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Chemistry of the Metal Carbonyls. Part 77.¹ Some Reactions of the Platinumtriosmium Complexes $[Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)]$ with Donor Molecules; X-Ray Crystal Structures of $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)_2]$ and $[OsPt_2(CO)_5(PPh_3)_2(\mu_3-MeC_2Me)]^{\dagger}$

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The compounds $[Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)]$ react with CO, PPh₃, or AsPh₃ to give complexes $[Os_3Pt(\mu-H)_2 (CO)_{10}(PR_3)L]$ [PR₃ = P(cyclo-C₆H₁)₃, L = CO; PR₃ = PPh₃, L = PPh₃ or AsPh₃]. Hydrogen-1 and ³¹P n.m.r. data for the compounds are discussed, and a single-crystal X-ray diffraction study has been carried out on the compound $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)_2]$, crystals of which are triclinic, space group $P\hat{1}$, 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 $\gamma = 120.87(3)$ 91.06(4)°. The structure has been refined to R 0.041 (R' 0.044) for 5 794 independent reflections (2.9 \leq 20 \leq 60°, Mo- K_{α} 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 $[Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)]$. In $[Os_3Pt(\mu-H)_2-H)_2$ $(CO)_{10}(PPh_3)_{\circ}$ 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 $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)]$ 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 Os₃Pt cluster of the precursor. One of the complexes was characterised as [OsPt₂(CO)₅- $(PPh_3)_2(\mu_3-MeC_2Me)]$ 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 $\beta = 113.82(5)^\circ$. The structure has been refined to R 0.031 (R' 0.033) for 4 438 independent reflections (2.9 \leq 20 \leq 55°, Mo-K_a 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 $\mu_3(\eta^2 - \|)$. The osmium atom carries three terminal CO ligands, and each platinum a CO and PPh₃ 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- $(C_{2}H_{4})_{2}(PR_{3})$ [PR₃ = P(cyclo-C₆H₁₁)₃, PPh₃, or PBu^t₂-Me] react with $[Os_3(\mu-H)_2(CO)_{10}]$ to afford the tetrametallic compounds $[Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)]$. An Xray 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 hydridoligands. 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 $[Os_3Pt(\mu-H)_2(CO)_{10}]$ (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 $[Os_3Pt(\mu-H)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ (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
$$\Longrightarrow$$

[Os₃Pt(μ -H)₂(CO)₁₁{P(cyclo-C₆H₁₁)₃}] (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 $[Os_3(\mu-H)_2(CO)_{10}]$, with 46 valence electrons, also reacts reversibly with CO, affording the 48-electron compound $[Os_3H(\mu-H)(CO)_{11}]$.^{4,5}

The ³¹P and ¹H n.m.r. spectra of (2) were informative. The ³¹P spectrum showed a singlet (δ -50.4 p.p.m.) with ¹⁹⁵Pt 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

⁺ 1,2,2,2,3,3,3,4,4-Decacarbonyl-1,2;3,4-di- μ -hydrido-1,3bis(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(μ -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(μ -H)Os proton in both the conversion of (1) (τ 16.93) into (2) (τ 27.60), and $[Os_3(\mu-H)_2(CO)_{10}]$ (τ 20.9) into $[Os_3H(\mu-H)(CO)_{11}]$ $(\tau 29.97)$. 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 hydridoligands 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 $[\text{Re}_4(\mu-\text{H})_4(\text{CO})_{12}]$ (τ 15.08).⁹ In the 60electron dianion cluster $[\text{Re}_4(\mu-\text{H})_4(\text{CO})_{13}]^{2-}$ the hydridoligands 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 $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)]$ (3) with either PPh₃ or AsPh₃ gave the adducts $[Os_3Pt(\mu-H)_2(CO)_{10}-(PPh_3)L]$ (4, L = PPh₃; 5, L = AsPh₃). It was also possible to prepare (4) directly from $[Os_3(\mu-H)_2(CO)_{10}]$ 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 highfield 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 ¹⁹⁵Pt coupling can be attributed to a bridging hydrido-ligand Os(μ -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(μ -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 ³¹P 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 ³¹P n.m.r. spectrum.

The ³¹P{¹H-decoupled} n.m.r. spectrum of (4) at -60 °C had singlet resonances at $\delta -30.7$ 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 PPh₃ ligand is bonded to platinum and the other to osmium. The presence of a signal at $\delta -31.2$ p.p.m. in the ³¹P n.m.r. spectrum of the triphenylarsine derivative (5), with ¹⁹⁵Pt 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 variabletemperature ³¹P 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 -34.4and 6.5 p.p.m., close to the main resonances at -30.5and 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 ¹⁹⁵Pt coupling of ca. 2 800 Hz on the resonance at -34.4 p.p.m. With ¹⁹⁵Pt coupling of the magnitude proposed the up-field satellites of both isomers are roughly coincident, and any broadening would be minimal. The ambient temperature ³¹P n.m.r. spectrum of (5) showed a similar differential broadening in the ¹⁹⁵Pt 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 I 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 dis-

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cussed 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 PPh₃ 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 $[W_2(\mu-H)(CO)_{10}]^{-,13}$ 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



 $\begin{array}{ll} \mbox{Figure 1} & \mbox{Molecular structure of (4), [Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)_2],} \\ & \mbox{showing the crystallographic numbering sequence} \end{array}$

 Os_3Pt system vary considerably from that expected for a regular tetrahedron.

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) = $112.7(1)^{\circ}$ 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)-Ptfavours 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 hydridoligands. 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 PPh₃ 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)

	1 (-)		
Atom	x	γ	z
Pt	-0.131.66(3)	0.191.36(2)	0.235.01(2)
Os(1)	-0.17974(3)	$0.361\ 37(2)$	$0.025 \ 61(2)$
Os(2)	-0.08589(3)	$0.145\ 65(2)$	0.07449(2)
Os(3)	$0.025\ 27(3)$	$0.316\ 24(2)$	0.21999(2)
$H(\hat{l})'$	-0.0345	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)	-0.2906(8)	0.010 9(8)	$0.114\ 7(7)$
C(11)	-0.1619(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)	-0.1046(10)	$0.387 \ 0(9)$	-0.0505(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)	$-0.016\ 1(11)$	$0.158\ 7(10)$	-0.0065(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)	$0.537\ 7(8)$	$0.325 \ 9(7)$
Triphen	ylphosphine group 1		
$\mathbf{P}(\mathbf{i})$	-0.1714(9)	0 223 3/2)	0.372.0/2)
C(41)	$-0.111 \pm (2)$ 0.285 6(10)	0.225.3(2) 0.136.3(0)	0.346.5(8)
C(42)	-0.269.0(10)	0.150 0(0)	0.4154(8)
C(42)	-0.3531(11)	-0.0202(10)	0.3871(9)
C(44)	-0.4510(11)	-0.008.6(10)	0.295.8(9)
C(45)	-0.471.5(11)	0.0744(10)	0.226.7(9)
C(46)	-0.383.0(11)	0.1433(9)	0.2527(8)
C(51)	-0.210.9(11)	0.356.5(9)	0.387(3(8))
C(52)	-0.140.0(11)	0.4400(10)	0.3913(9)
C(53)	-0.165.9(13)	0.5426(11)	$0.405\ 2(9)$
C(54)	-0.2496(13)	0.562 1(12)	0.417 8(10)
C(55)	-0.3133(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)	-0.0649(10)	0.2001(9)	$0.511 \ 3(8)$
C(62)	$0.026\ 6(14)$	0.1495(13)	0.5314(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)
Triphen	vlphosphine group 2		•
D/9)	0.946.9/9	0.261.1/9	0 149 9(9)
r(4) = c(71)	- 0.340 2(2)	0.001 1(2) A 979 Q(Q)	-0.144 2(2) -0.256 2(7)
C(79)	-0.370 0(9)	0.213 0(0)	-0.200 0(1)
C(12)	$-0.470 \ 3(10)$	0.200 1(9)	-0.352 1(8)
C(73)	-0.4304(10)	0.2000(3) 0.140 4(19)	$-0.442 \ 9(0)$
C(74) C(75)	-0.4131(13)	0.1434(12) 0.1579(12)	-0.351.6(10)
C(76)	-0.9880(11)	0.2187(10)	-0.257.7(9)
C(81)	-0.376.2(10)	0.488.7(8)	-0.2017(8)
C(82)	-0.387.3(11)	0.5732(9)	-0.1429(8)
C(83)	-0.4014(12)	0.6725(11)	-0.1807(10)
C(84)	-0.4035(12)	0.689 8(11)	-0.2794(10)
C(85)	-0.3892(12)	0.609 2(11)	-0.3334(10)
C(86)	-0.3745(11)	0.506 0(10)	-0.2987(9)
C(91)	-0.4618(10)	0.321 3(9)	-0.129 1(8)
C(92)	$-0.545\ 5(13)$	0.3821(11)	-0.1505(10)
C(93)	-0.6314(15)	0.345 4(15)	-0.1300(12)
C(94)	-0.6228(13)	0.247 8(12)	— 0.088 9(10)
C(95)	-0.5356(12)	$0.184 \ 2(10)$	— 0.068 6(9) [′]
C(96)	-0.4516(11)	$0.217\ 7(10)$	-0.0854(8)

compared with the Os(2)-Os(3) bond [2.773(1) Å]. For the PPh₃ 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

TABLE 2.

Important int	eratomic	distances	(Å)	and	bond	angles	(°)
for the	complex	[Os ₃ Pt(µ	$-H_2$	$(CO)_1$	(PPh	$_{3})_{2}], v$	vith
estimated	standard	deviation	s in	parei	ntheses	5	

(a) Distances			
Pt-Os(1) 3	530(2)	$O_{S}(3) - C(31)$	1.87(1)
Pt - Os(2) = 2	717(1)	$O_{S}(3) - C(32)$	1.87(1)
Pt = Os(2) 2	848(2)	$O_{S}(3) - C(33)$	1 89(1)
$\Omega_{\rm e}(1) - \Omega_{\rm e}(2) = 3$	043(2)	03(3) 0(33)	1.00(1)
$O_{S}(1) = O_{S}(2) = 0$	014(2)	C(01) = O(01)	1 14(9)
$O_{3}(1) = O_{3}(0) = 2$.914(2)	C(01) = O(01)	1.14(2) 1.16(1)
OS(3) = OS(2) = 2	.113(2)	C(11) = O(11)	1.10(1)
D4 D/1) 0	910/9	C(12) = O(12)	1.10(2)
Pt-P(1) = 2	.310(3)	C(13) = O(13)	1.14(2)
Os(1) - P(2) = 2	.307(3)	C(21) = O(21)	1.08(1)
DI ((01)	0.0 (1)	C(22) = O(22)	1.10(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)	1.39
Os(2) - C(23) = 1	.90(1)	mean	
		P-C (phosphines)	1.83
		mean	
(b) Angles			
$O_{s}(1) - Pt - O_{s}(2)$	5651(3)	$O_{S}(1) - O_{S}(2) - O_{S}(3)$	59 92(4)
$P_{s(1)} = P_{t-O_{s}(3)}$	53.07(3)	Pt = Os(3) = Os(1)	75 56(4)
$D_{s}(2) - Pt - O_{s}(3)$	59 79(9)	Pt = Os(3) = Os(2)	57 80(3)
$P_{1} = O_{1}(1) = O_{2}(2)$	48.19(9)	$O_{s}(1) - O_{s}(2) - O_{s}(2)$	64 44(3)
2t - Os(1) - Os(2)	51 97(9)	$Pt=O_{2}(2)=O_{2}(2)$	75 26(2)
$\frac{1}{2} \frac{1}{2} \frac{1}$	55 49(1)	$D_{t=O_{2}(2)=O_{2}(1)}$	69 49(2)
$D_{S(2)} = O_{S(1)} = O_{S(3)}$	109 6(5)	$\Gamma (-Os(2)-Os(3))$	170(9)
S(01) = Pt = Os(1)	102.0(0)	O(01) - C(01) - Pt	170(2)
C(01) = Pt = Os(2)	10.8(5)	O(11) = C(11) = Os(1)	170(1)
U(11) = Os(1) = Pt	110.0(0)	O(12) - C(12) - Os(1)	177(1)
$\mathcal{L}(11) - Os(1) - Os(3)$	91.9(3)	O(13) - C(13) - Os(1)	166(1)
U(12) - Os(1) - Os(2)	89.0(3)	O(21) - C(21) - Os(2)	177(1)
U(12) - Os(1) - Os(3)	89.1(3)	O(22) - C(22) - Os(2)	178(1)
U(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

with only small deviations, CO(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°. 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



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

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

TABLE 3

comparison	or corresponding metal-metal separations	5
	(Å) in complexes (1) and (4)	
	(, F (-, (-,	

	. ,	1 () ()		
Complex (1) ^a		Com	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 7	fable 2.	

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 PPh₃ 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)

J.C.S. Dalton

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 [Os₃(H)(μ -H)(CO)₁₀(PPh₃)] [3.018 5(6) Å] ¹⁵ and [Os₃W(μ -H)₃(CO)₁₁(η -C₅H₅)] [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 $[Os(1)-C(13)-O(13) \ 167(2)^{\circ}]$. 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 $[Fe_2Mn(\mu_3-PPh)(CO)_8(\eta-C_5H_5)]$, 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 AsPh₃, 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 $[Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)]^{2-}$. Lewis and co-workers 18 have shown that the bicapped tetrahedral cluster $[Os_6(CO)_{18}]$ is reversibly reduced to the dianion [Os₆(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 $[E_p = -0.90 \text{ V}, vs. \text{ a calomel}]$ electrode 1 mol dm⁻³ in LiCl; $(i_p)_{red}/(i_p)_{ox} = 1.0$], but the peak separation $[(E_p)_{red} - (E_p)_{ox} = 180 \text{ mV}$ 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 $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)]^{2-}$ seemed feasible. However, attempted reduction of (3) with sodium amalgam failed to give an isolable product on addition of NCl(PPh₃)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 $[Os_3(\mu-H)_2(CO)_{10}]$ with various alkenes and alkynes has been well documented.¹⁹⁻²¹ Contrary to the behaviour of $[Os_3(\mu-H)_2(CO)_{10}]$, 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.

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 $[Os_3(\mu-CO)-(CO)_9(\mu_3-\eta^2-MeC_2Me)]$. 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 ¹⁹⁵Pt satellites [J(PtH) 34 Hz], suggesting the presence of a symmetrical arrangement PtC(Me)=C(Me)Pt. The ³¹Pn.m.r. spectrum showed a singlet at $\delta -13.3$ p.p.m. with two sets of ¹⁹⁵Pt satellites as expected ²⁴ for a (Ph₃P)Pt-Pt(PPh₃) group [/(PtP) 3 366, 165; /(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 *I*(PtPt) are generally insensitive to Pt-Pt separations.²⁵ The ¹³C n.m.r. spectrum of (6) showed a resonance at § 191.9 p.p.m. with a large ¹⁹⁵Pt-¹³C coupling (1 309 Hz) indicative of PtCO groups, while a singlet at δ 182.1 p.p.m. with no ¹⁹⁵Pt 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 ¹⁹⁵Pt satellites visible [J(PtC) 607 Hz] instead of the expected two for a group PtC(Me)=C(Me)Pt. The ¹³C n.m.r. spectrum of the complex $[(cod)PtC(CH_2SiMe_3)=C(CH_2SiMe_3)Pt(cod)]$ (cod = cyclo-octa-1,5-diene) has the acetylenic-carbon resonance signal at δ 140.4 p.p.m. with J(PtC) = 642and 215 Hz.²⁶ The lack of a second set of ¹⁹⁵Pt 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 molecula. structure is shown in Figure 3, along with the atomic numbering scheme. As expected from the n.m.r. data, the molecular fragment $Ph_3P(OC)Pt-C(Me)=C(Me)Pt(CO)PPh_3$ 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

TABLE 4

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

Atom	x	У	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)	$0.158 \ 97(2)$
cin	-0.028.9(10)	0.618.0(5)	0.245.7(4)
C(2)	-0.0285(10)	0.5374(5)	0.2171(4)
C(2)	-0.0480(10)	0.001 ± 0.001	0.217 1(4) 0.157 5(9)
C(3)	-0.1407(8)	0.5257(4)	0.1373(3)
C(4)	-0.2330(11)	0.587 7(5)	0.1183(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)	-0.1193(8)	0.2480(4)	$0.105\ 7(3)$
Č(31)	0.006.4(10)	0.5342(5)	0.081.3(4)
	-0.021.5(6)	0.565.4(3)	0.035 2(3)
	-0.0210(0)	0.200 9(5)	0.137.8(4)
O(32)	0.1210(11)	0.335 2(3)	0.1373(4)
O(32)	0.1678(7)	0.345 2(4)	$(0.120 \ 1(3))$
C(33)	0.203 8(12)	0.537 6(6)	0.207 6(5)
O(33)	$0.296 \ 4(8)$	$0.571 \ 3(4)$	$0.239\ 0(3)$
Tripher	nylphosphine group 1		
P(1)	0.006.9(2)	0.4564(1)	0.356.7(1)
CIAN	0 158 9(10)	0 495 3(4)	0.416.7(4)
C(49)	0.202.1/10)	0.477 6(5)	0 470 8(4)
C(44)	0.2021(10)	0.477 0(0)	0.513 0(4)
C(43)	0.3110(11)	0.508 7(5)	0.5234(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)	-0.0280(10)	0.373 9(5)	$0.396\ 2(4)$
C(52)	-0.1000(10)	0.379 9(5)	0.4311(4)
C(53)	-0.120.5(11)	0.3184(5)	0.465.1(4)
C(54)	0.053.5(11)	0.250 0(5)	0.465.5(4)
$C(3\pm)$	-0.0000(11)	0.200 0(0)	0.491.6(5)
C(30)	0.0194(13)	0.2433(0)	0.4310(3)
C(56)	0.0319(12)	0.305 4(5)	0.390 1(4)
C(61)	-0.1214(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)	-0.3511(11)	0.553~6(5)	0.3116(4)
C(64)	-0.3231(11)	$0.626\ 7(5)$	0.339.6(4)
C(65)	-0.194.7(12)	0 646 1(5)	0.373.1(4)
	-0.091.2(11)	0 596 6(5)	0 381 9(4)
C(00)	-0.091 2(11)	0.000 0(0)	0.001 0(4)
Tripher	nylphosphine group 2		
$\mathbf{p}(\mathbf{y})$	0.388 5(2)	0 388 8(1)	0.126.6(1)
C(71)	-0.5000(2)	0.470 7(5)	0.1200(1)
$C(T_1)$	-0.5012(10)	0.470 7(5)	0.1119(4)
C(72)	-0.619 5(10)	0.4754(5)	0.059 8(4)
C(73)	-0.7029(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)	-0.5448(11)	$0.591\ 3(5)$	$0.149\ 2(4)$
C(76)	-0.4640(10)	$0.530\ 5(4)$	0.154.5(4)
Č(81)	-0.4811(10)	0.320.6(4)	0.065.4(4)
C(82)	-0.456.7(11)	0.320.7(5)	0.012.1(4)
C(02)	-0.594.9(11)	0.968 5(5)	0.026 6(4)
0(03)	- 0.024 3(11)	0.200 0(0)	~ 0.000 0(4)
U(84)	-0.0121(11)	0.219 9(0)	-0.0300(4)
C(85)	-0.6390(12)	$0.220\ 3(5)$	$0.022 \ 8(5)$
C(86)	-0.5717(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)	-0.3000(12)	0.271 6(5)	0.289 9(4)
C(94)	-0.401.8(12)	0.2884(6)	0.305.9(4)
C(95)	-0.502.3(12)	0 336 9(6)	0 269 3(5)
CIGEN	0 406 2(12)	0.266 0(6)	0.207 5(0)
U(90)		0.300 0(0)	0.410 3(0)

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 ¹³C n.m.r. spectrum, as mentioned above, showed only 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)



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

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

TABLE 5

Important interatomic distances (Å) and bond angles (°) for the complex [OsPt₂(CO)₅(PPh₃)₂{C₂(CH₃)₂}], with estimated standard deviations in parentheses

(a) Distances			
Pt(1) - Pt(2) Pt(1) - Os	3.033(2) 2.664(2)	C(01) - O(01) C(02) - O(02)	1.17(1)
Pt(2)-Os	2.669(2)	C(31) - O(31)	1.14(1)
Pt(1) - C(2)	2.060(8)	C(32) - O(32) C(33) - O(33)	1.16(1) 1.16(1)
Pt(2)-C(3)	2.055(7)		
Os-Ć(2)	2.22(1)	C(1)-C(2)	1.54(1)
Os-C(3)	2.23(1)	C(2) - C(3) C(3) - C(4)	1.40(1) 1.52(1)
Pt(1) - P(1)	2.310(3)	-(-)	(-/
Pt(2) - P(2)	2.300(4)		
		C–C (phenyl)	1.40
Pt(1)-C(01)	1.87(1)	mean	1.00
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) Pt(2) = C(2) = C(2)	113.0(0)	C(31) = Os = Pt(2) C(22) = Os = Pt(1)	101.4(4) 101.5(2)
C(1) - C(2) - C(2)	125.0(5)	C(32) = Os = Pt(1) 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)	$O_{S}-C(33)-O(33)$	176(1)

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 OsPt₂ 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

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 [Co₂Pt₂(CO)₈(PPh₃)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 $[Pt_2\{\mu-(CF_3)_2CO\}(cod)_2]$,³¹ 2.692(3) Å in $[\{Pt(\mu-H)(SiEt_3)[P(C_6H_{11})_3]\}_2]$,³² and 2.790—2.752(7) Å in $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$.³³ If no Pt-Pt bond is assumed in compound (6) the platinum atoms have a 16electron configuration and the osmium atom an 18electron 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 - C - C - 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 ³¹P 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 ³¹P and ¹⁹⁵Pt couplings [J(PH) 3, J(PtH) 34 Hz], whilst the other showed only ¹⁹⁵Pt coupling [J(PtH) 36 Hz]. A ³¹P n.m.r. spectrum had the expected pattern for a R₃-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 Os₃Pt 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 $[{}^{2}H_{1}]$ chloroform was used as solvent for n.m.r. studies.

Reaction of the Complex $[Os_3Pt(\mu-H)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ with Carbon Monoxide.—A solution of (1) (0.15 g,

0.1 mmol) in diethyl ether (20 cm³) was saturated with CO gas. Reduction in volume to *ca*. 5 cm³ by increasing the rate of CO bubbling, and cooling to -20 °C, gave bright yellow *crystals* of $[Os_3Pt(\mu-H)_2(CO)_{11}\{P(cyclo-C_6H_{11})_3\}]$ (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%); ν_{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, C₆H₁₁), 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]; ³¹P (¹H-decoupled), δ -50.4 p.p.m. [s, J(PtP) 2 409 Hz].

Reactions of $[Os_3Pt(\mu-H)_2(CO)_{10}(PPh_3)]$.--(a) With PPh₃. (i) To a stirred solution of (3) (0.2 g, 0.15 mmol) in diethyl ether (30 cm³) was added PPh₃ (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 [Os₃Pt(µ-H)₂(CO)₁₀(PPh₃)₂] (4) (0.19 g, 75%) (Found: C, 35.1; H, 2.1. $C_{46}H_{32}O_{10}Os_{3}P_{2}Pt$ requires C, 35.1; H, 2.1%), m.p. 142–150 °C (decomp.), v_{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, $Os(\mu-H)Pt$, J(PH) 18, J(PtH)590], and 27.55 [d, 1 H, Os(μ -H)Os, J(PH) 14 Hz]; ³¹P (1H-decoupled), $\delta = -30.7$ [s, PPt, J(PtP) = 2.501] and 7.3 p.p.m. (POs); ³¹P (¹H-decoupled, -50 °C), $\delta -34.4$ (s, PPt), -30.5 [s, PPt, J(PtP) 2 495 Hz], 6.5 (s, POs), and 7.3 p.p.m. (s, POs); ³¹P (selectively decoupled), $\delta - 30.9$ [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 $[Os_3(\mu-H)_2(CO)_{10}]$ (0.46 g, 0.55 mmol) in diethyl ether (60 cm³) 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 AsPh₃. Brownish yellow crystals of the compound $[Os_3Pt(\mu-H)_2(CO)_{10}(AsPh_3)(PPh_3)]$ (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 AsPh₃ (0.03 g, 0.08 mmol) and compound (3) (0.1 g, 0.08 mmol), as described in (i) above. Compound (5) had v_{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]; ³¹P (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 cm³), 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 cm³), and shown to be crystals of the complex [OSPt₂(CO)₅-(PPh₃)₂(μ_3 - η^2 -MeC₂Me)] (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 $[Os_3(\mu-H)_2(CO)_9(\mu_3-\eta^2-MeC_2Me)]$ (8) (combined yield 0.22 g), and bright yellow material containing the two complexes $[Os_3(\mu-H)_2(CO)_8(PPh_3)(\mu_3-\eta^2-MeC_2Me)]$ (9) and $[OsPt_2(CO)_6(PPh_3)(\mu_3-\eta^2-MeC_2Me)]$ (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.), $v_{max.}$ 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]. ³¹P (¹H-decoupled), δ –13.3 p.p.m. [s, J(PtP) 3 366 and 165, J(PtPt) 57 Hz]; ¹³C {¹H-decoupled, in the presence of [Cr($C_5H_8O_2$)₃], δ 191.9 [s, PtCO, J(PtC) 1 309], 182.1 (s, OsCO), 155.5 [s, CMe, 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]; v_{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), ν_{max} at 2103w, 2077vs, 2053vs, 2027s, 2017s, 2007vs, 1997m, and 1981m 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. $C_{30}H_{23}O_8$ -Os₃P requires C, 32.4; H, 2.1%), m.p. 178—184 °C (decomp.), ν_{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]; ³¹P (¹H-decoupled), δ 1.2 p.p.m.

(v) Complex (10) (Found: C, 31.7; H, 2.1. $C_{28}H_{21}O_{6}$ -OsPPt₂ requires C, 31.6; H, 2.0%), m.p. 135—139 °C (decomp.), v_{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]; ³¹P (¹H-decoupled), δ -20.7 p.p.m. [s, J(PPt) 3 406 and 171 Hz].

Crystal Structure Determinations.—(i) Complex (4), [Os₃- $Pt(\mu-H)_2(CO)_{10}(PPh_3)_2]$. Crystals of (4) grow as yellow triclinic (pseudo-hexagonal) prisms. Diffracted intensities were collected at 200 K from a crystal of dimensions 0.25 imes0.15 imes 0.35 mm on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leq 2\theta \leq 60.0^{\circ}$, according to methods described earlier.^{34,35} Of the total 7167 reflections measured, 5 794 had $I \ge 2.5\sigma(I)$ 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 = 1572.4, Triclinic, a = 14.427(7), b = 12.793(5), c = 14.151(6) Å, $\alpha = 92.33(3)$, $\beta = 120.87(3)$, $\gamma = 91.06(4)^{\circ}$, U = 2238(4)Å³, $D_m = 2.35$ (flotation), Z = 2, $D_c = 2.33$ g cm⁻³, F(000) = 1448, Mo- K_{α} X-radiation (graphite monochromator), $\bar{\lambda} = 0.71069$ Å, μ (Mo- K_{α}) = 124.0 cm⁻¹, space group $P\bar{I}$ (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 $w = 1/\sigma^2(F_0)$, where $\sigma(F_0)$ 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.

 $[OsPt_2(CO)_5(PPh_3)_2\{C_2(CH_3)_2\}].$ Complex (6), (ii)Crystals of (6) grow as yellow prisms. Conditions of data collection were as for (4) except in the following particulars: crystal size: $0.20 \times 0.15 \times 0.30$ mm; 20 range: $2.9-55.0^{\circ}$; total no. of reflections measured: 5 942, of which 4 438 had $I \ge 2.5\sigma(I)$; check reflections: 4 0 2, 1 4 1, 1 $\overline{1}$ $\overline{9}$, monitored every 50 reflections and showed no significant decay; A* ranged from 6.24 to 3.54.

Crystal data for (6). $C_{45}H_{36}O_5OsP_2Pt_2$, M = 1.299.1, Monoclinic, a = 11.143(8), b = 17.458(12), c = 23.443(15)Å, $\beta = 113.82(5)^{\circ}$, U = 4.172(5) Å³, $D_{\rm m}$ not measured, Z = 4, $D_c = 2.07$ g cm⁻³, F(000) = 2.432, Mo- K_{α} Xradiation (graphite monochromator), $\tilde{\lambda} = 0.710.69$ Å, μ (Mo- K_{α}) = 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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