# Alkyne Complexes of Platinum. Part 3.[1] The Synthesis and Crystal Structure of Bis(diphenylacetylene)platinum, and Studies on Related Compounds

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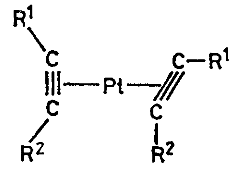
The bis(alkyne)platinum complexes $[Pt(R^1C_2R^2)_2]$ [$R^1 = R^2 =$ Ph, $CH_2SiMe_3$, $C_6H_4OMe$-4, or $C(OH)Me_2$; $R^1 = Bu^t$, $R^2 = SiMe_3$; $R^1 =$ Ph, $R^2 = SiMe_3$] have been prepared by treating $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) with excess of the alkyne. This method was unsuccessful for the synthesis of the related compounds $[Pt(R^1C_2R^2)_2]$ ($R^1 = R^2 =$ Me, Et, $Bu^t$, or $C_6H_4Me$-4; $R^1 = Bu^t$, $R^2 =$ Me; $R^1 =$ Ph, $R^2 =$ Me) but these species are readily prepared from $[Pt(C_2H_4)_3]$ and the respective alkynes. A single-crystal *X*-ray diffraction study of $[Pt(PhC_2Ph)_2]$ has shown that the crystals are monoclinic, space group *P*2/*n*, with $Z = 2$ in a unit cell of dimensions $a = 13.163(5)$, $b = 6.062(2)$, $c = 14.354(7)$ Å, and $\beta = 115.04(3)°$. The structure has been solved by heavy-atom methods from automated diffractometer data, and refined to *R* 0.038 (*R'* 0.046) for 3 433 reflections. The molecule adopts an essentially tetrahedral configuration, the angle between the two Pt–C–C planes being 82°. The platinum atom lies on a crystallographic two-fold axis of rotation, at a mean distance of 2.022(5) Å from the acetylenic carbon atoms which are 1.291(5) Å apart. Co-ordination of the diphenylacetylene to the metal shows the expected bending of the phenyl groups away from the platinum atom [Ph–C–C 153.2(5)°]. The acetylenic stretches in the i.r. spectra of the complexes $[Pt(R^1C_2R^2)_2]$ occur in the range 1 840—1 924 cm$^{-1}$, *ca.* 150 cm$^{-1}$ above the corresponding bands in the spectra of complexes $[Pt(R^1C_2R^2)(PR_3)_2]$, reflecting less metal–acetylene back bonding in the former. For all the complexes $[Pt(R^1C_2R^2)_2]$ there is a downfield shift of the acetylenic-carbon resonances in the $^{13}C$ n.m.r. spectra of 30—40 p.p.m. upon metal co-ordination.

Equimolar amounts of $[Pt(cod)_2]$ and PhC≡CPh afford $[Pt(PhC_2Ph)(cod)]$, while a second mol of the acetylene yields $[Pt(PhC_2Ph)_2]$. In contrast, in the presence of excess of the alkynes 4-$MeC_6H_4C{\equiv}CC_6H_4Me$-4', $C_6F_5C{\equiv}CC_6F_5$, and 4-$MeOC_6F_4C{\equiv}CC_6F_4OMe$-4', $[Pt(cod)_2]$ yields monoalkyne complexes [Pt(alkyne)(cod)]. Treatment of the fluoroarylalkyne-platinum compounds with $CNBu^t$ gives $[Pt(R^1C_2R^2)(CNBu^t)_2]$ ($R^1 = R^2 = C_6F_5$ or $C_6F_4OMe$-4). Addition of $[Pt(PhC_2Ph)_2]$ to light petroleum solutions containing excess of L = $CNBu^t$, $PMe_3$, $PEt_3$, or $PPh_3$ yields the complexes $[Pt(PhC_2Ph)L_2]$. By using samples containing enriched $Ph^{13}C{\equiv}CPh$, $^{13}C$ n.m.r. chemical shifts and $^{195}Pt$–$^{13}C$ coupling constants have been measured for these compounds, and for those species containing phosphine ligands the $^{31}P$ n.m.r. spectra also recorded.

MANY alkyne complexes of platinum(0) of the type [Pt(alkyne)$(PPh_3)_2$] have been prepared and studied.[2-4] These molecules adopt a trigonal-planar configuration in the crystal with the acetylene molecule approaching the geometry of a *cis*-olefin.[5] Some years ago Rochon and Theophanides[6] described a series of compounds [Pt(alkyne)$_2$] involving 1,4-dihydroxy-substituted acetylenes, prepared by reducing $K_2[PtCl_4]$ in ethanol in the presence of the alkyne. A single-crystal *X*-ray diffraction study[7] on $[Pt\{Et_2(HO)CC_2C(OH)Et_2\}_2]$ revealed that the midpoints of the two acetylenic ligands and the metal atom form a linear arrangement with these ligands on either side of the metal and with their C–C axes essentially perpendicular to each other. Compounds of platinum in which alkynes are the only ligands should be useful precursors in further syntheses. A possible route to such species might involve reaction of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) or $[Pt(C_2H_4)_3]$[8] with acetylenes. The results described in this paper were obtained with this objective in mind.[9]

## RESULTS AND DISCUSSION

Reaction of an excess of diphenylacetylene with $[Pt(cod)_2]$ in light petroleum at room temperature affords the pale yellow crystalline complex $[Pt(PhC_2Ph)_2]$ (1). Unfortunately this synthesis proved not to have general applicability, several alkynes forming either uncharacterisable polynuclear species, as does acetylene, or complexes of the type [Pt(alkyne)(cod)], as discussed below. However, this difficulty is easily circumvented by employing $[Pt(C_2H_4)_3]$, which with stoicheiometric amounts of alkyne affords a series of compounds [Pt(alkyne)$_2$] (2)—(7) (Table 1). This route has the advantage of simplifying purification procedures due to the volatility



| | $R^1$ | $R^2$ |
|---|---|---|
| (1) | Ph | Ph |
| (2) | Me | Me |
| (3) | Et | Et |
| (4) | $Bu^t$ | Me |
| (5) | Ph | Me |
| (6) | $C_6H_4Me$-4 | $C_6H_4Me$-4 |
| (7) | $Bu^t$ | $Bu^t$ |
| (8) | $Bu^t$ | $SiMe_3$ |
| (9) | Ph | $SiMe_3$ |
| (10) | $CH_2SiMe_3$ | $CH_2SiMe_3$ |
| (11) | $C_6H_4OMe$-4 | $C_6H_4OMe$-4 |
| (12) | $C(OH)Me_2$ | $C(OH)Me_2$ |

of ethylene and the absence of free cyclo-octa-1,5-diene. Complexes (8)—(12), however, were prepared from [Pt(cod)$_2$] in a similar manner to (1).

The species [Pt(MeC$_2$Me)$_2$] (2) and [Pt(EtC$_2$Et)$_2$] (3) were both very unstable even in the solid state, decomposing $< -25$ °C, and identification rests solely on spectroscopic studies. Indeed, it was only possible to isolate pure white needles of (2) on one of many attempts. As the alkyl substituent becomes more substituted, the thermal stability of the platinum complexes increases and hence [Pt(Bu$^t$C$_2$Bu$^t$)$_2$] (7) is stable at ambient temperatures. The trimethylsilyl derivatives (8) and (9) are very soluble in hydrocarbon solvents; indeed, the former could not be isolated as a solid.

TABLE 1

Bis(alkyne)platinum complexes [Pt(R$^1$C$_2$R$^2$)$_2$] [a]

| Complex | R$^1$ | R$^2$ | Synthetic route [b] | Yield (%) | Analysis (%) C | Analysis (%) H |
|---|---|---|---|---|---|---|
| (1) | Ph | Ph | A | 82 | 61.2 (60.9) | 3.8 (3.6) |
| (2) [c] | Me | Me | B | 45 | | |
| (3) [c] | Et | Et | B | 6 | | |
| (4) [c] | Bu$^t$ | Me | B | 74 | | |
| (5) | Ph | Me | B | 61 | 49.8 (50.6) | 3.6 (3.8) |
| (6) | C$_6$H$_4$Me-4 | C$_6$H$_4$Mc-4 | B | 74 | 61.7 (63.2) | 4.6 (4.6) |
| (7) | Bu$^t$ | Bu$^t$ | B | 8 | 61.0 (60.9) | 7.9 (7.7) |
| (8) | Bu$^t$ | SiMe$_3$ | A | 95 | 44.1 (42.9) | 7.5 (7.2) |
| (9) | Ph | SiMe$_3$ | A | 44 | 48.6 (48.9) | 5.2 (5.2) |
| (10) | CH$_2$SiMe$_3$ | CH$_2$SiMe$_3$ | A | 31 | 41.5 (41.0) | 7.4 (7.6) |
| (11) | C$_6$H$_4$OMe-4 | C$_6$H$_4$OMe-4 | A | 95 | 57.2 (57.1) | 4.2 (4.2) |
| (12) | C(OH)Me$_2$ | C(OH)Me$_2$ | A | 59 | 39.6 (40.1) | 6.0 (5.9) |

[a] Calculated values are given in parentheses. [b] Method A, from [Pt(cod)$_2$]; B, from [Pt(C$_2$H$_4$)$_3$] (see text). [c] Too unstable to obtain satisfactory elemental analysis (see text).

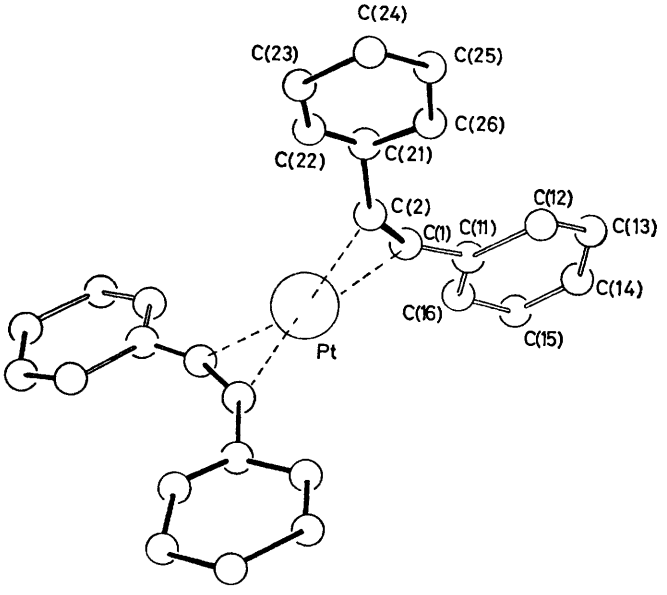


FIGURE 1 Molecular structure of [Pt(PhC$_2$Ph)$_2$] showing the atomic numbering scheme

The aryl-alkyne complexes (1), (6), and (11) are all air-stable as solids, but both (1) and (6) are unstable in diethyl ether above 0 °C. Complex (11) can be safely recrystallised from chloroform. The most stable species listed in Table 1, both in the solid state and in solution, proved to be [Pt{Me$_2$(HO)CC$_2$C(OH)Me$_2$}$_2$] (12). This compound was synthesised from [Pt(cod)$_2$], a greatly improved method over that reported previously.[6]

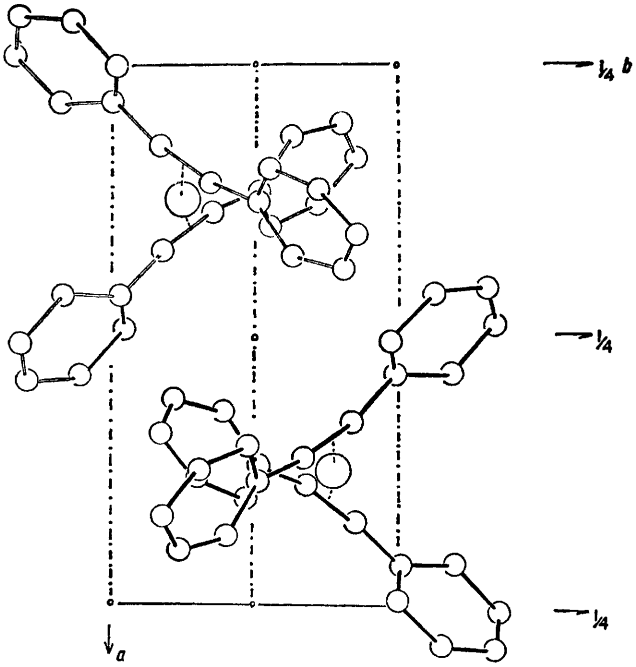


FIGURE 2 Contents of the unit cell of (1) viewed down $c^*$ towards the origin

A single-crystal $X$-ray diffraction study was carried out on (1). The structural results are summarised in Figure 1, which also shows the atom-numbering system, and in Tables 2 and 3. The packing of the molecules within the monoclinic unit cell is shown in Figure 2. The two diphenylacetylene molecules adopt the same geometry about the metal atom as was found[7] for the acetylene ligands in [Pt{Et$_2$(HO)CC$_2$C(OH)Et$_2$}$_2$]. Thus the dihedral angle between the planes defined by Pt, C(1), C(2) and Pt, C(1'), C(2') in (1) is 82° (Table 4), whereas the corresponding angle in [Pt{Et$_2$(HO)CC$_2$C(OH)Et$_2$}$_2$] is 86°. The bond distances [2.022(5) Å] between the platinum atom and the acetylenic carbon atoms

TABLE 2

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (1)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Pt * | 0.25 | 0.234 64(3) | 0.25 |
| C(1) | 0.341 3(3) | 0.156 2(6) | 0.171 5(3) |
| C(11) | 0.425 8(3) | −0.008 8(6) | 0.183 8(3) |
| C(12) | 0.498 5(4) | 0.014 3(6) | 0.136 2(3) |
| H(12) | 0.490(5) | 0.141(11) | 0.092(5) |
| C(13) | 0.579 3(4) | −0.146 4(7) | 0.148 6(4) |
| H(13) | 0.622(6) | −0.124(11) | 0.104(5) |
| C(14) | 0.586 5(4) | 0.331 8(7) | 0.209 6(4) |
| H(14) | 0.646(5) | −0.437(9) | 0.218(5) |
| C(15) | 0.516 0(4) | −0.355 2(6) | 0.257 5(4) |
| H(15) | 0.518(4) | −0.480(8) | 0.294(4) |
| C(16) | 0.434 5(4) | −0.195 3(7) | 0.245 1(3) |
| H(16) | 0.383(6) | −0.198(10) | 0.288(5) |
| C(2) | 0.275 2(4) | 0.317 5(6) | 0.125 0(3) |
| C(21) | 0.235 1(3) | 0.489 1(5) | 0.047 5(3) |
| C(22) | 0.140 6(4) | 0.614 4(7) | 0.034 2(3) |
| H(22) | 0.098(5) | 0.576(9) | 0.077(5) |
| C(23) | 0.108 3(5) | 0.790 9(8) | −0.035 2(4) |
| H(23) | 0.037(5) | 0.871(10) | −0.046(5) |
| C(24) | 0.169 1(4) | 0.842 2(7) | −0.090 1(4) |
| H(24) | 0.145(4) | 0.960(8) | −0.137(4) |
| C(25) | 0.262 4(4) | 0.716 6(7) | −0.078 9(4) |
| H(25) | 0.301(9) | 0.737(8) | −0.127(8) |
| C(26) | 0.295 5(4) | 0.540 5(6) | −0.010 0(3) |
| H(26) | 0.363(5) | 0.452(10) | 0.005(5) |

* On two-fold axis; $x$ and $z$ not refined.

in (1) are very slightly shorter than that [2.054(11) Å] found in the hydroxyacetylene complex. This is as expected since a Ph substituent would be more electronegative than a C(OH)Et$_2$ group, leading to enhanced back bonding in (1).[5] The distance C(1)–C(2) [1.291(5) Å] in (1) is shorter than that measured [1.35(3) Å] for [Pt{Et$_2$(HO)CC$_2$C(OH)Et$_2$}$_2$].[7] However, the large standard deviation involved in the latter value precludes detailed discussion of the relative degrees of back bonding in the two complexes based on the acetylenic C–C distances.

TABLE 3

Bond lengths (Å) and angles (°) for complex (1)

(*a*) Distances

| | | | |
|---|---|---|---|
| Pt–C(1) | 2.022(5) | | |
| Pt–C(2) | 2.021(5) | | |
| C(1)–C(2) | 1.291(5) | | |
| C(1)–C(11) | 1.450(6) | C(2)–C(21) | 1.449(5) |
| C(11)–C(12) | 1.399(8) | C(21)–C(22) | 1.400(7) |
| C(12)–C(13) | 1.396(7) | C(22)–C(23) | 1.400(6) |
| C(13)–C(14) | 1.402(7) | C(23)–C(24) | 1.375(9) |
| C(14)–C(15) | 1.377(9) | C(24)–C(25) | 1.396(8) |
| C(15)–C(16) | 1.400(7) | C(25)–C(26) | 1.394(6) |
| C(16)–C(11) | 1.407(6) | C(26)–C(21) | 1.402(8) |
| C(12)–H(12) | 0.97(7) | C(22)–H(22) | 1.02(8) |
| C(13)–H(13) | 1.03(9) | C(23)–H(23) | 1.01(7) |
| C(14)–H(14) | 0.98(7) | C(24)–H(24) | 0.94(5) |
| C(15)–H(15) | 0.92(5) | C(25)–H(25) | 1.02(13) |
| C(16)–H(16) | 1.09(9) | C(26)–H(26) | 0.98(7) |

(*b*) Angles

| | | | |
|---|---|---|---|
| C(1)–Pt–C(2) | 37.2(1) | C(1)–C(2)–Pt | 71.4(3) |
| C(1)–Pt–C(1′) * | 152.8(1) | C(2)–C(1)–Pt | 71.3(3) |
| C(2)–Pt–C(2′) * | 151.2(1) | | |
| C(1)–Pt–C(2′) | 155.9(1) | | |
| C(2)–Pt–C(1′) | 155.9(1) | | |
| C(2)–C(1)–C(11) | 154.1(5) | C(1)–C(2)–C(21) | 152.4(5) |
| C(16)–C(11)–C(12) | 119.6(4) | C(22)–C(21)–C(26) | 119.4(4) |
| C(11)–C(12)–C(13) | 120.6(4) | C(21)–C(26)–C(25) | 120.2(5) |
| C(12)–C(13)–C(14) | 119.1(6) | C(26)–C(25)–C(24) | 119.7(6) |
| C(13)–C(14)–C(15) | 120.7(5) | C(25)–C(24)–C(23) | 120.4(4) |
| C(14)–C(15)–C(16) | 120.6(4) | C(24)–C(23)–C(22) | 120.4(5) |
| C(15)–C(16)–C(11) | 119.3(5) | C(23)–C(22)–C(21) | 119.7(5) |
| C(1)–C(11)–C(16) | 119.1(5) | C(2)–C(21)–C(26) | 119.9(4) |
| C(1)–C(11)–C(12) | 121.3(3) | C(2)–C(21)–C(22) | 120.5(5) |

* Atoms C(1′) and C(2′) are related to C(1) and C(2) by a two-fold rotation axis.

The molecular structure of greatest interest for comparison with (1) is that of [Pt(PhC$_2$Ph)(PPh$_3$)$_2$].[10] Unfortunately, the *X*-ray diffraction studies on the latter compound were difficult due to the existence of mono- and tri-clinic forms. However, it is firmly established that in [Pt(PhC$_2$Ph)(PPh$_3$)$_2$] the metal is in an essentially trigonal configuration, but with the tilt of the acetylenic bond with respect to the P–Pt–P plane being about 10°. The benzene rings of the acetylene are bent back at an angle of 40° from linear. In complex (1) this bend-back angle (α) is 27°, suggesting less back bonding than in [Pt(PhC$_2$Ph)(PPh$_3$)$_2$], as would be expected in view of the σ-donor properties of the triphenylphosphine ligands. This is supported by the relative frequencies of the C≡C stretching vibrations in the i.r. spectra of the two complexes, discussed below. The platinum–carbon and the acetylenic C–C distances in (1) and in [Pt(PhC$_2$Ph)(PPh$_3$)$_2$] are very similar, but because of the difficulties encountered in the study of the triphenylphosphine complex comparisons are not useful. However, *X*-ray diffraction studies[11] have also been carried out on the closely related species [Pt(PhC$_2$Me)(PPh$_3$)$_2$]. In the latter the co-ordination around the platinum is also essentially trigonal if the co-ordinated triple bond of the alkyne is assumed to occupy one co-ordination site. The departure of the *cis*-bent MeC≡CPh moiety from linearity is approximately 40°, as in the diphenylacetylene analogue. The co-ordinated C≡C length is 1.277(25) Å and the mean Pt–C distance is 2.029(15) Å. Within experimental error, both these distances are the same as those found for (1).

TABLE 4

Some least-squares planes for complex (1) in the form $Ax + By + Cz = D$, where $x$, $y$, and $z$ are fractional co-ordinates[a]

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

$$6.843x + 3.958y + 4.003z = 3.640$$

Plane (2):[a] Pt, C(1′), C(2′)

$$6.833x - 3.976y + 3.973z = 1.768$$

Plane (3):[b] C(11), C(12), C(13), C(14), C(15), C(16)

$$4.569x + 2.943y + 8.325z = 3.452$$

Plane (4): C(21), C(22), C(23), C(24), C(25), C(26)

$$3.962x + 3.727y + 7.652z = 3.111$$

Angles (°) between the least-squares planes: (1)–(2) 82; (1)–(3) 20; (3)–(4) 9; (1)–(4) 16.

[a] Atoms C(1′) and C(2′) are related to C(1) and C(2) by the two-fold rotation axis through Pt. [b] Maximum deviation from least-squares planes through the 14 C and the Pt atom of Pt(C$_2$Ph$_2$) is 0.26 Å.

Having established the pseudo-tetrahedral structure for (1), and following the earlier result[7] with [Pt{Et$_2$(HO)CC$_2$C(OH)Et$_2$}$_2$], the question arises as to whether in the compounds (1)—(12) rotation of the acetylene ligands occurs in solution around the axis formed by the metal and the midpoint of the C≡C linkages. Extended-Hückel calculations [12] have shown that the molecular symmetry found for the [Pt(alkyne)$_2$] species is favoured over the alternative structure in which the platinum and the four contact-carbon atoms are coplanar, because of enhanced $\pi$ back donation in the ' tetrahedral ' structure. Nevertheless, in solution the barrier to rotation might be low enough to allow dynamic behaviour. Variable-temperature $^1$H n.m.r. studies on complexes (1)—(12) (Table 1) would not, however, lead to detection of rotation of acetylene ligands since with non-rotation there would not be inequivalence of protons on substituent groups. A rotational process could only be observed with those [Pt(alkyne)$_2$] complexes derived from unsymmetrical alkynes of the type RC≡CR$^1$R$^2$R$^3$, provided $R^1 \neq R^2 \neq R^3$ or $R^1 = R^2 \neq R^3$. By preparing complexes of the type [Pt{RC$_2$C(OH)Me$_2$}$_2$] it was hoped to carry out variable-temperature $^1$H n.m.r. studies to measure the free energy of activation for rotation, since the methyl substituents are inequivalent if there is no alkyne rotation, whereas equivalence arises if rotation occurs. However, this study [13] proved futile. Although it was established that alkyne rotation did not occur at ambient temperatures, in contrast to ethylene rotation in the species [Pt(C$_2$H$_4$)$_2$(PR$_3$)],[14] the broadness of the resonances and the temperature-dependent shifts suggested the presence of rotamers of the alkyl groups. Above 50 °C, collapse to a single Me resonance was observed, but because of these complications no values of the free energy of rotation could be calculated.

The acetylene stretches of transition-metal alkyne complexes in the i.r. have long been used for characterisation, and to assess the degree of metal–acetylene $\pi$ back bonding. For the complex [Pt(PhC$_2$Ph)(PPh$_3$)$_2$] $\nu_{max.}$(C≡C) occurs at 1 754 compared with 2 223 cm$^{-1}$ (Raman) for the free acetylene. With (1) the corresponding band appears at 1 881 cm$^{-1}$, indicating a lower degree of metal–ligand back bonding than in the triphenylphosphine complex. Table 5 lists for complexes (1)—(12) the values of $\nu_{max.}$(C≡C), together with those for the uncomplexed acetylenes. Also given is the change in frequencies [$\Delta\nu$(C≡C)] upon co-ordination.[15,16] These are (280—340 cm$^{-1}$) not as large as those found (450—510 cm$^{-1}$) for complexes [Pt(RC$_2$R)(PR$_3$)$_2$],[17,18] nor for the compounds [Pt(RC$_2$R)(cod)] discussed below.

Two inferences may be drawn from the i.r. data in Table 5. First, there is little change in $\Delta\nu$(C≡C) between the aryl- and the alkyl-acetylene complexes. This is perhaps surprising when the difference in inductive effects between a tertiary-butyl and a phenyl substituent is considered. The data provide, however, fairly strong evidence that complexes (2)—(4) have the postulated structure. Secondly, the introduction of a trimethylsilyl substituent onto the acetylenic carbon results in a lowering of $\Delta\nu$(C≡C) relative to that experienced by the other complexes. The measurement of vertical ionisation potentials, and i.r.[19] and $^{13}$C n.m.r.[20] spectroscopic studies, has provided evidence for considerable electron delocalisation from a carbon–carbon triple bond into empty *d* orbitals of a substituent silicon atom. Thus for the acetylenes involved in complexes (8), (9), and [Pt(Me$_3$SiC$_2$CH$_2$SiMe$_3$)$_2$] [$\nu_{max.}$(C≡C) 1 857 cm$^{-1}$, $\Delta\nu$(C≡C) 307 cm$^{-1}$],[13] the canonical form $R{-}\overset{+}{C}{=}C{=}\overset{-}{Si}Me_3$ must be considered to operate in the free acetylene leading to smaller values of $\Delta\nu$(C≡C) upon metal co-ordination. It is this effect, rather than $\pi$ back bonding, which is responsible for the data for (8) and (9) in Table 5.

TABLE 5

Infrared data (cm$^{-1}$) for the complexes [Pt(R$^1$C$_2$R$^2$)$_2$] (1)—(12), [Pt(R$^1$C$_2$R$^2$)(cod)] (13)—(17), and [Pt(R$^1$C$_2$R$^2$)(CNBu$^t$)$_2$] (18)—(20)

| Complex | R$^1$ | R$^2$ | $\nu_{max.}$(C≡C) free ligand | $\nu_{max.}$(C≡C) complex [a] | $\Delta\nu$(C≡C) [b] |
|---|---|---|---|---|---|
| (1) | Ph | Ph | 2 223 | 1 881 | 342 |
| (2) | Me | Me | 2 270 [c] | 1 924 | 346 |
| (3) | Et | Et | | 1 910 | |
| (4) | Bu$^t$ | Me | 2 246 | 1 906 | 350 |
| (5) | Ph | Me | 2 234 | 1 892 | 342 |
| (6) | C$_6$H$_4$Me-4 | C$_6$H$_4$Me-4 | 2 212 | 1 872 | 340 |
| (7) | Bu$^t$ | Bu$^t$ | 2 238 | 1 890 | 348 |
| (8) | Bu$^t$ | SiMe$_3$ | 2 155 | 1 845 | 310 |
| (9) | Ph | SiMe$_3$ | 2 125 | 1 840 | 285 |
| (10) | CH$_2$SiMe$_3$ | CH$_2$SiMe$_3$ | 2 193 [d] | 1 878 | 315 |
| (11) | C$_6$H$_4$OMe-4 | C$_6$H$_4$OMe-4 | 2 214 | 1 873 | 341 |
| (12) | C(OH)Me$_2$ | C(OH)Me$_2$ | 2 224 | 1 879 | 345 |
| (13) | Ph | Ph | 2 223 | 1 740 | 483 |
| (14) | C$_6$H$_4$Me-4 | C$_6$H$_4$Me-4 | 2 212 | 1 744 | 468 |
| (15) | C$_6$F$_5$ | C$_6$F$_5$ | 2 246 | 1 750 | 496 |
| (16) | C$_6$F$_4$OMe-4 | C$_6$F$_4$OMe-4 | 2 234 | 1 733 | 501 |
| (17) | CF$_3$ | CF$_3$ | 2 300 | 1 790 [e] | 510 |
| (18) | C$_6$F$_5$ | C$_6$F$_5$ | 2 246 | 1 769 | 477 |
| (19) | C$_6$F$_4$OMe-4 | C$_6$F$_4$OMe-4 | 2 234 | 1 736 | 498 |
| (20) | Ph | Ph | 2 223 | 1 741 | 482 |

[a] Measured in Nujol. [b] $\Delta\nu$(C≡C) = $\nu_{max.}$(C≡C) for free alkyne — $\nu_{max.}$(C≡C) for metal-co-ordinated alkyne. [c] Ref. 15. [d] Ref. 19. [e] Ref. 1(*a*).

Davies and Payne [15] have observed a linear correlation between $\Delta\nu(C{\equiv}C)$ and the bend-back angle ($\alpha$) for a number of acetylene complexes involving different transition metals. Interestingly, the parameters for (1) [$\Delta\nu(C{\equiv}C)$ 342 cm$^{-1}$, $\alpha = 27°$] place it at an intermediate position on the straight line between the extremes of the cationic 'electron-poor' platinum(II) complex *trans*-$[PtMe(MeC_2Me)(PMe_2Ph)_2]^+$ and the neutral 'electron-rich' platinum(0) complex $[Pt(CF_3C_2CF_3)(PPh_3)_2]$.

As a preliminary to measuring the $^{13}C$ n.m.r. spectra of the complexes (1)—(12), the spectra of the acetylene ligands themselves were recorded, so as to obtain values for the chemical shifts of the acetylenic carbon atoms of the free ligands (Table 6). In order to make correct assignments several other acetylenes were measured, and data for these are also included in Table 6.

TABLE 6

Carbon-13 n.m.r. chemical shifts ($\delta$)[a] for the acetylenic carbon atoms in the molecules $R^1C{\equiv}CR^2$ and in the complexes $[Pt(R^1C_2R^2)_2]$

| | | | Free acetylene[b] | | Platinum complex[c] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $CR^1$ | $CR^2$ | $CR^1$ | $\Delta(CR^1)$ | $^1J(PtCR^1)$ | $CR^2$ | $\Delta(CR^2)$ | $^1J(PtCR^2)$ | $\Delta(C_{mean})$ | $^1J(PtC_{mean})$ |
| (2)[d] | Me | Me | 74.3 | 74.3 | | | | | | | | |
| (3) | Et | Et | 80.9 | 80.9 | 121.3 | 40.4 | 266 | 121.3 | 40.4 | 266 | 40.4 | 266 |
| (7) | Bu$^t$ | Bu$^t$ | 86.8 | 86.8 | 128.4 | 41.6 | 286 | 128.4 | 41.6 | 286 | 41.6 | 286 |
| (1) | Ph | Ph | 89.6 | 89.6 | 124.8 | 35.2 | 311 | 124.8 | 35.2 | 311 | 35.2 | 311 |
| (6)[e] | $C_6H_4Me$-4 | $C_6H_4Me$-4 | 88.6 | 88.6 | 124.4 | 36.5 | 310 | 124.4 | 36.5 | 310 | 36.5 | 310 |
| (11)[f] | $C_6H_4OMe$-4 | $C_6H_4OMe$-4 | 87.9 | 87.9 | 123.7 | 35.8 | 290 | 123.7 | 35.8 | 290 | 35.8 | 290 |
| (10) | $CH_2SiMe_3$ | $CH_2SiMe_3$ | 75.5 | 75.5 | 113.0 | 37.5 | 266 | 113.0 | 37.5 | 266 | 37.5 | 266 |
| | $SiMe_3$ | $SiMe_3$ | 113.8 | 113.8 | | | | | | | | |
| | $C(SiMe_3)_3$ | $C(SiMe_3)_3$ | 79.1 | 79.1 | | | | | | | | |
| (4) | Bu$^t$ | Me | 87.8 | 73.7 | 130.8 | 41.6 | 292 | 113.5 | 39.8 | 260 | 40.7 | 276 |
| (5) | Ph | Me | 85.8 | 79.8 | 121.9 | 36.1 | 276 | 118.5 | 38.7 | 303 | 37.4 | 290 |
| | $SiMe_3$ | Me | 83.1[g] | 102.3 | | | | | | | | |
| (8) | Bu$^t$ | $SiMe_3$ | 115.0[h] | 81.7 | 151.9 | 36.0 | 415 | 114.2 | 32.6 | 131 | 34.3 | ·273 |
| (9) | Ph | $SiMe_3$ | 105.1[i] | 93.8[i] | 139.0 | 33.9 | 423 | 128.3 | 34.5 | 171 | 34.2 | 297 |
| | $CH_2SiMe_3$[j] | $SiMe_3$ | 105.6[k] | 83.0[k] | 137.0 | 31.4 | 372 | 112.7 | 34.1 | 137 | 32.8 | 255 |
| | $C_6H_4Me$-4 | Ph | 88.9 | 89.7 | | | | | | | | |
| | $C_6H_4OMe$-4 | Ph | 88.0 | 89.3 | | | | | | | | |

[a] Hydrogen-1 decoupled; chemical shifts ($\delta$) relative to $SiMe_4$, positive values to high frequency. Coupling constants in Hz. [b] Measured in $CDCl_3$. [c] Measured at −60 °C in $CDCl_3$, unless otherwise stated. [d] Spectrum of complex not recorded, due to instability. [e] Spectrum of complex measured at −15 °C. [f] Spectrum of complex recorded at 10 °C. [g] $^1J(SiC)$ 87, $^2J(SiC)$ 17 Hz. [h] $^1J(SiC)$ 87, $^2J(SiC)$ 16 Hz. [i] Lit.,[20] 104.4 [$^2J(SiC)$ 16.1] and 92.5 p.p.m. [$^1J(SiC)$ 83.6 Hz]. [j] Data for complex from ref. 13. [k] Assignment may be reversed.

Assignment of acetylenic-carbon signals was generally based on comparison with those of related alkynes. For example, $MeC_2Me$ has an acetylenic-carbon resonance at 74.3 p.p.m. and Bu$^t$C$_2$Bu$^t$ at 86.8 p.p.m.; it therefore follows that the resonance of Bu$^t$C$_2$Me at 87.8 p.p.m. is assigned to *C*Bu$^t$ and that at 73.7 p.p.m. to *C*Me. The increasing inductive effect of progressively more substituted alkyl groups is seen in the deshielding of the acetylenic carbons in the series $MeC_2Me$ (74.3), $EtC_2Et$ (80.9), and Bu$^t$C$_2$Bu$^t$ (86.8 p.p.m.).

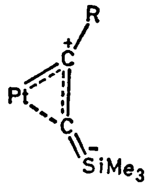
Whereas differences among the aryl alkynes are fairly small, the chemical shifts of the acetylenic carbons of the alkynes with trimethylsilyl substituents proved rather anomalous. Assignment of these resonances by comparison with those in related species containing only hydrocarbon substituents was quickly found to be inaccurate and misleading. However, prolonged data collection in the presence of the paramagnetic relaxant $[Cr(acac)_3]$ (acac = pentane-2,4-dionate) allowed positive identification of the acetylenic carbons bound directly to silicon by virtue of their large silicon–carbon coupling constants (Table 6). This method has previously been used[20] to assign the acetylenic carbon resonances in $PhC{\equiv}CSiMe_3$.

Although deshielding of the acetylenic carbon $Me_3Si\mathit{C}$ relative to $Me_3SiCH_2\mathit{C}$ is expected, the deshielding of the second acetylenic carbon $Me_3SiC\mathit{C}$ in the alkynes $Me_3SiC_2R$ is attributed to a significant contribution of a dipolar resonance form $Me_3Si{-}C{\equiv}C{-}R \longleftrightarrow Me_3\bar{S}i{=}C{=}\overset{+}{C}{-}R$, mentioned above. This proposal has been substantiated by the measurement[21] of $^1J(C{\equiv}C)$ in the alkyne $Et_3SiC_2SiEt_3$. The value of 101.4 Hz is midway between that observed for an alkyl- or aryl-substituted triple bond (150—180 Hz) and the value for ethylene (67.6 Hz).

The $^{13}C$ n.m.r. resonances of the acetylenic carbons of compounds (1)—(12) are also listed in Table 6. For all complexes there is a downfield shift of the acetylenic resonances [$\Delta(CR)$] of the order of 30—40 p.p.m. upon metal co-ordination. Mean values for the asymmetrically substituted alkynes have been calculated, and are listed on the right-hand side of the Table. This averaging process reduces the variation in $\Delta(CR)$ and, when applied also to the one-bond platinum–carbon coupling constant, shows the mean value of this parameter to be surprisingly constant (255—310 Hz). Assignment of the acetylenic resonances of the asymmetrically substituted alkyne complexes was based on the assumption that the downfield shift of the acetylenic carbons on metal co-ordination would be of the same magnitude for each carbon. However, verification of this assignment was provided for complex (9) by the synthesis of $Ph^{13}C{\equiv}CSiMe_3$ and a study of its spectrum which enabled a positive assignment to be made.

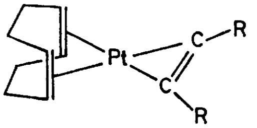
The $^{13}$C n.m.r. spectra of the alkyl-alkyne complexes (3), (4), and (7) show only a small variation of the n.m.r. parameters with respect to increasing inductive effect. This is illustrated by the small increase in the mean values of Δ(*C*R) and $^{1}J$(PtC) along the series [Pt(EtC$_2$Et)$_2$] (3), [Pt(Bu$^t$C$_2$Me)$_2$] (4), and [Pt(Bu$^t$C$_2$Bu$^t$)$_2$] (7). The data for the aryl-alkyne complexes (1), (6), and (11) are, as expected, essentially very similar except for a slightly smaller value of $^{1}J$(PtC) for (11). No explanation can be found to account for this observation.

Once again, data for the silyl-alkyne-platinum complexes proved the most interesting. It will be observed (Table 6) that there is a large difference in the coupling constants between the trimethylsilyl-substituted acetylenic carbon and the alkyl- or aryl-substituted carbon. However, the mean value of $^{1}J$(PtC) does not differ substantially from other values obtained, and also reflects the presence of the alkyl or aryl substituent. Thus, the order of average values of $^{1}J$(PtC) in the bis(alkyne)platinum complexes [Pt(Me$_3$SiCH$_2$C$_2$SiMe$_3$)$_2$] [13] (255) < [Pt(Bu$^t$C$_2$SiMe$_3$)$_2$] (8) (273) < [Pt(PhC$_2$SiMe$_3$)$_2$] (9) (297 Hz) is mirrored in the series [Pt(Me$_3$SiCH$_2$C$_2$CH$_2$SiMe$_3$)$_2$] (10) (266) < [Pt(Bu$^t$C$_2$Bu$^t$)$_2$] (7) (286) < [Pt(PhC$_2$Ph)$_2$] (1) (311 Hz). The explanation for the large disparity between the silyl- and the alkyl- or aryl-substituted acetylenic carbons [values of $^{1}J$(PtC) being a factor of 2.5 to 3 times larger in the latter than in the former] is found in the polarised canonical form mentioned previously for the free alkyne. The relatively positively charged acetylenic carbon carrying the alkyl or aryl substituent will attract a disproportionate amount of *s*-electron density from the electron-rich platinum(0) nucleus. This can be represented in an extreme form as shown below. It is this larger *s*-electron density in the Pt–CR bond which increases the platinum–carbon coupling constant. The opposite argument of course applies to the silyl-substituted carbon. This electronic polarisation should manifest itself structurally, not only by differing bend-back angles, but primarily in the difference between the acetylenic carbon–platinum bond lengths; that carrying the trimethylsilyl substituent should be significantly longer.

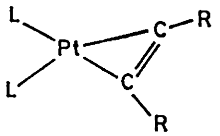


It was mentioned earlier that [Pt(cod)$_2$] reacts with certain alkynes to afford complexes [Pt(alkyne)(cod)]. We have also found that mixing equimolar amounts of [Pt(cod)$_2$] and diphenylacetylene at −20 °C affords the complex (13), which can react with a second mol of diphenylacetylene to give (1). This demonstrates that complexes (1) and (8)—(12) form *via* stepwise replacement of cyclo-octa-1,5-diene. In some cases, however, this second step does not occur and it is only possible to obtain the [Pt(alkyne)(cod)] species even in the presence of excess of alkyne. Thus the pentane-mediated reactions of [Pt(cod)$_2$] with excess or stoicheiometric amounts of 4-MeC$_6$H$_4$C≡CC$_6$H$_4$Me-4′, C$_6$F$_5$C≡CC$_6$F$_5$, and 4-MeOC$_6$F$_4$C≡CC$_6$F$_4$OMe-4′ affords the complexes (14), (15), and (16), respectively. The related compound (17) has previously been prepared.[1a]

Reaction of compounds (15) and (16) with tertiary-butyl isocyanide results in displacement of the cod ligand and formation of the complexes (18) and (19), respectively. Compounds (14)—(16), and (18) and (19), were fully characterised by i.r. (Table 5) and $^1$H n.m.r. spectroscopy, and by microanalysis. It is assumed that trigonal-planar stereochemistry for the metal occurs in complexes (13)—(20) as has been found in several *X*-ray diffraction studies of molecules of this type.[10,11,15,22,23]



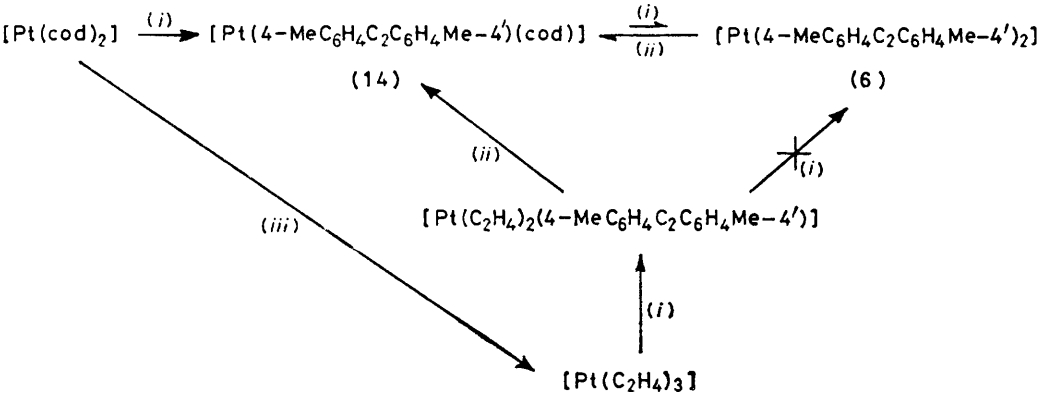
| | R |
|---|---|
| (13) | Ph |
| (14) | $C_6H_4Me$-4 |
| (15) | $C_6F_5$ |
| (16) | $C_6F_4OMe$-4 |
| (17) | $CF_3$ |



| | L | R |
|---|---|---|
| (18) | CNBu$^t$ | $C_6F_5$ |
| (19) | CNBu$^t$ | $C_6F_4OMe$-4 |
| (20) | CNBu$^t$ | Ph |
| (22) | $PMe_3$ | Ph |
| (23) | $PEt_3$ | Ph |
| (25) | $PEt_3$ | Me |
| (26) | $AsEt_3$ | Ph |

During the course of our work we also prepared the complex [Ni(4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′)(cod)] (21) by treating [Ni(cod)$_2$] with 4-MeOC$_6$F$_4$C≡CC$_6$F$_4$OMe-4′. The i.r. spectrum of (21) shows $\nu_{max.}$(C≡C) at 1 788 cm$^{-1}$ [Δν(C≡C) 446 cm$^{-1}$]. Data for the platinum analogue (16) are given in Table 5.

Formation of the cyclo-octa-1,5-diene complexes (15)—(17) rather than the [Pt(alkyne)$_2$] compounds might be expected for the fluoro-organoacetylenes since they are better π acceptors than the corresponding alkyl-, aryl-, or silyl-acetylenes as evidenced by the greater lowering [Δν(C≡C)] of $\nu_{max.}$(C≡C) (Table 5). The enhanced electron-withdrawing properties presumably result in a greater degree of σ donation to the platinum from the cod ligand which raises the energy for further cod displacement. However, the isolation of (14) rather than [Pt(4-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me-4′)$_2$] (6) was unexpected, since at first sight it seems unlikely that there is much difference between 4-MeC$_6$H$_4$C≡CC$_6$H$_4$Me-4′ and PhC≡CPh in donor acceptor ability, as evidenced by the similar Δν(C≡C) values for complexes (1) and (6) (Table 5). Because the isolation of (14) might be due to a solubility effect, the reaction of [Pt(cod)$_2$] with alkyne was repeated in diethyl ether but with the same result. Prior displacement of the cyclo-octa-1,5-diene with ethylene, thus generating [Pt(C$_2$H$_4$)$_3$] in the presence of cod, also produced compound (14). This suggests that either an equilibrium exists between (6) and (14) (Scheme) and that the latter is favoured or that (6) is never formed by this route. After the initial displacement of ethylene from $[Pt(C_2H_4)_3]$ by the alkyne, presumably affording $[Pt(C_2H_4)_2(4\text{-}MeC_6H_4C_2C_6H_4Me\text{-}4')]$, ethylene substitution in the latter by the cod present may be more favourable than that by $4\text{-}MeC_6H_4C{\equiv}CC_6H_4Me\text{-}4'$. To test this idea, a suspension of (6) in light petroleum was treated with cyclo-octa-1,5-diene. Within 5 min compound (6) had dissolved affording a light brown solution. Removal of volatile material *in vacuo* and i.r. examination of the white residue revealed it to be a mixture of (14) and the uncomplexed alkyne. This result not only favours preferential formation of (14) when an ethylene-saturated solution of $[Pt(cod)_2]$ is treated with $4\text{-}MeC_6H_4C{\equiv}CC_6H_4Me\text{-}4'$ but also indicates that the equilibrium (14) + $4\text{-}MeC_6H_4C{\equiv}CC_6H_4Me\text{-}4' \rightleftharpoons$ (6) + cod lies far to the left.



SCHEME Formation of complexes (6) and (14) (*i*) + $4\text{-}MeC_6H_4C_2C_6H_4Me\text{-}4'$; (*ii*) + cod; (*iii*) + $C_2H_4$

Comparison of the $^{13}C$ n.m.r. spectrum of complex (13) with that of (14) shows by virtue of their coupling constants $^1J(^{195}Pt\text{-}^{13}C)$, 455 and 453 Hz respectively, that there is virtually no difference in the *s* component of the platinum–acetylene bond. The smaller $\Delta\nu(C{\equiv}C)$ value (Table 5) of complex (14) is perhaps therefore attributable to less $\pi$-back bonding to the alkyne in this compound, the inductive effect of the methyl-group substituents possibly having raised the energy of the antibonding orbitals of the alkyne. As a result, in complex (14) $\pi$-back bonding from platinum to the cod ligand is enhanced resulting in stronger platinum–diene bonding than in (13). This presumably accounts for the isolation by Muetterties *et al.*[24] of both $[Ni(4\text{-}MeC_6H_4C_2C_6H_4Me\text{-}4')(cod)]$ and $[Ni_2(\mu\text{-}4\text{-}MeC_6H_4C_2C_6H_4Me\text{-}4')(cod)_2]$ from the reaction between $[Ni(cod)_2]$ and $4\text{-}MeC_6H_4C{\equiv}CC_6H_4Me\text{-}4'$ whereas only the dinickel species $[Ni_2(\mu\text{-}PhC_2Ph)(cod)_2]$, which requires greater back donation to the alkyne, is formed from similar reaction of $[Ni(cod)_2]$ and diphenylacetylene.

Addition of (1) to light petroleum solutions containing excess of $CNBu^t$, $PMe_3$, $PEt_3$, or $PPh_3$ affords complexes (20), (22), (23), and the long known compound $[Pt(PhC_2Ph)(PPh_3)_2]$,[10,25] respectively. Rochon and Theophanides[6] have reported that excess of triphenylphosphine would only replace one alkyne ligand from bis(hydroxyalkyne)platinum complexes such as (12). We have observed that this behaviour is not typical of all $[Pt(alkyne)_2]$ complexes. Thus, for example, $CNBu^t$ replaces both alkyne ligands in (9) to give $[Pt_3(CNBu^t)_6]$.[26]

The $^{13}C$ n.m.r. parameters for the acetylene-carbon atoms in complexes (13), (20), (22), (23), $[Pt(PhC_2Ph)(PPh_3)_2]$, and $[Pt(PhC_2SiMe_3)(PPh_3)_2]$ (24), $[Pt(MeC_2Me)(PEt_3)_2]$ (25), and $[Pt(PhC_2Ph)(AsEt_3)_2]$ (26) are given in Table 7. Complexes (24)—(26) were prepared from $[Pt(cod)_2]$, the appropriate acetylene and 2 mol of $PPh_3$, $PEt_3$, or $AsEt_3$, respectively. Except for complexes (23) and (25), which are very soluble, all the measurements were made on samples with 25% enrichment of $Ph^{13}C{\equiv}CR$ (R = Ph or $SiMe_3$). Whereas the acetylene resonances of complexes (13), (20), and (26) consisted only of a singlet with platinum satellites, those of the platinum complexes (22), (23), (25), and $[Pt(PhC_2Ph)(PPh_3)_2]$, which contain chemically equivalent tertiary phosphine ligands, consisted of a five-line multiplet with platinum satellites typical of an AA'X system. Whilst this multiplet only allowed determination of $|J(AX) + J(BX)|$ [*viz.* $|^2J(PC) + {}^2J(P'C)|$], measurement of the $^{31}P$ n.m.r. spectrum of a $^{13}C$-enriched sample of (21) allowed all the constants to be determined (Table 7).

Complex (24) was synthesised to ascertain whether the polarisation effect observed for the $[Pt(RC_2SiMe_3)_2]$ compounds, discussed earlier, would also be operative for a trigonal complex. Although the central $^{13}C$ resonance consisted of the usual multiplet associated with an ABX spin system, the relevant coupling constants were easily determined from the first-order $^{195}Pt$ satellites. Comparison of $^1J(PtC)$ of (24) with the value for $[Pt(PhC_2Ph)(PPh_3)_2]$ suggests that the effect operates to some degree.

The limited number of $^{13}C$ n.m.r. studies carried out on alkynes bonded to platinum makes comparisons between different types of complex difficult. Moreover, long relaxation times associated with acetylenic carbons have made certain available data suspect. The acetylenic carbons of platinum(II) species appear to undergo an upfield shift of 8—17 p.p.m. upon co-ordination.[27] In contrast, the acetylenic carbons in the complexes [Pt-

(alkyne)$_2$] and [Pt(alkyne)L$_2$] experience, respectively, a 31—42 and 35—44 p.p.m. downfield shift. Coupling constants are also smaller in the platinum(II) complexes, a range of 132—183 Hz being observed.[27] Mention must be made of the parameters reported [28] for the complexes *trans*-[PtMe(MeC$_2$Me)(PMe$_2$Ph)$_2$][PF$_6$] [acetylenic carbon resonance at 69.5 p.p.m., with $^1J$(PtC) 18 Hz] and [Pt(MeC$_2$Me)(PPh$_3$)$_2$] [δ 112.8 p.p.m., $^1J$(PtC) 52 Hz]. The value of $^1J$(PtC) for the latter complex differs so greatly from those of the corresponding compounds (13)—(26) in Table 7 that we felt compelled to reinvestigate its $^{13}$C n.m.r. spectrum. Fortunately [Pt(MeC$_2$Me)(PPh$_3$)$_2$] is readily soluble in [$^2$H$_2$]dichloromethane and in the presence of the paramagnetic relaxation reagent tris(pentane-2,4-dionato)chromium the natural-abundance $^{13}$C n.m.r. spectrum revealed the expected five-line AA′X pattern (δ 113.1 p.p.m.) flanked by identical five-line $^{195}$Pt satellites, as observed in the cases mentioned above. The value of $^1J$(PtC) (274 Hz) obtained from this spectrum agrees well with our other observations. A closer inspection of the separation of lines in the central pattern suggests that the previous workers [28] have mistaken the outer lines of this pattern for the $^{195}$Pt satellites. It follows that the bonding arguments put forward by these workers, based on their incorrect value of $^1J$(PtC), must also be in error.

TABLE 7

Selected $^{13}$C [a] and $^{31}$P [b] n.m.r. data for complexes [Pt(PhC$_2$R)L$_2$] and [Pt(MeC$_2$Me)L$_2$]

| Complex | δ(Ph*C*) or δ(Me*C*) | Δδ(Ph*C*) or Δδ(Me*C*)[c] | Other $^{13}$C resonances (δ) | $^{31}$P(δ) |
|---|---|---|---|---|
| (13) [Pt(PhC$_2$Ph)(cod)] | 132.5<br>(455) | 42.9 | 130.4 [Ph(56)], 128.6 (Ph), 123.5 (Ph)<br>89.9 [CH(89)], 30.7 [CH$_2$(10)] | |
| (20) [Pt(PhC$_2$Ph)(CNBu$^t$)$_2$] | 126.7 [d]<br>(332) | 37.1 | 139.8 [CPt(1 415)], 130.7 [Ph(42)],<br>128.0 (Ph), 126.2 (Ph), 56.6 (*C*Me$_3$),<br>30.6 (Me) | |
| (22) [Pt(PhC$_2$Ph)(PMe$_3$)$_2$] | 131.0<br>(281) {64} | 41.4 | 138.0 (Ph), 128.4 [Ph(33)], 127.8 (Ph),<br>124.7 (Ph), 20.9 [Me(39) {32}] | 29.2 [e] [*J*(PP) 27, *J*(PC) ±73,<br>*J*(P′C) ∓ 9, *J*(PtP) 3 110] |
| (23) [Pt(PhC$_2$Ph)(PEt$_3$)$_2$] | 131.9 [d]<br>(291) {65} | 42.3 | 136.2 (Ph), 127.8 (Ph), 127.7 [Ph(24)],<br>124.7 (Ph), 21.0 [CH$_2$(27) {27}],<br>8.7 [Me(23)] | 10.5 [*J*(PtP) 3 261] |
| [Pt(PhC$_2$Ph)(PPh$_3$)$_2$] | 127.9<br>(299) {61} | 38.3 | | 27.2 [*J*(PtP) 3 445] |
| (24) [Pt(PhC$_2$SiMe$_3$)(PPh$_3$)$_2$] | 146.8 [f]<br>(387) | 41.7 | | 28.0 [*J*(PP) 42, *J*(PtP) 3 534]<br>29.0 [*J*(PP) 42, *J*(PtP) 3 784] |
| (25) [Pt(MeC$_2$Me)(PEt$_3$)$_2$] | 117.1<br>(281) {60} | 43.8 | 22.2 [CH$_2$(27) {27}], 13.6 [C*Me*(22) {22}],<br>8.9 [Me(23)] | |
| (26) [Pt(PhC$_2$Ph)(AsEt$_3$)$_2$] | 125.0<br>(361) | 35.0 | 136.4 (Ph), 128.3 (Ph), 128.2 [Ph(33)],<br>125.6 (Ph), 19.3 [CH$_2$(33)], 10.0 [Me(13)] | |
| [Pt(MeC$_2$Me)(PPh$_3$)$_2$] | 113.1<br>(274) {52} | 38.8 | 10.1 [Me(27) {18}] | 31.2 [*J*(PtP) 3 454] |

[a] Hydrogen-1 decoupled; chemical shifts (δ) in p.p.m. relative to SiMe$_4$, positive values to high frequency. Coupling constants in Hz, *J*(PtC) in parentheses, |*J*(PC) + *J*(P′C)| in braces. Measured in CDCl$_3$ at −50 °C unless otherwise stated. [b] Hydrogen-1 decoupled chemical shifts (δ) in p.p.m. relative to 85% H$_3$PO$_4$ (external), positive values to high frequency. Measured in CDCl$_3$ at room temperature unless otherwise stated. [c] Downfield chemical-shift difference observed on complexation of the acetylene. [d] Measured in CD$_3$C$_6$D$_5$–C$_6$H$_6$ at −50 °C, AB spectrum. [e] Measured at −40 °C. [f] *J*(PC) ± 56, *J*(P′C) ±9 Hz.

## EXPERIMENTAL

Hydrogen-1 and $^{31}$P n.m.r. studies were made with JEOL PFT and PS 100 spectrometers. All spectra were measured in CDCl$_3$ unless stated otherwise. 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. 30—40 °C.

The complexes [Pt(cod)$_2$], [Pt(C$_2$H$_4$)$_3$],[8] [Pt$_3$(CNBu$^t$)$_6$],[26] and [Ni(cod)$_2$] [29] were prepared by literature methods. The alkynes 4-MeOC$_6$F$_4$C≡CC$_6$F$_4$OMe-4′, C$_6$F$_5$C≡CC$_6$F$_5$,[30] Bu$^t$C≡CBu$^t$,[31] Bu$^t$C≡CSiMe$_3$,[32] PhC≡CSiMe$_3$,[20] Me$_3$SiCH$_2$C≡CCH$_2$SiMe$_3$,[19] Me$_3$SiCH$_2$C≡CSiMe$_3$,[33] Me$_3$SiC≡CSiMe$_3$,[34] (Me$_3$Si)$_3$CC≡CC(SiMe$_3$)$_3$,[35] 4-MeC$_6$H$_4$C≡CPh, and 4-MeOC$_6$H$_4$C≡CPh [36] were also prepared by literature methods, and 4-MeC$_6$H$_4$C≡CC$_6$H$_4$Me-4′ and 4-MeOC$_6$H$_4$C≡CC$_6$H$_4$OMe-4′ were obtained by relevant modifications of a synthetic procedure [37] devised for PhC≡CPh. The other alkynes used were commercial samples. Enriched Ph$^{13}$C≡CPh was synthesised by the method of Gough and Trippett.[38] Preparation of PPh$_2$(OMe) required for this synthesis was as for PPh$_2$(OEt).[39] Enriched Ph$^{13}$COCl was prepared by thionyl chloride treatment of benzoic acid,[40] obtained from the reaction of phenylmagnesium bromide with $^{13}$CO$_2$ generated from Ba[$^{13}$CO$_3$].[41] Enriched Ph$^{13}$C≡CSiMe$_3$ [$\nu_{max.}$($^{13}$C≡C) 2 083 cm$^{-1}$] was synthesised by treating [42] Ph$^{13}$C≡CH with LiBu$^n$, followed by addition of SiMe$_3$Cl.

Analytical and yield data for the complexes [Pt(R$^1$C$_2$R$^2$)$_2$] are given in Table 1.

*Preparation of the Bis(alkyne)platinum Complexes* (1)—(12).—(*a*) The complex [Pt(cod)$_2$] (0.205 g, 0.5 mmol) was added portion-wise (15 min) to a stirred solution of diphenylacetylene (0.35 g, 2 mmol) in light petroleum (5 cm$^3$). After stirring for 15 min the volume was reduced *in vacuo* to *ca.* 3 cm$^3$. The supernatant liquid was removed with a syringe and the solid washed (5 × 3 cm$^3$) with light petroleum. Drying *in vacuo* afforded white *microcrystals* of [Pt(PhC$_2$Ph)$_2$] (1) (0.225 g), m.p. 140—145 °C (decomp.); $\nu_{max.}$ at 1 881m (C≡C) 1 595w, 1 575w, 1 490w, 1 445m, 1 330vw, 1 310vw, 1 300vw, 1 290w, 1 270w, 1 180w, 1 160w, 1 075m, 1 035w, 995vw, 980w, 915m, 880m, 830m, 755s, 730m, 690s, 630w, 615w, 580m, 550m, and 510s cm$^{-1}$.

(*b*) To a solution of [Pt(C$_2$H$_4$)$_3$] (0.136 g, 0.5 mmol) in light petroleum (5 cm$^3$) at −40 °C was added MeC$_2$Me (0.21 g, 4 mmol) in light petroleum (2 cm$^3$). The solution was warmed to −25 °C over 4 h by which time it became dark. Filtration through alumina (1 × 7 cm) at −40 °C, reduction of the volume of solution *in vacuo* (−40 °C), and crystallisation (−78 °C) afforded white *needles* of [Pt(MeC$_2$Me)$_2$] (2) (70 mg); $\nu_{\max.}$ at 1 924s (C≡C), 1 367m, 1 204m, 1 127m, 1 036s,br, 805w, 742s, and 576s cm$^{-1}$; $^1$H n.m.r. ([$^2$H$_8$]toluene, −60 °C), τ 7.65 [s, 12 H, $^3J$(PtH) 53 Hz].

(*c*) The compound [Pt(EtC$_2$Et)$_2$] (3) was isolated as white *crystals* in a manner similar to (2); $\nu_{\max.}$ at 1 910s (C≡C), 1 467s, 1 379s, 1 311s, 1 257w,br, 1 119w, 1 088m, 1 066m, 931m, 791m,br, 743w,br, and 668w cm$^{-1}$; $^{13}$C n.m.r. (−60 °C), δ 121.3 [s, *C*CH$_2$, $^1J$(PtC) 266], 17.8 (s, CH$_2$), and 15.6 p.p.m. [s, Me, $^3J$(PtC) 59 Hz].

(*d*) To a solution of [Pt(C$_2$H$_4$)$_3$] (0.136 g, 0.5 mmol) in light petroleum (5 cm$^3$) at −40 °C was added Bu$^t$C$_2$Me (0.13 g, 1.7 mmol) in the same solvent (10 cm$^3$). The solution was kept between −50 and −30 °C for 6 h while nitrogen was bubbled through. The volume was then reduced *in vacuo* (−40 °C) to *ca.* 2 cm$^3$ and the product crystallised at −78 °C. The supernatant liquid was removed, the product redissolved in light petroleum and filtered through alumina (1 × 1 cm) at −30 °C. The solution was reduced in volume to *ca.* 1 cm$^3$ (−40 °C). Crystallisation at −78 °C afforded white *crystals* of [Pt(Bu$^t$C$_2$Me)$_2$] (4) (0.098 g) dried at −30 °C *in vacuo*; $\nu_{\max.}$ at 1 906s (C≡C), 1 386m, 1 371s, 1 270w, 1 251s, 1 205m, 1 052s,br, 1 030m, 930w, 834m, 729m,br, 611m, and 490w cm$^{-1}$. N.m.r.: $^1$H (−60 °C) τ 7.36 [s, 6 H, Me, $^3J$(PtH) 52 Hz] and 7.72 (s, 18 H, Bu$^t$); $^{13}$C (−50 °C), δ 130.8 [s, *C*CMe$_3$, $^1J$(PtC) 292], 113.5 [s, *C*Me, $^1J$(PtC) 260], 31.2 [s, C(*C*H$_3$)$_3$, $^3J$(PtC) 34 Hz], 29.3 (s, *C*Me$_3$), and 9.5 p.p.m. (s, Me).

(*e*) To a solution of [Pt(C$_2$H$_4$)$_3$] (0.11 g, 0.394 mmol) in light petroleum (5 cm$^3$) at −50 °C was added an excess of PhC$_2$Me (0.2 cm$^3$). The solution was warmed to −20 °C over 2 h, by which time an off-white powder had precipitated. The product was washed with cold (−20 °C) light petroleum (3 × 5 cm$^3$) and dried *in vacuo* (−10 °C) affording off-white *microcrystals* of [Pt(PhC$_2$Me)$_2$] (5) (0.102 g); $\nu_{\max.}$ at 3 065w, 3 044w, 1 892w (C≡C), 1 592w, 1 571w, 1 486s, 1 471s, 1 444s, 1 438m, 1 311w, 1 242w, 1 235w(sh), 1 174w, 1 168w(sh), 1 153w, 1 071m, 1 049w,br, 1 027w, 1 002w, 937w, 925w, 768s, 762s, 754m, 748w, 724w, 695s, 688s, 613w, 539w, and 510w cm$^{-1}$. N.m.r.: $^1$H (−50 °C), τ 2.35—2.80 (m, 10 H, Ph) and 7.19 [s, 6 H, Me, $^3J$(PtH) 50 Hz]; $^{13}$C (−50 °C), δ 130.5 [s, Ph, β-C, $^3J$(PtC) 59], 128.3 (s, Ph, γ-C), 127.5 (s, Ph, δ-C), 123.4 (s, Ph, α-C), 121.9 [s, *C*Ph, $^1J$(PtC) 276], 118.5 [s, *C*Me, $^1J$(PtC) 303 Hz], and 10.8 p.p.m. (s, Me).

(*f*) To a suspension of 4-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me-4′ (0.103 g, 0.5 mmol) in light petroleum (10 cm$^3$) was added a solution of [Pt(C$_2$H$_4$)$_3$] (0.056 g, 0.2 mmol) in the same solvent (5 cm$^3$). After *ca.* 1 min a fine white precipitate resulted. The suspension was stirred for 30 min and the supernatant liquid removed. The product was washed with light petroleum (2 × 10 cm$^3$) and dried *in vacuo* affording [Pt(4-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me-4′)$_2$] (6) as white *microcrystals* (0.09 g), m.p. (*in vacuo*) 167 °C (decomp.); $\nu_{\max.}$ at 1 872w (C≡C), 1 606w, 1 510w, 1 502w, 1 409w, 1 309w, 1 215w, 1 180m, 1 112w, 1 040w, 1 028w, 892w, 828s, 820s, 782m, 720w, 688w, 630w, 559m, 525m, and 521(sh) cm$^{-1}$. N.m.r.: $^1$H τ 2.10—2.81 (m, 16 H, C$_6$H$_4$) and 7.60 (s, 12 H, Me); $^{13}$C (−15 °C), δ 139.3 (s, C$_6$H$_4$, δ-C), 130.7 [s, C$_6$H$_4$, β-C, $^3J$(PtH) 61], 129.2 (s, C$_6$H$_4$, γ-C), 124.4 [s, *C*C$_6$H$_4$, $^1J$(PtC) 310 Hz], 121.9 (s, C$_6$H$_4$, α-C), and 21.6 p.p.m. (s, Me).

(*g*) To a solution of [Pt(C$_2$H$_4$)$_3$] (0.136 g, 0.5 mmol) in light petroleum (10 cm$^3$) at −30 °C was added Bu$^t$C$_2$Bu$^t$ (0.152 g, 1.1 mmol). The solution was warmed to room temperature over 2 h and all volatiles were then removed *in vacuo*. The resultant oil was recrystallised from ethanol as pale yellow *crystals* of [Pt(Bu$^t$C$_2$Bu$^t$)$_2$] (7) (0.020 g); $\nu_{\max.}$ at 1 890m (C≡C), 1 479m, 1 460m, 1 391m, 1 366s, 1 268m, 1 230m, 1 202m, 1 034m, 992m, 851m, 797w, 683m, and 539w cm$^{-1}$. N.m.r.: $^1$H (−60 °C), τ 7.75 (s, 36 H, Bu$^t$); $^{13}$C (−50 °C), δ 128.4 [s, *C*Bu$^t$, $^1J$(PtC) 286], 31.8 [s, Me, $^3J$(PtC) 37 Hz], and 28.6 p.p.m. (s, *C*Me$_3$).

(*h*) The compound [Pt(Bu$^t$C$_2$SiMe$_3$)$_2$] (8) was isolated as a yellow *oil* in an analogous manner to (7); $\nu_{\max.}$ at 2 990s, 2 945m, 2 920m, 2 890m, 1 895w,br, 1 845m (C≡C), 1 590w,-br, 1 522w, 1 481m, 1 461m, 1 410w, 1 402w, 1 370m, 1 269(sh), 1 259s, 1 109w,br, 1 039m,br, 954s, 939m, 858vs,br, 771m, 709m, 668m, and 627m cm$^{-1}$. N.m.r.: $^1$H ([$^2$H$_6$]benzene), τ 8.58 (s, 18 H, Bu$^t$) and 9.61 (s, 18 H, Me); $^{13}$C (−50 °C), δ 151.9 [s, *C*Bu$^t$, $^1J$(PtC) 415], 114.2 [s, *C*SiMe$_3$, $^1J$(PtC) 131], 31.5 [s, C(*C*H$_3$)$_3$, $^3J$(PtC), 35], 29.6 (s, *C*Me$_3$), and 0.2 p.p.m. [s, Si(CH$_3$)$_3$, $^3J$(PtC) 24 Hz].

(*i*) To PhC$_2$SiMe$_3$ (0.35 g, 2.0 mmol) in light petroleum (10 cm$^3$) at −20 °C was added portionwise [Pt(cod)$_2$] (0.205 g, 0.5 mmol). The solution was warmed to room temperature with stirring (10 min). All volatiles were removed *in vacuo*, the residue dissolved in light petroleum and cooled (−78 °C) to yield black crystals. The supernatant liquid was removed and the crystals redissolved in light petroleum and filtered through alumina (1 × 5 cm). The resultant clear solution was reduced *in vacuo* in volume and cooled (−78 °C) to yield white *crystals* of [Pt(PhC$_2$SiMe$_3$)$_2$] (9) (0.12 g), m.p. (*in vacuo*) 81—82 °C; $\nu_{\max.}$ at 3 076w, 3 062w, 3 021w, 1 966w, 1 951w, 1 880w, 1 846s (C≡C), 1 834s (C≡C), 1 593m, 1 573w, 1 484s, 1 445s, 1 438(sh), 1 411w, 1 331w, 1 309w, 1 289w, 1 259m, 1 251s, 1 211m, 1 172m, 1 071m, 1 027m, 1 002w, 923m, 901(sh), 879s,br, 843s,br, 763s, 703m, 693s, 673m, 653s, 624m, 602m, 544s, 512w, 419w, and 352w cm$^{-1}$. N.m.r.: $^1$H ([$^2$H$_6$]benzene), τ 2.06 (m, 4 H, Ph), 2.92 (m, 6 H, Ph), and 9.50 (s, 18 H, Me); $^{13}$C (−50 °C), δ 139.0 [s, *C*Ph, $^1J$(PtC) 423], 131.2 [s, Ph, β-C, $^3J$(PtC) 60], 129.3 (s, Ph, δ-C), 128.4 (s, Ph, γ-C), 128.3 [s, *C*SiMe$_3$, $^1J$(PtC) 171], 124.4 (s, Ph, α-C), and 0.0 p.p.m. [s, Me, $^3J$(PtC) 22 Hz].

(*j*) To Me$_3$SiCH$_2$C$_2$CH$_2$SiMe$_3$ (0.670 g, 3.4 mmol) in light petroleum (10 cm$^3$) was added [Pt(cod)$_2$] (0.615 g, 1.5 mmol). The dark brown solution was stirred for 20 min, then all volatiles were removed *in vacuo*. The residue was redissolved in light petroleum, filtered through alumina (1 × 7 cm), and cooled (−25 °C) to produce colourless *crystals* of [Pt(Me$_3$SiCH$_2$C$_2$CH$_2$SiMe$_3$)$_2$] (10). A further crop was obtained by cooling to −78 °C (0.275 g), m.p. (*in vacuo*) 75—76 °C; $\nu_{\max.}$ at 1 878w (C≡C), 1 419w, 1 399w,1 294w, 1 259s, 1 155s, 857s,br, 843s,br, 808w, 763w, 705m,br, and 680w cm$^{-1}$. N.m.r.: $^1$H ([$^2$H$_6$]benzene) τ 6.59 [s, 4 H, CH$_2$, $^2J$(PtH) 65 Hz] and 9.81 (s, 18 H, Me); $^{13}$C (−50 °C), δ 113.0 [s, *C*CH$_2$, $^1J$(PtC) 266 Hz], 13.4 (s, CH$_2$), and −1.6 p.p.m. (s, Me).

(*k*) To a suspension of [Pt(cod)$_2$] (0.274 g, 0.667 mmol) in diethyl ether (10 cm$^3$) and light petroleum (10 cm$^3$) was added 4-MeOC$_6$H$_4$C$_2$C$_6$H$_4$OMe-4′ (0.30 g, 1.4 mmol). The suspension was stirred overnight and all volatiles were then removed *in vacuo*. The residue was washed with light petroleum (3 × 20 cm$^3$) and dried *in vacuo* affording [Pt(4-MeOC$_6$H$_4$C$_2$C$_6$H$_4$OMe-4′)$_2$] (11) as off-white *microcrystals* (0.269 g), m.p. (*in vacuo*) 168 °C; $\nu_{\max.}$ at 1 873w (C≡C), 1 607s, 1 569m, 1 515s, 1 503m, 1 443m, 1 414w, 1 312s, 1 304s, 1 283w, 1 253vs, 1 183m, 1 172vs, 1 134w, 1 097m, 1 035s, 890m, 837vs, 807m, 776w, 726w, 699m, 621w, 577m, 565w, and 540m cm$^{-1}$. N.m.r.: $^{1}$H $\tau$ 2.05—3.09 (m, 16 H, C$_6$H$_4$), and 6.13 (s, 12 H, OMe); $^{13}$C (10 °C), $\delta$ 160.0 (s, C$_6$H$_4$, $\delta$-C), 132.0 [s, C$_6$H$_4$, $\beta$-C, $^{3}J$(PtC) 60], 123.7 [s, *C*C$_6$H$_4$, $^{1}J$(PtC) 290 Hz], 117.2 (s, C$_6$H$_4$, $\alpha$-C), 113.7 (s, C$_6$H$_4$, $\gamma$-C), and 55.2 p.p.m. (s, OMe).

(*l*) To a solution of Me$_2$(HO)CC$_2$C(OH)Me$_2$ (0.09 g, 0.63 mmol) in toluene (10 cm$^3$) was added [Pt(cod)$_2$] (0.125 g, 0.30 mmol). The solution was stirred for 5 min after which time a fine gelatinous precipitate had developed. Precipitation was completed with light petroleum (20 cm$^3$) and the supernatant liquid removed. The product was recrystallised from acetone as white *needles* of [Pt{Me$_2$(HO)CC$_2$C(OH)Me$_2$}$_2$] (12) (0.090 g); $\nu_{\text{max.}}$ at 3 295vs,vbr, 1 889s (C≡C), 1 472s,br, 1 430m,br, 1 385s, 1 371s, 1 246m, 1 181vs,br, 978s, 952w, 868s, 852w, 748m,br, 706m, 602w, 561w, and 500w cm$^{-1}$.

*Preparation of the Complexes* [Pt(alkyne)(cod)] (13)—(16).—(*a*) To a suspension of [Pt(cod)$_2$] (0.411 g, 1 mmol) in light petroleum (10 cm$^3$, −20 °C) was added diphenylacetylene (0.178 g, 1 mmol) dissolved in the same solvent (5 cm$^3$) with stirring. After 15 min, pale pink *crystals* of [Pt(PhC$_2$Ph)(cod)] (13) formed, and were washed with light petroleum and dried *in vacuo* at 0 °C (0.40 g, 85%), m.p. 84—85 °C (Found: C, 54.0; H, 4.7. C$_{22}$H$_{22}$Pt requires C, 54.9; H, 4.6%); $\nu_{\text{max.}}$ at 3 060m, 1 736s (C≡C), 1 595m, 1 495s, 1 450s, 1 165m, 1 080s, 1 035s, 980m, 770vs, 725m, 700s, and 530s cm$^{-1}$. N.m.r.: $^{1}$H (−20 °C), $\tau$ 2.60 (m, 10 H, Ph), 4.20 [s, 4 H, CH, $^{2}J$(PtH) 58 Hz], and 7.56 (s, 8 H, CH$_2$).

A sample of [Pt(Ph$^{13}$C≡CPh)(cod)] was prepared in an analogous manner using Ph$^{13}$C≡CPh.

(*b*) To a suspension of 4-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me-4′ (0.206 g, 1.0 mmol) in light petroleum (20 cm$^3$) was added [Pt(cod)$_2$] (0.411 g, 1.0 mmol). The mixture was stirred for 2 h, allowed to settle, and the supernatant liquid removed. The precipitate was washed with light petroleum (2 × 10 cm$^3$) and dried *in vacuo* affording [Pt(4-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me-4′)(cod)] (14) as pale yellow *microcrystals* (0.473 g, 93%), m.p. 107—110 °C (decomp.) (Found: C, 56.0; H, 5.2. C$_{24}$H$_{26}$Pt requires C, 56.6; H, 5.1%); $\nu_{\text{max.}}$ at 1 744 (C≡C), 1 504m,br, 1 339w, 1 307w, 1 248w, 1 185w, 1 175w, 1 163w, 1 109w, 1 023w, 969m, 900w, 889w, 849w, 827s, 788w, 778w, 721w, 699w, 567w, and 527m cm$^{-1}$. N.m.r.: $^{1}$H (−50 °C), $\tau$ 2.58 (m, 8 H, C$_6$H$_4$), 4.24 [s, 4 H, CH, $^{2}J$(PtH) 57 Hz], and 7.60 (s, 8 H + 6 H, CH$_2$ + Me); $^{13}$C (−50 °C), $\delta$ 137.2 (s, C$_6$H$_4$, $\delta$-C), 131.6 [s, *C*C$_6$H$_4$, $^{1}J$(PtC) 453], 130.2 [s, C$_6$H$_4$, $\beta$-C, $^{3}J$(PtC) 56], 129.0 (s, C$_6$H$_4$, $\gamma$-C + $\alpha$-C), 89.5 [s, CH, $^{1}J$(PtC) 90 Hz], 30.6 (s, CH$_2$), and 21.5 p.p.m. (s, Me).

(*c*) To a solution of C$_6$F$_5$C$_2$C$_6$F$_5$ (0.306 g, 0.85 mmol) in light petroleum (35 cm$^3$) was added [Pt(cod)$_2$] (0.176 g, 0.43 mmol). The resultant yellow solution was cooled, stirred for 30 min, then cooled (−78 °C) to remove excess of C$_6$F$_5$C$_2$C$_6$F$_5$. Removal and concentration of the supernatant liquid resulted in the precipitation of light yellow *crystals* of [Pt(C$_6$F$_5$C$_2$C$_6$F$_5$)(cod)] (15) (0.111 g, 39%), m.p. (*in vacuo*) 121—122 °C (decomp.) (Found: C, 39.9; H, 1.8; F, 28.9. C$_{22}$H$_{12}$F$_{10}$Pt requires C, 39.9; H, 1.8; F, 28.7%); $\nu_{\text{max.}}$ at 1 750m (C≡C), 1 512s, 1 493vs, 1 408m, 1 341w, 1 326w, 1 307w, 1 190w, 1 176w, 1 151w, 1 110m, 1 042m, 1 026s, 1 006s, 995vs, 983(sh), 916m, 871w, 830(sh), 823m, 790m, 772w, 742w, 720m, 667w, 586w, and 470w cm$^{-1}$; $^{1}$H n.m.r. ([$^{2}$H$_6$]benzene) $\tau$ 4.51 [s, 4 H, CH, $^{2}J$(PtH) 61 Hz], and 7.12 (m,br, 8 H, CH$_2$).

(*d*) To a supension of [Pt(cod)$_2$] (0.205 g, 0.5 mmol) in diethyl ether (10 cm$^3$) was added 4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′ (0.191 g, 0.5 mmol). After *ca.* 2 min all insoluble material had dissolved to give a yellow solution. This was stirred for 20 min, all volatiles were removed *in vacuo*, and the product was washed with light petroleum (2 × 5 cm$^3$) and dried *in vacuo* affording [Pt(4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′)(cod)] (16) as yellow *microcrystals* (0.281 g, 87%). An analytical sample of (16) (Found: C, 42.4; H, 2.6. C$_{24}$H$_{18}$F$_8$O$_2$Pt requires C, 42.1; H, 2.6%), m.p. (*in vacuo*) 107—110 °C, was obtained by recrystallisation from diethyl ether–light petroleum; $\nu_{\text{max.}}$ at 1 733m (C≡C), 1 639m, 1 583w, 1 498s, 1 479s,br, 1 431s, 1 417s, 1 401m, 1 334w, 1 326w, 1 303w, 1 284w, 1 202m, 1 194(sh), 1 167m, 1 125m, 1 059s, 993s, 922s, 877w, 872w, 822w, 784m, 761w, 741w, 715w, 675w, 634w, and 465w cm$^{-1}$; $^{1}$H n.m.r. ([$^{2}$H$_6$]acetone), $\tau$ 4.39 [s, 4 H, CH, $^{2}J$(PtH) 61], 5.84 [t, 6 H, OCH$_3$, $^{5}J$(FH) 1 Hz], and *ca.* 6.6 (m, 8 H, CH$_2$).

*Synthesis of the Complex* [Ni(4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′)(cod)].—To a solution of [Ni(cod)$_2$] (0.138 g, 0.5 mmol) in diethyl ether (10 cm$^3$) was added 4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′ (0.191 g, 0.5 mmol). The suspension was stirred for 6 h to form a cloudy deep yellow solution. The solution was filtered and cooled (−20 °C) for 4 d affording orange *crystals* of [Ni(4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′)(cod)] (21) (0.254 g, 89%) (Found: C, 52.4; H, 3.3. C$_{24}$H$_{18}$F$_8$NiO$_2$ requires C, 52.5; H, 3.3%); $\nu_{\text{max.}}$ at 1 788m (C≡C), 1 642w, 1 531m, 1 506s, 1 481s, 1 437s, 1 422m, 1 247w, 1 204m, 1 170w, 1 133w, 1 124w, 1 062s, 996s, 956w, 926w, 883w, 865w, 814w, 791w, 755w, 733w, 713w, 709w, 629w, and 571w cm$^{-1}$; $^{1}$H n.m.r. ([$^{2}$H$_6$]benzene), $\tau$ 4.45 (s, 4 H, CH), 6.57 [t, 6 H, OCH$_3$, $^{5}J$(FH) 1 Hz], and 8.05 (s, br, 8 H, CH$_2$).

*Preparation of the Complexes* [Pt(alkyne)(CNBu$^{t}$)$_2$] (18)—(20).—(*a*) A solution of (15) (0.173 g, 0.261 mmol) in light petroleum (15 cm$^3$) was treated with excess of CNBu$^{t}$. The yellow crystals which formed immediately were filtered off and recrystallised from light petroleum as yellow *needles* of [Pt(C$_6$F$_5$C$_2$C$_6$F$_5$)(CNBu$^{t}$)$_2$] (18) (55 mg, 29%), m.p. (*in vacuo*) 291 °C (decomp.) (Found: C, 40.4; H, 2.8; N, 3.9. C$_{24}$H$_{18}$F$_{10}$N$_2$Pt requires C, 40.1; H, 2.5; N, 3.9%); $\nu_{\text{max.}}$ at 2 254s (NC), 2 216s (NC), 1 769m (C≡C), 1 541s, 1 521s, 1 261w, 1 242m, 1 131m, 1 061w, 1 037m, 1 021s, 940w, 844w, 810w, and 739w cm$^{-1}$; $^{1}$H n.m.r. ([$^{2}$H$_6$]benzene), $\tau$ 8.96 (s, 18 H, CH$_3$).

(*b*) To a suspension of [Pt(cod)$_2$] (0.205 g, 0.5 mmol) in diethyl ether was added 4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′ (0.191 g, 0.5 mmol). The suspension was stirred for 2 min and excess of CNBu$^{t}$ was added. There was an immediate precipitate. Most of the solvent was removed *in vacuo* and the precipitate was filtered off, washed with light petroleum (3 × 5 cm$^3$), and dried *in vacuo* affording [Pt(4-MeOC$_6$F$_4$C$_2$C$_6$F$_4$OMe-4′)(CNBu$^{t}$)$_2$] (19) as light yellow *microcrystals* (0.281 g, 76%), m.p. (*in vacuo*) 101—102 °C (Found: C, 42.6; H, 3.5; N, 3.5. C$_{26}$H$_{24}$F$_8$N$_2$O$_2$Pt requires C, 42.0; H, 3.3; N, 3.8%); $\nu_{\text{max.}}$ at 2 188vs (NC), 2 151vs (NC), 1 736m (C≡C), 1 650m, 1 503m, 1 424s, 1 400w, 1 232m, 1 206s,br, 1 167m, 1 084m,br, 1 064s, 994s,br, 924w, 819m, 785m, 710s, 660w, 557w, 515m, and 424w cm$^{-1}$; $^{1}$H n.m.r., $\tau$ 5.93 [t, 6 H, OCH$_3$, $^{5}J$(FH) 1 Hz], and 8.84 (s, 18 H, CH$_3$).

(*c*) (*i*) To a solution of [Pt$_3$(CNBu$^{t}$)$_6$] (0.10 g, 0.092 mmol) in toluene (20 cm$^3$) was added diphenylacetylene (0.049 g, 0.277 mmol). The solution was stirred for 3 d and taken to dryness *in vacuo*. The residue was recrystallised from toluene–light petroleum as white *crystals* of [Pt(PhC$_2$Ph)(CNBu$^{t}$)$_2$] (20) (0.107 g, 72%), m.p. 145—146 °C (decomp.) (Found: C, 54.2; H, 5.4; N, 4.9. C$_{24}$H$_{28}$N$_2$Pt requires C, 53.4; H, 5.2; N, 5.2%); $\nu_{max.}$ at 2 154s (NC), 2 116s (NC), 1 741s ($C\equiv C$), 1 590s, 1 443s, 1 235s, 1 208s, 771s, 700s, 610m, 580m, 535m, and 520m cm$^{-1}$; $^1$H n.m.r., $\tau$ 2.05—3.0 (m, 10 H, Ph) and 8.45 (s, 18 H, Me).

(*ii*) To stirred solution of tertiary-butyl isocyanide (0.33 g, 4 mmol) in light petroleum (5 cm$^3$) was added compound (1) (0.55 g, 1 mmol). The initial clear colourless solution rapidly became cloudy and an off-white precipitate was formed. The supernatant liquid was removed and the product washed with light petroleum (4 × 5 cm$^3$) to afford white *microcrystals* of (20) (0.4 g, 75%).

*Preparation of the Complexes* [Pt(alkyne)$(PR_3)_2$].— (*a*) (*i*) Trimethylphosphine (2 mmol) was condensed (−196 °C) into a mixture of (1) (0.275 g, 0.5 mmol) and light petroleum (5 cm$^3$). On warming to room temperature, with stirring, a heavy white precipitate formed. After stirring for 5 min the mixture was cooled to 0 °C and the supernatant liquid removed affording white *microcrystals* of [Pt($PhC_2Ph$)-$(PMe_3)_2$] (22) (0.16 g, 60%), which were washed with light petroleum (4 × 5 cm$^3$) and dried *in vacuo* (Found: C, 45.6; H, 5.4. $C_{28}H_{28}P_2Pt$ requires C, 45.7; H, 5.4%); $\nu_{max.}$ at 1 725s ($C\equiv C$), 1 590s, 1 443m, 1 435w, 1 420m, 1 310m, 1 305m, 1 290s, 1 270w, 1 180w, 1 168w, 1 078m, 1 035m, 965s,br, 915m, 895w, 862m, 855m, 845w, 785m, 770s, 735s, 730m, 710s, 700s, 690w, 680m, 600m, 575m, 565m, and 515m cm$^{-1}$; $^1$H n.m.r., $\tau$ 2.2—3.0 (m, 10 H, Ph) and 8.7 [d, second order, 18 H, Me, $|^2J(PH) + {}^4J(PH)|$ 8, $^3J$(PtH) 27 Hz].

(*ii*) Complex (22) may also be prepared by treatment of [Pt(cod)$_2$] with 2 mol equivalents of trimethylphosphine, followed by 1 mol equivalent of diphenylacetylene (70%). A $^{13}$C-enriched sample was similarly prepared, $\nu_{max.}$($C\equiv C$) at 1 725 and 1 693 cm$^{-1}$.

(*b*) To a stirred suspension of compound (1) (0.275 g, 0.5 mmol) in light petroleum (5 cm$^3$) at 0 °C was added triethylphosphine (0.35 g, 3 mmol). The clear solution so produced was stirred for 5 min and then solvent was removed *in vacuo*. The oily product was freed from $PhC\equiv CPh$ by sublimation of the latter under high vacuum, and the residue was washed with light petroleum (2 × 2 cm$^3$) at −78 °C. The product [Pt($PhC_2Ph$)$(PEt_3)_2$] (23) was identified solely by its i.r. [$\nu_{max.}$($C\equiv C$) 1 765 and 1 736 cm$^{-1}$] and n.m.r. (Table 7) spectra.

(*c*) The compound [Pt(cod)$_2$] (0.10 g, 0.25 mmol) was added slowly with stirring to ethylene-saturated light petroleum (2 cm$^3$) at 0 °C. To this clear pale yellow solution was added enriched $Ph^{13}C\equiv CPh$ (45 mg, 0.25 mmol) and $PPh_3$ (0.13 g, 0.5 mmol). A cream precipitate formed immediately and, after stirring for another 10 min, solvent was removed *in vacuo*. The solid was washed with light petroleum (4 × 3 cm$^3$) and dried *in vacuo*. The off-white solid was identified as [Pt($Ph^{13}C\equiv CPh$)$(PPh_3)_2$] (0.18 g, 74%) by its i.r. spectrum [$\nu_{max.}$($C\equiv C$) at 1 743 and 1 722 cm$^{-1}$].

(*d*) To a stirred solution of $PhC_2SiMe_3$ (0.087 g, 0.5 mmol) in light petroleum (10 cm$^3$, −40 °C) was added [Pt(cod)$_2$] (0.205 g, 0.5 mmol). The solution was allowed to warm to room temperature, and $PPh_3$ (0.26 g, 1 mmol) was added. After stirring for another 20 min, a light grey precipitate formed which was washed with light petroleum (4 × 5 cm$^3$) and dried *in vacuo* to afford off-white *microcrystals* of [Pt-($PhC_2SiMe_3$)$(PPh_3)_2$] (24) (0.26 g, 60%), m.p. 132—133 °C (decomp.) (Found: C, 63.4; H, 5.3. $C_{47}H_{44}P_2PtSi$ requires C, 63.1; H, 5.3%); $\nu_{max.}$ at 1 741m,br ($C\equiv C$), 1 590m, 1 574w, 1 480m, 1 438s, 1 315w, 1 250m, 1 190w, 1 180w, 1 164w, 1 100s, 1 036m, 1 008w, 888s, 844s, 766m, 757m, 750m, 730w, 710s, 700s, 646w, 628w, 610w, 550s, 533s, 520s, 512m, 506w, 458w, 450s, and 428w cm$^{-1}$; $^1$H n.m.r. ([$^2H_6$]benzene), $\tau$ 2.25—3.30 (m, 35 H, Ph) and 9.87 (s, 9 H, Me).

A sample of [Pt($Ph^{13}C\equiv CSiMe_3$)$(PPh_3)_2$] [$\nu_{max.}$($C\equiv C$) 1 703 cm$^{-1}$] was prepared in an analogous manner using $Ph^{13}C\equiv CSiMe_3$.

(*e*) The complex [Pt(cod)$_2$] (0.62 g, 1.5 mmol) in ethylene-saturated light petroleum (20 cm$^3$) was treated with $PPh_3$ (0.79 g, 3 mmol) in the same solvent (20 cm$^3$) to produce a precipitate of [Pt($C_2H_4$)$(PPh_3)_2$]. To this suspension was added excess of but-2-yne, and the mixture stirred (1 h) to give [Pt($MeC_2Me$)$(PPh_3)_2$] [28] (0.9 g, 78%) as microcrystals (Found: C, 61.8; H, 4.8. Calc. for $C_{40}H_{36}P_2Pt$: C, 61.1; H, 4.7%); $\nu_{max.}$($C\equiv C$) at 1 812 cm$^{-1}$; $^1$H n.m.r. ([$^2H_6$]-benzene), $\tau$ 2.3—3.2 (m, 30 H) and 7.72 [m, 6 H, *J*(PtH) 45 Hz].

(*f*) The complexes [Pt($MeC_2Me$)$(PEt_3)_2$] (25) and [Pt-($Ph^{13}C\equiv CPh$)$(AsEt_3)_2$] (26) were prepared in a similar manner to that described for (22), and were identified by their $^{13}$C n.m.r. spectra (Table 7).

*Crystal-structure Determination of* [Pt($PhC_2Ph$)$_2$] (1).—Crystals of (1) grow as very pale yellow plates from diethyl ether at −40 °C; that for data collection was of dimensions 0.2 × 0.26 × 0.05 mm, and diffracted intensities were recorded at 200 K for the range $2.9 \leqslant 2\theta \leqslant 65°$ on a Syntex $P2_1$ four-circle diffractometer.[43] Of the total 4 712 recorded intensities, 3 433 had $I \geqslant 2\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption. Computations were carried out with the '*X*-ray' system of programs [44] available for the CDC 7600 at the London Computing Centre.

*Crystal data.* $C_{28}H_{20}Pt$, $M = 551.6$, Monoclinic, space group $P2/n$, $a = 13.163(5)$, $b = 6.062(2)$, $c = 14.354(7)$ Å, $\beta = 115.04(3)°$, $U = 1\,037.9(7)$ Å$^3$, $D_m = 1.76$, $Z = 2$, $D_c = 1.77$ g cm$^{-3}$, $F(000) = 532$, Mo-$K_\alpha$ *X*-radiation ($\lambda = 0.710\,69$ Å), $\mu$(Mo-$K_\alpha$) = 69.5 cm$^{-1}$.

*Structure solution and refinement.* The molecular structure was solved from electron-density difference syntheses following location of the platinum atom from a Patterson synthesis. Refinement was accomplished by full-matrix least squares with the C and Pt atoms having anisotropic thermal parameters, and all the hydrogen atoms were located and refined with isotropic temperature factors. Weights were applied according to the scheme $w^{-1} = \sigma^2(F_o) + \alpha(F^2)$, where $\alpha = 0.005$ and $\sigma(F_o)$ is the estimated standard deviation in $|F_{obs.}|$ based on counting statistics only. This gave a satisfactory weighting analysis with the refinement converging at *R* 0.038 (*R'* 0.046), with a mean shift-to-error ratio for the last cycles of 0.02 : 1 and a maximum of 0.2 : 1. The final electron-density difference synthesis showed some residual density around the platinum atom (<2 e Å$^{-3}$), but elsewhere no peaks >0.3 or < −0.4 e Å$^{-3}$. Scattering factors used were those of ref. 45 for Pt, ref. 46 for C, and ref. 47 for H, with appropriate corrections for the effects of anomalous dispersion for Pt ($\Delta f' = 2.352$, $\Delta f'' = 8.388$). The atomic co-ordinates are given in Table 2 and equations of some least-squares planes in Table 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 22842 (16 pp.)* as are all thermal parameters.

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

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