Reactions of Halogenohydridobis(triethylphosphine)platinum(II) with Trihalogenophosphines: Some Unusual Complexes of Pt^{II} containing Five-co-ordinated Phosphorus

Christopher W. Allen, E. A. V. Ebsworth,* Steven G. Henderson, David W. H. Rankin, Heather E. Robertson, Bryan Turner, and John D. Whitelock
Chemistry Department, Edinburgh University, West Mains Road, Edinburgh EH9 3JJ

^{31}P N.m.r. spectra show that $[PtClH(PEt_3)_2]$ reacts with PCl_3 in CH_2Cl_2 at 180 K to give $[PtCl_2H_2(PEt_3)_2]$, (**5**), and the previously unknown $[PtCl(PEt_3)_2(P'Cl_2)]$, (**4**). On warming to 240 K, complex (**5**) decomposes and (**4**) is reversibly protonated to give $[PtCl(PEt_3)_2(P'Cl_2H)]^+$. Above 240 K, (**4**) is converted into the novel $[PtCl(PEt_3)_2(P'Cl_2H_2)]$, (**8**). This complex is stable in solution up to 260 K, but decomposes irreversibly at higher temperatures. Changes in the n.m.r. spectra on adding HCl or BCl_3 are interpreted in terms of dissociation of (**8**) into $[PtCl(PEt_3)_2(P'ClH_2)]^+$ and $[HCl_2]^-$ or $[BCl_4]^-$. Reaction of $[PtBrH(PEt_3)_2]$ with PBr_3 at 160 K gives $[PtBr_2H(PEt_3)_2(P'Br_2)]$, which loses HBr at 190 K, giving $[PtBr(PEt_3)_2(P'Br_2)]$ and $[PtBr_2H_2(PEt_3)_2]$. At 240 K, $[PtBr(PEt_3)_2(P'Br_2H_2)]$ is produced. This persists for short periods at room temperature, and is stable at 170 K; addition of HBr or BBr_3 leads to the formation of $[PtBr(PEt_3)_2(P'BrH_2)]^+$ by loss of bromide ion. All these species were identified by n.m.r. spectroscopy.

We have recently[1,2] prepared complexes containing PCl_2 or PF_2 groups bound to six-co-ordinated Ir^{III} by the oxidative addition of PCl_3 or $PClF_2$ to *trans*-$[Ir(CO)Cl(PEt_3)_2]$. These complexes are unusual in that they contain three-co-ordinated phosphorus ligands, and so can be regarded as phosphines with one substituent of exceptional steric and electronic character; they can be used to prepare mixed-metal species with PF_2 bridges, and they can be converted into complexes containing unusual ligands such as PH_2Se by reaction at the PCl_2 or PF_2 groups.[2] Analogous complexes of Pt^{II} would have additional modes of reaction open to them, through the possibility of addition to the metal centre; their synthesis and chemical properties are therefore also of interest. Unfortunately, however, reaction between $PClF_2$ and *trans*-$[PtClH(PEt_3)_2]$ gives[3] the binuclear complex $[(Et_3P)_2ClPt(P'F_2)Pt(PEt_3)Cl_2]$ containing a PF_2 bridge in which P′ is four-co-ordinated. We have therefore investigated the reactions between PCl_3 or PBr_3 and $[PtClH(PEt_3)_2]$, (**1**), $[PtBrH(PEt_3)_2]$, (**2**), or $[PtHI(PEt_3)_2]$, (**3**), to try to prepare platinum complexes of three-co-ordinated P and to study their reactions.

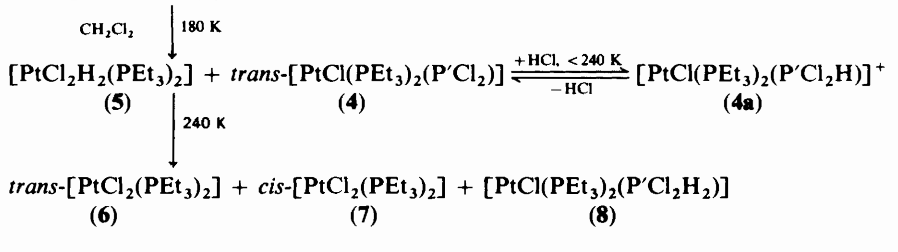
Results

Reaction between PCl_3 and complex (**1**) in CH_2Cl_2 is rapid at 180 K, and several products are formed as the solution is allowed to warm. The products depend on the initial ratios of reagents taken. With equimolar proportions, the process may be represented by Scheme 1. Most of the products are unstable in the reaction mixture and have not yet been isolated, but they have been identified by their n.m.r. spectra, using variations in the reaction conditions. Additional information has been obtained from reactions between PCl_3 and complex (**2**) or (**3**), and between PBr_3 and (**2**). The system will be considered in stages.

The Initial Reaction.—The ^{31}P-$\{^1H\}$ n.m.r. spectrum of an equimolar mixture of complex (**1**) and PCl_3 in CH_2Cl_2 showed no trace of (**1**) after an hour at 190 K. Peaks were observed due to the novel complex *trans*-$[PtCl(PEt_3)_2(P'Cl_2)]$, (**4**), and to $[PtCl_2H_2(PEt_3)_2]$, (**5**) [equation (1)]. The n.m.r. parameters

$$\textit{trans}\text{-}[PtClH(PEt_3)_2] + PCl_3 \longrightarrow \underset{\textbf{(4)}}{\textit{trans}\text{-}[PtClPEt_3)_2(P'Cl_2)]} + \underset{\textbf{(5)}}{[PtCl_2H_2(PEt_3)_2]} \qquad (1)$$

of complex (**5**) are well known.[4] The spectrum of (**4**) showed two resonances. One was a triplet $[^2J(PP') = 59.1$ Hz$]$ with Pt satellites $[^1J(PtP') = 465.4$ Hz$]$ at very high frequency ($\delta = 311.1$ p.p.m.), a region associated with metal–$P'Cl_2$ groups.[2,5] The other was a doublet ($\delta = 20.4$ p.p.m.) with the same coupling as the triplet splitting in the high-frequency resonance, and with platinum satellites. The chemical shift is



Scheme 1.

Table. N.m.r. parameters for complexes obtained in this work, with standard deviations in parentheses

	Complex	δ(P′)	δ(P)	δ(H)	^1J(PtP)	^1J(PtP′)	^1J(P′H)	^2J(PP′)	^2J(PtH)	^3J(PH)	T/K
(4)	$[\mathrm{PtCl(PEt_3)_2(P'Cl_2)}]$	311.1(5)	20.4(1)	—	2 638.5(3)	465.4(2)	—	59.1(2)	—	—	180
(9)	$[\mathrm{PtBr(PEt_3)_2(P'Cl_2)}]$	307.4(1)	18.3(1)	—	2 630(2)	370(2)	—	59.1(3)	—	—	180
(10)	$[\mathrm{PtI(PEt_3)_2(P'Cl_2)}]$	298.0(1)	13.4(1)	—	2 622(2)	245.8(3)	—	59.6(2)	—	—	180
(11)	$[\mathrm{PtBr(PEt_3)_2(P'Br_2)}]$	320.2(1)	17.7(1)	—	2 123(2)	185.6(2)	—	69.9(2)	—	—	176
(12)	$[\mathrm{PtBr_2H(PEt_3)_2(P'Br_2)}]$	277.0(1)	4.3(1)	−15.04(2)	1 741(2)	167.0(2)	—	44.9(2)	—	—	176
(4a)	$[\mathrm{PtCl(PEt_3)_2(P'Cl_2H)}]^+$	62.7(1)	23.0(2)	8.69(2)	1 943(5)	4 750(10)	550.2(2)	23.2(2)	235(1)	9.5(1)	180
(11a)	$[\mathrm{PtBr(PEt_3)_2(P'Br_2H)}]^+$	42.2(2)	15.5(1)	8.29(2)	2 083(5)	4 830(10)	500.5(2)	23.9(2)	218(5)	10.5(5)	200
(8)	$[\mathrm{PtCl(PEt_3)_2(P'Cl_2H_2)}]$	−71.0(10)	12.48(2)	6.22(2)	2 135(2)	4 725(10)	555(1)	30.5(5)	109.2(4)	8.4(2)	230
(8a)	$[\mathrm{PtCl(PEt_3)_2(P'ClH_2)}]^+$	−16.14(2)	17.34(2)	6.38(2)	1 989(2)	4 121(10)	487(2)	29.5(5)	112(1)	9.2(4)	230
(13)	$[\mathrm{PtBr(PEt_3)_2(P'Br_2H_2)}]$	−128.0(10)	4.22(2)	5.83(3)	2 168(3)	5 002(10)	569(1)	27.7(2)	117.3(2)	8.0(2)	250
(13a)	$[\mathrm{PtBr(PEt_3)_2(P'BrH_2)}]^+$	−53.5(1)	11.83(2)	5.66(2)	1 974(2)	4 112(5)	484.7(5)	27.2(2)	112.8(2)	8.8(3)	180

Shifts are given to high frequency of $\mathrm{SiMe_4}$ (^{1}H) or 85% $\mathrm{H_3PO_4}$ (^{31}P) for solutions in $\mathrm{CD_2Cl_2}$.

characteristic of $\mathrm{PEt_3}$ complexes, and the value of ^1J(PtP), 2 638.5 Hz, shows that the complex contained four-co-ordinated Pt. The resonance due to P′ was not affected when proton coupling was restored, and in the proton resonance spectrum the only Pt*H* peaks were those due to complex **(5)**. These observations show that **(4)** was $[\mathrm{PtCl(PEt_3)_2(P'Cl_2)}]$. As the solution was allowed to warm, this complex reacted further (see below), but it has been obtained as the only Pt-containing product from reactions between **(1)** and a large excess of $\mathrm{PCl_3}$, or from **(1)**, $\mathrm{PCl_3}$, and $\mathrm{NMe_3}$ in 1:1:1 molar ratio. We have been able to obtain this complex as an oil, and will report on its reactions in more detail elsewhere. Its n.m.r. parameters are given in the Table.

The products of the initial reactions between $\mathrm{PCl_3}$ and complex **(2)** or **(3)** were very unstable, and we have not been able to characterise them so fully. The ^{31}P-{^{1}H} n.m.r. spectrum of an equimolar solution of **(2)** and $\mathrm{PCl_3}$ in $\mathrm{CH_2Cl_2}$ showed three singlet resonances with platinum satellites in the *P*Et$_3$ region; we assign these on the basis of coupling constants and chemical shifts[4] to $[\mathrm{PtCl_2H_2(PEt_3)_2}]$, $[\mathrm{PtBrClH_2(PEt_3)_2}]$, and $[\mathrm{PtBr_2H_2(PEt_3)_2}]$; the relative intensities were roughly 1:40:40. In addition there were two triplet resonances with platinum satellites in the high-frequency region, each associated with a doublet with platinum satellites in the *P*Et$_3$ region. One set of doublets and triplets corresponds with the spectrum of complex **(4)**. The parameters of the other set, which was initially about twice as strong, were similar, but the chemical shifts and coupling constants were rather smaller. We identify this species, **(9)**, as *trans*-$[\mathrm{PtBr(PEt_3)_2(P'Cl_2)}]$. The chemical shifts were consistent with $\mathrm{PtBr(P'Cl_2)}$ rather than with $\mathrm{PtCl(P'Br_2)}$, particularly when taken with those of the products of the reaction between **(2)** and $\mathrm{PBr_3}$ (see below), and the value of ^1J(PtP) shows clearly that Pt was four- and not six-co-ordinated; no additional Pt*H* resonance was observed in the proton resonance spectrum. It appears that the initial reaction is like that between complex **(1)** and $\mathrm{PCl_3}$, but that halogen exchange has taken place, favouring PtBr in six-co-ordinated complexes [equation (2)]. The close correspondence of the parameters of one of the products to those of complex **(4)**, and the observation of five sets of resonances, show that any exchange of halogen at Pt or P′ must be slow on the n.m.r. time-scale at this temperature.

$$\textit{trans-}[\mathrm{PtBrH(PEt_3)_2}] + \mathrm{PCl_3} \longrightarrow \textit{trans-}[\mathrm{PtCl(PEt_3)_2(P'Cl_2)}] + \textit{trans-}[\mathrm{PtBr(PEt_3)_2(P'Cl_2)}] + [\mathrm{PtCl_2H_2(PEt_3)_2}] + [\mathrm{PtBrClH_2(PEt_3)_2}] + [\mathrm{PtBr_2H_2(PEt_3)_2}] \quad (2)$$

Reaction between complex **(3)** and $\mathrm{PCl_3}$ under the same conditions gave a similar mixture of products, except that in this system there was about ten times as much $[\mathrm{PtH_2I_2(PEt_3)_2}]$ as $[\mathrm{PtClH_2I(PEt_3)_2}]$ and we did not detect **(5)**. As before, there were two sets of high-frequency triplets with associated *P*Et$_3$ doublets; one, the stronger, was assigned from its parameters to **(4)**, and the other to *trans*-$[\mathrm{PtI(PEt_3)_2(P'Cl_2)}]$, **(10)**. The n.m.r. parameters are given in the Table.

Reaction between $\mathrm{PBr_3}$ and complex **(2)** was somewhat different; by working at very low temperatures we were able to detect an unstable platinum(IV) complex formed by oxidative addition of $\mathrm{PBr_3}$ to **(2)**. If the reaction was allowed to occur in $\mathrm{CH_2Cl_2}$ at temperatures above 200 K, we observed no P′ resonances in the high-frequency region. If the solution was not allowed to warm above 176 K, however, there were two triplet resonances at about +300 p.p.m., each with platinum satellites and associated $\mathrm{PEt_3}$ doublets. We assign one set of resonances to *trans*-$[\mathrm{PtBr(PEt_3)_2(P'Br_2)}]$, **(11)**, on the basis of its n.m.r. parameters. The chemical shifts of the second species, **(12)**, were similar, but the couplings to Pt were much smaller, suggesting that the Pt might be six-co-ordinated. In the proton resonance spectrum there was an additional Pt*H* triplet with platinum satellites at −15.04 p.p.m., a shift associated with H *trans* to halogen[4,6] in complexes of six-co-ordinated $\mathrm{Pt^{IV}}$. We were able to show by heteronuclear double resonance that the P′ resonance, the *P*Et$_3$ resonance, and the new hydride resonance were due to the same species; though ^2J(P′PtH) was not observed, irradiation at the *P*Et$_3$ frequency collapsed the triplet in the Pt*H* resonance. We therefore identify complex **(12)** as $[\mathrm{PtBr_2H(PEt_3)_2(P'Br_2)}]$, formed by oxidative addition of $\mathrm{PBr_3}$ to **(2)** [equation (3)]. The only other resonances were due to **(2)** and to $[\mathrm{PtBr_2H_2(PEt_3)_2}]$. The proportion of **(12)** formed was reduced if a large excess of $\mathrm{PBr_3}$ was taken. As the solution was allowed to warm to 200 K, the peaks due to **(12)** shrank and vanished; those due to **(11)** persisted to 200 K, but disappeared at higher temperatures.

$$[\mathrm{PtBrH(PEt_3)_2}] + \mathrm{PBr_3} \longrightarrow [\mathrm{PtBr_2H(PEt_3)_2(P'Br_2)}] \quad (3)$$

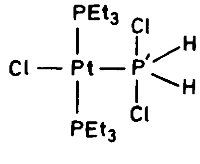
The Second Stage {*Protonation of* $[\mathrm{PtCl(PEt_3)_2(P'Cl_2)}]$}.—If the equimolar solution of $\mathrm{PCl_3}$ and complex **(1)** from which **(4)** was obtained was allowed to warm to temperatures between 180 and 240 K, the triplet due to P′ broadened greatly and shifted to lower frequency; at 40 MHz the high-frequency satellite could still be observed, but the low-frequency satellite became too broad to detect. The *P*Et$_3$ resonances changed relatively little. As the temperature approached 240 K, the changes in the P′resonance began to be reversed: the main peak moved back towards 300 p.p.m., and the satellites moved with it. These peculiar changes can be understood from the results of adding HCl. If a two-fold molar excess of HCl was added to the solution at 180 K, the P′ resonance shifted to 62.7 p.p.m. and became a relatively sharp triplet with platinum satellites; when proton coupling was restored, this peak showed a wide doublet splitting [^1J(P′H) = 550.2 Hz]; the changes in chemical shift and coupling constant for the *P*Et$_3$ resonance were much smaller. There is clearly an equilibrium between (**4**), HCl, and the protonated species (**4a**) [equation (4)]. At low temperatures

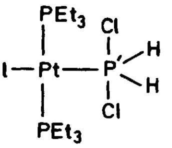
$$\underset{(\mathbf{4})}{[\mathrm{PtCl(PEt_3)_2(P'Cl_2)}]} + \mathrm{HCl} \rightleftharpoons \underset{(\mathbf{4a})}{[\mathrm{PtCl(PEt_3)_2(P'Cl_2H)}]^+} + \mathrm{Cl^-} \quad (4)$$

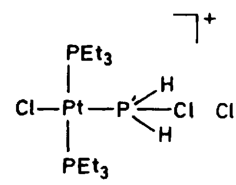
in the presence of excess of HCl the equilibrium lies to the right. With a deficit of HCl there is a fast exchange between (**4**) and (**4a**), giving average positions for the P′ resonance and for each of its satellites; as the temperature is raised, the equilibrium shifts to the left, perhaps through evaporation of HCl from the solution. Addition of a 1:1 mixture of HCl and BCl$_3$ to a solution of complex (**4**) gave a solution whose ^{31}P-{^{1}H} and ^{1}H n.m.r. spectra corresponded with those of (**4a**); the ^{11}B spectrum showed the sharp ($w \sim 2$ Hz) line at 7.6 p.p.m. associated[7] with [BCl$_4$]$^-$. The n.m.r. parameters for complex (**4a**) are given in the Table.

Solutions of PBr$_3$ and complex (**2**) at 200 K gave resonances that resembled those due to (**4a**), and these have been assigned by analogy to protonated (**11**), *i.e.* (**11a**); the parameters are given in the Table. The amount of (**11a**) in these solutions was always small, however, and was not significantly increased by adding HBr; further reaction occurred much more readily in the bromide system, giving products described in the next section.

Formation of Species containing Five-co-ordinated Phosphorus.—If the equimolar solution of PCl$_3$ and complex (**1**) was allowed to warm to temperatures between 240 and 260 K, the resonances due to (**4**), (**4a**), and (**5**) slowly disappeared, and new resonances grew in their place; this happened faster and at lower temperatures if the PCl$_3$ was not rigorously freed from HCl. Among the new resonances, peaks due to complexes (**6**) and to (**7**) were identified from their chemical shifts and from ^1J(PtP). In addition to these, there were peaks that we assign to a most unusual and unexpected complex, (**8**). These consisted of a doublet with platinum satellites in the *P*Et$_3$ region, and a triplet with platinum satellites at −71 p.p.m. The very low chemical shift suggests[2,8] P$^{\mathrm{V}}$ rather than P$^{\mathrm{III}}$. When proton coupling was restored, the resonance at −71 p.p.m. split into a wide triplet [^1J(P′H) = 555 Hz]; in the proton resonance spectrum, there was a wide doublet of triplets with platinum satellites [δ = 6.22 p.p.m. ^2J(PtH) = 109.2; ^3J(PH) = 8.4 Hz]. The P′ resonance was reasonably sharp if the temperature was kept between 200 and 260 K; at higher temperatures it broadened significantly, but sharpened again on recooling if the solution was not kept at temperatures above 260 K for long. The proton resonance was sharpest at 260 K, and broadened as the temperature was lowered. If the solution was kept at higher temperatures, peaks due to complex (**8**) shrank and vanished, and the end-products were (**6**), (**7**), and [PEt$_3$H]$^+$.


(**8**)


(**8**)


(**8a**)

The n.m.r. spectra show the structure of the co-ordination skeleton of the complex. The value of ^1J(PtP) (2 135 Hz) shows that the platinum atom is four-co-ordinated,[4] and the proton-coupled P′ resonance shows that P′ is bound to Pt and to two H atoms and is at least four-co-ordinated;[9] the value of ^1J(P′H) is rather large for four-co-ordinated P bound to two H atoms and a metal (though not impossibly so), but it seems quite consistent with five-co-ordinated P′. There are two possible structures for (**8**); the complex might be molecular, with five-co-ordinated P′, or cationic, (**8a**), with four-co-ordinated P′. Experiments with BCl$_3$ and with HCl lead us to conclude that the complex is best represented by the molecular form (**8**). If PCl$_3$ and complex (**1**) are allowed to react together in the presence of an equimolar proportion of BCl$_3$ or a four-fold excess of HCl, the reaction stops at (**4a**); the further reaction to give species based on (**8**) is inhibited. If, however, PCl$_3$ and (**1**) are allowed to react until (**8**) has been formed, and an equimolar amount of BCl$_3$ is then added, there is a marked change in the n.m.r. parameters associated with (**8**). The resonance due to P′ shifts from −71 to −16.1 p.p.m., and there are large reductions in ^1J(PtP′) and in ^1J(P′H), with smaller changes in other parameters. The ^{11}B resonance is at 7.4 p.p.m., close to the value for [BCl$_4$]$^-$, though the line is broader ($w \sim 20$ Hz) than usual for this species. We suggest that BCl$_3$ has removed Cl$^-$ from the equilibrium between (**8**) and (**8a**), generating the cation (**8a**). Addition of a two-fold molar excess of HCl to a solution containing complex (**8**) leads to similar but smaller changes; for instance, δ(P′) is −36 p.p.m.; we suppose that HCl acts as a weaker acceptor for Cl$^-$, forming [HCl$_2$]$^-$, and so does not shift the equilibrium fully to the right. Addition of a large excess of NPr$_4$Cl to a solution of PCl$_3$ and complex (**1**) before formation of (**8**) also inhibits formation of (**8**), but addition to a solution already containing (**8**) does not lead initially to significant changes in the n.m.r. parameters of (**8**), though on standing at 220 K the peaks due to P′ broaden and on prolonged standing at this temperature the spectrum changes further. We conclude that, in the absence of a chloride-ion acceptor, complex (**8**) is present in CH$_2$Cl$_2$ in the molecular form, with little or no dissociation into (**8a**) and Cl$^-$. The parameters in the Table for the molecular species are those taken from such a solution, and those for (**8a**) are taken from the solution to which an equimolar proportion of BCl$_3$ had been added. The chemical shift for P′ in molecular (**8**) varied by 1—2 p.p.m. from one solution to another, and by about the same amount with a change in temperature of 40 K.

Experiments with PBr$_3$ and complex (**2**) supported these conclusions. When the solution containing PBr$_3$ and (**2**) was allowed to warm above 220 K, peaks due to a complex analogous to (**8**), *i.e.* (**13**), appeared and rapidly grew stronger. They remained relatively sharp even at 280 K for short periods, suggesting that (**13**) is more stable than (**8**). Addition of HBr at 200 K did not alter the general pattern of the spectrum, but shifted the resonance due to P′; with a two-fold proportion of HBr the resonance shifted from −128 to −65.6 p.p.m., and with a four-fold proportion it shifted to −60.9 p.p.m., with large decreases in ^1J(PtP′) and smaller changes in other parameters.

We presume that added HBr has led to the formation of the cation (**13a**) and $[HBr_2]^-$ [equation (5)]. Addition of an

$$[PtBr(PEt_3)_2(P'Br_2H_2)] + HBr \rightleftharpoons [PtBr(PEt_3)_2(P'BrH_2)]^+ + [HBr_2]^- \quad (5)$$

equimolar amount of BBr_3 (based on Pt initially taken) to the solution of PBr_3 and complex (**2**) at 200 K gave a solution with several unidentified resonances in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, but peaks due to (**13a**) were strong and well defined; that due to P′ had shifted to −53.5 p.p.m., with a corresponding drop in $^1J(PtP')$ and in $^1J(P'H)$ and smaller changes in other parameters. The ^{11}B n.m.r. spectrum showed a fairly sharp line ($w \sim 7$ Hz) at − 23.3 p.p.m., assigned[7,10] to $[BBr_4]^-$. Addition of a four-fold molar proportion of NPr_4Br (based on Pt initially taken) did not perturb the n.m.r. parameters of complex (**13**) significantly. We conclude that (**13**) is present in CH_2Cl_2 in the molecular form unless a bromide-ion acceptor is added; the parameters for (**13**) in the Table are from the solution in CH_2Cl_2, and those for (**13a**) are from a solution to which BBr_3 had been added.

Reacting Ratio.—It is hard to determine the stoicheiometry of the reactions that give complex (**8**), because of parallel decomposition reactions forming (**6**) and (**7**). In the bromide system, PBr_3 is a difficult material to transfer quantitatively, but careful experiments using a standard solution of PBr_3 in CH_2Cl_2 showed that excess of PBr_3 was present after prolonged reaction at 250 K unless the starting ratio of PBr_3:(**2**) was less than 1:2. This implies that the overall reaction to form (**13**) may be written as in equation (6). However, complex (**13**) was

$$PBr_3 + 2[PtBrH(PEt_3)_2] \longrightarrow [PtBr_2(PEt_3)_2] + [PtBr(PEt_3)_2(P'Br_2H_2)] \quad (6)$$

unstable at 260 K in the absence of excess of PBr_3.

Reactions with an Excess of $[PtHX(PEt_3)_2]$.—Reaction between PCl_3 and an excess of complex (**1**) in CH_2Cl_2 gave (**4**), (**5**), and (**1**) at temperatures up to 300 K; no further products were detected on standing. The reaction between PBr_3 and an excess of complex (**2**) was more complicated. At 175 K, resonances were detected due to (**2**), to $[PtBr_2H_2(PEt_3)_2]$, to (**11**), and to (**12**); in this system, the resonances due to (**12**) faded quickly at 180 K, but those due to (**11**) persisted to 250 K. When the solution was shaken for about a minute at room temperature and then cooled again to 250 K, peaks due to complex (**11**) became very weak indeed; resonances were observed due to *cis*- and *trans*-$[PtBr_2(PEt_3)_2]$, to (**2**), to $[PtBr_2H_2(PEt_3)_2]$, to $[Pt(PEt_3)_3H]^+$, and to a small amount[11] of $[(Et_3P)_2BrPt(P'H_2)PtBr(PEt_3)_2]^+$.

Attempts to Fluorinate P′ *in* $[PtBr(PEt_3)_2(P'Br_2H_2)]$.—In order to try to demonstrate directly that P′ in complex (**13**) was bound to two halogen atoms as well as to two H atoms and Pt, we tried to fluorinate it with $GeMe_3F$, a mild fluorinating agent that was unlikely to react in other ways with the rest of the molecule. Treatment of a solution in dichloromethane containing (**13**) with $GeMe_3F$ in equimolar proportions or in excess led to very complicated reactions at low temperatures; HF was eliminated, and many platinum complexes were formed. The results did not help to confirm the formulation of (**13**).

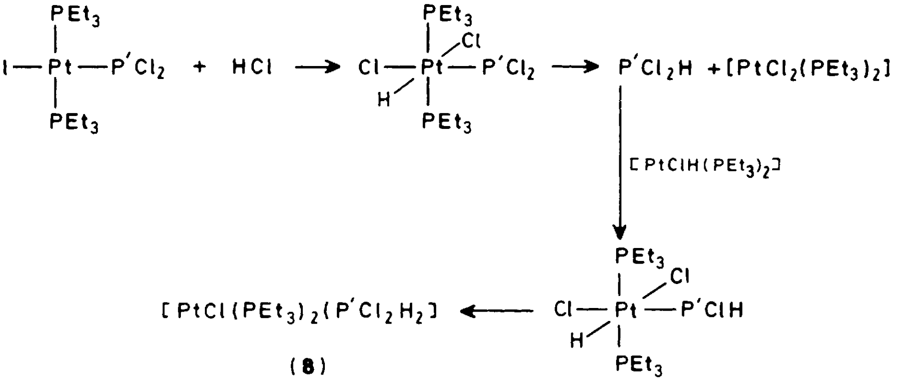
Discussion

The most unexpected process in the systems we describe here is the formation of the species (**8**) and (**13**) which we formulate as platinum(II) complexes of five-co-ordinated phosphorus. The initial reactions between (**1**) or (**2**) and the corresponding phosphorus(III) halide present no surprises. The detection of the six-co-ordinated platinum species (**12**) at very low temperatures in the reaction between (**2**) and PBr_3 confirms that the initial step involves oxidative addition of P–Br to Pt^{II}, as in the analogous reaction between PX_3 and $[Ir(CO)X(PEt_3)_2]$, but with Ir the product is stable to reductive elimination, and the reaction stops at this stage; in the platinum systems, the initially formed six-co-ordinated complex eliminates HX, which is taken up by excess of $[PtHX(PEt_3)_2]$ to give $[PtH_2X_2(PEt_3)_2]$. This shows that the substitution of H by PX_2 reduces the susceptibility of Pt^{II} to oxidative addition. The stability of $[PtY(PEt_3)_2(P'X_2)]$ in the reaction solutions is very sensitive to both X and Y; indeed, the only product of this type stable enough for us to isolate it is (**4**). We intend to study the reactions of complex (**4**) in more detail; here we are concerned with the behaviour of (**4**) and its analogues in the reaction system.

It is hard to see how species of the type $[PtX(PEt_3)_2(P'X_2)]$ are transformed into $[PtX(PEt_3)_2(P'H_2X_2)]$. The transformation must involve HX, yet addition of an excess of HCl to the reaction mixture of (**4**) and (**5**) inhibits the formation of (**8**). We suggest that this is because an excess of HCl protonates P′, and it follows that protonation is not involved in transforming $P'Cl_2$ into $P'Cl_2H_2$. Moreover, $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ does not react with HCl below 240 K, and at higher temperatures the reaction involves displacement of PCl_3 with formation of IrH rather than protonation of $P'Cl_2$. While $P'Cl_2$ is likely to be more electron-rich when bound to Pt^{II} than to Ir^{III}, we believe that $^{31}P\text{-}\{^1H\}$ *n.m.r. spectra* of equimolar solutions of complex (**1**) and PCl_3 show that the PCl_2 group of (**4**) is protonated reversibly between 200 and 250 K with no sign that this is a step in the formation of (**8**). It seems more likely that the metal atom is involved in this reaction. It is possible that HCl might add reversibly to (**4**) if the concentration of HCl were maintained at the right level; this addition could be followed by elimination of PCl_2H and rapid readdition (see below). We should have to suppose that the bound PClH added HCl so fast that we could not detect PCl_2H either bound or free. We know that platinum(IV) complexes such as (**5**) lose HX reversibly, but that dissociation is slight; the presence of (**5**) might thus impose a close control on the concentration of free HCl (Scheme 2).

It is worth noting that complex (**13**) is formed much more readily than (**8**) is; this implies that the metal is likely to be involved in the conversion of $P'X_2$ into $P'H_2X_2$, since PtBr is much more readily formed than is PBr. Since we have not been able to isolate either (**8**) or (**13**), our formulation of them as complexes of five-co-ordinated phosphorus must rest on a detailed analysis of the n.m.r. parameters. There is no doubt that the ligands contain two P′–H bonds and $^1J(P'H)$ is so large that P′ must be either four- or (more probably) five-co-ordinated; there is no direct evidence to show which it is, but we believe that our experiments with BCl_3 make it very probable that the molecular formulation is correct. As would have been expected on ionisation, P′ shifts to high frequency, and $^1J(P'H)$ drops to a value fully consistent with four-co-ordinated P′. We also believe that the formation of $[(Et_3P)_2BrPt(P'H_2)PtBr(PEt_3)_2]^+$ in the system containing PBr_3 and an excess of (**2**) is more consistent with the formation of molecular (**13**). It is possible to envisage transfer of Br_2 from P′ to (**2**); the resulting $[PtBr(PEt_3)_2(P'H_2)]$ could then displace Br^- from $[PtBr_2(PEt_3)_2]$ to give the PH_2-bridged species. Loss of Br^+ from the cation (**13a**) seems much less likely, particularly if (**13a**) had been formed by loss of Br^- from (**13**).

The observations we have made show that in the species (**8**) and (**13**) the unique phosphorus atom P′ is at least four-co-ordinated. It is conceivable that (**8**) and (**13**) contain five-co-ordinated Pt rather than P′, and should be written as



Scheme 2.

$[PtX_2(PEt_3)_2(P'H_2X)]$. Such species would be expected to lose halide ion from Pt on the addition of halide-ion acceptors. However, we do not believe that loss of halide ion from the metal would lead to the very large changes in P' n.m.r. parameters on the addition of BX_3 or HX, and so we regard this formulation as improbable. We cannot exclude the possibility that these species are anionic and contain six-co-ordinated P', being of the form $[PtX(PEt_3)_2(P'H_2X_3)]^-$. There are no analogous compounds on whose n.m.r. parameters we could base a distinction between these anions and the molecular (**8**) or (**13**). The value of ^1J(PH) drops slightly[12] from PF_4H to PF_5H^-; ^1J(P'H) is relatively large in (**8**) and in (**13**), which seems rather more in keeping with the molecular representation. Moreover, there is no obvious cation that could be present as a counter ion. But until we isolate either complex (**8**) or (**13**), this possibility is likely to remain, though in the context of general chemistry of P^V we regard it as improbable.

N.M.R. Parameters.—The very high-frequency shifts for $P'X_2$ ligands in these platinum complexes are fully in keeping with what has been observed in related complexes of other metals. The P' resonance moves to lower frequency when for a given X the halogen on Pt is changed from Cl to Br to I; there is, however, a substantial shift to high frequency between (**4**) and (**11**). Oxidation at Pt shifts P' to low frequency. The most unusual parameters in this group of complexes, however, are the values of ^1J(PtP'), which are exceptionally small. In most complexes of Pt^{II} in which P is also four-co-ordinated, ^1J(PtP) is over 2 000 Hz; here, with three-co-ordinated P', ^1J(PtP') ranges from 465.4 to 185.6 Hz. For $P'Cl_2$ species, this coupling constant drops as the halogen *trans* to P' changes from Cl (465.4) to Br (370) to I (245.8 Hz); since the two ligands involved share a common orbital, so large a change is understandable. There is a further drop in ^1J(PtP') as Pt is oxidised, from 185.6 in complex (**11**) to 167.0 Hz in (**12**). This drop is smaller than expected for a change in co-ordination from four to six, implying that in these systems at least ^1J(PtP') is affected by other factors. In platinum(II) complexes with four-co-ordinated P *trans* to halogen, ^1J(PtP) is around 3 000—4 000 Hz; in our compounds, ^1J(PtP') with P' *trans* to halogen is around 4 000—5 000 Hz, whether P' is formulated as four- or five-co-ordinated.

The parameters associated with P' in complexes (**8**), (**13**), (**8a**), and (**13a**) have already been discussed in some detail. The values for the proton chemical shifts are reasonable for such species, and ^1J(PtP'), though large, is not exceptionally so in any of these species. It is worth noting that the chemical shift of P' in the chloride species (**8**) and (**8a**) is to high frequency of its value in the corresponding bromide; the shift from chloride to bromide is in the same direction[13] in PX_5 or POX_3, but in the opposite direction in PX_3 and in $PtP'X_2$, emphasising that species derived from (**8**) and (**13**) contain oxidised phosphorus.

Experimental

Volatile compounds were manipulated using vacuum systems fitted with greased glass or greaseless Sovirel taps; air-sensitive involatile materials were transferred under dry N_2 in glove-bags or in a Vacuum Atmospheres glove-box; purity was checked spectroscopically and (where appropriate) by measurement of vapour pressure. N.m.r. spectra were recorded using JEOL FX60Q (for ^{31}P), Bruker WP80A (for ^1H and ^{19}F), WP200 and WH360 (for ^1H and ^{31}P) spectrometers.

Platinum starting materials were prepared by standard methods. Boron and phosphorus trihalides were purchased. Phosphorus trichloride was purified in the vacuum system and measured by direct weighing. Phosphorus tribromide was not volatile enough for this; it was purified by bubbling dry N_2 through it for 5 min, followed by freeze-degassing, and measured using a standard solution in CD_2Cl_2: roughly the required amount was transferred to CD_2Cl_2 in a calibrated dispenser vessel in a glove-bag, using a syringe, and the concentration determined gravimetrically by precipitation of AgBr after hydrolysis. Typical experiments are described below.

(*a*) *Reaction of Complex* (**1**) *with* PCl_3.—An n.m.r. tube containing complex (**1**) (0.05 mmol) was attached to a vacuum system by a ground-glass joint and CD_2Cl_2 was added, followed by a weighed amount of PCl_3. The solution was kept at 90 K, and allowed to melt in the probe of the n.m.r. machine; spectra were obtained over a range of temperatures.

(*b*) *Reaction of Complex* (**1**) *with* PCl_3 *followed by* HCl.—The reaction mixture of complex (**1**) and PCl_3 was prepared as in (*a*), and kept at 200 K (30 min) before a measured amount of HCl was added; the tube was sealed, and spectra recorded.

(*c*) *Reaction of Complex* (**8**) *with* HCl.—An n.m.r. tube was made with a glass breakseal, as well as the usual ground-glass joint. A reaction mixture of complex (**1**) and PCl_3 was prepared as in (*a*), and the tube was sealed. The spectrum was monitored as the solution warmed until strong resonances due to (**8**) were observed. The contents of the tube were then frozen and the appropriate amount of HCl added through the breakseal. The tube was then resealed and the spectrum of the products obtained.

(*d*) *Reaction of Complex* (**8**) *with* NPr_4Cl.—A solution of complex (**1**) and PCl_3 was prepared in an n.m.r. tube with a breakseal as described in (*c*), and the reaction was allowed to continue until strong resonances due to (**8**) were observed. A weighed amount of NPr_4Cl was then added through the breakseal under vacuum, giving a ratio NPr_4Cl:PCl_3 of 4:3, and the tube was resealed.

(*e*) *Reaction of Complex* (**2**) *with* PBr_3.—The contents of an n.m.r. tube containing complex (**2**) (0.05 mmol) in a 1:1 mixture of CD_2Cl_2 and Et_2O were frozen and PBr_3 added either in rough quantity using the vacuum system or in accurately measured amounts using the standard solution and the dispenser. Spectra were recorded at temperatures from 150 K.

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