Synthesis of *trans*-Di-μ-hydrido-bis(silyl)bis(trialkylphosphine)diplatinum Complexes: Crystal and Molecular Structure of Di-μ-hydrido-bis(tricyclohexylphosphine)bis(triethylsilyl)diplatinum

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Bis(ethylene)(tricyclohexylphosphine)platinum reacts with silanes SiR_3H [SiR_3 = $SiCl_3$, $SiClMe_2$, $SiMe_2Ph$, $SiMe_2(CH_2Ph)$, $SiMe_2Et$, $SiEt_3$, or $Si(OEt)_3$] to give hydrido-bridged diplatinum complexes [$\{Pt(\mu\text{-}H)(SiR_3)[P(C_6H_{11})_3]\}_2$]. The complex [$\{Pt(\mu\text{-}H)(GeMe_3)[P(C_6H_{11})_3]\}_2$] has been similarly prepared using trimethylgermane. A single-crystal *X*-ray diffraction study of [$\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2$] shows that the crystals are monoclinic, with space group $P2_1/c$ and $Z = 4$ in a unit cell of dimensions $a = 20.72(2)$, $b = 13.88(1)$, $c = 18.97(1)$ Å, and $\beta = 101.15(7)°$. The structure has been determined by heavy-atom methods from automated diffractometer data and refined to R 0.071 (R' 0.083) for 3 100 independent reflections. The results establish that the six atoms $(SiPtP)_2$ comprising the main skeleton of the molecule are significantly non-coplanar with a dihedral angle of 21° between the two SiPtP planes. There is a platinum–platinum separation of 2.692 Å. The bridging hydrido-ligands have not been located. An interesting property of the diplatinum complexes is the absence in their ^1H n.m.r. spectra of a high-field resonance. However, n.m.r. studies on [$\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t{}_2)\}_2$] show that this class of complex is dynamic, and the signal corresponding to the hydrido-bridge occurs at *ca.* τ 7. This low-field PtH resonance, coupled with deuteriation studies, and bridge-cleavage reactions with C_2H_4, CO, $P(OPh)_3$, Bu^tNC, PMe_3, and $AsMe_2Ph$, provides evidence for asymmetric $Pt(\mu\text{-}H)_2Pt$ bridges.

THE availability of bis(cyclo-octa-1,5-diene)platinum,[1] [$Pt(cod)_2$], has made it possible to use this reactive species as a precursor to many new organoplatinum compounds. We have previously reported the use of [$Pt(cod)_2$] in the synthesis of [$Pt_3(CNBu^t)_6$] [2] and [$Pt\{P(C_6H_{11})_3\}_2$],[3] and in the preparation of various acetylene,[4] allyl,[5] fluoro-olefinic,[6] and hexafluoroacetone [7] complexes. Moreover, ethylene-saturated solutions of [$Pt(cod)_2$] react with tricyclohexylphosphine to give the platinum(0) complex [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$].[8] This complex undergoes oxidative-addition reactions with triorganosilanes to afford diplatinum complexes [$\{Pt(\mu\text{-}H)(SiR_3)[P(C_6H_{11})_3]\}_2$],[9] which we have recently shown to be effective hydrosilylation catalysts.[10] In this paper we give details of their synthesis and molecular structure.

RESULTS AND DISCUSSION

The oxidative insertion of platinum(0) complexes into Si–H bonds is well established in reactions of [$Pt(PPh_3)_4$] or [$Pt(C_2H_4)(PPh_3)_2$] with SiR_3H which afforded *cis*-[$PtH(SiR_3)(PPh_3)_2$].[11] It was therefore to be expected that the complex [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$] would similarly react with SiR_3H, but it was far from evident as to what would be the nature of the final product, assuming loss of ethylene and initial formation of a three-co-ordinate platinum(II) species [$PtH(SiR_3)\{P(C_6H_{11})_3\}$].

Treatment of [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$] in toluene or light petroleum with the silanes SiR_3H [SiR_3 = $SiMe_2Et$, $SiEt_3$, $SiMe_2Ph$, $SiMe_2(CH_2Ph)$, $SiClMe_2$, $SiCl_3$, and $Si(OEt)_3$] gives in good yield air-stable yellow crystalline complexes (Table 1). Trimethylgermane reacted in a similar manner. That these new compounds were diplatinum complexes was indicated by their ^{31}P (^1H-decoupled) n.m.r. spectra, data from which are summarised in Table 2. Singlet signals were observed having two sets of ^{195}Pt satellites arising from molecules with up to one active platinum nucleus. Molecules with

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[7] M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278.

[8] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 450.

[9] M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Chem. Comm.*, 1976, 671.

[10] M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, 1977, 1519, 1525.

[11] C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.* 1972, **43**, C5; J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 881.

two ^{195}Pt atoms gave rise to a superimposed AA′XX′ spectrum. In order to establish the molecular structure of this family of complexes a single-crystal *X*-ray diffraction study was made on the product from $SiEt_3H$ and $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$.

TABLE 1

Diplatinum complexes $[\{Pt(\mu\text{-}H)(MR_3)(PR'_3)\}_2]$ (M = Si or Ge) [a]

Complex [b]	M.p. (θ_c/°C) (decomp.)	Yield (%)	Analysis (%) C	Analysis (%) H
$[\{Pt(\mu\text{-}H)(SiMe_2Et)[P(C_6H_{11})_3]\}_2]$ [c,d]	140—150	88	50.5 (50.2)	8.4 (8.1)
$[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$	142—143	47	48.5 (48.7)	8.4 (8.3)
$[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$	130—140	95	50.6 (51.0)	7.6 (7.4)
$[\{Pt(\mu\text{-}H)[SiMe_2(CH_2Ph)][P(C_6H_{11})_3]\}_2]$ [e,]	136—139	95	53.4 (53.2)	8.2 (7.6)
$[\{Pt(\mu\text{-}H)(SiClMe_2)[P(C_6H_{11})_3]\}_2]$ [e]	135—140	60	44.3 (44.0)	7.3 (7.1)
$[\{Pt(\mu\text{-}H)(SiCl_3)[P(C_6H_{11})_3]\}_2]$ [c,g]	178	95	39.4 (39.3)	5.9 (5.8)
$[\{Pt(\mu\text{-}H)[Si(OEt)_3][P(C_6H_{11})_3]\}_2]$ [h]	183—193	82	45.4 (45.1)	7.6 (7.7)
$[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t_2)\}_2]$	128—131	60	35.2 (34.7)	7.2 (7.2)
$[\{Pt(\mu\text{-}H)(GeMe_3)[P(C_6H_{11})_3]\}_2]$ [c,i]	120—124	96	45.9 (46.0)	7.9 (7.4)

[a] Calculated values are given in parentheses. [b] All the complexes are pale yellow. [c] Crystallises with one molecule of toluene. [d] P, 5.3 (5.1%). [e] Crystallises with half a molecule of toluene. [f] P, 3.6 (4.8%); *M*(benzene), 1 148 (1 298). [g] *M*(benzene), 1 196 (1 314). [h] P, 5.0 (4.8%); *M*(benzene), 1 276 (1 279). [i] P, 5.8 (4.8%).

TABLE 2

Phosphorus-31 and ^{1}H n.m.r. data [a]

Complex	^{31}P (δ/p.p.m.)		^{1}H (τ)
$[\{Pt(\mu\text{-}H)(SiMe_2Et)[P(C_6H_{11})_3]\}_2]$ [b]	−63.6 [*J*(PPt) 3 237, 61]		9.0—7.6 (m,br, MeSi, EtSi, C_6H_{11}), 7.8 (s, *Me*Ph), 6.22 [t, PtH, *J*(PH) 51]
$[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$	−63.2 [*J*(PPt) 3 228, 60]		9.0—7.6 (m,br, EtSi, C_6H_{11}), 6.66 [t, PtH, *J*(PH) 52]
$[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$	−63.1 [*J*(PPt) 3 188, 70]		9.1—7.9 (m,br, MeSi, C_6H_{11}), 2.7 and 1.8 (m, Ph)
$[Pt(\mu\text{-}H)[SiMe_2(CH_2Ph)][P(C_6H_{11})_3]\}_2]$ [b]			9.0—7.6 (m,br, CH_2Si, C_6H_{11}), 8.7 (s, MeSi), 7.8 (s, *Me*Ph)
$[\{Pt(\mu\text{-}H)(SiClMe_2)[P(C_6H_{11})_3]\}_2]$ [b]			9.0—7.6 (m,br, MeSi, C_6H_{11}), 7.8 (s, *Me*Ph)
$[\{Pt(\mu\text{-}H)(SiCl_3)[P(C_6H_{11})_3]\}_2]$ [b]			9.0—7.6 (m,br, C_6H_{11}), 7.8 (s, *Me*Ph)
$[\{Pt(\mu\text{-}H)[Si(OEt)_3][P(C_6H_{11})_3]\}_2]$	−66.3 [*J*(PPt) 3 127, 82]		8.54 [t, *Me*CH_2O, *J* (HH) 7], 8.0 (m,br, C_6H_{11}), 5.80 [q, C*H*$_2$O, *J*(HH) 7]
$[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t_2)\}_2]$	−67.8 [*J*(PPt) 3 125, 68]	75 °C	8.66 [Bu^t, *J*(PH) 13], 8.19 [Me, *J*(PH) 9, *J*(PtH) 45], 7.05 [PtH, *J*(PtH) 681, *J*(PH) 52], 6.0 [CH_2O, *J*(HH) 7]
		25 °C	8.70 [Bu^t, *J*(PH) 13], 8.69 (*Me*CH_2O), 8.21 [Me, *J*(PH) 9, *J*(PtH) 45], 6.87 [PtH, *J*(PH) 51], 5.97 [CH_2O, *J*(HH) 7]
		−60 °C	8.69 [Bu^t, *J*(PH) 14], 8.23 [Me, *J*(PH) 9, *J*(PtH) 47], 6.65 [PtH, *J*(PtH) 456, 894; *J*(PH) 104, 0], 5.94 [CH_2O, *J*(HH) 7]
$[\{Pt(\mu\text{-}H)(GeMe_3)[P(C_6H_{11})_3]\}_2]$	−62		
cis-$[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}(CNBu^t)]$	−48.7 [*J*(PPt) 1 455, *J*(PSi) 145]		13.1 [d, PtH, *J*(PtH) 960, *J*(PH) 21], 8.96 (s, Bu^t), 8.84 [d, MeSi, *J*(PH) 3, *J*(PtH) 32], 8.2 (m,br, C_6H_{11}), 2.65 and 1.87 (m, Ph)
cis-$[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}(PMe_3)]$	−48.5 [*J*(PPt) 1 525, *J*(PP) 14, *J*(PSi) 150] 20.7 [*J*(PPt) 2 330, *J*(PP) 14]		12.9 [d of d, PtH, *J*(PH) 160, 22], 9.0 [d, MeSi, *J*(PH) 2, *J*(PtH) 28], 8.70 [d, Me_3P, *J*(PH) 8, *J*(PtH) 26], 8.4 (m,br, C_6H_{11}), 2.7 and 2.0 (m, Ph)
cis-$[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}(AsMe_2Ph)]$	−50.6 [*J*(PPt) 1 592, *J*(PSi) 151]		9.0 (s,br, MeSi), 8.68 (s, MeAs), 8.5 (m, br, C_6H_{11}), 2.9—1.7 (m, Ph)

[a] Measured in C_6D_6; ^{31}P chemical shifts proton-decoupled relative to external H_3PO_4, coupling constants in Hz. [b] See footnotes *c* and *e* of Table 1.

The molecular structure is shown in Figure 1, and the contents of the unit cell in Figure 2. Table 3 gives internuclear distances (uncorrected for thermal effects) and bond angles. The six Si, P, and Pt atoms comprising the central skeleton of the molecule are significantly non-coplanar with a dihedral angle of 21° between the two planes defined by P(1),Pt(1),Si(1) and P(2),Pt(2),Si(2). The Pt–Pt separation [2.692(3) Å] is longer than the sum (2.62 Å) of the covalent radii but examples exist [7,12] of di- and poly-nuclear platinum complexes, with and without bridging ligands, having Pt–Pt distances both smaller and larger than that in $[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$.

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[12] K. P. Wagner, R. W. Hess, P. M. Treichel, and J. C. Calabrese, *Inorg. Chem.*, 1975, **14**, 1121 and refs. therein.

Although bridging hydrogen atoms were not located by the *X*-ray crystallographic study, the dihedral angle of 21° is perhaps indicative of their presence, and may be compared with the 26° dihedral angle between the two PNiP planes in $[\{Ni(\mu\text{-}H)[(cyclo\text{-}C_6H_{11})_2P(CH_2)_3P\text{-}(cyclo\text{-}C_6H_{11})_2]\}_2]$, although it must be recognised that in the latter complex,[13] where the bridging hydrogen atoms were located by the *X*-ray diffraction study, the metal is in an oxidation state I as compared with II in the platinum complex. The SiPtP angle of 102° (mean value) in $[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$ is also somewhat suggestive of the presence of Pt–H–Pt bridges, otherwise there seems no good reason why this angle should deviate so much from 120° for trigonal co-ordinated platinum. The smaller angle of 102° seems unlikely to be due to intramolecular steric interactions since the shortest non-bonded contacts occur between hydrogen atoms on adjacent molecules.

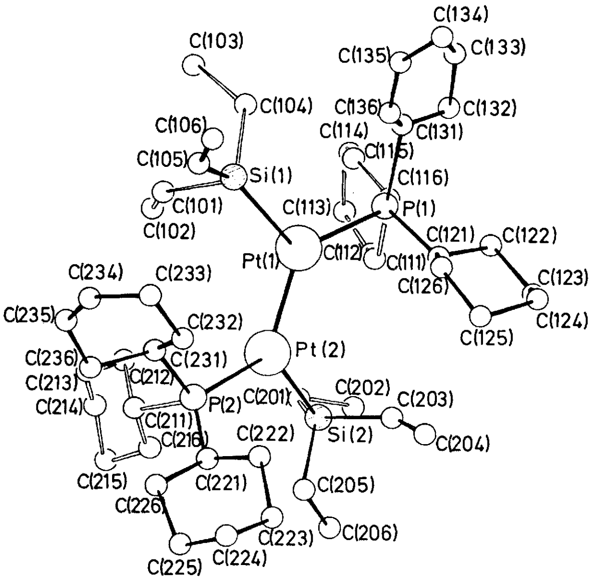


FIGURE 1 A molecule of $[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$ showing the crystallographic numbering system and omitting hydrogen atoms

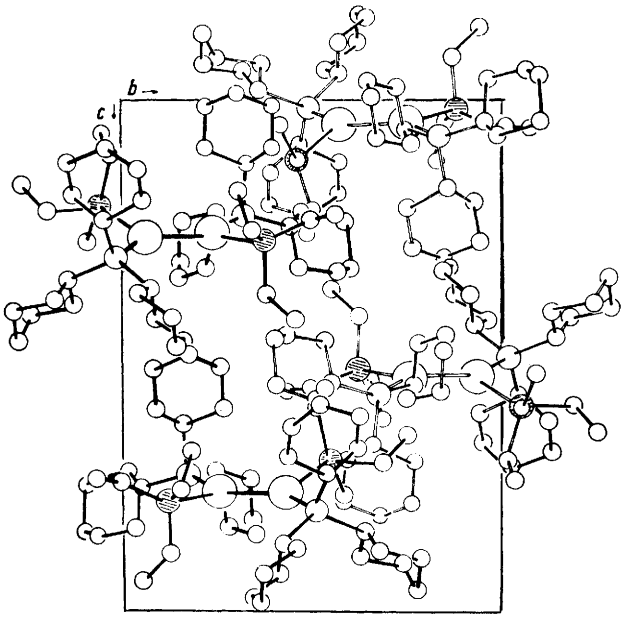


FIGURE 2 Contents of the unit cell of $[\{Pt(\mu\text{-}H)(SiEt_3)\text{-}[P(C_6H_{11})_3]\}_2]$ viewed on to the *bc* plane seen down $-a^*$

The ethyl groups of both crystallographically independent $SiEt_3$ ligands show high thermal activity. It would be unwise to attach significance to the deviations from exact tetrahedral geometry in these and in the phosphine ligands within the limitations of the data. The cyclohexyl groups adopt chair conformations.

Attempts to detect hydrido-ligands in the diplatinum complexes by i.r. and n.m.r. spectroscopy were initially inconclusive. In the i.r. spectra of the complexes a broad band was observed in the range 1 545—1 695 cm^{-1}. Generally, for hydridometal derivatives in which hydrogen is in a position bridging two metal atoms the hydrogen mode is shifted to even lower energy, *ca.* 1 100 ± 300 cm^{-1}.[14] However, deuteriation studies described below indicate that the bands near 1 600 cm^{-1} are due to $Pt(\mu\text{-}H)Pt$ bridges. The diplatinum complexes showed no resonance in their ^1H n.m.r. spectra above τ 12, from which it might be inferred that there was no hydrogen bonded to platinum. However, chemical evidence for the existence of $Pt(\mu\text{-}H)Pt$ bridges came from a study of the reactivity of the complex $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ towards various reagents.

Treatment of $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ with t-butyl isocyanide, trimethylphosphine, or dimethylphenylarsine afforded the terminal-hydridoplatinum complexes $[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}L]$ ($L = CNBu^t$, PMe_3, or $AsMe_2Ph$), apparently formed by symmetrical cleavage of the $Pt(\mu\text{-}H)_2Pt$ bridges. The spectroscopic properties of these products showed clearly the presence of PtH groups. In the i.r. spectra of the three complexes strong Pt–H stretching bands occurred near 2 100 cm^{-1}. In their ^1H n.m.r. spectra (Table 2), the trimethylphosphine and t-butyl isocyanide derivatives showed a high-field resonance near τ 13. The dimethylphenylarsine derivative was relatively insoluble so that a PtH resonance signal could not be detected in its spectrum.

The stereochemistry of the complexes $[PtH(SiMe_2Ph)\text{-}\{P(C_6H_{11})_3\}L]$ is established from features of their n.m.r. spectra (Table 2). Their ^{31}P spectra all show a resonance near −50 p.p.m., assignable to the phosphorus nucleus of the $P(C_6H_{11})_3$ ligand, with a large $^{31}P\text{–}^{29}Si$ coupling. The magnitude of this coupling is indicative of a *trans*-$[(C_6H_{11})_3P{\cdot}Pt{\cdot}SiMe_2Ph]$ arrangement. Moreover, the signal at 20.7 p.p.m. due to the PMe_3 group in the ^{31}P spectrum of $[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}\text{-}(PMe_3)]$ shows no $^{31}P\text{–}^{29}Si$ coupling, and has only a small

[13] K. Jonas, unpublished work; see P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1, p. 145.

[14] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

coupling to the other phosphorus nucleus which, therefore, must be *cis* to it. In the ^{1}H n.m.r. spectrum of [PtH(SiMe$_2$Ph){P(C$_6$H$_{11}$)$_3$}L] the hydrido-resonance near τ 13 shows for L = CNBu^t, J(PH) 21 Hz, while from a partially decoupled ^{31}P spectrum for L = PMe$_3$, J(PH) 160 (PMe$_3$) and 22 Hz [P(C$_6$H$_{11}$)$_3$]. These coupling constants establish conclusively that both in the t-butyl isocyanide and in the trimethylphosphine derivatives the hydrido-ligand is *cis* to the tricyclohexylphosphine group. Moreover, the 160-Hz Me$_3$^{31}P–H coupling shows that in the trimethylphosphine complex the hydride is *trans* to this ligand. Thus in these complexes the hydrido- and dimethylphenylsilyl ligands are *cis* to each other.

TABLE 3

Internuclear distances (Å) and bond angles (°) in [{Pt(μ-H)(SiEt$_3$)[P(C$_6$H$_{11}$)$_3$]}$_2$] *

Pt(1)–Pt(2)	2.692(3)	P(1)–Pt(1)–Pt(2)	131.3(2)
Pt(1)–P(1)	2.277(9)	Si(1)–Pt(1)–Pt(2)	125.1(3)
Pt(1)–Si(1)	2.338(11)	P(1)–Pt(1)–Si(1)	103.2(3)
Pt(2)–P(2)	2.264(9)	P(2)–Pt(2)–Si(2)	101.8(3)
Pt(2)–Si(2)	2.335(11)	P(2)–Pt(2)–Pt(1)	133.6(2)
		Si(2)–Pt(2)–Pt(1)	123.5(3)
Tricyclohexylphosphine ligands			
P(1)–C(111)	1.86(3)	C(111)–P(1)–Pt(1)	112(1)
C(111)–C(112)	1.55(4)	C(111)–C(112)–C(113)	111(2)
C(112)–C(113)	1.55(4)	C(112)–C(113)–C(114)	109(3)
C(113)–C(114)	1.51(4)	C(113)–C(114)–C(115)	113(2)
C(114)–C(115)	1.56(5)	C(114)–C(115)–C(116)	108(3)
C(115)–C(116)	1.59(5)	C(115)–C(116)–C(111)	109(2)
C(116)–C(111)	1.56(4)	C(116)–C(111)–C(112)	112(2)
		C(112)–C(111)–P(1)	109(2)
		C(116)–C(111)–P(1)	111(2)
P(1)–C(121)	1.86(3)	C(121)–P(1)–Pt(1)	104(1)
C(121)–C(122)	1.60(5)	C(121)–C(122)–C(123)	106(3)
C(122)–C(123)	1.58(5)	C(122)–C(123)–C(124)	108(3)
C(123)–C(124)	1.64(5)	C(123)–C(124)–C(125)	104(3)
C(124)–C(125)	1.56(5)	C(124)–C(125)–C(126)	112(3)
C(125)–C(126)	1.47(6)	C(125)–C(126)–C(121)	111(3)
C(126)–C(121)	1.59(4)	C(126)–C(121)–C(122)	106(2)
		C(122)–C(121)–P(1)	119(2)
		C(126)–C(121)–P(1)	113(2)
P(1)–C(131)	1.86(3)	C(131)–P(1)–Pt(1)	122(1)
C(131)–C(132)	1.52(5)	C(131)–C(132)–C(133)	107(3)
C(132)–C(133)	1.55(5)	C(132)–C(133)–C(134)	110(3)
C(133)–C(134)	1.58(5)	C(133)–C(134)–C(135)	105(3)
C(134)–C(135)	1.53(6)	C(134)–C(135)–C(136)	109(3)
C(135)–C(136)	1.54(6)	C(135)–C(136)–C(131)	110(3)
C(136)–C(131)	1.55(5)	C(136)–C(131)–C(132)	112(2)
		C(132)–C(131)–P(1)	117(2)
		C(136)–C(131)–P(1)	112(2)
		C(111)–P(1)–C(121)	104(1)
		C(121)–P(1)–C(131)	102(1)
		C(131)–P(1)–C(111)	110(1)
P(2)–C(211)	1.90(3)	C(211)–P(2)–Pt(2)	116(1)
C(211)–C(212)	1.57(5)	C(211)–C(212)–C(213)	107(3)
C(212)–C(213)	1.72(6)	C(212)–C(213)–C(214)	111(4)
C(213)–C(214)	1.32(7)	C(213)–C(214)–C(215)	117(5)
C(214)–C(215)	1.54(8)	C(214)–C(215)–C(216)	111(4)
C(215)–C(216)	1.53(6)	C(215)–C(216)–C(211)	108(3)
C(216)–C(211)	1.53(5)	C(216)–C(211)–C(212)	114(3)
		C(212)–C(211)–P(2)	103(2)
		C(216)–C(211)–P(2)	111(2)
P(2)–C(221)	1.86(3)	C(221)–P(2)–Pt(2)	118(1)
C(211)–C(222)	1.52(4)	C(221)–C(222)–C(223)	111(3)
C(222)–C(223)	1.56(5)	C(222)–C(223)–C(224)	104(3)
C(223)–C(224)	1.65(6)	C(223)–C(224)–C(225)	100(3)
C(224)–C(225)	1.63(6)	C(224)–C(225)–C(226)	108(3)
C(225)–C(226)	1.58(5)	C(225)–C(226)–C(221)	107(3)
C(226)–C(221)	1.54(5)	C(226)–C(221)–C(222)	109(3)
		C(222)–C(221)–P(2)	114(2)
		C(226)–C(221)–P(2)	117(2)
P(2)–C(231)	1.84(4)	C(231)–P(2)–Pt(2)	106(1)
C(231)–C(232)	1.48(5)	C(231)–C(232)–C(233)	114(3)
C(232)–C(233)	1.53(7)	C(232)–C(233)–C(234)	107(3)
C(233)–C(234)	1.69(7)	C(233)–C(234)–C(235)	122(5)
C(234)–C(235)	1.43(7)	C(234)–C(235)–C(236)	104(4)
C(235)–C(236)	1.59(7)	C(235)–C(236)–C(231)	109(3)
C(236)–C(231)	1.66(5)	C(236)–C(231)–C(232)	108(3)
		C(236)–C(231)–P(2)	116(2)
		C(232)–C(231)–P(2)	112(2)
		C(211)–P(2)–C(221)	105(1)
		C(211)–P(2)–C(231)	103(1)
		C(221)–P(2)–C(231)	108(1)
Triethylsilyl ligands			
Si(1)–C(101)	1.87(5)	C(101)–Si(1)–Pt(1)	108(2)
C(101)–C(102)	1.50(8)	C(102)–C(101)–Si(1)	110(4)
Si(1)–C(104)	1.84(4)	C(104)–Si(1)–Pt(1)	121(1)
C(104)–C(103)	1.56(6)	C(103)–C(104)–Si(1)	119(3)
Si(1)–C(105)	1.87 †	C(105)–Si(1)–Pt(1)	100 †
C(105)–C(106)	1.55 †	C(106)–C(105)–Si(1)	132 †
		C(101)–Si(1)–C(104)	107(2)
		C(101)–Si(1)–C(105)	107(2)
		C(104)–Si(1)–C(105)	112(1)
Si(2)–C(201)	2.07(3)	C(201)–Si(2)–Pt(2)	100(1)
C(201)–C(202)	1.54(6)	C(202)–C(201)–Si(2)	110(2)
Si(2)–C(203)	1.88(4)	C(203)–Si(2)–Pt(2)	115(1)
C(203)–C(204)	1.49(7)	C(204)–C(203)–Si(2)	112(3)
Si(2)–C(205)	1.91(4)	C(205)–Si(2)–Pt(2)	121(1)
C(205)–C(206)	1.56(6)	C(206)–C(205)–Si(2)	112(3)
		C(201)–Si(2)–C(203)	108(2)
		C(201)–Si(2)–C(205)	108(1)
		C(203)–Si(2)–C(205)	104(2)

* Estimated standard deviations in parentheses. † C(105) and C(106) were not refined (see text).

In contrast to the reactions with CNBu^t, PMe$_3$, or AsMe$_2$Ph, the diplatinum complex [{Pt(μ-H)(SiMe$_2$Ph)-[P(C$_6$H$_{11}$)$_3$]}$_2$] reacts with an excess of P(OPh)$_3$ to give the platinum(0) complex [Pt{P(OPh)$_3$}$_4$], while examination of the i.r. spectrum of the reaction mixture revealed the presence of liberated SiMe$_2$(Ph)H [$\nu_{max.}$(SiH) at 2 136 cm^{-1}]. With a deficiency of P(OPh)$_3$ the diplatinum complex afforded [Pt{P(C$_6$H$_{11}$)$_3$}{P(OPh)$_3$}$_2$]. Reaction with ethylene gave [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}], and with carbon monoxide gave the known triplatinum complex [{Pt(μ-CO)[P(C$_6$H$_{11}$)$_3$]}$_3$].[15]

It was anticipated that reaction of [Pt(C$_2$H$_4$)$_2$-{P(C$_6$H$_{11}$)$_3$}] with SiMe$_2$(Ph)D would yield [{Pt(μ-D)-(SiMe$_2$Ph)[P(C$_6$H$_{11}$)$_3$]}$_2$]. However, when this reaction was carried out the i.r. spectrum of the product still contained a band at 1 610 cm^{-1}, albeit greatly reduced in intensity. A stronger band appeared in the spectrum at 1 163 cm^{-1}. The relation between these bands makes it reasonable to assign the latter to a Pt(μ-D)Pt group and the former to a Pt(μ-H)Pt bridge. Evidently, in the reaction with SiMe$_2$(Ph)D some deuterium–hydrogen exchange occurs, presumably by reversal of some of the steps in the hydrosilylation mechanism discussed earlier,[10] but no attempt was made to identify deuteriated products.

Reaction of the partially deuteriated product from SiMe$_2$(Ph)D and [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}] with PMe$_3$ gave a mixture of the mononuclear deuteriated and non-deuteriated hydrides *cis*-[PtD(SiMe$_2$Ph){P(C$_6$H$_{11}$)$_3$}-

[15] A. Albinati, G. Carturan, and A. Musco, *Inorg. Chim. Acta*, 1976, **16**, L3.

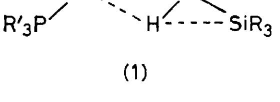
$(PMe_3)]$ {$\nu_{max.}$(PtD) at 1 470 cm^{-1}; ^{2}D n.m.r., τ 12.9 [d of d, J(PD) 24 and 3, J(PtD) 122 Hz]} and *cis*-$[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}(PMe_3)]$ (see above). A similar mixture of deuteriated and non-deuteriated mononuclear platinum hydrides was obtained in a reaction with CNBu^t. The relative intensities of the i.r. bands and n.m.r. signals showed that the deuteriated species predominated in the mixtures of mononuclear hydrides produced in these reactions.

From the above results it is evident that the diplatinum complex obtained from the reaction of $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ with $SiMe_2(Ph)H$ contains hydride bonded to platinum, and that this complex can react to afford either the '$[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}]$' moiety, which can be captured by a σ-donor molecule L, or with strong π acceptors can revert to platinum(0) species.

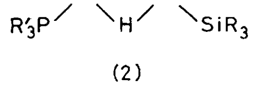
The disturbing feature of the apparent absence of a Pt*H* signal in the ^{1}H n.m.r. spectra of the diplatinum complexes appeared at first to be compounded by the results of Brown *et al.*[16] These workers have recently characterised binuclear bis(diphenylphosphino)methane cationic complexes of platinum containing both bridging and terminal hydrido-ligands. In the complex $[Pt_2H_2(\mu\text{-}H)(dppm)_2]Cl$ (dppm = $Ph_2PCH_2PPh_2$), for example, the n.m.r. resonances for terminal Pt*H* and bridging Pt(μ-*H*)Pt appear at τ 16.8 [^1J(PtH) 1 162, ^2J(PtH) 116 Hz] and 15.8 [^1J(PtH) 540 Hz], respectively. Thus it appears that in a complex containing a symmetrical Pt(μ-H)Pt group a high-field n.m.r. signal near τ 16 is to be expected. The absence of a signal in this region for the complexes $[\{Pt(\mu\text{-}H)(SiR_3)[P(C_6H_{11})_3]\}_2]$ indicates that either (*i*) the resonance is not seen because the molecules are undergoing dynamic behaviour in solution and the measurement (at 30 °C) is being made near the coalescence temperature, or (*ii*) the Pt(μ-H)Pt bridge bonding is of a 'non-classical' kind giving rise to a hydride resonance with an unusual chemical shift. A combination of (*i*) and (*ii*) could also not be neglected. In view of these considerations, detailed n.m.r. experiments were carried out on the complex $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t{}_2)\}_2]$, prepared by treating $SiH(OEt)_3$ with $[Pt(C_2H_4)_2(PMeBu^t{}_2)]$. The complex $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t{}_2)\}_2]$ was chosen for study in order to simplify the τ 5—10 region of the n.m.r. spectrum. Diplatinum complexes containing cyclohexyl groups and alkyl substituents on silicon show n.m.r. bands which tend to obscure signals below τ 10. Moreover, the chosen complex is considerably more soluble than the tricyclohexylphosphine derivatives.

From this n.m.r. study, resonances due to the protons in the PMeBu$^t{}_2$ and $Si(OEt)_3$ groups were readily assigned, the chemical shifts and coupling constants being invariant with temperature (Table 2). However, of considerable significance was the observation of another signal the shift of which varied, from τ 7.05 at 75 °C to τ 6.65 at —60 °C. Moreover, this resonance showed in the —60 °C limiting spectrum two couplings of 456 and 894 Hz, whereas at 25 °C broadening of the signal made these couplings unobservable. At 75 °C a single coupling of 681 Hz was measured. The magnitudes[14] of these coupling constants clearly show that they are due to hydride bonded to platinum, and this was confirmed by a ^{1}H-{^{195}Pt} INDOR measurement at 30 °C which gave a platinum resonance at —44 p.p.m. [relative to 21.4 MHz ($SiMe_4$ at 100 MHz)] with J(PtP) 3 122 Hz and an average J(PtH) 678 Hz. This ^{195}Pt–^{1}H coupling is in excellent agreement with that obtained from the ^{1}H spectrum at 75 °C.

The nature of the platinum satellites in the signal at τ 6.65 in the spectrum of $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t{}_2)\}_2]$ at —60 °C shows that the μ-H proton is associated more closely with one metal atom than with the other. However, the complex is undergoing dynamic behaviour at elevated temperatures. It is of interest that the time-averaged J(PtH) value of 681 Hz found at 75 °C is of similar magnitude to that observed[16] for the symmetrically bridged hydride in the cation $[Pt_2H_2(\mu\text{-}H)(dppm)_2]^+$ discussed above. The discovery of two distinct J(PtH) values in the spectrum of $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t{}_2)\}_2]$ at low temperatures leads us to propose that the diplatinum complexes contain unsymmetrical Pt(μ-H)Pt bridge bonds; there still remains, however, a need to account for the relatively low chemical shift, τ 9, below that found in $[Pt_2H_2(\mu\text{-}H)(dppm)_2]^+$. Although several of the diplatinum complexes listed in Table 2 were too insoluble to allow identification of a Pt(μ-H)Pt signal in their n.m.r. spectra, nevertheless such resonances were identified at τ 6.22 and 6.66 in the spectra of $[\{Pt(\mu\text{-}H)(SiR_3)[P(C_6H_{11})_3]\}_2]$ (SiR_3 = $SiMe_2Et$ or $SiEt_3$, respectively). Moreover, these Pt(μ-*H*)Pt resonances in the room-temperature ^{1}H n.m.r. spectra in the τ 6.2—6.9 region are similar in shift but somewhat upfield from that we have measured (τ 5.8) for the hydrogen bonded to silicon in the silane $SiH(OEt)_3$. It thus seems possible that the apparently abnormally low chemical shift for the Pt(μ-H)Pt resonance in the diplatinum complexes $[\{Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ is the result of incipient Pt(μ-H)Si bridging in solution, so that the bonding is better represented by the multicentre interaction (1) rather than (2). Asymmetric Pt(μ-H)Pt bridges might be expected because of the strong *trans* influence of SiR_3 groups[17] since a given μ-H atom is *trans* to silicon on one platinum atom but is *trans* to phosphorus on the other. This in itself could be sufficient to account for the two ^{195}Pt–^{1}H coupling constants mentioned above, but does not explain the chemical-shift value being similar to that found in silanes. Moreover, the *trans*



(1)



(2)

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[16] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L27, *J.C.S. Dalton*, 1978, 516.

[17] J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 1343.

influence of the SiR_3 group on one platinum atom would serve to move the hydrogen *trans* to it towards the silicon on the other platinum atom.

An unsymmetrical bridged hydrido-structure (1) in which there is also interaction between the silicon atoms and the bridge system correlates well with the chemical reactivity of these complexes, referred to above where they either revert to $Pt(PR'_3)$ and SiR_3H, or form mononuclear platinum(II) hydrido-complexes $[PtH(SiR_3)(PR'_3)L]$. A relatively weak Pt–Pt interaction seems to be indicated by the *J*(PtPt) value of 92 Hz obtained from the ^{31}P spectrum of $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t_2)\}_2]$. This may be compared with values of 760, 1 770, 5 345, and 8 197 Hz in the complexes $[\{PtCl(CO)(PPh_3)\}_2]$, $[\{Pt(\mu\text{-}CO)(PMeBu^t_2)\}_3]$, $[Pt_2\{\mu\text{-}(CF_3)_2CO\}(cod)_2]$, and $[\{PtCl(\mu\text{-}dppm)\}_2]$, respectively.[18] We have drawn attention above to the relatively long Pt–Pt distance, but whether this can be related to the low *J*(PtPt) value is not clear at the present time.

The concept of hydrido-bridging between a transition-metal atom and silicon was first proposed by Graham and his co-workers [19] for the complexes $[Re_2H_2(\mu\text{-}SiR_2)(CO)_8]$ (R = Me or Ph), based on n.m.r. and *X*-ray crystallographic data.[20] However, the results of recent *X*-ray crystallographic studies,[21,22] while failing to locate the hydrido-ligands, have been interpreted as providing evidence against the existence of Re(μ-H)Si or Mn(μ-H)Si interaction in several complexes where it was thought to occur. Nevertheless, even if there is no incipient M–H · · · Si interaction in the solid in the manganese or rhenium complexes it might occur in solution, as indicated by the observed ^1H–^1H coupling between the methyl and ReH protons in $[Re_2H_2(\mu\text{-}SiMe_2)(CO)_8]$.[19] Moreover, whereas the Re*H* resonance in the latter occurs (τ 20.56) well above τ 10, nevertheless it is τ 6.5 below that found (τ 27.1) in the spectrum of $[\{Re(\mu\text{-}H)(CO)_4\}_3]$ [14] where the bridging $SiMe_2$ has been replaced by an $Re(CO)_4$ group. This compares with a decrease in shift of τ 9 between the Pt(μ-*H*)Pt resonances in $[Pt_2H_2(\mu\text{-}H)(dppm)_2]Cl$ and $[\{Pt(\mu\text{-}H)[Si(OEt)_3](PMeBu^t_2)\}_2]$.

In (1) the platinum atoms could be interacting with bonding pairs of electrons in $H{:}SiR_3$, as proposed by Hart-Davis and Graham [23] for the interaction of the manganese group $[Mn(CO)_2(\eta\text{-}C_5H_5)]$ with $SiPh_3H$ in the complex $[MnH(SiPh_3)(CO)_2(\eta\text{-}C_5H_5)]$. In the case of (1) the second platinum atom is assisting in the rupture of the Si–H bond. Moreover, it may be pointed out that the interactions implied by (1) could well be related to the mode of activation [24] by platinum of alkanes so that H–D exchange occurs.

It is evident from the work reported herein, relating to the ideas implied by formulation (1), that further structural studies on the species $[\{Pt(\mu\text{-}H)(SiR_3)(PR_3)\}_2]$ are merited.

EXPERIMENTAL

N.m.r. studies were made with JEOL PFT and PS 100 spectrometers. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Experiments were carried out under a dry oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction having b.p. 40—60 °C. The triorganosilanes were prepared by reduction of chlorotriorganosilanes with lithium tetrahydridoaluminate. Tricyclohexylphosphine- and methyldi-t-butylphosphine-bis(ethylene)platinum were synthesised using procedures described elsewhere.[25]

Preparation of the Diplatinum Complexes $[\{Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$.—The following representative syntheses are given for the complexes listed in Table 1.

(*a*) The complex $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.3 g, 0.5 mmol) was suspended in toluene (5 cm^3) contained in a Schlenk tube, and triethoxysilane (0.3 cm^3, 1.6 mmol) was added slowly with a syringe. The mixture was stirred for 2 h, during which time a pale yellow precipitate formed. The latter was filtered off, washed with n-hexane (3 × 3 cm^3), and dried *in vacuo* giving pale yellow *crystals* of $[\{Pt(\mu\text{-}H)[Si(OEt)_3][P(C_6H_{11})_3]\}_2]$ (0.3 g, 82%): $\nu_{max.}$ at 1 608m,br, 1 305m, 1 272m, 1 240w, 1 200m, 1 183s, 1 171s, 1 133vs, 1 105vs, 1 070vs,br, 1 012s, 940vs,br, 910s, 900s, 860vs, 838m, 830m, 780vs, 763vs, 751vs, 748vs, 700vs, 535vs, 518vs, and 503vs cm^{-1}.

(*b*) The complex $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.3 g, 0.6 mmol) was placed with toluene (5.0 cm^3) in a tube fitted with a Westef high-pressure stopcock and attached to a vacuum line. Trichlorosilane (2.3 g, 1.6 mmol) was distilled into the tube cooled to −196 °C. The reaction vessel was warmed to room temperature, gas evolution was observed, and a pale yellow precipitate appeared. After 15 min, 0.35 g (95%) of $[\{Pt(\mu\text{-}H)(SiCl_3)[P(C_6H_{11})_3]\}_2]$ was recovered as in (*a*): $\nu_{max.}$ at 1 607w, 1 500s, 1 332s, 1 305vs, 1 298s, 1 275s, 1 238m, 1 208m, 1 180vs, 1 137s, 1 120m, 1 083m, 1 057m, 1 010vs, 928s, 908s, 898s, 858vs, 830m, 758vs, 750vs, 740vs, 708vs, 582vs, 558vs, 540vs, 530vs (sh), 520vs, 508vs, 478s, and 468s cm^{-1}.

(*c*) An excess of $SiH(OEt)_3$ (0.5 g, 3 mmol) was added to $[Pt(C_2H_4)_2(PMeBu^t_2)]$ (0.66 g, 1.6 mmol) in light petroleum (5 cm^3) at 0 °C. After 20 min, volatiles were removed *in vacuo*, and the oily residue crystallised at −78 °C from light petroleum (5 cm^3) to give yellow crystals of $[\{Pt(\mu\text{-}H)[Si(OEt_3)](PMeBu^t_2)\}_2]$ (0.5 g, 60%): $\nu_{max.}$ at 1 617m, 1 300m, 1 170m, 1 117 (sh), 1 105s, 1 079s, 1 027w, 948s, 897s, 822m, 773s, 739s, 712s, 589w, 524s, 486m, and 447w cm^{-1}.

Reactions of $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$.—(*a*) *With t-butyl isocyanide*. The complex $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ (0.61 g, 0.5 mmol) was suspended in diethyl ether (20 cm^3) in a Schlenk tube, and Bu^tNC (0.19 g, 2.1 mmol) was added. The initial yellow solid dissolved immediately, and after 0.5 h at room temperature the solvent was removed *in vacuo*. The residue was dissolved

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[18] N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, R. J. Goodfellow, M. Murray, and J. L. Spencer, *J. Chem. Research*, 1978, (*S*) 228; (*17*) 2962.

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[22] M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1977, **16**, 2321, 2325.

[23] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1971, **94**, 4388 and refs. therein.

[24] D. E. Webster, *Adv. Organometallic Chem.*, 1977, **15**, 147.

[25] J. L. Spencer, *Inorg. Synth.*, 1978, **19**, in the press.

in light petroleum (5 cm^3), and the solution cooled in a refrigerator for 4 h. A syringe was used to remove solvent from the solid formed, the latter was washed (4 × 3 cm^3) with light petroleum, and the white *crystals* of [PtH(SiMe$_2$Ph){P(C$_6$H$_{11}$)$_3$}(CNBu^t)] (0.3 g, 45%), m.p. 122 °C (*in vacuo*), were dried *in vacuo* (Found: C, 53.6; H, 8.1; N, 2.6. C$_{31}$H$_{54}$NPPtSi requires C, 53.6; H, 7.8; N, 2.0%): $\nu_{max.}$ at 3 046w, 2 148vs,br, 2 110 (sh), 2 050w (PtH), 1 426m, 1 400w, 1 348w, 1 327w, 1 304w, 1 297w, 1 268w, 1 238 (sh), 1 230s, 1 204m, 1 195m, 1 183m, 1 178m, 1 173w, 1 118m, 1 105m, 1 090w, 1 048w, 1 033w, 1 005w, 922w, 896m, 857m, 832s, 803vs, 745s, 730s, 712m, 690w, 672w, 650w, 524m, 510w, 480m, 417s, and 393m cm^{-1}.

(*b*) *With trimethylphosphine.* A sealed tube fitted with a Westef high-pressure stopcock was charged with [{Pt(μ-H)(SiMe$_2$Ph)[P(C$_6$H$_{11}$)$_3$]}$_2$] (0.61 g, 0.5 mmol) and diethyl ether (20 cm^3). The tube was attached to a vacuum system, cooled with liquid nitrogen, and trimethylphosphine (1.5 g, 2 mmol) distilled into it. After 0.5 h at room temperature the reaction mixture was filtered through an alumina column (1 × 0.75 cm^2). Solvent was removed *in vacuo*, the residual oil dissolved in light petroleum, and the solution cooled in a refrigerator overnight. Solvent was removed with a syringe, and the solid washed with light petroleum and dried *in vacuo*. Crystallisation from diethyl ether–light petroleum gave white *crystals* of [PtH(SiMe$_2$Ph){P(C$_6$H$_{11}$)$_3$}(PMe$_3$)] (0.25 g, 35%), m.p. 80 °C (decomp.) (*in vacuo*) (Found: C, 50.8; H, 8.2. C$_{29}$H$_{54}$P$_2$PtSi requires C, 50.6; H, 8.2%): $\nu_{max.}$ at 3 068w, 3 050w, 2 054s, 1 488w, 1 429m, 1 340w, 1 326vw, 1 308m, 1 298w, 1 288m, 1 276w, 1 240m, 1 233ms, 1 207m, 1 184m, 1 128m, 1 109m, 1 081w, 1 061w, 1 038w, 1 016m, 961s, 946s, 927w, 898m, 860s, 830s, 816s, 772w, 758m, 742s, 725m, 713s, 683m, 645s, 537m, 527m, 490s, 452w, and 414s cm^{-1}.

(*c*) *With dimethylphenylarsine.* A suspension of [{Pt(μ-H)(SiMe$_2$Ph)[P(C$_6$H$_{11}$)$_3$]}$_2$] (0.48 g, 0.4 mmol) in diethyl ether (15 cm^3) was treated with dimethylphenylarsine (0.2 cm^3, 1.3 mmol) in a Schlenk tube. The mixture was stirred (2 h) at room temperature, solvent was reduced in volume to *ca.* 3 cm^3, and the solution left in a refrigerator overnight. As in (*a*) above, white *crystals* were obtained of [PtH(SiMe$_2$Ph)(AsMe$_2$Ph){P(C$_6$H$_{11}$)$_3$}] (0.19 g, 30%), m.p. 110 °C (decomp.) (*in vacuo*) (Found: C, 51.2; H, 7.0. C$_{34}$H$_{56}$AsPPtSi requires C, 51.4; H, 7.1%): $\nu_{max.}$ at 3 060w, 3 040w, 2 115s, 1 590br,w, 1 520br,w, 1 485w, 1 427m, 1 310w, 1 303w, 1 272w, 1 265w, 1 246m, 1 239m, 1 204w, 1 189w, 1 181m, 1 174w, 1 134w, 1 120w, 1 092m, 1 035w, 1 014w, 912w,b, 895w, 873m, 858m, 839m,s, 829w, 802s, 748s, 735s, 723s, 704m,s, 688w, 673w, 653m, 596m, 533w, 522m, 487w, 477m, 425m, 409m,s, and 392m,s cm^{-1}.

(*d*) *With triphenyl phosphite.* The diplatinum complex (0.6 g, 0.5 mmol) in diethyl ether (15 cm^3) was treated with freshly distilled P(OPh)$_3$ (0.6 g, 2 mmol) leading to precipitation of a white solid. Solvent was partially removed to a volume of *ca.* 10 cm^3, and the remainder removed with a syringe. The residue was washed with diethyl ether and crystallised from tetrahydrofuran–diethyl ether giving white crystals of [Pt{P(OPh)$_3$}$_4$] [26,27] (0.28 g, 27%) (Found: C, 59.8; H, 4.2. Calc. for C$_{72}$H$_{60}$O$_{12}$P$_4$Pt: C, 60.2; H, 4.2%): ^{31}P n.m.r., δ −98.8 p.p.m. [s with Pt satellites, *J*(PPt) 5 842 Hz]. The silane SiMe$_2$(Ph)H was identified as a product of this reaction from its i.r. spectrum (comparison with authentic sample).

In another experiment, a deficiency of P(OPh)$_3$ (0.24 cm^3, 0.91 mmol) with [{Pt(μ-H)(SiMe$_2$Ph)[P(C$_6$H$_{11}$)$_3$]}$_2$] (0.61 g, 0.5 mmol) in diethyl ether afforded a yellow solution. After filtration through an alumina pad (1 × 0.75 cm^2) and evaporation of the solvent, the residue was dissolved in light petroleum giving yellow *crystals* of [Pt{P(C$_6$H$_{11}$)$_3$}{P(OPh)$_3$}$_2$] (0.28 g, 25%), m.p. 139—141 °C (*in vacuo*) (Found: C, 59.2; H, 6.1. C$_{54}$H$_{63}$O$_6$P$_3$Pt requires C, 59.2; H, 5.8%). N.m.r. spectra: ^{1}H in CH$_2$Cl$_2$, τ 9.60—7.90 (br m, 33 H, C$_6$H$_{11}$) and 2.90 (br m, 30 H, Ph); ^{31}P in C$_6$D$_6$, δ −177.6 [d, PhO*P*, *J*(PP) 182, *J*(PtP) 7 034 Hz] and −62.8 p.p.m. [t, C$_6$H$_{11}$*P*, *J*(PP) 182, *J*(PtP) 4 021 Hz]. $\nu_{max.}$ at 3 070w, 3 046w, 1 596s, 1 493vs, 1 297w, 1 240 (sh), 1 230m, 1 215s, 1 205vs, 1 180m, 1 172m, 1 080w, 1 035w, 1 015w, 937m, 916s, 890vs, 836w, 782s, 769s, 738m, 715m, 700s, 636w, 605m, 570m, 558w, 515 (sh), 508m, and 475m cm^{-1}.

(*e*) *With ethylene.* The diplatinum complex (0.61 g, 0.5 mmol) and toluene (10 cm^3) were placed in a tube fitted with a Westef stopcock and attached to the vacuum line. Ethylene (3 mmol) was condensed into the tube, and the vessel was heated at 60 °C (3 min) and then allowed to stand (15 h) at room temperature. Solvent was removed *in vacuo* giving [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}] (0.15 g, 25%) (Found: C, 49.6; H, 8.3. Calc. for C$_{22}$H$_{41}$PPt: C, 49.7; H, 7.8%). The i.r. spectrum was identical with that of an authentic sample.

(*f*) *With carbon monoxide.* A suspension of the diplatinum complex (0.61 g, 0.5 mmol) in diethyl ether (20 cm^3) was treated with a stream of CO gas. A brown precipitate formed which after 1 h was filtered off, the known [15] complex [{Pt(μ-CO)[P(C$_6$H$_{11}$)$_3$]}$_3$] (0.23 g, 46%) being recovered by crystallisation from dichloromethane–diethyl ether (Found: C, 45.7; H, 6.8. Calc. for C$_{57}$H$_{99}$O$_3$P$_3$Pt$_3$: C, 45.3; H, 6.6%): $\nu_{max.}$(CO) at 1 837w, 1 798s, 1 781vs, and 1 767vs cm^{-1}.

Deuteriation Studies.—The complex [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}] (1.05 g, 2 mmol), suspended in light petroleum (15 cm^3), was treated with SiMe$_2$(Ph)D (1 cm^3, *ca.* 6 mmol) at room temperature for 3 h. The yellow solid product (see Discussion section) was washed with diethyl ether (3 × 3 cm^3) and dried *in vacuo* (Found: C, 51.4; H, 7.9. Calc. for C$_{52}$H$_{88}$D$_2$P$_2$Pt$_2$Si$_2$: C, 51.0; H, 7.6%): $\nu_{max.}$(PtH) at 1 610w,br, $\nu_{max.}$(PtD) at 1 163m,br cm^{-1}. This product, evidently a mixture of [{Pt(μ-D)(SiMe$_2$Ph)[P(C$_6$H$_{11}$)$_3$]}$_2$] and non-deuteriated Pt(μ-H)Pt species, was treated with Bu^{t}NC and with PMe$_3$ as in (*a*) and (*b*) above to form mononuclear platinum deuterides. From PMe$_3$, white crystals (35%) (Found: C, 50.2; H, 8.2. Calc.: C, 50.6; H, 8.2%). For ^{2}H n.m.r. and i.r. data see Discussion section. From Bu^{t}NC, white crystals (60%) (Found: C, 53.9; H, 8.2; N, 1.8. Calc.: C, 53.5; H, 7.9; N, 2.0%). N.m.r. spectra: ^{2}H, τ 13.1 [d, *J*(PtD) 146 Hz]; ^{31}P, −48.5 p.p.m. [*J*(PtP) 1 450, *J*(SiP) 145 Hz]. $\nu_{max.}$(PtH) at 2 110, $\nu_{max.}$(PtD) at 1 485 cm^{-1}.

Crystal-structure Determination of [{Pt(μ-H)(SiEt$_3$)[P(C$_6$H$_{11}$)$_3$]}$_2$].—The complex crystallises as yellow prisms from light petroleum, and the crystal used for data collection was of dimensions *ca.* 0.2 × 0.1 × 0.18 mm. Diffracted intensities were recorded on a Syntex *P*2$_1$ four-circle diffractometer for $2.9 \leqslant 2\theta \leqslant 40°$, according to methods described earlier.[28] Of the total of 5 189 reflections, 3 100 were ' observable ' according to the criterion

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$I \geqslant 2\sigma(I)$ (σ is the estimated standard deviation of the measured intensity based on counting statistics). The observed reflections only were used to solve and refine the structure. Corrections were made for Lorentz polarisation, but not for the effects of *X*-ray absorption since although the crystal shape was irregular the relative path-length changes were small.

TABLE 4

Final positional (fractional co-ordinate) factors for [{Pt(μ-H)(SiEt$_3$)[P(C$_6$H$_{11}$)$_3$]}$_2$], with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt(1)	0.276 30(6)	0.254 43(10)	0.316 63(6)
Pt(2)	0.241 66(6)	0.067 44(9)	0.315 29(7)
Tricyclohexylphosphine ligands			
P(1)	0.370 5(4)	0.327 1(6)	0.299 3(4)
C(111)	0.376(1)	0.333(2)	0.203(1)
C(112)	0.360(1)	0.233(2)	0.168(2)
C(113)	0.366(1)	0.234(2)	0.088(2)
C(114)	0.321(1)	0.311(2)	0.049(2)
C(115)	0.338(2)	0.414(2)	0.080(2)
C(116)	0.331(1)	0.413(2)	0.162(2)
C(121)	0.436(1)	0.241(2)	0.340(2)
C(122)	0.509(1)	0.255(2)	0.325(2)
C(123)	0.549(2)	0.161(2)	0.353(2)
C(124)	0.557(2)	0.158(3)	0.441(2)
C(125)	0.485(2)	0.149(3)	0.454(2)
C(126)	0.444(1)	0.233(2)	0.425(2)
C(131)	0.394(1)	0.451(2)	0.331(1)
C(132)	0.459(2)	0.489(3)	0.319(2)
C(133)	0.462(1)	0.598(2)	0.338(2)
C(134)	0.458(2)	0.612(3)	0.420(2)
C(135)	0.390(2)	0.576(3)	0.427(2)
C(136)	0.384(2)	0.468(2)	0.409(2)
P(2)	0.151 8(4)	−0.011 1(6)	0.337 0(5)
C(211)	0.086(2)	−0.038(2)	0.255(2)
C(212)	0.074(2)	0.061(3)	0.215(2)
C(213)	0.023(2)	0.042(3)	0.133(3)
C(214)	0.044(2)	−0.031(4)	0.100(3)
C(215)	0.055(2)	−0.128(4)	0.140(3)
C(216)	0.107(2)	−0.118(3)	0.209(2)
C(221)	0.165(1)	−0.126(2)	0.387(2)
C(222)	0.224(2)	−0.127(2)	0.448(2)
C(223)	0.244(2)	−0.231(3)	0.474(2)
C(224)	0.183(2)	−0.267(3)	0.512(2)
C(225)	0.124(2)	−0.274(3)	0.442(2)
C(226)	0.105(2)	−0.168(2)	0.414(2)
C(231)	0.110(2)	0.074(2)	0.388(2)
C(232)	0.148(2)	0.088(3)	0.462(2)
C(233)	0.122(2)	0.171(4)	0.502(2)
C(234)	0.040(2)	0.157(3)	0.491(2)
C(235)	0.000(3)	0.138(4)	0.422(3)
C(236)	0.033(2)	0.046(3)	0.394(2)
Triethylsilyl ligands			
Si(1)	0.205 7(5)	0.384 2(8)	0.322 5(6)
C(101)	0.120(2)	0.347(3)	0.280(3)
C(102)	0.116(3)	0.324(6)	0.202(3)
C(103)	0.162(2)	0.575(3)	0.267(2)
C(104)	0.220(2)	0.503(3)	0.285(2)
C(105) †	0.209	0.390	0.422
C(106) †	0.177	0.459	0.468
Si(2)	0.295 7(4)	−0.054 0(7)	0.264 4(6)
C(201)	0.271(2)	−0.017(2)	0.157(2)
C(202)	0.329(2)	−0.037(3)	0.120(2)
C(203)	0.388(2)	−0.051(3)	0.291(2)
C(204)	0.411(2)	−0.081(4)	0.367(3)
C(205)	0.274(2)	−0.187(2)	0.274(2)
C(206)	0.306(2)	−0.253(3)	0.224(2)

† C(105) and C(106) were not refined (see text).

Crystal data. $C_{48}H_{98}P_2Pt_2Si_2$, $M = 1\,185.5$, Monoclinic, space group $P2_1/c$, $a = 20.72(2)$, $b = 13.88(1)$, $c = 18.97(1)$ Å, $\beta = 101.15(7)°$, $U = 5\,355$ Å^3, $D_m = 1.45$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.47$ cm^{-3}, $F(000) = 2\,400$, Mo-$K_{\bar{\alpha}}$ *X*-radiation, graphite monochromator (λ 0.710 69 Å), μ(Mo-$K_{\bar{\alpha}}$) = 56.2 cm^{-1}.

Structure solution and refinement. The structure was solved by heavy-atom methods and refined by blocked-matrix least squares, with anisotropic thermal parameters for the Pt, Si, and P atoms only. Refinement ceased at *R* 0.071 (*R′* 0.083) with the two ethyl carbon atoms C(105) and C(106) fixed. No clearly defined alternative position, or positions for partial occupation, could be found, but these atoms had shown very large thermal parameters from the start and oscillated when free to do so. Hydrogen atoms were not included in the calculation since several of the ethyl and cyclohexyl carbon atoms could not be well defined, showing moderately large positional errors. The final difference density synthesis showed no peaks >0.9 or < -1.1 e Å^{-3}, except at *ca.* 2 e Å^{-3} between the two platinum atoms where the bridging hydrogen atoms might be expected to be located. However, since no absorption correction had been applied, little significance can be attached to these rather diffuse peaks.

Atomic scattering factors used were those of ref. 29 for H, ref. 30 for C and P, and ref. 31 for Si and Pt. Those for Pt, Si, and P were corrected for the effects of anomalous dispersion (Pt $\Delta f' = 2.352$, $\Delta f'' = 8.388$; Si $\Delta f' = 0.072$, $\Delta f'' = 0.071$; P $\Delta f' = 0.096$, $\Delta f'' = 0.095$). Weights were applied [32] according to the scheme $1/w = \sigma(F_o) + \alpha|F_o|$, where $\alpha = 0.05$ and $\sigma(F_o)$ is the estimated standard deviation in $|F_{\text{obs.}}|$ based on counting statistics. The mean shift-to-error ratio in the final four cycles of refinement was 0.061 : 1 with a maximum of 0.4 : 1. Positional parameters are given in Table 4, and some least-squares planes in Table 5. All the computational work was carried out at the University of London Computing Centre using the '*X*-Ray' system of programs.[32] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22235 (16 pp.).*

TABLE 5

Equations of least-squares planes for [{Pt(μ-H)(SiEt$_3$)-[P(C$_6$H$_{11}$)$_3$]}$_2$] in the form $Ax + By + Cz = D$, where *x*, *y*, *z* are fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane 1: P(1), Pt(1), Si(1)

$$2.758x + 0.688y + 17.939z = 6.617$$

[Pt(2) −0.25, P(2) −0.16, Si(2) −1.09]

Plane 2: P(2), Pt(2), Si(2)

$$6.869x - 3.524y + 15.699z = 6.372$$

[Pt(1) −0.40, P(1) −0.28, Si(1) −1.25]

Angle between planes: 21°

We thank the S.R.C. for support, the Greek Government for the award of a Scholarship (to C. A. T.), and Drs. R. J. Goodfellow, M. Murray, and B. F. Taylor for ^{2}H and INDOR n.m.r. measurements.

[7/1878 *Received*, 26*th October*, 1977]

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

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