Reactions of Bis(ethylene)(tertiary phosphine)platinum Complexes with Phenylethynyl Derivatives of Titanium and Silicon; Crystal Structure of (μ-Dimethylsilanediyl)(σ-phenylethynyl)[μ-(1-σ:1—2-η-phenylethynyl)]-bis(tricyclohexylphosphine)diplatinum (*Pt–Pt*)

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Bis(ethylene)(tertiary phosphine)platinum complexes $[Pt(C_2H_4)_2(PR_3)]$ [PR_3 = P(cyclo-$C_6H_{11})_3$, PMe_2Ph, $PMePh_2$, PPh_3, or PPr^i_2Ph] react with bis(cyclopentadienyl)bis(phenylethynyl)titanium to give compounds $[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PR_3)]$ in which the PhC≡C–Ti–C≡CPh group acts as a bidentate ligand to platinum. In contrast, dimethylbis(phenylethynyl)silane reacts with $[Pt(C_2H_4)_2(PR_3)]$ [$PR_3 = P(C_6H_{11})_3$, $PMeBu^t_2$, or PPr^i_2Ph] to give diplatinum complexes $[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)(PR_3)_2]$. A single-crystal *X*-ray diffraction study has established the structure of the product from $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ and $[Si(C{\equiv}CPh)_2Me_2]$. Crystals are monoclinic, space group $P2_1/c$ (no. 14), with a = 12.44(1), b = 26.12(4), c = 15.832(8) Å, β = 97.99(6)°, and Z = 4. The structure has been determined by analysis of 5 131 unique data with $F > 4\sigma(F)$ collected to $2\theta \leqslant 50°$ (Mo-K_α radiation) at 200 K on a four-circle diffractometer, and refined to R 0.053 (R' 0.041). The results establish a molecular structure with an $SiMe_2$ group asymmetrically bridging a Pt–Pt separation of 2.703(1) Å. Two C≡CPh groups are σ-bonded to one metal atom (formally Pt^{IV}) but one is also η^2-co-ordinated to the other platinum (formally Pt^{II}). The P–Pt–Pt–P skeleton is non-linear with PPtPt angles of 165.2(1) and 148.0(1)°. Dimethylbis(phenylethynyl)silane reacts with $[Pt(C_2H_4)(PPh_3)_2]$, without carbon–silicon bond cleavage, to give mono- and di-platinum η^2 complexes $[Pt\{\eta\text{-}PhC{\equiv}CSi(C_2Ph)Me_2\}(PPh_3)_2]$ and $[Pt_2\{\eta\text{-}(PhC{\equiv}C)_2SiMe_2\}(PPh_3)_4]$.

PLATINUM complexes $[Pt(\eta\text{-}RC_2R)(PR_3)_2]$ have been known for many years.[1-3] Recently it has been shown that platinum(0) forms several other types of acetylene complex. These include monoplatinum compounds $[Pt(\eta\text{-}RC_2R)_2]$,[4,5] the first examples of which were described by Rochon and Theophanides,[6] as well as di- and tri-platinum species, *e.g.* $[Pt_2\{\mu_2\text{-}(\eta\text{-}PhC_2Ph)\}(PMe_3)_4]$,[7] $[Pt_2\{\mu_2\text{-}(\eta\text{-}Me_3SiC_2SiMe_3)\}(\eta\text{-}Me_3SiC_2SiMe_3)_2]$,[5] and $[Pt_3\{\mu_2\text{-}(\eta^2\text{-}PhC_2Ph)\}_2(PEt_3)_4]$.[7] An interesting aspect of our work, however, has been our failure to isolate species of the type $[Pt(\eta\text{-}RC_2R)_2(PR_3)]$, yet the corresponding ethylene complexes $[Pt(\eta\text{-}C_2H_4)_2(PR_3)]$ [8] exist and have an extensive chemistry.[9-11] The latter do not react with acetylenes to give the former, but instead afford a mixture of products, including the bridged $[Pt\{\mu\text{-}(RC_2R)\}Pt]$ compounds mentioned above. However, the report [12] that $[Ni(CO)_4]$ reacts with $[Ti(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)_2]$ (1) to give the chelate complex (2) made it seem possible that (1) would react with $[Pt(C_2H_4)_2(PR_3)]$ in a similar manner, release of ethylene yielding complexes in which the titanium compound acts, *via* its acetylenic ligands, as a bidentate group to platinum.

RESULTS AND DISCUSSION

Addition of solid $[Ti(C{\equiv}CPh)_2(\eta\text{-}C_5H_5)_2]$ (1) to solutions or suspensions of the complexes $[Pt(C_2H_4)_2(PR_3)]$ [PR_3 = P(cyclo-$C_6H_{11})_3$, PMe_2Ph, $PMePh_2$, PPh_3, or PPr^i_2Ph] in diethyl ether affords at room temperature red solutions. The latter yield air-stable orange crystalline compounds having compositions corresponding to the anticipated addition of a single $Pt(PR_3)$ group to (1). Whereas complex (1) showed in its i.r. spectrum a C≡C stretching band at 2 075 cm^{-1}, the new compounds had no band in this region, but instead there was an absorption near 1 800 cm^{-1}. The latter is in the region for acetylenic groups co-ordinated to platinum. Thus the diacetylene complex $[Pt(PhC_4Ph)(PPh_3)_2]$ exhibits bands at 1 725 cm^{-1} (co-ordinated C≡C group) and at 2 170 cm^{-1} (unco-ordinated C≡C group),[13] while for $[Pt(PhC_2Ph)_2]$ $\nu_{max.}$(C≡C) occurs at 1 881 cm^{-1}.[4] The ^{31}P n.m.r. spectra of the products (Table 1) all showed a singlet resonance, with a ^{31}P–^{195}Pt satellite pattern corresponding to the presence in the molecules of a single $Pt(PR_3)$ group. The compounds are accordingly formulated as the chelate complexes (3)—(7). This implies that the four acetylenic carbon atoms in these compounds are present in two environments, and in agreement with this the ^{13}C n.m.r. spectrum (^{1}H-decoupled) of (7) shows resonances for the carbon atoms bonded to platinum at 189.5 [d, J(PC) 4, J(PtC) 58 Hz] and 114.4 p.p.m. [d, J(PC) 9, J(PtC) 273 Hz]. The resonance at 189.5 p.p.m. has an unusually low chemical shift and hence we tentatively assign it to the two carbon atoms bonded to both titanium and platinum.

Formation of the complexes (3)—(7) prompted an investigation of reactions of the compounds $[Pt(C_2H_4)_2(PR_3)]$ with $[Si(C{\equiv}CPh)_2Me_2]$ in order to establish whether the latter would also act as a bidentate ligand to the $Pt(PR_3)$ groups. The complexes $[Pt(C_2H_4)_2(PR_3)]$ [PR_3 = P(cyclo-$C_6H_{11})_3$, $PMeBu^t_2$, or PPr^i_2Ph] on treatment with dimethylbis(phenylethynyl)silane at room temperature gave pale yellow or white solids. Examination of the ^{31}P n.m.r. spectra of the products (8)—(10) showed (Table 1) that they were diplatinum complexes containing non-equivalent PR_3 ligands since each spectrum had two resonances, with coupling to two different ^{195}Pt nuclei. Moreover, the spectrum of (9) revealed ^{29}Si–^{31}P couplings of 140 and 16 Hz, the former being associated with the resonance at −43.4 p.p.m.

TABLE 1

Hydrogen-1 and phosphorus-31 n.m.r. data [a]

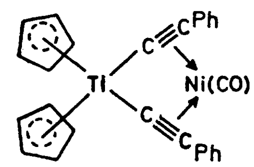
Complex	^{1}H	^{31}P
$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PR_3)]$		
(3) $PR_3 = P(C_6H_{11})_3$	2.74 (m, 10 H, Ph), 4.57 (s, 10 H, C_5H_5), 8.0—9.50 (m, br, 33 H, C_6H_{11})	−42.1 [s, *J*(PPt) 4 376]
(4) PMe_2Ph	2.65—2.95 (m, 15 H, Ph), 4.47 (s, 10 H, C_5H_5), 8.61 [d, 6 H, *J*(PH) 9, *J*(PtH) 39]	8.2 [s, *J*(PPt) 4 640]
(5) $PMePh_2$	2.82 (m, 10 H, Ph), 3.08 (m, 10 H, Ph), 4.52 (s, 10 H, C_5H_5), 8.38 [d, 3 H, *J*(PH) 9, *J*(PtH) 40]	−10.2 [s, *J*(PPt) 4 722]
(6) PPh_3	2.80 (m, 15 H, Ph), 3.22 (m, 10 H, Ph), 4.53 (s, 10 H, C_5H_5)	−32.4 [s, *J*(PPt) 4 805]
(7) $PPr^i{}_2Ph$	2.60 (m, 15 H, Ph), 4.57 (s, 10 H, C_5H_5), 7.86 (m, 2 H, C*H*Me$_2$), 9.17 [d of d, 6 H, Me, *J*(PH) 17, *J*(HH) 7], 9.28 [d of d, 6 H, Me, *J*(PH) 15, *J*(HH) 7]	−47.0 [s, *J*(PPt) 4 614]
$[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma : 1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)(PR_3)_2]$		
(8) $PR_3 = P(C_6H_{11})_3$	2.75 (m, 10 H, Ph), 7.70—9.15 (m, br, 66 H, C_6H_{11}), 8.76 (s, 6 H, MeSi)	−55.0 [d, *J*(PP) 41, *J*(PPt) 5 286 and 308], −38.5 [d, *J*(PP) 41, *J*(PPt) 2 576 and 0] [b]
(9) $PMeBu^t{}_2$	2.20—3.00 (m, 10 H, Ph), 8.21 [d, 3 H, Me, *J*(PH) 8, *J*(PtH) 33], 8.54 [s, 6 H, SiMe$_2$, *J*(PtH) 14 and 8], 8.80 (m, 21 H, Me and Bu^t), 8.97 [d, 18 H, Bu^t, *J*(PH) 13] [c]	−54.5 [d, *J*(PP) 42, *J*(PPt) 5 592 and 312], −43.4 [d, *J*(PP) 42, *J*(PPt) 2 742 and 11] [c]
(10) $PPr^i{}_2Ph$	2.20—3.30 (m, 15 H, Ph), 6.86 and 7.54 (m, 4 H, C*H*Me$_2$), 8.60 and 9.05 [m, 12 H, Me, *J*(PH) 16, *J*(HH) 7], 8.78 (s, 6 H, SiMe$_2$)	−61.0 [d, *J*(PP) 45, *J*(PPt) 5 515 and 335], −42.4 [d, *J*(PP) 45, *J*(PPt) 2 705 and 0]
$[Pt\{\eta\text{-}PhC{\equiv}CSi(C_2Ph)Me_2\}(PR_3)_2]$		
(12) $PR_3 = PPh_3$	2.40—3.28 (m, 40 H, Ph), 10.08 (s, 6 H, SiMe$_2$)	−26.9 [d, *J*(PP) 39, *J*(PPt) 3 492], −28.2 [d, *J*(PP) 39, *J*(PPt) 3 804]
(14) $PMePh_2$	2.48—3.10 (m, 30 H, Ph), 8.10 [m, 3 H, *J*(PH) 7, *J*(PtH) 28], 8.43 [m, 3 H, *J*(PH) 7, *J*(PtH) 30], *ca.* 10.0 (s, 6 H, MeSi)	−6.8 [s, *J*(PP) 43, *J*(PPt) 3 694], −6.8 [s, *J*(PP) 43, *J*(PPt) 3 410] [d]
(13) $[Pt_2\{\eta\text{-}(PhC{\equiv}C)_2SiMe_2\}(PPh_3)_4]$	2.24—3.16 (m, 70 H, Ph), 10.04 (s, 6 H, Me$_2$Si)	−29.1 [s, *J*(PP) 46, *J*(PPt) 3 795], −29.1 [s, *J*(PP) 46, *J*(PPt) 3 545] [d]

[a] ^{1}H chemical shifts in τ, ^{31}P chemical shifts in p.p.m. (to low frequency, relative to H_3PO_4 external), coupling constants in Hz. Recorded in [^{2}H]chloroform unless otherwise stated. [b] In [$^2H_2$]dichloromethane. [c] In [$^2H_6$]benzene. [d] AB pattern of spectrum can be inferred from satellite peaks.

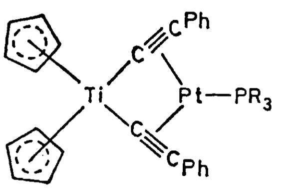
and the latter with that at −54.5 p.p.m. The detection of ^{29}Si–^{31}P couplings in the spectra seemed indicative of the presence in the molecule of P–Pt–Si bonding, which would in turn imply carbon–silicon bond cleavage in the reaction of $[Si(C{\equiv}CPh)_2Me_2]$ with $[Pt(C_2H_4)_2(PMeBu^t{}_2)]$. Moreover, in the ^{1}H n.m.r. spectrum the SiMe$_2$ group (τ 8.54) showed two *J*(PtH) values (14 and 8 Hz). These ^{31}P and ^{1}H n.m.r. data suggested the presence in the molecule of a skeletal arrangement $\mathrm{P\overline{Pt{-}SiMe_2{-}Pt}P}$.

The i.r. spectra of the complexes (8)—(10) showed two bands assignable to C≡C groups. One band near 2 100 cm^{-1} was indicative of a Pt–C≡CR group, as observed [14] in the spectra of the platinum(II) compounds $K_2[Pt(C_2R)_4]$. The second band near 1 960 cm^{-1} was at too high a frequency for an Si–C≡CPh group η^2-co-ordinated to platinum. Thus with the complex $[Pt(PhC_2SiMe_3)_2]$ ν(C≡C) occurs at 1 846 cm^{-1}.[5]

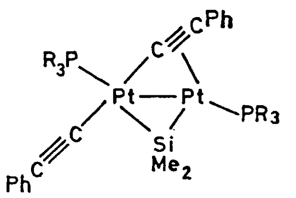
In order to establish the molecular structures of compounds (8)—(10) a single-crystal *X*-ray diffraction study was carried out on (8). The results of this study are given in Tables 2—4 and are illustrated in Figure 1, which also shows the crystallographic numbering system. The contents of the monoclinic unit cell are shown in Figure 2. It is at once apparent that in the reaction of $[Si(C{\equiv}CPh)_2Me_2]$ with $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ both PhC≡C groups have been cleaved from silicon, and have become bonded to Pt(2). The Pt(1)–Pt(2) separation [2.703(1) Å], although longer than the sum of the covalent radii (2.62 Å), is shorter than those measured in some platinum clusters, *e.g.* $[Pt_4(CO)_5(PMe_2Ph)_4]$ (2.752 and 2.790 Å),[15] and is little different from those found in several other diplatinum complexes, *e.g.* $[(Ph_3P)_2\overline{Pt{-}S{-}Pt}(CO)(PPh_3)]$ (2.647 Å) [16] and $[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$ (2.692 Å).[9] The metal–metal bond in (8) is bridged by a SiMe$_2$ group such that the Pt(1)SiPt(2) angle is 70.1(1) Å.



(2)



	PR$_3$
(3)	P(cyclo-C$_6$H$_{11}$)$_3$
(4)	PMe$_2$Ph
(5)	PMePh$_2$
(6)	PPh$_3$
(7)	PPr$^i{}_2$Ph



	PR$_3$
(8)	P(cyclo-C$_6$H$_{11}$)$_3$
(9)	PMeBu$^t{}_2$
(10)	PPr$^i{}_2$Ph

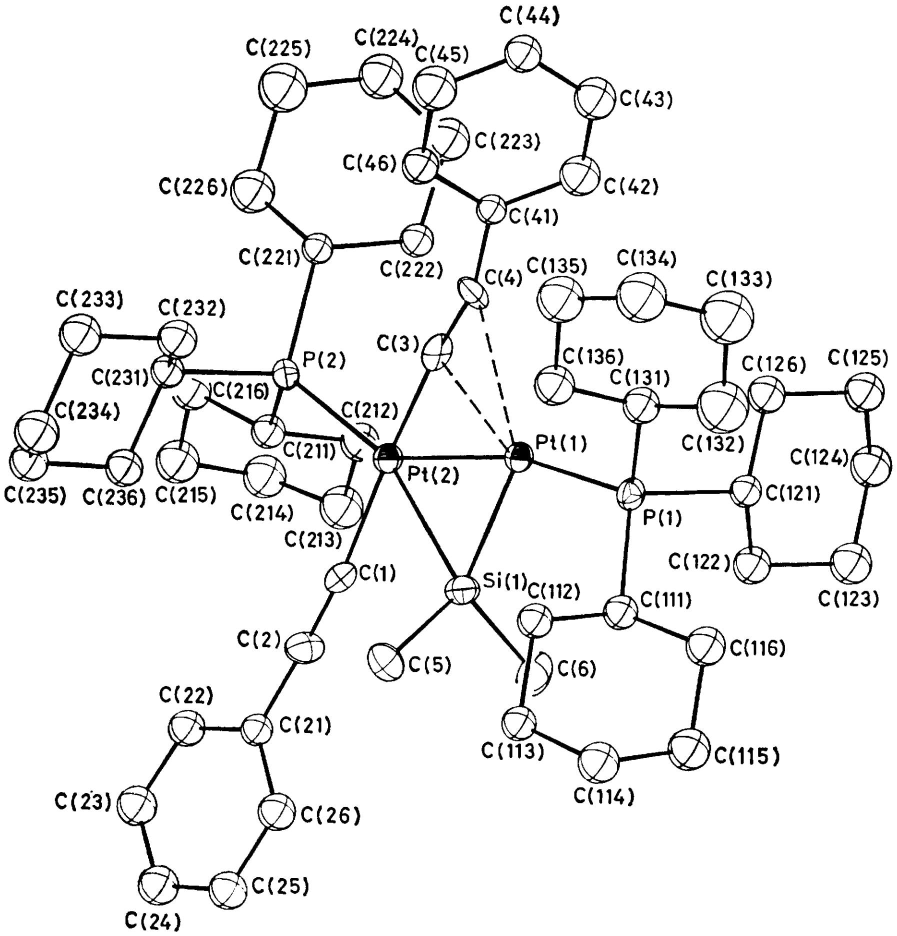


Figure 1 Molecular structure of the diplatinum complex (8)

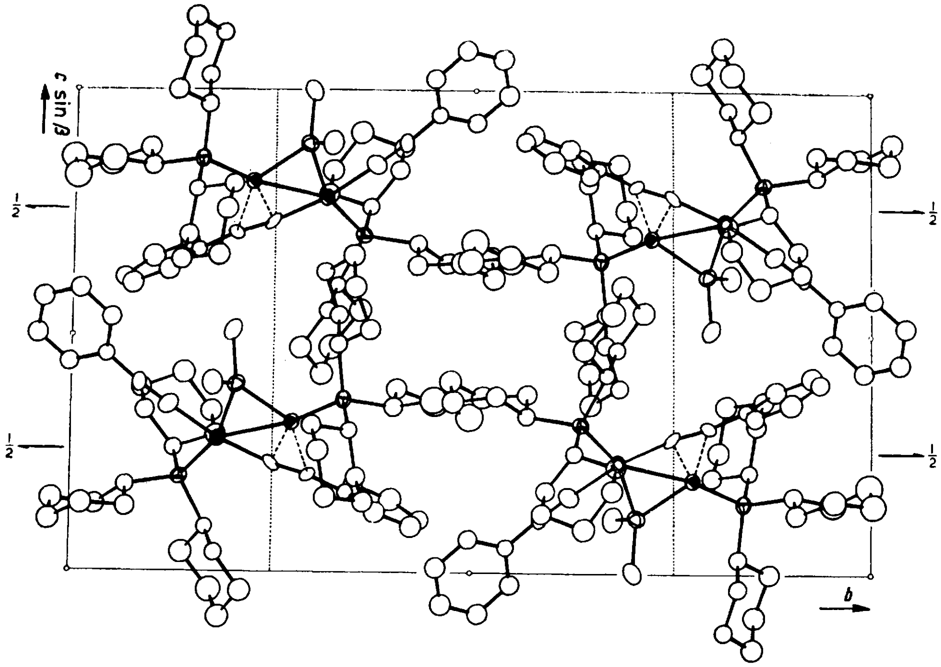


Figure 2 Contents of the monoclinic unit cell of complex (8)

Although acute this angle differs little from those found in the μ-SiR$_2$ bridged complexes $[\mathrm{Re_2H_2(\mu\text{-}SiEt_2)(CO)_8}]$ [75.7(3)°] [17] and $[\mathrm{Re_2H_2(\mu\text{-}SiEt_2)_2(CO)_7}]$ [73.6(1)°].[18] Bond distances in the terminal acetylide ligand are Pt(2)–C(1) 2.01(1) and C(1)–C(2) 1.20(2) Å, the latter corresponding to a triple bond [C(1)–C(2)–C(21) 174(1)°]. In the bridging acetylene group the distances are Pt(2)–C(3) 1.96(1) and C(3)–C(4) 1.26(1) Å, the C≡C

TABLE 2

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (8)

Atom	*x*	*y*	*z*
Pt(1)	0.329 37(4)	0.276 10(2)	0.307 95(3)
Pt(2)	0.235 03(4)	0.183 76(2)	0.274 09(3)
Si(1)	0.383 7(3)	0.206 1(1)	0.385 7(2)
C(5)	0.350 5(12)	0.201 3(5)	0.497 2(8)
C(6)	0.524 6(11)	0.176 9(5)	0.388 4(9)
PhC≡C groups			
C(1)	0.287 0(10)	0.121 8(5)	0.343 2(8)
C(2)	0.309 2(11)	0.085 0(5)	0.388 0(8)
C(21)	0.328 3(9)	0.043 5(4)	0.447 1(7)
C(22)	0.274 5(10)	−0.003 1(4)	0.430 8(8)
C(23)	0.288 9(11)	−0.043 0(5)	0.490 2(7)
C(24)	0.358 2(10)	−0.036 2(5)	0.565 7(8)
C(25)	0.414 0(11)	0.009 4(4)	0.583 8(8)
C(26)	0.397 8(10)	0.048 8(5)	0.523 4(7)
C(3)	0.191 3(10)	0.250 3(5)	0.222 6(7)
C(4)	0.172 3(12)	0.296 1(5)	0.199 8(8)
C(41)	0.119 5(8)	0.342 7(4)	0.164 8(7)
C(42)	0.173 4(11)	0.380 0(4)	0.123 8(8)
C(43)	0.121 0(10)	0.425 0(5)	0.094 5(8)
C(44)	0.015 3(9)	0.435 4(5)	0.107 9(8)
C(45)	−0.039 8(11)	0.399 2(4)	0.150 3(8)
C(46)	0.013 7(9)	0.353 9(5)	0.178 2(8)
Tricyclohexylphosphine group 1			
P(1)	0.440 3(3)	0.340 0(1)	0.354 8(2)
C(111)	0.506 6(10)	0.333 9(5)	0.467 8(7)
C(112)	0.424 0(10)	0.333 2(5)	0.530 3(7)
C(113)	0.477 2(10)	0.315 8(5)	0.618 9(7)
C(114)	0.569 5(12)	0.351 2(5)	0.651 2(9)
C(115)	0.652 7(12)	0.354 3(6)	0.587 7(9)
C(116)	0.598 5(11)	0.371 7(5)	0.499 9(8)
C(121)	0.555 4(10)	0.347 6(4)	0.291 5(7)
C(122)	0.630 1(11)	0.301 1(5)	0.301 9(8)
C(123)	0.726 2(11)	0.308 1(5)	0.250 6(8)
C(124)	0.685 6(11)	0.318 3(5)	0.155 7(8)
C(125)	0.611 4(11)	0.363 7(5)	0.145 5(8)
C(126)	0.516 3(11)	0.356 1(5)	0.197 9(7)
C(131)	0.369 3(11)	0.402 2(5)	0.339 3(8)
C(132)	0.433 2(15)	0.452 4(6)	0.352 1(11)
C(133)	0.362 6(15)	0.497 7(7)	0.317 8(11)
C(134)	0.259 7(14)	0.501 9(6)	0.356 8(11)
C(135)	0.196 9(13)	0.453 8(6)	0.346 8(10)
C(136)	0.265 4(11)	0.405 9(5)	0.376 3(8)
Tricyclohexylphosphine group 2			
P(2)	0.098 2(3)	0.136 3(1)	0.195 1(2)
C(211)	0.144 7(10)	0.069 3(5)	0.177 9(8)
C(212)	0.245 4(11)	0.068 7(5)	0.133 1(8)
C(213)	0.293 5(12)	0.013 8(5)	0.140 6(9)
C(214)	0.210 4(12)	−0.026 5(6)	0.106 3(9)
C(215)	0.110 4(12)	−0.022 7(5)	0.149 2(9)
C(216)	0.059 1(12)	0.031 0(5)	0.137 0(9)
C(221)	0.041 6(10)	0.167 9(4)	0.092 1(7)
C(222)	0.131 2(10)	0.181 1(5)	0.039 6(7)
C(223)	0.086 8(12)	0.213 6(5)	−0.037 9(9)
C(224)	−0.008 3(12)	0.188 8(6)	−0.089 8(9)
C(225)	−0.096 6(13)	0.175 2(6)	−0.036 2(10)
C(226)	−0.050 0(12)	0.140 7(6)	0.040 1(9)
C(231)	−0.021 8(10)	0.128 4(4)	0.252 9(8)
C(232)	−0.057 1(11)	0.180 6(5)	0.281 8(8)
C(233)	−0.155 7(11)	0.176 2(5)	0.330 8(8)
C(234)	−0.130 1(13)	0.141 1(5)	0.405 8(9)
C(235)	−0.094 3(11)	0.089 2(5)	0.377 1(8)
C(236)	0.004 8(11)	0.093 3(5)	0.330 0(8)

TABLE 3

Bond lengths (Å) and angles (°) for complex (8) with estimated standard deviations in parentheses

(*a*) Distances

Pt(1)–Pt(2)	2.703(1)	Si(1)–C(5)	1.873(13)
Pt(1)–Si(1)	2.255(4)	Si(1)–C(6)	1.906(14)
Pt(2)–Si(1)	2.444(4)		
PhC≡C groups *			
Pt(2)–C(1)	2.01(1)	C(23)–C(24)	1.385(9)
C(1)–C(2)	1.20(2)	C(24)–C(25)	1.388(9)
C(2)–C(21)	1.43(2)	C(25)–C(26)	1.401(8)
C(21)–C(22)	1.396(8)	C(21)–C(26)	1.392(8)
C(22)–C(23)	1.399(8)		
Pt(1)–C(3)	2.14(1)	C(42)–C(43)	1.393(9)
Pt(2)–C(3)	1.96(1)	C(43)–C(44)	1.388(9)
Pt(1)–C(4)	2.47(1)	C(44)–C(45)	1.393(9)
C(3)–C(4)	1.26(1)	C(45)–C(46)	1.398(9)
C(4)–C(41)	1.45(2)	C(41)–C(46)	1.393(8)
C(41)–C(42)	1.395(8)		
Tricyclohexylphosphine group 1			
Pt(1)–P(1)	2.226(3)	P(1)–C(131)	1.85(1)
P(1)–C(111)	1.87(1)	C(131)–C(132)	1.53(2)
C(111)–C(112)	1.52(2)	C(132)–C(133)	1.53(2)
C(112)–C(113)	1.53(2)	C(133)–C(134)	1.50(2)
C(113)–C(114)	1.51(2)	C(134)–C(135)	1.48(2)
C(114)–C(115)	1.54(2)	C(135)–C(136)	1.55(2)
C(115)–C(116)	1.53(2)	C(131)–C(136)	1.49(2)
C(111)–C(116)	1.54(2)		
P(1)–C(121)	1.87(1)		
C(121)–C(122)	1.52(2)		
C(122)–C(123)	1.55(2)		
C(123)–C(124)	1.54(2)		
C(124)–C(125)	1.50(2)		
C(125)–C(126)	1.55(2)		
C(121)–C(126)	1.51(1)		
Tricyclohexylphosphine group 2			
Pt(2)–P(2)	2.325(3)		
P(2)–C(211)	1.87(1)	C(224)–C(225)	1.52(2)
C(211)–C(212)	1.52(2)	C(225)–C(226)	1.55(2)
C(212)–C(213)	1.55(2)	C(221)–C(226)	1.49(2)
C(213)–C(214)	1.52(2)	P(2)–C(231)	1.87(1)
C(214)–C(215)	1.50(2)	C(231)–C(232)	1.52(2)
C(215)–C(216)	1.54(2)	C(232)–C(233)	1.54(2)
C(211)–C(216)	1.54(2)	C(233)–C(234)	1.50(2)
P(2)–C(221)	1.87(1)	C(234)–C(235)	1.52(2)
C(221)–C(222)	1.52(2)	C(235)–C(236)	1.53(2)
C(222)–C(223)	1.53(2)	C(231)–C(236)	1.52(2)
C(223)–C(224)	1.49(2)		

(*b*) Angles

Pt(1)–Si(1)–Pt(2)	70.1(1)		
Pt(1)–Si(1)–C(5)	118.7(5)		
Pt(1)–Si(1)–C(6)	122.8(5)		
Pt(2)–Si(1)–C(5)	114.9(5)		
Pt(2)–Si(1)–C(6)	121.4(5)		
C(5)–Si(1)–C(6)	106.0(6)		
PhC≡C ligands			
Pt(2)–C(1)–C(2)	174(1)	Pt(2)–C(3)–C(4)	171(1)
C(1)–C(2)–C(21)	174(1)	C(3)–C(4)–C(41)	163(1)
C(2)–C(21)–C(22)	121(1)	C(4)–C(41)–C(42)	123(1)
C(2)–C(21)–C(26)	121(1)	C(4)–C(41)–C(46)	120(1)
C(21)–C(22)–C(23)	121(1)	C(41)–C(42)–C(43)	121(1)
C(22)–C(23)–C(24)	119(1)	C(42)–C(43)–C(44)	121(1)
C(23)–C(24)–C(25)	121(1)	C(43)–C(44)–C(45)	119(1)
C(24)–C(25)–C(26)	118(1)	C(44)–C(45)–C(46)	119(1)
C(25)–C(26)–C(21)	122(1)	C(45)–C(46)–C(41)	123(1)
C(26)–C(21)–C(22)	118(1)	C(46)–C(41)–C(42)	117(1)
C(1)–Pt(2)–C(3)	171.2(5)		
C(1)–Pt(2)–Pt(1)	120.8(4)	C(3)–Pt(2)–Pt(1)	51.7(3)
C(1)–Pt(2)–Si(1)	69.2(4)	C(3)–Pt(2)–Si(1)	103.1(3)
		C(3)–Pt(1)–C(4)	30.8(4)

TABLE 3 (*Continued*)

(*b*) Angles (*Continued*)

Tricyclohexylphosphine group 1			
Pt(2)–Pt(1)–P(1)	165.2(1)	Pt(1)–P(1)–C(131)	110.6(4)
Si(1)–Pt(1)–P(1)	107.5(1)	P(1)–C(131)–C(132)	120(1)
Pt(1)–P(1)–C(111)	115.2(4)	P(1)–C(131)–C(136)	115(1)
P(1)–C(111)–C(112)	112.1(9)	C(131)–C(132)–C(133)	111(1)
P(1)–C(111)–C(116)	117.9(9)	C(132)–C(133)–C(134)	113(1)
C(111)–C(112)–C(113)	111(1)	C(133)–C(134)–C(135)	111(1)
C(112)–C(113)–C(114)	110(1)	C(134)–C(135)–C(136)	113(1)
C(113)–C(114)–C(115)	111(1)	C(135)–C(136)–C(131)	114(1)
C(114)–C(115)–C(116)	111(1)	C(136)–C(131)–C(132)	111(1)
C(115)–C(116)–C(111)	109(1)		
C(116)–C(111)–C(112)	109(1)		
Pt(1)–P(1)–C(121)	112.8(4)		
P(1)–C(121)–C(122)	111.0(8)		
P(1)–C(121)–C(126)	112.0(9)		
C(121)–C(122)–C(123)	111(1)		
C(122)–C(123)–C(124)	111(1)		
C(123)–C(124)–C(125)	111(1)		
C(124)–C(125)–C(126)	110(1)		
C(125)–C(126)–C(121)	112(1)		
C(126)–C(121)–C(122)	109(1)		
Tricyclohexylphosphine group 2			
Pt(1)–Pt(2)–P(2)	148.0(1)	Pt(2)–P(2)–C(231)	111.8(4)
Si(1)–Pt(2)–P(2)	160.0(1)	P(2)–C(231)–C(232)	109.4(8)
Pt(2)–P(2)–C(211)	111.0(4)	P(2)–C(231)–C(236)	111.1(9)
P(2)–C(211)–C(212)	111.7(9)	C(231)–C(232)–C(233)	112(1)
P(2)–C(211)–C(216)	117.3(9)	C(232)–C(233)–C(234)	110(1)
C(211)–C(212)–C(213)	108(1)	C(233)–C(234)–C(235)	110(1)
C(212)–C(213)–C(214)	112(1)	C(234)–C(235)–C(236)	112(1)
C(213)–C(214)–C(215)	111(1)	C(235)–C(236)–C(231)	109(1)
C(214)–C(215)–C(216)	111(1)	C(236)–C(231)–C(232)	110(1)
C(215)–C(216)–C(211)	107(1)		
C(216)–C(211)–C(212)	111(1)		
Pt(2)–P(2)–C(221)	113.0(4)		
P(2)–C(221)–C(222)	111.1(8)		
P(2)–C(221)–C(226)	115.9(9)		
C(221)–C(222)–C(223)	111(1)		
C(222)–C(223)–C(224)	112(1)		
C(223)–C(224)–C(225)	112(1)		
C(224)–C(225)–C(226)	110(1)		
C(225)–C(226)–C(221)	109(1)		
C(226)–C(221)–C(222)	112(1)		
P(2)–Pt(2)–C(1)	91.1(4)		
P(2)–Pt(2)–C(3)	96.3(3)		

* During refinement C–C bond lengths in the phenyl rings were kept restricted to 1.395 Å with σ 0.01 Å.

bond being elongated due to co-ordination to Pt(1) [Pt(1)–C(3) 2.14(1), Pt(1)–C(4) 2.47(1) Å]. The phenyl substituent on C(4) is bent away from Pt(1) such that the angle C(3)C(4)C(41) is 163(1)°. The plane defined by the carbon atoms of this phenyl substituent lies at 62° with respect to the Si(1)Pt(1)Pt(2) plane, whereas the plane of the phenyl ring of the terminal acetylide is essentially coplanar with the $SiPt_2$ plane.

The two phosphorus atoms differ considerably in their distances to the platinum atoms [Pt(1)–P(1) 2.226(3), Pt(2)–P(2) 2.325(3) Å] and in the angles PPtPt [P(1)Pt(1)Pt(2) 165.2(1), P(2)Pt(2)Pt(1) 148.0(1)°] and PPtSi[P(1)Pt(1)Si(1) 107.5(1), P(2)Pt(2)Si(1) 160.0(1)°]. Although the two Pt–P bond lengths differ, the observed distances fall within the range previously observed, namely 2.267(9)—2.331(5).[19] That Pt(2)–P(2) is longer than Pt(1)–P(1) can be attributed to the steric effects around Pt(2) which is five-co-ordinate, and to the *trans* influence of silicon.[20] The arrangement of the ligands about this metal atom is noteworthy in that Pt(2) has a surprisingly low root-mean-square deviation of 0.04 Å from the least-squares plane through the atoms Pt(1), P(2), Si(1), C(1), C(3), and Pt(2). Co-ordination around Pt(1) is effectively four, and the ligands are essentially coplanar with the metal atom, but they are not at the corners of a square. All the cyclohexyl groups are in a chair conformation.

Establishment of the molecular structure of complex (8) allows the spectroscopic properties of (8)—(10) to be understood. Thus the i.r. bands near 2 100 cm^{-1} can be assigned to the σ-bonded terminal acetylide groups, and the band of each complex near 1 960 cm^{-1} is due to the bridging acetylide ligand, the decrease in frequency being due to metal co-ordination. The n.m.r. spectra are also explicable as a result of the *X*-ray crystallographic study. Thus the observation of two ^{31}P resonance signals is readily understood. Moreover, the relative values of *J*(PtP) deduced from the spectra accord with the structure found for (8). In the latter, P(1) is essentially *trans* to Pt(2)[P(1)Pt(1)Pt(2) 165.2(1)°] whereas P(2) is *trans* with respect to the bridging silicon [P(2)Pt(2)Si 160.0(1)°]. Thus it would be anticipated that P(1) would experience a large coupling to both Pt(1) and Pt(2) whilst the corresponding values for P(2) would be considerably smaller due to the large *trans* influence of silicon.[20] Also the two-bond coupling *J*[P(2)Pt(1)] would be small as a result of the considerable deviation of angle P(2)Pt(2)Pt(1) [148.0(1)°] from linearity. It is reasonable, therefore, to assign the ^{31}P

TABLE 4

Some least-squares planes,* distances (Å) of atoms from planes being given in square brackets

Plane (i): Pt(1), Pt(2), Si(1)

$$-9.3863x + 5.3995y + 11.4271z = 1.9182$$

[P(1) −0.161, P(2) 0.126, C(1) −0.032, C(3) 0.181, C(4) 0.345]

Plane (ii): Si(1), C(5), C(6)

$$4.8110x + 23.4548y + 2.4439z = 7.6225$$

Plane (iii): C(21), C(22), C(23), C(24), C(25), C(26)

$$-10.3218x + 9.0691y + 8.6792z = 0.8814$$

[C(21) 0.004, C(22) −0.004, C(23) 0.0006, C(24) 0.003, C(25) −0.002, C(26) −0.001, C(2) 0.065, C(1) 0.24]

Plane (iv): C(41), C(42), C(43), C(44), C(45), C(46)

$$2.7209x + 11.3046y + 13.2293z = 6.3914$$

[C(41) −0.012, C(42) 0.013, C(43) −0.007, C(44) −0.0002, C(45) 0.001, C(46) 0.005, C(4) 0.068, C(3) −0.097]

Plane (v): Pt(1), Pt(2), Si(1), P(2), C(1), C(3)

$$-9.0374x + 4.9256y + 11.9601z = 2.1137$$

[Pt(1) −0.047, Pt(2) −0.055, Si(1) 0.046, P(2) 0.004, C(1) −0.002, C(3) 0.053, P(1) −0.175, C(2) 0.151, C(4) 0.177]

Plane (vi): Pt(1), Pt(2), Si(1), C(3), C(4)

$$-8.9388x + 4.0990y + 12.2050z = 2.0420$$

[Pt(1) −0.096, Pt(2) −0.044, Si(1) 0.080, C(3) −0.009, C(4) 0.070, P(1) −0.254, P(2) 0.021, C(1) 0.082]

Angles (°) between least-squares planes

	(ii)	(iii)	(iv)	(v)	(vi)
(i)	88.6	14.1	62.0	2.9	4.7
(ii)		85.3	48.9	88.4	89.7
(iii)			69.5	16.9	18.8
(iv)				60.0	59.8
(v)					2.1

* *x*, *y*, *z* are fractional crystal co-ordinates.

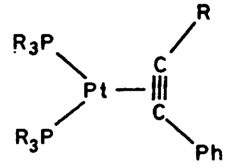
resonance in the spectrum of (8) at −55.0 p.p.m., and the corresponding signals in the spectra of (9) and (10) at −54.5 and −61.0 p.p.m., respectively, to the phosphorus nucleus [P(1)] bonded to the Pt atom in formal oxidation state II.

It may also be noted that in the ^{31}P spectrum of (9) it is the resonance at −43.4 p.p.m. which has the larger *J*(SiP) value (see above). This is also to be expected since this signal is due to the phosphorus bonded to the platinum in formal oxidation state IV with a *trans*-$Bu^t_2MeP–Pt–Si$ arrangement.

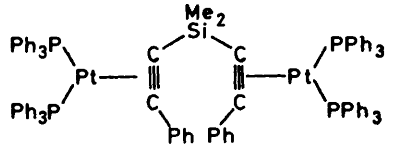
It is interesting that the titanium compound (1) and the silicon compound $[Si(C{\equiv}CPh)_2Me_2]$ apparently behave so differently towards $[Pt(C_2H_4)_2(PR_3)]$ [PR_3 = $P(C_6H_{11})_3$ or PPr^i_2Ph] in terms of the products produced. It is possible that, with dimethylbis(phenylethynyl)silane, chelate complexes analogous to (3) and (7) are initially formed, but these are then attacked by a second molecule of $[Pt(C_2H_4)_2(PR_3)]$ with Pt–Pt bond formation and concomitant rupture of the $Si–C_2Ph$ linkages. In other work [7] it has been shown that an acetylenic group can bridge two platinum atoms, so that an intermediate $[Pt\{\eta\text{-}(PhC{\equiv}C)_2SiMe_2\}(PR_3)]$ could attach a second $Pt(PR_3)$ moiety *via* C–C p_π–p_π bonds orthogonal to those used to co-ordinate the metal atom already present. Perhaps the two cyclopentadienyl ligands present in (3)—(7) sterically prevent co-ordination of a second $Pt(PR_3)$ moiety as a prelude to formation of structures similar to (8)—(10) with a $\mu\text{-}Ti(\eta\text{-}C_5H_5)_2$ group.

In contrast to the reactions of $[Pt(C_2H_4)_2(PR_3)]$ [$PR_3 = P(C_6H_{11})_3$, $PMeBu^t_2$, or PPr^i_2Ph] with $[Si(C{\equiv}CPh)_2Me_2]$, the compound $[Pt(C_2H_4)_2(PPh_3)]$ affords a yellow solid insoluble in benzene, chloroform, or diethyl ether, which analysed for the composition $[Pt_2\{Si(C{\equiv}CPh)_2Me_2\}(PPh_3)_2]$ (11). The insolubility of (11) prevented n.m.r. studies. In the i.r. spectrum a band at 1 842 cm^{-1} indicated the presence of a co-ordinated acetylene group. Complexes from $[Pt(C_2H_4)(PPh_3)_2]$ and dimethylbis(phenylethynyl)silane were more amenable to study. In 1 : 1 mol ratio these reactants gave $[Pt\{\eta\text{-}(PhC{\equiv}C)Si(C_2Ph)Me_2\}(PPh_3)_2]$ (12) with characteristic $\nu_{max.}(C{\equiv}C)$ bands at 2 164 and 1 712 cm^{-1}. In the spectrum of $[Si(C{\equiv}CPh)_2Me_2]$ the C≡C stretch occurs at 2 159 cm^{-1}. The ^{31}P n.m.r. spectrum of (12) was of the AB type (Table 1) in accord with the structure proposed.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ and $[Si(C{\equiv}Ph)_2Me_2]$ in a 2 : 1 mol ratio afforded the diplatinum compound (13) [$\nu_{max.}(C{\equiv}C)$ at 1 750 and 1 724 cm^{-1}]. Cleavage of $Si–C_2Ph$ linkages did not occur in these reactions, and the products (12) and (13) are analogous to those obtained from reactions of the platinum compound with 1,4-diphenylbuta-1,3-diyne and hexa-2,4-diyne.[13]



(12) $PR_3 = PPh_3$, R = $Si(C{\equiv}CPh)Me_2$
(14) $PR_3 = PMePh_2$, R = $Si(C{\equiv}CPh)Me_2$



(13)

The bis(ethylene)platinum complex $[Pt(C_2H_4)_2(PMePh_2)]$ also reacted with $[Si(C{\equiv}CPh)_2Me_2]$ to give a monoplatinum compound. Surprisingly the product was the bis(tertiary phosphine)platinum complex (14). Evidently side reactions occur, and (14) was formed in only *ca.* 10% yield.

The ^{31}P n.m.r. spectra of (13) and (14) both showed only one sharp resonance. However, the pattern of the ^{195}Pt satellite peaks confirmed the expected AB nature of the spectra, in which evidently the non-equivalent phosphorus nuclei have coincidental chemical shifts.

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 in Schlenk tubes under a dry

TABLE 5

Platinum–titanium and –silicon phenylethynyl compounds

	Compound	M.p. (θ_c/°C) [b]	Yield (%)	Analyses (%) [a]	
				C	H
(3)	$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}\{P(C_6H_{11})_3\}]$	222—223	80	61.8 (61.7)	6.4 (6.2)
(4)	$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PMe_2Ph)]$	>180	47	57.3 (57.2)	4.4 (4.4)
(5)	$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PMePh_2)]$	168	53	58.3 (60.4)	4.4 (4.3)
(6)	$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PPh_3)]$	>150	74	63.3 (62.9)	4.6 (4.2)
(7)	$[Pt\{\eta\text{-}(PhC{\equiv}C)_2Ti(\eta\text{-}C_5H_5)_2\}(PPr^i_2P)]$	>160	78	59.5 (59.3)	5.2 (5.1)
(8)	$[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma : 1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)\{P(C_6H_{11})_3\}_2]$	183—184	58	53.8 (53.5)	7.0 (6.8)
(9)	$[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma : 1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)(PMeBu^t_2)_2]$	153—155	23	44.5 (44.5)	5.9 (6.0)
(10)	$[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma : 1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)(PPr^i_2Ph)_2]$	142—145	21	48.6 (48.5)	5.6 (5.2)
(11)	$[Pt_2\{Si(C{\equiv}CPh)_2Me_2\}(PPh_3)_2]$	176	30	55.2 (55.2)	4.3 (3.9)
(12)	$[Pt\{\eta\text{-}(PhC{\equiv}C)Si(C_2Ph)Me_2\}(PPh_3)_2]$	130—132	80	65.6 (66.2)	5.1 (4.3)
(13)	$[Pt_2\{\eta\text{-}(PhC{\equiv}C)_2SiMe_2\}(PPh_3)_4]$	92—95	70	64.2 (63.6)	5.0 (4.5)
(14)	$[Pt\{\eta\text{-}(PhC{\equiv}C)Si(C_2Ph)Me_2\}(PMePh_2)_2]$		11	60.6 (61.7)	5.1 (4.9)

[a] Calculated values are given in parentheses. [b] With decomposition.

oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction having a b.p. 40—60 °C. The complexes $[Pt(C_2H_4)_2(PR_3)]$ were prepared using procedures described elsewhere.[8,21] Analytical data for the new compounds are given in Table 5.

Preparation of the Platinum–Titanium Complexes $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}(PR_3)]$.—(*a*) $PR_3 = P(cyclo\text{-}C_6H_{11})_3$. Solid $[Ti(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ (0.19 g, 0.5 mmol) was added to $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.26 g, 0.5 mmol) suspended in diethyl ether (15 cm^3) in a Schlenk tube. The mixture precipitated an orange solid, which was washed with diethyl ether and dried *in vacuo* to give *crystals* of $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}\{P(C_6H_{11})_3\}]$ (3). $\nu_{max.}$ at 3 050w(br), 1 814m(C≡C), 1 591m, 1 482m, 1 296w, 1 270w, 1 224w, 1 196w, 1 172w, 1 125w, 1 113w, 1 066w, 1 023w, 1 015w, 1 005w, 920w, 898w, 851w, 808vs, 762s, 740w, 733w, 700s, 586w, 534w, 515w, 506(sh), and 490w cm^{-1}.

(*b*) $PR_3 = PMe_2Ph$. Bis(cyclo-octa-1,5-diene)platinum [21,22] (0.38 g, 0.9 mmol) was added to 15 cm^3 of ethylene-saturated light petroleum and treated with PMe_2Ph (1 mmol). Solvent was removed *in vacuo* to give a brown residue which was dissolved in diethyl ether (15 cm^3), and filtered through an alumina pad (2 × 0.75 cm^2). The resulting solution was treated with $[Ti(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ (0.38 g, 1 mmol) to give (5 min) a yellow-orange solid. The solvent was removed, and the solid washed with diethyl ether and recrystallised from dichloromethane–diethyl ether to give *crystals* of $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}(PMe_2Ph)]$ (4). $\nu_{max.}$ at 3 070w(br), 1 838w, 1 800m(C≡C), 1 591m, 1 482s, 1 436m, 1 304w, 1 281w, 1 275w, 1 203vw, 1 186vw, 1 155vw, 1 106w, 1 069m, 1 028m, 1 016m, 953m, 920(sh), 916s, 846m, 832w, 822s, 813vs, 801s, 766s, 761s, 747s, 736s, 718w, 705s, 697s, 596w, 582w, 538w, 486w, and 443m cm^{-1}.

(*c*) $PR_3 = PMePh_2$. The complex $[Pt(C_2H_4)_2(PMePh_2)]$ (0.23 g, 0.5 mmol) in diethyl ether (10 cm^3) was treated with $[Ti(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ (0.19 g, 0.5 mmol) with stirring for 15 min. The mixture was filtered through an alumina pad, solvent was removed *in vacuo*, and the residue recrystallised from dichloromethane–light petroleum to give orange *crystals* of $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}(PMePh_2)]$ (5). $\nu_{max.}$ at 3 050w(br), 1 842w(br), 1 800m(C≡C), 1 590m, 1 482s, 1 434s, 1 304w, 1 260w(br), 1 180w, 1 155w, 1 100m, 1 067m, 1 027m, 1 013m, 907m, 895s, 848m, 816vs, 804vs, 762s, 750s, 744(sh), 730m, 700s, 624w, 583w, 540w, 520w, 507s, 498s, 457m, and 437m cm^{-1}.

(*d*) $PR_3 = PPh_3$. Similarly, $[Pt(C_2H_4)_2(PPh_3)]$ (0.51 g, 1 mmol) in diethyl ether (25 cm^3) treated with $[Ti(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ (0.38 g, 1 mmol) gave yellow-orange *crystals* of $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}(PPh_3)]$ (6). $\nu_{max.}$ at 3 065w, 1 819w, 1 792m(C≡C), 1 591m, 1 567w, 1 485s, 1 445s, 1 264w, 1 187w, 1 175w, 1 157w, 1 097w, 1 069w, 1 026m, 1 018m, 1 000w, 908w, 893w, 817s, 807vs, 763s, 758s, 740m, 705s, 699s, 631w, 602w, 588w, 543s, 533w, 526w, 516m, and 503m cm^{-1}.

(*e*) $PR_3 = PPr^i{}_2Ph$. The complex $[Pt(C_2H_4)_2(PPr^i{}_2Ph)]$ (0.45 g, 1 mmol) and $[Ti(C\equiv CPh)_2(\eta\text{-}C_5H_5)_2]$ (0.38 g, 1 mmol) in diethyl ether (15 cm^3) yielded orange *crystals* of $[Pt\{\eta\text{-}(PhC\equiv C)_2Ti(\eta\text{-}C_5H_5)_2\}(PPr^i{}_2Ph)]$ (7). $\nu_{max.}$ at 3 040w, 1 838w, 1 824m(C≡C), 1 595m, 1 438s, 1 435s, 1 252w, 1 245w, 1 142w, 1 072w, 1 028m, 1 019m, 916w, 892w, 882w, 846w, 822m, 808vs, 761s, 746m, 704s, 697s, 672m, 637m, 578w, 536m, 510m, 485w, and 434w cm^{-1}.

Preparation of Platinum–Silicon Complexes. Reactions of Dimethylbis(phenylethynyl)silane.—(*a*) *With* $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$. The compound $[Si(C\equiv CPh)_2Me_2]$ (0.14 g, 0.54 mmol) was added to $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.26 g, 0.48 mmol) in light petroleum (10 cm^3) at room temperature. The initial suspension turned orange in colour and a cream solid precipitated (2 h). Solvent was removed with a syringe, and the solid washed with light petroleum. A second crop of *crystals* of $[Pt_2(\sigma\text{-}C\equiv CPh)\{\mu\text{-}(1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C\equiv CPh)\}(\mu\text{-}SiMe_2)\{P(C_6H_{11})_3\}_2]$ (8) was obtained from the light petroleum washings after 2 d. $\nu_{max.}$ at 3 050w(br), 2 100s and 1 945s(C≡C), 1 592m, 1 585m, 1 478m, 1 399w, 1 295w, 1 266w, 1 232m, 1 226m, 1 205w, 1 176m, 1 127w, 1 108w, 1 075w, 1 048w, 1 024w, 1 003m, 916w, 898w, 887w, 850m, 837m, 817w, 757vs, 740m, 691m, 671w, 553w, 524m, 493w, and 474w cm^{-1}.

(*b*) *With* $[Pt(C_2H_4)_2(PMeBu^t{}_2)]$. The compound $[Si(C\equiv CPh)_2Me_2]$ (0.26, 1 mmol) was added to $[Pt(C_2H_4)_2(PMeBu^t{}_2)]$ (0.38 g, 1 mmol) in light petroleum (10 cm^3) at room temperature, and the mixture stirred for 1 h. Solvent was removed *in vacuo* and the residue dissolved in hexane (1 cm^3) from which grew cream *crystals* of $[Pt_2(\sigma\text{-}C\equiv CPh)\{\mu\text{-}(1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C\equiv CPh)\}(\mu\text{-}SiMe_2)(PMeBu^t{}_2)_2]$ (9). $\nu_{max.}$ at 3 070w, 2 104m, and 1 965m(br)(C≡C), 1 590m, 1 490s, 1 290w, 1 236m, 1 230m, 1 203m, 1 186m, 1 070w, 1 024m, 943w, 905m, 886s, 878m(sh), 846m, 818m, 770s, 762s, 722m, 698s, 674w, 602w, 582m, 554w, 530w, 492w, and 474m cm^{-1}.

(*c*) *With* $[Pt(C_2H_4)_2(PPr^i{}_2Ph)]$. Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was added to an ethylene-saturated solution of light petroleum (10 cm^3) at 0 °C, and then the solution was treated with $PPr^i{}_2Ph$ (0.19 g, 1 mmol). The mixture was reacted with $[Si(C\equiv CPh)_2Me_2]$ (0.26 g, 1 mmol) for 1 h, solvent was removed *in vacuo*, and the residue was, after pumping (2 h), dissolved in diethyl ether (2 cm^3) affording cream *crystals*, washed with light petroleum–diethyl ether, of $[Pt_2(\sigma\text{-}C\equiv CPh)\{\mu\text{-}(1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C\equiv CPh)\}(\mu\text{-}SiMe_2)(PPr^i{}_2Ph)_2]$ (10). $\nu_{max.}$ at 3 050w(br), 2 108s, and 1 947m(br)(C≡C), 1 591m, 1 484s, 1 435s, 1 245m, 1 238m, 1 227m, 1 100w(br), 1 076w, 1 065w, 1 034w, 1 025m, 1 000w, 883w, 844w, 768m, 760vs, 745s, 695s, 673s, 638m, 554w, 536s, 524s, and 483m cm^{-1}

(*d*) *With* $[Pt(C_2H_4)_2(PPh_3)]$. The compound $[Pt(C_2H_4)_2(PPh_3)]$ (0.51 g, 1 mmol) suspended in diethyl ether (20 cm^3) at −50 °C was treated with $[Si(C\equiv CPh)_2Me_2]$ (0.26 g, 1 mmol). The mixture was warmed to room temperature and more $[Si(C\equiv CPh)_2Me_2]$ (1 mmol) was added, affording yellow *microcrystals*, dried *in vacuo* after washing with diethyl ether, of $[Pt_2\{Si(C\equiv CPh)_2Me_2\}(PPh_3)_2]$ (11). This complex was insoluble in benzene, diethyl ether, chloroform, or light petroleum. $\nu_{max.}$ at 3 045m, 1 842s(C≡C), 1 587m, 1 567w, 1 535m, 1 478s, 1 435s, 1 237m, 1 179m, 1 154m, 1 115w, 1 093s, 1 067w, 1 025m, 996w, 910w, 892m, 860m, 826m, 806m, 772m, 760m, 754m, 747s, 743s, 695vs, 630w(br), 582s, and 540s cm^{-1}.

(*e*) *With* $[Pt(C_2H_4)(PPh_3)_2]$. Ethylenebis(triphenylphosphine)platinum (0.77 g, 1 mmol) suspended in diethyl ether (15 cm^3) was treated with $[Si(C\equiv CPh)_2Me_2]$ (0.26 g, 1 mmol) at room temperature for 0.5 h. The yellow mixture was filtered through an alumina pad, and the solvent removed *in vacuo*. The resulting oil was dissolved in diethyl ether (5 cm^3), and light petroleum (10 cm^3) was added. After 15 h the solution afforded white *crystals*, washed with hexane, of $[Pt\{\eta\text{-}PhC\equiv CSi(C_2Ph)Me_2\}(PPh_3)_2]$ (12). $\nu_{max.}$ at 3 050w, 2 164m, 1 750w(br), and 1 712m(br)(C≡C), 1 588w, 1 568w, 1 482s, 1 436s, 1 247m, 1 220w, 1 195w, 1 182w, 1 159w, 1 116w, 1 094s, 1 068w, 1 027m, 1 000w, 908w, 882s, 848s, 834s, 811m, 785s, 766(sh), 758s, 744s, 706s(sh), 696s, 666w, 596w, 543s, 527s, 520s, 513s, 504s, 458w, 440w, and 423m cm^{-1}.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ (1 mmol) in a mixture of diethyl ether (15 cm^3) and toluene (5 cm^3) at reflux with $[Si(C{\equiv}CPh)_2Me_2]$ (0.13 g, 0.5 mmol) for 0.5 h afforded white *crystals* (from diethyl ether) of the diplatinum complex $[Pt_2\{\eta\text{-}(PhC{\equiv}C)_2SiMe_2\}(PPh_3)_4]$ (13). $\nu_{max.}$ at 3 040m, 1 750m, and 1 724m(br)(C≡C), 1 586w, 1 480s, 1 434s, 1 337w, 1 304w, 1 278w, 1 252w, 1 214w, 1 092s, 1 065w, 1 024w, 996w, 873m, 808m, 774w, 762w, 750m, 742m, 730w, 694vs, 539s, 521s, 508s, and 417m cm^{-1}.

(*f*) *With* $[Pt(C_2H_4)_2(PMePh_2)]$. The compound $[Pt(C_2H_4)_2(PMePh_2)]$ (0.44 g, 1 mmol) in diethyl ether (15 cm^3) at −50 °C was treated with $[Si(C{\equiv}CPh)_2Me_2]$ (0.26 g, 1 mmol) for 0.5 h. The mixture was warmed to room temperature and stirred overnight. After removal of solvent, the solid was extracted with diethyl ether (75 cm^3) and filtered twice through alumina (2 × 5 cm). The diethyl ether was removed *in vacuo* and the resulting oil dissolved in light petroleum–diethyl ether (1 : 1). White *crystals* of the complex $[Pt\{\eta\text{-}(PhC{\equiv}C)Si(C_2Ph)Me_2\}(PMePh_2)_2]$ (14) were obtained, washed with diethyl ether, and dried *in vacuo*. $\nu_{max.}$ at 3 070w, 3 050w, 2 158m, 1 783(sh), and 1 710s(C≡C), 1 588m, 1 484s, 1 438s, 1 305w, 1 282w, 1 241m, 1 217w, 1 192w, 1 155w, 1 098m, 1 066w, 1 025w, 997w, 913w, 893vs, 886s, 880s, 845s, 829m, 809m, 781m, 769s, 762s, 750s, 745s, 729s, 703vs, and 660w cm^{-1}.

X-*Ray Data Collection and Structure Determination*.—A pale yellow crystal of $[Pt_2(\sigma\text{-}C{\equiv}CPh)\{\mu\text{-}(1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C{\equiv}CPh)\}(\mu\text{-}SiMe_2)\{P(C_6H_{11})_3\}_2]$ (8) of dimensions *ca.* 0.05 × 0.05 × 0.18 mm was cut from a large crystal of rectangular shape, and diffracted intensities were collected at 200 K for $2.9 \leqslant 2\theta \leqslant 50°$ on a Syntex $P2_1$ four-circle diffractometer, according to methods described earlier.[23] Of the total 9 400, there were 5 131 unique reflections having $|F| \geqslant 4\sigma(F)$ and only these were used in solution and refinement of the structure. Three check reflections were monitored once every batch of 40. Corrections were applied for Lorentz, polarisation, and *X*-ray absorption effects. All computations were carried out with the SHELX system of programs.[24]

Crystal data. $C_{54}H_{82}P_2Pt_2Si$, $M = 1\,211.5$, Monoclinic, $a = 12.44(1)$, $b = 26.12(4)$, $c = 15.832(8)$ Å, $\beta = 97.99(6)°$, $U = 5\,094(10)$ Å^3, $D_m = 1.52$ (flotation), $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 2\,424$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 53.69$ cm^{-1}, space group $P2_1/c$ (no. 14).

The structure was solved by the heavy-atom method and all atoms (except H) were located by successive electron-density difference synthesis. The structure was refined by full-matrix least squares with anisotropic thermal parameters for the Pt, P, Si, acetylenic carbon, and methyl carbons of the $SiMe_2$ group. During refinement C–C bond lengths in the phenyl rings were restricted to 1.395 ± 0.01 Å. Hydrogen atoms were included at calculated positions (C–H 1.08 Å). Only common temperature factors for sets of chemically different hydrogen atoms were refined (Appendix B). Refinement converged at R 0.053 (R' 0.041). A weighting scheme of the form $w = 1.542/[\sigma^2(F) + 0.000\,1F^2]$, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >1.1 or <-0.9 e Å^{-3}, except in the region of the platinum atoms ($+1.4$ e Å^{-3}). Scattering factors were from ref. 25 for C, P, and Si, ref. 26 for H, and ref. 27 for Pt. Atomic positional parameters are in Table 2, interatomic distances and angles in Table 3, and some least-squares planes in Table 4. Observed and calculated structure factors, all thermal parameters, and positional parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22603 (32 pp.).†

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.