J(Pt-H) 12.8.

(iii) Preparation of [PtMeA_2(CO)](PF_6)

trans-PtMeA_2Cl (0.517 g., 1.07 mmoles) was dissolved in 15 ml. of acetone and carbon monoxide was bubbled through the solution. AgPF_6 (0.269 g., 1.07 mmoles) in 10 ml. of acetone was added and the solution was stirred under a CO atmosphere for 10 minutes. The silver chloride was removed by centrifugation and the volume of the solution was reduced to about 5 ml. and cooled in ice. Diethylether was added slowly with shaking. White crystals slowly precipitated so the flask was cooled at 0°C for 12 hours. The crystals were filtered, washed with ether and dried in vacuo. Yield was 0.535 g., 0.860 mmoles. m.p. 132°C. Analyses, Calculated for $PtAs_2PF_6OC_8H_{21}$: C, 15.41; H, 3.39. Found: C, 15.59; H, 3.13. Nmr in $CDCl_3$: δ(PtMe) 0.65; ^2J(Pt-H) 62.4; δ(AsMe) 1.75; ^3J(Pt-H) 24.8.

(iv) Preparation of [$PtClA_2(CO)$](PF_6)

Carbon monoxide was bubbled through a solution of _cis_-$PtCl_2A_2$ (0.327 g., 0.646 mmoles) in 15 ml. of acetone and $AgPF_6$ (0.162 g., 0.646 mmoles) was added. The solution was stirred for 15 minutes under a CO atmosphere and the AgCl was then removed by centrifugation to give a clear solution. The solvent was removed and the oil was taken up in 5 ml. of dichloromethane. Ether was added slowly with shaking to give a white crystalline solid. Yield was 0.265 g., 0.397 mmoles. m.p. 144°C. _Analyses_, Calculated for $PtAs_2PF_6OC_7H_{18}$: C, 13.05; H, 2.82; Cl, 5.52. Found: C, 12.99; H, 2.96; Cl, 5.80.

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