Chemistry of the Metal Carbonyls. Part 77.[1] Some Reactions of the Platinumtriosmium Complexes $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ with Donor Molecules; *X*-Ray Crystal Structures of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ and $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$†

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The compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ react with CO, PPh_3, or $AsPh_3$ to give complexes $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)L]$ [$PR_3 = P(cyclo\text{-}C_6H_{11})_3$, L = CO; $PR_3 = PPh_3$, L = PPh_3 or $AsPh_3$]. Hydrogen-1 and ^{31}P n.m.r. data for the compounds are discussed, and a single-crystal *X*-ray diffraction study has been carried out on the compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$, crystals of which are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 14.427(7)$, $b = 12.793(5)$, $c = 14.151(6)$ Å, $\alpha = 92.33(3)$, $\beta = 120.87(3)$, and $\gamma = 91.06(4)°$. The structure has been refined to R 0.041 (R' 0.044) for 5 794 independent reflections ($2.9 \leqslant 2\theta \leqslant 60°$, Mo-$K_\alpha$ *X*-radiation) collected at 200 K. The four metal atoms adopt a butterfly arrangement in contrast to the tetrahedral cluster structure of the 58-electron precursors $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$. In $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ the metal–metal bonding distances are Os–Pt 2.717(1) and 2.848(1) Å, and Os–Os 2.773(1), 2.914(1), and 3.043(1) Å. Evidence is presented for the two hydrido-ligands bridging the longer Os–Pt and Os–Os bonds. One triphenylphosphine ligand is attached to platinum and the other to osmium, and all the carbonyl ligands are terminally bound. Reaction of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$ with but-2-yne affords a mixture, from which five polynuclear metal complexes were isolated and studied by i.r. and n.m.r. spectroscopy. None of these products contained the Os_3Pt cluster of the precursor. One of the complexes was characterised as $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$ and its structure established by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 11.143(8)$, $b = 17.458(12)$, $c = 23.443(15)$ Å, and $\beta = 113.82(5)°$. The structure has been refined to R 0.031 (R' 0.033) for 4 438 independent reflections ($2.9 \leqslant 2\theta \leqslant 55°$, Mo-$K_\alpha$ *X*-radiation) collected at 200 K. The metal atoms form an isosceles triangle [Os–Pt 2.662(2) (mean), Pt–Pt 3.033(2) Å] bridged by a face-bonding but-2-yne molecule whose orientation with respect to the triangle is $\mu_3(\eta^2\text{-}\|)$. The osmium atom carries three terminal CO ligands, and each platinum a CO and PPh_3 group such that there is a cisoid arrangement OCPtPtCO; the Pt–Pt separation of 3.033(2) Å, however, suggests that there may be little direct metal–metal interaction.

WE have recently reported[1] that the complexes $[Pt(C_2H_4)_2(PR_3)]$ [$PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3, or $PBu^t{}_2Me$] react with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to afford the tetrametallic compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$. An *X*-ray crystallographic study revealed an essentially tetrahedral structure for these molecules, distortion from ideality being largely due to a lengthening of an Os–Pt and an Os–Os bond by two edge-bridging hydrido-ligands. An interesting feature of these tetranuclear compounds is that they possess five skeletal bond pairs for bonding of the $PtOs_3$ core, rather than the six bond pairs associated with tetrahedral molecules such as $[Ir_4(CO)_{12}]$.[2] As discussed earlier,[1] the apparent 'unsaturation' of the compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$, in the sense that they are 58 rather than 60 valence electron species, is probably related to the tendency of platinum to employ only 16 valence electrons in many of its compounds. However, it was of interest to investigate reactions of these cluster compounds with donor molecules in order to establish whether 60-electron configurations are readily attained, and if so whether or not the *closo* structure is preserved. A preliminary account of a portion of the results described in this paper has been given.[3]

RESULTS AND DISCUSSION

When CO gas is bubbled through solutions of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (1) in diethyl ether, within a few seconds the original green colour of the solution becomes bright yellow. However, when the CO atmosphere is removed the yellow solution acquires a green tinge due to reformation of the starting compound and establishment of the equilibrium shown below.

$$(1) + CO \rightleftharpoons [Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}] \quad (2)$$

Fortunately, crystals of compound (2) could be obtained by concentration of solutions under a CO atmosphere, and as a solid it was reasonably stable. Significantly $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, with 46 valence electrons, also reacts reversibly with CO, affording the 48-electron compound $[Os_3H(\mu\text{-}H)(CO)_{11}]$.[4,5]

The ^{31}P and ^1H n.m.r. spectra of (2) were informative. The ^{31}P spectrum showed a singlet (δ −50.4 p.p.m.) with ^{195}Pt coupling [J(PtP) 2 409 Hz], characteristic of a direct P–Pt bond. The ^1H n.m.r. of (2), measured at −60 °C because of dynamic behaviour, showed resonances due to the cyclohexyl groups and two high-field signals at τ 21.60 [J(PH) 11, J(PtH) 513 Hz] and 27.60 [J(PH) 3, J(PtH) 30 Hz]. The relative magnitudes of these coupling constants indicate that the signal at τ 21.60 is due to a hydrido-ligand bound directly to

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† 1,2,2,2,3,3,3,4,4,4-Decacarbonyl-1,2;3,4-di-μ-hydrido-1,3-bis(triphenylphosphine)-*cyclo*-platinumtriosmium (2 *Pt–Os*)(3 *Os–Os*) and 1,2,3,3,3-pentacarbonyl-1,2,3-μ_3-1,2-dimethylvinylene-1,2-bis(triphenylphosphine)-*cyclo*-diplatinumosmium (2 *Pt–Os*).

platinum whereas the hydrido-ligand giving the resonance at τ 27.60 is not. Moreover, the chemical shift of the latter is consistent with its assignment as a bridging $[Os(\mu\text{-}H)Os]$ group since this system is known to give resonances with shifts in this region.[6]

It is interesting to note that there is an up-field shift of *ca.* τ 10 in the resonance of the $Os(\mu\text{-}H)Os$ proton in both the conversion of (1) (τ 16.93) into (2) (τ 27.60), and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (τ 20.9) into $[Os_3H(\mu\text{-}H)(CO)_{11}]$ (τ 29.97). There is a much smaller change in chemical shift between the proton associated with the platinum atom in (1) (τ 18.44) and in (2) (τ 21.60). Although the factors which determine the chemical shifts of hydrido-ligands are complex,[7,8] it would appear that the electronic effects generated by changing from formally 'unsaturated' to 'saturated' cluster compounds are responsible for the up-field shifts. An anomalous low-field shift is found for the face-bridging hydrido-ligands in the 56-electron cluster $[Re_4(\mu\text{-}H)_4(CO)_{12}]$ (τ 15.08).[9] In the 60-electron dianion cluster $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$ the hydrido-ligands give ^1H n.m.r. signals at τ 26.7 and 27.3.[10]

The formation of (2) from (1) by addition of a molecule of CO results in an extra two valence electrons being added to the cluster as a whole, bringing the total to the 60 electrons associated with most tetranuclear metal systems which adopt tetrahedral structures as predicted by electron counting schemes.[2,11,12] However, because of the platinum atom present in (2) some structure other than tetrahedral may be expected.[1] It was essential, therefore, to carry out an *X*-ray diffraction study on (2) to ascertain whether there had been gross changes in the metal framework compared with (1). Unfortunately all crystals grown of (2) proved to be twinned, and so studies were directed towards reactions with other electron-pair donors to establish whether these paralleled the CO reaction, and also to obtain suitable crystals for diffraction work.

Reaction in diethyl ether at room temperature of the complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$ (3) with either PPh_3 or $AsPh_3$ gave the adducts $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)L]$ (4, L = PPh_3; 5, L = $AsPh_3$). It was also possible to prepare (4) directly from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Pt(C_2H_4)(PPh_3)_2]$, although in this synthesis the reaction proceeded in two stages, namely initial formation of the green complex (3), followed by a much slower reaction to give a yellow solution of (4).

Complexes (4) and (5) each showed two sets of high-field resonances in their ^1H n.m.r. spectra at -60 °C. For (4) signals occurred at τ 18.55 [*J*(PH) 18, *J*(PtH) 590 Hz] and 27.55 [*J*(PH) 14 Hz], and for (5) they were at τ 18.50 [*J*(PH) 20, *J*(PtH) 580 Hz] and 27.60. The resonances in the spectra of (4) and (5) which show strong ^{195}Pt coupling can be attributed to a bridging hydrido-ligand $Os(\mu\text{-}H)Pt$, as found[1] in compound (3) [τ 17.52, *J*(PH) 16, *J*(PtH) 590 Hz]. The signals at τ 27.55 and 27.60 in the spectra of (4) and (5), respectively, can be correspondingly assigned to $Os(\mu\text{-}H)Os$ groups. It was of interest that whereas the resonance in the triphenylarsine adduct at τ 27.60 was a singlet, the signal in (4) at τ 27.55 was a doublet due to ^{31}P coupling. This suggested that the added triphenylphosphine ligand in (4) had co-ordinated to one of the osmium atoms rather than to platinum. This was confirmed by an examination of the ^{31}P n.m.r. spectrum.

The $^{31}P\{^1H\text{-decoupled}\}$ n.m.r. spectrum of (4) at -60 °C had singlet resonances at δ -30.7 p.p.m. [*J*(PtP) 2 501 Hz] and 7.3 p.p.m. With selective ^1H decoupling these resonances became doublets with *J*(PH) 15 and 12 Hz, respectively. These data establish that in (4) one PPh_3 ligand is bonded to platinum and the other to osmium. The presence of a signal at δ -31.2 p.p.m. in the ^{31}P n.m.r. spectrum of the triphenylarsine derivative (5), with ^{195}Pt satellites and *J*(PPt) 2 502 Hz, of a similar magnitude to that found in the spectrum of compound (4), suggests that the two species are structurally analogous, an idea supported by the close similarity of their i.r. spectra in the CO region.

An interesting feature was observed in the variable-temperature ^{31}P n.m.r. spectrum of (4). At ambient temperature the down-field satellite of the signal at -30.7 p.p.m. and the signal itself were broadened relative to the up-field satellite and to the resonance due to the osmium-bound phosphorus nucleus at 7.3 p.p.m. At -50 °C this broadening had disappeared and two new peaks at very low intensity were observed at -34.4 and 6.5 p.p.m., close to the main resonances at -30.5 and 7.3 p.p.m. These observations are taken to indicate the presence of a second species isomeric with the first, and in equilibrium with it. At room temperature the rate of exchange between the two isomers is sufficiently fast compared with the time scale of the measurement that signals due to this second species are not clearly visible. On cooling to -50 °C, however, the rate of interconversion is slower and low intensity signals of the second isomer, representing only a few percent of the main complex, can be seen. The differential broadening of the low-field satellite can be explained by assuming a ^{195}Pt coupling of *ca.* 2 800 Hz on the resonance at -34.4 p.p.m. With ^{195}Pt coupling of the magnitude proposed the up-field satellites of both isomers are roughly coincident, and any broadening would be minimal. The ambient temperature ^{31}P n.m.r. spectrum of (5) showed a similar differential broadening in the ^{195}Pt satellites, whereas such an effect was not observed in the spectrum of (2).

Fortunately crystals of (4), grown from diethyl ether, proved to be of suitable quality for *X*-ray diffraction work, the results of which are summarised in Tables 1 and 2; the molecular structure with the atomic numbering scheme is shown in Figure 1. It is immediately apparent that the four metal atoms in (4) adopt a butterfly arrangement, in contrast to the tetrahedral structures of complex (1) established by *X*-ray crystallography, and of (3) inferred from spectroscopic properties which are similar to those of (1).[1] This result is in agreement with Wade's rules [2] and with Lauher's [11] results which predict that addition of two extra electrons to the cluster will result in scission of a metal–metal bond. Moreover, as discussed earlier [1] the presence of the platinum atom in the cluster gives rise to the structure expected for 62 valence electrons rather than the 60 electrons present in (4), *i.e.* C_{2v} symmetry occurs rather than T_d for the metal atoms.[11]

As established by the n.m.r. studies, the added PPh_3 ligand is bonded to an osmium atom [Os(1)]. The Os(1)–Pt distance of 3.530(1) Å is indicative of little if any direct metal–metal interaction. Metal–metal bonding distances between third-row transition elements of up to 3.504(1) Å have been observed, *e.g.* in the anion $[W_2(\mu\text{-}H)(CO)_{10}]^-$,[13] but in all such compounds bridging hydrido-ligands have been present. There was no evidence for hydrido-bridges across the Os(1)–Pt vector. The remaining metal–metal distances show more variation than those found in compound (1) [1] and in agreement with this the dihedral angles within the Os_3Pt system vary considerably from that expected for a regular tetrahedron.

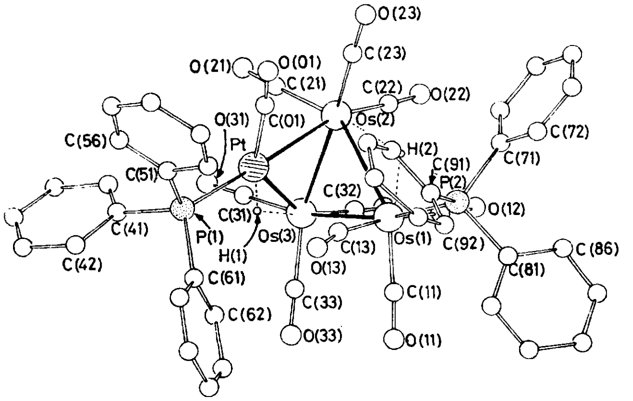


FIGURE 1 Molecular structure of (4), $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$, showing the crystallographic numbering sequence

Of the two bonding Pt–Os distances, Pt–Os(3) is *ca.* 0.1 Å longer than Pt–Os(2). The Os(1)–Os(2) separation is also *ca.* 0.1 Å longer than Os(1)–Os(3), and these longer Pt–Os and Os–Os linkages are postulated to be bridged by the two hydrido-ligands known to be present from the n.m.r. studies. In accord with the proposed location of the hydrido-ligands, the angles Pt–Os(3)–C(33) = 114.1(4), Os(3)–Pt–P(1) = 122.0(1), Os(1)–Os(2)–C(23) = 113.5(4), and Os(2)–Os(1)–P(2) = 112.7(1)° are widened, whereas other *cis*-M–M–ligand angles range from 76.8(5) to 106.7(6)°. Moreover, the staggering of the tricarbonyl groups on Os(2) and Os(3) with respect to the edges Os(1)–Os(2) and Os(3)–Pt favours location of the hydrido-ligands along these edges.[1] Calculations [14] also indicated the presence of sites of suitably low potential energy along these edges, the locations of which, at plausible distances of *ca.* 1.85 Å from the corresponding metal atoms, have been included in Table 1 as the co-ordinates of the two hydrido-ligands. This is in accord with the evidence from the ^1H n.m.r. spectrum at –60 °C which showed two distinct hydrido-ligands both coupled to separate phosphorus nuclei. There was no evidence, however, from Fourier synthesis of residual electron density in the positions discussed.

The *trans* influence [7] of the PPh_3 ligand results in lengthening of the Os(1)–Os(3) bond [2.914(1) Å] as

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (4)

Atom	*x*	*y*	*z*
Pt	–0.131 66(3)	0.191 36(2)	0.235 01(2)
Os(1)	–0.179 74(3)	0.361 37(2)	0.025 61(2)
Os(2)	–0.085 89(3)	0.145 65(2)	0.074 49(2)
Os(3)	0.025 27(3)	0.316 24(2)	0.219 99(2)
H(1)	–0.034 5	0.303 1	0.308 1
H(2)	–0.205 1	0.220 4	–0.016 8
C(01)	–0.225 9(11)	0.077 0(10)	0.155 5(9)
O(01)	–0.290 6(8)	0.010 9(8)	0.114 7(7)
C(11)	–0.161 9(11)	0.505 5(9)	0.070 0(8)
O(11)	–0.153 2(8)	0.592 4(7)	0.100 8(6)
C(12)	–0.104 6(10)	0.387 0(9)	–0.050 5(8)
O(12)	–0.063 5(8)	0.403 5(8)	–0.101 2(7)
C(13)	–0.261 3(10)	0.351 8(9)	0.101 5(8)
O(13)	–0.319 0(8)	0.363 7(7)	0.133 3(6)
C(21)	0.027 5(11)	0.063 3(9)	0.183 7(8)
O(21)	0.087 8(9)	0.014 1(8)	0.243 0(7)
C(22)	–0.016 1(11)	0.158 7(10)	–0.006 5(9)
O(22)	0.029 6(9)	0.165 3(8)	–0.053 6(7)
C(23)	–0.185 3(12)	0.035 7(11)	–0.018 6(10)
O(23)	–0.242 9(9)	–0.032 7(9)	–0.077 3(7)
C(31)	0.143 4(11)	0.254 4(10)	0.334 7(9)
O(31)	0.218 8(9)	0.216 3(8)	0.406 2(7)
C(32)	0.099 0(10)	0.345 4(8)	0.146 2(8)
O(32)	0.148 4(8)	0.364 3(8)	0.105 1(6)
C(33)	0.049 7(11)	0.453 0(9)	0.286 8(8)
O(33)	0.065 8(9)	0.537 7(8)	0.325 9(7)
Triphenylphosphine group 1			
P(1)	–0.171 4(2)	0.223 3(2)	0.372 0(2)
C(41)	–0.285 6(10)	0.136 3(9)	0.346 5(8)
C(42)	–0.268 1(10)	0.052 8(9)	0.415 4(8)
C(43)	–0.353 1(11)	–0.020 2(10)	0.387 1(9)
C(44)	–0.451 0(11)	–0.008 6(10)	0.295 8(9)
C(45)	–0.471 5(11)	0.074 4(10)	0.226 7(9)
C(46)	–0.383 0(11)	0.143 3(9)	0.252 7(8)
C(51)	–0.210 9(11)	0.356 5(9)	0.387 3(8)
C(52)	–0.140 0(11)	0.440 0(10)	0.391 3(9)
C(53)	–0.165 9(13)	0.542 6(11)	0.405 2(9)
C(54)	–0.249 6(13)	0.562 1(12)	0.417 8(10)
C(55)	–0.313 3(15)	0.476 3(14)	0.417 6(11)
C(56)	–0.294 3(12)	0.376 1(11)	0.402 2(9)
C(61)	–0.064 9(10)	0.200 1(9)	0.511 3(8)
C(62)	0.026 6(14)	0.149 5(13)	0.531 4(11)
C(63)	0.105 7(16)	0.129 1(16)	0.640 7(13)
C(64)	0.092 9(12)	0.161 0(11)	0.725 0(10)
C(65)	0.000 8(12)	0.214 5(10)	0.708 3(9)
C(66)	–0.076 3(11)	0.233 5(9)	0.598 8(8)
Triphenylphosphine group 2			
P(2)	–0.346 2(2)	0.361 1(2)	–0.142 2(2)
C(71)	–0.370 8(9)	0.273 8(8)	–0.259 3(7)
C(72)	–0.476 3(10)	0.266 1(9)	–0.352 7(8)
C(73)	–0.496 4(10)	0.205 0(9)	–0.442 9(8)
C(74)	–0.413 1(13)	0.149 4(12)	–0.444 6(11)
C(75)	–0.308 5(13)	0.157 2(12)	–0.351 6(10)
C(76)	–0.288 0(11)	0.218 7(10)	–0.257 7(9)
C(81)	–0.376 2(10)	0.488 7(8)	–0.201 7(8)
C(82)	–0.387 3(11)	0.573 2(9)	–0.142 9(8)
C(83)	–0.401 4(12)	0.672 5(11)	–0.180 7(10)
C(84)	–0.403 5(12)	0.689 8(11)	–0.279 4(10)
C(85)	–0.389 2(12)	0.609 2(11)	–0.333 4(10)
C(86)	–0.374 5(11)	0.506 0(10)	–0.298 7(9)
C(91)	–0.461 8(10)	0.321 3(9)	–0.129 1(8)
C(92)	–0.545 5(13)	0.382 1(11)	–0.150 5(10)
C(93)	–0.631 4(15)	0.345 4(15)	–0.130 0(12)
C(94)	–0.622 8(13)	0.247 8(12)	–0.088 9(10)
C(95)	–0.535 6(12)	0.184 2(10)	–0.068 6(9)
C(96)	–0.451 6(11)	0.217 7(10)	–0.085 4(8)

compared with the Os(2)–Os(3) bond [2.773(1) Å]. For the PPh_3 group attached to the platinum the effect on the Pt–Os distances is not as noticeable, due to the complication of the presence of the bridging hydrido-ligand. The geometry about the platinum atom is close to planar with only small deviations, C0(1) being 0.059 Å above the plane defined by Pt, Os(2), and Os(3), *i.e.* on the same side as Os(1), with P(1) 0.053 Å below. The dihedral angles between the faces of the tetrahedron defined by the four metal atoms can conveniently be listed as torsion angles, and are given at the end of Table 2. They range from 60.9 to 88.4°, the maximum value being the angle at the hinge of the butterfly. The dihedral angle for a regular tetrahedron is 70.5°.

TABLE 2

Important interatomic distances (Å) and bond angles (°) for the complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$, with estimated standard deviations in parentheses

(*a*) Distances

Pt–Os(1)	3.530(2)	Os(3)–C(31)	1.87(1)
Pt–Os(2)	2.717(1)	Os(3)–C(32)	1.87(1)
Pt–Os(3)	2.848(2)	Os(3)–C(33)	1.89(1)
Os(1)–Os(2)	3.043(2)		
Os(1)–Os(3)	2.914(2)	C(01)–O(01)	1.14(2)
Os(3)–Os(2)	2.773(2)	C(11)–O(11)	1.16(1)
		C(12)–O(12)	1.16(2)
Pt–P(1)	2.310(3)	C(13)–O(13)	1.14(2)
Os(1)–P(2)	2.357(3)	C(21)–O(21)	1.08(1)
		C(22)–O(22)	1.16(2)
Pt–C(01)	1.86(1)	C(23)–O(23)	1.16(2)
Os(1)–C(11)	1.89(1)	C(31)–O(31)	1.17(2)
Os(1)–C(12)	1.91(2)	C(32)–O(32)	1.16(2)
Os(1)–C(13)	1.96(2)	C(33)–O(33)	1.16(2)
Os(2)–C(21)	1.94(1)		
Os(2)–C(22)	1.88(2)	C–C (phenyl) mean	1.39
Os(2)–C(23)	1.90(1)		
		P–C (phosphines) mean	1.83

(*b*) Angles

Os(1)–Pt–Os(2)	56.51(3)	Os(1)–Os(2)–Os(3)	59.92(4)
Os(1)–Pt–Os(3)	53.07(3)	Pt–Os(3)–Os(1)	75.56(4)
Os(2)–Pt–Os(3)	59.72(2)	Pt–Os(3)–Os(2)	57.80(3)
Pt–Os(1)–Os(2)	48.12(2)	Os(1)–Os(3)–Os(2)	64.44(3)
Pt–Os(1)–Os(3)	51.37(3)	Pt–Os(2)–Os(1)	75.36(2)
Os(2)–Os(1)–Os(3)	55.43(1)	Pt–Os(2)–Os(3)	62.48(3)
C(01)–Pt–Os(1)	102.6(5)	O(01)–C(01)–Pt	170(2)
C(01)–Pt–Os(2)	76.8(5)	O(11)–C(11)–Os(1)	176(1)
C(11)–Os(1)–Pt	115.5(5)	O(12)–C(12)–Os(1)	177(1)
C(11)–Os(1)–Os(3)	91.9(3)	O(13)–C(13)–Os(1)	166(1)
C(12)–Os(1)–Os(2)	89.0(3)	O(21)–C(21)–Os(2)	177(1)
C(12)–Os(1)–Os(3)	89.1(3)	O(22)–C(22)–Os(2)	178(1)
C(13)–Os(1)–Os(2)	97.4(3)	O(23)–C(23)–Os(2)	177(1)
C(13)–Os(1)–Os(3)	93.9(3)	O(31)–C(31)–Os(3)	179(1)
C(21)–Os(2)–Pt	85.0(5)	O(32)–C(32)–Os(3)	177(1)
C(21)–Os(2)–Os(3)	85.5(3)	O(33)–C(33)–Os(3)	178(1)
C(22)–Os(2)–Os(1)	94.6(4)		
C(22)–Os(2)–Os(3)	95.0(3)	P(1)–Pt–Os(2)	125.4(11)
C(23)–Os(2)–Pt	106.7(6)	P(1)–Pt–Os(3)	122.0(1)
C(23)–Os(2)–Os(1)	113.5(4)		
C(31)–Os(3)–Pt	94.5(5)	P(2)–Os(1)–Pt	122.8(1)
C(31)–Os(3)–Os(2)	102.2(3)	P(2)–Os(1)–Os(2)	112.7(1)
C(32)–Os(3)–Os(1)	90.7(3)		
C(32)–Os(3)–Os(2)	91.2(3)		
C(33)–Os(3)–Pt	114.1(5)		
C(33)–Os(3)–Os(1)	94.5(3)		

(*c*) Dihedral angles (torsion angles of the metal skeleton)

Os(3)–Pt–Os(1)–Os(2)	75.0	Os(3)–Os(1)–Os(2)–Pt	66.4
Os(1)–Pt–Os(2)–Os(3)	63.4	Pt–Os(1)–Os(3)–Os(2)	60.9
Os(2)–Pt–Os(3)–Os(1)	68.9	Os(1)–Os(2)–Os(3)–Pt	88.4

It is interesting to compare the previously reported[1] structure for (1) with that of (4), given that the former contains a tricyclohexylphosphine ligand attached to platinum and the latter a triphenylphosphine group similarly bonded. Examination of the two molecular structures reveals that they are derived from different enantiomers, and comparison is easier from the representations in Figure 2 where they are shown with the same chirality. Apart from the changes in the co-ordination around the osmium atom bearing the phosphine ligand, there is remarkably little change in the structure of (4) in relation to (1), with the hydrido-ligands in the same corresponding positions, and the arrangement of the remaining ligands very similar. A detailed analysis of the metal–metal separations, however, is revealing (Table 3). Three metal–metal separations have changed significantly, but by far the greatest alteration is in the bond Pt–Os(2) in (1) which is broken in forming (4), where the separation now becomes 3.530(1) Å. The Os(1)–Os(3) bond in (4) is longer than the Os(1)–Os(2) bond in (1) due to the *trans* influence of the PPh_3 group on Os(1) in the former compound. More interestingly Os(1)–Os(2) in (4) is 0.25 Å longer than the corresponding bond in (1), and both of these are hydrogen-bridged. If any multiple-bond character exists for this bond in (1), then two conflicting factors will determine the interatomic distance, namely the tendency of the H bridge to lengthen the bond, and the tendency of multiple bonding to shorten it. The unsaturation of the 58-electron complex (1) can perhaps be to some extent ' localised ' in this Os(2)–Os(3) bond. Certainly the Os(1)(μ-H)Os(2)

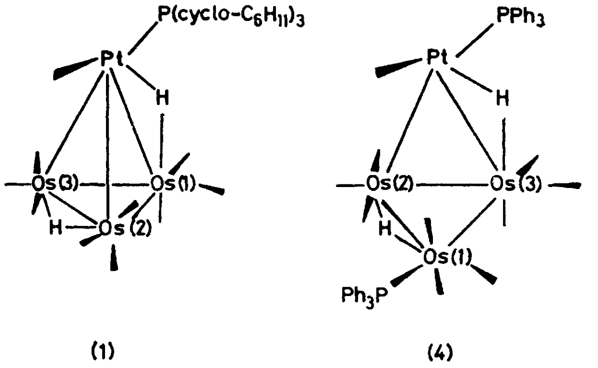


FIGURE 2 Diagrammatic representation of the structural framework of complexes (1) and (4), shown in similar orientation (see text)

TABLE 3

Comparison of corresponding metal–metal separations (Å) in complexes (1) and (4)

Complex (1) [a]		Complex (4) [b]	
Pt–Os(1)	2.863(1)	2.848(1)	Pt–Os(3)
Pt–Os(2)	2.791(1)	3.530(1)	Pt–Os(1)
Pt–Os(3)	2.832(1)	2.717(1)	Pt–Os(2)
Os(1)–Os(2)	2.777(1)	2.914(1)	Os(1)–Os(3)
Os(1)–Os(3)	2.741(1)	2.773(1)	Os(2)–Os(3)
Os(2)–Os(3)	2.789(1)	3.043(1)	Os(1)–Os(2)

[a] Data from ref. 1. [b] See Figure 1 and Table 2.

distance of 3.043(1) Å in (4) is not very different from the distances found for the similar single Os(μ-H)Os linkages in $[Os_3(H)(\mu\text{-}H)(CO)_{10}(PPh_3)]$ [3.018 5(6) Å] [15] and $[Os_3W(\mu\text{-}H)_3(CO)_{11}(\eta\text{-}C_5H_5)]$ [2.941(2) Å].[16]

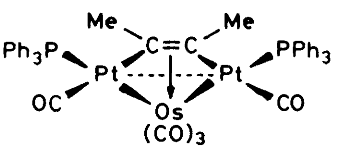
The molecular structure of (4) shows no other unusual features, apart from a slight bending in the C(13)O(13) carbonyl group [Os(1)–C(13)–O(13) 167(2)°]. However, there does not appear to be any semi-bridging character in this ligand since the Os(3)–C(13) separation is outside the normal van der Waals contact distance.

We referred earlier to the existence in solution of an equilibrium between compound (1) and its CO adduct (2). It seems very likely that the molecular structure of the latter involves a 'butterfly' arrangement of metal atoms as found for (4). Hence the equilibrium (1) + CO $\rightleftharpoons$ (2) is accompanied by metal–metal bond formation and bond breakage within the clusters. A similar behaviour has been noted in the reversible binding of CO by $[Fe_2Mn(\mu_3\text{-}PPh)(CO)_8(\eta\text{-}C_5H_5)]$, and the possible importance of such processes to catalysis involving clusters has been pointed out.[17]

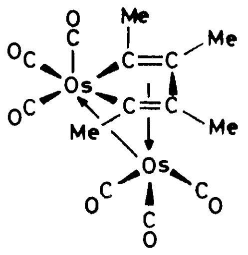
The ready reaction of (1) with CO, and (3) with PPh_3 or $AsPh_3$, and the concomitant rearrangement of the metal framework, led to the hope that such a process might also be accomplished by a simple two-electron reduction to give $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]^{2-}$. Lewis and co-workers [18] have shown that the bicapped tetrahedral cluster $[Os_6(CO)_{18}]$ is reversibly reduced to the dianion $[Os_6(CO)_{18}]^{2-}$ with an octahedral structure. In view of this observation the electrochemistry of complex (3) was investigated. The cyclic voltammogram of (3) in dichloromethane revealed a chemically reversible two-electron reduction [$E_p = -0.90$ V, *vs.* a calomel electrode 1 mol dm^{-3} in LiCl; $(i_p)_{red}/(i_p)_{ox} = 1.0$], but the peak separation [$(E_p)_{red} - (E_p)_{ox} = 180$ mV at a scan rate of 100 mV s^{-1}] shows the electron transfer to be slow. From this observation isolation of a salt of an anion $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]^{2-}$ seemed feasible. However, attempted reduction of (3) with sodium amalgam failed to give an isolable product on addition of $NCl(PPh_3)_2$, even though there was an obvious change in colour from the dark green solution of the neutral complex to dark red-purple. The solution decomposed after several hours to give brown insoluble material.

The facile formation of compounds (2), (4), and (5) suggested that a reaction between the 58-electron complex (3) and ethylene, or an alkyne, should be investigated. The ready reactions of the parent unsaturated complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with various alkenes and alkynes has been well documented.[19–21] Contrary to the behaviour of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, compound (3) was unreactive towards ethylene at room temperature. A solution stirred overnight under an ethylene atmosphere showed no change in colour or in its i.r. spectrum. Under similar conditions, however, but-2-yne reacted slowly, and thin-layer chromatography of the mixture showed that most of the sample of (3) had reacted to give a very complex mixture of products.

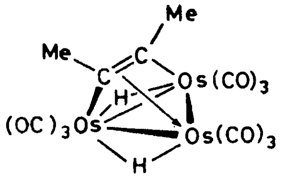
In order to optimise the reaction to obtain the most stable products, compound (3) was reacted with excess of MeC≡CMe at 60 °C in hexane for 4 days. Under these conditions the original dark green solution turned yellow, and bright yellow crystals of a compound (6) formed on the walls of the reaction vessel. The mother-liquor contained four other compounds (7)—(10) which proved difficult to separate. Although chromatography separated (7) and (8) from (9) and (10), further separation for spectroscopic studies had to be accomplished by crystal selection or sublimation. The various compounds were then characterised as follows.



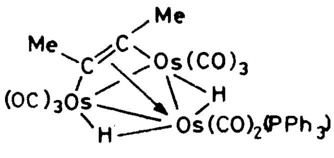
(6)



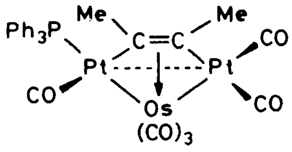
(7)



(8)



(9)



(10)

Compound (7) is a readily volatile colourless solid, the mass spectrum of which clearly showed a parent ion at *m/e* 658. A computer simulation for the isotope pattern $[C_{14}H_{12}O_6Os_2]^+$ closely resembled the observed spectrum, and strongly indicated this composition to be correct. The ^1H n.m.r. spectrum showed two singlets of equal intensity for two sets of equivalent Me groups. The i.r. spectrum of (7) in the carbonyl stretching region was very similar in number of bands, frequencies, and pattern to that reported [22] for a complex $[Os_2(CO)_6(C_4H_2Me_2)]$ which has been shown by *X*-ray crystallography [23] to have a structure like that proposed for (7), except that the two Me groups on the α carbons σ bonded to osmium are replaced by hydrogen atoms.

Compound (8) has been previously prepared and assigned the structure shown by Deeming *et al.*[19] It was first obtained by addition of hydrogen to $[Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^2\text{-}MeC_2Me)]$. The spectroscopic (i.r. and ^1H n.m.r.) properties of our product were identical with those previously reported,[19] except that we found that the high-field signals due to the Os(μ-H)Os groups were temperature dependent. At ambient temperatures only a broad singlet (τ 29.31) was visible which sharpens at 60 °C, whilst at −60 °C the spectrum appears as the two expected singlets at τ 27.43 and 31.19. There is thus site exchange between the protons.

Complex (6), which crystallised readily from the reaction mixture, could be obtained pure in sufficient quantity to allow full characterisation. The i.r. spectrum revealed five CO bands all in the region associated with terminal ligands. The ^1H n.m.r. spectrum showed signals due to the phenyl groups on the phosphorus and a methyl group singlet at τ 7.81 with ^{195}Pt satellites [J(PtH) 34 Hz], suggesting the presence of a symmetrical arrangement PtC(Me)=C(Me)Pt. The ^{31}P n.m.r. spectrum showed a singlet at δ −13.3 p.p.m. with two sets of ^{195}Pt satellites as expected[24] for a $(Ph_3P)Pt\text{-}Pt(PPh_3)$ group [J(PtP) 3 366, 165; J(PtPt) 57 Hz]. In view of the very small value for J(PtPt) it is tempting to correlate this with a very weak Pt–Pt interaction, as also implied by the *X*-ray crystallographic results described below, except that it has been shown that the magnitudes of J(PtPt) are generally insensitive to Pt–Pt separations.[25] The ^{13}C n.m.r. spectrum of (6) showed a resonance at δ 191.9 p.p.m. with a large $^{195}Pt\text{-}^{13}C$ coupling (1 309 Hz) indicative of PtCO groups, while a singlet at δ 182.1 p.p.m. with no ^{195}Pt satellites was assigned to osmium-bonded terminal CO ligands; the relative intensity of the two signals was *ca.* 2 : 3. The resonance due to the acetylenic carbon atoms was seen at δ 155.5 p.p.m. but with only one set of ^{195}Pt satellites visible [J(PtC) 607 Hz] instead of the expected two for a group PtC(Me)=C(Me)Pt. The ^{13}C n.m.r. spectrum of the complex $[(cod)\overline{PtC(CH_2SiMe_3)=C(CH_2SiMe_3)Pt}(cod)]$ (cod = cyclo-octa-1,5-diene) has the acetylenic-carbon resonance signal at δ 140.4 p.p.m. with J(PtC) = 642 and 215 Hz.[26] The lack of a second set of ^{195}Pt satellites in the spectrum of (6) of *ca.* 200 Hz may be attributed to the inherent difficulties of observing such low-intensity signals with the instrumentation available. Nevertheless, the similar J(PtC) values of 607 and 642 Hz for the two compounds suggests that (6) also contains a Pt-C(R)=C(R)Pt bridge system.

In order to establish unambiguously the molecular structure of (6), an *X*-ray diffraction study was carried out. The results are summarised in Tables 4 and 5, and the molecular structure is shown in Figure 3, along with the atomic numbering scheme. As expected from the n.m.r. data, the molecular fragment $Ph_3P(OC)Pt\text{-}C(Me)=C(Me)Pt(CO)PPh_3$ is present in the structure, giving the nucleus of the molecule idealised mirror (C_s) symmetry. An $Os(CO)_3$ group is bonded to the two platinum atoms and to the acetylenic carbon atoms C(2) and C(3). The molecule evidently undergoes dynamic behaviour in solution, since the *X*-ray diffraction results reveal that whereas C(31)O(31) and C(33)-O(33) occupy equivalent sites the carbonyl group C(32)O(32) is in a different environment, and yet the ^{13}C n.m.r. spectrum, as mentioned above, showed only

TABLE 4

Final atomic positional parameters (fractional co-ordinates) for the complex $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$ (6)

Atom	*x*	*y*	*z*
Pt(1)	0.034 53(3)	0.438 81(2)	0.265 07(1)
Pt(2)	−0.177 21(3)	0.409 16(2)	0.136 23(2)
Os	0.045 48(3)	0.484 98(2)	0.158 97(2)
C(1)	−0.028 9(10)	0.618 0(5)	0.245 7(4)
C(2)	−0.048 5(10)	0.537 4(5)	0.217 1(4)
C(3)	−0.146 7(8)	0.523 7(4)	0.157 5(3)
C(4)	−0.233 0(11)	0.587 7(5)	0.118 3(4)
C(01)	0.137 5(12)	0.349 9(5)	0.281 4(4)
O(01)	0.206 4(8)	0.296 9(4)	0.289 8(3)
C(02)	−0.142 8(11)	0.309 5(5)	0.116 5(4)
O(02)	−0.119 3(8)	0.248 0(4)	0.105 7(3)
C(31)	0.006 4(10)	0.534 2(5)	0.081 3(4)
O(31)	−0.021 5(6)	0.565 4(3)	0.035 2(3)
C(32)	0.121 0(11)	0.399 2(5)	0.137 8(4)
O(32)	0.167 8(7)	0.345 2(4)	0.126 1(3)
C(33)	0.203 8(12)	0.537 6(6)	0.207 6(5)
O(33)	0.296 4(8)	0.571 3(4)	0.239 0(3)
Triphenylphosphine group 1			
P(1)	0.006 9(2)	0.456 4(1)	0.356 7(1)
C(41)	0.158 9(10)	0.495 3(4)	0.416 7(4)
C(42)	0.202 1(10)	0.477 6(5)	0.479 8(4)
C(43)	0.311 6(11)	0.508 7(5)	0.523 4(4)
C(44)	0.384 4(11)	0.559 8(5)	0.504 7(4)
C(45)	0.345 8(12)	0.577 4(6)	0.442 8(5)
C(46)	0.235 1(11)	0.543 3(5)	0.398 2(4)
C(51)	−0.028 0(10)	0.373 9(5)	0.396 2(4)
C(52)	−0.100 0(10)	0.379 9(5)	0.431 1(4)
C(53)	−0.120 5(11)	0.318 4(5)	0.465 1(4)
C(54)	−0.053 5(11)	0.250 0(5)	0.465 5(4)
C(55)	0.019 4(13)	0.243 3(6)	0.431 6(5)
C(56)	0.031 9(12)	0.305 4(5)	0.396 1(4)
C(61)	−0.121 4(10)	0.522 8(4)	0.353 3(4)
C(62)	−0.251 1(10)	0.502 2(5)	0.319 1(4)
C(63)	−0.351 1(11)	0.553 6(5)	0.311 6(4)
C(64)	−0.323 1(11)	0.626 7(5)	0.339 6(4)
C(65)	−0.194 7(12)	0.646 1(5)	0.373 1(4)
C(66)	−0.091 2(11)	0.596 6(5)	0.381 9(4)
Triphenylphosphine group 2			
P(2)	−0.388 5(2)	0.388 8(1)	0.126 6(1)
C(71)	−0.501 2(10)	0.470 7(5)	0.111 9(4)
C(72)	−0.619 5(10)	0.475 4(5)	0.059 8(4)
C(73)	−0.702 9(11)	0.538 5(5)	0.052 9(4)
C(74)	−0.664 4(12)	0.595 9(5)	0.098 6(4)
C(75)	−0.544 8(11)	0.591 3(5)	0.149 2(4)
C(76)	−0.464 0(10)	0.530 5(4)	0.154 5(4)
C(81)	−0.481 1(10)	0.320 6(4)	0.065 4(4)
C(82)	−0.456 7(11)	0.320 7(5)	0.012 1(4)
C(83)	−0.524 3(11)	0.268 5(5)	−0.036 6(4)
C(84)	−0.612 1(11)	0.219 9(5)	−0.030 0(4)
C(85)	−0.639 0(12)	0.220 3(5)	0.022 8(5)
C(86)	−0.571 7(12)	0.270 9(5)	0.070 5(4)
C(91)	−0.397 3(10)	0.348 7(5)	0.196 3(4)
C(92)	−0.294 3(11)	0.301 9(5)	0.233 0(4)
C(93)	−0.300 0(12)	0.271 6(5)	0.289 9(4)
C(94)	−0.401 8(12)	0.288 4(6)	0.305 9(4)
C(95)	−0.502 3(12)	0.336 9(6)	0.269 3(5)
C(96)	−0.496 3(12)	0.366 0(6)	0.215 3(5)

one resonance for the $Os(CO)_3$ group at ambient temperature.

The but-2-yne fragment C(1)—C(4) is symmetrically σ bonded to the two platinum atoms [Pt(1)–C(2) 2.060(8) Å, Pt(2)–C(3) 2.055(7) Å] and η^2-bonded to the osmium atom [Os–C(2) 2.22(1) Å, Os–C(3) 2.23(1) Å]. The C(2)–C(3) separation of 1.40(1) Å and the angles about C(2) and C(3) suggest that the hybridisation of these carbon atoms is close to sp^2. The two platinum atoms do not lie exactly in the plane defined by C(1)—C(4) of the but-2-yne fragment. The interplanar angle between C(1)—C(4) and Pt(1)–C(2)–C(3)–Pt(2) is 170°, with atoms C(1) and C(4) bending away from the Os atom. This mode of bonding of the acetylene molecule to the $OsPt_2$ triangle in (6) has been found [27] in many other trimetallic complexes, and is appropriately described as $\mu_3(\eta^2-\|)$.[28] In triosmium cluster chemistry a good example of this type of acetylene attachment is provided by $[Os_3(CO)_{10}(PhC_2Ph)]$.[29]

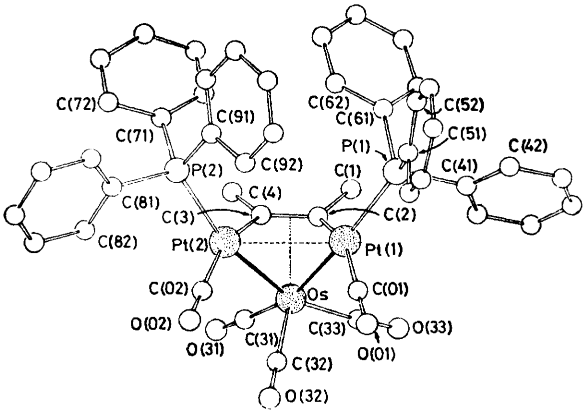


FIGURE 3 Molecular structure of (6), $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$, showing the crystallographic numbering sequence

TABLE 5

Important interatomic distances (Å) and bond angles (°) for the complex $[OsPt_2(CO)_5(PPh_3)_2\{C_2(CH_3)_2\}]$, with estimated standard deviations in parentheses

(a) Distances

Pt(1)–Pt(2)	3.033(2)	C(01)–O(01)	1.17(1)
Pt(1)–Os	2.664(2)	C(02)–O(02)	1.16(1)
Pt(2)–Os	2.669(2)	C(31)–O(31)	1.14(1)
		C(32)–O(32)	1.16(1)
Pt(1)–C(2)	2.060(8)	C(33)–O(33)	1.16(1)
Pt(2)–C(3)	2.055(7)		
Os–C(2)	2.22(1)	C(1)–C(2)	1.54(1)
Os–C(3)	2.23(1)	C(2)–C(3)	1.40(1)
		C(3)–C(4)	1.52(1)
Pt(1)–P(1)	2.310(3)		
Pt(2)–P(2)	2.300(4)		
		C–C (phenyl) mean	1.40
Pt(1)–C(01)	1.87(1)		
Pt(2)–C(02)	1.88(1)	P–C (phosphines) mean	1.83
Os–C(31)	1.90(1)		
Os–C(32)	1.88(1)		
Os–C(33)	1.90(1)		

(b) Angles

Pt(1)–Os–Pt(2)	69.33(3)	C(4)–C(3)–Pt(2)	124.6(6)
Os–Pt(1)–Pt(2)	55.42(4)	C(1)–C(2)–C(3)	120.4(7)
Os–Pt(2)–Pt(1)	55.25(3)	C(4)–C(3)–C(2)	121.7(7)
Pt(1)–C(2)–C(3)	113.5(5)	C(31)–Os–Pt(2)	101.4(4)
Pt(2)–C(3)–C(2)	113.1(5)	C(32)–Os–Pt(1)	101.5(3)
C(1)–C(2)–Pt(1)	125.0(5)	C(32)–Os–Pt(2)	91.8(4)
C(33)–Os–Pt(1)	88.2(4)	Pt(1)–C(01)–O(01)	176(1)
C(01)–Pt(1)–Os	100.7(4)	Pt(2)–C(02)–O(02)	178(1)
C(01)–Pt(1)–P(1)	102.7(4)	Os–C(31)–O(31)	177(1)
C(02)–Pt(2)–Os	104.0(4)	Os–C(32)–O(32)	178(1)
C(02)–Pt(2)–P(2)	97.8(4)	Os–C(33)–O(33)	176(1)

The Os–Pt distances [mean 2.666(2) Å] are shorter than the non-hydrido-bridged distance Os(2)–Pt [2.717(1) Å] in compound (4), and the two non-hydrido-bridged Os–Pt distances [mean 2.811(1) Å] in complex (1). The Pt(1)–Pt(2) separation of 3.033(2) Å is more than twice the covalent radius of platinum, and may be compared with the Pt–Pt separation of 2.987(4) Å in the 'butterfly' structure $[Co_2Pt_2(CO)_8(PPh_3)_2]$ [30] where no direct platinum–platinum bond is assumed or required. Platinum–platinum separations where bridging ligands are involved show very considerable variations, *e.g.* 2.585(1) Å in $[Pt_2\{\mu\text{-}(CF_3)_2CO\}(cod)_2]$,[31] 2.692(3) Å in $[\{Pt(\mu\text{-}H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$,[32] and 2.790—2.752(7) Å in $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$.[33] If no Pt–Pt bond is assumed in compound (6) the platinum atoms have a 16-electron configuration and the osmium atom an 18-electron closed shell. It thus seems likely that the Pt–Pt separation is determined by the steric requirements of the bridging but-2-yne group. Moreover, the C(2)–C(3) distance is reminiscent of an aromatic C–C bond distance [1.395(3) Å] and may imply some electron delocalization Pt$\overset{\text{---}}{\text{—}}C\overset{\text{---}}{\text{—}}C\overset{\text{---}}{\text{—}}$Pt, as in the η^4 bonding of a diene to an $M(CO)_3$ group, although the Pt–C distances in (6) are normal for σ bonds.[24]

Reaction of (3) with but-2-yne also gave compounds (9) and (10), isolated pure in only very small quantity. Structures were assigned on the basis of spectroscopic data. The ^1H n.m.r. spectrum of (9) had a singlet for the Me groups at τ 7.11, and a high-field doublet for the two hydrido-ligands at τ 28.58 [J(PH) 11 Hz]. The structure proposed assumes that the hydrido-ligands are equivalent, but other structures are possible if the molecule is fluxional. The ^{31}P n.m.r. spectrum showed the expected singlet (δ 1.2 p.p.m.). Complex (10) displayed two resonances due to the Me groups in its ^1H n.m.r. spectrum, one of which showed ^{31}P and ^{195}Pt couplings [J(PH) 3, J(PtH) 34 Hz], whilst the other showed only ^{195}Pt coupling [J(PtH) 36 Hz]. A ^{31}P n.m.r. spectrum had the expected pattern for a R_3-PPtPt group. The i.r. spectrum of (10) was very similar to that of (6).

No complexes were isolated from the reaction of (3) with but-2-yne which retained the Os_3Pt framework of (3). Evidently the tetranuclear cluster was easily degraded under the reaction conditions.

EXPERIMENTAL

The instrumentation and synthetic methods used have been described earlier.[1] Infrared measurements were made on cyclohexane solutions, and [$^2H_1$]chloroform was used as solvent for n.m.r. studies.

Reaction of the Complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ *with Carbon Monoxide.*—A solution of (1) (0.15 g, 0.1 mmol) in diethyl ether (20 cm^3) was saturated with CO gas. Reduction in volume to *ca.* 5 cm^3 by increasing the rate of CO bubbling, and cooling to −20 °C, gave bright yellow *crystals* of $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (2) (0.1 g, 66%) (Found: C, 25.8; H, 2.7. $C_{29}H_{35}O_{11}Os_3PPt$ requires C, 25.7; H, 2.6%); $\nu_{max.}$ at 2 091m, 2 077w, 2 051vs, 2 041vs, 2 023s, 2 019m, 2 011s, 1 987s, 1 975s(sh), 1 963w, and 1 943w cm^{-1}. N.m.r.: ^1H (−60 °C), τ 8.18—8.76 (br, 33 H, C_6H_{11}), 21.60 [d, 1 H, Os(μ-H)Pt, *J*(PH) 11, *J*(PtH) 513], and 27.60 [d, 1 H, Os(μ-H)Os, *J*(PH) 3, *J*(PtH) 30 Hz]; ^{31}P (^1H-decoupled), δ −50.4 p.p.m. [s, *J*(PtP) 2 409 Hz].

Reactions of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$.—(*a*) *With* PPh_3. (i) To a stirred solution of (3) (0.2 g, 0.15 mmol) in diethyl ether (30 cm^3) was added PPh_3 (0.04 g, 0.15 mmol). The solution was stirred overnight. Concentration of the solution, and cooling to −20 °C, gave bright yellow *crystals* of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ (4) (0.19 g, 75%) (Found: C, 35.1; H, 2.1. $C_{46}H_{32}O_{10}Os_3P_2Pt$ requires C, 35.1; H, 2.1%), m.p. 142—150 °C (decomp.), $\nu_{max.}$ at 2 075m, 2 041vs, 2 025vs, 2 013vs, 1 991s, 1 977s, 1 965s, 1 957w(sh), and 1 941m cm^{-1}. N.m.r.: ^1H (−60 °C), τ 2.56—2.62 (m, 30 H, Ph), 18.55 [d, 1 H, Os(μ-H)Pt, *J*(PH) 18, *J*(PtH) 590], and 27.55 [d, 1 H, Os(μ-H)Os, *J*(PH) 14 Hz]; ^{31}P (^1H-decoupled), δ −30.7 [s, PPt, *J*(PtP) 2 501] and 7.3 p.p.m. (POs); ^{31}P (^1H-decoupled, −50 °C), δ −34.4 (s, PPt), −30.5 [s, PPt, *J*(PtP) 2 495 Hz], 6.5 (s, POs), and 7.3 p.p.m. (s, POs); ^{31}P (selectively decoupled), δ −30.9 [d, PPt, *J*(PH) 15, *J*(PtP) 2 501] and 7.2 p.p.m. [d, POs, *J*(PH) 12 Hz].

(ii) To a stirred solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.46 g, 0.55 mmol) in diethyl ether (60 cm^3) was added $[Pt(C_2H_4)(PPh_3)_2]$ (0.42 g, 0.55 mmol). The solution turned grass green immediately, and then brownish yellow slowly. Concentration and cooling to −20 °C afforded yellow *crystals* of (4) (0.6 g, 70%).

(*b*) *With* $AsPh_3$. Brownish yellow *crystals* of the compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(AsPh_3)(PPh_3)]$ (5) (0.07 g, 54%), (Found: C, 34.5; H, 2.2. $C_{46}H_{32}AsO_{10}Os_3PPt$ requires C, 34.2; H, 1.9%), m.p. 140—145 °C (decomp.), were prepared from $AsPh_3$ (0.03 g, 0.08 mmol) and compound (3) (0.1 g, 0.08 mmol), as described in (i) above. Compound (5) had $\nu_{max.}$ at 2 077m, 2 043vs, 2 025vs, 2 013vs, 1 991s, 1 979s, 1 969m, 1 957(sh), and 1 943m cm^{-1}. N.m.r.: ^1H (−60 °C), τ 2.60 (m, 30 H, Ph), 18.50 [d, 1 H, Os(μ-H)Pt, *J*(PH) 20, *J*(PtH) 580 Hz], and 27.60 [s, 1 H, Os(μ-H)Os]; ^{31}P (^1H-decoupled), δ −31.2 p.p.m. [s, *J*(PtP) 2 502 Hz].

(*c*) *With but-2-yne.* A Carius tube, fitted with a Westef stopcock, was charged with compound (3) (1.1 g, 0.85 mmol) and hexane (140 cm^3), and but-2-yne (0.32 g, 6 mmol) was condensed into the reaction vessel *in vacuo*. The reactants were heated at 60 °C for 4 days, after which time bright yellow crystals had formed on the walls of the tube. These were recovered, washed with light petroleum (3 × 5 cm^3), and shown to be *crystals* of the complex $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}\eta^2\text{-}MeC_2Me)]$ (6) (0.25 g, 24%).

The mother-liquor from the reaction was concentrated *in vacuo* and chromatographed on alumina. Elution with light petroleum allowed separation into two fractions; a pale green crystalline material containing the two complexes $[Os_2(CO)_6(C_4Me_4)]$ (7) and $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^2\text{-}MeC_2Me)]$ (8) (combined yield 0.22 g), and bright yellow material containing the two complexes $[Os_3(\mu\text{-}H)_2(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}MeC_2Me)]$ (9) and $[OsPt_2(CO)_6(PPh_3)(\mu_3\text{-}\eta^2\text{-}MeC_2Me)]$ (10) (combined yield 0.28 g). Both mixtures were recrystallised from light petroleum to give crystals suitable for separation visually under a microscope. The compounds were characterised by the following data; (i) Complex (6) (Found: C, 41.1; H, 2.9. $C_{45}H_{36}O_5OsP_2Pt_2$ requires C, 41.6; H, 2.7%), m.p. 225—230 °C (decomp.), $\nu_{max.}$ at 2 047s, 2 015m, 2 009(sh), 1 961m, and 1 953m cm^{-1}. N.m.r.: ^1H, τ 2.76 (m, 30 H, Ph) and 7.81 [s, 6 H, Me, *J*(PtH) 34 Hz]. ^{31}P (^1H-decoupled), δ −13.3 p.p.m. [s, *J*(PtP) 3 366 and 165, *J*(PtPt) 57 Hz]; ^{13}C {^1H-decoupled, in the presence of $[Cr(C_5H_8O_2)_3]$}, δ 191.9 [s, Pt*C*O, *J*(PtC) 1 309], 182.1 (s, Os*C*O), 155.5 [s, *C*Me, *J*(PtC) 607 Hz], 132.7, 129.5 and 127.6 (Ph), 28.1 p.p.m. (s br, Me).

(ii) Complex (7), sublimes 100 °C *in vacuo* [Found: *M* (mass spectrum) 658. $C_{14}H_{12}O_6Os_2$ requires *M* 657.5]; $\nu_{max.}$ at 2 075m, 2 041s, 2 005s, 1 987w, 1 975m, and 1 963s cm^{-1}; ^1H n.m.r.: τ 7.37 (s, 3 H, Me) and 7.63 (s, 3 H, Me).

(iii) Complex (8), $\nu_{max.}$ at 2 103w, 2 077vs, 2 053vs, 2 027s, 2 017s, 2 007vs, 1 997m, and 1 981m cm^{-1}; ^1H n.m.r. (−60 °C): τ 7.20 (s, 6 H, Me), 27.43 [s, 1 H, Os(μ-H)Os], and 31.19 [s, 1 H, Os(μ-H)Os].

(iv) Complex (9) (Found: C, 32.5; H, 2.3. $C_{30}H_{23}O_8Os_3P$ requires C, 32.4; H, 2.1%), m.p. 178—184 °C (decomp.), $\nu_{max.}$ at 2 075m, 2 041s, 2 027m, 1 987m br, 1 969m, and 1 963w(sh) cm^{-1}. N.m.r.: ^1H, τ 2.58 (m, 15 H, Ph), 7.11 (s, 6 H, Me), and 28.58 [d, 2 H, Os(μ-H)Os, *J*(PH) 11 Hz]; ^{31}P (^1H-decoupled), δ 1.2 p.p.m.

(v) Complex (10) (Found: C, 31.7; H, 2.1. $C_{28}H_{21}O_6OsPPt_2$ requires C, 31.6; H, 2.0%), m.p. 135—139 °C (decomp.), $\nu_{max.}$ at 2 075s, 2 039s, 2 021s, 1 971m, and 1 965m cm^{-1}. N.m.r.: ^1H, τ 2.57 (m, 15 H, Ph), 6.99 [s, 3 H, Me, *J*(PtH) 36], and 7.80 [d, 3 H, Me, *J*(PH) 3, *J*(PtH) 34 Hz]; ^{31}P (^1H-decoupled), δ −20.7 p.p.m. [s, *J*(PPt) 3 406 and 171 Hz].

Crystal Structure Determinations.—(*i*) *Complex* (4), $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$. Crystals of (4) grow as yellow triclinic (pseudo-hexagonal) prisms. Diffracted intensities were collected at 200 K from a crystal of dimensions 0.25 × 0.15 × 0.35 mm on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 60.0°$, according to methods described earlier.[34,35] Of the total 7 167 reflections measured, 5 794 had $I \geqslant 2.5\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics; only these were used in the solution and refinement of the structure. Three check reflections ($\bar{3}\,\bar{3}\,7$, $6\,0\,\bar{5}$, $\bar{2}\,3\,\bar{1}$) were monitored every 40 reflections but showed no significant variation over the 246 h of crystal exposure to *X*-rays. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption;[36] A^* ranged from 5.32 to 3.57. All computations were carried out with the '*X*-Ray' system of programs [36] available for the CDC 7600 at the London Computing Centre.

Crystal data for (4). $C_{46}H_{32}O_{10}Os_3P_2Pt$, $M = 1\,572.4$, Triclinic, $a = 14.427(7)$, $b = 12.793(5)$, $c = 14.151(6)$ Å, $\alpha = 92.33(3)$, $\beta = 120.87(3)$, $\gamma = 91.06(4)°$, $U = 2\,238(4)$ Å^3, $D_m = 2.35$ (flotation), $Z = 2$, $D_c = 2.33$ g cm^{-3}, $F(000) = 1\,448$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 124.0 cm^{-1}, space group $P\bar{1}$ (no. 2).

Structure solution and refinement for (4). The metal atoms were located by vector methods and the sites of these were identified as Os or Pt by thermal parameter refinement. Successive electron-density difference syntheses revealed all non-hydrogen atoms. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for the osmium, platinum, and phosphorus atoms. All other non-hydrogen atoms were refined isotropically. The hydrogen atoms of the phenyl rings were incorporated at calculated positions but were not refined. The final electron-density difference synthesis did not reveal the locations of the bridging hydride ligands, but these were inferred by methods explained in the main text, including computation of potential energy minima.[14] Refinement converged at R 0.041 (R' 0.044), with a weighting scheme of the form $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the estimated error in the observed structure factor based on counting statistics. Scattering factors were from ref. 37 for C, O, and P, ref. 38 for H, and ref. 39 for Os and Pt, including corrections for the effects of anomalous dispersion for Os, Pt, and P. Atomic positional parameters for (4) are in Table 1, interatomic distances and bond angles in Table 2.

(*ii*) *Complex* (6), $[\mathrm{OsPt_2(CO)_5(PPh_3)_2\{C_2(CH_3)_2\}}]$. Crystals of (6) grow as yellow prisms. Conditions of data collection were as for (4) except in the following particulars: crystal size: 0.20 × 0.15 × 0.30 mm; 2θ range: 2.9—55.0°; total no. of reflections measured: 5 942, of which 4 438 had $I \geqslant 2.5\sigma(I)$; check reflections: 4 0 2, 1 4 1, $1\ \bar{1}\ \bar{9}$, monitored every 50 reflections and showed no significant decay; A^* ranged from 6.24 to 3.54.

Crystal data for (6). $\mathrm{C_{45}H_{36}O_5OsP_2Pt_2}$, $M = 1\,299.1$, Monoclinic, $a = 11.143(8)$, $b = 17.458(12)$, $c = 23.443(15)$ Å, $\beta = 113.82(5)°$, $U = 4\,172(5)$ Å^3, D_m not measured, $Z = 4$, $D_c = 2.07$ g cm^{-3}, $F(000) = 2\,432$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 103.8$ cm^{-1}, space group $P2_1/c$ (no. 14).

Structure solution and refinement for (6). Solution of a Patterson synthesis revealed a triangular array of metal atoms, and as one side of the triangle was much longer than the other two (equal) sides, it was evident that the two equal sides must join a central Os atom to two Pt atoms. The other non-hydrogen atoms were located by successive electron-density difference syntheses. Conditions of refinement were as for (4), and although again the hydrogen atoms were incorporated at calculated positions and were not refined, those of the butenyl ligand were clearly identifiable on the electron-density difference maps. The refinement converged at R 0.031 (R' 0.033). Atomic positional parameters for (6) are in Table 4, interatomic distances and bond angles in Table 5. Observed and calculated structure factors, all hydrogen-atom co-ordinates, and all thermal parameters for both (4) and (6) are listed in Supplementary Publication No. SUP 22899 (36 pp.).*

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

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