Alkyne Complexes of Platinum. Part 5.[1] Di- and Tri-platinum Complexes with Bridging Trimethylsilyl-substituted Alkyne Ligands; Crystal Structure of $[Pt_2(\mu\text{-}PhC_2SiMe_3)(C_8H_{12})_2]$ †

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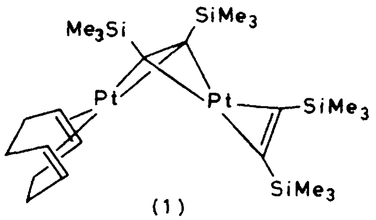
Bis(trimethylsilyl)acetylene in excess reacts with $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) to give the diplatinum complex $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(Me_3SiC_2SiMe_3)(cod)]$, whereas $[Pt(C_2H_4)_3]$ and the alkyne afford $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(Me_3SiC_2SiMe_3)_2]$. Reactions of $[Pt(cod)_2]$ with the alkynes $RC{\equiv}CSiMe_3$ (R = $SiMe_3$, $SiMe_2Bu^t$, CF_3, or Ph) in 2 : 1 mol ratio, or excess of alkyne in the case of $CF_3C{\equiv}CSiMe_3$, yields the diplatinum complexes $[Pt_2(\mu\text{-}RC_2SiMe_3)(cod)_2]$. The nickel compounds $[Ni_2(\mu\text{-}RC_2SiMe_3)(cod)_2]$ (R = $SiMe_3$ or Ph) have also been prepared. Reaction of $PhC{\equiv}CSiMe_3$ with $[Pt(cod)_2]$ in 1 : 1 mol ratio gives the triplatinum complex $[Pt_3(\mu\text{-}PhC_2SiMe_3)_2(cod)_2]$, which like $[Pt_2(\mu\text{-}PhC_2SiMe_3)(cod)_2]$ undergoes dynamic behaviour in solution, as revealed by variable-temperature n.m.r. studies. An *X*-ray crystallographic study on the latter was carried out. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 14.93(1)$, $b = 10.38(1)$, $c = 17.463(8)$ Å, $\beta = 112.79(6)°$. The structure has been refined to R 0.038 (R' 0.038) for 5 464 unique reflections to $2\theta \leqslant 60°$ (Mo-K_α, *X*-radiation) collected at 200 K. The PhC_2SiMe_3 ligand transversely bridges the Pt ··· Pt vector (2.914 Å) such that the dihedral angle between the two planes formed by the two Pt–μ–C_2 units is 97°. This, together with the long metal–metal distance and the essentially planar geometry about each platinum atom, is taken to imply little or no direct Pt–Pt bonding, with the two halves of the molecule held together by orthogonal π orbitals of the shared $PhC{\equiv}CSiMe_3$ ligand.

We have previously shown that reactions of $[Pt(C_2H_4)_3]$ or $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) with an excess of a variety of alkynes afford bis(alkyne)platinum complexes $[Pt(RC_2R')_2]$ [R = R' = Me, Et, Bu^t, Ph, C_6H_4Me-4, C_6H_4OMe-4, CH_2SiMe_3, or $C(OH)Me_2$; R = Bu^t, R' = Me or $SiMe_3$; R = Ph, R' = Me or $SiMe_3$].[2] Moreover, the alkyne ligands in these monoplatinum compounds are susceptible to attack by $Pt(PR_3)_2$ species, derived from $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt_2(\mu\text{-}cod)(PEt_3)_4]$, yielding di- or tri-platinum complexes, *e.g.* $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PPh_3)_2]$ or $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$.[1] During a detailed study of the i.r. and ^{13}C n.m.r. spectra of the $[Pt(RC_2R')_2]$ complexes it was observed that when R' = $SiMe_3$ the data were consistent with the trimethylsilyl group acting as an electron-withdrawing substituent. This property prompted a more comprehensive examination of the reactions of trimethylsilyl-substituted alkynes with $[Pt(cod)_2]$ and with $[Pt(C_2H_4)_3]$ in the expectation that further examples of mono-, di-, and tri-platinum alkyne complexes would be obtained.

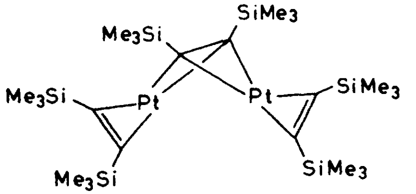
RESULTS AND DISCUSSION

Excess of bis(trimethylsilyl)acetylene reacts at room temperature with $[Pt(cod)_2]$ in light petroleum to give not the expected[2] bis(alkyne)monoplatinum complex $[Pt(Me_3SiC_2SiMe_3)_2]$ but the dinuclear platinum compound $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(Me_3SiC_2SiMe_3)(cod)]$ (1), an analogue of the diphenylacetylene complex $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PMe_3)_2]$.[1,3]

The structure of the orange-yellow crystalline compound (1) was established by its spectroscopic properties. In the i.r. spectrum a band at 1 817 cm^{-1} is characteristic of a terminally bound $Me_3SiC{\equiv}CSiMe_3$ ligand, and a weak band at 1 517 cm^{-1} may be attributed to the C–C stretch of the bridging ligand.[1,2] The ^1H n.m.r. spectrum showed signals for the non-equivalent $SiMe_3$ groups at τ 9.50 and 9.58 of equal intensity. The ^{13}C n.m.r. spectrum was particularly informative since



(1)



(2)

resonances due to the acetylenic carbon atoms could be observed. Two signals at 143.9 and 142.4 p.p.m., with J(PtC) 294 and 218 Hz respectively, can be assigned to the terminally bound alkyne ligand. The appearance of two resonances is to be expected because the *pseudo*-tetrahedral symmetry about the platinum atom Pt^b (Figure 1) renders C^β and C^γ non-equivalent. A signal centred at 106.8 p.p.m., with values of $^1J(Pt^aC^\alpha)$ and $^1J(Pt^bC^\alpha)$ of 326 and 219 Hz respectively, can be attributed to the two bridging acetylenic carbon atoms. The magnitudes of these couplings eliminate an acetylenic

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† Bis(η-cyclo-octa-1,5-diene)-μ-phenyl(trimethylsilyl)acetylene-diplatinum.

bonding mode of the type $\overline{\mathrm{PtC(SiMe_3)=C(SiMe_3)Pt}}$ in which the alkyne lies parallel to the metal–metal vector. Assignment of the satellite peaks to Pt^a and Pt^b is based on the observed influence of the cod ligand on ^{195}Pt–^{13}C couplings noted previously.[2]

Failure to isolate the compound [Pt(Me$_3$SiC$_2$SiMe$_3$)$_2$] by treating [Pt(cod)$_2$] with an excess of Me$_3$SiC≡CSiMe$_3$ prompted a study of the reaction of this alkyne with [Pt(C$_2$H$_4$)$_3$]. The product (2) was a yellow oil which slowly crystallised under high vacuum. Bands in the i.r. spectrum at 1 816 and 1 563 cm^{-1} suggested the presence of both terminal and bridging acetylene ligands. In accord with this observation, microanalysis and n.m.r. studies established the new compound as a diplatinum complex. The ^{1}H n.m.r. spectrum showed two resonances for the SiMe$_3$ groups at τ 9.48 [J(PtH) 1 Hz] and 9.58 of relative intensity 1 : 2, allowing the former signal to be assigned to the bridging ligand, and the latter to the terminal. The observed chemical shifts of the protons in (2) allows assignment of the signals in the spectrum of (1) at τ 9.50 and 9.58 to the bridging and terminal alkyne groups, respectively.

The observed pattern of resonance in the ^{13}C n.m.r. spectrum of (2) was especially informative concerning the structure of the molecule. The bridging alkyne ligand could adopt two configurations, either lying perpendicular to the platinum–platinum vector as shown, or lying parallel to a metal–metal bond in a diplatinacyclobutene structure $\overline{\mathrm{PtC(SiMe_3)=C(SiMe_3)Pt}}$. Both configurations have been observed in diplatinum complexes.[1,4,5] A μ-η^2-alkyne bonding mode would have a 1 : 8 : 18 : 8 : 1 ^{13}C resonance pattern arising from the probabilities of molecules being present containing zero, one, or two ^{195}Pt nuclei. In contrast a μ-η^1-alkyne bridged structure would be expected to exhibit a 1 : 1 : 4 : 1 : 1 resonance pattern, corresponding to the probabilities of the presence of diplatinum species containing either zero or one ^{195}Pt nucleus, overlapping a much smaller more complex AXX′ signal due to molecules with two ^{195}Pt nuclei. In (2) the resonance for the bridging acetylenic carbon C$^\alpha$ (Figure 1) occurs at δ 117.7 p.p.m., but unfortunately under the conditions of the measurement it appears with only one set of satellites [^1J(PtC) 210 Hz]. However, their magnitude and the absence of a further set of satellites of equal intensity indicated a 1 : 8 : 18 : 8 : 1 pattern to be present, with the weak outer signals being unobserved. This implies the presence of a transversely bridging alkyne in (2). The signals for the acetylenic terminally bound carbons C$^\beta$ and C$^\gamma$ were measured at 143.0 [^1J(PtC) 293] and 142.8 p.p.m. [^1J(PtC) 259 Hz], respectively.

Addition of one equivalent of Me$_3$SiC≡CSiMe$_3$ to two equivalents of [Pt(cod)$_2$] suspended in light petroleum afforded yellow microcrystals of (3), a platinum compound similar to the dinickel complex [Ni$_2$(μ-PhC$_2$Ph)-(cod)$_2$].[6] The i.r. spectrum of (3) revealed no terminal alkyne ligands to be present, but a band at 1 508 cm^{-1} was possibly attributable to the bridging alkyne. The

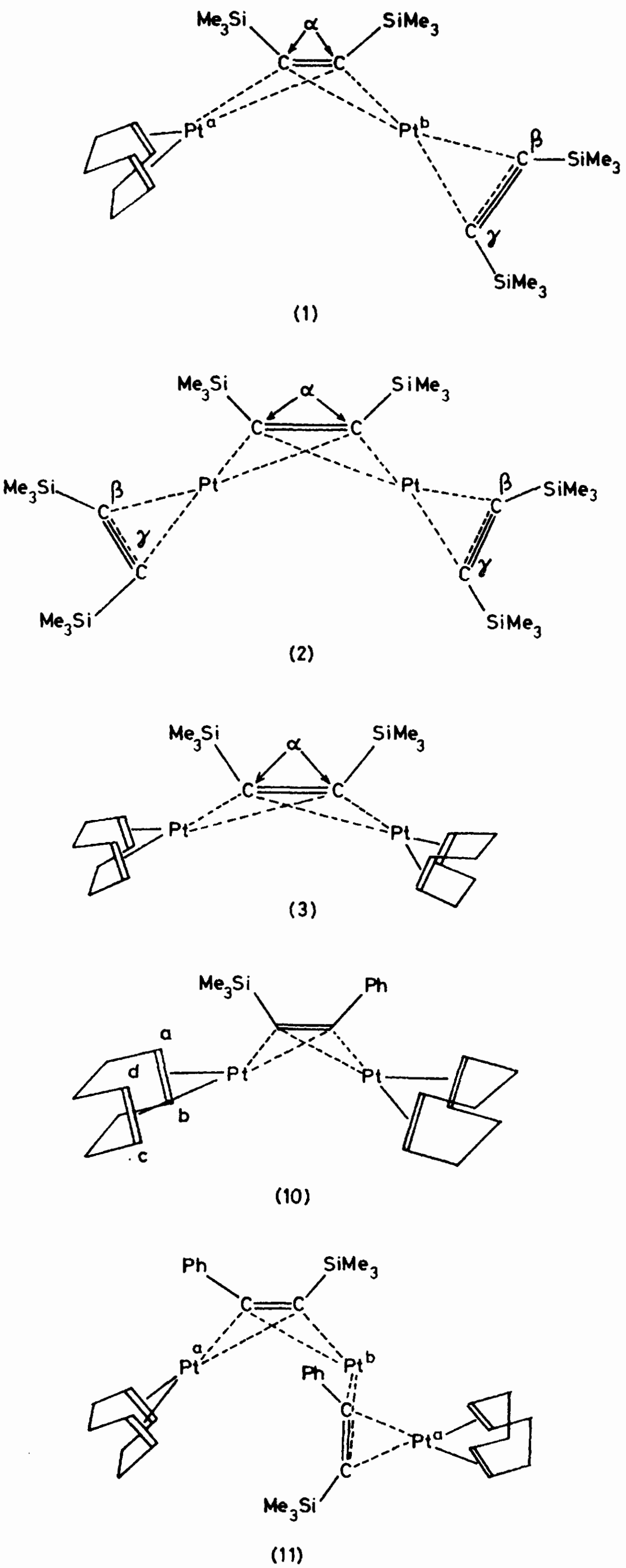


FIGURE 1 Labelling scheme for carbon and platinum atoms in complexes (1), (2), (3), (10), and (11) for n.m.r. discussion (see text)

^{1}H n.m.r. spectrum showed the expected resonances with the anticipated relative intensities (see Experimental section), including the observation of two cod CH resonances {τ 4.73 [^2J(PtH) 74 Hz] and 5.43 [^2J(PtH) 46 Hz]}, in accord with the structure proposed. Definitive evidence for the structure came from the ^{13}C n.m.r. spectrum measured at −45 °C (Figure 2) where the C$^\alpha$ resonance at 84.4 p.p.m. [^1J(PtC) 329 Hz] is an excellent example of a 1 : 8 : 18 : 8 : 1 multiplet.

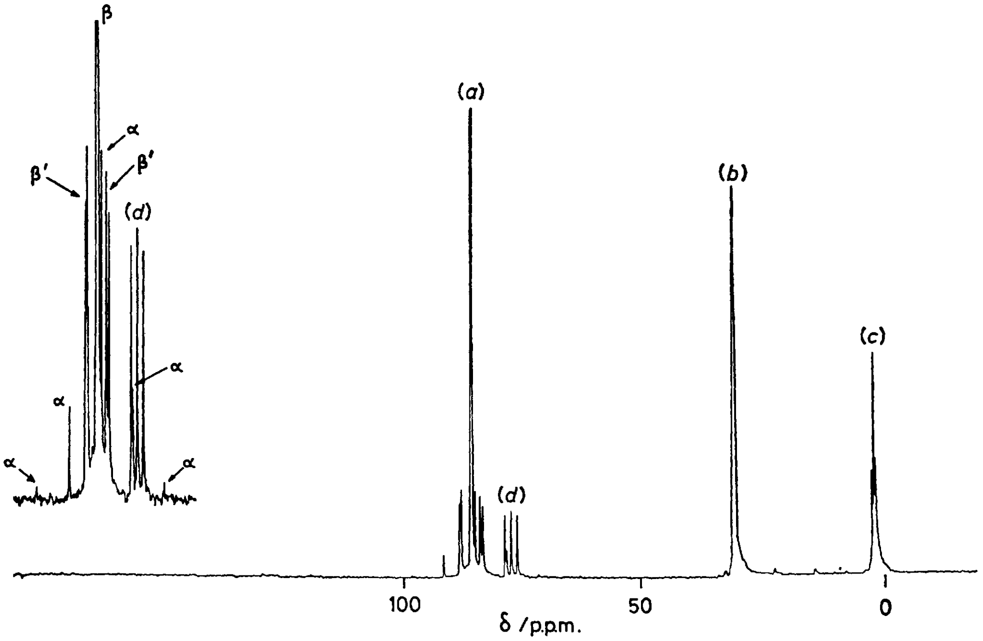
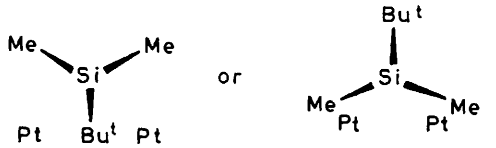


FIGURE 2 Carbon-13 n.m.r. spectrum of complex (3) at −45 °C. (*a*) Signals due to *C*H of cod and carbon atoms $Me_3SiC\equiv$, with their ^{195}Pt satellites; (*b*) *C*H$_2$ resonances of cod; (*c*) *C*H$_3$Si signal; (*d*) CDCl$_3$ solvent peaks. Inset: Peaks α, of relative intensity 1 : 8 : 18 : 8 : 1, are due to $Me_3SiC\equiv$ carbon nuclei. β is *C*H resonance, with β′ indicating ^{195}Pt satellites

Complexes (1)—(3) provide good demonstrations of species wherein two platinum atoms are held together by the orthogonal π orbitals of the bridging alkyne without the need to postulate a metal–metal bond, the metal atoms adopting 16-electron configurations. Moreover, it is interesting to compare the $J(^{195}Pt\text{-}^{13}CSiMe_3)$ values for the three compounds which show that these parameters depend on the ligand *trans* to the acetylenic carbons, and are virtually independent of the co-ordination at the other platinum centre. Thus in (1) there is a 326 Hz coupling of C$^\alpha$ (Figure 1) with the ^{195}Pt of the Pt(cod) group and a 219 Hz coupling with the ^{195}Pt of the Pt(η^2-$Me_3SiC_2SiMe_3$) group. In the symmetrically terminally substituted diplatinum compounds (2) and (3), ^1J(PtC$^\alpha$) is 210 and 329 Hz, respectively, these values comparing well with the respective couplings in (1).

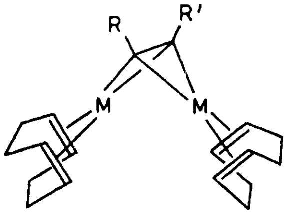
Complex (4) was prepared in an analogous manner to (3). Once again the ^{13}C n.m.r. spectrum proved very informative. Four *C*H(cod) signals were observed in the ^{13}C n.m.r. spectrum in accord with the proposed structure, and the expected two acetylenic carbon resonances were observed at δ 84.9 p.p.m. [*C*SiMe$_3$, ^1J(PtC) 316 Hz] and 82.6 [*C*SiMe$_2$Bu^t, ^1J(PtC) 327 Hz]. However, although the CSi*Me*$_3$ signal had the 1 : 8 : 18 : 8 : 1 platinum satellite pattern expected for the assumed structure, the Si(*C*H$_3$)$_2$Bu^t carbon had double platinum satellites (1 : 1 : 4 : 1 : 1). Measurement of the ^{195}Pt spectrum produced only a single resonance (δ = 619 p.p.m.), establishing that the two platinum nuclei are equivalent. The ^{195}Pt–Si(*C*H$_3$)$_2$Bu^t satellite pattern must therefore arise from restricted rotation of the SiMe$_2$Bu^t group around the acetylenic carbon–silicon bond. Since only one resonance is observed for the two methyl groups, these must be symmetrically disposed between the two platinums, as shown below.



Reaction of an excess of $Me_3SiC\equiv CCF_3$ with [Pt-(cod)$_2$] gave the diplatinum compound (5), which with excess of CNBu^t afforded [Pt$_2$(μ-$Me_3SiC_2CF_3$)(CNBu^t)$_4$] (6), both compounds giving ^{1}H and ^{19}F n.m.r. spectra (see Experimental section) in agreement with the structures proposed.

It has been suggested previously that alkyl substituted alkynes do not yield isolable bridged-alkyne dinickel compounds due to steric factors.[6] However, we have found that sterically demanding $Me_3SiC\equiv CSiMe_3$ reacts readily with [Ni(cod)$_2$] to afford a red dinickel complex (7) [$\nu_{max.}$ ($C\equiv C$) 1 526 cm^{-1}; ^{13}C n.m.r. δ (p.p.m.) 115.9 (*C*SiMe$_3$)]. For comparative purposes the complex [Ni_2(μ-PhC_2Ph)(cod)$_2$] (8), first synthesised by Muetterties and co-workers,[6] was prepared using diphenylacetylene ^{13}C-enriched at an acetylenic carbon atom. This species in its ^{13}C n.m.r. spectrum showed a resonance for *C*Ph at 106.7 p.p.m.

Reaction of PhC≡CSiMe$_3$ with [Ni(cod)$_2$] yields compound (9) [$\nu_{max.}$($C\equiv C$) 1 531 cm^{-1}]. From the ^{13}C n.m.r. spectrum the bridging-alkyne carbon atoms were identified at δ (p.p.m.) 119.9 (*C*Ph) and 101.1 (*C*SiMe$_3$), and the expected four resonances for the CH and CH_2 groups of the cod ligands were also clearly seen.



	M	R	R'
(3)	Pt	SiMe$_3$	SiMe$_3$
(4)	Pt	SiMe$_3$	SiMe$_2$Bu^t
(5)	Pt	SiMe$_3$	CF_3
(7)	Ni	SiMe$_3$	SiMe$_3$
(8)	Ni	Ph	Ph
(9)	Ni	SiMe$_3$	Ph
(10)	Pt	SiMe$_3$	Ph

Although [Pt(cod)$_2$] reacts with excess of PhC≡CSiMe$_3$ to form the bis(alkyne) complex [Pt(PhC$_2$SiMe$_3$)$_2$],[2] a synthetic approach similar to that used for the synthesis of compound (3) affords the analogous orange complex (10). A band in the i.r. spectrum at 1 504 cm^{-1} was attributed to a modified acetylenic stretch by comparison with a band observed at 1 495 cm^{-1} in the ^{13}C-enriched species [Pt_2(μ-Ph$^{13}C\equiv C$SiMe$_3$)(cod)$_2$]. Variable-temperature ^{13}C n.m.r. studies revealed that complex (10) undergoes dynamic behaviour in solution. At −15 °C the methine carbons of the cod ligands appear as two resonances [δ(p.p.m.) 88.9 and 87.9, with *J*(PtC) 98 and 111 Hz, respectively], rather than the four expected from the proposed structure. The acetylenic carbon resonances were observed at 92.9 [*C*Ph, *J*(PtC) 440 Hz] and 73.8 p.p.m. [*C*SiMe$_3$, *J*(PtC) 259 Hz], the relatively large difference in *J*(PtC) for the acetylenic carbons being attributable to the polarisation effect of the SiMe$_3$ group discussed previously.[2] Cooling to −90 °C resulted in a broadening of the two *C*H signals almost to the coalescence point as well as the appearance of two *C*H_2 resonances, first seen as a single resonance at −15 °C. However, variable-temperature ^{13}C n.m.r. measurements of a sample of (10) prepared from Ph$^{13}C\equiv$CSiMe$_3$ showed the *C*Ph signal to be virtually temperature invariant. Unfortunately the limiting spectrum could not be attained, although it would seem likely that this would be comparable with the spectrum of the dinickel analogue (9), with four environments observable for the CH and the CH_2 groups.

It is surprising that the platinum complex (10) shows dynamic behaviour whereas the nickel compound (9) does not. This observation prompted a single-crystal *X*-ray diffraction study of (10) to establish beyond doubt the molecular structure of this molecule, and by inference that of the other diplatinum species described in this paper. The molecular structure is shown in Figure **3**, along with the atomic numbering scheme, and the crystallographic data are summarised in Tables 1—3. Figure **4** shows the packing of the molecules in the unit cell.

TABLE 1

Atomic positional (fractional co-ordinates) parameters for complex (10), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt(1)	0.210 8(0)	0.154 0(0)	0.159 3(0)
Pt(2)	0.255 0(0)	0.067 3(0)	0.019 0(0)
Trimethylsilyl(phenyl)acetylene ligand			
Si(1)	0.378 2(1)	0.352 1(2)	0.123 7(1)
C(21)	0.345 5(6)	0.489 3(8)	0.178 8(5)
C(22)	0.486 7(6)	0.265 8(8)	0.199 1(5)
C(23)	0.412 3(7)	0.418 2(9)	0.038 7(5)
C(1)	0.177 1(5)	0.218 9(6)	0.040 1(4)
C(2)	0.277 9(5)	0.237 1(7)	0.086 3(4)
C(11)	0.095 9(5)	0.294 4(7)	−0.014 8(4)
C(12)	0.108 0(5)	0.422 9(7)	−0.034 9(5)
C(13)	0.029 3(6)	0.495 6(8)	−0.088 2(5)
C(14)	−0.062 8(6)	0.439 7(9)	−0.122 6(5)
C(15)	−0.076 1(6)	0.313 6(10)	−0.102 8(5)
C(16)	0.001 3(5)	0.241 1(8)	−0.049 8(5)
Cyclo-octadiene ligands			
C(101)	0.311 6(5)	0.053 9(7)	0.274 7(4)
C(102)	0.290 7(6)	0.175 7(8)	0.297 1(4)
C(103)	0.218 5(6)	0.199 9(8)	0.338 2(5)
C(104)	0.114 9(5)	0.232 7(7)	0.277 9(4)
C(105)	0.084 7(5)	0.160 9(8)	0.196 5(4)
C(106)	0.102 1(5)	0.032 0(7)	0.187 2(5)
C(107)	0.152 4(7)	−0.060 0(8)	0.260 0(6)
C(108)	0.264 1(6)	−0.070 5(7)	0.283 7(5)
C(201)	0.382 2(6)	−0.066 3(7)	0.067 8(5)
C(202)	0.383 4(5)	−0.007 4(7)	−0.002 7(5)
C(203)	0.353 0(6)	−0.072 8(8)	−0.087 6(5)
C(204)	0.246 5(5)	−0.054 4(8)	−0.144 5(4)
C(205)	0.177 6(5)	−0.038 9(7)	−0.100 7(4)
C(206)	0.180 4(6)	−0.120 3(8)	−0.034 5(5)
C(207)	0.248 3(7)	−0.234 3(8)	−0.004 2(5)
C(208)	0.343 3(7)	−0.202 8(8)	0.069 9(5)

The molecule has a structure analogous to that of [Ni_2(μ-PhC_2Ph)(cod)$_2$],[6] consisting of two Pt(cod) groups bound to the orthogonal orbitals of the bridging alkyne. This is exemplified by the 96.9° angle between the planes Pt(1), C(1), C(2) and Pt(2), C(1), C(2) (Table **3**). The metal–metal separation (2.914 Å) is considerably longer than the sum of the covalent radii (2.60 Å) and compares with 2.904 Å found in [Pt_3(μ-PhC_2Ph)$_2$-(PEt$_3$)$_4$].[1] In the complexes [Co_2Pt_2(CO)$_8$(PPh$_3$)$_2$],[7] [Fe_2Pt_2(μ-H)(μ-CO)$_3$(CO)$_5$(PPh$_3$)$_2$]$^-$, and [Fe_2Pt_2(μ-H)$_2$-(CO)$_8$(PPh$_3$)$_2$] [8] the Pt ··· Pt separations are 2.987(4), 2.966(1), and 2.998(2) Å, and these species are considered to have butterfly arrangements of the metal atoms with little or no direct Pt–Pt bonding. In several ligand-bridged diplatinum complexes the metal–metal distance is *ca.* 2.63 Å. It would thus seem that the metal–metal distance in (10) is largely determined by the stereochemistry associated with the bonding of the platinum atoms to the two orthogonal π orbitals of the alkyne. This concept, leading to a butterfly configuration for the Pt(μ-C_2)Pt group, has the merit of assigning each metal atom a 16-electron configuration, a common feature of platinum chemistry. Moreover, around each metal atom there is near perfect planar configuration. The angles between the pairs of planes Pt(1), C(101,102), C(105,106) and Pt(1), C(1), C(2), and Pt(2), C(1), C(2) and Pt(2), C(201,202), C(205,206) are 2.5 and 5.7°, respectively (Table 3).

The μ-C–C bond at 1.42(1) Å is rather long compared with that found [1.38(2) Å] for the C–C bonds of the bridging diphenylacetylene molecules in [$Pt_3(\mu$-$PhC_2Ph)_2(PEt_3)_4$], and may reflect a weakening of this bond by p_π–d_π interaction with the silicon. The variation in electronic effects of the $SiMe_3$ and Ph substituents is seen in the different bend-back angles of 33.6(6) and 42.7(6)°. The cod ligands in (10) adopt their customary ' tub ' configuration, and their bond distances and angles call for no comment.

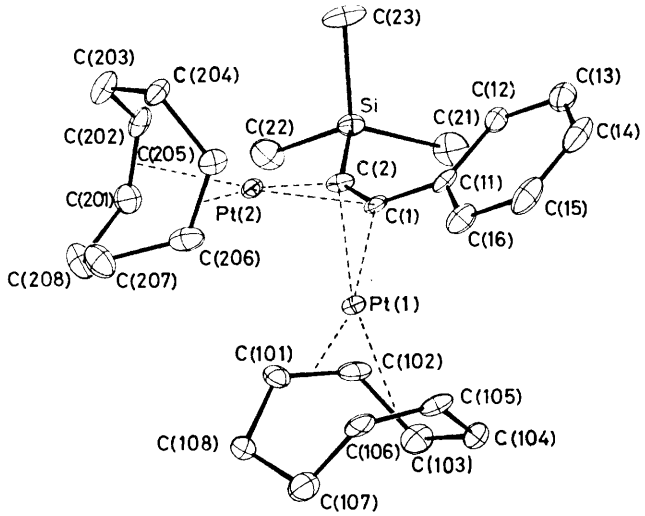
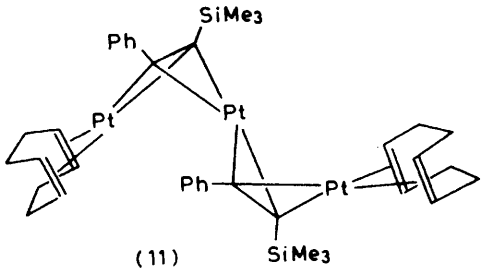


FIGURE 3 The molecular structure of the complex [$Pt_2(\mu$-$PhC_2SiMe_3)(cod)_2$] (10) showing the atom numbering



(11)

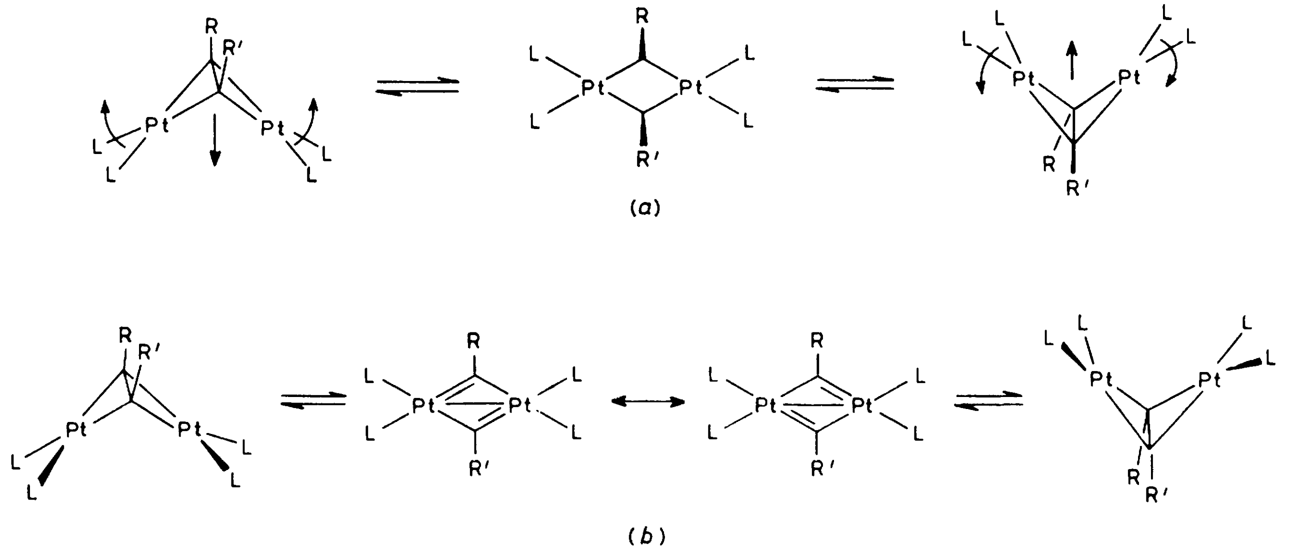
Reaction of PhC≡CSiMe$_3$ with [$Pt(cod)_2$] in 1 : 1 mol ratio, which would have been expected[2] to afford the compound [$Pt(PhC_2SiMe_3)(cod)$], yielded a red, crystalline triplatinum complex (11). A band in the i.r. spectrum of (11) at 1 546 cm^{-1} is probably due to a modified C≡C stretch, since by preparing the complex from a 50% ^{13}C-enriched sample of Ph^{13}C≡CSiMe$_3$ this absorption decreased in intensity and a band appeared at 1 516 cm^{-1}. Thus (11) is structurally analogous to [$Pt_3(\mu$-$PhC_2Ph)_2(PEt_3)_4$].[2] Examination of the ^{1}H and ^{13}C n.m.r. spectra of (11) revealed that, like (10), it underwent dynamic behaviour in solution. Thus at room temperature in the ^{1}H n.m.r. spectrum only two C*H* resonances were observed at τ 4.78 [^2J(PtH) 64] and 4.60 [^2J(PtH) 56 Hz], whereas four signals would be expected for the static structure. Similarly, at −5 °C the ^{13}C n.m.r. spectrum showed only two resonances for the *C*H groups {δ (p.p.m.) 88.9 [J(PtC) 94] and 87.5 [J(PtC) 115 Hz]} and two signals for the *C*H$_2$ groups (δ 31.2 and 30.5). The presence in the molecule of platinum atoms in two different environments was shown by studies on a sample of (11) prepared from ^{13}C-enriched Ph^{13}C≡CSiMe$_3$. The Ph*C* resonance at 108.0 p.p.m. had double satellites [^1J(Pt^{a}C) 496 and ^1J(Pt^{b}C) 288 Hz]. The bands in the ^{13}C spectrum of (11) broaden on cooling, as occurs with complex (10). Although the limiting spectrum for (11) could not be obtained, the enriched ^{13}*C*Ph resonance was observed firstly to collapse and then sharpen into three distinct signals flanked by ^{195}Pt satellites attributable to ^{195}Pt^a (Figure 1). The satellites of ^{195}Pt^b could not be resolved. Inspection of molecular models of (11) suggest the existence of three conformers, one of which has two different *C*Ph environments. Hence four *C*Ph resonances might have been expected instead of the three observed. However, the signals were not of equal intensity suggesting that coincidence of peaks occurs.

A dynamic process of this type involving a di- or trinuclear platinum acetylene complex has not been previously observed, and it is, therefore, interesting to consider the possible reaction paths involved. Dissociative processes can be excluded, since ^{195}Pt–^{13}C couplings are observed both on the acetylenic *C*Ph and cyclo-octa-1,5-diene *C*H nuclei at all temperatures.

Rotation of the cod ligands would result in site equivalence of C^a with C^c, and C^b with C^d [Figure 1, complex (10)]. However, this process does not account for the observation in the ^{13}C spectrum of (11) of only one *C*Ph resonance at −5 °C when three are observed at −90 °C, because in (11) equivalence of the *C*Ph sites arises from the relative orientations of the alkynes rather than the cod ligands.

A second process which could be envisaged is a ' butterfly-wing inversion ' in which the bridging acetylene ligand passes through an intermediate where the two platinum atoms and the two acetylenic carbon atoms are all coplanar. Such a process [Scheme 1(*a*)] would cause equivalence of C^a with C^b, and C^c with C^d. However, the involvement of an intermediate containing two planar four-co-ordinate carbon atoms makes this unlikely. A geometrically related and more plausible reaction path is illustrated in Scheme 1(*b*), which involves cleavage of the central acetylenic C–C bond to form a planar bis-carbyne complex. Such a process is consistent with the experimental observations, and it is interesting that molecules containing the cyclic fragment $\overline{\mathrm{MC(R)MC(R)}}$ (M = Nb, Mo, or W) have been reported.[9,10] Moreover, reaction of [Fe(CO)$_5$] with Et$_2$NC≡CNEt$_2$ has been shown [11] to result in apparent cleavage of the carbon–carbon triple bond and the formation of the dinuclear complex [{Fe(CO)$_3$(μ-CNEt$_2$)}$_2$].

Another mechanism for the dynamic behaviour of (10) to be considered is rotation of the alkyne above the platinum–platinum vector which would produce site exchange of C^a with C^d, and C^b with C^c (Figure 1). Furthermore, such a process, like that illustrated in Scheme 2, would account for the appearance of a single CPh resonance at ambient temperatures in the spectrum of (11). It is envisaged that such a rotation could take place *via* tetrahedrane-type transition states, involving platinum–platinum bond formation (Scheme 2). This could occur *via* a breathing motion from the butterfly structure. Rupture of the transverse carbon–platinum bonds in these intermediates would produce the ' twisted ' diplatinacyclobutene structures (A)—(D), which could interconvert as shown. This ' flipping ' motion would produce the plane of symmetry in the molecule. Reformation of the dimetallatetrahedrane configuration can then occur from which can be obtained, *via* Pt–Pt bond cleavage, the rotated species (E) and (F). Although this is an attractive reaction path, an estimation [12] by the extended Hückel method of the barrier to rotation from (E) to (C) and from (F) to (D) in bridged alkyne–metal complexes of this type indicates a barrier of 50 kcal mol^{-1},* the primary cause of the large barrier being an avoided crossing between filled and unfilled *a* orbitals. Although the barrier to apparent rotation may be lowered to some extent by squeezing together the two platinum atoms in the postulated intermediate it is thought that this would not be sufficient to achieve the facile process observed experimentally.[12]



SCHEME 1

Recently [13] evidence has been presented to suggest that in certain mononuclear complexes an acetylene can function as a four-electron donor, which in valence-bond terms can be regarded as a chelating dicarbene complex. Extension of this idea to a bridged acetylene, which in this bonding mode is of course already a four-electron ligand, leads to the suggestion that the bridged acetylene system can transform into a bridging dicarbene system, which (Scheme 3) could undergo a conformation change thus effecting the conversion of a transversely bridged acetylene into a dimetallacyclobutene, which is geometrically equivalent to a rotation above the Pt • • • Pt vector.

Clearly further studies will be required to establish firmly which reaction paths are followed, and it is interesting to note that alkyne rotation in the diplatinacyclobutene compound [Pt$_2$(μ-η^1-CF$_3$C$_2$CF$_3$)(cod)$_2$] readily occurs.[14]

It is envisaged that formation of the di- and triplatinum complexes occurs as shown in Scheme 4. Initial displacement of cod by an alkyne affords the species [Pt(alkyne)(cod)]. Although this type of complex was not isolated with the alkynes used in the present study, several such compounds were characterised earlier.[2] Moreover, although the compounds [Pt(RC$_2$SiMe$_3$)(cod)] (R = SiMe$_3$ or Ph) were not isolated they were detected by i.r. spectroscopy [R = SiMe$_3$, $\nu_{max.}$(C≡C) 1 717 cm^{-1}; R = Ph, $\nu_{max.}$(C≡C) 1 709 cm^{-1}] in the reaction mixtures, but were impossible to obtain pure. If excess of PhC≡CSiMe$_3$ is employed the complex [Pt(PhC$_2$SiMe$_3$)$_2$] is produced.[2] However, perhaps through a combination

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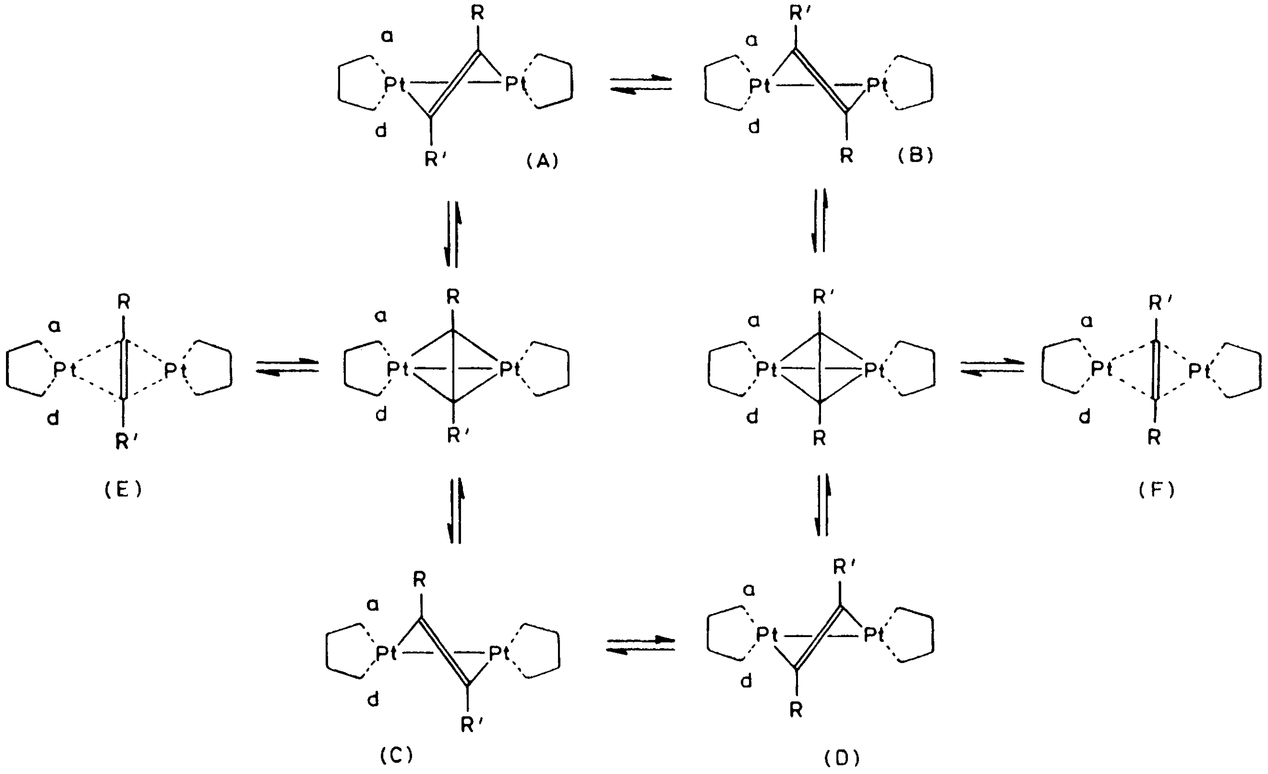
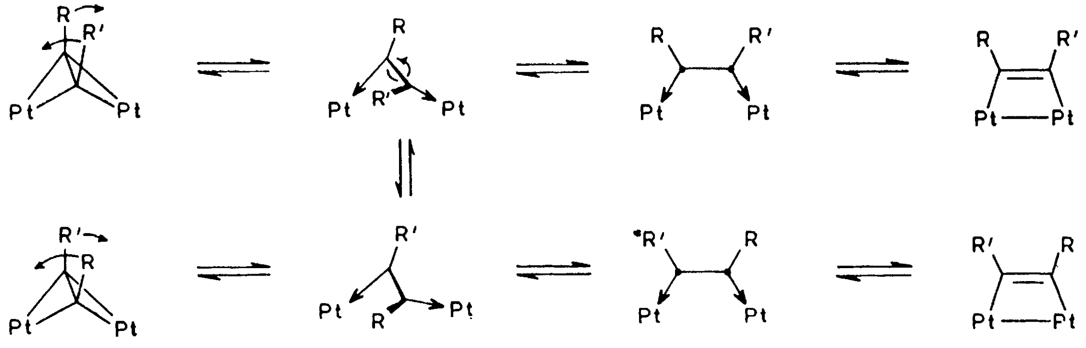
* Throughout this paper: 1 cal = 4.184 J.

of the steric and electron-withdrawing properties of the $SiMe_3$ groups, the compound $[Pt(Me_3SiC_2SiMe_3)_2]$ appears not to exist.

A series of kinetically controlled reactions starting from initial formation of the species [Pt(alkyne)(cod)] can be invoked (Scheme 4). Attack by $[Pt(\eta^2\text{-cod})(\eta^4\text{-cod})]$, derived from $[Pt(cod)_2]$, on the p_π—p_π orbital of the alkyne which is essentially not involved in metal bonding in the monoplatinum species [Pt(alkyne)(cod)] would afford the diplatinum compounds (3)—(5), and (10). Formation of (1) can be accounted for by displacement of cod from (3) by excess of $Me_3SiC_2SiMe_3$. Alternatively, the alkyne ligand in $[Pt(Me_3SiC_2SiMe_3)(cod)]$ might displace cod from a second molecule to give (1). However, the absence of (1) as a product in the synthesis of (3) argues against this proposal. In a controlled experiment an equimolar ratio of $[Pt(cod)_2]$ and $Me_3SiC{\equiv}CSiMe_3$ were stirred together at room temperature and the reaction followed by i.r. spectroscopy. After 30 min bands due to $[Pt(Me_3SiC_2SiMe_3)(cod)]$, $[Pt(cod)_2]$, and the complexes (1) and (3), as well as the free alkyne were observed. This result implies not only that the co-ordinated alkyne of $[Pt(Me_3SiC_2SiMe_3)(cod)]$ is as reactive if not more reactive than free $Me_3SiC{\equiv}CSiMe_3$, but that stepwise formation of these complexes does indeed occur.

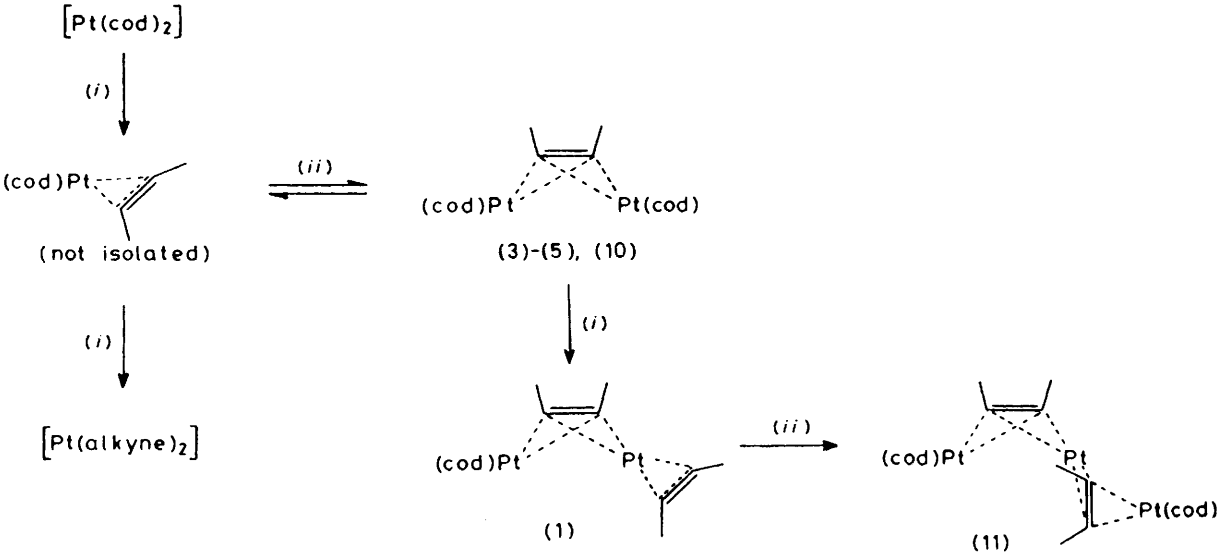


SCHEME 2



SCHEME 3

Further evidence for successive cod displacement by alkyne followed by attack on the co-ordinated alkyne by $[Pt(cod)_2]$ was uncovered in the reaction of the latter with $PhC{\equiv}CSiMe_3$ in a 3 : 2 mol ratio. This resulted not in the precipitation of complex (11), but instead (10) was produced. Addition of a further mol equivalent of $PhC{\equiv}CSiMe_3$ resulted in formation of (11). Thus it can be argued that build up of the triplatinum complex occurs *via* the diplatinum compound.



SCHEME 4 Formation of alkyne-bridged di- and tri-platinum complexes. (*i*) + Alkyne, (*ii*) + $[Pt(cod)_2]$

EXPERIMENTAL

The instrumentation used and experimental methods employed were as described previously.[1,2] The various alkynes, including ^{13}C-enriched species, were obtained as described earlier.[2] Light petroleum refers to that fraction of b.p. 40—60 °C. Infrared spectra were measured as Nujol mulls. All ^1H n.m.r. spectra were measured in $[^2H_6]$benzene at room temperature unless otherwise stated. Fluorine-19 chemical shifts are relative to CCl_3F (0.0 p.p.m.). The ^{13}C n.m.r. data are ^1H-decoupled, and chemical shifts are relative to $SiMe_4$, positive values to high frequency. For carbon and platinum atom notations see Figure 1.

Synthesis of the Diplatinum Complexes (1)—(5) *and* (10).—(*a*) To a light petroleum (20 cm^3) solution of $Me_3SiC{\equiv}CSiMe_3$ (1.15 g, 6.75 mmol) was added $[Pt(cod)_2]$ (0.9 g, 2.19 mmol). The cloudy yellow solution was stirred for 1 h, and all volatiles were then removed *in vacuo*. The residue was crystallised from light petroleum (−78 °C). Final purification was achieved by redissolution of the crystals in light petroleum, filtration through an alumina pad (1 × 5 cm), and reduction of the solvent volume *in vacuo* followed by crystallisation (−78 °C, 15 h) to afford yellow-orange *crystals* of $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(Me_3SiC_2SiMe_3)(cod)]$ (1) (0.35 g, 38%) (Found: C, 34.8; H, 5.9. $C_{24}H_{48}Pt_2Si_4$ requires C, 34.4; H, 5.8%); $\nu_{max.}$ at 1 817s (C≡C), 1 595w, 1 486s, 1 403m, 1 338w, 1 313w, 1 245vs, 1 172w, 1 079w, 996w, 960m, 914s, 873vs, 845vs, 773s, 700m, 642m, 623m, 502w, 479w, and 455vw cm^{-1}; ^1H n.m.r. τ 4.57 [s, 4 H, CH, ^2J(PtH) 63], 7.92 [s, 8 H, CH_2, ^3J(PtH) 23 Hz], 9.50 (s, 18 H, $SiMe_3$), and 9.58 (s, 18 H, $SiMe_3$); ^{13}C ($[^2H_1]$chloroform, −45 °C), δ (p.p.m.) 143.9 [C^β or C^γ, $^1J(Pt^bC)$ 294], 142.4 [C^β or C^γ, $^1J(Pt^bC)$ 218], 106.8 [C^α, $^1J(Pt^aC)$ 326, $^1J(Pt^bC)$ 219], 87.1 [CH, ^1J(PtC) 123], 87.1 [CH, ^1J(PtC) 93 Hz], 30.1 (CH_2), 0.9 ($SiMe_3$), and −0.3 ($SiMe_3$).

(*b*) To a solution of $[Pt(C_2H_4)_3]$ (0.162 g, 0.58 mmol) in light petroleum (5 cm^3, 0 °C) under an ethylene atmosphere was added $Me_3SiC{\equiv}CSiMe_3$ (0.2 g, 1.16 mmol) in light petroleum (2 cm^3). Within a few seconds ethylene was evolved and the solution turned yellow. The ethylene atmosphere was replaced by nitrogen and the solution stirred for a further 30 min. All volatiles were removed *in vacuo* and the residue redissolved in light petroleum and passed through an alumina pad (1 × 5 cm). Removal of solvent *in vacuo* afforded an oil which after a prolonged period (150 h) *in vacuo* gave yellow crystals of $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(Me_3SiC_2SiMe_3)_2]$ (2) in almost quantitative yield, m.p. (*in vacuo*) 80—81 °C (Found: C, 31.7; H, 6.0. $C_{24}H_{54}Pt_2Si_6$ requires C, 32.0; H, 6.0%), $\nu_{max.}$ at 1 816s (C≡C), 1 563m (C≡C), 1 397w, 1 247s, 1 091w,br, 1 017w,br, 868vs,vbr, 845vs,vbr, 812m, 761m, 697m, 636m, and 622m cm^{-1}; ^1H n.m.r., τ 9.48 [s, 18 H, $SiMe_3$, ^4J(PtH) 1 Hz], and 9.58 (s, 36 H, $SiMe_3$); ^{13}C ($[^2H_1]$chloroform, −60 °C), δ (p.p.m.) 143.0 [C^β or C^γ, ^1J(PtC) 293], 142.8 [C^β or C^γ, ^1J(PtC) 259], 117.7 [C^α, ^1J(PtC) 210], 0.7 [$SiMe_3$ (bridging), ^3J(PtC) 24 Hz], 0.2 ($SiMe_3$), and −0.1 ($SiMe_3$).

(*c*) To a suspension of $[Pt(cod)_2]$ (0.25 g, 0.61 mmol) in light petroleum (10 cm^3) was added $Me_3SiC{\equiv}CSiMe_3$ (0.052 g, 0.305 mmol) in the same solvent (5 cm^3). The clear yellow solution was stirred for 45 min. After removal of all volatiles *in vacuo*, the residue was redissolved in light petroleum and unchanged $[Pt(cod)_2]$ removed by crystallisation (−78 °C). The supernatant liquid was passed through a short column of alumina (1 × 5 cm) and the solvent removed *in vacuo* to afford yellow *microcrystals* of $[Pt_2(\mu\text{-}Me_3SiC_2SiMe_3)(cod)_2]$ (3) (90%), m.p. (*in vacuo*) 134—135 °C (Found: C, 36.8; H, 5.8. $C_{24}H_{42}Pt_2Si_2$ requires C, 37.1; H, 5.5%); $\nu_{max.}$ at 1 508w (C≡C), 1 431w, 1 399m, 1 332w, 1 306w, 1 298w, 1 260w, 1 240s, 1 219w, 1 189w, 1 175w, 1 151w, 1 071w, 999w, 988w, 927w, 848s, 832s, 763m, 752m, 723w, 689m, and 615w cm^{-1}; ^{1}H n.m.r. τ 4.73 [m, 4 H, CH, ^2J(PtH) 74], 5.43 [m, 4 H, CH, ^2J(PtH) 46], 7.99 (m, 8 H, CH_2), 8.12 (s, 8 H, CH_2), and 9.41 [s, 18 H, $SiMe_2$, ^4J(PtH) 2 Hz]; ^{13}C ([$^2H_1$]chloroform, −45 °C), δ (p.p.m.) 85.3 [CH_2, ^1J(PtC) 99], 85.2 [CH, ^1J(PtC) 120], 84.4 [C$^\alpha$, ^1J(PtC) 329], 30.8 (CH_2), 30.6 (CH_2), and 2.0 [$SiMe_3$, ^3J(PtC) 20 Hz].

TABLE 2

Bond lengths (Å) and angles (°) for the complex [Pt_2(μ-PhC_2SiMe_3)(cod)$_2$] (10)

(a) Distances

Pt(1)–Pt(2)	2.914(0)		
Pt(1)–C(1)	2.055(6)	Pt(2)–C(1)	2.072(7)
Pt(1)–C(2)	2.087(7)	Pt(2)–C(2)	2.072(7)
Pt(1)–C(101)	2.249(7)	Pt(2)–C(201)	2.237(8)
Pt(1)–C(102)	2.246(7)	Pt(2)–C(202)	2.233(7)
Pt(1)–C(105)	2.220(7)	Pt(2)–C(205)	2.247(7)
Pt(1)–C(106)	2.257(7)	Pt(2)–C(206)	2.258(8)
Pt(1)–C(101,102)	2.136 *	Pt(2)–C(201,202)	2.126
Pt(1)–C(105,106)	2.123	Pt(2)–C(205,206)	2.138
C(1)–C(2)	1.42(1)	C(1)–C(11)	1.45(1)
C(11)–C(12)	1.41(1)	C(12)–C(13)	1.40(1)
C(13)–C(14)	1.40(1)	C(13)–C(15)	1.39(1)
C(15)–C(16)	1.39(1)	C(11)–C(16)	1.42(1)
C(2)–Si(1)	1.828(7)	Si(1)–C(21)	1.887(8)
Si(1)–C(22)	1.873(8)	Si(1)–C(23)	1.876(8)
C(101)–C(102)	1.39(1)	C(201)–C(202)	1.38(1)
C(102)–C(103)	1.53(1)	C(202)–C(203)	1.53(1)
C(103)–C(104)	1.51(1)	C(203)–C(204)	1.53(1)
C(104)–C(105)	1.51(1)	C(204)–C(205)	1.51(1)
C(105)–C(106)	1.39(1)	C(205)–C(206)	1.42(1)
C(106)–C(107)	1.54(1)	C(206)–C(207)	1.51(1)
C(107)–C(108)	1.56(1)	C(207)–C(208)	1.54(1)
C(101)–C(108)	1.51(1)	C(201)–C(208)	1.54(1)

(*b*) Angles

C(2)–C(1)–C(11)	137.3(6)	C(1)–C(2)–Si(1)	146.4(6)
C(1)–C(11)–C(12)	121.4(6)	C(1)–C(11)–C(16)	120.9(7)
C(11)–C(12)–C(13)	121.2(7)	C(12)–C(13)–C(14)	119.7(8)
C(13)–C(14)–C(15)	119.8(8)	C(14)–C(15)–C(16)	121.0(8)
C(15)–C(16)–C(11)	120.6(8)	C(12)–C(11)–C(16)	117.7(7)
C(2)–Si(1)–C(21)	109.7(4)	C(21)–Si(1)–C(22)	109.0(4)
C(2)–Si(1)–C(22)	107.7(4)	C(22)–Si(1)–C(23)	107.8(4)
C(2)–Si(1)–C(23)	113.2(4)	C(23)–Si(1)–C(21)	109.4(4)
C(101)–C(102)–C(103)	123.8(7)	C(201)–C(202)–C(203)	124.5(7)
C(102)–C(103)–C(104)	114.9(6)	C(202)–C(203)–C(204)	114.7(6)
C(103)–C(104)–C(105)	113.0(6)	C(203)–C(204)–C(205)	115.2(6)
C(104)–C(105)–C(106)	125.9(7)	C(204)–C(205)–C(206)	122.6(7)
C(105)–C(106)–C(107)	123.9(7)	C(205)–C(206)–C(207)	123.6(7)
C(106)–C(107)–C(108)	113.2(6)	C(206)–C(207)–C(208)	113.7(7)
C(107)–C(108)–C(101)	114.2(6)	C(207)–C(208)–C(201)	114.1(6)
C(108)–C(101)–C(102)	125.5(7)	C(208)–C(201)–C(202)	124.4(7)
Pt(1)–C(1)–Pt(2)	89.8(3)	Pt(1)–C(2)–Pt(2)	89.0(3)
Pt(1)–C(1)–C(2)	71.2(4)	Pt(1)–C(2)–C(1)	68.8(4)
Pt(2)–C(1)–C(2)	70.0(4)	Pt(2)–C(2)–C(1)	70.0(4)
C(101)–Pt(1)–C(102)	36.1(3)	C(201)–Pt(2)–C(202)	36.0(3)
C(101)–C(102)–Pt(1)	72.0(4)	C(201)–C(202)–Pt(2)	72.1(4)
C(102)–C(101)–Pt(1)	71.8(4)	C(202)–C(201)–Pt(2)	71.9(3)
C(105)–Pt(1)–C(106)	36.0(3)	C(205)–Pt(2)–C(206)	36.7(3)
C(105)–C(106)–Pt(1)	70.5(4)	C(205)–C(206)–Pt(2)	71.2(4)
C(106)–C(105)–Pt(1)	73.4(4)	C(206)–C(205)–Pt(2)	72.1(4)

* C(*n*,*m*) indicates the midpoint of the line joining the atoms C(*n*) and C(*m*).

(*d*) Yellow-orange *microcrystals* of [Pt_2(μ-$Me_3SiC_2SiMe_2$-Bu^t)(cod)$_2$] (4) were prepared as described for (3). An analytical sample was obtained by recrystallisation from light petroleum at −78 °C (Found: C, 40.2; H, 6.3. $C_{27}H_{48}Pt_2Si_2$ requires C, 39.6; H, 6.0%); $\nu_{max.}$ at 3 024w, 1 511m,br (C≡C), 1 504m,br (C≡C), 1 464s, 1 429m, 1 411s, 1 381w, 1 353w, 1 330m, 1 303w, 1 259w, 1 238s, 1 215w, 1 187w, 1 172w, 1 151w, 1 070w, 1 002w, 985w, 948w, 941m, 915s, 880w, 831s,br, 813s, 799s, 760m, 749m, and 662m cm^{-1}; ^{1}H n.m.r., τ 4.76 [s,br, 4 H, CH, ^2J(PtH) 65], 5.09 [s,br, 4 H, CH, ^2J(PtH) 50 Hz], 7.99 (s,br, 8 H, CH_2), 8.13, (s,br, 8 H, CH_2), 8.79 (s, 9 H, Bu^t), 9.61 (s, 9 H, $SiMe_3$), and 9.67 (s, 6 H, $SiMe_2$); ^{13}C ([$^2H_2$]dichloromethane), δ (p.p.m.) 87.4 [CH, ^1J(PtC) 119, ^2J(PtC) 5], 87.0 [CH, ^1J(PtC) 100], 86.3 [CH, ^1J(PtC) 119], 86.3 [CH, ^1J(PtC) 91], 84.9 [CSi, ^1J(PtC) 316], 82.6 [CSi, ^1J(PtC) 327 Hz], 31.3 (CH_2), 31.2 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 27.4 (Bu^t), 18.0 [*C*Me_3, ^2J(PtC) 11],2.5 [$SiMe_3$, ^3J(PtC) 18], and −1.8 [$SiMe_2$, ^3J(PtC) 26, 12 Hz]; ^{195}Pt ([$^2H_2$]dichloromethane), δ [p.p.m. to high frequency of Ξ (^{195}Pt) = 21.4 MHz] 619 (s).

(*e*) A suspension of [Pt(cod)$_2$] (0.205 g, 0.5 mmol) in diethyl ether (5 cm^3) was treated with an excess of $CF_3C{\equiv}CSiMe_3$ (0.33 g, 2 mmol). After 3 h, the solution was passed through a short column of alumina and the solvent removed *in vacuo*. Recrystallisation from light petroleum–diethyl ether afforded yellow *crystals* of [Pt_2(μ-$CF_3C_2SiMe_3$)(cod)$_2$] (5) (0.12 g, 62%), m.p. >158 °C (decomp.) [Found: C, 34.3; H, 4.6%; *M* = 792 (in benzene). $C_{22}H_{33}F_3Pt_2Si$ requires C, 34.2; H, 4.3%; *M* 793]; $\nu_{max.}$ at 1 518m, 1 508m, 1 457vs, 1 400vw, 1 378s, 1 335m, 1 308m, 1 300vw, 1 252m, 1 240vs, 1 222m, 1 200vs, 1 195m, 1 160m, 1 100vs, 1 090vs, 990s, 962s, 955m, 940vs, 850vs, 840w, 820w, 770s, 760m, 751w, 700s, 620m, 550vw, and 445w cm^{-1}; ^{1}H n.m.r., τ 4.74 [s, 4 H, CH, ^2J(PtH) 60], 4.88 [s, 4 H, CH, ^2J(PtH) 60 Hz], 8.40 (s, 16 H, CH_2), and 9.60 (s, 9 H, $SiMe_3$); ^{19}F (benzene), δ (p.p.m.) 49.8 [s, CF_3, ^3J(PtF) 136 Hz].

(*f*) To a suspension of [Pt(cod)$_2$] (0.566 g, 1.38 mmol) in light petroleum (10 cm^3) was added $PhC{\equiv}CSiMe_3$ (0.12 g, 0.69 mmol). The [Pt(cod)$_2$] dissolved to give a red-yellow solution from which precipitated an orange solid. The suspension was stirred for 30 min, and then most of the solvent was removed *in vacuo*. The supernatant solution was removed from the product, which was washed with light petroleum (2 × 5 cm^3) and dried *in vacuo* affording orange *microcrystals* of [Pt_2(μ-PhC_2SiMe_3)(cod)$_2$] (10) (0.3 g, 56%). An analytical sample was crystallised from diethyl ether as dark red *crystals*, m.p. (*in vacuo*) 135—136 °C (decomp.) (Found: C, 41.7; H, 5.1. $C_{27}H_{38}Pt_2Si$ requires C, 41.5; H, 4.9%); $\nu_{max.}$ at 3 056w, 3 036w, 1 596w, 1 514m, 1 504s (C≡C), 1 447s, 1 432m, 1 384m, 1 307w, 1 301w, 1 253w, 1 245m, 1 240s, 1 222w, 1 177w, 1 167w, 1 159w, 1 085w, 1 031w, 953m, 945m, 912s, 868m, 842s, 832s, 822m, 771m, 761m, 752m, 698s, 647w, 620w, 600w, 584w, and 443w cm^{-1}; ^{1}H n.m.r., τ 2.47—3.10 (m, 5 H, Ph), 4.77 [s, 4 H, CH, ^2J(PtH) 60], 5.08 [s, 4 H, CH, ^2J(PtH) 60 Hz], 8.72 (s, 6 H, CH_2), and 9.54 (s, 9 H, $SiMe_3$); ^{13}C ([$^2H_2$]dichloromethane, −15 °C), δ (p.p.m.) 143.6 [Ph, α-C, ^2J(PtC) 32], 128.0 [Ph, β-C, ^3J(PtC) 39], 127.8 [Ph, γ-C, ^4J(PtC) 21], 123.6 [Ph, δ-C, ^5J(PtC) 7], 92.9 [*C*Ph, ^1J(PtC) 440], 88.9 [CH, ^1J(PtC) 98], 87.9 [CH, ^1J(PtC) 111], 73.8 [*C*$SiMe_3$, ^1J(PtC) 259], 31.1 (CH_2), and 2.3 [$SiMe_3$, ^3J(PtC) 20 Hz]; ^{13}C (−90 °C), δ (p.p.m.) 90.5 [*C*Ph, ^1J(PtC) 443 Hz], 32.3 (CH_2), and 30.3 (CH_2).

Synthesis of [Pt_3(μ-PhC_2SiMe_3)$_2$(cod)$_2$].—Orange-red *microcrystals* of [Pt_3(μ-PhC_2SiMe_3)$_2$(cod)$_2$] (11) (0.17 g, 50%) were prepared in a similar manner to complex (10) using [Pt(cod)$_2$] (0.39 g, 0.95 mmol) and $PhC{\equiv}CSiMe_3$ (0.17 g, 0.95 mmol). An analytical sample of (11) was obtained as dark red *crystals* from diethyl ether, m.p. (*in vacuo*) 113—115 °C (decomp.) (Found: C, 39.7; H, 4.6. $C_{35}H_{52}Pt_3Si_2$ requires C, 39.7; H, 4.6%), $\nu_{max.}$ at 3 074w, 3 061w, 3 047w, 1 596m, 1 546m,br (C≡C), 1 471s, 1 444m, 1 432m, 1 338w, 1 313w, 1 305w, 1 255(sh), 1 245s, 1 196w, 1 185w, 1 170m, 1 078m, 1 069w, 1 029w, 1 005w, 995w, 967w, 956w, 906m, 888m, 856(sh), 846s, 839(sh), 819m, 767s, 761w, 726w, 696s, 654w, 625w, 605w, and 564w cm^{-1}; ^{1}H n.m.r., τ 2.39—2.84 (m, 10 H, Ph), 4.60 [s, 4 H, CH, ^2J(PtH) 56], 4.78 [s, 4 H, CH, ^2J(PtH) 64 Hz], 8.06 (s, 16 H, CH_2), and 9.58 (s, 18 H, $SiMe_3$); ^{13}C ([$^2H_2$]dichloromethane, −5 °C), δ (p.p.m.) 139.0 [Ph, α-C, ^2J(PtC) 18], 129.6 [Ph, β-C, ^3J(Pt^{a}C) 48, ^3J(Pt^{b}C) 26], 128.0 (Ph, γ-C), 125.6 (Ph, δ-C), 108.0 [*C*Ph, ^1J(Pt^{a}C) 496, ^1J(Pt^{b}C) 288], 89.9 [CH, ^1J(PtC) 94], 87.5 [CH, ^1J(PtC) 115], 31.2 (CH_2), 30.5 (CH_2), and 0.9 [$SiMe_3$, ^3J(PtC) 20 Hz]; (−90 °C), δ (p.p.m.) 108.2 [*C*Ph, ^1J(Pt^{a}C) 505], 107.3 [*C*Ph, ^1J(Pt^{a}C) 492], and 106.3 [*C*Ph, ^1J(Pt^{a}C), 489, ^2J(Pt^{a}C) 18 Hz].

Synthesis of [$Pt_2(\mu\text{-}Me_3SiC_2CF_3)(CNBu^t)_4$].—(*a*) A diethyl ether (10 cm^3) solution of $CF_3C{\equiv}CSiMe_3$ (0.33 g, 2 mmol) was treated portionwise with [$Pt_3(CNBu^t)_6$] (0.15 g, 0.14 mmol). After 3 h the mixture was filtered through an alumina pad, and solvent removed *in vacuo*. The residue was washed with light petroleum (4 × 2 cm^3) affording pale cream *microcrystals* of [$Pt_2(\mu\text{-}Me_3SiC_2CF_3)(CNBu^t)_4$] (6) (0.14 g, 75%), m.p. >144 °C (decomp.) (Found: C, 34.7; H, 4.8; N, 6.0. $C_{26}H_{45}F_3N_4Pt_2Si$ requires C, 35.1; H, 5.1; N, 6.3%); $\nu_{max.}$ at 2 140vs (NC), 2 118vs (NC), 1 460vs, 1 398w, 1 378vs, 1 238s, 1 210vs, 1 100s, 1 072s, 940vs, 850s, 838s, 755w, 725m, 690m, 618m, 510m, and 452w cm^{-1}; ^{1}H n.m.r., τ 8.94 (s, 18 H, Bu^t), 8.98 (s, 18 H, Bu^t), and 9.24 (s, 9 H, $SiMe_3$); ^{19}F (benzene), δ (p.p.m.) 47.8 [s, CF_3, ^3J(PtF) 128 Hz].

(*b*) A solution of complex (5) in diethyl ether (10 cm^3) was treated with an excess of CNBu^t. After 2 h, the solution was reduced *in vacuo* to *ca.* 2 cm^3, and light petroleum (5 cm^3) added. The resultant precipitate was isolated and washed with light petroleum (3 × 2 cm^3) affording [$Pt_2(\mu\text{-}Me_3SiC_2CF_3)(CNBu^t)_4$] (6) (0.07 g, 78%).

Synthesis of the Dinickel Complexes (7) *and* (9).—(*a*) To a suspension of [$Ni(cod)_2$] (0.55 g, 2.0 mmol) in light petroleum (10 cm^3) was added $Me_3SiC{\equiv}CSiMe_3$ (0.34 g, 2.0 mmol) After five minutes all the [$Ni(cod)_2$] had dissolved to give a red solution. Stirring was continued for 4 h, then all volatiles were removed *in vacuo*. The residue was dissolved in light petroleum, filtered through a pad of Florisil (1 × 5 cm), and all the light petroleum removed *in vacuo*, affording maroon *microcrystals* of [$Ni_2(\mu\text{-}Me_3SiC_2SiMe_3)(cod)_2$] (7) (90%) (Found: C, 61.3; H, 9.4. $C_{24}H_{42}Ni_2Si_2$ requires C, 62.7; H, 10.0%); $\nu_{max.}$ at 3 040w, 1 526m (C≡C), 1 488s, 1 435m, 1 331w, 1 305w, 1 253s, 1 181w, 1 078w, 1 023w, 984w, 900s, 881m, 848vs,br, 764m, 739w, 725w, 685w, and 619w cm^{-1}; ^{1}H n.m.r., τ 4.69 (s, 4 H, CH), 4.97 (s,br, 4 H, CH), 7.92 (s,br, 16 H, CH_2), and 9.65 (s, 18 H, $SiMe_3$); ^{13}C ([$^2H_6$]benzene), δ (p.p.m.) 115.9 (s, *C*SiMe$_3$), 94.5 (CH), 93.7 (CH), 30.5 (CH_2), and 2.1 ($SiMe_3$).

(*b*) Maroon *crystals* (0.35 g, 72%), recrystallised from light petroleum (−78 °C), of [$Ni_2(\mu\text{-}PhC_2SiMe_3)(cod)_2$] (9) were prepared in a similar manner to (7) using [$Ni(cod)_2$] (0.55 g, 2.0 mmol) and $PhC{\equiv}CSiMe_3$ (0.55 g, 3.2 mmol) (Found: C, 63.2; H, 7.3. $C_{27}H_{38}Ni_2Si$ requires C, 63.8; H, 7.5%); $\nu_{max.}$ at 3 050w, 1 588s, 1 551s, 1 531m (C≡C), 1 522m, 1 471s, 1 431w, 1 329w, 1 302w, 1 299w, 1 251w, 1 243s, 1 220w, 1 183w, 1 162w, 1 066m, 1 022w,br, 914m, 892m, 890m, 836vs,br, 754m, 740w, 694s, 633m, and 616w cm^{-1}; ^{1}H n.m.r., τ *ca.* 2.6 (m, 5 H, Ph), 4.6—5.45 (m, 8 H, CH), *ca.* 8.15 (m, 16 H, CH_2), and 9.61 (s, 9 H, $SiMe_3$); ^{13}C ([$^2H_6$]benzene), δ (p.p.m.) 141.5 (Ph, α-C), 128.8 (Ph), 126.5 (Ph), 123.7 (Ph, δ-C), 119.9 (*C*Ph), 101.1 (*C*SiMe$_3$), 98.8 (CH), 96.6 (CH), 95.4 (CH), 94.6 (CH), 30.7 (s, CH_2 + CH_2), 30.5 (CH_2), 30.1 (CH_2), and 2.1 [$SiMe_3$, ^1J(SiC) 58 Hz].

TABLE 3

Some least-squares planes in the complex [$Pt_2(\mu\text{-}PhC_2SiMe_3)$}$(cod)_2$] in the form $Ax + By + Cz = D$, where *x*, *y*, and *z* are fractional crystal co-ordinates

(*i*) C(201,202), C(205,206), Pt(2)
$$-6.059x - 5.531y + 14.700z = 1.638$$

(*ii*) C(101,102), C(105,106), Pt(1)
$$-3.329x + 9.802y + 5.412z = 1.670$$

(*iii*) Pt(1), C(1), C(2)
$$-4.671x + 9.453y + 6.467z = 1.501$$

(*iv*) Pt(2), C(1), C(2)
$$-5.981x - 5.174y + 15.088z = -1.587$$

(*v*) C(1), C(2), Si(1), C(11)
$$-8.540x + 2.374y + 16.552z = -0.355$$

Angles (°) between planes

(*i*)–(*iv*) 2.5; (*ii*)–(*iii*) 5.7; (*iii*)–(*iv*) 96.9; (*iii*)–(*v*) 53.1; (*iv*)–(*v*) 43.9.

X-Ray Data Collection and Structure Determination.—Crystals of [$Pt_2(\mu\text{-}PhC_2SiMe_3)(cod)_2$] (10) grow as small orange-red prisms, that selected for data collection was of dimensions *ca.* 0.1 × 0.6 × 0.2 mm. Diffracted intensities were collected at 200 K for 2.9 ⩽ 2θ ⩽ 60° on a Syntex $P2_1$ four-circle diffractometer, according to methods described earlier.[15] Of the total recorded 8 508 intensities, there were 5 464 unique reflections having $|F| \geqslant 5\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics, and

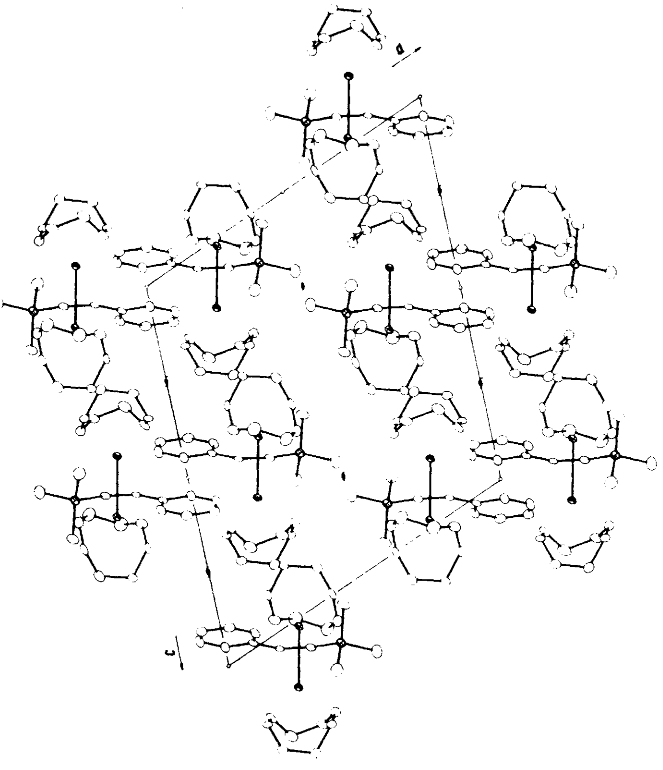


FIGURE 4 Contents of the monoclinic unit cell of complex (10) viewed down the *b* axis towards the origin

only these were used in the solution and refinement of the structure. Three check reflections ($1\,0\,\bar{8}$, $2\,1\,\bar{1}$, $1\,2\,1$) were monitored once every 40. Corrections were applied for Lorentz, polarisation, and X-ray absorption effects. All computations were carried out with the 'SHELX' system of programs.[16]

Crystal data. $C_{27}H_{38}Pt_2Si$, $M = 780.9$, Monoclinic, $a = 14.93(1)$, $b = 10.38(1)$, $c = 17.463(8)$ Å, $\beta = 112.79(6)^\circ$, $U = 2\,496(3)$ Å^3, $D_m = 2.00$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.03$ g cm^{-3}, $F(000) = 1\,480$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 108.12$ cm^{-1}, space group $P2_1/c$ (no. 14).

The platinum and silicon atoms were located from a Patterson synthesis and the carbon atoms by successive electron-density difference syntheses. The structure was refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Most of the hydrogen atoms were included at calculated positions and only common temperature factors for chemically equivalent hydrogen atoms were refined. Of those on the C=C bonds, only five were successfully located from difference-density syntheses. Refinement converged at R 0.038 (R' 0.038). A weighting scheme of the form $w = 1.332\,9/[\sigma^2F + 0.000\,82|F|^2]$, 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 >1.4 or <-3.5 e Å^{-3}, except in the region of the platinum atoms (2.2 e Å^{-3}). The scattering factors were from ref. 17 for carbon and silicon, ref. 18 for hydrogen, and ref. 19 for Pt, including corrections for the effects of anomalous dispersion for Pt ($\Delta f'$ -2.353, $\Delta f''$ 8.388) and Si ($\Delta f'$ 0.072, $\Delta f''$ 0.071). Atomic positional parameters are in Table 1, interatomic distances in Table 2, and some least-squares planes in Table 3. Packing of the molecules in the monoclinic unit cell is shown in Figure 4. Observed and calculated structure factors, all thermal parameters, and the positional parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22960 (28 pp.).*

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