Some Four- and Five-co-ordinate Cations of Platinum(II) containing Alkylphosphine and Hydride Ligands

By **E. A. V. Ebsworth,* Joyce M. Edward, Francis J. S. Reed,** and **John D. Whitelock,** Department of Chemistry, West Mains Road, Edinburgh EH9 3JJ

Hydrogen-1 and ^{31}P n.m.r. spectroscopy have been used to study the equilibrium of *trans*-[PtH(I)(PEt$_3$)$_2$] with an additional phosphine L [mol ratio 1 : 1, L = PMe$_{3-n}$H$_n$ (n = 0—3) or PEt$_3$] in CD$_2$Cl$_2$ solution. The spectra are temperature dependent and the cation [PtH(PEt$_3$)$_2$L]$^+$ is observed at −90 °C. These cations (except L = PH$_3$) have been isolated as [BPh$_4$]$^-$ salts from reactions in methanol. A mixture of *trans*-[PtH(I)(PEt$_3$)$_2$] and PMeH$_2$ (mol ratio 1 : 2) gives completely reversible temperature-dependent n.m.r. spectra from which the formation of [PtH(PMeH$_2$)$_2$(PEt$_3$)$_2$]$^+$ is inferred. Reaction of [PtH(PEt$_3$)$_3$]$^+$ with PMeH$_2$, PMe$_2$H, or PMe$_3$ at −90 °C in CD$_2$Cl$_2$ gives well resolved spectra of [PtH(PEt$_3$)L$_3$]$^+$. The spectra show the five-co-ordinate cations to have a trigonal-bipyramidal structure with the PEt$_3$ groups in equatorial positions.

WE have been interested in the reactions of silylphosphines with platinum substrates [1,2] and in order to provide a firm basis for our interpretation of n.m.r. data we have now completed a study of the reactions of the simple methylphosphines, PMe$_{3-n}$H$_n$ (n = 0—3) with *trans*-[PtH(X)(PEt$_3$)$_2$] (X = Cl or I) and [PtH(PEt$_3$)$_3$]-[BPh$_4$].

It is well known that *trans*-[PtH(X)(PEt$_3$)$_2$] will react with neutral donor ligands to set up equilibrium (i).

$$\textit{trans}\text{-[PtH(X)(PEt}_3)_2] + \text{L} \longrightarrow [\text{PtH(L)(PEt}_3)_2]\text{X} \quad \text{(i)}$$

In many cases the cationic complex has been isolated by addition of a large anion.[3-5] The n.m.r. spectra of these isolated cations have been extensively reported and second-order effects in both ^{1}H and ^{31}P spectra have been discussed.[6,7] However, there is little information on either the rate of phosphine exchange or the position of equilibrium in (i), apart from a detailed and definitive study by Meakin *et al.*[8] of the reaction of [PtH(PEt$_3$)$_3$]$^+$ with PEt$_3$. These workers observed the ^{31}P n.m.r. spectrum of [PtH(PEt$_3$)$_4$]$^+$ at −131 °C. We have investigated the related systems (i) in which L = PH$_3$, PMeH$_2$, PMe$_2$H, or PMe$_3$; this series is particularly suitable for study of ^{31}P n.m.r. spectroscopy since the ^{31}P chemical shift by P′ in L either free or co-ordinated is sufficiently different from that of PEt$_3$ to give essentially first-order spectra, while there is a steady and consistent change in basicity across the series. We have also obtained evidence for five-co-ordinate species in the reactions of *trans*-[PtH(I)(PEt$_3$)$_2$] with excess of PMeH$_2$ and in the reaction of [PtH(PEt$_3$)$_3$]$^+$ with the three methylphosphines.

TABLE 1

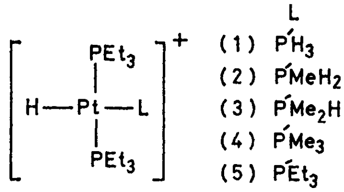
Phosphorus-31 n.m.r. parameters for the cations [PtH(PEt$_3$)$_2$L]$^+$ in CD$_2$Cl$_2$ at −80 °C

Complex	δ(P) [a]	^1J(PtP)/Hz	δ(free P′) [b]	δ(P′)	^1J(PtP′)/Hz	^2J(PP′)/Hz
(1)	16.9	2 377	−239.7	−138.0	1 610	24
(2)	16.0	2 379	−165.5	−89.4	1 700	24
(3)	17.2	2 421	−90.0	−50.0	1 830	24
(4)	16.2	2 495	−62.0	−20.6	1 915	22
(5)	15.2	2 510	−20.4	+2.3	2 000	20

[a] In p.p.m., positive to high frequency of 85% H$_3$PO$_4$. [b] P′ = Phosphine L *trans* to hydride; in CD$_2$Cl$_2$–SiMe$_4$ at 25 °C.

RESULTS AND DISCUSSION

Four-co-ordinate Cations.—The reactions with methylphosphines described by equilibrium (i) were carried out originally in n.m.r. tubes. The added phosphine was condensed on to a frozen solution of *trans*-[PtH(I)(PEt$_3$)$_2$] in CD$_2$Cl$_2$ and the tube sealed and stored at −196 °C. The tubes were then transferred cold to the spectrometer and ^{31}P n.m.r. spectra were obtained immediately at −80 °C. In each case the initial spectrum showed that only the cationic complexes (1)—(5) were present. The spectra were sharp at −80 °C except for (1) which had to be cooled to −90 °C to resolve ^2J(PP′). The n.m.r. data are given in Table 1.



$$\left[\begin{array}{c} \text{PEt}_3 \\ | \\ \text{H—Pt—L} \\ | \\ \text{PEt}_3 \end{array}\right]^+$$

As complex (1) was warmed above −90 °C the couplings ^2J(PP′) and then ^1J(PtP′) were lost and the resonances broadened, although there was little change in chemical shifts. At >−30 °C decomposition occurred and an insoluble yellow precipitate was formed. This type of decomposition was only observed with L = PH$_3$

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[8] P. Meakin, A. D. English, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **98**, 414, 422.

and could be caused by elimination of H_2 or HI and the formation of insoluble bridged complexes.[2] The dependence of the ^{31}P n.m.r. spectrum of (2) on temperature was completely reversible between −80 °C and room temperature. The couplings $^{2}J(PP')$ and $^{1}J(PtP')$ were lost on warming to −50 °C and at room temperature the resonances were very broad, but there was no significant change in the chemical shift of either phosphine over this temperature range. With (3) the couplings $^{2}J(PP')$ and $^{1}J(PtP')$ were lost by −20 °C but the spectra were not completely reversible with temperature and it appeared that some exchange of PEt_3 and PMe_2H was occurring. For both (4) and (5) only the $^{2}J(PP')$ coupling was not resolved in the room-temperature spectrum and, although the resonances were broad, $^{1}J(PtP')$ was still observed. As with L = PMe_2H, it appeared that the PMe_3 complex disproportionated and the temperature dependence was not reversible.

TABLE 2

Hydrogen-1 n.m.r. parameters for the cations $[PtH(PEt_3)_2L]^+$ in CD_2Cl_2 at −70 °C

Complex	$\delta(H_A)$ [a]	$^{1}J(PtH_A)$ [b]/Hz	$^{2}J(PH_A)$/Hz	$^{2}J(P'H_A)$/Hz	$\delta(H_B)$	$^{1}J(P'H_B)$	$\delta(H_C)$	$\delta(Pt)$ [c]
(1)	−4.30	+1 073	−14	n.o. [d]	4.69	354		−378
(2)	−4.60	+948	−14	+172	4.84	362	1.70	−365
(3)	−5.10	+900	−14.5	+168	5.20	360	1.78	−325
(4)	−6.12	+800	−16	+166			1.89	n.r. [e]
(5)	−5.90	+788	−15	+158				−204

[a] H_A = Pt–*H*, H_B = P–*H*, H_C = P–CH_3. In p.p.m. positive to high frequency of $SiMe_4$. [b] Signs relative to positive $^{1}J(Pt-P)$ (D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 2370). [c] By double-resonance methods, in p.p.m. positive to high frequency of 21 392 145 Hz (see ref. in footnote *b*). [d] n.o. = Not observed. [e] n.r. = Not recorded; also $^{2}J(PtH_B)$, $^{3}J(H_AH_B)$, $^{3}J(H_BH_C)$, $^{3}J(PtH_C)$, and $^{3}J(PH_B)$ were not observed.

Hydrogen-1 n.m.r. spectra were obtained from freshly made-up mixtures over the range −70 °C to room temperature. The low-temperature data for cations (1)—(5) are given in Table 2. The spectra were broad even at low temperature and not all the expected couplings were resolved. The temperature dependences of the Pt–H resonances were consistent with those observed in the ^{31}P n.m.r. spectra. For (2) and (3) both $^{2}J(PH)$ and $^{2}J(P'H)$ were lost at room temperature but the chemical shifts and $^{1}J(PtH)$ coupling did not change significantly. For (4) and (5) only $^{2}J(PH)$ was lost and the resonances broadened at room temperature. Thus for complexes (2)—(5) both $^{1}J(PtP)$ and $^{1}J(PtH)$ were retained at all the temperatures studied.

The n.m.r. evidence therefore indicates that in CD_2Cl_2 the equilibrium in (i) is very much in favour of the cation. Since there is a large chemical-shift difference between free and co-ordinated L (see Table 1) and a large difference in hydride chemical shift between $[PtH(I)(PEt_3)_2]$ (−18 p.p.m.)[9] and corresponding cations, these results suggest that the equilibrium position is not strongly dependent on temperature. The temperature dependence of the spectra is therefore a result of the rate of intermolecular exchange of L and as expected this rate appears to depend on the basicity of L: the order of decreasing rate of exchange, L = PH_3 > $PMeH_2$ > PMe_2H > PMe_3 > PEt_3, is the order of increasing donor ability of the phosphine. We have also repeated most of these experiments with *trans*-$[PtCl(H)(PEt_3)_2]$ with virtually identical results and it seems that the nature of the halide has little effect on equilibrium (i). Because the error in measuring the amount of phosphine added (0.2 mmol) using standard vacuum-line methods is *ca.* 5% and because we do not know the solubilities of the more volatile phosphines, it is not possible to interpret these data more quantitatively.

Complexes (2)—(5) were isolated as their $[BPh_4]^-$ salt from the reaction of $[PtCl(H)(PEt_3)_2]$ and $Na[BPh_4]$ with the phosphine in methanol. It is notable that for (3) and (4) disproportionation of the isolated cations did not occur, suggesting that excess of phosphine is needed to cause exchange of PEt_3 and L, perhaps through a five-co-ordinate intermediate (see next section). Complex (1) could not be isolated in this way, even when excess of PH_3 and methanol were removed at −40 °C; extraction of the white residue with CH_2Cl_2 gave solutions containing only (5).

Five-co-ordinate Cations.—The reactions of $[PtH(I)(PEt_3)_2]$ with 2 mol equivalents of $PMeH_2$ in CD_2Cl_2 gave a pale yellow solution. No decomposition occurred, even after several hours at room temperature, and changes in the ^{31}P n.m.r. spectrum were completely reversible. These changes of ^{31}P n.m.r. parameters are given in Table 3. The ^{1}H n.m.r. spectrum at −60 °C showed a broad hydride resonance at −10.6 p.p.m. with platinum satellites [$^{1}J(PtH)$ 732 Hz]. This temperature dependence seemed best explained by a shift in equilibrium (ii) in favour of the five-co-ordinate species at low temperatures. It was not possible to decrease the temperature sufficiently to obtain the limiting spectrum of (6) and even at −90 °C the couplings $^{2}J(PP')$ and $^{1}J(PtP')$ were not resolved.

TABLE 3

Phosphorus-31 n.m.r. temperature dependence for $[PtH(I)(PEt_3)_2]$ + 2 $PMeH_2$ in CD_2Cl_2 [a]

θ_c/°C	$\delta(P)$	$^{1}J(PtP)$/Hz	$\delta(P')$ [b]
−90	−4.8	2 851	−136.0
−77	−4.1	2 835	−136 0
−62	−2.9	2 805	−135 3
−33	2.2	2 690	−133.0
−17	6.4	2 600	−131.0
30	*c*		−128.4

[a] See also footnotes to Table 1. [b] $^{1}J(PtP')$ not observed. [c] Usually broad.

It is likely that the stability of a five-co-ordinate platinum hydride containing both PEt_3 and a methyl-

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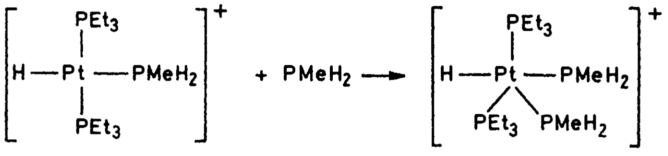
[9] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 854.

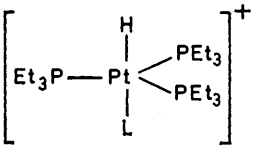
phosphine would be increased by utilising the maximum number of the more basic tertiary phosphines, yet conversely would be decreased by steric crowding factors, *e.g.* $[PtH(PEt_3)_4]^+$ (ref. 8) which has four bulky PEt_3 ligands is only observed at −131 °C. The best chance of observing five-co-ordinate species therefore appears to be the combination of three basic PEt_3 groups in $[PtH(PEt_3)_3]^+$ and one small methylphosphine. These reactions were carried out in n.m.r. tubes (in CD_2Cl_2) and great care was taken to prevent the reaction mixture warming to >−90 °C.



(ii)

(6)

For PH_3 the system was still exchanging fast at −95 °C, the triethylphosphines giving rise to a single broad resonance at 14.9 p.p.m. in the ^{31}P n.m.r. spectrum and PH_3 to a relatively sharp signal at −235.2 p.p.m. On warming the lines broadened, but at > −60 °C a reaction took place and an insoluble precipitate was formed. For $PMeH_2$, PMe_2H, and PMe_3 the five-co-ordinate cations (7)—(9) were clearly distinguished as the only species present in the original spectrum at −95 °C. The n.m.r. parameters for the three cations are given in Table 4. The ^1H n.m.r. spectra were obtained from the same reaction mixtures before they had been allowed to warm to >−90 °C. The trigonal-bipyramidal structure with equatorial PEt_3 groups is defined by the fact that only one ^{31}P chemical shift is observed for these groups and the large $^2J(P'H)$ coupling implies a mutually *trans* arrangement for these atoms. In all cases the $^2J(PP')$ coupling is clearly observed as a quartet splitting on P'. The large low-frequency shift of the PEt_3 ligands in the equatorial positions seems characteristic of the ^{31}P n.m.r. spectra of these five-co-ordinate platinum hydrides {*cf.* $[PtH_2(PEt_3)_3]$,[10] $\delta(P) = -3.25$ p.p.m.} and provides further evidence for equilibrium (ii). It is interesting to note that for both four- and five-co-ordinate cations both $^1J(PtP)$ and $^1J(PtP')$ increase, whereas $^1J(PtH)$ decreases, as the basicity of L increases. The increase in $^1J(PtP)$ is unexpected.



L
(7) $P'MeH_2$
(8) $P'Me_2H$
(9) $P'Me_3$

TABLE 4

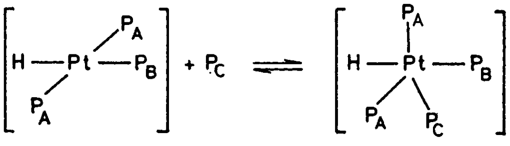
N.m.r. parameters for $[PtH(PEt_3)_3L][BPh_4]$ in CD_2Cl_2 at −90 °C [a]

Complex	δ(P)	^1J(PtP)/Hz	δ(P')	^1J(PtP')/Hz	^2J(PP')/Hz	δ(H)	^1J(PtH)/Hz	^2J(P'H)
(7)	−13.6	2 605	−131.1	1 536	33	−13.1	600	170
(8) [b]	−14.4	2 628	−88.7	1 932	34	−13.6	540	170
(9)	−14.1	2 667	−56.3	2 115	31	−13.8	490	150

[a] See also footnotes to Table 1. [b] $^1J(P'H)$ 340 Hz (off-resonance ^{31}P spectrum).

On warming the mixtures ^{31}P resonances quickly broaden. The coupling $^2J(PP')$ is lost at −80 °C and by −60 °C the platinum satellites have disappeared. At room temperature the triethylphosphines give a broad resonance at *ca.* 12 p.p.m. and the methylphosphine a relatively sharp signal close to the chemical shift of the free phosphines. For $L = PMeH_2$ the temperature dependence of the spectra is almost reversible, but although on returning to −90 °C the chemical shifts and $^1J(PtP')$ couplings are those originally observed for (7) the coupling $^2J(PP')$ is not resolved. For PMe_2H and PMe_3 the room-temperature spectra rapidly change and become uninterpretable as new broad resonances are observed. Cooling does not then sharpen the spectra. This is consistent with exchange of L with PEt_3 in the cation $[PtH(PEt_3)_3]$.$^+$ It is expected that the extent of such an exchange would be determined by the relative basicity of the phosphines.

The fact that the five-co-ordinate complex with the methylphosphine axial and *trans* to hydride is the first observed product in these reactions requires some discussion. Meakin *et al.*[8] have concluded that the equilibrium (iii) ($P_A = P_B = P_C = PEt_3$) involves a phosphine in the equatorial plane and that the unique phosphine *trans* to hydride does not take part in the exchange process. If this simple mechanism of addition also applies to the present methylphosphines, then the initial five-co-ordinate complex must undergo an immediate rearrangement to transfer P_C to an axial position. In order to obtain further information we have also followed the reaction of PEt_3 with *trans*-$[PtH(PMe_2H)(PEt_3)_2]^+$. Again the major product observed in the original ^{31}P n.m.r. spectrum at −95 °C was (8) with PMe_2H in the axial position [although in this case *ca.* 20% of the in-



(iii)

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[10] J. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

tensity occurred as an unidentified broad resonance at -10.1 p.p.m. with platinum satellites, ^1J(PtP) 2 800 Hz]. This implies that we are observing the more stable structure in these reactions rather than the initial addition geometry. The structure with the three bulky PEt_3 groups in equatorial positions would be expected to be more stable on steric grounds {*cf.* [IrH(CO)$(PPh_3)_3$],[11] [CoH$(N_2)(PPh_3)_3$],[12] and [RuH(NO)$(PPh_3)_3$] [13]}. Our results are therefore consistent with those of Meakin *et al.*, assuming a rapid intramolecular rearrangement of the addition product to give the sterically more stable isomer. It seems unlikely that we could devise an experiment to prevent this rearrangement using this system and our existing equipment.

EXPERIMENTAL

N.m.r. and i.r. measurements were made as in ref. 1. The complexes *trans*-[PtH(X)$(PEt_3)_2$] (X = Cl or I) and [PtH$(PEt_3)_3$][BPh_4] and the methylphosphines were prepared by standard methods. Dichlorodideuteriomethane was dried over CaH_2 and distilled immediately before use. N.m.r. tube reactions were carried out as follows. The platinum substrate (0.1—0.2 mmol) was weighed into a 5-mm n.m.r. tube blown on to a B.10 cone and attached to a standard Pyrex-glass vacuum line. Dichlorodideuteriomethane (0.4 cm^3) was condensed into the tube and the substrate dissolved. A measured amount of the phosphine was condensed into the tube at -196 °C and the tube was sealed and stored at this temperature.

Preparation of Hydrido(methylphosphine)bis(triethylphosphine)platinum(II) *Tetraphenylborate* (2).—The complex *trans*-[PtCl(H)$(PEt_3)_2$] (1.0 mmol) and Na[BPh_4] (1.0 mmol) were dissolved in MeOH in a Schlenk tube connected *via* a glass tap adaptor to a vacuum line, and the solution was degassed. Methylphosphine (1.1 mmol) was condensed into the tube at -190 °C and the mixture allowed to warm to room temperature with vigorous shaking. The resulting white precipitate was filtered off under nitrogen and washed with cold methanol. Drying *in vacuo* gave the pure product as a white powder, m.p. 76—79 °C, stable indefinitely *in vacuo* or under dry nitrogen but unstable in air (Found: C, 55.75; H, 6.90. $C_{37}H_{56}BP_3Pt$ requires C, 55.6; H, 7.0%). Infrared spectrum in Nujol: ν(P–H) at 2 355vw, ν(Pt–H) at 2 050m cm^{-1}.

The following complexes were prepared by similar methods but were stable in air and were recrystallised from methanol: [PtH$(PMe_2H)(PEt_3)_2$][BPh_4] (3) (Found: C, 56.0; H, 7.18. $C_{38}H_{58}BP_3Pt$ requires C, 56.1; H, 7.12%), m.p. 124—125 °C, ν(P–H) at 2 340vw, ν(Pt–H) at 2 060m cm^{-1} in Nujol; [PtH$(PMe_3)(PEt_3)_2$][BPh_4] (4) (Found: C, 56.7; H, 7.39. $C_{39}H_{60}BP_3Pt$ requires C, 56.6; H, 7.39%), m.p. 118—120 °C, ν(Pt–H) at 2 060 cm^{-1} in Nujol.

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