

Platinum Hydrides containing Silyl or Germyl Ligands. Crystal Structure of *trans*-Hydridosilylbis(tricyclohexylphosphine)platinum(II)

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The reaction between *trans*-[PtH₂{P(C₆H₁₁)₃}₂] and MH₃X (M = Si, X = H, Cl, or SiH₃; M = Ge, X = H) gives *trans*-[PtH(Y){P(C₆H₁₁)₃}₂] (Y = MH₂X). Reaction intermediates, thought to be [PtH₂(Y)P{(C₆H₁₁)₃}₂], have been detected by ³¹P n.m.r. spectroscopy at low temperatures, except for X = H. Except when Y = Si₂H₆, the products have been isolated as air-stable crystalline solids, and the structure of the title complex has been determined. The crystals are monoclinic, space group *P*2₁/*n*, with *a* = 1 317.9, *b* = 1 277.7, *c* = 2 347.8 pm, and β = 106.96°. The structure has been solved with 4 165 diffractometer data and refined to *R* 0.049. No reaction is observed between MH₃X and *trans*-[PtH(Z){P(C₆H₁₁)₃}₂] (Z = Cl or SiH₃) or between SiMeH₃ and *trans*-[PtH₂{P(C₆H₁₁)₃}₂].

In previous papers we have reported the reactions of some silyl and germyl hydrides with transition-metal substrates.¹⁻³ With *trans*-[PtCl(H)(PEt₃)₂] it was found that reaction with MH₃Q (M = Si or Ge; Q = Cl, H, Me, or MH₃) invariably yielded *trans*-[PtCl(MH₂Q)(PEt₃)₂] and dihydrogen. A six-co-ordinate dihydrido-platinum intermediate was postulated but was not observed spectroscopically. Recently, there has been considerable interest in the stabilisation of platinum hydrides by bulky phosphine ligands⁴⁻⁷ and we have now completed a study of the reactions of one of these hydrides, *trans*-[PtH₂{P(C₆H₁₁)₃}₂],⁸ with some simple silyl and germyl compounds.

RESULTS

No reaction between *trans*-[PtCl(H){P(C₆H₁₁)₃}₂] and any silyl or germyl compound was observed at room temperature in CD₂Cl₂ solution. After several days, solutions turned brown but there was no evidence in either the ³¹P or ¹H n.m.r. spectra for a reaction of the platinum complex.

The reaction between *trans*-[PtH₂{P(C₆H₁₁)₃}₂] and SiH₄ in CD₂Cl₂ was followed by ³¹P n.m.r. spectroscopy. No reaction occurred until the mixture was warmed to room temperature, when the product, *trans*-[PtH(SiH₃){P(C₆H₁₁)₃}₂] (I), was quickly formed with the evolution of dihydrogen. The product was isolated by removing the solvent *in vacuo* and recrystallised from hexane as colourless air-stable crystals, suitable for X-ray analyses. The reaction of Si₂H₆ with [PtH₂{P(C₆H₁₁)₃}₂] appeared to proceed similarly. In the ³¹P n.m.r. spectrum, resonances were observed consistent with the formation of [PtH₂(Si₂H₅){P(C₆H₁₁)₃}₂] at -80 °C and subsequent decomposition to yield [PtH(Si₂H₅){P(C₆H₁₁)₃}₂] at room temperature. However, in this case the product was very insoluble and attempts at isolation led to decomposition.

The reaction of *trans*-[PtH₂{P(C₆H₁₁)₃}₂] with SiClH₃ or GeH₄ proceeded cleanly to give the complexes *trans*-[PtH(SiClH₂){P(C₆H₁₁)₃}₂] or *trans*-[PtH(GeH₃){P(C₆H₁₁)₃}₂].

¹ J. E. Bentham, S. Craddock, and E. A. V. Ebsworth, *J. Chem. Soc. (A)*, 1971, 587.

² E. A. V. Ebsworth and D. Leitch, *J.C.S. Dalton*, 1973, 1287.

³ D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 2370.

⁴ T. G. Attig and H. C. Clark, *Canad. J. Chem.*, 1975, **53**, 3466.

⁵ G. Bracher, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem. Internat. Edn.*, 1975, **14**, 563.

⁶ M. Green, J. A. K. Howard, J. Proud, J. L. Spenser, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Chem. Comm.*, 1976, 671.

[PtH₂(Y){P(C₆H₁₁)₃}₂]. These products, too, were stable in air and easily purified by recrystallisation from hot benzene. In both these reactions it was possible to detect an intermediate by ³¹P n.m.r. spectroscopy at -80 °C before the reactants had been allowed to warm above this temperature. The ³¹P n.m.r. parameters of the intermediates are comparable with those found for the intermediate formed^{9a} on addition of HCl to *trans*-[PtH₂{P(C₆H₁₁)₃}₂] at -80 °C and which decomposed to [PtCl(H){P(C₆H₁₁)₃}₂] above -60 °C, and the values of the platinum-phosphorus couplings are consistent with *trans*-bis(phosphine)platinum(IV) complexes² (see Table 1). Although the resonances broadened under

TABLE 1

Phosphorus-31 n.m.r. data

Y	[PtH(Y){P(C ₆ H ₁₁) ₃ } ₂] δ(P) ^{a,b}	¹ J(Pt-P)/Hz	[PtH ₂ (Y){P(C ₆ H ₁₁) ₃ } ₂] δ(P) ^c	¹ J(Pt-P)/Hz
H	50.54	2 784		
Cl	38.21	2 763	30.70	1 773
SiH ₃	40.42	2 615	n.o.	n.o.
GeH ₃	39.45	2 638	33.12	1 811
SiClH ₂	40.55	2 615	33.49	1 790
Si ₂ H ₅	40.50	2 600	33.12	1 797

^a Chemical shifts in p.p.m., positive to high frequency of 85% H₃PO₄. Measured in CD₂Cl₂. n.o. = Species not observed.

^b At room temperature. ^c At -80 °C.

conditions of off-resonance decoupling that produced a sharp triplet from ³J(PH) in [PtH₂{P(C₆H₁₁)₃}₂] the hydride coupling to phosphorus was not resolved. Unfortunately, it was not possible to obtain convincing ¹H n.m.r. spectra as at these low temperatures the solutions were too dilute for continuous-wave (c.w.) methods and the dynamic range problem caused by large cyclohexyl resonances made Fourier-transform methods inadequate with our equipment. However, the circumstantial evidence strongly suggests that we are observing trihydride species of the type *trans*-[PtH₂(MH₂Y){P(C₆H₁₁)₃}₂] formed by oxidative addition.

It was possible to record ¹H n.m.r. spectra for the platinum(II) products using c.w. methods and these data are given in Table 2. The sizes and multiplicities of the couplings are consistent with the *trans* formulations given, but

⁷ J. Forries, M. Green, J. L. Spenser, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1006.

⁸ B. L. Shaw and M. F. Uttley, *J.C.S. Chem. Comm.*, 1974, 918.

⁹ (a) E. A. V. Ebsworth and F. J. S. Reed, unpublished work; (b) 'X-RAY '76', ed. J. M. Stewart, Technical Report TR-466, Computer Science Centre, University of Maryland, Maryland, U.S.A.

the coupling $^3J(\text{HH})$ was only resolved for *trans*-[PtH-(GeH₃)₂{P(C₆H₁₁)₃}₂] and so the SiClH₂ and SiH₃ groups are not defined by the spectra. The relatively high-frequency hydride chemical shift, the small value of $^1J(\text{PtH})$, and the

Cell dimensions and X-ray intensity data were obtained with a Nonius CAD4 diffractometer, using graphite-monochromatised Mo- K_α radiation. Twenty reflections having $25 < \theta < 30^\circ$ were used to refine the cell dimensions. Data

TABLE 2
Hydrogen-1 n.m.r. data for [PtH(Y){P(C₆H₁₁)₃}₂]

Y	$\delta(\text{H})^a$	$^1J(\text{Pt-H})$	$^2J(\text{P-H})$	$^3J(\text{H-H}')$	$\delta(\text{H}')$	$^2J(\text{Pt-H}')$	$^3J(\text{P-H}')$
		Hz				Hz	
H	-3.92 ^b	794	16				
Cl	-18.66 ^b	1 296	12.5				
SiH ₃	-0.75 ^c	528	15	0	3.76	20	3
GeH ₃	-4.46 ^c	866	12	3	3.40	57	3
SiClH ₂	-0.50 ^{c,d}	756	15	0	n.o.		

^a Chemical shifts in p.p.m. positive to high frequency of SiMe₄.
^c At 50 °C in C₆H₆. ^d Using a computer of average transients.

n.o. = Species not observed. ^b At room temperature in CD₂Cl₂.

low value of $\nu(\text{Pt-H})$ in the i.r. spectrum all suggest that the *trans* influences of the silyl and germly ligands are comparable with that of hydride in these complexes.

Crystal Data and Structure Determination.—C₃₆H₇₀P₂PtSi,

TABLE 3

Fractional co-ordinates ($\times 10^4$) (with standard deviations) for (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pt	4 605.7(2)	1 982.0(3)	1 509.0(1)
Si	5 737(2)	3 425(2)	1 486(2)
P(1)	3 052(2)	2 896(2)	1 237(1)
C(1)	2 587(7)	3 169(7)	1 896(4)
C(2)	2 407(7)	2 177(7)	2 217(4)
C(3)	2 013(9)	2 447(9)	2 749(5)
C(4)	2 782(9)	3 153(9)	3 180(5)
C(5)	3 000(9)	4 135(9)	2 873(5)
C(6)	3 371(7)	3 878(7)	2 336(4)
C(7)	3 069(7)	4 208(7)	901(4)
C(8)	2 171(8)	4 977(8)	880(4)
C(9)	2 432(9)	6 048(9)	679(5)
C(10)	2 666(9)	5 987(9)	78(5)
C(11)	3 514(9)	5 204(9)	85(5)
C(12)	3 255(8)	4 133(8)	292(4)
C(13)	1 990(7)	2 099(6)	734(4)
C(14)	905(7)	2 589(8)	490(4)
C(15)	96(8)	1 796(8)	1 418(4)
C(16)	463(8)	1 286(8)	-353(5)
C(17)	1 542(8)	809(8)	-106(5)
C(18)	2 356(7)	1 593(7)	236(4)
P(2)	5 915(2)	767(2)	1 844(1)
C(19)	6 114(6)	516(7)	2 643(4)
C(20)	5 204(8)	-53(8)	2 783(4)
C(21)	5 400(8)	-195(9)	3 444(5)
C(22)	5 589(9)	832(9)	3 767(5)
C(23)	6 525(9)	1 397(9)	3 648(5)
C(24)	6 324(8)	1 552(8)	2 983(4)
C(25)	7 263(7)	1 122(7)	1 815(4)
C(26)	8 205(8)	494(8)	2 179(4)
C(27)	9 240(8)	1 029(8)	2 169(5)
C(28)	9 291(9)	1 191(9)	1 539(5)
C(29)	8 347(9)	1 768(9)	1 171(5)
C(30)	7 318(8)	1 245(8)	1 186(4)
C(31)	5 512(6)	-509(6)	1 472(4)
C(32)	6 257(8)	-1 431(8)	1 670(5)
C(33)	5 707(8)	-2 438(8)	1 382(5)
C(34)	5 364(10)	-2 354(10)	727(5)
C(35)	4 597(9)	-1 428(10)	512(5)
C(36)	5 146(8)	-422(8)	801(5)

$M = 788$, Monoclinic, $a = 1 317.9(4)$, $b = 1 277.7(3)$, $c = 2 347.8(3)$ pm, $\beta = 106.96^\circ$, $U = 3.681$ nm³, $D_m = 1 380$, $Z = 4$, $D_c = 1 384$ kg m⁻³, Mo- K_α radiation, $\lambda = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 4.04$ mm⁻¹, space group $P2_1/n$ (no. 14) (conditions for reflection: $h0l$, $h + l = 2n$; $0k0$, $k = 2n$).

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

were collected for one asymmetric unit up to $\theta = 22^\circ$ using a crystal having dimensions *ca.* $0.8 \times 0.6 \times 0.4$ mm. Of 4 500 independent data measured, 4 165 could be classed as observed, and the structure was solved and refined using these. Absorption corrections were applied, the largest being approximately four times the smallest. The position of the platinum atom was found from a Patterson synthesis, and the other non-hydrogen atoms were found by successive difference-Fourier syntheses. Positions for the hydrogen atoms of the cyclohexyl groups were calculated assuming tetrahedral carbon atoms and C-H bond lengths of 110 pm. They were assigned fixed temperature factors (B 0.03 nm²) and not refined. The positions of the hydrogen atoms bonded to silicon and platinum could be vaguely inferred from a difference-Fourier map, but were not included in the structure-factor calculations. In the last few cycles of block-diagonal least-squares refinement a weighting scheme of the form $w = 70/|F_o|$ for $|F_o| > 70$ and $w = 1$ otherwise was used, and the Pt, Si, and P atoms were given anisotropic temperature factors. At convergence $R = 0.049$ and the maximum shift-to-error for a parameter was 0.6. Positional parameters are given in Table 3. The structure-factor table and thermal parameters are deposited as Supplementary Publication No. SUP 22291 (25 pp.).* The X-RAY '76' computer programs of Stewart *et al.*^{6b} were used for all the crystallographic calculations.

DISCUSSION

Although the reactions by which these complexes are formed have been known for some time the complexes themselves show unusual stability. Platinum complexes with hydride *trans* to silyl or germly are very uncommon. Furthermore, although SiH₃ complexes are usually sensitive to air and moisture, as are species containing chlorine bound to silicon, the complexes described here are remarkably stable and unreactive. This unreactivity can be understood in the light of the details of the structure of (1).

Distances and angles for (1) are summarised in Tables 4 and 5 and a stereoscopic view of the complex molecule is given in the Figure. The molecule has molecular C_s (m) symmetry within experimental error. The platinum atom lies 6 pm from the plane determined by the silicon and phosphorus atoms.

All the interatomic distances are normal except the Pt-Si bond, which is significantly longer than that reported in other compounds: 231.7 (ref. 10) or 229.3

¹⁰ P. B. Hitchcock, *Acta Cryst.*, 1976, **B32**, 2014.

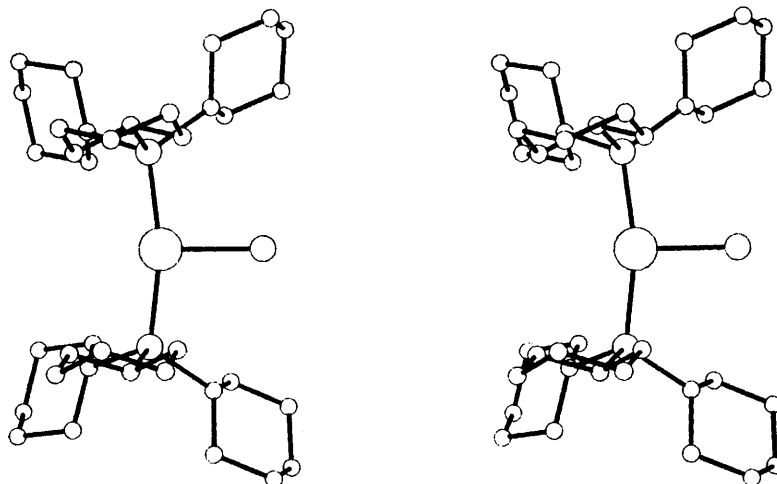
pm.¹¹ In both these cases, however, Si is *trans* to chloride, and the sort of difference observed may be explained in terms of differing *trans* influences between

TABLE 4

Selected bond lengths (pm) and angles (°) in (1). Quantities related by molecular symmetry are placed on the same line

Atoms	Bond or angle	Atoms	Bond or angle
Pt-Si	238.2(3)		
Pt-P(1)	228.0(2)	Pt-P(2)	228.3(2)
P(1)-C(1)	185.5(10)	P(2)-C(19)	184.4(9)
P(1)-C(7)	185.7(9)	P(2)-C(25)	185.4(10)
P(1)-C(13)	185.1(8)	P(2)-C(31)	185.3(9)
P(1)-Pt-P(2)	166.17(9)		
P(1)-Pt-Si	96.57(9)	P(2)-Pt-Si	96.82(9)
Pt-P(1)-C(1)	110.5(3)	Pt-P(2)-C(19)	109.8(3)
Pt-P(1)-C(7)	117.4(3)	Pt-P(2)-C(25)	117.2(3)
Pt-P(1)-C(13)	110.3(3)	Pt-P(2)-C(31)	110.6(3)
P(1)-C(1)-C(2)	113.1(6)	P(2)-C(19)-C(20)	114.6(5)
P(1)-C(1)-C(6)	110.7(6)	P(2)-C(19)-C(24)	109.3(6)
P(1)-C(7)-C(8)	119.3(7)	P(2)-C(25)-C(26)	119.1(7)
P(1)-C(7)-C(12)	111.5(6)	P(2)-C(25)-C(30)	112.5(6)
P(1)-C(13)-C(14)	118.0(6)	P(2)-C(31)-C(32)	117.9(6)
P(1)-C(13)-C(18)	111.8(7)	P(2)-C(31)-C(36)	112.8(6)

chloride and hydride. Distortion of bond angles is marked in the tricyclohexylphosphine ligands. The very large values of Pt-P(1)-C(7) and P(1)-C(7)-C(8) and the related Pt-P(2)-C(25) and P(2)-C(25)-C(26) are outstanding. These distinctions occur at the cyclohexyl



Stereoscopic view of (1), viewed normal to the co-ordination plane

rings closest to the silyl group, and are related to the close approach of C(7) and C(25) to Si (353 and 352 pm respectively). These rings produce an effective envelope, which will contribute greatly to the observed unreactivity of the SiH₃ group. On the hydride side of the molecule the enveloping is also pronounced. In particular, hydrogen atoms on C(2), C(4), and C(6) are between 250 and 300 pm of the corresponding substituents of C(20), C(22), and C(24). The 'protecting' effect may be clearly inferred from the Figure. Very

¹¹ C. Eaborn, K. J. Odell, A. Pidcock, and G. R. Scollary, *J.C.S. Chem. Comm.*, 1976, 317.

¹² A. Albinati, A. Musco, G. Carturan, and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219.

similar dispositions of tricyclohexylphosphine are found in *trans*-[Pt{P(C₆H₁₁)₃}₂(HCS₂)]¹² where the placing of the atomic co-ordinates on a consistent axial system gives a near superimposition for much of the molecule.

EXPERIMENTAL

N.m.r. and i.r. measurements were made as in ref. 13. All the manipulations were carried out *in vacuo* or under a dry nitrogen atmosphere. Platinum starting materials

TABLE 5

Summary of parameters for cyclohexyl rings. Thirty six independent values of each parameter are involved

Parameter	Minimum	Maximum	Mean	e.s.d.	
				of	Mean
C-C bonds (pm)	147.4	153.5	151.8	1.4	1.5
C-C-C angles (°)	108.6	112.4	111.0	0.9	0.8
C-C-C-C torsion angles (°)	53.6	58.6	56.1	1.3	1.2

and the silyl and germyl compounds were made by standard methods. Solvents were dried and freshly distilled before use.

Standard methods for n.m.r.-tube reactions were used. The platinum substrate (0.1 nmol) was weighed into an n.m.r. tube blown on to a B.10 cone and attached to a standard Pyrex-glass vacuum line. Dichlorodideuterio-methane was condensed into the tube and the complex completely dissolved. The silyl or germyl compound was

then condensed into the tube which was sealed and stored at -196 °C.

Preparation of trans-Hydridosilylbis(tricyclohexylphosphine)platinum(II) (1).—The complex [PtH₂{P(C₆H₁₁)₃}₂] (0.5 mmol) was dissolved in CH₂Cl₂ (5 cm³) in a Schlenk tube and SiH₄ (0.6 mmol) was condensed into the tube from a vacuum line. The mixture was warmed to room temperature with vigorous shaking and then allowed to stand for 2 h. A white precipitate was formed. The solvent was removed *in vacuo* to yield the curdy product which was recrystallised from hexane by slow evaporation of the solvent in a stream of nitrogen (Found: C, 53.5; H, 8.70. C₃₆H₇₀P₂PtSi requires C, 54.85; H, 8.70%), m.p. 178—

¹³ E. A. V. Ebsworth, J. M. Edward, and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 1667.

180 °C (with decomp.); i.r. spectrum in Nujol, $\nu(\text{SiH})$ at 2 025 and 2 020 (strong), $\nu(\text{PtH})$ at 1 860s cm^{-1} .

The complexes *trans*- $[\text{PtH}(\text{SiClH}_2)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ (2) and *trans*- $[\text{PtH}(\text{GeH}_3)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ (3) were prepared by a similar method but recrystallised from hot benzene. For (2) (Found: C, 52.65; H, 8.30. $\text{C}_{36}\text{H}_{69}\text{ClP}_2\text{PtSi}$ requires C, 52.55; H, 8.45%), m.p. 205—210 °C (with decomp.); i.r. spectrum in Nujol, $\nu(\text{SiH})$ at 2 050, 2 025, and 2 000 (strong), $\nu(\text{PtH})$ at 1 872s cm^{-1} . For (3) (Found: C, 52.05; H,

8.60. $\text{C}_{36}\text{H}_{70}\text{GeP}_2\text{Pt}$ requires C, 51.95; H, 8.45%), m.p. 195—198 °C (with decomp.); i.r. spectrum in Nujol, $\nu(\text{PtH})$ at 1 915vs, br cm^{-1} .

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