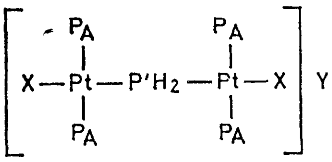
Monobridged Binuclear Platinum Complexes. Part 1. Some Phosphido-bridged Diplatinum Complexes of Triethylphosphine

By **E. A. V. Ebsworth,* Bernard J. L. Henner,** and **Francis J. S. Reed,** Department of Chemistry, West Mains Road, Edinburgh EH9 3JJ

The complexes $[\{PtX(PEt_3)_2\}_2PH_2]Y$ (X = H, Y = Cl or Br; X = Y = Cl or Br) have been prepared, and the structures of two isomers in $CDCl_3$ solution have been determined by ^{31}P n.m.r. spectroscopy. Both isomers are linked by single PH_2 bridges. The halide complexes partly decompose to give $[(Et_3P)X_2Pt(\mu\text{-}PH_2)PtX(PEt_3)_2]$ in $CDCl_3$ solution. Analogous iodide complexes have been identified from their ^{31}P n.m.r. spectra but could not be isolated. The bridging PH_2 group is relatively stable, and the spectroscopic parameters suggest that it has a greater *trans* influence than PEt_3 in these complexes.

Few platinum dimers linked by a single atom are known. One example is[1] $[Cl_3Pt(SMe_2)PtCl_3]^{2-}$ and we have recently shown that SH and SeH groups form complexes similar to (1).[2] The dicyclohexylphosphido-group has recently been reported to link two $Ni(CO)_3$ units in the complex $[\{Ni(CO)_3\}_2P(C_6H_{11})_2]$,[3] but a series of platinum complexes of PPh_2 reported earlier by Chatt and Davidson[4] were all doubly bridged. These workers commented that the PPh_2 bridge was easily the strongest known in the platinum(II) series of complexes.

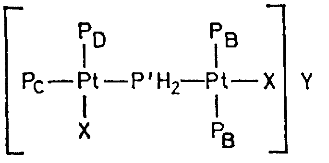
trans-trans cation



$$\left[X-\overset{P_A}{\underset{P_A}{Pt}}-P'H_2-\overset{P_A}{\underset{P_A}{Pt}}-X\right]Y$$

(1) X = H, Y = Cl or Br
(2) X = Y = Cl
(3) X = Y = Br
(4) X = Y = I

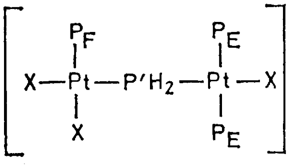
cis-trans cation



$$\left[P_C-\overset{P_D}{\underset{X}{Pt}}-P'H_2-\overset{P_B}{\underset{P_B}{Pt}}-X\right]Y$$

(5) X = H, Y = Cl
(6) X = Y = Cl
(7) X = Y = Br
(8) X = Y = I

neutral complex



$$\left[X-\overset{P_F}{\underset{X}{Pt}}-P'H_2-\overset{P_E}{\underset{P_E}{Pt}}-X\right]$$

(9) X = Cl
(10) X = Br
(11) X = I

A—F are referred to in Tables 1—3. The ethyl groups bound to P_A—P_F have been omitted for clarity

A study of the reactions of $PH_{3-n}(SiH_3)_n$ with some transition-metal complexes revealed that addition of $SiH_3(PH_2)$ to *trans*-$[PtCl(H)(PEt_3)_2]$ gave resonances in the ^{31}P n.m.r. spectrum corresponding to the phosphido-bridged complex (1).[5] The reaction mixture also contained *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$, which was previously characterised as the product from the reaction of $SiClH_3$ and $[PtCl(H)(PEt_3)_2]$,[6] and $[PtH(PEt_3)_3]^+$. It was thought that (1) could be made free from side products by the use of $SiMe_3(PH_2)$, since Si–C, unlike Si–H, bonds are unreactive towards $[PtCl(H)(PEt_3)_2]$. We have now completed our initial investigation of the reaction of $SiMe_3(PH_2)$ with a range of platinum–triethylphosphine substrates, and in this paper we present evidence for the formation of a number of novel complexes containing a single PH_2 bridge.

---

[1] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1974, 576.

[2] E. A. V. Ebsworth, H. M. Ferrier, B. J. L. Henner, D. W. H. Rankin, F. J. S. Reed, H. E. Robertson, and J. D. Whitelock, *Angew. Chem.*, 1977, **89**, 495.

[3] K. Jonas and L. Schieferstein, *Angew. Chem. Internat. Edn.*, 1976, **15**, 622.

[4] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433.

[5] J. M. Edward, Ph.D. Thesis, Edinburgh University, 1976.

[6] J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1971, 597.

The best available method for studying this type of reaction is ^{31}P n.m.r. spectroscopy, the products often being clearly defined by J(Pt–P) and J(P–P) couplings. In this case, the analysis is helped by the large difference in chemical shift between PH_2 and PEt_3, as a consequence of which most of the spectra are first order. For this reason the reactions were first carried out in n.m.r. tubes. It soon became apparent that it was necessary to have completely homogeneous reaction conditions, otherwise local concentrations of $SiMe_3(PH_2)$ gave insoluble precipitates and solutions containing mainly $[PtX(PEt_3)_3]^+$ (X = H or halide).

RESULTS

trans-trans Cations (1)—(4).—The reaction of *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl or Br) with $SiMe_3(PH_2)$ in $CDCl_3$ (mol ratio 2 : 1) was complete within 5 min at room temperature, giving a pale yellow solution. The major product in each case was complex (1), identified from its ^{31}P n.m.r. spectrum. The symmetrical bridging environment of the PH_2 group is defined by the platinum satellites (1 : 8 : 18 : 8 : 1) and further confirmed by the observation of a three-bond Pt–P coupling to the P nuclei of the triethylphosphine group. The additional ^2J(P–P), ^1J(P–H), and ^3J(P–H) couplings and multiplicities unambiguously define structure (1). A significant magnitude for the coupling ^2J(Pt–Pt) in this system would give extra resonances about the triethylphosphine–platinum satellites [7] and these were not observed.

TABLE 1

Phosphorus-31 n.m.r. parameters [a] for the *trans-trans* isomers in $CDCl_3$ at −50 °C

	Parameter							
Complex	δ(P′)	^2J(P′–P_A)	^1J(Pt–P′)	^1J(P′–H) [b]	^2J(P′–H) [c]	δ(P_A)	^1J(Pt–P_A)	^3J(Pt–P_A)
(1)	−169.7	18	1 202	280	137	16.6	2 537	12
(2)	−152.0	20	2 804	347		12.8	2 260	27
(3)	−147.8	20	2 788	348		9.2	2 238	31
(4)	−148.7	20	2 631	338		2.2	2 215	28

[a] Chemical shifts (δ/p.p.m.) were all positive to high frequency. Standards: ^1H, $SiMe_4$; ^{31}P, 85% H_3PO_4. The accuracy of the coupling constants (J) is ± 5 Hz. [b] From non-decoupled spectra. [c] From partially decoupled spectrum.

With $[PtH(I)(PEt_3)_2]$ the reaction was less straightforward. Observation of the ^{31}P spectrum at −50 °C before warming to room temperature shows that in this case a reaction has occurred and a monomeric product of the type *trans*-$[PtH(PEt_3)_2(PH_2Q)]$ is formed. It seems likely that Q is $SiMe_3$, but we cannot establish this from the spectroscopic parameters we recorded. On warming to room temperature this species decomposes to give a mixture of products. Only about half the peaks in the ^{31}P n.m.r. spectrum of the reaction mixture correspond to complex (1). The only other product we could identify from the ^{31}P spectrum was free PH_3. The remaining strong resonance (δ 16.1 p.p.m.) had platinum satellites [^1J(Pt–P) 2 413 Hz].

Solutions in $CDCl_3$ of the chloride and the bromide of cation (1) were stable at room temperature for several days. However, in the presence of a two-fold excess of $[PtH(Cl)(PEt_3)_2]$, *ca.* 25% decomposition had occurred within 2 h involving formation of $[PtH(PEt_3)_3]^+$. After 24 h this was the major species present and the solution was dark orange. No decomposition products of the PH_2 group were detected.

Complexes (2)—(4) were formed as the initial products from the reaction of *trans*-$[PtX_2(PEt_3)_2]$ and $SiMe_3(PH_2)$ in $CDCl_3$ (mol ratio 2 : 1). For the chloride, reaction did not occur until the solutions reached room temperature and then slow isomerisation took place. With the bromide, reaction was more rapid and with the iodide the initial reaction was complete at −46 °C and the product (4) isomerised at higher temperatures. The structures of these complexes are completely defined by their ^{31}P n.m.r. spectra. As with the hydride (1), no evidence for ^2J(PtPt) was found.

cis-trans Cations (5)—(8).—Complexes (1)—(3) isomerised at room temperature in $CDCl_3$ solution; after *ca.* 2 h an equilibrium concentration of *ca.* 5, 30, and 90% respectively of the *cis-trans* isomers (5)—(7) was obtained. For the iodide, isomerisation from (4) to (8) was complete after warming the solution to room temperature for a few minutes. The ^{31}P n.m.r. parameters are given in Table 2 and the couplings and multiplicities are consistent with the formulations given. The long-range ^3J(Pt–P) coupling is only observed here for the resonance of the triethylphosphine *trans* to the bridging PH_2 group. Again there is no indication of ^2J(PtPt). The spectrum of (7) is shown in Figures 2 and 3.

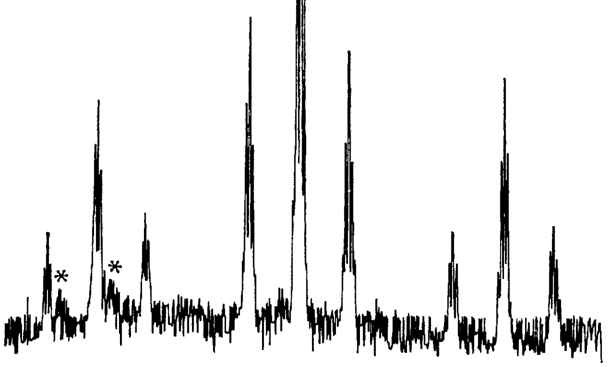


FIGURE 1 Phosphorus-31 n.m.r. spectrum of the PH_2 part of complex (2) in $CDCl_3$ at −50 °C. *Not* ^1H decoupled. The asterisks correspond to complex (6)

---

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965.

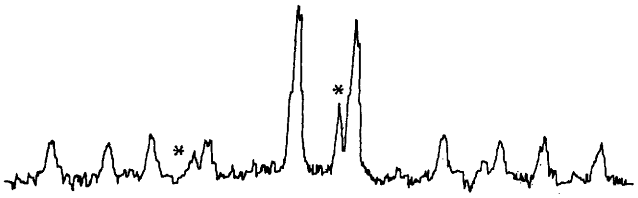


FIGURE 2 ^{31}P-{^{1}H} N.m.r. spectrum of the PH_2 part of complex (7) in $CDCl_3$ at −60 °C. The asterisk corresponds to complex (10)

Neutral Complexes (9)—(11).—While the hydride complexes (1) and (5) are stable in $CDCl_3$ solution for several days, with the halide complexes another PH_2-bridged species was observed, the proportion of which increased in the order Cl < Br < I. The ^{31}P n.m.r. parameters for the PH_2 group are well defined and are listed in Table 3. They show the PH_2 group to be bound to two chemically distinct platinum nuclei and also to be coupled to three *cis*-phosphorus nuclei. This suggests that the neutral species (9)—(11) are being formed. For the iodide this neutral complex was the major product after 2 h at room temperature [*ca.* 90%, the relative amounts of (8) and (11) being independent of temperature] and it was possible to assign the PEt_3 resonances. However, for the chloride and bromide the concentration of the neutral complex never exceeded *ca.* 30% of the total reaction mixture and it was not possible to positively distinguish its PEt_3 resonances from those of the cationic isomers present. The evidence for the structures of these neutral complexes is therefore less certain than for the cations, but our formulation is consistent with the change in ^{31}P n.m.r. parameters with change of halide. We have also prepared and characterised a PF_2-bridged analogue of (11).[8] The iodide, (11), decomposed in $CDCl_3$ at room temperature to give increasing amounts of *trans*-[$PtI_2(PEt_3)_2$] and a resonance at 20.2 p.p.m., without platinum satellites, due to [PEt_3H]$^+$. Small amounts of this phosphonium ion were detected with the other halides after long standing, but other decomposition products were not identified.

TABLE 2

Phosphorus-31 n.m.r. prameters * for the *cis-trans* isomers in $CDCl_3$

	Parameter							
Complex	$\delta(P')$	$^{2}J(P'-P_C)$	$^{2}J(P'-P_B)$	$^{1}J(Pt-P')$	$^{1}J(P'-H)$	$\delta(P_B)$	$^{2}J(P_B-P')$	$^{1}J(Pt-P_B)$
(5)	−168.6	277	17	1 205 1 347	n.o.	7.6	17	2 554
(6)	−117.1	363	18(q)	3 054 1 887	324	11.7	22	2 316
(7)	−121.8	363	14(d) 22(t)	3 090 1 830	325	7.3	21	2 302
(8)	−136.6	365	n.o.	2 048 1 745	320	−0.3	19	2 277

Complex	$\delta(P_C)$	$^{2}J(P_C-P')$	$^{1}J(Pt-P_C)$	$^{3}J(Pt-P_C)$	$\delta(P_D)$	$^{2}J(P_D-P')$	$^{1}J(Pt-P_D)$
(5)	17.4	n.o.	2 592	n.o.	7.6	17	1 968
(6)	14.6	17	2 256	18	3.5	17(t)	3 366
(7)	10.1	17	2 240	16	2.9	16(t)	3 365
(8)	4.4	17	2 236	n.o.	2.7	12(d)	3 247

* Complexes (5)—(7) were examined at room temperature, (8) at −20 °C. d = Doublet, q = quartet, t = triplet, n.o. = not observed. See also footnote *a* in Table 1.

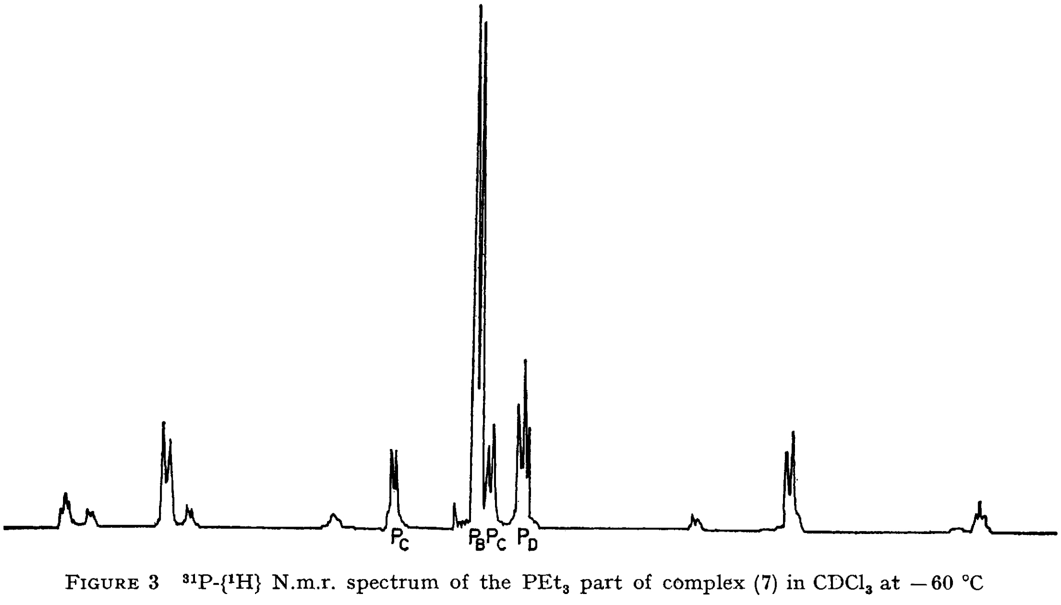


FIGURE 3 ^{31}P-{^{1}H} N.m.r. spectrum of the PEt_3 part of complex (7) in $CDCl_3$ at −60 °C

Preparative Reactions.—All attempts to isolate complex (1) from reactions in $CHCl_3$ or CH_2Cl_2 resulted in the formation of intractable gums, as did attempts to stabilise the

---

[8] J. Whitelock and E. A. V. Ebsworth, unpublished work.

cation by addition of $[BPh_4]^-$ or $[BF_4]^-$. However, in toluene a similar reaction slowly formed a microcrystalline precipitate and after washing with diethyl ether the pure complex (1) was obtained in *ca.* 80% yield. The pale yellow complex is indefinitely stable at room temperature under dry nitrogen but decomposes rapidly in air, the P–H stretching band disappearing from the i.r. spectrum.

The reaction of *trans*-$[PtX_2(PEt_3)_2]$ (X = Cl or Br) with $SiMe_3(PH_2)$ in toluene gave white solids with elemental analyses corresponding to (2) and (6), and (3) and (7) respectively. On redissolving in $CDCl_3$ and recording ^{31}P n.m.r. spectra at -50 °C before warming to room temperature, the solids were shown to be the *cis-trans* isomers (6) and (7). Complexes (1), (6), and (7) all gave conducting solutions in CH_2Cl_2.

TABLE 3

Phosphorus-31 n.m.r. parameters * of the neutral complexes at room temperature in $CDCl_3$

	Parameter								
Complex	$\delta(P')$	$^2J(P'-P)$	$^1J(Pt-P')$	$\delta(P_E)$	$^2J(Pt-P_E')$	$^1J(Pt-P_E)$	$\delta(P_F)$	$^2J(P_F-P')$	$^1J(Pt-P_F)$
(9)	-120.9	n.o.	2 630 1 880	11.7	21	2 332	n.o.	n.o.	n.o.
(10)	-124.9	11	2 680 1 850	7.45	22	2 320	4.1	13	3 260
(11)	-138.7	11	2 630 1 758	0.0	19	2 302	5.8	n.o.	3 140

* See footnote *a* in Table 1.

An attempt was made to convert the *cis-trans* cations (6) and (7) completely into the neutral isomers by warming them to 50 °C under toluene for several hours. The only identifiable product after this treatment was *cis*-$[PtX_2(PEt_3)_2]$ (X = Cl or Br).

DISCUSSION

We have found that the first product obtained on reaction of *trans*-$[PtX_2(PEt_3)_2]$ (X = Cl, Br, or I) or *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl or Br) with $SiMe_3(PH_2)$ is the *trans-trans* complex. By analogy with the reaction of other phosphines with these platinum substrates, a possible mechanism involves an initial displacement of halide to form a cationic monomer, as shown in (1) for $[PtCl(H)(PEt_3)_2]$.

$$\begin{tikzcd}
 & {[PtCl(H)(PEt_3)_2] + SiMe_3(PH_2)} \arrow[r] & {[PtH(PEt_3)_2\{PH_2(SiMe_3)\}Cl]} \arrow[d] \\
(1) & {[\{PtH(PEt_3)_2\}PH_2]^+} & {[PtH(PH_2)(PEt_3)_2] + SiMe_3Cl} \arrow[l, "{[PtCl(H)(PEt_3)_2]}"']
\end{tikzcd}$$

A similar mechanism is possible in the other cases. As only this one product is formed and the intermediates are not detected the implication is that the final bridging step is fast. Thus the $Pt-PH_2$ group appears a much better nucleophile than either $SiMe_3(PH_2)$ or PH_3. This is reinforced by the sharpness of the

$$[PtCl(H)(PEt_3)_2] + PH_3 \rightleftharpoons [PtH(PH_3)(PEt_3)_2]Cl \text{ (ref. 9)} \quad (2)$$

i.e. in this case:

$$[PtCl(H)(PEt_3)_2] + PH_2R \rightleftharpoons [PtH(PEt_3)_2(PH_2R)]Cl$$
$$R = PtH(PEt_3)_2$$

^{31}P n.m.r. spectrum of complex (1) at room temperature which shows that no exchange parallel to (2) takes place. The equilibrium analogous to (2) was not observed in a mixture of $[PtCl(H)(PEt_3)_2]$ and $SiMe_3(PH_2)$ at low temperature, the ^{31}P n.m.r. spectrum at -60 °C showing only sharp resonances due to the starting materials. An alternative mechanism involving oxidative addition as the first step is possible, *i.e.* as in (3). The reaction between $SiMe_3(PH_2)$ and *trans*-$[PtH(I)(PEt_3)_2]$ is clearly somewhat different. The unstable species initially formed could correspond to a cation like that postulated in the first step of (1); on the other hand, the formation of PH_3 could well come from reductive elimination from a six-co-ordinate species like that in (3).

The *trans* influence of the bridging PH_2 group may be judged, from the low value of the $J(Pt-P_c)$ coupling in these complexes (Table 2) and the Pt–H stretching frequency of 2 030 cm^{-1} for complex (1) compared to 2 120 cm^{-1} in $[PtH(PEt_3)_3]^+$, to be greater than that of PEt_3. This high *trans* influence, weakening the $Pt-P_c$ bond, also accounts for the equilibrium between the *cis-trans* and the neutral isomer.

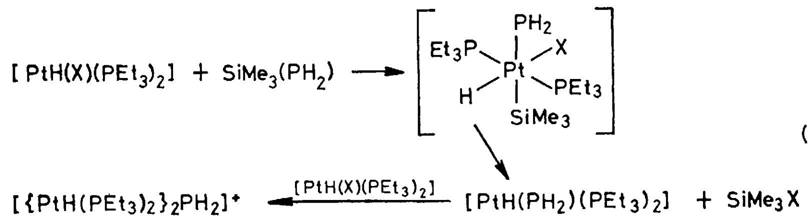
A study of molecular models of the *trans-trans* complexes (assuming tetrahedral co-ordination about the PH_2 bridge) reveals that the PEt_3 groups are considerably hindered regardless of the twist angle between the co-ordination planes round platinum. This steric strain is noticeably relieved by isomerisation to the *cis-trans* isomer, the most favourable conformation being with the two platinum co-ordination planes at right angles to each other. We have obtained no evidence for the formation of a *cis-cis* isomer in any of these reactions, and the reaction of *cis*-$[PtX_2(PEt_3)_2]$ with $SiMe_3(PH_2)$ (X = Cl or Br) gave only complexes (6) and (9), and (7) and (10) respectively. An attempt to produce a *cis-cis* isomer by the reaction of $SiMe_3(PH_2)$ with

---

[9] E. A. V. Ebsworth, J. M. Edward, F. J. S. Reed, and J. D. Whitelock, *J.C.S. Dalton*, submitted for publication.

$[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ was not successful because of the extreme insolubility of the products.

We have also investigated the reactions of $SiMe_3(PH_2)$ with $[NPr^n_4][PtCl_3(PEt_3)]$, $[Pt_2Cl_4(PEt_3)_2]$, and $[PtH(PEt_3)_3][BPh_4]$ but in no instance was it possible clearly to define the products.


(3)

EXPERIMENTAL

N.m.r. and i.r. measurements were made as described in ref. 10. All the manipulations were carried out *in vacuo* or in a dry nitrogen atmosphere. Platinum-containing starting materials were prepared by standard methods. Solvents were dried and freshly distilled before use.

Trimethylphosphinosilane was prepared from $P(SiMe_3)_3$ (supplied by Laramie Chemical Company) by a modification of the literature method.[11-13] To $P(SiMe_3)_3$ (10 mmol) was added water (10 mmol) in diglyme (0.7 cm^3) and the mixture shaken at room temperature for 12 h. Vacuum distillation through traps at -24 and -96 to -196 °C separated a mixture of $SiMe_3(PH_2)$ and $O(SiMe_3)_2$ at -96 °C. The ratio of the proportions of these components as measured by ^1H n.m.r. was usually 70 : 30 and this mixture was used in these reactions.

Standard Method for N.M.R. Tubes.—The platinum substrate (0.1 mmol) was weighed into an n.m.r. tube blown on to a B 10 cone and connected *via* a detachable tap to a vacuum line. Deuteriochloroform (0.5 cm^3) was condensed into the tube and the complex was completely dissolved (if possible). The compound $SiMe_3(PH_2)$ (0.05 mmol) was then condensed into the tube in four equal portions, the mixture being warmed to -46 °C and shaken in between each addition. The tube was then sealed and stored at -196 °C.

Preparation of μ-Phosphido-bis[hydridobis(triethylphosphine)platinum(II)] *Chloride* (1).—$[PtCl(H)(PEt_3)_2]$ (1 mmol) was dissolved in toluene (2 cm^3) in a Schlenk tube and $SiMe_3(PH_2)$ (0.5 mmol) condensed into the tube on a vacuum line. The mixture was warmed to room temperature with vigorous shaking and allowed to stand for 2 h, a pale yellow precipitate being formed. The solvent was removed with a syringe under a nitrogen atmosphere and the solid was washed twice with diethyl ether (5 cm^3) and dried *in vacuo* to yield the pure complex (Found: C, 31.05; H, 6.95. Calc. for $C_{24}H_{64}ClP_5Pt_2$: C, 30.9; H, 6.85%), ν(Pt–H) at 2 030s cm^{-1}, ν(P–H) at 2 280m cm^{-1}; decomposes at >85 °C. Complexes (6) and (7) were prepared by similar methods starting from *trans*-$[PtX_2(PEt_3)_2]$ (X = Cl or Br): $[\{PtCl(PEt_3)_2\}_2PH_2]Cl$ (Found: C, 29.0; H, 6.10. Calc. for $C_{24}H_{62}Cl_3P_5Pt_2$: C, 28.75; H, 6.20%), ν(P–H) at 2 290br cm^{-1}, decomposes at >118 °C; $[\{PtBr(PEt_3)_2\}_2PH_2]Br$ (Found: C, 25.65; H, 5.45. Calc. for $C_{24}H_{62}Br_3P_5Pt_2$: C, 25.4; H, 5.50%), ν(P–H) at 2 300br cm^{-1}, decomposes at >125 °C.

We thank Johnson, Matthey Ltd. for lending us platinum starting materials, and I.C.I. Ltd. for the award of a Fellowship (to F. J. S. R.).

[7/1475 *Received*, 15*th August*, 1977]

---

[10] E. A. V. Ebsworth, J. M. Edward, and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 1667.

[11] H. Burger and W. Goetz, *J. Organometallic Chem.*, 1968, **12**, 451.

[12] H. Burger, W. Goetz, and W. Arvodny, *Spectrochim. Acta*, 1970, **A26**, 671.

[13] E. Fluck, H. Burger, and W. Goetze, *Z. Naturforsch.*, 1967, **B22**, 912.