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CHEMISTRY OF METAL HYDRIDES

XI*. PREPARATION AND SPECTROSCOPIC ASPECTS OF SOME HYDRIDO DIPHENYLMETHYL- AND DIMETHYLPHENYL-PHOSPHINE COMPLEXES OF PLATINUM(II)

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SUMMARY

Useful new hydrido diphenylmethyl- and dimethylphenyl-phosphine platinum(II) complexes have been synthesized by the reduction of *cis*-$PtX_2(PR_3)_2$ ($X=Cl$, Br, I and NCS; $PR_3=PPh_2Me$: $X=Cl$ and Br; $PR_3=PMe_2Ph$) or *trans*-$Pt(CN)_2(PPh_2Me)_2$ with sodium borohydride. Cationic hydrido platinum(II) complexes were also prepared via the interesting intermediate, *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+$, or from the reaction of *trans*-$PtH(CN)(PR_3)_2$ ($PR_3=PPh_2Me$ and PMe_2Ph) with a neutral strong ligand such as a phosphine or an alkyl isocyanide in the presence of $NaPF_6$. Proton NMR and infrared spectroscopic studies of these complexes provide information concerning:

(*a*), the existence of different crystalline modifications of *trans*-$PtH(CN)(PPh_2Me)_2$;

(*b*), the relative *trans* influence of both thiocyanato and isothiocyanato ligands;

(*c*), the magnetic anisotropic effect of the isoelectronic ligands, CN^-, CNR and CO;

(*d*), the facile phosphine exchange reactions of *trans*-$PtH(CN)(PPh_2Me)_2$ and *trans*-$Pt(CN)_2(PPh_2Me)_2$.

INTRODUCTION

There has been much interest in both the spectroscopic behavior[1-6] and chemical reactivity toward olefins[7-11] of hydrido complexes of platinum(II). Several methods[1,6,12,13], are available for the preparation of neutral hydrido complexes of the type, *trans*-$PtHX(PR_3)_2$ where $X=$halide, the reaction of *cis*-$PtX_2(PR_3)_2$ with hydrazine being most frequently successful. However, few examples have been reported of hydrido diphenylmethyl-, dimethylphenyl- or trimethyl-phosphine complexes of platinum(II); previously, only *trans*-$PtHX(PMe_2Ph)_2$ ($X=Cl$ and

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[*] For Part X see ref. 15.

TABLE 2

PROTON NMR[a] AND INFRARED DATA FOR SOME PLATINUM(II) HYDRIDES

Compound	*ν(Pt–H) (cm⁻¹)*		*Hydrido proton*			*Phosphine-methyl protons*		
	Nujol	*(In CH_2Cl_2)*	*τ(H)*	*J(Pt–H)*	*J(P–H)*	*τ(P–CH_3)*	*J(Pt–CH_3)*	*J(P–CH_3)*
PtHX(PPh$_2$Me)$_2$								
X = Cl	2220	(2219)	26.40 t	1260	14.5	7.83 t	32.0	7.0
Br	2208	(2210)	24.90 t	1302	13.0	7.73 t	32.0	6.5
I	2180	(2185)	22.09 t	1332	12.5	7.61 t	33.5	6.5
NO_3	2275	(2269)	32.90 t	1316	15.0	7.81 t	34.0	6.5
-NCS	2252	(2230)	27.02 br	1072		7.80 t	34.0	7.0
-SCN	2177	(2170)	22.18 t	1204	14.0	7.72 t	33.5	6.5
CN[b]	2059	(2059)	17.37 t	768	14.0	7.59 t	36.0	7.0
	2032							
[PtH(PPh$_2$Me)$_2$L]$^+$PF$_6^-$								
L[c] = A	2178		27.20 t	1080	14.5	7.87 t[d]	41.0	6.5
B	2188		26.53 t	1073	14.0	7.99 t[e]	39.5	6.5
p-$CH_3C_6H_4NC$	ca. 2100		16.10 t	872	13.5	7.54 t[f]	40.0	6.0
PPh_2Me	2082		15.39 x	840	{ 18.0	8.14 t	36.5	8.0
					167	8.45 d	21.5	8.0
Acetone	2275		33.60 t	1458	14.5	7.84 t	43.0	6.5
[PtH(PMe$_2$Ph)$_3$]$^+$PF$_6^-$	2079		17.10 x	880	{ 20.0	8.04 t	39.5	7.5
					170	8.84 d	20.5	9.0

[a] τ in ppm relative to internal TMS (τ = 10.00) and J in Hz, all obtained in CH_2Cl_2. d = doublet; t = triplet; x = doublet of triplets; br = broad singlet.

[b] NMR at −30°.

[c] A = 2-methylpyridine, B = 2,4,6-trimethylpyridine.

[d] τ(o-CH_3) 7.73, J(Pt-CH_3) 5.5 Hz.

[e] τ(o-CH_3) 7.58, J(Pt-CH_3) 6.5 Hz. τ(p-CH_3) 7.87.

[f] τ(p-CH_3) 7.71.

Br)[14] has been obtained in rather low yields by the hydrazine reduction method. Platinum complexes containing these phosphines should be especially useful in that they should have good solubilities and their proton NMR spectra may provide much stereochemical information. The change of phosphine may also cause slight but significant modifications in the chemical properties of the complexes. In extending our studies of metal hydrides[15] and other platinum(II) compounds[16,17], we now report the preparation of several neutral as well as cationic hydrido platinum(II) complexes of dimethylphenyl- and diphenylmethyl-phosphines. Some interesting aspects have been observed in their proton NMR and infrared spectra, and some of the new complexes have specific reactivities toward olefins which will be reported in a later paper.

RESULTS AND DISCUSSION

Several new hydrido platinum(II) complexes have been prepared as follows:

$$cis\text{-PtX}_2(\text{PR}_3)_2 + \text{NaBH}_4 \xrightarrow[\text{HCl}]{\text{MeOH}} trans\text{-PtHX}(\text{PR}_3)_2 \qquad (1)$$

$PR_3 = PPh_2Me; X = Cl$, Br, I and NCS
$PR_3 = PMe_2Ph; X = Cl$ and Br

This method is more convenient than the hydrazine reduction method[14] in that a higher yield of *trans*-$PtHX(PMe_2Ph)_2$ is obtained. Moreover, *trans*-$PtHX(PPh_2Me)_2$ can not be obtained by the hydrazine method but can be synthesized by the above reaction. *trans*-$PtH(CN)(PPh_2Me)_2$ was similarly prepared from *trans*-$Pt(CN)_2(PPh_2Me)_2$ and $NaBH_4$ although the dimethylphenylphosphine analogue could not be prepared this way. The latter was prepared by reduction with $NaBH_4$ of a 1/1 mixture of *trans*-$Pt(CN)_2(PMe_2Ph)_2$ and *cis*-$PtCl_2(PMe_2Ph)_2$ in methanol. *trans*-$PtH(CN)(PPh_2Me)_2$ was also prepared by the reaction of $Pt(PPh_2Me)_4$ with HCN in benzene solution, or from *trans*-$PtHCl(PPh_2Me)_2$ and sodium cyanide. It is of interest to note that slightly different infrared spectra* were observed according to the mode of crystallization of *trans*-$PtH(CN)(PPh_2Me)_2$ as shown in the Experimental Section.

A proton NMR spectrum in methylene chloride or toluene solution showed only signals assignable to the *trans* complex. The existence of different forms in the solid state is therefore probably not due to *cis*–*trans* isomerism but to different crystalline modifications of the *trans* form. A similar change in crystalline modification was reported for *trans*-$PtHCl(PPh_3)_2$[19,20].

The infrared spectrum of *trans*-$PtH(NCS)(PPh_2Me)_2$ in the solid state also exhibits two Pt–H and two C≡N stretching bands; however, this may be explained in terms of the existence of two isomers associated with the platinum–thiocyanate linkage because the infrared spectrum in methylene chloride solution also showed two bands attributable to the Pt–H stretching mode, and this is in agreement with

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* Assignments were made by comparison with analogous *trans*-$PtH(CN)(PEt_3)_2$[1,18] although examination of the infrared spectra of both *trans*-$PtH(CN)(PEt_3)_2$ and *trans*-$PtD(CN)(PEt_3)_2$ suggested[18] that the degree of vibrational coupling between ν(Pt–H) and ν(C≡N) is as large as 25 cm^{-1}.

TABLE 1

MELTING POINTS AND ANALYTICAL DATA FOR SOME PLATINUM(II) HYDRIDES

Compound	*M.p.* (°C)	*Analysis found (calcd.)* %		
		C	*H*	*Halogen or N*
$PtHX(PPh_2Me)_2$				
X=Cl	119–121 dec.	49.32	4.09	5.62
		(49.41)	(4.31)	(5.61)
Br	127–129 dec.	46.12	4.17	11.70
		(46.17)	(4.02)	(11.81)
I	121–123 dec.	43.08	3.77	17.65
		(43.17)	(3.76)	(17.54)
NO_3	103–105 dec.	47.27	4.13	2.00
		(47.49)	(3.99)	(2.13)
NCS	132–134	49.52	4.31	2.29
		(49.54)	(4.16)	(2.14)
CN	133–135 dec.	51.85	4.18	2.62
		(52.09)	(4.37)	(2.25)
$PtH(CN)(PMe_2Ph)_2$	116–118 dec.	41.16	4.52	2.91
		(40.97)	(4.65)	(2.81)
$[PtH(PPh_2Me)_2L]PF_6$				
L[a]=A	135 dec.	46.25	4.21	1.75
		(46.05)	(4.11)	(1.68)
B	155–157 dec.	47.40	4.47	1.64
		(47.34)	(4.44)	(1.62)
p-$CH_3C_6H_4NC$	[b]	47.59	4.05	1.72
		(47.56)	(3.98)	(1.63)
PPh_2Me	170–171	49.88	4.49	
		(49.74)	(4.28)	
$[PtH(PMe_2Ph)_2L]PF_6$				
L=p-$CH_3C_6H_4NC$	98–100 dec.	39.08	3.95	1.84
		(39.24)	(4.12)	(1.91)
PMe_2Ph	142–144	38.13	4.46	
		(38.15)	(4.54)	
$Pt(CN)_2(PPh_2Me)_2$	248–249	52.07	4.07	
		(51.93)	(4.05)	
$Pt(CN)_2(PMe_2Ph)_2$	198–199	41.34	4.24	
		(41.31)	(4.24)	

[a] A=2-methylpyridine, B=2,4,6-trimethylpyridine. [b] No definite melting point

the proton NMR spectrum (see below). No change in the solid state infrared spectrum was found after recrystallization from methylene chloride or benzene.

The proton NMR spectrum of *trans*-$PtH(NCS)(PPh_2Me)_2$ shows two sets of resonances for both hydrido and phosphine–methyl protons (the isothiocyanato isomer is higher in concentration) (Table 2). Although the hydrido resonances of the isothiocyanato isomer are so broad due to coupling with the nitrogen-14 quadrupole[2] that the stereochemistry cannot be deduced, the triplet (1/2/1) patterns[21] for the phosphine–methyl protons clearly show this isomer to have the *trans* configuration.

Even though the existence of two isomers of *trans*-$PtH(NCS)(PEt_3)_2$ and of *trans*-$PtH(NCS)(AsEt_3)_2$ was reported on the basis of the proton NMR spectra[2], there was some ambiguity about the assignment of the Pt–H stretching bands. Chatt and Shaw reported[1] that ν(Pt–H) for *trans*-$PtH(-NCS)(PEt_3)_2$ occurred at 2195 cm^{-1} in the solid state and at 2112 cm^{-1} in hexane solution, and no infrared evidence was found for the existence of the thiocyanato isomer in solution or in the solid state. However, values of 2210 cm^{-1} and 2160 cm^{-1} were reported for *trans*-$PtH(-NCS)(PEt_3)_2$ and *trans*-$PtH(-SCN)(PEt_3)_2$ in chloroform solution respectively[22]. We now assign, in accordance with this latter report, the bands at 2252 cm^{-1} (Nujol) and 2230 cm^{-1} (methylene chloride) to ν(Pt–H) of the isothiocyanato isomer, and the bands at 2177 cm^{-1} (Nujol) and 2170 cm^{-1} (methylene chloride) to ν(Pt–H) of the thiocyanato isomer of *trans*-$PtH(NCS)(PPh_2Me)_2$. This assignment is also strongly supported by the relationship of ν(Pt–H) with τ(Pt–H) which is discussed below. The strong bands at 2080 cm^{-1} and 2113 cm^{-1} in the solid state can be assigned to the ν(C≡N) modes for Pt–NCS and Pt–SCN isomers, respectively[23], and one of the three bands at 824 cm^{-1}, 843 cm^{-1} and 853 cm^{-1} to the ν(C–S) mode of the former isomer[23]. This absorption for the Pt–SCN isomer may be overlapped with strong bands at 690 cm^{-1} or 735 cm^{-1} due to phosphine–ligand vibrations.

It has been previously reported[2,4,6], that differences in both ν(Pt–H) and τ(Pt–H), but not in J(Pt–H), for *trans*-$PtHX(PR_3)_2$ can be related to the relative *trans* influence of the group X. Green *et al.* suggested[4] that, in a closely related series of complexes such as *trans*-$PtH(OOCR)(PEt_3)_2$, a linear correlation between ν(Pt–H) and τ(Pt–H) can be related to a change in the Pt–H bond distance, while they could not find any correlation between ν(Pt–H) and τ(Pt–H)[1] for *trans*-$PtHX(PEt_3)_2$ where X changes from CN through a series of ligands to NO_3. Nevertheless, if ν(Pt–H) is plotted against τ(Pt–H) for *trans*-$PtHX(PPh_2Me)_2$ (methylene chloride solutions), and also for *trans*-$PtHX(PPh_3)_2$ [$CDCl_3$ (NMR) or in the solid state (IR)][6], a good correlation is seen except for X=CN and NO_3 (Fig. 1). Such a com-

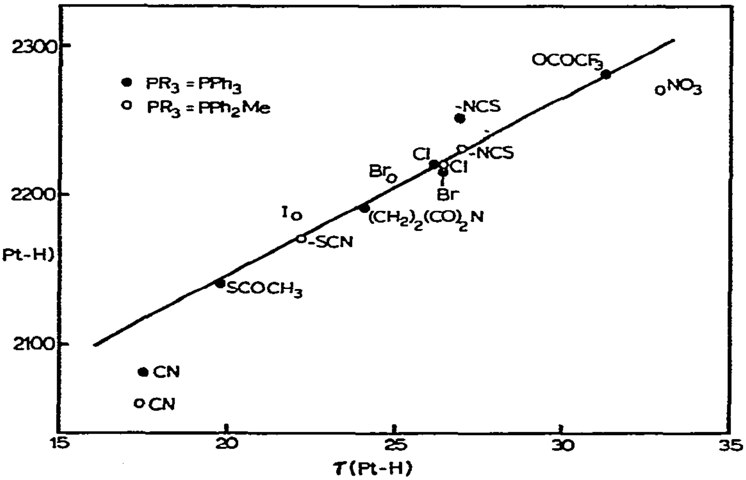

Fig. 1. Correlation between ν(Pt–H) (in cm^{-1}) and τ(Pt–H) (in ppm) for *trans*-$PtHX(PR_3)_2$.

parison of the diphenylmethylphosphine and triphenylphosphine complexes is not unreasonable since the change of phosphine appears to have little effect on the values of ν(Pt–H) and τ(Pt–H). Moreover, solvent effects on the NMR spectra do not seem very important, and ν(Pt–H) values in CH_2Cl_2 solutions and Nujol mulls are almost identical (Table 2). Although it may be argued that the linearity shown here is accidental, particularly since the number of the complexes studied is limited, some interesting features are apparent from this Figure. We assume that the changes in these values are still dominated mainly by changes in the Pt–H bond distance, although there is no obvious explanation for those points which deviate from the linear relationship. Notable are the positions of both the isothiocyanato and thiocyanato isomers. A previous report[6] described both ν(Pt–H) and τ(Pt–H) of *trans*-$PtH(NCS)(PPh_3)_2$ as having anomalously high values in view of the known position of NCS in the *trans effect* series. However, we suggest that the values shown in the Fig. are not unexpected because they reflect the *trans influence* series, which is defined as the ability of the ligand A to weaken the bond *trans* to A in the equilibrium state, while the *trans* effect includes the thermodynamic contribution from the activated complex[24,25]. The two series are therefore, not necessarily parallel. Thus, the *trans* influence of –SCN is reasonably close to that of another *S*-bonded ligand, $SCOCH_3$ or a soft base, I, and that of –NCS to that of Cl.

One interpretation for the deviation of cyanide may be that vibrational coupling between ν(Pt–H) and ν(C≡N) may lead to a lower frequency of ν(Pt–H). π-Bonding[22] or a very large ΔE term in the equation describing the paramagnetic shielding coefficient due to Pt-5*d* electrons for a hydrido resonance[26] seems unlikely to account for this anomaly for X=CN since these effects would produce a less shielded hydrido resonance. On the other hand, a small ΔE value for $X=NO_3$ may be partly responsible for the slightly larger value of τ(Pt–H) observed for this complex than would be expected from the linear relationship. The strong diamagnetic anisotropic effect of the cyanide group[27] may cause some shift of the resonance of the hydridic hydrogen to high field since that hydrogen nucleus lies on the C≡N bond axis which is a more shielded region. The magnitude of this kind of anisotropy is determined by the $1/R^3$ term (R = distance between the proton under consideration and the center of C≡N group) as well as the $[3\cos^2\alpha-1]$ term (α = angle between the C≡N axis and the line joining the proton and the center of the C≡N group). Although estimation of the exact amount of this anisotropic contribution to the chemical shift of a hydrido proton seems difficult because of the lack of molecular parameters, its value can not be large enough to explain completely the deviation observed for the cyanide complex, particularly when the value of 45 Hz (obtained at 40 MHz), calculated for the anisotropic contribution from a C≡N group to an α-proton of acrylonitrile[27], is taken into account.

It is also interesting to compare the chemical shifts of the phosphine–methyl protons. As shown in Table 2, $\tau(P\text{–}CH_3)$ of *trans*-$PtH(CN)(PPh_2Me)_2$ is considerably smaller than those of the other complexes, except for X=I. This is probably due to the magnetic anisotropy of the C≡N or Pt–I bonds[28]. Although there must be some restriction to the rotation of the phosphine ligands, some of the possible molecular configurations may be such that the methyl protons are now in a less shielded region due to the anisotropy of the CN group. A similar effect by the Pt–I bond is thought[28] to produce the low field chemical shift of the phosphine–methyl protons in *trans*-

$PtI_2(PMe_3)_2$. It is of interest to note that τ(P–CH_3) for *trans*-[$PtH(PPh_2Me)_2$-(p-$CH_3C_6H_4NC$)]$^+PF_6^-$ (Table 2) is very close to that of *trans*-$PtH(CN)(PPh_2Me)_2$, and also that τ(P–CH_3) values for seven compounds of the type *trans*-[PtMe-$(PMe_2Ph)_2(RNC)]^+$ (τ 8.10–7.96)[29] are significantly smaller than the values for ten complexes of the type *trans*-$[PtMe(PMe_2Ph)_2L]^+$ (τ 8.66–8.16)[30] except for L=CO (τ 7.92). These facts are probably not due to electronegativity differences of ligands, but rather to the anisotropy of C≡N groups, because both the cyanide and alkylisocyanides are rather better σ-donors than other ligands and the alkylisocyanides are not good π-acceptors[29]. This is also in agreement with the fact that CN^-, CNR and CO ligands are all isoelectronic so that they show the same kind of anisotropic contribution.

Proton NMR spectra of analytically pure samples of *trans*-$PtH(CN)(PPh_2Me)_2$ and *trans*-$Pt(CN)_2(PPh_2Me)_2$ showed at 31° only a broad singlet due to the phosphine–methyl protons, and in the former complex the hydrido resonance appeared as a 1/4/1 triplet (^{195}Pt satellites) with no indication of ^{31}P–^{1}H coupling. At –30°, the spectrum appeared with the phosphine–methyl protons showing a 1/2/1 triplet accompanied by ^{195}Pt satellites due to mutually *trans* phosphine methyls[21] and hydrido resonances with ^{31}P–^{1}H coupling. This can be interpreted in terms of an intermolecular phosphine exchange, the rate of which is fast enough to show a broad singlet for the phosphine–methyl protons in the presence of strong phosphorus–phosphorus virtual coupling[31] and no ^{31}P–^{1}H coupling in the hydrido resonances at room temperature. Mixing *trans*-$Pt(CN)_2(PPh_2Me)_2$ and *trans*-$Pt(CN)_2(PMe_2Ph)_2$ resulted in the immediate formation of *trans*-$Pt(CN)_2(PPh_2Me)(PMe_2Ph)$ which is in equilibrium with the two reactants. This is confirmed by the low temperature NMR spectrum (Table 3), which also indicates intermolecular phosphine exchange.

TABLE 3

PROTON NMR DATA FOR SOME *trans*-$Pt(CN)_2(PR_3)_2$[a]

Compound	*τ(CH₃)*	*J(Pt–CH₃)*	*J(P–CH₃)*
$Pt(CN)_2(PPh_2Me)_2$[b]	7.59 t	35.9	6.8
$Pt(CN)_2(PMe_2Ph)_2$	7.93 t	32.0	7.5
$Pt(CN)_2(PPh_2Me)(PMe_2Ph)$[b]	7.67 x[c]	Not resolved	Not resolved
	7.83 x[d]	34.0	Not resolved

[a] τ in ppm relative to internal TMS (τ=10.00), and J in Hz obtained in CH_2Cl_2. t=triplet, x=complex. [b] At –30°. [c] From PPh_2Me. [d] From PMe_2Ph.

Similar mixed phosphine–arsine complexes of Pd^{II} and Pt^{II} were reported to be formed only after a day[28]. One possible explanation of such a fast phosphine exchange is that the strong coordinating ability of the CN ligands weakens the Pt–phosphine bonds which then are very susceptible to replacement by either phosphine ligands attached to other molecules or trace amounts of free phosphines which could not have been removed by ordinary recrystallization procedures. However, the latter possibility seems unlikely because no significant change was observed in the spectrum of *trans*-$Pt(CN)_2(PPh_2Me)_2$ at room temperature when 1 mole percent of a chlorine-bridged dimer, $[Pt_2Cl_2(PPh_3)_4]^{2+}$, which reacts rapidly with phosphine, was added to this solution. A similar phosphine exchange has also been found in several cationic alkylisocyanide complexes, *trans*-$[PtMe(PMe_2Ph)_2(CNR)]^+$[29].

Cationic hydrido complexes

The chloride in *trans*-$PtHCl(PEt_3)_2$ is labile because of the strong *trans* effect of the hydrido ligand and a series of cationic complexes of the type, *trans*-$[PtH(PEt_3)_2L]^+$ have previously been prepared by the reaction of the chloride with a neutral ligand in the presence of $NaClO_4$[3]. Even the cyanide in *trans*-$PtH(CN)(PEt_3)_2$ can be replaced in this way with phosphines[32], and we also have observed that the cyanide in *trans*-$PtH(CN)(PR_3)_2$ ($PR_3 = PPh_2Me$ and PMe_2Ph) can be substituted by an alkylisocyanide or a phosphine in the presence of $NaPF_6$ in acetone solution, but not with much weaker ligands such as pyridine.

$$\textit{trans}\text{-PtH(CN)(PR}_3)_2 + L + NaPF_6 \xrightarrow{\text{acetone}} \textit{trans}\text{-[PtH(PR}_3)_2L]^+PF_6^- + NaCN$$

$PR_3 = PPh_2Me$; $L = PPh_2Me$ and $p\text{-}CH_3C_6H_4NC$
$PR_3 = PMe_2Ph$; $L = PMe_2Ph$ and $p\text{-}CH_3C_6H_4NC$

These direct displacement reactions of chloride or cyanide are limited to particular ligands, so we have used a more general method to prepare some cationic hydrido complexes via *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+$ *in situ* which is stable in solution at room temperature for a couple of hours.

$$\textit{trans}\text{-PtHBr(PPh}_2\text{Me)}_2 + AgPF_6 \xrightarrow{\text{Acetone}/CH_2Cl_2}$$

$$\textit{trans}\text{-[PtH(PPh}_2\text{Me)}_2\text{(Acetone)]}^+PF_6^- + AgBr \xrightarrow{L}$$

$$\textit{trans}\text{-[PtH(PPh}_2\text{Me)}_2L]^+PF_6^- \qquad (3)$$

L = 2-methylpyridine, 2,4,6-trimethylpyridine, PPh_2Me and $p\text{-}CH_3C_6H_4NC$

The acetone complex is particularly useful in that acetone can be easily replaced by olefins to give at first hydrido olefin complexes of platinum(II) and then olefin insertion products[33]. Although the solid acetone complex can not be isolated pure, the infrared spectrum of the crude product of *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+PF_6^-$ showed ν(C=O) for coordinated acetone at 1660 cm^{-1} and ν(Pt–H) at 2275 cm^{-1}. The proton NMR spectrum in methylene chloride solution showed the highest chemical shift and the largest ^{195}Pt–^{1}H coupling constant for a platinum(II) hydrido proton resonance (Table 2). This clearly indicates the very weak *trans* influence of an acetone ligand, in agreement with the above ready replacement reactions. Similar properties were also observed for *trans*-$[PtMe(PMe_2Ph)_2(Acetone)]^+$[34]. Attempts to isolate *trans*-$[PtH(PPh_2Me)_2(CO)]^+$ were unsuccessful and decomposition occurred readily in solution to give a platinum(0) cluster compound, $Pt_3(CO)_3(PPh_2Me)_4$[35].

In addition to the comparison of relative *trans* influences of the ligand L in *trans*-$[PtH(PR_3)_2L]^+$ by comparisons of $^1J(^{195}Pt\text{–}^1H)$, other information can be obtained from the values of $^3J(^{195}Pt\text{–P–C–}^1H)$ for the phosphine–methyl protons *trans* to X in $[PtX(PMe_2Ph)_3]^+$ (X = H, Me or Cl). This value for X = H (20.5 Hz) is very close to that for X = Me (18.5 Hz)[30] but much smaller than that for X = Cl (40 Hz)[30], which suggests that $^3J(^{195}Pt\text{–P–C–}^1H)$ is also dependent on the relative *trans* influence of the group X.

EXPERIMENTAL

cis-$PtCl_2(PR_3)_2$ ($PR_3 = PPh_2Me$ and PMe_2Ph) were prepared by the reported method[36]. *cis*-$PtX_2(PR_3)_2$ (X = Br, I and NCS) were prepared by the reaction of the corresponding chloride and NaX in methanol, and the products were used *in situ* for the reaction with sodium borohydride. Tetrakis(diphenylmethylphosphine)-platinum(0) was prepared from K_2PtCl_4 and excess of the phosphine in ethanol to which potassium hydroxide was added[37]. Melting points were uncorrected. All the products prepared in this study are white or pale-yellow solids. Microanalyses were performed by Dr. A. B. Gygli, Toronto (Table 1). Infrared spectra were obtained using Beckman IR 10 and 7 spectrophotometers, the samples being either in Nujol mulls or in methylene chloride solutions. All spectra were calibrated against the spectrum of polystyrene film. Proton NMR spectra were recorded in methylene chloride solutions on a Varian HA-100 spectrometer using TMS as internal standard.

Preparation of trans-$Pt(CN)_2(PPh_2Me)_2$

To an acetone solution (30 ml) of *cis*-$PtCl_2(PPh_2Me)_2$ (0.67 g) was added 0.27 g of freshly prepared silver cyanide (from $AgNO_3$ and NaCN in aqueous solution). The mixture was kept at 50° for 5 h with stirring. After filtering off the precipitate of silver chloride, the solvent was removed under reduced pressure. The solid was recystallized from methylene chloride/n-pentane twice to give fine crystals (0.45 g; 70%).

trans-$Pt(CN)_2(PMe_2Ph)_2$ was prepared in the same manner from *cis*-$PtCl_2(PMe_2Ph)_2$ and AgCN (78% yield).

Preparation of trans-$PtHCl(PPh_2Me)_2$

To a suspension of *cis*-$PtCl_2(PPh_2Me)_2$ (1.0 g) in methanol (15 ml) was added dropwise a methanol solution of sodium borohydride (concentration 0.01 g/ml) with stirring under nitrogen until a pale-yellow clear solution was obtained. Dilute methanolic HCl solution (1 ml of 12 *N* HCl in 10 ml MeOH) was added under nitrogen until the solution became slightly acidic. The solvent was then removed under reduced pressure and the residual mixture was extracted with benzene (3 × 10 ml). The benzene extract was evaporated to a volume of 5 ml, and n-pentane was added to give white crystals of *trans*-$PtHCl(PPh_2Me)_2$ (0.76 g, 80%).

trans-$PtHBr(PPh_2Me)_2$ (78% yield), *trans*-$PtHI(PPh_2Me)_2$ (92%) and *trans*-$PtH(NCS)(PPh_2Me)_2$ (70%) were similarly prepared from *cis*-$PtX_2(PPh_2Me)_2$ (X = Br, I and NCS), respectively. *trans*-$PtH(NCS)(PPh_2Me)_2$ was also prepared from *trans*-$PtHCl(PPh_2Me)_2$ and NaNCS in acetone (56%) in a manner similar to that for *trans*-$PtH(NCS)(PEt_3)_2$.

trans-$PtHCl(PMe_2Ph)_2$ (90%; m.p. 101–103°, lit.[14] 102–104°, ν(Pt–H) 2195 cm^{-1} (Nujol)) and *trans*-$PtHBr(PMe_2Ph)_2$ (75%; m.p. 110–112°, lit.[14] 112°, ν(Pt–H) 2184 cm^{-1} (Nujol)) were prepared using the same method as that described for *trans*-$PtHCl(PPh_2Me)_2$ above.

Preparation of trans-$PtH(CN)(PPh_2Me)_2$

(*i*). To a stirred suspension of 0.24 g of *trans*-$Pt(CN)_2(PPh_2Me)_2$ in 10 ml of methanol was added slowly 0.028 g of sodium borohydride in 2 ml of methanol under nitrogen. The solution became pale-yellow and clear, and the solvent was evaporated under vacuum. The residual mixture was extracted with benzene (3 × 3 ml). The benzene extract was then evaporated to a volume of 3 ml, and n-pentane was added to give 0.1 g of white fluffy crystals (42%). This product showed m.p. 133–138° and ν(Pt–H) 2032 cm^{-1}, ν(C≡N) 2131 and δ(Pt–H) 803 cm^{-1}. This product was further recrystallized from methylene chloride/n-pentane to give a fine crystalline material which had m.p. 133–135°, ν(Pt–H) 2059, ν(C≡N) 2138 and δ(Pt–H) 812 cm^{-1}. In methylene chloride solution, ν(Pt–H) 2059 and ν(C≡N) 2140 cm^{-1}.

(*ii*). Through a benzene solution (5 ml) of 0.17 g of tetrakis(diphenylmethylphosphine)platinum(0) was passed HCN gas (generated by the reaction of aqueous NaCN and conc. H_2SO_4) until the initial color of the solution (green) changed to pale-yellow. n-Pentane (30 ml) was added to this solution to give white, powder *trans*-$PtH(CN)(PPh_2Me)_2$ (0.05 g, 47%). A similar change in the infrared spectra according to the solvent used for recrystallization was observed.

trans-$PtH(CN)(PMe_2Ph)_2$ was prepared by the reduction of a 1/1 mixture of *trans*-$Pt(CN)_2(PMe_2Ph)_2$ and *cis*-$PtCl_2(PMe_2Ph)_2$ in methanol with sodium borohydride, using the same procedure as that described for the diphenylmethylphosphine analogue (63%). The infrared spectrum in Nujol mull showed ν(Pt–H) 2037, ν(C≡N) 2130 and δ(Pt–H) 805 cm^{-1}. The proton NMR spectrum in methylene chloride solution showed τ(Pt–H) 17.51 (triplet), J(Pt–H) 812 Hz and J(P–H) 17.0 Hz for a hydrido proton, and $\tau(P\text{–}CH_3)$ 7.99 (triplet), $J(Pt\text{–}CH_3)$ 36.0 Hz and $J(P\text{–}CH_3)$ 7.0 Hz for the phosphine–methyl protons.

Preparation of trans-$PtH(NO_3)(PPh_2Me)_2$

To a stirred solution of 0.34 g of *trans*-$PtHI(PPh_2Me)_2$ in acetone (8 ml) was added dropwise 0.084 g of $AgNO_3$ in 1 ml H_2O/2 ml CH_3OH mixture. Silver iodide was filtered off and the solvent was evaporated under reduced pressure. The residual solid was recrystallized from benzene/n-pentane to give *trans*-$PtH(NO_3)(PPh_2Me)_2$ (0.184 g, 60%).

Reaction of trans-$PtH(CN)(PR_3)_2$ with a phosphine or alkylisocyanide

In a typical reaction, to an acetone solution (10 ml) of *trans*-$PtH(CN)(PPh_2Me)_2$ (0.18 g) and $NaPF_6$ (0.06 g) was added 0.034 g of *p*-tolylisocyanide. The solution was evaporated under reduced pressure, and the residual mixture was extracted with methylene chloride (10 ml). The methylene chloride extract was passed through a Florisil-column and n-pentane was added to methylene chloride solution to give 0.12 g of pale-yellow *trans*-$[PtH(PPh_2Me)_2(p\text{-}CH_3C_6H_4NC)]^+PF_6^-$. Similarly, $[PtH(PPh_2Me)_3]^+PF_6^-$ (66%), *trans*-$[PtH(PMe_2Ph)_2(p\text{-}CH_3C_6H_4NC)]^+PF_6^-$ (56%) and $[PtH(PMe_2Ph)_3]^+PF_6^-$ (66%) were prepared.

Preparation of trans-$[PtH(PPh_2Me)_2L]^+PF_6^-$ via trans-$[PtH(PPh_2Me)_2(Acetone)]^+PF_6^-$

In a typical preparation, to a methylene chloride solution (1 ml) of *trans*-$PtHBr(PPh_2Me)_2$ (0.135 g) was added with stirring 0.05 g of $AgPF_6$ in 0.2 ml of acetone. Silver bromide was filtered off to give a pale-yellow clear solution of *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+PF_6^-$. 0.24 g of 2,4,6-trimethylpyridine (B) was added to this solution, and the solvent evaporated. The residual solid was recrystallized from methylene chloride/n-pentane to give 0.10 g of *trans*-$[PtH(PPh_2Me)_2B]^+PF_6^-$ (58%). When n-pentane was added to a methylene chloride solution of *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+PF_6^-$, a yellowish-green solid was obtained which showed ν(C=O) at 1660 cm^{-1} and a rather weak band for ν(Pt–H) at 2275 cm^{-1}. Other cationic hydrido complexes were similarly prepared. However, if carbon monoxide was bubbled through a methylene chloride solution of *trans*-$[PtH(PPh_2Me)_2(Acetone)]^+PF_6^-$, the color changed to reddish-brown, and the infrared spectrum of the red product which was obtained on addition of n-pentane showed bands at 2170 and 2070 cm^{-1}, which probably are due to *trans*-$[PtH(PPh_2Me)_2(CO)]^+PF_6^-$, and bands at 1840 cm^{-1}, 1795 cm^{-1} and 1770 cm^{-1} which are consistent with those reported for $Pt_3(CO)_3(PPh_2Me)_4$[35].

REFERENCES

1 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1962) 5075.
2 J. Powell and B. L. Shaw, *J. Chem. Soc.*, (1965) 3879.
3 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, (1968) 3074.
4 P. W. Atkins, J. C. Green and M. L. H. Green, *J. Chem. Soc. A*, (1968) 2275.
5 R. R. Dean and J. C. Green, *J. Chem. Soc. A*, (1968) 3047.
6 D. M. Roundhill, P. B. Tripathy and B. W. Renoe, *Inorg. Chem.*, 10 (1971) 727.
7 H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 89 (1967) 529.
8 H. C. Clark, K. R. Dixon and W. J. Jacobs, *J. Amer. Chem. Soc.*, 90 (1968) 2259.
9 J. Chatt, R. S. Coffey, A. Gough and D. T. Thompson, *J. Chem. Soc. A*, (1968) 190.
10 P. R. Brookes and R. S. Nyholm, *Chem. Commun.*, (1970) 169.
11 A. J. Deeming, B. F. G. Johnson and J. Lewis, *Chem. Commun.*, (1970) 598.
12 H. C. Clark, K. R. Dixon and W. J. Jacobs, *J. Amer. Chem. Soc.*, 91 (1969) 1346.
13 R. Ugo, *Coord. Chem. Rev.*, 3 (1968) 319.
14 J. Chatt, C. Eaborn, S. D. Ibekwe and P. N. Kapoor, *J. Chem. Soc. A*, (1970) 1343.
15 W. J. Cherwinski and H. C. Clark, *Inorg. Chem.*, 10 (1971) 2263.
16 M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 10 (1971) 1711.
17 H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 10 (1971) 18 and references therein.
18 P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 5446.
19 A. F. Clemmit and F. Glockling, *J. Chem. Soc. A*, (1969) 2163.
20 I. Collamati, A. Furlani and G. Attioli, *J. Chem. Soc. A*, (1970) 1694.
21 R. K. Harris, *Can. J. Chem.*, 42 (1964) 2275.
22 G. Socrates, *J. Inorg. Nucl. Chem.*, 31 (1969) 1667.
23 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed., Wiley, (1970), p. 187.
24 A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. A*, (1966) 1707.
25 S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 90 (1968) 6669.
26 A. D. Buckingham and D. J. Stephens, *J. Chem. Soc.*, (1964) 4583.
27 G. S. Reddy, J. G. Goldstein and L. Mandell, *J. Amer. Chem. Soc.*, 83 (1961) 1300.
28 D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest and J. G. Smith, *J. Chem. Soc. A*, (1969) 2134.
29 H. C. Clark and L. E. Manzer, *Inorg. Chem.*, in press.
30 H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 9 (1970) 1226.
31 J. P. Fackler, Jr., *Inorg. Chem.*, 9 (1970) 2625.
32 M. Giustiniani, G. Dolcetti and U. Belluco, *J. Chem. Soc. A*, (1969) 2047.
33 H. C. Clark and H. Kurosawa, *Chem. Commun.*, (1971) 957.
34 M. H. Chisholm, H. C. Clark and L. E. Manzer, *Inorg. Chem.*, in press.
35 J. Chatt and P. Chini, *J. Chem. Soc. A*, (1970) 1538.
36 S. O. Grim, R. L. Keiter and W. M. Farlane, *Inorg. Chem.*, 6 (1967) 1133.
37 P. Chini and G. Longoni, *J. Chem. Soc. A*, (1970) 1542.