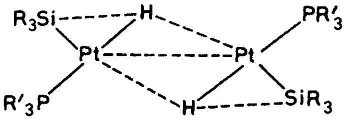
# Synthesis of Bis-μ-diorganosilanediyl-*af*-dihydridobis(triorganophosphine)diplatinum Complexes: Crystal and Molecular Structure of $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$

By **Mary Auburn, Miguel Ciriano, Judith A. K. Howard, Martin Murray, Nicholas J. Pugh, John L. Spencer, F. Gordon A. Stone,** and **Peter Woodward,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compound $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ decomposes in hexane at reflux to give in low yield (10%) the diplatinum complex $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$. A single-crystal *X*-ray diffraction study shows that the crystals are monoclinic, space group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions $a$ = 9.158(2), $b$ = 11.725(3), $c$ = 20.252(9) Å, and $\beta$ = 92.37(3)°. The structure has been solved by heavy-atom methods from automated diffractometer data, and refined to $R$ 0.065 ($R'$ 0.080) for 5 998 reflections. The molecule is constrained crystallographically to $C_i$ symmetry, and the two platinum atoms are asymmetrically bridged by two dimethylsilyl groups, giving two distinct Pt–Si bond lengths [2.420(2) and 2.324(2) Å]. The Pt, Si, and P atoms are essentially coplanar, with a P–Pt–Pt angle of 159.5(1) ° and a Pt–Pt distance of 2.708(1) Å. Hydrido-ligands have been located *trans* to the shorter Pt–Si bonds at a distance of 1.78 Å from the Pt atoms, sites which are also only 1.72 Å from the other Si atoms. These hydrido-ligands might therefore be considered to bridge the longer Pt–Si bonds, and in any case complete very distorted ' square ' planar configurations around the Pt atoms. The tricyclohexylphosphine ligands show no unusual features, and possess the usual chair conformation for the $C_6$ rings. The complex $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ may be synthesised in high yield by treating $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ with $SiMe_2H_2$, and similar reactions afford the compounds $[\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$ [R = Me, $PR'_3$ = $PMeBu^t_2$, $PPr^i_2Ph$, or $PPh_3$; R = Ph, $PR'_3$ = $P(C_6H_{11})_3$, $PPh_3$, $PPr^i_2Ph$, or $PMeBu^t_2$] from $SiR_2H_2$ (R = Me or Ph). These hydridoplatinum complexes do not show $^1H$ n.m.r. resonances above $\tau$ 10, but the $^2H$ spectrum of $[\{Pt^2H(\mu\text{-}SiMe_2)(PMeBu^t_2)\}_2]$ has a signal due to $^2HPt$ at $\tau$ 8.13. This property, and the occurrence in the i.r. spectra of all the complexes $[\{PtH(\mu\text{-}SiR_2)(PR_3)\}_2]$ of $\nu(PtH)$ bands at *ca.* 1 650 cm$^{-1}$, are interpreted as indicating the presence of delocalised three-centre two-electron Pt–H–Si bonding in the title compounds.

We have recently described [1] a series of diplatinum complexes $[\{Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$, formed by oxidative addition of triorganosilanes $SiR_3H$ to the platinum(0) species $[Pt(C_2H_4)_2(PR'_3)]$.[2] The di-μ-hydrido-bis(silyl)-bis(trialkylphosphine)diplatinum compounds showed unusual spectroscopic properties in that in their $^1H$ n.m.r. spectra the hydrido-ligands had resonance signals in the range $\tau$ 6.2—6.9, and their i.r. spectra had a band between 1 500 and 1 700 cm$^{-1}$ which deuteriation showed was due to Pt(μ-H)Pt bridges. The i.r. bands are higher in energy than those generally found (1 100 ± 300 cm$^{-1}$) in complexes containing a hydrido-ligand bridging two metal atoms.[3] This observation, and especially the relatively low-field shifts of the proton signals, led to the proposal that in addition to bridging the platinum atoms, the hydrido-ligands interact with the silicon atoms as in (1). In order to extend our knowledge of these and related silicon–platinum complexes the following studies were carried out.



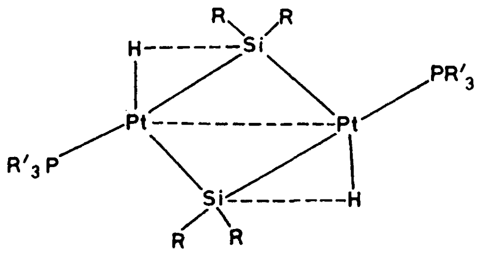
(1)

RESULTS AND DISCUSSION

It had been observed [1] that reactions of the diplatinum complexes (1) with ethylene at 60 °C lead to recovery of the species $[Pt(C_2H_4)_2(PR_3)]$. Triorganosilanes were not detected as products, presumably because hydrosilylation of the excess of ethylene present occurs.[4] However, treatment of the compounds (1) with $P(OPh)_3$ released $SiR_3H$ and formed $[Pt\{P(OPh)_3\}_4]$. The formation of $[Pt(C_2H_4)_2(PR_3)]$ on heating in the presence of ethylene suggested that thermal decomposition of the complexes (1) in the absence of the olefin should be examined.

Refluxing the complex [1; $SiR_3$ = $SiMe_2Ph$, $PR'_3$ = $P(C_6H_{11})_3$] in hexane (0.5 h) afforded in low yield (*ca.* 10%) a white microcrystalline solid (2).[5] The i.r. spectrum revealed a band at 1 655m(br) cm$^{-1}$ which was initially thought to be due to a Pt(μ-H)Pt group, because of the results described above. The $^1H$ n.m.r. spectrum was of interest in that it showed no resonances assignable to a phenyl group, and as in the parent compound there was no signal above $\tau$ 10. The $^{31}P$ ($^1H$-decoupled) n.m.r. spectrum had a pattern centred at −52.6 p.p.m. which was clearly indicative of the presence of a PPtPtP chain [$^1J(PPt)$ 3 982, $^2J(PPt)$ 253, and $J(PtPt)$ 2 853 Hz]. It was thus evident that the thermal decomposition of $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ had produced another type of diplatinum complex but one from which the phenyl group had been lost.

In order to establish the molecular structure of (2) a single-crystal *X*-ray diffraction study was carried out on a crystal grown by slow evaporation of a tetrahydrofuran solution. The structural results are summarised in Figure 1, which also shows the atom-numbering system, and in Tables 1 and 2. The packing of the molecules within the monoclinic unit cell is shown in Figure 2. The two platinum atoms are bridged asymmetrically by



| | R | PR'3 |
|---|---|---|
| (2) | Me | $P(C_6H_{11})_3$ |
| (3) | Me | $PMeBu^t_2$ |
| (4) | Me | $PPr^i_2Ph$ |
| (5) | Me | $PPh_3$ |
| (6) | Ph | $P(C_6H_{11})_3$ |
| (7) | Ph | $PPh_3$ |
| (8) | Ph | $PPr^i_2Ph$ |
| (9) | Ph | $PMeBu^t_2$ |

two dimethylsilyl groups, giving two distinct Pt–Si bond lengths [2.324(2) and 2.420(2) Å]. The Pt, Si, and P atoms are approximately coplanar (see Table 3) and the geometry of the central four-membered ring system is strongly suggestive of Pt ··· Pt interaction. The Pt–Pt distance of 2.708(1) Å, while longer than the sum of the covalent radii (2.62 Å), is nevertheless well within the range of known Pt–Pt bonds,[6] and the acuteness of the angle [69.5(3)°] at the ' tetrahedral ' Si atoms would not be necessary unless Pt ··· Pt interaction formed an integral part of the bonding mechanism. The environment of each Pt atom, although essentially planar, is excessively distorted from the ideal square, and the Pt–P bond does not lie on the central Pt–Pt axis of the Pt–Si ring system [PPtPt' 159.5(1)°]. Indeed, the angles around Pt [P–Pt–Si 104.5(2), P–Pt–Si' 144.6(3), and Si–Pt–Si' 110.4(3)°] are strongly suggestive of a missing hydride within the P–Pt–Si' angle. The largest residual feature on the final electron-density difference synthesis was in fact a peak, identifiable as the missing

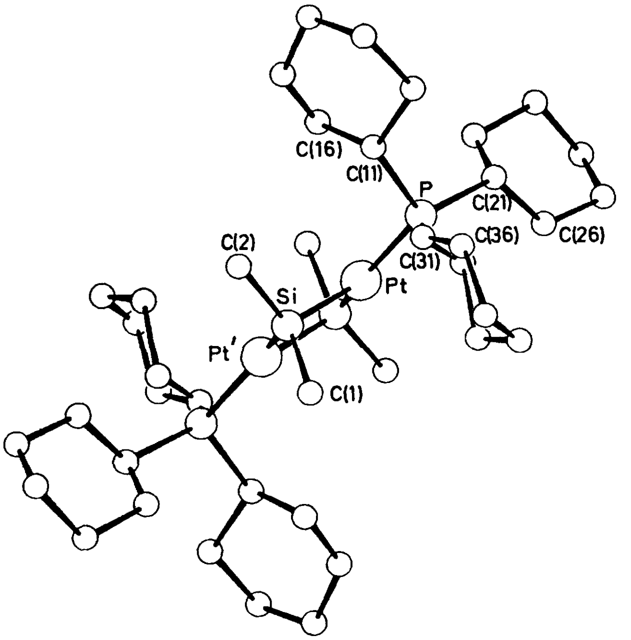


FIGURE 1 Molecular structure of $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$, showing the atom-numbering system for the crystallographic asymmetric unit. The atom H(01), not indicated on the diagram, bridges the Si–Pt' bond

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt | 0.117 76(3) | 0.062 20(2) | 0.020 72(1) |
| P | 0.260 09(21) | 0.180 77(16) | 0.084 39(9) |
| Si | −0.052 79(27) | −0.008 39(20) | 0.092 07(11) |
| H(01) | −0.192 4 | −0.089 3 | 0.057 5 |
| C(1) | −0.001 4(11) | −0.130 3(8) | 0.148 7(4) |
| H(101) | 0.075 8 | −0.175 9 | 0.131 0 |
| H(102) | −0.080 8 | 0.177 8 | 0.157 3 |
| H(103) | 0.035 1 | −0.088 1 | 0.187 9 |
| C(2) | −0.162 5(10) | 0.090 7(8) | 0.143 3(4) |
| H(201) | −0.240 2 | 0.043 9 | 0.154 9 |
| H(202) | −0.223 7 | 0.162 4 | 0.124 9 |
| H(203) | −0.108 5 | 0.114 8 | 0.181 4 |
| C(11) | 0.149 6(8) | 0.302 5(6) | 0.112 4(3) |
| H(11) | 0.104 2 | 0.259 8 | 0.152 8 |
| C(12) | 0.236 7(10) | 0.405 3(7) | 0.140 8(4) |
| H(121) | 0.317 7 | 0.379 3 | 0.173 7 |
| H(122) | 0.281 8 | 0.431 1 | 0.104 9 |
| C(13) | 0.134 3(12) | 0.494 3(8) | 0.168 6(4) |
| H(131) | 0.188 2 | 0.560 4 | 0.190 6 |
| H(132) | 0.089 8 | 0.455 3 | 0.196 0 |
| C(14) | 0.021 6(12) | 0.533 4(8) | 0.117 0(5) |
| H(141) | 0.082 3 | 0.582 0 | 0.075 1 |
| H(142) | −0.034 1 | 0.598 6 | 0.144 0 |
| C(15) | −0.067 9(11) | 0.431 0(7) | 0.088 5(5) |
| H(151) | −0.105 4 | 0.403 6 | 0.121 5 |
| H(152) | −0.153 8 | 0.467 1 | 0.048 1 |
| C(16) | 0.034 8(8) | 0.341 0(7) | 0.059 4(4) |
| H(161) | −0.034 4 | 0.270 3 | 0.047 8 |
| H(162) | 0.091 7 | 0.341 1 | 0.024 0 |
| C(21) | 0.417 6(8) | 0.246 5(6) | 0.043 4(4) |
| H(21) | 0.481 9 | 0.302 1 | 0.085 0 |
| C(22) | 0.372 7(8) | 0.322 1(7) | −0.016 4(3) |
| H(221) | 0.316 7 | 0.284 9 | −0.053 1 |
| H(222) | 0.312 3 | 0.370 1 | 0.000 2 |
| C(23) | 0.508 2(9) | 0.372 1(7) | −0.047 7(4) |
| H(231) | 0.479 7 | 0.415 5 | −0.082 8 |
| H(232) | 0.566 9 | 0.413 8 | −0.019 1 |
| C(24) | 0.610 7(11) | 0.278 7(7) | −0.070 6(4) |
| H(241) | 0.695 5 | 0.325 3 | −0.098 0 |
| H(242) | 0.550 2 | 0.229 4 | −0.111 8 |
| C(25) | 0.655 8(9) | 0.204 8(7) | −0.012 2(4) |
| H(251) | 0.692 4 | 0.257 0 | 0.019 1 |
| H(252) | 0.726 5 | 0.140 9 | −0.027 2 |
| C(26) | 0.525 8(9) | 0.154 4(6) | 0.022 3(4) |
| H(261) | 0.555 0 | 0.079 7 | 0.055 3 |
| H(262) | 0.463 2 | 0.098 9 | −0.007 6 |
| C(31) | 0.348 5(9) | 0.124 2(7) | 0.162 7(4) |
| H(31) | 0.429 7 | 0.164 7 | 0.174 3 |
| C(32) | 0.388 6(10) | −0.003 0(7) | 0.155 3(4) |
| H(321) | 0.438 4 | −0.020 7 | 0.119 8 |
| H(322) | 0.265 6 | −0.035 5 | 0.147 9 |
| C(33) | 0.462 5(11) | −0.051 8(8) | 0.218 2(4) |
| H(331) | 0.557 7 | −0.034 9 | 0.224 7 |
| H(332) | 0.483 2 | −0.118 3 | 0.212 7 |
| C(34) | 0.372 7(12) | −0.033 9(8) | 0.277 9(4) |
| H(341) | 0.252 8 | −0.077 2 | 0.271 7 |
| H(342) | 0.421 3 | −0.058 9 | 0.324 8 |
| C(35) | 0.339 5(11) | 0.093 6(9) | 0.286 1(4) |
| H(351) | 0.295 6 | 0.133 1 | 0.323 0 |
| H(352) | 0.438 6 | 0.102 0 | 0.293 8 |
| C(36) | 0.260 4(10) | 0.139 8(8) | 0.223 8(4) |
| H(361) | 0.170 8 | 0.099 4 | 0.217 2 |
| H(362) | 0.242 0 | 0.218 0 | 0.229 4 |

terminal hydrido-ligand [H(01)], at a distance 1.78 Å from the Pt′ atom but also, interestingly, 1.72 Å from the Si atom; the sum of the van der Waals radii for Si and H is 3.2 Å. These distances may be compared with Pt–H 1.66 Å in $[PtH(SB_9H_{10})(PEt_3)_2]$ [7] and Si–H 1.8 Å in $[Mn(\eta\text{-}C_5H_5)H(SiPh_3)(CO)_2]$.[8] Although the location of H(01) may be described vaguely as *trans* to the shorter Si–Pt bond, the angle Si–Pt–H is in fact 155° with the deviation from linearity, of course, towards the other Si atom. Hydrogen atoms which bridge metal–silicon bonds, and which involve the silicon atom as being in a state of incipient five-co-ordination, have been studied previously. Of particular interest, because of its similarity to the present study, is the compound $[\{WH(\mu\text{-}SiEt_2)(CO)_4\}_2]$ in which a central planar $\overline{\mathrm{WSiWSi}}$ unit carries two hydride ligands (one per W atom) which are each associated with a different Si atom.[9] The two distinct W–Si distances [2.586(5) and 2.703(4) Å] differ by approximately the same margin (*ca.* 0.1 Å) as do our present Pt–Si distances but, as the authors of that study point out,[9] had the bonding been a linear insertion of H into the W–Si bond to give W · · · H · · · Si, a difference of as much as 0.4 Å might be expected. They inferred, therefore, a bent W(μ-H)Si arrangement, with the H atom bridging the longer W–Si bond, but unfortunately the H atom was not located in the *X*-ray diffraction study. We are here able to give direct evidence for an exactly similar arrangement in the title compound.*

TABLE 2

Interatomic distances (Å) and bond angles (°) in $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$

(*a*) Distances

| | | | |
|---|---|---|---|
| Pt–Si | 2.324(2) | C(14)–C(15) | 1.55(1) |
| Pt′–Si | 2.420(2) | C(15)–C(16) | 1.55(1) |
| Pt–Pt′ | 2.708(1) | C(16)–C(11) | 1.54(1) |
| Pt–P | 2.271(2) | P–C(21) | 1.861(8) |
| Pt′–H(01) | 1.78 | C(21)–C(22) | 1.54(1) |
| Si–H(01) | 1.72 | C(22)–C(23) | 1.53(1) |
| Si–C(1) | 1.881(10) | C(23)–C(24) | 1.53(1) |
| C(1)–H(101) | 0.97 | C(24)–C(25) | 1.51(1) |
| C(1)–H(102) | 0.94 | C(25)–C(26) | 1.53(1) |
| C(1)–H(103) | 0.98 | C(26)–C(21) | 1.54(1) |
| Si–C(2) | 1.887(10) | P–C(31) | 1.872(7) |
| C(2)–H(201) | 0.94 | C(31)–C(32) | 1.54(1) |
| C(2)–H(202) | 1.07 | C(32)–C(33) | 1.53(1) |
| C(2)–H(203) | 0.94 | C(33)–C(34) | 1.51(1) |
| P–C(11) | 1.853(7) | C(34)–C(35) | 1.54(3) |
| C(11)–C(12) | 1.54(1) | C(35)–C(36) | 1.53(1) |
| C(12)–C(13) | 1.53(1) | C(36)–C(31) | 1.52(1) |
| C(13)–C(14) | 1.51(1) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| Si–Pt–Si′ | 110.4(3) | C(13)–C(14)–C(15) | 110.9(8) |
| Pt–Si–Pt′ | 69.5(3) | C(14)–C(15)–C(16) | 110.4(8) |
| Pt–Si–C(1) | 119.5(3) | C(15)–C(16)–C(11) | 110.0(7) |
| Pt–Si–C(2) | 120.8(3) | P–C(21)–C(22) | 113.7(5) |
| C(1)–Si–C(2) | 105.1(4) | P–C(21)–C(26) | 110.7(5) |
| Pt′–H(01)–Si | 87.6 | C(26)–C(21)–C(22) | 109.8(6) |
| Si–Pt–P | 104.5(2) | C(21)–C(22)–C(23) | 110.5(6) |
| Si′–Pt–P | 144.6(4) | C(22)–C(23)–C(24) | 111.7(7) |
| Pt–P–C(11) | 109.7(2) | C(23)–C(24)–C(25) | 109.0(7) |
| Pt–P–C(21) | 116.0(2) | C(24)–C(25)–C(26) | 112.8(7) |
| Pt–P–C(31) | 118.8(3) | C(25)–C(26)–C(21) | 112.3(6) |
| C(11)–P–C(21) | 105.1(3) | P–C(31)–C(32) | 110.9(5) |
| C(21)–P–C(31) | 102.0(3) | P–C(31)–C(36) | 115.0(6) |
| C(31)–P–C(11) | 103.7(3) | C(36)–C(31)–C(32) | 109.4(7) |
| P–C(11)–C(12) | 115.8(6) | C(31)–C(32)–C(33) | 112.4(6) |
| P–C(11)–C(16) | 112.2(5) | C(32)–C(33)–C(34) | 112.3(8) |
| C(16)–C(11)–C(12) | 111.0(6) | C(33)–C(34)–C(35) | 109.8(8) |
| C(11)–C(12)–C(13) | 110.8(7) | C(34)–C(35)–C(36) | 110.2(7) |
| C(12)–C(13)–C(14) | 111.4(7) | C(35)–C(36)–C(31) | 112.4(7) |

Crystallographic studies [10] on $[\{ReH_2(\mu\text{-}SiEt_2)(CO)_3\}_2]$ and $[Re_2H_2(\mu\text{-}SiEt_2)_2(CO)_7]$, on the other hand, have revealed a central ring system with all Si–Re bond lengths equal; the results have been interpreted as indicating the presence of normal terminal hydrido-ligands on the rhenium atoms which are, however, constrained in their locations by intramolecular contacts with the CO ligands. A related study [11] of the rhenium complex $[Re(\eta\text{-}C_5H_5)H(SiPh_3)(CO)_2]$ claims to have located the hydrido-ligand at a distance of 1.7 Å from the rhenium but at a non-bonding distance of 2.2 Å from the silicon. The shorter silicon–hydrido-ligand distance of 1.8 Å found in the manganese analogue, mentioned above, is not repeated with the rhenium compound, and again, by inference, steric factors are invoked to explain the close contacts observed with the former. It is implied [9] that the W(μ-H)Si bridges in $[\{WH(\mu\text{-}SiEt_2)(CO)_4\}_2]$ might be caused by the same kind of interactions involving steric crowding by the other ligands. However, we consider that the evidence supporting two-electron three-centre Pt(μ-H)Si bonds in $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ (2) is very strong, including spectroscopic data for compound (3) presented below. Moreover, such bonding is obviously related to various M · · · H · · · C interactions (M = Mo, Fe, Ru, Rh, Pd, and Pt) which have been shown by diffraction studies to range from incipient [12] to strong.[13,14] The perturbation of a Si–H bond by a metal in the manner indicated for (1)—(9) is similar to that proposed for the metal activation of C–H bonds of arenes and alkanes.[15,16]

TABLE 3

Equations of some least-squares planes for $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ in the form $Ax + By + Cz = D$, where $x, y, z$ are fractional crystal co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (1): Pt, Si′, Pt′

$$-4.865x + 9.841y - 1.891z = 0.000$$

[P 0.354, H(01′) 0.052, C(1) −1.558, C(2) 1.412]

Plane (2): Si, C(1), C(2)

$$7.566x + 5.598y + 5.362z = 0.047$$

Plane (3): Pt, Si, P

$$-5.510x + 8.937y - 4.325z = -0.183$$

[H(01) 0.196, C(1) −1.618, C(2) 1.269]

Angles (°) between planes:

(1)–(2) 85.8; (1)–(3) 9.3; (2)–(3) 78.2

The *X*-ray study having established the molecular structure of the complex $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ (2), it was possible to devise a more suitable synthesis for this and related compounds. In earlier work [17] we had shown that pentamethyldisilane and $[Ru_3(CO)_{12}]$ react

---

* In reference 5, from preliminary interpretation of the data, it was incorrectly stated that the hydrido-ligands bridge the shorter Pt–Si bonds and, therefore, occupy sites *trans* to the longer Pt–Si bonds. In fact the reverse situation is true.

TABLE 4

Diplatinum complexes $[\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$ [a]

| | Complex [b] | M.p. ($\theta_c$/°C) (decomp.) | $\nu_{max.}$(PtH) ($cm^{-1}$) | Yield (%) | Analysis (%) | |
|---|---|---|---|---|---|---|
| | | | | | C | H |
| (2) | $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ | 180—184 | 1 655m | 80 [c] | 45.0 (44.9) | 8.0 (7.5) |
| (3) | $[\{PtH(\mu\text{-}SiMe_2)(PMeBu^t{}_2)\}_2]$ | 216—218 | 1 634s | 40 | 32.0 (31.8) | 7.1 (6.8) |
| | $[\{Pt^2H(\mu\text{-}SiMe_2)(PMeBu^t{}_2)\}_2]$ | 216—218 | 1 180s [d] | 66 | 32.9 (31.8) | 7.3 (6.8) |
| (4) | $[\{PtH(\mu\text{-}SiMe_2)(PPr^i{}_2Ph)\}_2]$ | >200 | 1 650s | 22 | 37.6 (37.5) | 6.3 (5.8) |
| (5) | $[\{PtH(\mu\text{-}SiMe_2)(PPh_3)\}_2]$ | >160 | 1 625m | 35 | 46.1 (46.0) | 4.8 (4.7) |
| (6) | $[\{PtH(\mu\text{-}SiPh_2)[P(C_6H_{11})_3]\}_2]$ | 200—220 | 1 655m | 35 | 54.5 (54.7) | 6.9 (6.7) |
| (7) | $[\{PtH(\mu\text{-}SiPh_2)(PPh_3)\}_2]$ | >160 | 1 635m | 60 | 56.1 (56.2) | 4.2 (4.1) |
| (8) | $[\{PtH(\mu\text{-}SiPh_2)(PPr^i{}_2Ph)\}_2]$ | *ca.* 140 | 1 655m | 30 | 50.1 (50.0) | 6.1 (5.2) |
| (9) | $[\{PtH(\mu\text{-}SiPh_2)(PMeBu^t{}_2)\}_2]$ | >210 | 1 652m | 30 | 47.0 (46.8) | 6.0 (6.0) |

[a] Calculated values are given in parentheses. [b] All complexes are white or cream. [c] From $SiMe_2H_2$. [d] $\nu_{max.}$(PtD)

to give a complex $[\{Ru(\mu\text{-}SiMe_2)(SiMe_3)(CO)_3\}_2]$ with bridging dimethylsilyl groups, and hence the reaction of $Si_2Me_5H$ and $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ was investigated. Although this reaction did produce the desired compound (2) the yield was only marginally superior to that obtained from the pyrolysis of $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$. As an alternative synthetic approach, the reaction between $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ and dimethylsilane was next investigated. Hydrogen was evolved at room temperature and (2) was produced in 80% yield. A series of related compounds (3)—(9) (Table 4) was similarly prepared from dimethyl- or diphenyl-silane and the complexes $[Pt(C_2H_4)_2(PR_3)]$ [$PR_3$ = $PMeBu^t{}_2$, $P(C_6H_{11})_3$, $PPr^i{}_2Ph$, or $PPh_3$]. The new compounds, with the exception of the triphenylphosphine derivatives, are air stable.

In the i.r. spectra of the compounds there are broad bands of medium intensity near 1 650 $cm^{-1}$ (Table 4). As mentioned earlier, in the spectra of the complexes (1) similar bands have been ascribed to Pt($\mu$-H)Pt absorptions perturbed by interaction of the hydrido-ligands with silicon.[1] In order to establish that the i.r. bands near 1 650 $cm^{-1}$ in the compounds listed in Table 4 were due to a Pt–H bond, the complex $[\{Pt^2H(\mu\text{-}SiMe_2)(PMeBu^t{}_2)\}_2]$ was prepared from $SiMe_2{}^2H_2$. The i.r. spectrum showed a strong band at 1 180 $cm^{-1}$ and a very weak band at 1 635 $cm^{-1}$. The relationship between these two bands, together with the absence of the former in the spectrum of the non-deuteriated species, leads to assignment of the absorption at 1 180 $cm^{-1}$ as being due to a Pt–$^2$H stretch. In hydridoplatinum complexes, Pt–H absorptions in the i.r. generally occur [3,18] in the

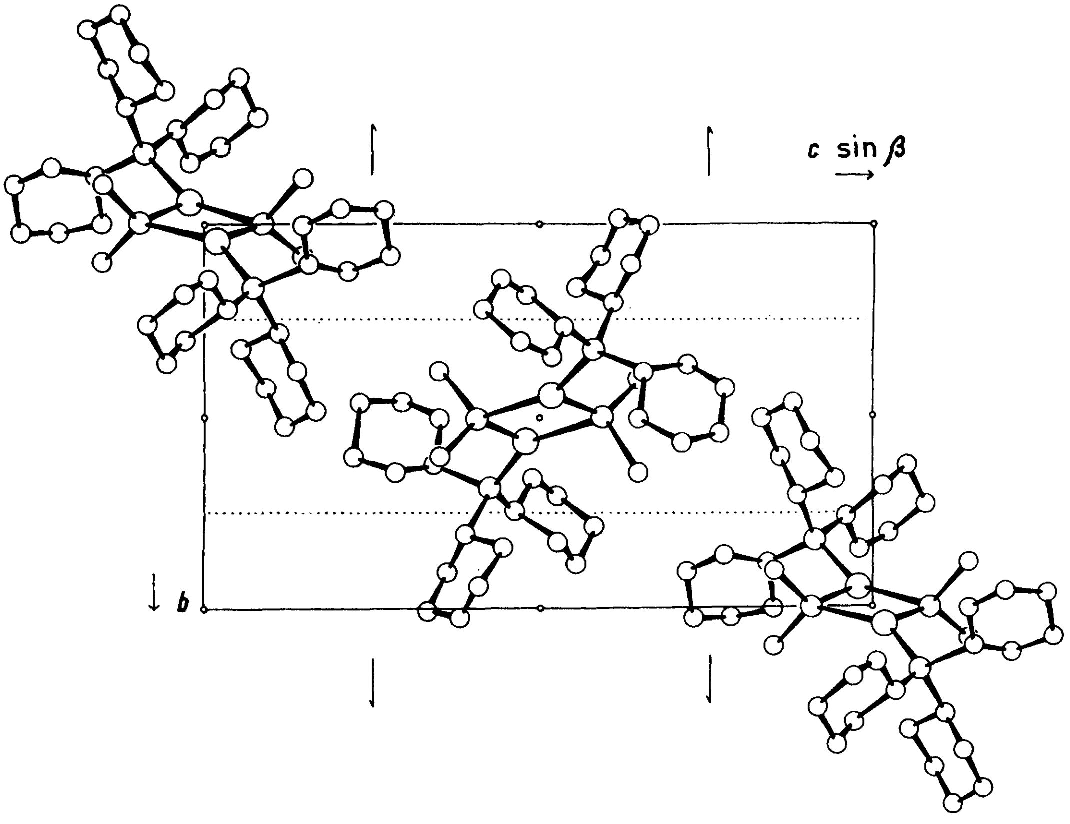


FIGURE 2 Contents of the monoclinic unit cell of (2) viewed down *a*, looking towards the origin

range 2 000—2 300 cm$^{-1}$, for terminally bound hydride. However, these frequencies depend on the *trans* influence of the other ligands present, and this property presumably accounts for $\nu_{max.}$(PtH) in the complex *trans*-[PtH(SiH$_3$){P(C$_6$H$_{11}$)$_3$}$_2$] occurring at as low a frequency as 1 860 cm$^{-1}$,[19] the very strong *trans* influence of silicon groups being well established.[20] Although silicon groups are *trans* to hydride in the compounds [{PtH($\mu$-SiR$_2$)(PR'$_3$)}$_2$], it seems unlikely that the occurrence of Pt–H stretches at as low an energy as *ca.* 1 650 cm$^{-1}$ is entirely due to the *trans* influence of silicon, and it thus seems possible that the band frequencies are a further manifestation of Pt($\mu$-H)Si interaction, as indicated by the *X*-ray diffraction results.

TABLE 5

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

| Complex | $^{31}$P($\delta$/p.p.m.) | $^1$H($\tau$) |
|---|---|---|
| [{PtH($\mu$-SiMe$_2$)[P(C$_6$H$_{11}$)$_3$]}$_2$] | −52.6 [*J*(PtP) 3 982, 253; *J*(PP) 59; *J*(PtPt) 2 853] | 7.60—8.95 (m, 66 H, C$_6$H$_{11}$), 8.62 (s, 12 H, MeSi) |
| [{PtH($\mu$-SiMe$_2$)(PMeBu$^t_2$)}$_2$] | −52.5 [*J*(PtP) 4 132, 282; *J*(PP) 61; *J*(PtPt) 3 331] | [b] 8.11 [t, 2 H, PtH, *J*(PtH) 608, 120; *J*(PH) 13], 8.21 [d, 6 H, MeP, *J*(PtH) 49, *J*(PH) 7], 6.88 [d, 36 H, Bu$^t$, *J*(PH) 13] |
| [{PtH($\mu$-SiMe$_2$)(PPr$^i_2$Ph)}$_2$] | −57.8 [*J*(PtP) 4 089, 277; *J*(PP) 62] | 2.36—2.90 (m, 10 H, Ph), 7.72 (m, 4 H, CH), 8.44 (s, 12 H, MeSi), 8.85 [d of d, 12 H, MeC, *J*(PH) 16, *J*(HH) 7], 9.04 [d of d, 12 H, MeC, *J*(PH) 16, *J*(HH) 7] |
| [{PtH($\mu$-SiMe$_2$)(PPh$_3$)}$_2$] | −35.8 [*J*(PtP) 4 237, 319; *J*(PP) 64] | 2.05—2.90 (m, 30 H, Ph), 9.08 (s, 12 H, MeSi) |
| [{PtH($\mu$-SiPh$_2$)[P(C$_6$H$_{11}$)$_3$]}$_2$] | −53.7 [*J*(PtP), 3 971, 231; *J*(PP) 57] | 1.80—2.76 (m, 20 H, Ph), 7.80—9.20 (m, br, 66 H, C$_6$H$_{11}$) |
| [{PtH($\mu$-SiPh$_2$)(PPh$_3$)}$_2$] | | 2.85—3.04 (m, 50 H, Ph) |
| [{PtH($\mu$-SiPh$_2$)(PPr$^i_2$Ph)}$_2$] | −57.6 [*J*(PtP), 4 103, 256; *J*(PP) 60] | 2.08—3.10 (m, 30 H, Ph), 7.80 (m, 4 H, CH), 9.12 [d of d, 12 H, MeC, *J*(PH) 16, *J*(HH) 7], 9.30 [d of d, 12 H, MeC, *J*(PH) 16, *J*(HH) 7] |
| [{PtH($\mu$-SiPh$_2$)(PMeBu$^t_2$)}$_2$] | −52.7 [*J*(PtP), 4 105, 252; *J*(PP) 60; *J*(PtPt) 2 477] | 1.96—2.78 (m, 20 H, Ph), 8.42 [d, 6 H, MeP, *J*(PH)7, *J*(PtH) 51], 9.07 [d, 36 H, Bu$^t$, *J*(PH) 13] |

[a] Measured in C$_6$D$_6$; coupling constants in Hz, $^{31}$P chemical shifts (proton-decoupled) are given to low frequency of 85% H$_3$PO$_4$ (external). [b] Measured from the Fourier-transform spectrum; signal for Me$_2$Si group obscured by Bu$^t$ resonance. For signal for PtH see text.

The $^1$H n.m.r. spectra of the compounds [{PtH($\mu$-SiR$_2$)(PR'$_3$)}$_2$] (Table 5), like those of the species [{Pt($\mu$-H)(SiR$_3$)(PR'$_3$)}$_2$], show no resonances above $\tau$ 10. Initial studies on (2)—(9) were somewhat frustrated by the low solubility of most of the compounds. Even when this was overcome with (3) no signals ascribable to a hydrido-ligand could be observed, in spite of extensive searches of the low-frequency region and accumulation of large numbers of transients of the Fourier-transform $^1$H spectrum. In view of our earlier observation [1] that the n.m.r. resonances for the bridging hydrido-ligands in the compounds (1) occur in the range $\tau$ 6—7, it seemed possible that the HPt signals in the spectra of the bis-$\mu$-diorganosilanediyl-*af*-dihydridobis(tertiary phosphine)-diplatinum complexes (2)—(9) might be obscured by the resonances from the phosphine and/or silyl groups. To overcome this problem the $^2$H spectrum of the complex [{Pt$^2$H($\mu$-SiMe$_2$)(PMeBu$^t_2$)}$_2$] was studied. At ambient temperatures a poorly resolved triplet (separations *ca.* 1 Hz) was observed at $\tau$ 8.13 with two sets of platinum satellites [*J*($^2$HPt) 93.3 and 18.5 Hz] each of which showed doublet fine structure (*J* 2 Hz). Two further weak signals, triplets like the central peak, were observed with a separation of 111.8 Hz, showing that the two $^2$H–Pt coupling constants have the same sign. The fine structure arises from phosphorus coupling [*J*($^2$HP) 2 Hz], which in the central peak and the double satellites gives rise to triplets, due to the chemical equivalence of the two phosphorus nuclei and the *J*(PP) coupling of 61 Hz.

The observation of separate deuterium–platinum coupling constants, also observed in the spectrum run at 70 °C, shows that each deuterium atom is associated with one platinum and is not exchanging between the two metal atoms.

In the light of these results, the $^1$H n.m.r. spectrum of (3) was re-examined. The expected triplet at $\tau$ 8.13 could not be observed due to the strong signal of the phosphine methyl groups; however, the platinum satellites were observed at high gain as two poorly resolved doublets [*J*(HPt) 608, *J*(HP) 13 Hz] symmetrically placed about $\tau$ 8.11. These values correspond to those calculated from the $^2$H n.m.r. results by the relationship $J(^2\text{H})/J(^1\text{H}) = \gamma(^2\text{H})/\gamma(^1\text{H})$. Also observed was the high-frequency component of the doublet caused by the other platinum splitting, for which *J*(HPt) is calculated as 120 Hz.

The identification of the $^1$H resonance in (3) at such a low field as $\tau$ 8.1 lends further support to the concept of three-centre bonding Pt($\mu$-H)Si, since HPt resonances have been typically measured in the range $\tau$ 13—27 while HSi signals are generally observed near $\tau$ 6. However, Ebsworth *et al.*[19] have recently recorded a chemical shift of $\tau$ 10.75 for the hydrido-ligand in *trans*-[PtH(SiH$_3$){P(C$_6$H$_{11}$)$_3$}$_2$] and so evidently a *trans*-silicon group has a substantial effect in moving the signal to low field. A further example of this phenomenon is the change which occurs in the n.m.r. shift of the hydrido-bridging ligand in the cations $[Pt_2X_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ (dppm = $Ph_2PCH_2PPh_2$) from $\tau = 26.6$ to $\tau = 15.85$ as X *trans* to the hydride is changed from Cl to H.[21] Thus since the hydrido-ligands in the compounds $[\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$ are essentially *trans* to an organosilyl group some shift to low field is to be expected in these compounds also. However, in view of the relatively low-frequency $\nu_{max.}$(PtH) i.r. bands, and the estimation of an H · · · Si distance of 1.72 Å from the *X*-ray crystallographic study, discussed above, it seems that the apparently anomalous HPt n.m.r. shifts must arise in part from a bonding interaction Pt–H–Si.

The $^{31}P$ spectra (with $^1H$ decoupling) of the compounds $[\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$ (Table 5) are particularly informative and are in accord with the diorganosilyl-bridged structures. For all the compounds, except (7) which was both insoluble and unstable, a basic singlet is observed for molecules containing no $^{195}Pt$ nuclei. Molecules with one $^{195}Pt$ nucleus give rise to two pairs of doublets resulting from coupling between the two phosphorus nuclei. Finally, weak signals are observed from the 11.4% of molecules which contain two $^{195}Pt$ nuclei, and which give spectra corresponding to the $[AX]_2$ spin system.[22] For the compounds (2), (3), and (9), these signals were sufficiently intense to allow a value of *J*(PtPt) to be determined (Table 5). These couplings lie between 2 477 and 3 331 Hz, and are remarkably large when compared with the values obtained previously (*ca.* 90 Hz)[1,22] for the hydrido-bridged compounds (1), in spite of very similar Pt–Pt distances, 2.708(1) and 2.692(3) Å respectively, in the two types of compound.

We have no experimental evidence for the mode of formation of the complexes (2)—(9) but a possible route, in view of the implication of radicals in some reactions of $d^{10}$ metal derivatives with substrates,[23] could be as shown in the Scheme.

$$[Pt(C_2H_4)_2(PR'_3)] \xrightarrow[-C_2H_4]{+SiR_2H_2} [Pt(SiR_2H)(PR'_3)] + H\,(\rightarrow H_2)$$

$$[Pt(SiR_2H)(PR'_3)] \longrightarrow [PtH(SiR_2)(PR'_3)] \longrightarrow [\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$$

SCHEME

The hydrido-bridges of the compound $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ are cleaved by CO and $CNBu^t$ giving the triplatinum complex $[\{Pt(\mu\text{-}CO)[P(C_6H_{11})_3]\}_3]$ and the monoplatinum complex $[PtH(SiMe_2Ph)(CNBu^t)\{P(C_6H_{11})_3\}]$, respectively.[1] It was of interest, therefore, to investigate reactions of CO and $CNBu^t$ with (2). The former reacted instantly with a toluene solution of the μ-disilyl-diplatinum compound affording $[\{Pt(\mu\text{-}CO)[P(C_6H_{11})_3]\}_3]$, as had occurred with the compound $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$. t-Butyl isocyanide also reacted rapidly at room temperature with (2) to produce in low yield a white or cream species the nature of which was not established with certainty, but which appears to be the compound $[PtBu^t(CN)(CNBu^t)\{P(C_6H_{11})_3\}]$. Evidence for this formulation is based on chemical analysis and on the following observations.

(*i*) The $^{31}P$ n.m.r. spectrum showed a singlet resonance with $^{195}Pt$ satellites corresponding to coupling with only one platinum nucleus in the molecule. Moreover, the value measured (1 057 Hz) for $^1J$(PPt) is relatively low, indicating an arrangement *trans*-$RPtP(C_6H_{11})_3$ in which the group R is strongly *trans* directing (*e.g.* $Bu^t$). It may be noted that the $^{31}P$ n.m.r. spectrum of $[PtMe(CN)(Ph_2PCH_2CH_2PPh_2)]$ showed *J*(PPt) *trans* to the ligand Me to be 1 633 Hz.[24]

(*ii*) The i.r. spectrum had bands at 2 195vs(br) and 2 136vs $cm^{-1}$. The former is assigned to the NC stretch of the isocyanide ligand, as observed in the spectrum of $[PtH(SiMe_2Ph)(CNBu^t)\{P(C_6H_{11})_3\}]$.[1] The band at 2 136 $cm^{-1}$ is not only intense but very sharp, and was initially thought to be due to a Pt–H stretch. However, the $^1H$ n.m.r. spectrum of the monoplatinum complex revealed no resonance above τ 10. Moreover, reaction of the deuterio-complex $[\{Pt^2H(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ with $CNBu^t$ afforded the same compound with no shift of the i.r. absorption at 2 136 $cm^{-1}$. Accordingly, the latter is assigned to a cyano-ligand, and in support of this conclusion it may be noted that the corresponding band in the i.r. spectrum of the compound $[PtMe(CN)(Ph_2PCH_2CH_2PPh_2)]$ occurs[24] at 2 135 $cm^{-1}$.

(*iii*) The $^1H$ n.m.r. spectrum, in addition to showing broad signals due to the $C_6H_{11}$ groups (τ 8.0—9.2), had resonances corresponding to the presence in the molecule of two $Bu^t$ groups in different environments. A sharp singlet resonance at τ 9.05 may be assigned to the $CNBu^t$ ligand.[1] The second resonance at τ 7.92 was a doublet with platinum satellites [$^4J$(PH) 7, $^3J$(PtH) 51 Hz]. This signal is assigned to a σ-bonded butyl group, since coupling between the latter and the ligated phosphorus atom could only be observable if the $Bu^t$ group were directly bonded to the metal atom. Moreover, the value of 51 Hz for $^3J$(PtH) compares well with those found for $^3J$(PtH) in the anion $[PtPr^iCl_2(CO)]^-$ (66.6 Hz)[25] and in the cycloheptenyl complex $[Pt(\sigma\text{-}C_7H_{11})(OCOCF_3)(PPh_3)_2]$ (67 Hz).[26]

The mode of formation of $[PtBu^t(CN)(CNBu^t)\{P(C_6H_{11})_3\}]$ from $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ and $CNBu^t$ is not clear but must involve cleavage of a C–N bond of the t-butyl isocyanide. It is of interest to note that $CNBu^t$ reacts with $K_2[PtCl_4]$ in aqueous solution to give initially a salt $[Pt(CNBu^t)_4][PtCl_4]$ which with excess of t-butyl isocyanide yields $[Pt(CN)_2(CNBu^t)_2]$ and butanol.[27]

## EXPERIMENTAL

Hydrogen-1 and $^{31}P$ n.m.r. studies were made with JEOL PFT and PS 100 spectrometers, $^2H$ measurements with the JEOL PFT 100 using a $^{19}F$ lock. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Experiments were carried out in Schlenk tubes 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 diorganosilanes were prepared by reduction of dichlorodiorganosilanes with lithium tetrahydridoaluminate. The bis(ethylene)triorganophosphine platinum complexes were synthesised using procedures described elsewhere.[2] Analytical data for new compounds are given in Table 4.

*Synthesis of* $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ *from* $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$.—The compound *trans*-di-μ-hydrido-bis(dimethylphenylsilyl)bis(tricyclohexylphosphine)diplatinum (1.22 g, 1 mmol) was refluxed in hexane (15 $cm^3$) for 0.5 h, giving a brown suspension which was filtered through an alumina pad. Removal of solvent *in vacuo* gave a yellow oil which was dissolved in diethyl ether (3 $cm^3$). After leaving the solution in the refrigerator overnight, cream *microcrystals* of $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ (2) (0.10 g, 10%), washed with diethyl ether (5 × 1 $cm^3$), were obtained: $\nu_{max.}$ at 1 655m(br), 1 340w, 1 300w, 1 290w, 1 268w, 1 231m, 1 226m, 1 199m, 1 178w, 1 170m, 1 113m, 1 005m, 997m, 910w, 883m, 850m, 835m, 828s, 785s, 748s, 733s, 723m, 705w, 668m, 649s, 519s, 472m, and 452w $cm^{-1}$.

*Preparation of the Diplatinum Complexes* $[\{PtH(\mu\text{-}SiR_2)(PR'_3)\}_2]$.—The following representative syntheses are given for the complexes (2)—(9) listed in Table 4.

(*a*) The complex $[Pt(C_2H_4)_2(PMeBu^t_2)]$ (0.38 g, 1 mmol) in light petroleum (10 $cm^3$) was treated with dimethylsilane (3 mmol). The yellow solution was stirred at room temperature (2 h), and then the solvent was removed *in vacuo*. The resulting oil was dissolved in hexane (1 $cm^3$) and placed in a refrigerator affording after 15 h white *microcrystals* of $[\{PtH(\mu\text{-}SiMe_2)(PMeBu^t_2)\}_2]$ (3) (0.17 g, 40%), washed with hexane (4 × 0.5 $cm^3$) and dried *in vacuo*: $\nu_{max.}$ at 1 634s(br), 1 365s, 1 361s, 1 290s, 1 237s, 1 228s, 1 198w, 1 178m, 1 022s, 941w, 887s, 830s, 816m, 790s, 736m, 720m, 673w, 649m, 600w, and 578m $cm^{-1}$.

A similar synthesis using $SiMe_2{}^2H_2$ with $[Pt(C_2H_4)_2(PMeBu^t_2)]$ gave white microcrystals of $[\{Pt^2H(\mu\text{-}SiMe_2)(PMeBu^t_2)\}_2]$ (0.30 g, 66%): $\nu_{max.}$ at 1 635w, 1 365s, 1 361s, 1 290s, 1 237s, 1 228s, 1 180s(br), 1 022s, 941w, 887s, 830s, 816m, 790s, 736m, 720m, 673w, 649m, 600w, and 578m $cm^{-1}$.

(*b*) The complex $[Pt(C_2H_4)_2(PPh_3)]$ (0.51 g, 1 mmol) suspended in light petroleum (10 $cm^3$) was treated with dimethylsilane (4 mmol) with stirring for 1 h at room temperature. Solvent was removed with a syringe, and the remaining solid was washed with toluene (2 × 1 $cm^3$) and diethyl ether to afford white slightly air-sensitive *microcrystals* of $[\{PtH(\mu\text{-}SiMe_2)(PPh_3)\}_2]$ (5) (0.18 g, 35%): $\nu_{max.}$ at 3 050w(br), 1 625m(br), 1 475m, 1 432s, 1 233m, 1 177w, 1 152w, 1 093s, 1 066w, 1 025w, 1 000w, 835m, 791w, 747s, 698vs, 651m, 536vs, 515s, 495m, 454w, and 427w $cm^{-1}$.

(*c*) The complex $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.26 g, 0.5 mmol) in light petroleum (10 $cm^3$) was treated with diphenylsilane (0.28 g, 1.5 mmol) at room temperature. The orange solution was stirred (0.5 h), giving a white solid. Solvent was removed with a syringe and the remaining solid was washed with light petroleum (2 × 3 $cm^3$) and dried *in vacuo* to give white *microcrystals* of $[\{PtH(\mu\text{-}SiPh_2)[P(C_6H_{11})_3]\}_2]$ (6) (0.11 g, 35%): $\nu_{max.}$ at 3 060w, 1 655m(br), 1 448s, 1 430s, 1 296w, 1 261m, 1 225w, 1 192m, 1 182m, 1 176m, 1 167w, 1 130m, 1 096s, 1 027w, 1 006w, 917w, 900w, 890w, 853m, 830w(br), 746s, 710s, 702s, 535w, 517w, 490s, 450s, 434w, 390w, and 376m $cm^{-1}$.

*Reaction between Pentamethyldisilane and Bis(ethylene)tricyclohexylphosphineplatinum*.—The compound $Si_2Me_5H$ (0.2 g, 1.5 mmol) was slowly added to a stirred suspension of $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.26 g, 0.5 mmol) in diethyl ether (10 $cm^3$) at room temperature. The resulting brown suspension after 0.5 h was filtered through an alumina pad (1 × 0.5 $cm^3$) to give a yellow solution from which the compound $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ (2) (36 mg, 15%) was obtained as white crystals, identified by comparison of the i.r. spectrum with an authentic sample.

*Reaction of the Compound* $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$ *with t-Butyl Isocyanide*.—To a stirred suspension of (2) (0.54 g, 0.5 mmol) in diethyl ether (10 $cm^3$) was added sufficient $CNBu^t$ (0.25 g, 3 mmol) to dissolve the solid. The mixture was stirred for 0.5 h and then filtered through a small pad of alumina (1 × 0.75 $cm^3$), giving an orange solution. Solvent was removed *in vacuo* and the residue was dissolved in a mixture (1 : 1) of light petroleum and diethyl ether (10 $cm^3$). After standing for 2 h white *crystals*, washed with light petroleum (3 × 3 $cm^3$), of the compound $[PtBu^t(CN)(CNBu^t)\{P(C_6H_{11})_3\}]$ (0.1 g, 15%), m.p. 244—246 °C (decomp.), were obtained (Found: C, 52.3; H, 9.0; N, 4.3. $C_{28}H_{51}N_2PPt$ requires C, 52.4; H, 8.0; N, 4.4%): $\nu_{max.}$ at 2 195s, 2 136s, 1 352w, 1 298w, 1 268w, 1 231w, 1 199w, 1 177m, 1 151w, 1 130w, 1 110w, 1 005w, 916w, 901w, 889w, 850m, 819w, 740m, 540m, 516m, 492w, and 469w $cm^{-1}$. N.m.r.: $^1H([^2H_6]benzene)$, τ 7.92 [d, $PtC(Me)_3$, 9 H, *J*(PH) 7, *J*(PtH) 52 Hz], 9.05 [s, 9 H, $CNC(Me)_3$], and 8.0—9.2(m br, 33 H, $C_6H_{11}$); $^{31}P([^2H_6]benzene)$, −25.8 p.p.m. [s, *J*(PtP) 1 057 Hz].

*Crystal-structure Determination of* $[\{PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]\}_2]$.—The complex crystallises as colourless needles; the crystal used for data collection was of dimensions *ca.* 0.27 × 0.17 × 0.15 mm and was mounted in a Lindemann tube. Diffracted intensities were recorded at 200 K on a Syntex $P2_1$ four-circle diffractometer for $2.9 \leqslant 2\theta \leqslant 40°$, according to methods described earlier.[28] Of the total (7 123) measured intensities, 5 998 were deemed 'observed' according to the criterion $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. The intensities were corrected for the effects of *X*-ray absorption.

*Crystal data.* $C_{40}H_{80}P_2Pt_2Si_2$, $M = 1\,069.6$, Monoclinic, $a = 9.158(2)$, $b = 11.725(3)$, $c = 20.252(9)$ Å, $\beta = 92.37(3)°$, $U = 2\,172.7(13)$ Å$^3$, $D_m$(flotation) = 1.51 g $cm^{-3}$, $Z = 2$, $D_c = 1.53$ g $cm^{-3}$, $F(000) = 1\,068$, space group $P2_1/c$, Mo-$K_\alpha$ *X*-radiation (graphite monochromator) $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 69.2 $cm^{-1}$

The platinum atoms were located from a Patterson synthesis, and the rest of the atoms (including hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. In order to locate the hydride atom as accurately as possible, the positional and isotropic thermal parameters for all other H atoms were held constant in the later stages of the refinement. The refinement converged at *R* 0.065 (*R'* 0.080) with a mean shift-to-error ratio in the last cycle of 0.04. A weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.001\,5F^2$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.8 or < −0.6 e Å$^{-3}$, except in the immediate vicinity of the Pt atom. Scattering factors were from ref. 29 for C, Si, P, and Pt, and from ref. 30 for H. Corrections for the effects of anomalous dispersion were applied for Pt ($\Delta f'$ −2.35, $\Delta f''$ 8.39), Si ($\Delta f'$ 0.07, $\Delta f''$ 0.07) and P ($\Delta f'$ 0.09, $\Delta f''$ 0.09).[31] All computational work was carried out at the University of London Computer Centre with the '*X*-Ray' system of programs.[32] Observed and calculated structure factors, together with all thermal parameters, are listed in Supplementary Publication No. SUP 22666 (26 pp.).*

We thank the S.R.C. for support, the Spanish Ministry of Education and Science for a scholarship (to M. C.), and Dr. B. F. Taylor for $^2$H n.m.r. measurements.

[9/428 *Received, 15th March, 1979*]

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, 1978, 801.

[2] N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. C. S. Dalton*, 1978, 1337.

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

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

[5] M. Ciriano, M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *Adv. Chem. Ser.*, 1978, **167**, 111.

[6] 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.

[7] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 2571.

[8] W. L. Hutcheon, Ph.D. dissertation, University of Alberta, 1971; see also *Chem. Eng. News.*, 1970, **48**, 75.

[9] M. J. Bennett and K. A. Simpson, *J. Amer. Chem. Soc.*, 1971, **93**, 7156.

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

[11] R. A. Smith and M. J. Bennett, *Acta Cryst.*, 1977, **B33**, 1113.

[12] D. M. Rae, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1972, 1273.

[13] F. A. Cotton, T. LaCour, and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754.

[14] J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Amer. Chem. Soc.*, 1978, **100**, 7407.

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

[16] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[17] A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3469.

[18] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[19] E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed, and R. O. Gould, *J.C.S. Dalton*, 1978, 1167.

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

[21] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J.C.S. Dalton*, 1978, 517.

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

[23] M. F. Lappert and P. W. Lednor, *Adv. Organometallic Chem.*, 1976, **14**, 345.

[24] T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.

[25] J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson, and M. Murray, *J.C.S. Dalton*, 1978, 872.

[26] M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, 1971, **93**, 3797.

[27] L. Malatesta, *Progr. Inorg. Chem.*, 1959, **1**, 375; L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley–Interscience, New York, 1969, p. 169.

[28] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[29] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[30] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[31] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[32] Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.