Alkyne Complexes of Platinum. Part 4.[1] Stepwise Formation of Di- and Tri-platinum Complexes with Bridging Alkyne Ligands; Crystal Structure of $[Pt_3\{\mu\text{-}(\eta^2\text{-}PhC_2Ph)\}_2(PEt_3)_4]$ †

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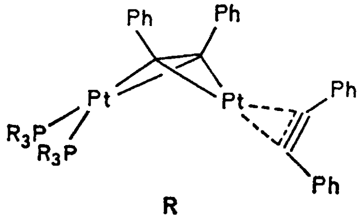
Reaction of the compound $[Pt(PhC_2Ph)_2]$ with $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ (cod = cyclo-octa-1,5-diene) affords diplatinum complexes $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PR_3)_2]$ (R = Ph or Et). The triphenylphosphine compound has also been prepared by treating PhC≡CPh with $[Pt(C_2H_4)_2(PPh_3)]$. The terminal alkyne ligand in $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PPh_3)_2]$ bonds a third platinum atom on treatment with $[Pt(C_2H_4)(PPh_3)_2]$ to give the triplatinum complex $[Pt_3(\mu\text{-}PhC_2Ph)_2(PPh_3)_4]$. The latter can also be prepared by addition of 2 mol equivalents of $[Pt(C_2H_4)(PPh_3)_2]$ to $[Pt(PhC_2Ph)_2]$, and the triethylphosphine-triplatinum analogue is similarly obtained using $[Pt_2(\mu\text{-cod})(PEt_3)_4]$. In view of the novelty of these compounds, a single-crystal *X*-ray diffraction study has been carried out on $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$, crystals of which are monoclinic, space group *C*2/*c* (no. 15), with $Z = 4$ in a unit cell of dimensions $a = 17.047(2)$, $b = 13.677(2)$, $c = 25.073(3)$ Å, and $\beta = 105.79(1)°$. The structure has been solved by heavy-atom methods from 3 038 intensity data $[I \geqslant 3.0\sigma(I)]$ measured on a four-circle diffractometer at 300 K, and refined to *R* 0.047 (*R'* 0.046). The three platinum atoms adopt an open V-shaped configuration with an internuclear distance of 2.90_4 Å and an interbond angle of 144°, while the acetylenic units form transverse bridges across the two Pt–Pt vectors on the convex side of the V. The phenyl groups bend away from the metal atoms to give a C–C–Ph angle of 139°, and the whole molecule is constrained crystallographically to C_2 symmetry. The ethyl groups of the phosphine ligands are ill defined and possibly disordered.

The diplatinum complexes $[Pt_2(\mu\text{-}RC_2R)(PMe_3)_4]$ (R = Ph or C_6F_5) have also been prepared, and $[Pt_2(\mu\text{-}PhC_2Ph)(PEt_3)_4]$ characterised spectroscopically. Reaction of $[Pt(PhC_2Ph)(CNBu^t)_2]$ with $[Pt(C_2H_4)(PPh_3)_2]$ yields *trans*-$[Pt_2(\mu\text{-}PhC_2Ph)(CNBu^t)_2(PPh_3)_2]$, scrambling of the $CNBu^t$ and PPh_3 ligands having occurred. The stereochemistry of this complex, and its $PhC{\equiv}CC_6H_4OMe$-4 analogue, has been established by ^{31}P and ^{13}C-labelling n.m.r. studies. The modes of formation of the various compounds are discussed.

In the preceding paper[1] we reported the synthesis of several bis(acetylene)platinum complexes and an *X*-ray crystallographic study on the compound $[Pt(PhC_2Ph)_2]$. The platinum atom in the latter species is in an essentially tetrahedral (D_{2d}) environment with respect to the four ligated carbon atoms since the dihedral angle between the planes defined by the two η^2-C_2Pt fragments is 84°. In the complexes $[Pt(alkyne)_2]$, as well as in the related monoplatinum compounds $[Pt(alkyne)L_2]$ [L_2 = cyclo-octa-1,5-diene (cod), L = PR_3 or CNR], the currently held view of the metal–acetylene bonding is that it involves overlap of a π bonding orbital of the acetylene with a vacant metal hybrid orbital to produce a σ bond, with concomitant overlap of a filled metal *d* orbital with the π^* antibonding orbital of the ligand to afford a π bond.[2-5] It is generally assumed that the π and π^* orbitals of the acetylene which are orthogonal to those employed in donor–acceptor bonding to the metal play no part, or at best an insignificant role, in the interaction of the carbon atoms with the metal. Consequently, it seemed likely that this set of π and π^* orbitals could bond a second metal atom, thereby converting an η^2-terminal acetylene ligand into a bridging ligand. Many complexes are known in which an acetylene transversely bridges two metal atoms,[6-8] but it had not been appreciated that these dimetal compounds might form *via* the intermediacy of mononuclear metal acetylene species. It was in order to investigate this possibility in the case of platinum that the results described in this paper were obtained.[9]

RESULTS AND DISCUSSION

Reaction of $[Pt(PhC_2Ph)_2]$ (1) with 1 mol equivalent of $[Pt(C_2H_4)(PPh_3)_2]$ in light petroleum at room temperature affords the yellow complex (2). The ^{31}P n.m.r. spectrum of (2) showed a signal at 26.6 p.p.m. with satellite peaks indicating coupling to ^{195}Pt nuclei in two environments (Table 1), in accord with the desired result, based on the ideas expressed above. The i.r. spectrum of (2) showed a band at 1 842 cm^{-1} assignable to $\nu_{max.}$(C≡C) of the terminally bound diphenylacetylene ligand. The corresponding band in the spectrum of (1) occurs at 1 881 cm^{-1}. Formation of (2) can be regarded as displacement of ethylene from $[Pt(C_2H_4)(PPh_3)_2]$ by one of



	R
(2)	Ph
(3)	Et
(4)	Me

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† *cd*-Bis(μ-diphenylacetylene)-*abef*-tetrakis(triethylphosphine)-triplatinum.

TABLE 1

Hydrogen-1 decoupled ^{31}P n.m.r. chemical shifts and coupling constants [a]

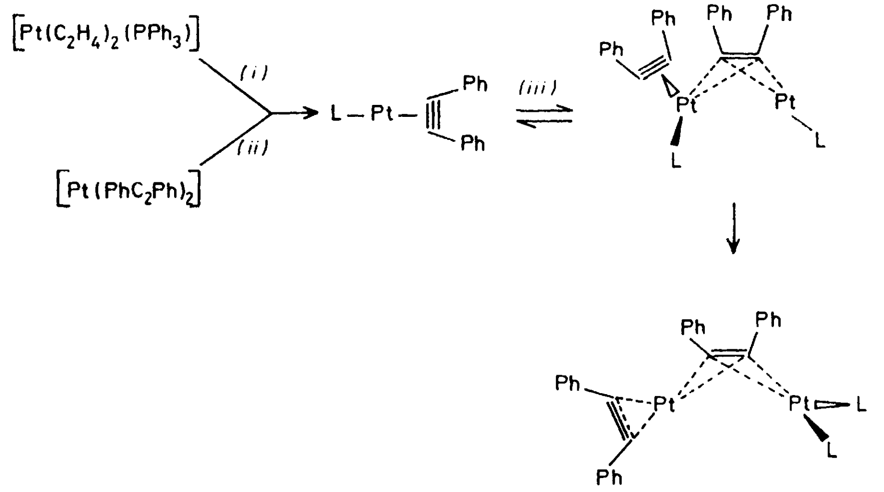
Compound	Solvent	δ	^1J(PtP)	^2J(PtP)	Other coupling constants
$[Pt(PhC_2Ph)(PMe_3)_2]$ [b]	C_6D_6	30.1	3 235		^2J(PP) 27 [c]
$[Pt(PhC_2Ph)(PEt_3)_2]$ [b]	$CDCl_3$	10.5	3 261		
$[Pt(PhC_2Ph)(PPh_3)_2]$ [b]	$CDCl_3$	27.2	3 445		
$[Pt(C_6F_5C_2C_6F_5)(PMe_3)_2]$	C_6D_6	30.7	3 314		
$[Pt(PhC_2Ph)(CNBu^t)(PPh_3)]$ [d]	$CDCl_3$	28.6	3 198		
$[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PPh_3)_2]$	$CDCl_3$	26.6	3 769	41	
$[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PEt_3)_2]$ [e]	C_6D_6–C_6H_5Me	16.0	3 619	45	
$[Pt_2(\mu\text{-}PhC_2Ph)(PEt_3)_4]$ [f]	C_6D_6–C_6H_5Me	3.8	3 350	−79	
$[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PMe_3)_2]$ [g]	C_6D_6	20.4	3 530	44	^1J(PtPt) 1 006
$[Pt_2(\mu\text{-}PhC_2Ph)(PMe_3)_4]$ [h]	C_6D_6–C_6H_5Me	31.3	3 340	−83	^3J(PP) 15, ^3J(PP′) 10, ^2J(PP) 13, ^1J(PtPt) 470
$[Pt_2(\mu\text{-}C_6F_5C_2C_6F_5)(PMe_3)_4]$	C_6D_6–C_6H_5Me	32.9	3 470	−74	^5J(PF) *ca.* 10
trans-$[Pt_2(\mu\text{-}PhC_2Ph)(CNBu^t)_2(PPh_3)_2]$ [e]	C_6D_6–C_6H_5Me	21.8	3 332	−68	^3J(PP) 10
trans-$[Pt_2(\mu\text{-}PhC_2C_6H_4OMe\text{-}4)(CNBu^t)_2(PPh_3)_2]$ [i]	C_6D_6–C_6H_5Me	21.7	3 325	−69	^3J(PP) 10
		21.9	3 354	−68	
$[Pt_3(\mu\text{-}PhC_2Ph)_2(PPh_3)_4]$ [j]	CD_2Cl_2–CH_2Cl_2	26.0	3 615		^2J(PP) 40
		23.3	3 884		
$[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$ [e,j]	$CDCl_3$	12.1	3 670		^2J(PP) 36
		10.7	3 498		

[a] Chemical shifts are measured positive in p.p.m. to low field of 85% H_3PO_4, at room temperature, unless otherwise stated; coupling constants are in Hz. [b] Ref. 1. [c] Measured from the spectrum of $[Pt(Ph^{13}C{\equiv}CPh)(PMe_3)_2]$. [d] Ref. 13. [e] Measured at −40 °C. [f] Measured at −20 °C. Complex not isolated, see text. [g] J(PtPt) from ^1H-{^{195}Pt} INDOR experiment. [h] Measured at −60 °C. [i] Measured at −30 °C, AB spectrum, calculated values. [j] Approximately an AB spectrum (see text).

the acetylene ligands of (1). Reaction of the latter with $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ [10] affords the diplatinum compound (3) [$\nu_{max.}$(C≡C) 1 842 cm^{-1}; ^{31}P n.m.r., see Table 1].

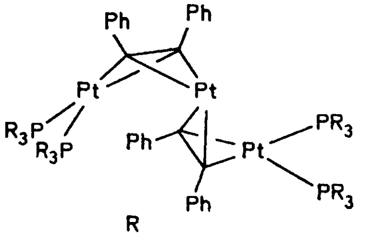
A single-crystal *X*-ray diffraction study [11] of the trimethylphosphine analogue (4), prepared serendipitously in poor yield by addition of 1 equivalent of trimethylphosphine to (1), demonstrated the salient structural features of this class of dinuclear complex. Thus one platinum atom is bonded to two alkyne ligands, the co-ordination around this metal atom being not dissimilar to the pseudo-tetrahedral symmetry of complex (1). However, one of these alkyne ligands transversely bridges the platinum–platinum vector with its metal-bonded carbon atoms essentially coplanar with the atoms of the PtP_2 group. The species (2)—(4) can be regarded as comprising either a $[Pt(PhC_2Ph)(PR_3)_2]$ unit with a $Pt(\eta^2\text{-}PhC_2Ph)$ fragment bonded *via* the orthogonal orbitals of the bridging alkyne, or a $[Pt(PhC_2Ph)_2]$ molecule with a $Pt(PR_3)_2$ moiety attached in a similar manner.

Complex (2) was also obtained by treating $[Pt(C_2H_4)_2(PPh_3)]$ [12] with 1 mol equivalent of diphenylacetylene at 0 °C. This synthesis, which must involve phosphine migration, illuminates the process by which the diplatinum complex (4) is formed by addition of trimethylphosphine to (1). In both reactions, a 14-electron species $[Pt(PhC_2Ph)(PR_3)]$ is probably first formed; indeed, evidence has been obtained for the existence of complexes $[Pt(RC_2R)(PPh_3)]$ (R = Ph or C_6H_4Me-4) by treating $[Pt(C_2H_4)_2(PPh_3)]$ with PhC_2Ph or 4-$MeC_6H_4C_2C_6H_4Me$-4′.[13] A co-ordinatively unsaturated complex $[Pt(PhC_2Ph)(PR_3)]$ could well dimerise forming an unstable dimetal intermediate, the platinum atoms being held together by the orthogonal π orbitals of the bridging diphenylacetylene ligand (Scheme). The dimetal intermediate contains both a 16-electron 'trigonal' planar unit and a 14-electron 'linear' unit. The terminal alkyne could rotate through 90° and swing round to adopt a pseudotetrahedral disposition around the



SCHEME Formation of $[Pt_2\{\mu\text{-}(\eta^2\text{-}PhC_2Ph)\}(\eta^2\text{-}PhC_2Ph)L_2]$ (L = PR_3). (*i*) PhC_2Ph, (*ii*) PMe_3, (*iii*) $[Pt(PhC_2Ph)L]$

platinum with respect to the bridging alkyne. This could displace a phosphine ligand so that it migrates to the more electron-deficient metal nucleus, thereby enhancing back bonding.



R
(5) Ph
(6) Et

The reactions which yielded (2)—(4) can in principle be extended so as to add a further platinum atom *via* utilisation of the π orbital of the *terminal* alkyne in these diplatinum compounds. In order to test this idea, complex (2) was treated with 1 equivalent of $[Pt(C_2H_4)(PPh_3)_2]$, a reaction which afforded red-purple crystals of the triplatinum compound (5). The latter could also be prepared directly from (1) by addition of 2 equivalents of $[Pt(C_2H_4)(PPh_3)_2]$. Compound (5) was characterised by analysis, and by the absence of any band in the i.r. spectrum at *ca.* 1 800 cm^{-1} corresponding to a terminally bonded alkyne ligand. The ^{31}P n.m.r. spectrum was complex, consisting of a basic AB pattern with easily observed one-bond satellites (Table 1).

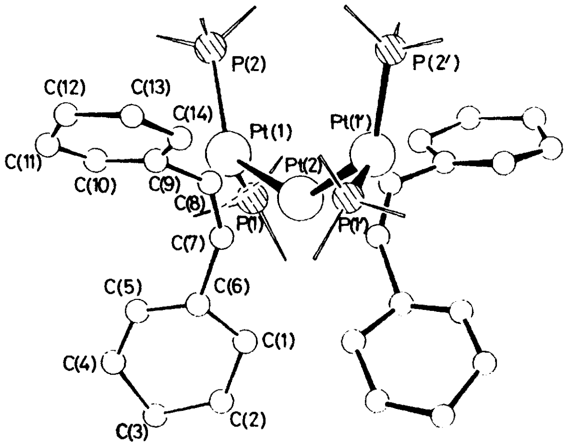


FIGURE 1 Molecular configuration of (6) showing the crystallographic numbering sequence. The ethyl groups have been omitted

Red-orange crystals of the triplatinum compound (6) were prepared by adding $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ to (1) in light petroleum. Comparison of the i.r. spectra of (5) and (6) indicated that a strong band at *ca.* 1 600 cm^{-1} may be attributed to the bridging alkyne ligands. In view of the novelty of these triplatinum compounds a single-crystal *X*-ray diffraction study was undertaken on complex (6).

TABLE 2

Atomic positional co-ordinates (fractional cell co-ordinates) for $[Pt_3(\mu\text{-PhC}_2Ph)_2(PEt_3)_4]$ (6), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	−0.045 0(10)	−0.024 6(10)	0.174 3(6)
C(2)	−0.065 3(12)	−0.118 6(11)	0.158 7(7)
C(3)	−0.138 8(11)	−0.137 7(12)	0.122 5(8)
C(4)	−0.190 2(12)	−0.064 6(14)	0.105 4(7)
C(5)	−0.168 3(11)	0.029 7(12)	0.121 9(7)
C(6)	−0.096 3(8)	0.052 1(9)	0.157 8(5)
C(7)	−0.073 6(8)	0.153 0(9)	0.174 7(4)
C(8)	−0.107 0(8)	0.236 0(9)	0.191 0(5)
C(9)	−0.183 4(9)	0.265 3(9)	0.199 7(6)
C(10)	−0.254 4(12)	0.265 9(13)	0.159 9(9)
C(11)	−0.372 2(12)	0.296 6(15)	0.167 6(9)
C(12)	−0.331 3(13)	0.330 6(16)	0.215 2(10)
C(13)	−0.262 2(15)	0.341 3(17)	0.255 5(10)
C(14)	−0.185 7(12)	0.307 8(15)	0.247 1(8)
C(15)	−0.036 3(16)	0.175 7(22)	0.008 1(10)
C(16)	−0.107 3(14)	0.130 6(20)	0.000 2(9)
C(17)	0.097 4(14)	0.285 4(15)	0.053 2(9)
C(18)	0.147 7(16)	0.245 3(16)	0.017 4(10)
C(19)	0.077 4(16)	0.099 7(17)	0.094 7(10)
C(20)	0.147 8(12)	0.108 8(17)	0.152 7(10)
C(21)	−0.088 4(16)	0.497 6(12)	0.171 7(10)
C(22)	−0.102 1(15)	0.598 1(16)	0.169 6(10)
C(23)	−0.121 2(18)	0.466 4(19)	0.059 0(10)
C(24)	−0.174 4(17)	0.426 5(19)	0.024 2(11)
C(25)	0.024 6(14)	0.517 4(17)	0.107 5(12)
C(26)	0.089 5(15)	0.508 1(17)	0.146 1(10)
H(1)	0.014 5(10)	−0.010 6(10)	0.202 0(6)
H(2)	−0.023 2(12)	−0.177 5(11)	0.174 6(7)
H(3)	−0.155 7(11)	−0.211 2(12)	0.108 3(8)
H(4)	−0.249 5(12)	−0.078 8(14)	0.077 5(7)
H(5)	−0.211 3(11)	0.087 7(12)	0.106 0(7)
H(6)	−0.255 2(12)	0.240 9(13)	0.118 9(9)
H(7)	−0.382 5(12)	0.293 7(15)	0.134 1(9)
H(8)	−0.388 7(13)	0.350 1(16)	0.222 8(10)
H(9)	−0.261 9(15)	0.373 6(17)	0.294 9(10)
H(10)	−0.129 9(12)	0.317 5(15)	0.279 6(8)
H(11)	0.000 5(16)	0.125 2(22)	−0.007 9(10)
H(12)	−0.047 5(16)	0.240 5(22)	−0.017 5(10)
H(13)	−0.132 8(14)	0.114 5(20)	−0.043 2(9)
H(14)	−0.147 9(14)	0.178 8(20)	0.014 1(9)
H(15)	−0.099 9(14)	0.063 5(20)	0.023 8(9)
H(16)	0.141 3(14)	0.315 8(15)	0.088 8(9)
H(17)	0.059 7(14)	0.343 4(15)	0.030 5(9)
H(18)	0.183 1(16)	0.303 6(16)	0.006 4(10)
H(19)	0.106 4(16)	0.215 9(16)	−0.019 7(10)
H(20)	0.188 0(16)	0.188 3(16)	0.038 6(10)
H(21)	0.105 5(16)	0.076 5(17)	0.063 1(10)
H(22)	0.032 5(16)	0.046 5(17)	0.098 5(10)
H(23)	0.177 9(12)	0.039 6(17)	0.164 9(10)
H(24)	0.119 1(12)	0.132 6(17)	0.183 9(10)
H(25)	0.192 1(12)	0.162 6(17)	0.148 5(10)
H(26)	−0.046 0(16)	0.479 3(12)	0.210 9(10)
H(27)	−0.147 3(16)	0.466 3(12)	0.169 6(10)
H(28)	−0.124 3(15)	0.618 8(16)	0.204 4(10)
H(29)	−0.145 5(15)	0.620 4(16)	0.131 5(10)
H(30)	−0.044 3(15)	0.633 4(16)	0.172 9(10)
H(31)	−0.091 0(18)	0.519 3(19)	0.039 5(10)
H(32)	−0.162 6(18)	0.503 6(19)	0.078 0(10)
H(33)	−0.213 6(17)	0.480 2(19)	0.001 4(11)
H(34)	−0.211 0(17)	0.373 9(19)	0.038 8(11)
H(35)	−0.139 4(17)	0.389 6(19)	0.000 2(11)
H(36)	0.003 5(14)	0.590 9(17)	0.111 2(12)
H(37)	0.030 9(14)	0.506 4(17)	0.066 2(12)
H(38)	0.129 7(15)	0.561 7(17)	0.136 0(10)
H(39)	0.113 0(15)	0.435 7(17)	0.142 9(10)
H(40)	0.085 7(15)	0.520 1(17)	0.187 9(10)
P(1)	0.031 6(3)	0.213 0(3)	0.077 8(2)
P(2)	−0.052 1(3)	0.435 8(3)	0.119 2(2)
Pt(1)	−0.037 76(4)	0.273 09(4)	0.135 78(2)
Pt(2)	0.000 00	0.206 87(5)	0.250 00

The molecular structure of (6), including the crystallographic numbering sequence, is shown in Figure 1, and a stereoscopic view in Figure 2. Tables 2 and 3 list the atomic positional parameters and the bond lengths and angles, respectively, while Table 4 gives the equations and dihedral angles of some least-squares planes. Figure 3 shows the contents of the monoclinic unit cell.

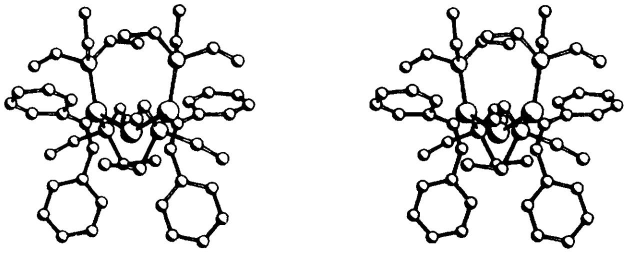


FIGURE 2 Stereoscopic view of the molecular structure of (6) including the ethyl groups

The three platinum atoms adopt an open V-shaped configuration [Pt(1)–Pt(2) 2.904(1) Å; Pt(1)–Pt(2)–Pt(1′) 144°], and the whole molecule is constrained to two-fold symmetry by a crystallographic two-fold axis through Pt(2). The acetylenic units form transverse bridges across the two Pt–Pt vectors on the convex side of the V. The phenyl rings of the diphenylacetylene ligands bend away from the metal nucleus to give a C–C–Ph angle of 139(1)°; the dihedral angle between the planes of the phenyl rings is 120°. The four central carbon atoms of the diphenylacetylene themselves remain coplanar, but the two phenyl rings, C(1)—C(6) and C(9)—C(14), are twisted around their C–Ph bonds by +43 and −53°, respectively (Table 4). The Pt–P distance [2.264(4) Å] and the Pt–P–C angles (Table 3) are indicative of normal phosphine geometry, but the carbon atoms of the triethylphosphine are ill defined and there may be some disorder.

Of over-riding interest, however, is the co-ordination state of the platinum atoms. Around the outer Pt atom, Pt(1), the atoms P(1), P(2), and C(7), C(8) of the acetylene are all coplanar, and Pt(1) is displaced from this plane towards Pt(2) by only *ca.* 0.08 Å (Table 4). Apart from any interaction with Pt(2), therefore, atom Pt(1) is in near-perfect planar triangular co-ordination. The P–Pt–P angle is 107°, but the acetylenic carbon atoms subtend an angle of 38° at Pt(1), thus making the P–Pt(1)–C angles also 107°. The question to be resolved is whether any significant Pt(1)–Pt(2) bonding interaction occurs. The interatomic distance, 2.904(1) Å, is longer than has been

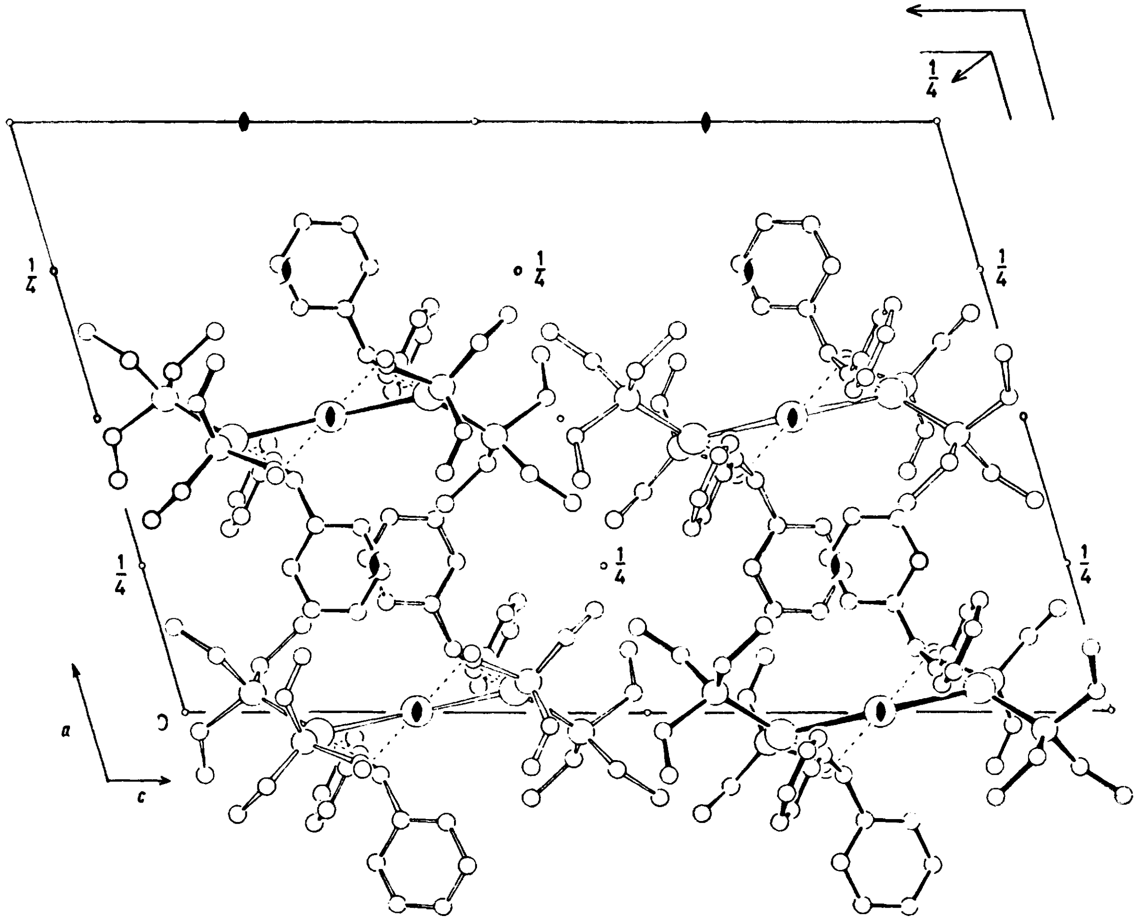


FIGURE 3 Contents of the monoclinic unit cell viewed in projection down *b* looking towards the origin

found in some other bridged diplatinum complexes (2.647(2) Å in $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$,[14] 2.632(2) Å in $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$,[15] and 2.627(1) Å in $[Pt_2W\{\mu\text{-}CPh(OMe)\}(CO)_6(PMeBu^t_2)_2]$ [16]), but too short to be considered non-bonding unless other evidence can be adduced. Two pointers suggest that the interaction is weak or zero. (*i*) The electron configuration of the Pt atoms: if no direct Pt–Pt bond exists the platinum atoms have a 16-electron configuration which is very common, whereas an 18-electron configuration would require a double bond between the metal atoms, for which a distance of 2.904 Å is extremely unlikely. (*ii*) The angle subtended at the midpoint of the acetylenic link by Pt(1) and Pt(2) is 95°, suggesting that the bonding is primarily due to the orthogonal π orbitals of the acetylene, and this largely determines the metal–metal distances. A theoretical treatment supports this view.[17]

TABLE 3

Bond distances (Å) and angles (°) for the complex $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$ (6), with estimated standard deviations in parentheses

(*i*) Distances

(*a*) Pt co-ordination

Pt(1)–P(1)	2.264(4)	Pt(1)–Pt(2)	2.904(1)
Pt(1)–P(2)	2.265(4)		
Pt(1)–C(7)	2.086(11)	Pt(2)–C(7)	2.096(11)
Pt(1)–C(8)	2.110(12)	Pt(2)–C(8)	2.051(12)

(*b*) PhC_2Ph

C(1)–C(2)	1.362(18)	C(9)–C(10)	1.343(20)
C(2)–C(3)	1.357(21)	C(10)–C(11)	1.373(22)
C(3)–C(4)	1.321(22)	C(11)–C(12)	1.300(24)
C(4)–C(5)	1.373(21)	C(12)–C(13)	1.334(26)
C(5)–C(6)	1.345(18)	C(13)–C(14)	1.451(23)
C(6)–C(1)	1.356(17)	C(14)–C(9)	1.333(20)
C(6)–C(7)	1.465(16)		
C(7)–C(8)	1.379(16)		
C(8)–C(9)	1.435(17)		

(*c*) Et_3P groups

P(1)–C(15)	1.886(23)	C(15)–C(16)	1.326(27)
P(1)–C(17)	1.730(18)	C(17)–C(18)	1.503(22)
P(1)–C(19)	1.734(23)	C(19)–C(20)	1.618(28)
P(2)–C(21)	1.808(20)	C(21)–C(22)	1.392(23)
P(2)–C(23)	1.694(21)	C(23)–C(24)	1.204(28)
P(2)–C(25)	1.802(23)	C(25)–C(26)	1.263(27)

(*ii*) Angles

C(6)–C(1)–C(2)	123(2)	P(1)–C(17)–C(18)	122(2)
C(1)–C(2)–C(3)	119(2)	P(1)–C(19)–C(20)	109(2)
C(2)–C(3)–C(4)	119(2)	P(2)–C(21)–C(22)	121(2)
C(3)–C(4)–C(5)	121(2)	P(2)–C(23)–C(24)	138(2)
C(4)–C(5)–C(6)	123(2)	P(2)–C(25)–C(26)	110(2)
C(5)–C(6)–C(1)	115(1)	Pt(1)–P(1)–C(15)	113(1)
C(5)–C(6)–C(7)	122(1)	Pt(1)–P(1)–C(17)	122(1)
C(1)–C(6)–C(7)	123(1)	Pt(1)–P(1)–C(19)	117(1)
C(6)–C(7)–C(8)	140(1)	Pt(1)–P(2)–C(21)	112(1)
Pt(1)–C(7,8)–Pt(2) [a]	95	Pt(1)–P(2)–C(23)	115(1)
C(7)–C(8)–C(9)	138(1)	Pt(1)–P(2)–C(25)	126(1)
C(8)–C(9)–C(10)	124(1)	Pt(2)–Pt(1)–P(1)	120.4(1)
C(8)–C(9)–C(14)	120(1)	Pt(2)–Pt(1)–P(2)	118.1(1)
C(14)–C(9)–C(10)	115(2)	Pt(2)–Pt(1)–C(7,8) [a]	42
C(9)–C(10)–C(11)	124(2)	P(1)–Pt(1)–P(2)	106.8(2)
C(10)–C(11)–C(12)	121(2)	P(1)–Pt(1)–C(7,8)	125
C(11)–C(12)–C(13)	119(2)	P(2)–Pt(1)–C(7,8)	127
C(12)–C(13)–C(14)	120(2)	Pt(1)–Pt(2)–Pt(1′) [b]	144
C(13)–C(14)–C(9)	121(2)	Pt(1)–Pt(2)–C(7,8) [a]	43
P(1)–C(15)–C(16)	125(2)	C(7,8)–Pt(2)–C(7′,8′) [a,b]	169

[a] C(7,8) is the midpoint of the C(7)–C(8) bond. [b] Primes denote atoms related to one another by the two-fold axis through Pt(2) (see text).

Around the central metal atom [Pt(2)] the two co-ordination sites of the acetylenes form another very open V shape (nearly linear, the angle being 169° to the mid-points of each acetylene), inverted relative to Pt(1)–Pt(2)–Pt(1′). The V planes are at an angle of 37°.

TABLE 4

Equations of some least-squares planes for complex (6); distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): C(7), C(8), Pt(1), P(1), P(2)

$$11.268x + 1.726y + 13.335z = 1.778$$

[C(7) −0.022, C(8) −0.010, Pt(1) 0.078, P(1) −0.021, P(2) −0.026]

Plane (2): C(7), C(8), Pt(2), C(7′), C(8′)

$$-14.157x + 0.000y + 19.108z = 4.777$$

[C(7) −0.373, C(8) 0.373, Pt(2) 0.000]

Plane (3): Pt(1), Pt(2), Pt(1′)

$$17.027x + 0.000y - 5.635z = -1.409$$

Plane (4): C(1), C(2), C(3), C(4), C(5), C(6)

$$-10.698x - 1.609y + 22.851z = 4.532$$

Plane (5): C(9), C(10), C(11), C(12), C(13), C(14)

$$4.226x + 12.574y - 9.063z = 0.798$$

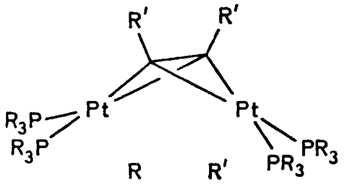
Angles (°) between least-squares planes:

(1)–(2) 98; (1)–(3) 46; (2)–(3) 37; (4)–(5) 120

Some torsion angles (°):

C(5)–C(6)–C(7)–C(8)	43
C(6)–C(7)–C(8)–C(9)	−3
C(7)–C(8)–C(9)–C(10)	−53

During the course of the work we were able to isolate other diplatinum complexes containing μ-η^2-alkyne ligands. Thus a solution of $[Pt(cod)_2]$ in light petroleum saturated with ethylene gas, on treatment with 2 mol equivalents of trimethylphosphine and 0.5 mol equivalent of diphenylacetylene, gave yellow crystals of compound (7). The latter had no band in its i.r. spectrum readily assignable to an 'acetylenic' C–C stretch; however, comparison with the spectrum of a sample containing *ca.* 25% ^{13}C enrichment of one of the acetylenic carbons suggests that a weak band at 1 491 cm^{-1} may be associated with a modified C–C stretch. The ^1H n.m.r. spectrum of (7) was in accord with the structure proposed, integration giving a 1 : 4 ratio for acetylene : phosphine protons. Conclusive evidence for the structure, including the transverse bonding of the diphenylacetylene across the platinum–platinum vector, came from measurement of the ^{31}P and ^{13}C n.m.r. spectra.



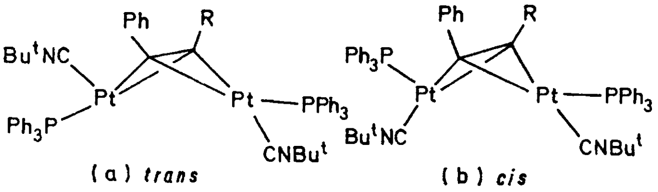
	R	R′
(7)	Me	Ph
(8)	Et	Ph
(9)	Me	C_6F_5

The ^{31}P spectrum showed a single resonance with double platinum satellites, and well resolved Pt–P and P–P couplings. The fine details of this spectrum were simulated from computer iterations and consequently a well defined value of ^1J(PtPt) was obtained (Table 1). Whilst this spectrum demonstrated that all phosphine environments in complex (7) are equivalent and the molecule is dinuclear, information concerning the co-ordination mode of the diphenylacetylene was obtained from the ^{13}C n.m.r. spectrum of a sample of (7) with 25% ^{13}C enrichment of an acetylenic carbon. The signal at 80.8 p.p.m. due to this carbon proved to be a deceptively simple quintet with platinum satellites [^1J(PtC) 278 Hz]. These satellites suggest that they and the central resonance are the inner components of a 1 : 8 : 18 : 8 : 1 resonance pattern expected for a carbon atom situated symmetrically between two platinum atoms, the situation arising when an alkyne ligand lies across the Pt–Pt vector. Moreover, the observed ^{13}C chemical shift and the magnitude of ^1J(PtC) are those expected for this type of bridge bonding rather than the alternative diplatinacyclobutene structure $\overline{\mathrm{Pt{-}C(Ph){=}C(Ph){-}Pt}}$.[18,19]

Comparison of the ^{13}C n.m.r. parameters of complex (7) with those of [Pt(PhC$_2$Ph)(PMe$_3$)$_2$] [*C*Ph resonance 131.0 p.p.m., ^1J(PtC) 280 Hz] [1] demonstrate that an upfield shift of 50.2 p.p.m. occurs for the acetylene contact-carbon resonance upon bonding to another metal centre [Pt(η^2-RC$_2$R) $\longrightarrow$ Pt{μ-(η^2-RC$_2$R)}Pt]. Since the chemical shift observed for [Pt(PhC$_2$Ph)(PMe$_3$)$_2$] occurs in the region associated with *sp*^{2}-hybridised (olefinic) carbons, the observed increase in shielding of the ‘ olefinic ’ alkyne-monoplatinum species on co-ordination to a second metal atom indicates that the alkyne takes on some ‘ metallacyclopropane ’ character [*cf.* the chemical shifts for ethylene (122.8 p.p.m.) *versus* cyclopropane (−2.6 p.p.m.) [20,21]]. Thus on the basis of the changes in ^{13}C chemical shifts, the platinum-bonded carbon atoms in (7) may be regarded in the valence-bond approximation as intermediate in hybridisation between *sp*^{2} and *sp*^{3}. For [Pt(PhC$_2$Ph)(PMe$_3$)$_2$] and (7) the ^1J(PtC) values are similar, suggesting the same degree of *s* character and hence σ bonding for both compounds. The degree of π back bonding would be relatively greater in (7), leading to a further decrease in the C≡C bond order and consequential lowering of $\nu_{\text{max.}}$(C≡C) as is observed {*viz.* 1 725 cm^{-1} for [Pt(PhC$_2$Ph)(PMe$_3$)$_2$] *versus* 1 491 cm^{-1} for (7), see above}.

The triethylphosphine complex (8) was detected by ^{31}P n.m.r. spectroscopy (Table 1) in solutions obtained by addition of 1 mol equivalent of PhC$_2$Ph to [Pt$_2$(μ-cod)(PEt$_3$)$_4$], and also in the mother-liquors of (6). However, it was not possible to isolate crystals of (8). Moreover, complex (7) proved unstable. In these circumstances a study was made using C$_6$F$_5$C≡CC$_6$F$_5$ in the expectation that the electronegative pentafluorophenyl groups would enhance the stability of the resulting diplatinum compound. This proved to be the case, resulting in the isolation of complex (9) in good yield and stable up to *ca.* 150 °C. The ^{31}P n.m.r. spectrum was of similar pattern to that of (7) although ^{31}P–^{19}F coupling caused some broadening of the observed peaks. Interestingly, similar coupling was not observed in the spectrum of [Pt(C$_6$F$_5$C$_2$C$_6$F$_5$)(PMe$_3$)$_2$] (10), prepared for spectral comparisons.

The availability of [Pt(PhC$_2$Ph)(CNBu^t)$_2$] [1] suggested the synthesis of a μ-PhC$_2$Ph compound with tertiary-butyl isocyanide ligands on one platinum atom and tertiary phosphine ligands on the other. Accordingly equimolar amounts of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and [Pt(PhC$_2$Ph)(CNBu^t)$_2$] were stirred together in light petroleum giving a yellow complex (11). Once again, selective ^{13}C enrichment suggested that an absorption in the i.r. at 1 516 cm^{-1} may be associated with a modified acetylenic C≡C stretch. The ^{31}P n.m.r. spectrum (Table 1), however, was of a pattern corresponding to the presence of a R$_3$P–Pt–Pt–PR$_3$ skeleton. Thus scrambling of the ligands had occurred, leading to the formation of one of the two possible isomers (11a) or (11b).



(a) *trans* (b) *cis*

	R
(11)	Ph
(12)	C$_6$H$_4$OMe-4

To elucidate the stereochemistry of the single isomer formed, the analogous complex (12) was prepared *in situ* from [Pt(PhC$_2$C$_6$H$_4$OMe-4)(CNBu^t)$_2$] (13) and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] for a ^{31}P n.m.r. study. Since the *cis* isomer (12b) has a plane of symmetry through the C–C bond and the midpoint of the Pt–Pt vector, this isomer has identical environments for the phosphorus nuclei. Moreover, since the *trans* isomer (12a) lacks the C$_2$ axis found in the diphenylacetylene analogue (11a), the phosphine ligands are not equivalent in the former species. Since the observed ^{31}P n.m.r. spectrum of (12) has an AB doublet as its central component, rather than the singlet expected for equivalent ^{31}P nuclei, the *trans* configuration (12a) must be assumed for (12), and by inference a similar stereochemistry (11a) can be assumed for (11) also.

In addition to the main doublet resonance, the ^{31}P n.m.r. spectrum of (12a) showed two signals of equal intensity at 28.7 [^1J(PtP) 3 205] and 28.3 p.p.m. [^1J(PtP) 3 284 Hz] attributable to the presence of monoplatinum complexes as impurities. By comparison with the spectrum of [Pt(PhC$_2$Ph)(CNBu^t)(PPh$_3$)] [13] (Table 1) these two peaks can be assigned to the two possible isomers of [Pt(PhC$_2$C$_6$H$_4$OMe-4)(CNBu^t)(PPh$_3$)] (14), their presence in solution indicating how readily the di- and tri-nuclear platinum species dissociate.

The tendency of the di- and tri-platinum complexes to dissociate, together with the relatively long platinum–platinum distances [2.890(2) Å in (4), and 2.904(1) Å in

(6)], suggests little metal–metal interaction in these platinum(0) complexes, as discussed above. Moreover, in the related nickel compound $[Ni_2(\mu\text{-}PhC_2Ph)(cod)_2]$ [22] it seems unlikely that any metal–metal bonding exists either,[17] the two metal centres being held together by the steric constraints of the bridging alkyne. The values of ^1J(PtPt) for complexes (4) and (7) (1 006 and 470 Hz, respectively) unfortunately provide little insight into metal–metal interactions.[23] However, several general conclusions can be drawn from the available spectroscopic data on the compounds containing bridging alkyne ligands. (*i*) The C–C bond order is decreased considerably in passing from the mono- to the di-platinum compounds, as evidenced by the lowering of $\nu_{max.}$(C≡C). (*ii*) On the basis of changes in ^{13}C n.m.r. chemical shifts, rehybridisation of the platinum-bonded carbon atoms occurs in passing from the monoplatinum complexes to those containing bridging acetylene ligands, corresponding to approximately sp^2 hybridisation in the former and sp^3 in the latter. (*iii*) An increase in ^1J(PtP) in the relative order $[Pt(RC_2R)L_2] < [Pt_2(\mu\text{-}RC_2R)L_4] \ll [Pt_3(\mu\text{-}RC_2R)_2L_4] < [Pt_2(RC_2R)_2L_2]$ may be associated with an increase in π back donation from the platinum to the bridging acetylene groups. (*iv*) The π-acceptor ability of the alkyne is of importance in stabilising bridged complexes, since the available ^{13}C n.m.r. data indicate that the degree of σ bonding does not significantly change when the alkyne adopts a μ-η^2-bridging mode.

EXPERIMENTAL

The instrumentation used and experimental methods were as described earlier.[1] Carbon-13 chemical shifts are relative to $SiMe_4$ (0.0 p.p.m.), and ^{31}P chemical shifts are relative to external 85% H_3PO_4 (0.0 p.p.m.) and are positive to low field. Infrared bands were recorded in Nujol. Light petroleum refers to that fraction of b.p. 30—40 °C. The compounds $[Pt(cod)_2]$,[24] $[Pt(PhC_2Ph)_2]$,[1] $[Pt(PhC_2Ph)(CNBu^t)_2]$,[1] $[Pt(C_2H_4)_2(PPh_3)]$,[12] $[Pt_2(\mu\text{-}cod)(PEt_3)_4]$ [10] $Ph^{13}C{\equiv}CPh$,[1] and $C_6F_5C_2C_6F_5$ [25] were prepared by literature methods. The complex $[Pt(C_2H_4)(PPh_3)_2]$ was prepared by dissolving $[Pt(cod)_2]$ in light petroleum saturated with ethylene, followed by addition of 2 mol equivalents of PPh_3.

Preparations.—$[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PPh_3)_2]$. (*i*) To a suspension of $[Pt(PhC_2Ph)_2]$ (0.138 g, 0.25 mmol) in light petroleum (10 cm^3) was added $[Pt(C_2H_4)(PPh_3)_2]$ (0.187 g, 0.25 mmol). After stirring for 2 h, a yellow precipitate formed which was isolated, washed with light petroleum (2 × 3 cm^3), and dried *in vacuo* affording yellow *microcrystals* of $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PPh_3)_2]$ (2) (78 mg, 25%), m.p. (*in vacuo*) >250 °C (Found: C, 61.2; H, 4.3. $C_{64}H_{50}P_2Pt_2$ requires C, 60.5; H, 4.0%); $\nu_{max.}$ 3 058w, 1 840m (C≡C), 1 603m, 1 596m, 1 573w, 1 483m, 1 439s, 1 314w, 1 270w, 1 189w, 1 165w, 1 103s, 1 078w, 1 037m, 1 009w, 922w, 891w, 814w, br, 765s, 754s, 712(sh), 702vs, 599m, 573m, 543s, 529s, 518s, 509(sh), and 431w cm^{-1}.

(*ii*) To a solution of PhC_2Ph (26 mg, 0.146 mmol) in diethyl ether (1 cm^3) at 0 °C was added a solution of $[Pt(C_2H_4)_2(PPh_3)]$ (75 mg, 0.146 mmol) in diethyl ether (5 cm^3). The yellow solution was stirred (45 min) at 0 °C. Addition of light petroleum (30 cm^3) gave a yellow precipitate which was washed with light petroleum (2 × 5 cm^3) and dried *in vacuo* affording (2) (50 mg, 50%).

$[Pt(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PEt_3)_2]$. The complex $[Pt_2(\mu\text{-}cod)(PEt_3)_4]$ was prepared from PEt_3 (0.118 g, 1.0 mmol) and $[Pt(cod)_2]$ (0.205 g, 0.5 mmol) in light petroleum (10 cm^3). After stirring (15 min) all volatile material was removed *in vacuo* and the residue dissolved in light petroleum (15 cm^3) and added to a suspension of $[Pt(PhC_2Ph)_2]$ (0.276 g, 0.5 mmol) in light petroleum (10 cm^3). The mixture was stirred (1 h) and then evaporated *in vacuo*. The oil remaining was dissolved in diethyl ether, filtered through a Florisil pad (1 × 3 cm), and all solvent removed *in vacuo*. The oil was triturated with light petroleum affording, from diethyl ether–light petroleum, yellow-orange *crystals* of $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PEt_3)_2]$ (3) (0.272 g, 55%), m.p. (*in vacuo*) 141—142 °C (decomp.) (Found: C, 49.2; H, 5.2. $C_{40}H_{50}P_2Pt_2$ requires C, 48.9; H, 5.1%); $\nu_{max.}$ at 3 055w, 1 842m (C≡C), 1 600s, 1 541w,br, 1 488s, 1 445s, 1 419w, 1 259w, 1 160w, 1 074w, 1 038s, 918w, 884w, 777s, 761vs, 743m, 737m, 726m, 702s, 697s, 634m, 593m, 571s, 556m, and 519m cm^{-1}; ^{1}H n.m.r. ([$^2H_1$]chloroform), τ 2.02—3.07 (m, 20 H, Ph), 8.39 (m, 12 H, CH_2), and 9.01 (m, 18 H, CH_3).

$[Pt_3(\mu\text{-}PhC_2Ph)_2(PPh_3)_4]$. (*i*) A mixture of $[Pt(PhC_2Ph)_2]$ (0.100 g, 0.181 mmol) and freshly prepared $[Pt(C_2H_4)(PPh_3)_2]$ (0.271 g, 0.363 mmol) was suspended in light petroleum (40 cm^3) and stirred for 4 h. The mixture was evaporated *in vacuo* and the residue washed with diethyl ether (50 cm^3). The solid was recrystallised from dichloromethane–light petroleum giving purple *crystals* of $[Pt_3(\mu\text{-}PhC_2Ph)_2(PPh_3)_4]$ (5) (66 mg, 18%), m.p. (*in vacuo*) 148—150 °C (decomp.) (Found: C, 59.7; H, 4.5. $C_{100}H_{50}P_4Pt_3$ requires C, 60.3; H, 4.1%); $\nu_{max.}$ at 3 052w, 1 595m (C≡C), 1 571w,br, 1 479m, 1 438s, 1 189w, 1 162w, 1 099s, 1 077w, 1 037w, 1 007w, 919w, 851w, 776w, 748m, 700s, 627w, 578w, 551(sh), 538s, 526s, 517s, 504m, 459w, and 429w cm^{-1}.

(*ii*) A mixture of (2) (0.240 g, 0.189 mmol) and $[Pt(C_2H_4)(PPh_3)_2]$ (0.141 g, 0.189 mmol) was suspended in light petroleum (20 cm^3) and stirred for 2 h. Removal of the solvent *in vacuo* gave a residue which on washing with diethyl ether (3 × 10 cm^3) and light petroleum (10 cm^3) and on drying *in vacuo* afforded complex (5) (0.13 g, 35%).

$[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$. A light petroleum solution of $[Pt_2(\mu\text{-}cod)(PEt_3)_4]$ (0.227 mmol), prepared as described above, was added to a suspension of $[Pt(PhC_2Ph)_2]$ (0.125 g, 0.227 mmol) in light petroleum (15 cm^3). The resultant red solution was stirred for 15 min, filtered, and then crystallised (−10 °C) overnight to give red-orange *crystals* of $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$ (6) (0.120 g, 35%), washed with light petroleum (2 × 2 cm^3), m.p. (*in vacuo*) 143—148 °C (decomp.) (Found: C, 43.8; H, 5.6. $C_{52}H_{80}P_4Pt_3$ requires C, 44.2; H, 5.7%); $\nu_{max.}$ at 3 064m, 1 600vs (C≡C), 1 561m, 1 486s, 1 440s, 1 412w, 1 302w,br, 1 251m, 1 067w, 1 050(sh), 1 032s, 995w, 984w, 766s, 758(sh), 742(sh), 737m, 714m, 695s, and 688(sh) cm^{-1}; ^{1}H n.m.r. (CH_2Cl_2), τ 2.53—3.13 (m, 20 H, Ph), 8.43 (m, 24 H, CH_2), and 9.09 (m, 36 H, CH_3).

$[Pt_2(\mu\text{-}PhC_2Ph)(PMe_3)_4]$. To light petroleum (10 cm^3) saturated with ethylene at 0 °C was slowly added $[Pt(cod)_2]$ (0.205 g, 0.5 mmol). Once all the solid had dissolved, a solution of trimethylphosphine (1 mmol) in light petroleum was added. After stirring (5 min) at 0 °C, diphenylacetylene (44 mg, 0.25 mmol) was added and the solution was stirred at room temperature for 2 h. The cloudy white suspension slowly turned to a clear dark yellow solution. Following removal of some solvent *in vacuo* the product was allowed to crystallise at −20 °C. Clear yellow *prisms* of $[Pt_2(\mu\text{-}PhC_2Ph)(PMe_3)_4]$ (7) (80 mg, 18%) were separated by hand from a white precipitate also formed, and were indefinitely stable at 0 °C under nitrogen, m.p. (*in vacuo*) 128—130 °C (decomp.) (Found: C, 35.6; H, 5.3. $C_{26}H_{46}P_4Pt_2$ requires C, 35.7; H, 5.3%); $\nu_{max.}$ at 1 589m, 1 491m ($C\equiv C$), 1 410w, 1 295w, 1 275m, 1 060w, 1 020w, 935s,br, 835w, 765m, 710m, 690m, 670w, 660w, and 570w, cm^{-1}; ^{1}H n.m.r. ([$^{2}H_8$]toluene), τ 2.10—2.85 (m, 10 H, Ph), 8.50 [second-order multiplet, 36 H, Me, ^{3}J(PtH) 28, $|^{2}J(PH) + {}^{4}J(PH)|$ *ca.* 7 Hz].

Complex (7) was also synthesised from 25%-enriched $Ph^{13}C\equiv CPh$, $\nu_{max.}$ at 1 590s, 1 523w, 1 495s, 1 489s, 1 478s, 1 436m, 1 428w, 1 412m, 1 295m, 1 277s, 1 272m, 1 060w, 1 020w, 935s,br, 835m, 765s, 710m, 690s, 670m, 660m, and 570w cm^{-1}.

[$Pt_2(\mu$-$C_6F_5C_2C_6F_5)(PMe_3)_4$]. This complex was prepared in an analogous manner to that of (7). Removal of solvent *in vacuo* gave yellow *microcrystals* of [$Pt_2(\mu$-$C_6F_5C_2C_6F_5)(PMe_3)_4$] (9) (0.3 g, 70%), m.p. 155—156 °C (decomp.) (Found: C, 28.6; H, 3.6; F, 18.3. $C_{26}H_{36}F_{10}P_4Pt_2$ requires C, 29.6; H, 3.4; F, 18.0%); $\nu_{max.}$ at 1 504s,br, 1 307w, 1 303w, 1 288m, 1 284w, 1 261w, 1 086s, 1 006m, 988s, 949s,br, 894w, 857m, 853w, 802w, 784w, 758w, 743m, 705w, 686w, 677m, 660w, 621w, 581w, and 480w cm^{-1}.

[$Pt(C_6F_5C_2C_6F_5)(PMe_3)_2$]. To a stirred suspension of [$Pt(cod)_2$] (0.205 g, 0.5 mmol) in light petroleum (10 cm^3) was added a solution of trimethylphosphine (1 mmol) in light petroleum. Decafluorotolan, $C_6F_5C_2C_6F_5$ (0.179 g, 0.5 mmol), was added, giving a colourless solution which on stirring (5 min) afforded a heavy white precipitate. This solid was washed with light petroleum (4 × 5 cm^3) and dried *in vacuo* to afford white *microcrystals* of [$Pt(C_6F_5C_2C_6F_5)(PMe_3)_2$] (10) (0.255 g, 70%), m.p. 161—162 °C (decomp.) (Found: C, 33.9; H, 2.8; P, 8.5. $C_{20}H_{18}F_{10}P_2Pt$ requires C, 34.0; H, 2.6; P, 8.8%); $\nu_{max.}$ at 1 701s ($C\equiv C$), 1 510s, 1 468s, 1 439w, 1 428m, 1 404w, 1 319w, 1 308m, 1 299w, 1 290s, 1 110s, 1 039w, 1 018s, 994s, 968s, 954m, 944m, 927w, 867w, 859m, 854w, 819m, 778m, 740s, 714w, 690w, 680m, 665m, 635w, 585w, and 550w cm^{-1}.

trans-[$Pt_2(\mu$-$PhC_2Ph)(CNBu^t)_2(PPh_3)_2$]. To a suspension of [$Pt(PhC_2Ph)(CNBu^t)_2$] (0.10 g, 0.18 mmol) in light petroleum (10 cm^3) was added [$Pt(C_2H_4)(PPh_3)_2$] (0.14 g, 0.18 mmol) with stirring for 2 h. A dark red solution formed and then a yellow precipitate, thereby leaving a clear yellow supernatant liquid. The precipitate was washed with light petroleum (4 × 5 cm^3) and dried (*in vacuo*) to afford yellow *microcrystals* of [$Pt_2(\mu$-$PhC_2Ph)(CNBu^t)_2(PPh_3)_2$] (11a) (0.18 g, 80%), m.p. 121—122 °C (decomp.) (Found: C, 57.4; H, 4.9; N, 1.7. $C_{60}H_{58}N_2P_2Pt_2$ requires C, 57.2; H, 4.6; N, 2.2%); $\nu_{max.}$ at 2 110s,br (NC), 1 590m, 1 516m ($C\equiv C$), 1 440m, 1 238w, 1 216m, 1 102m, 1 036w, 1 006w, 732w, 702s, 600w, 562w, 532s, 522m, and 512m cm^{-1}; ^{1}H n.m.r. ([$^{2}H_6$]benzene), τ 2.20—3.30 (m, 40 H, Ph) and 9.13 (s, 18 H, Bu^t).

trans-[$Pt_2(\mu$-$PhC_2C_6H_4OMe$-$4)(CNBu^t)_2(PPh_3)_2$]. The complex [$Pt(PhC_2C_6H_4OMe$-$4)(CNBu^t)_2$] (13) was prepared in an analogous manner to [$Pt(PhC_2Ph)(CNBu^t)_2$] [1] and its identity verified by i.r. spectroscopy, $\nu_{max.}$ at 2 162s (NC), 2 128s (NC), 1 735m ($C\equiv C$), 1 590m,br, 1 562w, 1 501m, 1 459m, 1 440m, 1 408w, 1 393w, 1 298m, 1 249s, 1 209m,br, 1 182w, 1 172w, 1 163m, 1 127w, 1 103w, 1 069w, 1 032w, 892w, 838m, 815w, 798w, 779w, 762m, 732w, 694m, 589w, 542m, 528m, 508w, 450w, and 409w cm^{-1}.

Equivalent mol amounts of (13) and [$Pt(C_2H_4)(PPh_3)_2$] were stirred as a slurry in light petroleum. The reaction was periodically monitored by the removal of solvent *in vacuo* and observation of the disappearance of the terminal acetylene i.r. stretch of complex (13) at 1 735 cm^{-1}. When this band disappeared (*ca.* 2 h), the residue was dissolved in toluene and its ^{31}P n.m.r. spectrum recorded (Table 1).

Crystal-structure Determination of [$Pt_3(\mu$-$PhC_2Ph)_2(PEt_3)_4$] (6).—Crystals of (6) grow as orange prisms from diethyl ether. The crystals shatter on cooling and decompose in *X*-rays. Intensities were therefore collected at room temperature in the range $2.9 \leqslant 2\theta \leqslant 50°$ on a Syntex $P2_1$ four-circle diffractometer, with a scan rate varying up to 0.488° s^{-1} according to the magnitude of a preliminary 2-s count. A net intensity decrease of 16.5% was observed by monitoring three standard reflections during the 90 h of crystal exposure, for which correction was subsequently made. The intensities were also corrected for the effects of *X*-ray absorption [μ(Mo-K_α) = 72.8 cm^{-1}], the crystal dimensions being 0.35 ($110/\bar{1}\bar{1}0$), 0.23 ($010/0\bar{1}0$), and 0.20 ($001/00\bar{1}$) mm. Of the total 4 975 independent reflections, 3 038 satisfied the criterion $I/\sigma(I) > 3.0$ and were used in the refinement of the structure.

Crystal data. $C_{52}H_{80}P_4Pt_3$, M = 1 414.3, Monoclinic, a = 17.047(2), b = 13.677(2), c = 25.073(3) Å, β = 105.79(1)°, D_m = 1.58, Z = 4, D_c = 1.67 g cm^{-3}, U = 5 625(1) Å^3, $F(000)$ = 2 744, space group $C2/c$, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 72.8 cm^{-1}.

The structure was solved by heavy-atom methods assuming space-group symmetry *Cc*. Successive electron-density difference syntheses following the location of the platinum atoms revealed all non-hydrogen atoms, giving a molecular structure with two-fold symmetry in the *b* direction. Consequently, all further refinement was carried out in space group *C2/c* using blocked-matrix least-squares methods.[26] Anisotropic thermal parameters were used for all non-hydrogen atoms, and the hydrogen atoms themselves were incorporated at calculated positions with a fixed isotropic thermal parameter U = 0.03 Å^2. Despite the successful location of the ethyl-carbon atoms, refinement consistently produced high thermal parameters for these atoms. No consistent disorder model could be found, and as these atoms have no relevance to the interest of the structure they have been omitted from Figure 1. They are included, however, in both the stereoscopic view (Figure 2) and in the molecular packing diagram (Figure 3) where the molecule nearest to the origin corresponds to the atomic co-ordinates listed in Table 2. From this diagram the ethyl-carbon atom labels C(15)—C(26) can be readily identified. Refinement converged at R 0.047 (R' 0.046) with an optimised weighting scheme $w = 0.779/[\sigma^2(F) + 0.000\,3(F)^2]$. A final electron-density difference synthesis showed peaks at *ca.* 1.0 e Å^{-3} in the region of the Pt atoms but no peaks >0.8 or < −0.8 e Å^{-3} elsewhere. Atomic scattering factors were those of ref. 27 for Pt, P, and C, those for Pt being corrected for anomalous dispersion [28] (Pt, $\Delta f'$ −2.35, $\Delta f''$ 8.39). Scattering factors for hydrogen were from ref. 29. All computational work was carried on the South-Western Universities' Network with the SHELX system of programs.[26] Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22843 (19 pp.).*

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

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