Silyl and Germyl Complexes of Platinum and Palladium. Part 4.[1] Reactions between Four-co-ordinated Halogenohydridobis(triethylphosphine)-platinum(II) Complexes and Silyl-amines or -phosphines

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Reactions between $NH(SiH_3)_2$ and *trans*-[PtH(I)$(PEt_3)_2$] give *trans*-[PtI$(PEt_3)_2(H_2SiNHSiH_3)$] and *trans*-[{PtI$(PEt_3)_2(SiH_2)$}$_2$NH]; with $N(SiH_3)_3$, only *trans*-[PtI$(PEt_3)_2\{H_2SiN(SiH_3)_2\}$] is formed, probably for steric reasons. With $PH_2(SiH_3)$ or $PH(SiH_3)_2$, PH_3 and *trans*-[PtI$(PEt_3)_2(SiH_3)$] are produced; $P(SiH_3)_3$ reacts with a four-fold excess of *trans*-[PtH(I)$(PEt_3)_2$] to give PH_3 and *trans*-[PtI$(PEt_3)_2(SiH_3)$], but with reacting ratios (phosphine : Pt) between 1 : 1 and 2 : 1 the products are *trans*-[PtI$(PEt_3)_2\{H_2SiP(SiH_3)_2\}$] and *trans*-[{PtI$(PEt_3)_2$-$(SiH_2)$}$_2PSiH_3$]. The only silyl compound of this series to give an identifiable species with *trans*-[PtCl(H)$(PEt_3)_2$] is $PH_2(SiH_3)$ which produces *trans,trans*-[$PH_2\{PtH(PEt_3)_2\}_2$]$^+$. The complexes described have been characterised by ^1H and ^{31}P n.m.r. spectroscopy and by heteronuclear double resonance. Most of these reactions are considered to involve derivatives of six-co-ordinate platinum as intermediates.

IN earlier papers [1-4] we have discussed the reactions between platinum complexes *trans*-[PtX(H)$(PEt_3)_2$] (X = Cl, Br, or I) and silyl halides or silyl derivatives of the elements of Group 6. Here we describe reactions of some silyl-amines and -phosphines with *trans*-[PtH(I)-$(PEt_3)_2$] or the corresponding chloro-complex.

RESULTS

Reactions of $N(SiH_3)_3$.—*With* trans-[PtH(I)$(PEt_3)_2$]. When a solution in toluene containing equimolar amounts of $N(SiH_3)_3$ and *trans*-[PtH(I)$(PEt_3)_2$] was allowed to warm from 177 K, no apparent reaction occurred until the system had reached room temperature. A slow effervescence began at that stage, and reaction appeared complete after 15 min. The n.m.r. spectrum of the resulting solution showed a resonance due to H_2, and peaks that could be assigned to the protons of the monoplatinum complex *trans*-[PtI$(PEt_3)_2\{H_2SiN(SiH_3)_2\}$], formed by reaction (1)

$$N(SiH_3)_3 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow H_2 + trans\text{-}[PtI(PEt_3)_2\{H_2SiN(SiH_3)_2\}] \quad (1)$$

that involves elimination of H_2. The SiH_3 resonance appeared with ^{195}Pt satellites, but neither $^4J(HH)$ nor $^5J(HP)$ was detected. The SiH_2 resonance was a 1 : 2 : 1 triplet with platinum satellites; the central peak was one sixth the height of the central peak in the SiH_3 resonance. The spectra of a sample made from $^{15}N(SiH_3)_3$ in 90% enrichment showed additional doublet splittings on each line. Various n.m.r. parameters were determined by direct observation of the ^{31}P spectrum and by heteronuclear double resonance; they are given in Tables 1 and 2 and are discussed below. The mono complex was the only silyl species detected in the system, even when a three-fold molar excess of the platinum complex was used initially.

With trans-[PtCl(H)$(PEt_3)_2$]. Reaction in toluene of the two reagents in equimolar proportions was slow; the ^1H n.m.r. spectrum seemed unchanged after 30 min at room temperature. After a somewhat longer period, the resonance due to $N(SiH_3)_3$ disappeared suddenly and the solution separated into two phases. There was no evidence of the presence of $SiClH_3$ in either phase, although the lower phase, being very viscous, gave poor n.m.r. spectra. The ^{31}P

TABLE 1

Chemical shifts for platinum complexes of $N(SiH_3)_3$, $NH(SiH_3)_2$, and $P(SiH_3)_3$

Complex	δ(SiH_3)	δ(SiH_2)	δ(PEt$_3$)	δ(Si–^{15}N/Si–P)	δ(^{195}Pt)
trans-[PtI$(PEt_3)_2(H_2SiNHSiH_3)$]	4.23	4.04	12.8	n.s.	−400
trans-[{PtI$(PEt_3)_2(SiH_2)$}$_2$NH]		4.14	13.0	n.s.	−388
trans-[PtI$(PEt_3)_2\{H_2SiN(SiH_3)_2\}$] *	4.58	4.39	10.7	−64.3	−378
trans-[PtI$(PEt_3)_2\{H_2SiP(SiH_3)_2\}$]	4.07	3.69	9.23	−345.2	−315
trans-[{PtI$(PEt_3)_2(SiH_2)$}$_2PSiH_3$]	4.08	n.o.	9.47	−308.1	n.o.

Standards: ^{15}N, $[NMe_4]I$; ^{31}P, 85% H_3PO_4; ^{195}Pt, 0.5 mol dm^{-3} *trans*-[PtCl(H)$(PEt_3)_2$] in CH_2Cl_2 at 300 K; ^1H, $SiMe_4$. All shifts positive to high frequency. n.o. = Not observed, n.s. = not studied.

* δ(^{29}Si) for SiH$_3$ groups = −41.4 p.p.m. (relative to $SiMe_4$ = 0, positive to high frequency).

TABLE 2

Coupling constants (Hz) for platinum complexes derived from $N(SiH_3)_3$, $NH(SiH_3)_2$, and $P(SiH_3)_3$. The SiH_3 groups are labelled A and the SiH_2 groups are labelled B

Complex	$^2J(H_A-^{15}N/P)$	$^2J(H_B-^{15}N/P)$	$^3J(H_B-P)$	$^2J(H_B-Pt)$	$^4J(H_A-Pt)$	$^1J(PtP)$	$^2J(Pt-^{15}N/P)$	$^3J(P-^{15}N/P)$	$^1J(^{29}Si_AH_A)$	$^1J(Si^{15}N/P)$
trans-[PtI$(PEt_3)_2(H_2SiNHSiH_3)$] *	n.s.	n.s.	9.5	86	8	2 520	n.s.	n.s.	n.o.	n.s.
trans-[{PtI$(PEt_3)_2(SiH_2)$}$_2$NH]	n.s.	n.s.	9	84		2 565	n.s.	n.s.	n.o.	n.s.
trans-[PtI$(PEt_3)_2\{H_2SiN(SiH_3)_2\}$]	−4.2	−4.5	+9.5	+90	+6	+2 446	−30	<0.2	−208	+12
trans-[PtI$(PEt_3)_2\{H_2SiP(SiH_3)_2\}$]	+16.5	+14	+8.0	n.o.	+9.5	+2 437	219	1.6	−206	45
trans-[{PtI$(PEt_3)_2(SiH_2)$}$_2PSiH_3$]	+16.0	n.o.	n.o.	n.o.	9.5	2 525	230	n.o.	n.o.	50

In $^{15}NH(SiH_3)_2$ ^3J(HH) 4 ± 1 and $^1J(^{29}SiH)$ 209 ± 1 Hz. Signs of coupling constants, which were determined only where they are explicitly given, were measured relative to ^1J(PtP) assumed positive. n.o. = Not observed, n.s. = not studied.

* $^3J[H_A-(N)H]$ 3 ± 1; $^3J[H_B-(N)H]$ = 2 ± 1 Hz.

[1] Part 3, E. A. V. Ebsworth, J. M. Edward, and D. W. H. Rankin, preceding paper.

[2] Part 2, J. E. Bentham and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1971, 2091.

[3] J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1971, 587.

[4] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 2370.

spectrum of the upper phase showed that the main component containing phosphorus was *trans*-$[PtCl(H)(PEt_3)_2]$. In the lower phase there were 1 : 4 : 1 pseudo-triplet patterns for four different phosphine complexes of platinum (see Table 3); one set of peaks could be assigned to *trans*-$[PtCl(H)(PEt_3)_2]$ and another to the cation [5] $[PtH(PEt_3)_3]^+$. The other two species were not identified. Their ^{31}P n.m.r. parameters [δ −28 and −31 p.p.m.; $^1J(PtP)$ 1 280 and *ca.* 1 280 Hz] are very close to those observed for unidentified complexes found in the reactions between $Se(SiH_3)_2$ and *trans*-$[PtCl(H)(PEt_3)_2]$ or its bromo-analogue [1] (see Table 4).

In an attempt to prevent the separation into two phases, the reaction was allowed to occur in CH_2Cl_2. Three sets of broad resonances (5.1, 4.7, and 4.4 p.p.m.) were observed in the ^1H spectrum in addition to very sharp peaks due to the solvent and to H_2, with two Pt*H* resonances. One of the Pt*H* resonances [−16.6 p.p.m., $^2J(PtH)$ 1 230 Hz] was due to *trans*-$[PtCl(H)(PEt_3)_2]$; the other [−8.75 p.p.m., $^2J(PtH)$ 720 Hz; sharpened by irradiation at δ(P) −26 p.p.m.] was broad. The ^{31}P spectrum of the solution showed that the main phosphorus-containing components were *trans*-$[PtCl(H)(PEt_3)_2]$ and a complex containing platinum [δ(P) −26.6 p.p.m., $^1J(PtH)$ 1 285 Hz]. Trace amounts of *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$ and $[PtH(PEt_3)_3]^+$ were also present.

Reactions of $NH(SiH_3)_2$.—*With* trans-$[PtH(I)(PEt_3)_2]$. Pure disilylamine is very difficult to prepare,[6] and our samples were all contaminated with small amounts of $N(SiH_3)_3$ and SiH_4. However, the course of the reaction between $NH(SiH_3)_2$ and *trans*-$[PtH(I)(PEt_3)_2]$ could be established clearly. When equimolar amounts of the reagents were allowed to mix in toluene or methylene chloride at room temperature there was a vigorous effervescence; H_2 was evolved, and the n.m.r. spectrum of the solution showed that a monoplatinum complex had been formed [equation (2)]. The SiH_3 resonance of the product showed the

$$NH(SiH_3)_2 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(H_2SiNHSiH_3)] + H_2 \quad (2)$$

expected 1 : 4 : 1 pseudo-triplet pattern, with an additional small doublet splitting due to the N*H* proton. Similarly, the SiH_2 resonance (a 1 : 2 : 1 triplet with ^{195}Pt satellites) showed an additional doublet splitting. The N*H* resonance itself was not observed; this sort of resonance is notoriously difficult to detect in secondary silylamines unless ^{15}N-substituted species are studied, and we did not make any $^{15}NH(SiH_3)_2$ for this purpose. The ^{31}P spectra give values for the phosphorus chemical shift of the platinum complex, and also showed the presence of small amounts of *trans*-$[PtI(PEt_3)_2(SiH_3)]$ and *trans*-$[PtI(PEt_3)_2\{H_2SiN(SiH_3)_2\}]$, formed by reaction of *trans*-$[PtH(I)(PEt_3)_2]$ with the impurities mentioned above. With an initial two-fold molar excess of the platinum hydride the same silylaminomonoplatinum complex was first formed, but the ultimate product was the bis complex [equation (3)]. The SiH_2 resonance of

$$trans\text{-}[PtI(PEt_3)_2(H_2SiNHSiH_3)] + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[\{PtI(PEt_3)_2(SiH_2)\}_2NH] + H_2 \quad (3)$$

this product showed the expected 1 : 2 : 1 pattern with ^{195}Pt satellites, each peak showing a further doublet split-

TABLE 3

N.m.r. parameters for the cation *trans,trans*-$[PH_2\{PtH(PEt_3)_2\}_2]^+$. Labelling: Pt*H* = H_E; P*H* = H_F; *P*H_2 = P^1; and *P*Et_3 = P^2

Solvent	δ(H_E)	δ(H_F)	δ(P^1)	δ(P^2)	δ(^{195}Pt)
	p.p.m.				
C_7D_8	−5.6 ± 0.01	n.o.	−172.0 ± 0.1	17.4 ± 0.1	n.m.
CD_2Cl_2	−5.7 ± 0.01	n.o.	−170.0 ± 0.1	17.0 ± 0.1	n.m.

	$^1J(P^1H_F)$	$^1J(PtH_E)$	$^2J(P^2H_E)$	$^2J(P^1H_E)$	$^1J(PtP^2)$	$^1J(PtP^1)$	$^2J(P^1P^2)$
	Hz						
C_7D_8	300	908	15	126	2 525	1 230	17.4
CD_2Cl_2	n.o.	n.o.	15	127	2 536	1 210	18.4
	±5	±10	±5	±5	±5	±10	±1

n.m. = Not measured, n.o. = not observed.

TABLE 4

Some n.m.r. parameters for unidentified intermediates in reactions between silyl compounds and platinum hydrides

Reaction system	δ(Pt*H*) p.p.m.	$^1J(PtH)$ Hz	δ(P) p.p.m.	$^1J(PtP)$ Hz	Ref.
$Se(SiH_3)_2$/*trans*-$[PtBr(H)(PEt_3)_2]$	n.o.	n.o.	−32	1 220	1
	n.o.	n.o.	−33.1	1 200	1
$S(SiH_3)_2$/*trans*-$[PtCl(H)(PEt_3)_2]$	−13.56	1 098	−17.4	n.o.	1
	−8.78	664	4.1	n.o.	1
$Se(SiH_3)_2$/*trans*-$[PtCl(H)(PEt_3)_2]$	−13.78	1 136	−20.1	n.o.	1
	−8.32	652	1.0	n.o.	1
			−31.0	1 228	1
			−32.8	1 214	1
			−30.2	1 250	1
$NH(SiH_3)_2$/*trans*-$[PtCl(H)(PEt_3)_2]$			−28	1 280	*
$N(SiH_3)_3$/*trans*-$[PtCl(H)(PEt_3)_2]$			−28	1 280	*
			−31	1 280	*
$N(SiH_3)_3$/*trans*-$[PtCl(H)(PEt_3)_2]$	−8.75	720	−26.6	1 285	*

* This work.

[5] T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846.
[6] D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 1215.

ting. The n.m.r. parameters for both complexes are given in Tables 1 and 2 and are discussed below.

With trans-$[PtCl(H)(PEt_3)_2]$. Disilylamine and *trans*-$[PtCl(H)(PEt_3)_2]$ reacted immediately with effervescence in toluene at room temperature. The ^1H n.m.r. spectrum of the resulting yellow solution was ill defined; a peak possibly due to $SiClH_3$ was observed. The ^{31}P spectrum showed that substantial amounts of *trans*-$[PtCl(H)(PEt_3)_2]$ remained, and *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$ had been formed. An intermediate was also produced [δ(P) -28 p.p.m., ^1J(PtP) 1 280 Hz], but its resonances disappeared after 30 min. A similar study of the reaction in methylene chloride gave no more definite results.

Reactions of $P(SiH_3)_3$.—*With* trans-$[PtH(I)(PEt_3)_2]$. When the two reagents were allowed to mix in equimolar proportions in toluene at 213 K there was a slow effervescence; H_2 was evolved and some $P(SiH_3)_3$ remained. In the ^1H n.m.r. spectrum a strong doublet with ^{195}Pt and ^{29}Si satellites was observed, with a much weaker doublet of 1 : 2 : 1 triplets (too weak to detect ^{195}Pt satellites). The doublet splittings in each of these resonances were shown by heteronuclear double resonance to be associated with the same phosphorus nucleus (δ -345 p.p.m.). These observations can all be interpreted in terms of the formation of a monoplatinum complex with elimination of H_2 [equation (4)]. In keeping with this interpretation the ^{31}P spectrum

$$P(SiH_3)_3 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2\{H_2SiP(SiH_3)_2\}] + H_2 \quad (4)$$

of the system showed two resonances besides that due to excess of $P(SiH_3)_3$. One of these resonances appeared with ^1H decoupled as a 1 : 4 : 1 pseudo-triplet [δ(P) 9.2 p.p.m., ^1J(PtP) 2 437 Hz] with a small additional doublet splitting [^3J(PP) 1.6 Hz] on each line. This resonance is assigned to the P nuclei of the PEt_3 groups. The other resonance (δ -345 p.p.m.) also appeared as a 1 : 4 : 1 pseudo-triplet [^2J(PtP) 219 Hz] when ^1H was decoupled; it had silicon satellites [$^1J(^{29}SiP)$ 45 Hz]. With proton coupling retained, this resonance showed seven of the nine lines expected if $^2J(H_3SiP)$ and $^2J(H_2SiP)$ are indistinguishable; from the ^1H spectra the difference in coupling constants should be 1.5 Hz. The identity of this species is established beyond reasonable doubt; the values of δ(P) and ^1J(SiP) for the silylphosphorus nucleus are not very different from those [7] for $P(SiH_3)_3$ [δ(P) -373 p.p.m., ^1J(SiP) 42 Hz]. We have to assume that the phosphorus is equally coupled to both types of silicon nucleus.

The ^{31}P spectrum of a reaction mixture containing a two-fold excess of *trans*-$[PtH(I)(PEt_3)_2]$ showed additional peaks at 9.47 and -308.1 p.p.m. The former was of the usual 1 : 4 : 1 pseudo-triplet form [^1J(PtP) 2 525 Hz]; each line was somewhat broadened even when protons were decoupled, but no additional splittings were resolved. The latter had ^{195}Pt satellite lines (J 230 Hz; identity confirmed by heteronuclear double resonance), but the overall pattern of the resonance was a 1 : 8 : 18 : 8 : 1 quintet and not the expected 1 : 4 : 1 pseudo-triplet. The chemical shift of this resonance, and the observation of ^{29}Si satellites [^1J(SiP) 50 Hz], show that this P nucleus is bound to silicon; the relative intensities of the Pt satellites can be understood if the phosphorus nuclei concerned are each bound to two platinum atoms, *i.e.* if the compound is a diplatinum complex [equation (5)]. Unfortunately the peak at δ -308 p.p.m. showed no resolved fine structure when the spectrum was recorded with ^1H coupling retained. However, it is quite likely that restricted rotation and/or increased differences between $^2J(H_3SiP)$ and $^2J(H_2SiP)$ might prevent

$$trans\text{-}[PtI(PEt_3)_2\{H_2SiP(SiH_3)_2\}] + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[\{PtI(PEt_3)_2(SiH_2)\}_2PSiH_3] + H_2 \quad (5)$$

resolution; even in the corresponding resonance of *trans*-$[PtI(PEt_3)_2\{H_2SiP(SiH_3)_2\}]$ the peaks are broad. In the ^1H spectrum only the SiH_3 resonance could be identified, with its platinum satellites. No trace of a tris complex was detected in either ^1H or ^{31}P spectra. The n.m.r. parameters are given in Tables 1 and 2 and are discussed below.

The mono- and di-platinum complexes of trisilylphosphine described above were formed if the molar proportions of *trans*-$[PtH(I)(PEt_3)_2]$ and $P(SiH_3)_3$ were between 1 : 1 and 2 : 1. When a four-fold excess of *trans*-$[PtH(I)(PEt_3)_2]$ was used initially the reaction followed a different path. The main products were PH_3 and *trans*-$[PtI(PEt_3)_2(SiH_3)]$, although $PH(SiH_3)_2$ was identified as an intermediate. The identities of these products were determined beyond doubt by the many n.m.r. parameters that could be determined for each. Small amounts of *trans*-$[\{PtI(PEt_3)_2(SiH_2)\}_2PSiH_3]$ were also present among the products of the 1 : 4 reaction, but none of the mono complex was detected.

With trans-$[PtCl(H)(PEt_3)_2]$. When $P(SiH_3)_3$ was allowed to react with a two- or three-fold molar excess of *trans*-$[PtCl(H)(PEt_3)_2]$ in toluene at 213 K the initial ^1H spectrum showed peaks due to $P(SiH_3)_3$, $PH(SiH_3)_2$, $SiClH_3$, SiH_4, and H_2. After some minutes at 213 K, the $PH(SiH_3)_2$ resonances disappeared and peaks due to PH_3 and *trans*-$[PtCl(PEt_3)_2(SiH_3)]$ developed. At room temperature both reaction systems separated into two phases within *ca.* 1 min. The ^{31}P spectra were very broad; only peaks due to *trans*-$[PtCl(H)(PEt_3)_2]$ and $[PtH(PEt_3)_3]^+$ could be identified.

Reactions of Disilylphosphine.—With trans-$[PtH(I)(PEt_3)_2]$. When $PH(SiH_3)_2$ was allowed to react with an equimolar amount of *trans*-$[PtH(I)(PEt_3)_2]$ in toluene at 233 K effervescence occurred. The ^1H spectrum initially observed contained peaks due to $PH(SiH_3)_2$, $PH_2(SiH_3)$, and PH_3, with trace amounts of H_2 and SiH_4; the ^{31}P spectrum showed the presence of $PH(SiH_3)_2$ and $PH_2(SiH_3)$, but these compounds disappeared rapidly from the system. The main platinum-containing product was *trans*-$[PtI(PEt_3)_2(SiH_3)]$, although the ^{31}P spectrum showed the presence of a trace amount of *trans*-$[PtI(PEt_3)_2(SiH_2I)]$. The solution was pale yellow when reaction was complete and contained a fine white precipitate.

With trans-$[PtCl(H)(PEt_3)_2]$. A rapid reaction occurred when $PH(SiH_3)_2$ and a two-fold molar excess of *trans*-$[PtCl(H)(PEt_3)_2]$ were allowed to warm to room temperature in toluene. The resonances due to $PH(SiH_3)_2$ disappeared and the solution quickly separated into two phases. The ^{31}P spectra were very broad; the only species identified were *trans*-$[PtCl(H)(PEt_3)_2]$ and $[PtH(PEt_3)_3]^+$.

Reactions of $PH_2(SiH_3)$.—(a) *With* trans-$[PtH(I)(PEt_3)_2]$. When equimolar proportions of $PH_2(SiH_3)$ and *trans*-$[PtH(I)(PEt_3)_2]$ were allowed to react in toluene at 195 K effervescence occurred and a cloudy white solution was produced. Effervescence stopped after 2 min at room temperature. The end products were identified as H_2, PH_3, and *trans*-$[PtI(PEt_3)_2(SiH_3)]$; unchanged *trans*-$[PtH(I)(PEt_3)_2]$

[7] E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1966, **62**, 3282; D. J. Hutchison, unpublished work.

was present if an initial two-fold excess of this reagent was used. The solution contained a sticky yellow precipitate.

(b) *With* trans-$[PtCl(H)(PEt_3)_2]$. The reaction between $PH_2(SiH_3)$ and a two-fold molar excess of *trans*-$[PtCl(H)(PEt_3)_2]$ in toluene was very fast at 233 K; no $PH_2(SiH_3)$ was detected even in the initial ^1H spectrum. When warmed to room temperature the solution bubbled vigorously and separated into two phases. The ^1H spectrum of the lower phase contained a broad resonance at −5.6 p.p.m. showing a wide doublet splitting of 127 Hz with ^{195}Pt satellites. The doublet splitting was collapsed by irradiation at a ^{31}P frequency corresponding to δ(P) −177 p.p.m. Peaks in the high-frequency region were very broad and only resonances due to PEt_3 groups could be recognised. The ^{31}P spectrum contained peaks due to *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$ and two additional resonances. One [δ(P) 17.4 p.p.m.] was a 1 : 4 : 1 pseudo-triplet with an additional doublet splitting (17.4 Hz) when protons were decoupled. The other, a broad resonance, was centred at −172 p.p.m. This seemed to have a 1 : 2 : 1 triplet structure, but the separations between adjacent lines (1 230 Hz) were so large that they could only be associated with $^1J(PtP)$. The relative intensities were consistent with a species in which the phosphorus was bound to two platinum atoms; the natural abundance of ^{195}Pt (33%) would then lead to a quintet pattern of relative intensities 1 : 8 : 18 : 8 : 1. From the weakness of the central peaks it is not surprising that we failed to observe the weak outer lines. The individual lines were too broad for any additional small couplings to be detected. We attempted to record the spectrum with ^1H couplings retained. The centre line then appeared to split into a triplet of triplets, with couplings of 300 and 127 Hz. The spectrum was of poor quality, and the description of the triplets is not definitive, because of the breadth of the lines. However, all our observations are consistent with the identification of the species responsible for these peaks as *trans,trans*-$[PH_2\{PtH(PEt_3)_2\}_2]^+$ which could have been formed by reactions (6)—(8). The reaction was repeated

$$PH_2(SiH_3) + trans\text{-}[PtCl(H)(PEt_3)_2] \longrightarrow SiClH_3 + trans\text{-}[PtH(PEt_3)_2(PH_2)] \quad (6)$$

$$trans\text{-}[PtH(PEt_3)_2(PH_2)] + trans\text{-}[PtCl(H)(PEt_3)_2] \longrightarrow trans,trans\text{-}[PH_2\{PtH(PEt_3)_2\}_2]Cl \quad (7)$$

$$SiClH_3 + trans\text{-}[PtCl(H)(PEt_3)_2] \longrightarrow H_2 + trans\text{-}[PtCl(PEt_3)_2(SiClH_2)] \quad (8)$$

using methylene chloride as solvent; the same resonances were observed, with additional peaks in the ^1H and ^{31}P spectrum that were assigned to $[PtH(PEt_3)_3]^+$. The peaks in this spectrum were sharper than those obtained for the solution in toluene, and the solution remained a single phase throughout. Unsuccessful attempts were made to detect the ^1H resonances of the PH_2 protons; since these resonances might well show splittings due to coupling with one unique and four possibly equivalent phosphorus nuclei, as well as with platinum in two equivalent sites and perhaps two hydride protons, it is possible to understand why we could not find these peaks. The n.m.r. parameters for the diplatinum cation are given in Table 3.

DISCUSSION

Our previous studies of the reactions between *trans*-$[PtX(H)(PEt_3)_2]$ and silyl halides [1] have led to the identification of a range of complexes containing silicon bound to platinum, formed by the well known reaction (9).

$$SiXH_3 + trans\text{-}[PtX(H)(PEt_3)_2] \longrightarrow trans\text{-}[PtX(PEt_3)_2(SiXH_2)] + H_2 \quad (9)$$

With $S(SiH_3)_2$ or $Se(SiH_3)_2$, similar products [type (I)] are formed if X = I or Br [equations (10) and (11)].

$$S(SiH_3)_2 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(H_2SiSSiH_3)] + H_2 \quad (10)$$

$$trans\text{-}[PtI(PEt_3)_2(H_2SiSSiH_3)] + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[\{PtI(PEt_3)_2(SiH_2)\}_2S] \quad (11)$$

However, if X = Cl a different type of product, (II), is formed [equation (12)]. In none of these systems did we

$$Se(SiH_3)_2 + 2\ trans\text{-}[PtCl(H)(PEt_3)_2] \longrightarrow trans\text{-}[PtCl(PEt_3)_2(SiClH_2)] + trans\text{-}[PtH(PEt_3)_2(SeSiH_3)] + H_2 \quad (12)$$

detect *trans*-$[PtX(PEt_3)_2(SiH_3)]$, a complex formed in the reaction between SiH_4 and *trans*-$[PtX(H)(PEt_3)_2]$.

The reactions between $NH(SiH_3)_2$ or $N(SiH_3)_3$ and *trans*-$[PtH(I)(PEt_3)_2]$ fit in with the general pattern of the reactions of type (I). It is at first sight surprising that $NH(SiH_3)_2$ should give both a mono and a bis complex, whereas $N(SiH_3)_3$ gives only a mono complex; however, we have made molecular models of these species, and it is clear that a bis complex of $N(SiH_3)_3$ would be extremely crowded. The difference between $N(SiH_3)_3$ and $NH(SiH_3)_2$ is almost certainly steric. The reactions with the silylphosphines are somewhat different. With them it appears that there are two possible routes. One [equations (4) and (5)] is analogous to the reactions of $S(SiH_3)_2$ or related species with *trans*-$[PtH(I)(PEt_3)_2]$. The other [type (III)] involves elimination not of H_2 but of PH species as in equations (13)—(15). Mono- and di-

$$P(SiH_3)_3 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(SiH_3)] + PH(SiH_3)_2 \quad (13)$$

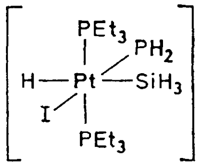
$$PH(SiH_3)_2 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(SiH_3)] + PH_2(SiH_3) \quad (14)$$

$$PH_2(SiH_3) + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(SiH_3)] + PH_3 \quad (15)$$

silylphosphines react exclusively according to reactions of type (III); trisilylphosphine reacts according to type (I) if the platinum hydride is not present in large excess.

We have therefore three types of reaction to consider. The first is well understood; the most probable mechanism is through oxidative addition of SiH across platinum. We have considered the second type as taking place through one of two possible mechanisms: either a four-centre exchange mechanism, or oxidative addition of Si–S or Si–Se across platinum followed by elimination of the most stable products. The third type could also proceed through either of these types of mechanism. It is perhaps less likely here, though, that a four-centre mechanism would be involved in exchanging H and

SiH_3. If oxidative addition is the first step, then the intermediate would be of the form:



(A)

It may well be that the most stable products of elimination from this intermediate would be PH_3 and *trans*-[PtI$(PEt_3)_2(SiH_3)$]. However, there are some difficulties about this type of mechanism in relation to the products we have observed. Mono- and di-silylphosphine react exclusively according to this scheme; trisilylphosphine, however, reacts in this manner only in the presence of a large excess of platinum complex. When a small excess of platinum hydride is used, reaction is according to type (I). It is hard to understand why the excess of platinum hydride should determine which route is followed. We can explain our observations in terms of intermediate (A) if we suppose that Si–P addition is fast but that there is a strong steric influence on the equilibrium concentration of this adduct. Addition of Si–H is slower, but elimination of H_2 from the adduct once formed is rapid. The presence of a large excess of *trans*-[PtH(I)$(PEt_3)_2$] could be sufficient to lead to the formation of enough of intermediate (A) to induce reaction according to type (III).

In many of these reaction systems we have detected intermediates whose ^{31}P n.m.r. parameters are unusual. Some at least of these complexes contain H bound to Pt; several give ^{31}P chemical shifts in the region -28 to -32 p.p.m., an unusual region for PEt_3 groups, and $^1J(PtP)$ is unusually low (*ca.* 1 200 Hz). The n.m.r. parameters we have observed for some of these complexes are given in Table 4. Given that the resonance in each case is a single peak, there is either only one PEt_3 group in these species or all the PEt_3 groups are mutually equivalent. These intermediates could be like (A) postulated for type (III).

It is worth noting that we have not detected the formation of any complexes of the elements of Group 5 analogous to *trans*-[PtH$(PEt_3)_2(SSiH_3)$], formed in reactions of $S(SiH_3)_2$ or $Se(SiH_3)_2$ with *trans*-[PtCl(H)$(PEt_3)_2$]. This can be understood in terms of the thermodynamics for the nitrogen compounds; in the hypothetical equilibrium (16), the constant would be expected to favour the left-hand side. Of all the silyl

$$N(SiH_3)_3 + trans\text{-}[PtCl(H)(PEt_3)_2] \rightleftharpoons trans\text{-}[PtH\{N(SiH_3)_2\}(PEt_3)_2] + SiClH_3 \quad (16)$$

derivatives of the elements of Group 5 we have studied, only one gave a product with *trans*-[PtCl(H)$(PEt_3)_2$] that we could identify. This was $PH_2(SiH_3)$ [equations (6)—(8)]. The first stage of this reaction process, involving formation of *trans*-[PtH$(PEt_3)_2(PH_2)$], is just like the reaction between $SiH_3(SH)$ and the same platinum complex.

It is not easy to understand why we found no evidence for the formation of species like *trans*-[PtH$(PEt_3)_2$-$\{P(SiH_3)_2\}$]. It is possible that such a species would then react further to expel chloride from another molecule of platinum hydride, forming a dimeric cation $[P(SiH_3)_2\{PtH(PEt_3)_2\}_2]^+$ like $[PH_2\{PtH(PEt_3)_2\}_2]^+$. Further addition of Si–P from $P(SiH_3)_2$ bound to Pt would also be possible, leading to the formation of polymeric species. Alternatively it might be very crowded sterically.

There is much we do not understand about these reactions. However, we believe that we have clearly identified three different types of product that are formed in reactions between silyl compounds and hydrides of four-co-ordinate platinum. We hope to discover more about these processes and in particular about the nature of the intermediates.

N.M.R. Spectra.—(a) *Silyl complexes*. There is little remarkable in the chemical shifts we have measured for the platinum derivatives of silylamines and silylphosphines. The ^1H chemical shifts are all in the general region expected, as are the ^{31}P chemical shifts of the *P*Et_3-groups. The chemical shifts of ^{31}P nuclei bound to silicon moved to high frequency as first one and then a second silyl group of $P(SiH_3)_3$ was substituted by platinum. The ^{195}Pt chemical shifts are normal for derivatives [6] of four-co-ordinate Pt^{II}; the ^{15}N chemical shift is not far from its value for $N(SiH_3)_3$. The coupling constants, too, are unremarkable; in contrast to *trans*-[PtI$(PEt_3)_2(H_2SiOSiH_3)$], for which $^4J(HPt)$ was not resolved, $^4J(HPt)$ was 6 Hz for *trans*-[PtI$(PEt_3)_2(H_2SiNHSiH_3)$] and 8 Hz for *trans*-[PtI$(PEt_3)_2\{H_2SiN(SiH_3)_2\}$].

(b) *trans,trans*-$[PH_2\{PtH(PEt_3)_2\}_2]^+$. We did not detect the P*H* resonance of this species. The Pt*H* chemical shift is consistent with what would be expected for H *trans* to P; the ^{31}P chemical shift of the bridging PH_2 group is not far from those for PH_3 and for transition-metal complexes of this ligand. Of the coupling constants, $^1J(PH)$ is normal for four-co-ordinated phosphorus, and $^1J(PtH)$ is normal for four-co-ordinate platinum. The coupling constant between ^{195}Pt and the P atoms of the PEt_3 groups is much the same as for other complexes of four-co-ordinate platinum with two mutually *trans* PEt_3 groups. However, $^1J(Pt\text{–}PH_2)$ is rather small for such a species; the low value is probably associated with the presence of H *trans* to the P nucleus.

EXPERIMENTAL

Experimental procedures are described in previous publications. Compounds were prepared by standard methods, except for $PH(SiH_3)_2$ which was obtained [8] by treating $Li[P(SiH_3)_2]$ with H_2S.

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