Silyl and Germyl Complexes of Platinum and Palladium. Part 3.[1] Reactions between Silyl and Germyl Derivatives of Group 6 and Four-co-ordinate Halogenohydridobis(triethylphosphine)platinum(II) Complexes

By **E. A. V. Ebsworth,*** **Joyce M. Edward,** and **David W. H. Rankin,** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reactions between $Y(MH_3)_2$ (Y = O, S ,or Se; M = Si or Ge) and *trans*-$[PtX(H)(PEt_3)_2]$ (X = Cl, Br, or I) have been investigated by n.m.r. spectroscopy. When X = Br or I and M = Si, *trans*-$[PtX(PEt_3)_2(H_2SiYSiH_3)]$ and *trans*-$[\{PtX(PEt_3)_2(SiH_2)\}_2Y]$ are formed; for M = Ge, the reactions are similar but the products are thermally unstable. When X = Cl, $S(SiH_3)_2$ and $Se(SiH_3)_2$ give *trans*-$[PtH(PEt_3)_2(YSiH_3)]$ and *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$; for M = Ge, the reactions are complicated and the products thermally unstable. Reaction between $SiH_3(SH)$ and *trans*-$[PtH(I)(PEt_3)_2]$ gives *trans*-$[PtI(PEt_3)_2(SiH_2SH)]$; with *trans*-$[PtCl(H)(PEt_3)_2]$, *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$ and *trans*-$[PtCl(PEt_3)_2(SH)]$ are formed. The complexes have been characterised by ^1H and ^{31}P n.m.r. spectra; ^{195}Pt, and in some cases ^{29}Si, ^{77}Se, and ^{125}Te, chemical shifts have been determined by heteronuclear double resonance.

IN earlier papers [1-3] we have described studies of the reactions of some simple silyl and germyl compounds with hydrides of four-co-ordinate platinum, *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl, Br, or I). We have characterised the products, which are unstable and reactive, by n.m.r. spectroscopy, using heteronuclear double resonance to determine parameters for ^{195}Pt and certain other magnetic nuclei.[4] We describe here a similar study of the reactions between disilyl or digermyl derivatives of elements of Group 6 and the same platinum hydrides.

RESULTS AND DISCUSSION

Reactions between trans-$[PtH(I)(PEt_3)_2]$ *and* $Y(MH_3)_2$.—The reaction between *trans*-$[PtH(I)(PEt_3)_2]$ and $S(SiH_3)_2$ or $Se(SiH_3)_2$ is very like that between the same platinum hydride and $SiClH_3$. When a solution in toluene containing equimolar proportions of the two reagents was allowed to warm to room temperature there was a vigorous reaction; hydrogen was evolved and a small amount of SiH_4 was formed. In the ^1H n.m.r. spectrum of the resulting solution there were peaks due to SiH_4 and to three other Si*H* species. Two of these resonances (A and B) appeared together, and were associated with an initial product. One resonance (B) showed a 1 : 2 : 1 triplet pattern (due to coupling with P) with platinum satellites; the size of *J*(HPt) strongly suggested that this resonance was due to Si*H* with the silicon atom directly bound to Pt. The second resonance (A) was a 1 : 4 : 1 ' pseudo-triplet ' due to Si*H* coupled to Pt; no coupling to P was detected. By double resonance we found that the platinum nuclei associated with resonances A and B had the same chemical shift, showing that resonances A and B came from the same molecule. We assign these peaks to the SiH_3 and the SiH_2 resonances of a monoplatinum species formed by reaction (1). The relative intensities are consistent with this

$$S(SiH_3)_2 + trans\text{-}[PtH(I)(PEt_3)_2] \longrightarrow trans\text{-}[PtI(PEt_3)_2(H_2SiSSiH_3)] + H_2 \quad (1)$$

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

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

[3] D. W. W. Anderson, E. A. V. Ebsworth, J. K. MacDougall, and D. W. H. Rankin, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2259.

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

assignment, and it is reasonable that $^{5}J(H\mathrm{SiSSiPt}P)$ should be too small to affect the spectrum. For $[\mathrm{PtI(PEt_3)_2(H_2SiSeSiH_3)}]$ we were able to detect ^{77}Se satellites to resonance A and so to measure the ^{77}Se chemical shift; for both compounds we obtained δ(^{29}Si) for resonance A, again by double resonance.

TABLE 1

Some n.m.r. parameters for *trans*-$[\mathrm{PtX(PEt_3)_2(H_2MYMH_3)}]$ and *trans*-$[\{\mathrm{PtX(PEt_3)_2(MH_2)}\}_2\mathrm{Y}]$ (M = Si or Ge; X = Cl, Br, or I; Y = O, S, Se, or Te). MH$_3$ Groups are labelled A, MH$_2$ groups are labelled B

Complex	δ(H_A)	δ(H_B)	δ(P)	δ(^{195}Pt)	$^{2}J(\mathrm{Pt}H_B)$	$^{3}J(\mathrm{P}H_B)$	$^{4}J(\mathrm{Pt}H_A)$	$^{1}J(\mathrm{PtP})$	$^{1}J(\mathrm{Si}H_A)$	$^{2}J(\mathrm{Y}H_A)$
		p.p.m.					Hz			
trans-$[\mathrm{PtI(PEt_3)_2(H_2SiOSiH_3)}]$	4.66	5.06	13.08	−327 [a] −314 [b]	+121.5(2)	+8.5(2)	N.o.	+2 450(5)	216(1)	
trans-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{O}]$		5.14	13.30	−309 [a]	+114.5(2)	+7.5(2)		+2 590(5)		
trans-$[\mathrm{PtI(PEt_3)_2(H_2SiSSiH_3)}]$	4.59	4.02	9.10	340 [a] 338 [c]	+86.0(2)	+8.5(2)	17(2)	+2 448(5)	216.5(1)	
trans-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{S}]$		4.16	9.31	−341 [a]	+82.0(2)	+9.0(2)		+2 538(5)		
trans-$[\mathrm{PtI(PEt_3)_2(H_2SiSeSiH_3)}]$	4.23	3.96	8.36	−327 [a] −316 [d]	+90.0(2)	+9.0(2)	17.5(2)	+2 403(5)	216.5(1)	13.5(2)
trans-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{Se}]$		3.99	8.58	−306 [d]	+86.0(2)	+9.5(2)		+2 491(5)		
trans-$[\mathrm{PtI(PEt_3)_2(H_2SiTeSiH_3)}]$	3.85	3.42	6.86	−285 [a]	+86.7(2)	+9.4(2)	15.5(2)	+2 386(5)	215.5(1)	23.0(2)
trans-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{Te}]$		3.48	7.21	−281 [a]	+82.0(2)	+9.3(2)		+2 468(5)		
trans-$[\mathrm{PtBr(PEt_3)_2(H_2SiOSiH_3)}]$	4.70	5.04	16.55	−234 [a] −224 [b]	+116.0(2)	+7.7(2)	<0.2	+2 570(5)		
trans-$[\{\mathrm{PtBr(PEt_3)_2(SiH_2)}\}_2\mathrm{O}]$		5.12	16.68	−209 [b]	+111.0(2)	+7.5(2)		+2 633(5)		
trans-$[\mathrm{PtBr(PEt_3)_2(H_2SiSSiH_3)}]$	4.56	3.96	13.14	−216 [a] −217 [b]	+87.0(2)	+8.8(2)	16.0(2)	+2 468(5)	N.o.	
trans-$[\{\mathrm{PtBr(PEt_3)_2(SiH_2)}\}_2\mathrm{S}]$		4.02	13.52	−206 [b]	+80.0(2)	+9.0(2)		+2 537(5)		
trans-$[\mathrm{PtBr(PEt_3)_2(H_2SiSeSiH_3)}]$	4.28	3.70	12.75	−195 [a]	+87.5(2)	+8.8(2)	17.5(2)	+2 423(5)	N.o.	N.o.
trans-$[\{\mathrm{PtBr(PEt_3)_2(SiH_2)}\}_2\mathrm{Se}]$		3.77	13.0	−191 [a] 188 [b]	+82.0(2)	+9.3(2)		+2 525(5)		
trans-$[\mathrm{PtCl(PEt_3)_2(H_2SiOSiH_3)}]$	4.69	5.05	18.76	−155 [a]	111.5(2)	7.5(2)	<0.2	2 590(5)	216(1)	
trans-$[\{\mathrm{PtCl(PEt_3)_2(SiH_2)}\}_2\mathrm{O}]$		5.11	18.90	−149 [b] −137 [b]	105(2)	7.0(2)		2 669(5)		
trans-$[\mathrm{Pt(H_2GeSGeH_3)I(PEt_3)_2}]$	4.76	4.18	5.8	−373 [a]	169.0(5)	8.3(2)	18.0(2)	2 377(30)		
trans-$[\{\mathrm{Pt(GeH_2)I(PEt_3)_2}\}_2\mathrm{S}]$		4.22	5.8	N.o.	158.0(5)	7.0(2)		N.o.		
trans-$[\mathrm{Pt(H_2GeSeGeH_3)I(PEt_3)_2}]$	4.40	3.80	5.8	−367 [c]	168.0(5)	8.0(2)	19.0(2)	2 434(20)		
trans-$[\{\mathrm{Pt(GeH_2)I(PEt_3)_2}\}_2\mathrm{Se}]$		3.89	6.0	−350 [c]	158.0(5)	7.5(2)		2 430(30)		

All spectra were measured in toluene or [^{2}H$_8$]toluene. Signs of coupling constants were determined where these are explicitly stated. The parameters were scarcely affected by temperature except for δ(^{195}Pt), for which temperatures are given. Chemical shifts are all measured as positive to high frequency. The standards are: ^{1}H, SiMe$_4$; ^{31}P, 85% H$_3$PO$_4$; ^{29}Si, SiMe$_4$ in CHCl$_3$; ^{77}Se, 20% SeMe$_2$ in CH$_2$Cl$_2$; ^{125}Te, 20% TeMe$_2$ in CH$_2$Cl$_2$; ^{195}Pt, 0.5 mol dm^{-3} *trans*-$[\mathrm{PtCl(H)(PEt_3)_2}]$ in CH$_2$Cl$_2$ at 300 K.

[a] 233 K. [b] 273 K. [c] 213 K. [d] 273 K.

The third resonance, C, was also a 1 : 2 : 1 triplet with platinum satellites. It grew after resonances A and B had appeared and as they decayed; in the 1 : 1 system, resonances A—C were present together, but when a 2 : 1 molar excess of platinum hydride was used the main product was the complex giving resonance C. We conclude that this compound is the diplatinum complex formed by reaction of the initial platinum complex with excess of platinum hydride [equation (2)]. It was

$$trans\text{-}[\mathrm{PtI(PEt_3)_2(H_2SiSSiH_3)}] + [\mathrm{PtH(I)(PEt_3)_2}] \longrightarrow trans\text{-}[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{S}] + \mathrm{H_2} \quad (2)$$

more difficult to characterise the products of the reaction between *trans*-$[\mathrm{PtH(I)(PEt_3)_2}]$ and O(SiH$_3$)$_2$. The initial product gave two resonances as in the other system; whereas resonance B showed the expected pattern of a 1 : 2 : 1 triplet with platinum satellites, resonance A was a single peak. If the initial product of the reaction between disiloxane and *trans*-$[\mathrm{PtH(I)(PEt_3)_2}]$ is $[\mathrm{PtI(PEt_3)_2(H_2SiOSiH_3)}]$, we have to explain why we do not see $^{4}J(H\mathrm{SiOSi}Pt)$. There are two possible reasons. There may be intermolecular exchange of SiH$_3$ groups that is fast on the n.m.r. time scale, which would lead to collapse of couplings though O; this explanation is not very convincing, since we found no other evidence of such exchange and the spectra were unaffected by cooling to 210 K. The other explanation is that couplings through oxygen might be smaller than through sulphur or selenium. There are other examples in silyl chemistry where this is true,[5] so we feel that this explanation is plausible. The bis complex *trans*-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{O}]$ was identified as before. Reaction between *trans*-$[\mathrm{PtH(I)(PEt_3)_2}]$ and Te(SiH$_3$)$_2$ gave mono and bis complexes *trans*-$[\mathrm{PtI(PEt_3)_2(H_2SiTeSiH_3)}]$ and *trans*-$[\{\mathrm{PtI(PEt_3)_2(SiH_2)}\}_2\mathrm{Te}]$, although the bis complex was only formed in the presence of excess of platinum hydride; however, in all the reactions with Te(SiH$_3$)$_2$ we observed the formation of substantial amounts of SiH$_4$ and *trans*-$[\mathrm{PtI(PEt_3)_2(SiH_2I)}]$. Satellites due to Te were observed for the SiH_3 resonances of *trans*-$[\mathrm{PtI(PEt_3)_2(H_2SiTeSiH_3)}]$, from which the Te chemical shift was determined by double resonance. All the solutions were stable for short periods at room temperature, but the products decomposed on prolonged standing.

Reaction between *trans*-$[\mathrm{PtH(I)(PEt_3)_2}]$ and S(GeH$_3$)$_2$ or Se(GeH$_3$)$_2$ in toluene led to the formation of *trans*-$[\mathrm{Pt(H_2GeSGeH_3)I(PEt_3)_2}]$ or its selenium analogue, but the germylplatinum complexes decomposed rapidly at room temperature. Reaction of S(GeH$_3$)$_2$ with a two-

[5] J. E. Drake and C. Riddle, *Quart. Rev.*, 1970, **24**, 263.

fold excess of *trans*-$[PtH(I)(PEt_3)_2]$ gave both mono and bis species; although formation of the mono complex began at 213 K, the presence of the bis species was not detected until the solution had reached room temperature. In an analogous reaction with $Se(GeH_3)_2$, peaks due to both mono- and di-platinum complexes were observed even when the solution was kept below 213 K.

Reactions between trans-$[PtBr(H)(PEt_3)_2]$ *and* $Y(MH_3)_2$.—Reactions between $Y(SiH_3)_2$ and *trans*-$[PtBr(H)(PEt_3)_2]$ gave products analogous to those formed with *trans*-$[PtH(I)(PEt_3)_2]$; their n.m.r. parameters are included in Table 1. The only differences were that with Y = O and S the reaction products included very small amounts of *trans*-$[PtBr(PEt_3)_2(SiBrH_2)]$, which were probably formed by the presence of trace amounts of HBr, and with the selenide the presence of two intermediates was detected in the ^{31}P spectrum of the reaction mixture at 223 K. These had $\delta(P)$ of -32 and -33.1 p.p.m., and $^1J(PtP)$ of 1 220 and 1 200 Hz respectively; the resonances disappeared as the reaction mixture was allowed to warm above this temperature.

The n.m.r. parameters for all these complexes are given in Table 1 and are discussed below.

Reaction between trans-$[PtCl(H)(PEt_3)_2]$ *and* $Y(MH_3)_2$.—When $S(SiH_3)_2$ or $Se(SiH_3)_2$ was treated with a two-fold molar excess of *trans*-$[PtCl(H)(PEt_3)_2]$ in toluene there was no effervescence if the solution was kept at 213 K, but the ^1H n.m.r. spectrum showed that $SiClH_3$ was present at that temperature together with peaks due to unidentified intermediate platinum hydrides (Table 2).

TABLE 2

N.m.r. parameters for intermediates found in reactions of $S(SiH_3)_2$ or $Se(SiH_3)_2$ with *trans*-$[PtCl(H)(PEt_3)_2]$

Group 6 element	$\delta(PtH)$ (± 0.02)	$\delta(^{31}P)$ (± 0.3)	$^2J(PH)$ (± 0.5)	$^1J(PtP)$ (± 0.5)
	p.p.m.		Hz	
S	-13.56	-17.4	13.0	1 098
	-8.32	4.1	10.0	664
Se	-13.78	-20.1	12.0	1 136
	-8.78	1.0	11.0	652

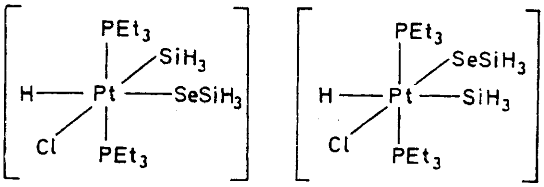
Values were recorded in toluene–tetramethylsilane at 213 K; the ^{31}P shift was measured relative to 85% H_3PO_4, taking shifts to high frequency as positive.

These species are likely to contain at least one sulphur or selenium atom per molecule, besides platinum, phosphorus, and silyl groups; the values for $^1J(PtP)$ suggest that in some of the species the platinum atoms may well be six-co-ordinate. When the solutions were allowed to warm to room temperature a vigorous effervescence began; when this had ceased peaks were observed in the ^1H and ^{31}P spectra due to *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$, whose identity was confirmed by the ^{195}Pt chemical shift.[4] Besides the single peak due to H_2, there were two other ^1H resonances: a 1 : 4 : 1 triplet (D) in the Si*H* region, with a further narrow doublet splitting on each line, and a resonance E in the Pt*H* region. Resonance E consisted of a wide 1 : 4 : 1 triplet [$^1J(PtH)$ *ca.* 1 200 Hz] with a narrower 1 : 2 : 1 triplet structure due to coupling with ^{31}P, and a narrower 1 : 3 : 3 : 1 quartet splitting on each line of the triplet. Irradiation at D collapsed the narrow quartet splitting in the main resonance of E, and the same Pt frequency collapsed the satellites to both D and E. It follows that the same species is responsible for peaks D and E; it contains one H bound to Pt and one SiH_3 group linked to Pt through at least one other atom [if SiH_3 were directly bound to Pt we would expect to see $^3J(HSiPtP)$]. The parameters associated with Pt imply that the platinum atom is four-co-ordinate; the Pt–*H* nucleus is equally coupled to two phosphorus nuclei, and the observation of $^4J(H_3SiMPtH)$ implies that H and SiH_3M are mutually *trans*. No peaks were observed that could be assigned to SiH_2Pt groups from this species. With $Se(SiH_3)_2$ as starting material, satellites of the SiH_3 resonance due to ^{77}Se were detected; satellites due to ^{77}Se were not observed on the Pt*H* resonance, presumably because the solution was too dilute. It follows from all these observations that the species responsible for the peaks D and E is *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ or its selenium analogue; the reaction has followed equation (3). With

$$S(SiH_3)_2 + 2\ trans\text{-}[PtCl(H)(PEt_3)_2] \longrightarrow trans\text{-}[PtH(PEt_3)_2(SSiH_3)] + trans\text{-}[PtCl(PEt_3)_2(SiClH_2)] \quad (3)$$

$Se(SiH_3)_2$ the solution separated on standing into two phases; it was impossible to obtain useful ^1H spectra of either phase as the lines were very broad, but the ^{31}P spectrum of the lower phase was the same as that of the initial products of the reaction. When $Se(SiH_3)_2$ was allowed to react with an equimolar quantity of *trans*-$[PtCl(H)(PEt_3)_2]$ the solution separated into two phases after a few minutes at room temperature. The ^{31}P n.m.r. spectrum showed peaks due to unidentified products (see Table 4).

Reaction between $Se(SiH_3)_2$ and *trans*-$[PtCl(H)(PEt_3)_2]$ in very concentrated solution in toluene gave very broad peaks in the ^1H spectrum because the solution was extremely viscous; the only peak of any significance was a broad resonance at -8.7 p.p.m. In the ^{31}P spectrum two peaks were observed, at $\delta(P)$ -31.0 and -32.8 p.p.m., with platinum satellites [$^1J(PtP)$ 1 228 and 1 214 Hz]. Irradiation at a P frequency corresponding to $\delta(P)$ -31 p.p.m. led to a slight sharpening in the Pt*H* resonance at -8.75 p.p.m. The chemical shifts and particularly the small PtP coupling constants imply that the species contain six-co-ordinate platinum. The ^{31}P n.m.r. parameters are remarkably close to those of the unidentified intermediates in the reaction between $Se(SiH_3)_2$ and *trans*-$[PtBr(H)(PEt_3)_2]$; if the species are identical, they must contain no halogen bound to platinum, although ^{31}P n.m.r. parameters are not very sensitive to the nature of the halogen bound to Pt. The ^{31}P spectrum of the concentrated solution contained no other resonances, and in particular none that we could assign to any complexes of four-co-ordinate platinum. The only species we can suggest that might give rise to the spectra observed in this solution are the postulated intermediates:



(7)

We have no idea why these should not have decomposed to give a complex of four-co-ordinate platinum. The nature of these intermediates is discussed further in the following paper.

Reaction of $O(SiH_3)_2$ with *trans*-$[PtCl(H)(PEt_3)_2]$ in either equimolar proportions or with a two-fold excess of platinum hydride in toluene gave H_2, *trans*-$[PtCl(PEt_3)_2(H_2SiOSiH_3)]$, *trans*-$[\{PtCl(PEt_3)_2(SiH_2)\}_2O]$, and *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$. When equimolar proportions of these reactants were allowed to react at 253 K the ^{31}P spectrum showed the presence of *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$, together with a second product [δ(P) 21.4 p.p.m., ^1J(PtP) 2 705 Hz] that may well have been *trans*-$[PtH(OSiH_3)(PEt_3)_2]$. The ^1H spectrum of this species could not be detected; the complex seems to be unstable at higher temperatures.

Reactions between *trans*-$[PtCl(H)(PEt_3)_2]$ and $S(GeH_3)_2$ or $Se(GeH_3)_2$ gave very unstable products. Various transitory resonances were observed at low temperature. The solution in toluene of the reaction mixture containing $S(GeH_3)_2$ separated into two phases after 1 min at room temperature; after a similar period, the only identifiable product of the reaction between *trans*-$[PtCl(H)(PEt_3)_2]$ and $Se(GeH_3)_2$ was *trans*-$[PtCl(GeClH_2)(PEt_3)_2]$.

The n.m.r. parameters for these complexes are given in Table 3 and are discussed below.

TABLE 3

N.m.r. parameters for *trans*-$[PtH(PEt_3)_2(YSiH_3)]$ (Y = O, S, or Se). MH_3 Groups are labelled A, Pt*H* protons are labelled C

	Y = O	S	Se *
$\delta(H_C)$/p.p.m.	N.o.	−11.68 (2)	−11.36 (2)
$\delta(H_A)$/p.p.m.	N.o.	−4.67 (2)	4.29 (2)
$\delta(^{31}P)$/p.p.m.	21.2 (5)	20.0 (5)	18.7 (5)
$\delta(^{195}Pt)$/p.p.m.	N.o.	−85 (1)	−165 (1)
$^1J(PtH_C)$/Hz	N.o.	+1 160 (1)	+1 216 (1)
$^2J(PH_C)$/Hz	N.o.	−14.0 (2)	−14.0 (2)
$^3J(PtH_A)$/Hz	N.o.	27.0 (2)	24.0 (2)
$^4J(H_AH_C)$/Hz	N.o.	+1.0 (2)	+1.0 (2)
$^1J(PtP)$/Hz	2 705 (5)	+2 665 (5)	+2 160 (5)

All values were recorded in $[^2H_8]$toluene at 223 K. Chemical shifts (positive to high frequency) are given relative to $SiMe_4$ (^1H) 85% H_3PO_4 (^{31}P), 0.5 mol dm^{-3} *trans*-$[PtCl(H)(PEt_3)_2]$ in CH_2Cl_2 at 300 K (^{195}Pt), or $SeMe_2$ (^{77}Se). Signs of coupling constants are based on the assumption that ^1J(PtH) is positive, and were determined only where explicitly stated.

* $\delta(^{77}Se)$ −743 ± 2.0 p.p.m., $^2J(SeH_A)$ 12.8 ± 0.5 Hz.

Reactions of $SiH_3(SH)$.—Silanethiol is formed in equilibrium when H_2S and disilyl sulphide react together.[6] Treatment of $S(SiH_3)_2$ with a large excess of H_2S over several weeks gives appreciable proportions of $SiH_3(SH)$, and equilibrium is reached slowly enough to allow us to obtain samples of silanethiol containing less than 20% disilyl sulphide by fractional distillation at low temperatures. Such samples were used without further purification.

(a) *With* trans-$[PtH(I)(PEt_3)_2]$. Equimolar proportions of $SiH_3(SH)$ and *trans*-$[PtH(I)(PEt_3)_2]$ were allowed to react together in toluene; a vigorous reaction began as soon as the solution reached room temperature. When effervescence ceased (10 min) the ^1H n.m.r. spectrum contained peaks due to H_2, H_2S, and *trans*-$[\{PtI(PEt_3)_2(SiH_2)\}_2S]$, together with new Si*H* and S*H* resonances that we assign to *trans*-$[PtI(PEt_3)_2(SiH_2SH)]$. The Si*H* resonance was a 1 : 2 : 1 triplet with platinum satellites, each line showing an additional narrow doublet splitting. The S*H* resonance showed a narrow triplet splitting due to coupling with the SiH_2 protons; this assignment was confirmed by heteronuclear double resonance; the signals were so weak that Pt satellites were not observed. The measured n.m.r. parameters are included in Table 4. There was no sign of any products of addition of SH or Si–S to platinum.

TABLE 4

N.m.r. parameters of *trans*-$[PtI(PEt_3)_2(SiH_2SH)]$ and $SiH_3(SH)$. SiH Protons are labelled A, SH protons are labelled D

	trans-$[PtI(PEt_3)_2(SiH_2SH)]$	$SiH_3(SH)$ [11]
$\delta(H_A)$/p.p.m.	4.21 (2)	4.05 (2)
$\delta(H_D)$/p.p.m.	0.40 (2)	−0.52 (2)
$\delta(^{31}P)$/p.p.m.	−9.6 (5)	
$\delta(^{195}Pt)$/p.p.m.	−353 (1)	
^2J(PtH)/Hz	85.0 (2)	
^3J(PH)/Hz	9.3 (5)	
^3J(PtH)/Hz	N.o.	
^3J(HH)/Hz	2.5 (5)	5.0 (5)
^1J(PtP)/Hz	24.19 (20)	

Chemical shifts are positive to high frequency of $SiMe_4$ (^1H), 85% H_3PO_4 (^{31}P), or 0.5 mol dm^{-3} *trans*-$[PtCl(H)(PEt_3)_2]$ in CH_2Cl_2 (^{195}Pt). All parameters were obtained from toluene solutions at 223 K.

(b) *With* trans-$[PtCl(H)(PEt_3)_2]$. Silanethiol was allowed to react with a two-fold excess of *trans*-$[PtCl(H)(PEt_3)_2]$ in CH_2Cl_2; a vigorous effervescence began when the solution reached room temperature. After 5 min effervescence ceased; the ^1H spectrum showed peaks due to H_2, a small amount of *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ [formed from reaction between the platinum complex and $S(SiH_3)_2$ present in $SiH_3(SH)$] and *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$. In addition, Pt*H* and S*H* resonances due to a new complex were detected. The Pt*H* resonance consisted of a 1 : 2 : 1 triplet with platinum satellites; each line showed a further narrow doublet splitting. The associated S*H* resonance at −0.12 p.p.m. also appeared as a 1 : 2 : 1 triplet with platinum satellites, and here each line showed a narrow doublet splitting. The two resonances were shown by double-resonance experiments to be associated with the same species, which we identify as *trans*-$[PtH(PEt_3)_2(SH)]$. Its

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[6] H. J. Emeleus, A. G. MacDiarmid, and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

formation can be understood in terms of steps (4) and (5). The n.m.r. parameters for *trans*-$[PtH(PEt_3)_2(SH)]$ are given in Table 5.

$$\textit{trans}\text{-}[PtCl(H)(PEt_3)_2] + SiH_3(SH) \longrightarrow \textit{trans}\text{-}[PtH(PEt_3)_2(SH)] + SiClH_3 \quad (4)$$

$$\textit{trans}\text{-}[PtCl(H)(PEt_3)_2] + SiClH_3 \longrightarrow \textit{trans}\text{-}[PtCl(PEt_3)_2(SiClH_2)] + H_2 \quad (5)$$

TABLE 5

N.m.r. parameters of *trans*-$[PtH(PEt_3)_2(SH)]$; Pt*H* labelled C, S*H* labelled D

$\delta(H_C)$	-10.08 (2) p.p.m.	$^1J(PtH)$	$+1\,012$ (5) Hz
$\delta(H_D)$	-0.12 (12) p.p.m.	$^2J(PtH_B)$	-44 (1) Hz
$\delta(^{31}P)$	19.1 (1) p.p.m.	$^2J(PH_C)$	-15 (1) Hz
$\delta(^{195}Pt)$	-139 (2) p.p.m.	$^3J(PH_D)$	$+8$ (1) Hz
		$^1J(PtP)$	$+2\,700$ (30) Hz
		$^3J(HH)$	2 (1) Hz

Chemical shifts are positive to high frequency of $SiMe_4$ (^1H), 85% H_3PO_4 (^{31}P), or 0.5 mol dm^{-3} *trans*-$[PtCl(H)(PEt_3)_2]$ in CH_2Cl_2 at 300 K (^{195}Pt). Signs of coupling constants are relative to $^1J(PtH)$ (assumed positive).

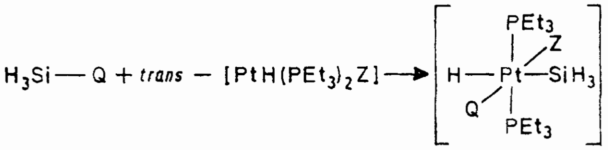
Possible Mechanisms.—The difference between the reactions of *trans*-$[PtCl(H)(PEt_3)_2]$ and of *trans*-$[PtBr(H)(PEt_3)_2]$ or *trans*-$[PtH(I)(PEt_3)_2]$ is striking. It is generally agreed that reactions between SiH compounds and platinum hydrides to give H_2 and Si–Pt complexes involve oxidative addition of SiH to Pt. We were unable to detect any intermediates in the reactions between $Y(SiH_3)_2$ and *trans*-$[PtH(I)(PEt_3)_2]$, but there is no reason to postulate a different type of mechanism; the products are what would have been expected by analogy with reactions of other silanes.

It is harder to decide what is responsible for the different reaction between $S(SiH_3)_2$ or $Se(SiH_3)_2$ and *trans*-$[PtCl(H)(PEt_3)_2]$. However, there are analogies in the reaction of silyl halides that may be helpful. It is known[1] that SiH_3I reacts rapidly with *trans*-$[PtCl(H)(PEt_3)_2]$ at low temperatures, before addition of SiH occurs, giving $SiClH_3$ and *trans*-$[PtH(I)(PEt_3)_2]$. This is an example of what is at least with halide substituents a general exchange process [equation (6)]. When Q is

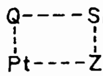
$$SiH_3Z + \textit{trans}\text{-}[PtH(PEt_3)_2Q] \rightleftharpoons SiH_3Q + \textit{trans}\text{-}[PtH(PEt_3)_2Z] \quad (6)$$

lighter or more electronegative than Z the equilibrium lies to the right; when Q is heavier or less electronegative than Z the opposite is true.[1] If we extend this analysis to include systems in which $Q = YSiH_3$ it is possible to correlate our observations with those made earlier. When $Z = Br$ or I, all the equilibria lie to the right. When $Z = Cl$, the equilibria might be expected to lie to the left when $Q = SSiH_3$ or $SeSiH_3$, but to the right when $Q = OSiH_3$. This is what we have observed: when $Z = Cl$ and $Q = SSiH_3$ or $SeSiH_3$ the products are *trans*-$[PtCl(PEt_3)_2(SSiH_3)]$ or its selenium analogue, whereas when $Q = OSiH_3$ we obtain as main products the results of Si–H addition to *trans*-$[PtCl(H)(PEt_3)_2]$.

This discussion sheds no light on the mechanism of exchange. We can envisage two possible paths. One, (7), involves oxidative addition of Si–Q to platinum. Elimination of $ZSiH_3$ or $QSiH_3$ would then depend on thermodynamic factors. The formation of the intermediate would have to be much faster than addition of Si–H to platinum. The alternative explanation would involve a four-centre exchange:



(7)



We cannot at present distinguish between these two possibilities. However, the formation of unidentified intermediates probably containing six-co-ordinate platinum in the reaction between *trans*-$[PtCl(H)(PEt_3)_2]$ and $S(SiH_3)_2$ or $Se(SiH_3)_2$ leads us to retain the former mechanism as a serious possibility.

It is interesting to consider what is formed in the reaction between $S(SiH_3)_2$ or $Se(SiH_3)_2$ and a two-fold excess of *trans*-$[PtCl(H)(PEt_3)_2]$. The initial product is $SiClH_3$; this must be formed in the presence of both *trans*-$[PtCl(H)(PEt_3)_2]$ and *trans*-$[PtH(PEt_3)(SSiH_3)]$. The end products are *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ and *trans*-$[PtCl(PEt_3)_2(SiClH_2)]$; the latter is formed by reaction between $SiClH_3$ and *trans*-$[PtCl(H)(PEt_3)_2]$. No products of any possible reaction between $SiClH_3$ and *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ were detected. Although steric factors could be involved, it seems likely that SiH addition to *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ is appreciably more difficult than to *trans*-$[PtCl(H)(PEt_3)_2]$, implying that the relevant *d*-electron ionisation potential of the former may be the higher.

N.M.R. Parameters.—(a) *Complexes containing* Si–Pt *bonds*. (i) *Chemical shifts*. For the mono complexes *trans*-$[PtX(PEt_3)_2(H_2SiYSiH_3)]$ both SiH_3 and SiH_2 resonances shifted to high frequency as Y changed from O to Te; the SiH_3 protons are substantially less sensitive to change in Y than are the SiH_2 protons, so that whereas for O the SiH_2 resonance was to high frequency of the SiH_3, for Te the opposite was true. For a given Y, the chemical shift of neither set of protons was affected by change in X. In each case the SiH_2 protons in the bis complexes *trans*-$[\{PtX(PEt_3)_2(SiH_2)\}_2Y]$ were to high frequency of the corresponding resonances in the appropriate mono complexes. In the series of mono or bis complexes with a given halogen bound to platinum, the ^{31}P resonance shifted to high frequency as Y was varied from Te to O; similarly, for a given Y the ^{31}P resonance shifted to high frequency as X was changed from I to Cl, a trend like that found in many other platinum phosphine complexes.[4] The chemical shifts of ^{195}Pt nuclei in these complexes are in the range where complexes of four-co-ordinate platinum are usually observed;[4,7] for a particular X and Y, the platinum resonance frequency scarcely changed from mono to bis species, but it was sensitive to change in X or Y. When X was kept the same, δ(Pt) moved to high frequency as Y was altered from Te to S, but for O the Pt resonance moved to low frequency. Such a change is often put down to electronic effects such as $(p \longrightarrow d)$ π bonding, but it may just as well be associated with the wide angle to be expected at Y in the oxygen species. As found for other platinum complexes,[7] $\delta(^{195}Pt)$ shifted substantially to low frequency as X was changed from Cl to I. The ^{195}Pt chemical shifts were, as in other systems,[8] found to change with temperature by 0.5—1 p.p.m. K^{-1}.

(ii) *Coupling constants.* All the values of $^1J(PtP)$ are typical for complexes of four-co-ordinate platinum. For given X, the value of J increased as Y was changed from Te to O; for given X and Y, the coupling was larger in bis than in mono complexes, but it was less affected if Y was kept the same and X was changed. The coupling between the B protons of the mono complexes and ^{195}Pt was substantially larger in the oxygen derivative than in the others, but changes in this coupling as Y was changed from S to Te were irregular; for a particular element Y there was a slight decrease in $^2J(HSiPt)$ as X was varied from I to Cl, and (for fixed X and Y) from mono to bis species. The coupling between the A protons and platinum, $^4J(HPt)$, is *ca.* 15—17 Hz for all the mono complexes, except when Y is O: this point is discussed above. For each complex, $^3J(HSiPtP)$ is *ca.* 7.5—9 Hz; in all the mono complexes, $^1J(^{29}SiH)$ for the A protons is 216 Hz, although the change from $Te(SiH_3)_2$ to $O(SiH_3)_2$ is 8 Hz.[9] The values for $^2J(HSiSe)$ and $^2J(HSiTe)$ are unremarkable.

There are so few values for coupling constants in the germanium complexes that trends cannot usefully be discussed.

All the values of $^1J(PtP)$, $^2J(PtH)$, and $^3J(PH)$ have the same sign; we assume that they are all positive, as in other similar molecules.

(b) *Complexes containing* Pt–Y *bonds.* For *trans*-$[PtH(PEt_3)_2(SSiH_3)]$ and its selenium analogue, the Pt*H* chemical shift is *ca.* −10.0 p.p.m., characteristic of H *trans* to an element with a high *trans* influence; the values are much the same as for *trans*-$[PtH(PEt_3)_2(SH)]$ or its selenium analogue, and δ is slightly the higher for the selenium derivative. The Si*H* chemical shifts are slightly to high frequency of those for other $SSiH_3$ or $SeSiH_3$ compounds. The other n.m.r. parameters are unremarkable, except perhaps for the value of $\delta(^{77}Se)$ for *trans*-$[PtH(PEt_3)_2(SeSiH_3)]$, which is to low frequency of the corresponding value[10] for $Se(SiH_3)_2$ but close to that[11] for $Li(SeSiH_3)$.

In the ^{31}P n.m.r. spectrum of the products of the reaction between $O(SiH_3)_2$ and *trans*-$[PtCl(H)(PEt_3)_2]$, a resonance with platinum satellites was observed that could tentatively be assigned to *trans*-$[PtH(OSiH_3)(PEt_3)_2]$. The ^{31}P chemical shift and $^1J(PtP)$ are both reasonable in terms of an extrapolation from the values for $[PtH(PEt_3)_2(SSiH_3)]$ and its selenium analogue, but the ^1H spectrum of this complex was not obtained and the identification is very tentative.

EXPERIMENTAL

The n.m.r. spectra were recorded using a Varian Associates XL 100 Fourier-transform spectrometer (for ^{31}P spectra) or a HA 100 continuous-wave instrument (for ^1H spectra). The latter was modified to accept a second radio frequency generated by a Schlumberger frequency synthesiser for heteronuclear double resonance.[4] Infrared spectra were recorded on a Perkin-Elmer 457 instrument.

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