Chemistry of the Metal Carbonyls. Part 76.[1] Platinum–Osmium Carbonyl Complexes derived from Decacarbonyldi-μ-hydrido-triosmium; *X*-Ray Crystal Structure of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ †

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Reactions between $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and the compounds $[Pt(C_2H_4)_2(PR_3)]$ $[PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3, or $PBu^t{}_2Me]$ afford tetranuclear metal complexes $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$. Examination of the variable-temperature ^1H n.m.r. spectra of these ' 58-electron ' clusters reveals dynamic behaviour with site exchange of the two hydrido-ligands, the energy barrier for this process for the $PBu^t{}_2Me$ derivative being *ca.* 58 kJ mol^{-1}. In order to establish the molecular structure of these complexes a single-crystal *X*-ray diffraction study was made on the compound containing the $P(cyclo\text{-}C_6H_{11})_3$ ligand. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 11.822(4)$, $b = 16.584(5)$, $c = 17.763(9)$ Å, and $\beta = 108.10(4)°$. The structure has been refined to R 0.035 (R' 0.038) for 5 737 reflections to $2\theta < 60°$ (Mo-K_α *X*-radiation) collected at 200 K. The metal atoms adopt a slightly asymmetric tetrahedral structure [Os–Os 2.777(1), 2.741(1), and 2.789(1) Å; Os–Pt 2.791(1), 2.832(1), and 2.863(1) Å]. The platinum atom is bonded to a CO group and to the $P(cyclo\text{-}C_6H_{11})_3$ ligand, and each osmium is attached to three CO groups. The hydrido-ligands bridge the longer of the Os–Os and Os–Pt bonds, as deduced from observation of residual electron densities, from widening of certain Pt–Os–CO and Os–Os–CO angles, from staggered conformations of two of the $Os(CO)_3$ groups with respect to the two longer edges of the tetrahedron, and from calculation of potential energy minima.

In developing the chemistry of carbonyl complexes containing heteronuclear metal–metal bonds,[2] some years ago we showed[3] that the zerovalent platinum complexes $[Pt(PR_3)_4]$ and $[Pt(olefin)(PR_3)_2]$ reacted with $[Fe_2(CO)_9]$ or $[Ru_3(CO)_{12}]$ to yield trinuclear iron– or ruthenium–platinum clusters such as $[Fe_2Pt(CO)_8(PMe_2Ph)_2]$ and $[RuPt_2(CO)_5(PPh_3)_3]$. During the course of this earlier work, we also obtained the tri- and tetranuclear metal species $[OsPt_2(CO)_5(PPh_3)_3]$ and $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ in low yields from $[OsH_2(CO)_4]$ and $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$. However, the major product of this reaction was $[OsH_2(CO)_3(PPh_3)]$. Moreover, we were unable to prepare osmium–platinum cluster compounds from reactions between $[Os_3(CO)_{12}]$ and $[Pt(PR_3)_4]$, the products being the complexes $[Os_3(CO)_{12-n}(PR_3)_n]$ ($n = 1$ or 2). With hindsight these results[3] can be attributed to two factors, namely, the now well established stability of the *triangulo*-structure of $[Os_3(CO)_{12}]$, which is preserved in many reactions,[4-10] and to the presence in solution of PR_3, produced by dissociation of $[Pt(PR_3)_4]$. Free PR_3 leads to preferential formation of the compounds $[Os_3(CO)_{12-n}(PR_3)_n]$ ($n = 1$ or 2) and $[OsH_2(CO)_3(PPh_3)]$, rather than the desired osmium–platinum containing species.

More recently two independent developments have prompted a more promising approach to the synthesis of tetranuclear osmium–platinum compounds. Firstly, the discovery[4] of the electronically unsaturated dihydrido-cluster complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has initiated development of an extensive chemistry of this novel compound, particularly *via* reactions with nucleophiles, with which it generally interacts under mild conditions.[11-15] Thus it seemed likely that $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ would be a more promising precursor to heteronuclear metal complexes containing osmium *via* low-valent metal addition reactions than $[Os_3(CO)_{12}]$. Secondly, in zerovalent platinum chemistry the discovery of $[Pt(C_2H_4)_3]$,[16] and its ready *in situ* conversion to the reactive species $[Pt(C_2H_4)_2(PR_3)]$[17] and $[Pt(C_2H_4)(PR_3)_2]$,[18] has provided a range of reagents which do not suffer from the disadvantage of tertiary phosphine dissociation of the Malatesta and Cenini[19] compounds $[Pt(PR_3)_4]$, referred to above. Moreover, we have demonstrated in a series of studies that the $Pt(PR_3)_2$ group oxidatively inserts into electron deficient *closo*-carbaboranes to give both *closo*- and *nido*-platinacarbaborane clusters.[20] It thus seemed likely that appropriately chosen zerovalent platinum compounds would add to the 46-electron complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. It has been suggested[21] that the $Os(\mu\text{-}H)_2Os$ group in this triosmium compound has bonding characteristics similar to the four-centre four-electron bonds of $B(\mu\text{-}H)_2B$ systems. A preliminary report on some aspects of the work described herein has appeared.[22]

RESULTS AND DISCUSSION

Addition of a light petroleum solution of $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ in the same solvent at room temperature resulted in a rapid colour change from deep purple to green. Chromatography of the mixture afforded the dark green or black crystalline compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (1), characterised by microanalysis, and by its ^1H and ^{31}P n.m.r. spectra.

At ambient temperatures the ^{31}P n.m.r. spectrum of (1) showed a singlet at δ −74.8 p.p.m. with ^{195}Pt satellites [J(PtP) 2 503 Hz]. This coupling is within the range found for complexes in which there is a direct P–Pt bond.[18] When selectively ^1H-decoupled, the signal became a doublet of separation 11 Hz, thus indicating

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† 1,2,2,2,3,3,3,4,4,4-Decacarbonyl-1,2;3,4-di-μ-hydrido-1-tricyclohexylphosphine-*tetrahedro*-platinumtriosmium.

a coupling between the phosphorus nucleus and one hydrido-ligand in (1). At room temperature the ^{1}H n.m.r. spectrum showed, in addition to the signals of the cyclohexyl groups, two broad singlets at τ 16.93 and 18.44, with only the latter displaying ^{195}Pt satellites [J(PtH) 583 Hz]. These data thus established that the higher field signal was due to a proton attached to platinum, as deduced from the partially decoupled ^{31}P spectrum.

Reaction of the complexes $[\mathrm{Pt(C_2H_4)_2(PR_3)}]$ ($\mathrm{PR_3} = \mathrm{PPh_3}$ or $\mathrm{PBu^t_2Me}$) with $[\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}]$ afforded the compounds $[\mathrm{Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)}]$ (2, $\mathrm{PR_3} = \mathrm{PPh_3}$; 3, $\mathrm{PR_3} = \mathrm{PBu^t_2Me}$) in 60—75% yield. The spectral properties of (2) and (3) were very similar to those of (1), and suggested that all three complexes were structurally analogous. The ^{1}H and ^{31}P n.m.r. spectra of the three complexes showed only minor differences in chemical shifts and coupling constants, apart from those resonances due to the organo-groups on the phosphine ligands.

The ^{1}H n.m.r. spectrum of (3) was examined over the range 100 °C to —30 °C, and revealed dynamic behaviour (Figure 1). At the upper limit there was one doublet resonance [τ 17.55, J(PH) 7, J(PtH) 284 Hz], while the limiting —30 °C spectrum showed a singlet at τ 16.83 and a doublet at τ 18.21 [J(PH) 15, J(PtH) 577 Hz]. The ^{1}H spectrum of (2) also revealed dynamic behaviour in this cluster, the limiting spectrum at —60 °C being very similar to that of (3) (Figure 1). We interpret these data as indicating a two-site exchange process between two hydrido-ligands in a pyramidal structure $\mathrm{Os_3Pt}$, probably containing Os(μ-H)Os and Pt(μ-H)Os bridge bonds. The activation energy for the process is estimated [23] as $\Delta G_{T_c}^\ddagger = 58 \pm 2$ kJ mol^{-1}. This value is comparable with those obtained [24] for the hydrido-site-exchange processes in $[\mathrm{Ru_4(\mu\text{-}H)_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)}]$ for which $\Delta G_{T_c}^\ddagger$ is calculated at 30 °C to be 50 kJ mol^{-1}. It is of interest that the value of J(PtH) of 577 Hz in the signal at τ 18.21 in the spectrum of (3) at —30 °C is very similar to that [J(PtH) 540 Hz] measured [25] for the bridging hydrido-ligand in the diplatinum cation $[\mathrm{Pt_2H_2(\mu\text{-}H)(Ph_2PCH_2PPh_2)}]^+$.

The ^{13}C n.m.r. spectrum of (3) at —70 °C was uninformative. Apart from resonances due to the Bu^t and Me groups, there was a sharp singlet at δ 193 [J(PtC) 30 Hz], and four other CO resonances observed as unresolved multiplets at 185, 182, 177, and 170 p.p.m. Evidently the CO ligands are still undergoing site exchange at —70 °C. The relatively poor solubility of compounds (1) and (2) precluded measurement of useful ^{13}C n.m.r. spectra.

The spectroscopic evidence discussed so far does not allow a definitive assignment of the structures of compounds (1)—(3). Hence a single-crystal X-ray diffraction study was carried out, and complex (1) was chosen because only it gave crystals of sufficiently high quality for X-ray diffraction. The results are summarized in Tables 1 and 2, and a view of the molecule with the atomic numbering scheme is shown in Figure 2.

A 'tetrahedral' metal framework is immediately apparent, with some asymmetry in the metal–metal distances discussed below. It is also evident that a CO ligand is attached to the platinum atom, so that in the reaction leading to the synthesis of (1) a CO ligand is transferred to this metal centre. This is a common feature of reactions of the complexes $[\mathrm{Pt(C_2H_4)_2(PR_3)}]$.[26]

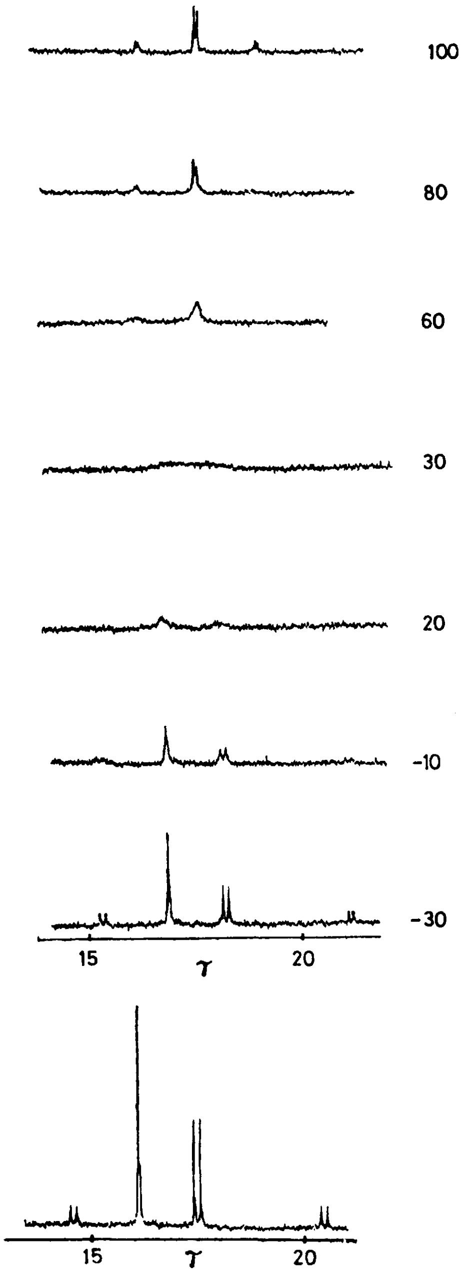


FIGURE 1 Hydrogen-1 n.m.r. spectra of compound (3) in the range τ 15—20, measured from 100 to —30 °C. The bottom spectrum is that of (2) at —60 °C

Within the metal framework the dihedral angles range from 68.2 to 72.8°, departing slightly from a regular tetrahedral geometry as a result of the slightly differing metal–metal bond distances (Table 2). Within the $\mathrm{Os_3}$

triangle the Os–Os separations may be compared with those found in [$Os_3(CO)_{12}$] [2.877(3) Å],[27] in [$Os_3(\mu\text{-}H)_2(CO)_{10}$] [2.814(1) and 2.683(1) Å (Os=Os)],[21] and within the central tetrahedron of [$Os_6(CO)_{18}$] [2.731(1)—2.807(1) Å].[28]

The two hydrido-ligands were detected by the presence of residual electron density in appropriate locations relative to the longest Os–Os and Pt–Os bonds, *viz.* Os(2)–Os(3) and Pt–Os(1). It is well known that metal–metal distances are lengthened by bridging hydrido-ligands.[29–31] Moreover, additional evidence for the location of the hydrido-ligands is the widening of the corresponding equatorial Pt–Os–CO and Os–Os–CO angles [Pt–Os(1)–C(12) 109.5(3), Pt–Os(1)–C(13) 108.1(3), Os(3)–Os(2)–C(22) 112.0(3), Os(3)–Os(2)–C(23) 112.0(3), Os(2)–Os(3)–C(31) 110.0(4), and Os(2)–Os(3)–C(32) 115.6(4)°], whereas the other *cis*-Pt–Os–CO and Os–Os–CO angles range over 81—105°.

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for the complex [$Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}$] (1)

Atom	*x*	*y*	*z*
Pt	−0.036 93(3)	0.270 07(2)	0.137 90(2)
Os(1)	0.080 87(3)	0.143 87(2)	0.243 11(2)
Os(2)	0.180 74(3)	0.208 20(2)	0.134 00(2)
Os(3)	0.173 25(3)	0.296 78(2)	0.265 82(2)
H(1) *	−0.070 3	0.177 4	0.184 6
H(2) *	0.273 7	0.281 6	0.205 2
C(01)	−0.000 7(8)	0.360 8(6)	0.088 2(6)
O(01)	0.022 6(8)	0.416 0(5)	0.057 8(5)
C(11)	0.231 7(9)	0.108 9(6)	0.304 7(6)
O(11)	0.325 1(7)	0.088 8(5)	0.342 1(5)
C(12)	0.006 0(10)	0.129 2(6)	0.323 1(6)
O(12)	−0.035 3(8)	0.120 4(5)	0.373 2(5)
C(13)	0.027 5(9)	0.043 6(6)	0.192 7(5)
O(13)	0.001 7(7)	−0.019 3(4)	0.162 5(4)
C(21)	0.089 9(9)	0.131 7(6)	0.059 9(6)
O(21)	0.033 8(7)	0.084 4(4)	0.014 0(4)
C(22)	0.220 9(10)	0.274 2(7)	0.057 2(7)
O(22)	0.246 8(8)	0.310 9(5)	0.009 6(5)
C(23)	0.321 9(9)	0.142 3(7)	0.156 6(6)
O(23)	0.404 7(7)	0.106 2(5)	0.169 7(5)
C(31)	0.185 2(11)	0.410 9(7)	0.246 3(6)
O(31)	0.181 9(8)	0.478 3(4)	0.234 2(4)
C(32)	0.311 8(9)	0.295 5(6)	0.351 3(6)
O(32)	0.401 0(8)	0.291 9(5)	0.400 3(5)
C(33)	0.077 6(10)	0.300 6(6)	0.337 2(6)
O(33)	0.028 5(7)	0.304 4(5)	0.381 6(5)
Tricyclohexylphosphine ligand			
P	−0.247 99(21)	0.271 21(14)	0.092 77(14)
C(41)	−0.302 9(9)	0.300 2(5)	0.175 6(6)
C(42)	−0.233 1(9)	0.371 8(6)	0.224 2(6)
C(43)	−0.278 1(11)	0.385 4(7)	0.296 0(6)
C(44)	−0.409 1(10)	0.403 7(8)	0.272 6(8)
C(45)	−0.478 8(10)	0.333 6(7)	0.221 8(7)
C(46)	−0.438 5(8)	0.316 6(6)	0.150 3(6)
C(51)	−0.325 2(9)	0.336 9(5)	0.007 2(5)
C(52)	−0.290 2(11)	0.314 9(6)	−0.067 8(6)
C(53)	−0.352 6(12)	0.369 7(7)	−0.135 8(7)
C(54)	−0.326 7(12)	0.459 0(6)	−0.116 2(7)
C(55)	−0.367 3(10)	0.479 4(6)	−0.045 2(6)
C(56)	−0.306 2(10)	0.427 7(6)	0.026 7(6)
C(61)	−0.312 6(8)	0.169 8(5)	0.061 1(6)
C(62)	−0.326 2(8)	0.117 4(6)	0.129 7(6)
C(63)	−0.381 7(10)	0.037 0(7)	0.096 7(6)
C(64)	−0.307 1(10)	−0.010 3(5)	0.054 7(6)
C(65)	−0.290 0(10)	0.040 8(6)	−0.011 9(6)
C(66)	−0.234 2(9)	0.123 6(5)	0.020 8(6)

* Calculated; see text.

In accordance with this positioning of the hydrogen atoms as edge-bridging ligands, projections of the structure onto the $\overline{\text{Os(2)–Os(3)–Pt}}$ and $\overline{\text{Os(1)–Pt–Os(3)}}$ planes show that the carbonyl ligands on Os(1) and Os(2), respectively, are staggered relative to the M–M bonds between these two atoms and the corresponding triangular faces.[32] Finally calculations [33] show that there are potential energy minima for sites for hydrido-ligand co-ordination along Os(1)–Pt and Os(2)–Os(3), these being of considerably lower energy than any other sites. For purposes of crystallographic computation, however, the hydride ligands were constrained during refinement to a M–H bond distance of 1.85 Å, based mainly on the Os–H distance found by neutron diffraction in [$Os_3(\mu\text{-}H)_2(CO)_{10}$].[21]

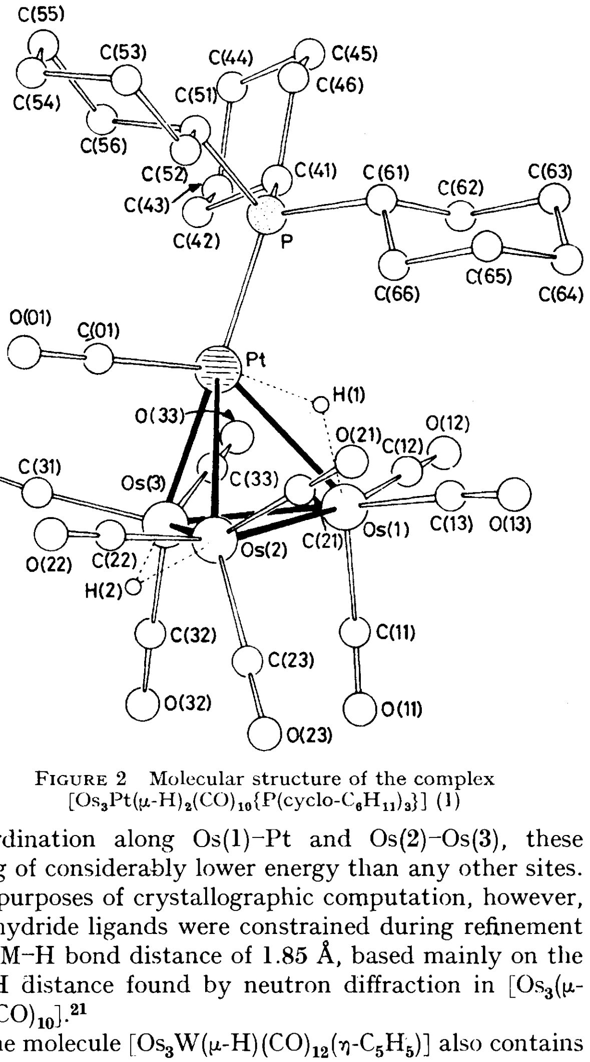


FIGURE 2 Molecular structure of the complex [$Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}$] (1)

The molecule [$Os_3W(\mu\text{-}H)(CO)_{12}(\eta\text{-}C_5H_5)$] also contains an Os(μ-H)Os group but with an Os–Os separation [2.932(2) Å] [34] significantly longer than in (1). Moreover, the non-hydrido-bridged Os–Os bonds in [$Os_3W(\mu\text{-}H)(CO)_{12}(\eta\text{-}C_5H_5)$] are also longer (average 2.792 Å) than the corresponding distances in (1) (average 2.759 Å). However, whereas [$Os_3W(\mu\text{-}H)(CO)_{12}(\eta\text{-}C_5H_5)$] has the customary six skeletal bond pairs [35] of a *closo*-tetrahedral structure, the platinum compound (1) has five such pairs, and is thus an ' unsaturated ' tetrahedral structure; this feature is probably responsible for the shorter bond distances in (1). It is interesting that the cluster complexes [$Co_2Pt_2(CO)_8(PPh_3)_2$][36] and [$Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2$] [22] also have five skeletal bond pairs

TABLE 2

Bond lengths (Å) and angles (°) for the complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ (1)

(*a*) Distances			
Pt–Os(1)	2.863(1)	Os(1)–Os(2)	2.777(1)
Pt–Os(2)	2.791(1)	Os(1)–Os(3)	2.741(1)
Pt–Os(3)	2.832(1)	Os(2)–Os(3)	2.789(1)
Pt–H(1)	1.85 *	Os(2)–H(2)	1.85 *
Os(1)–H(1)	1.85 *	Os(3)–H(2)	1.85 *
(*i*) Carbonyls			
Pt–C(01)	1.853(11)	C(01)–O(01)	1.149(14)
Os(1)–C(11)	1.867(10)	C(11)–O(11)	1.151(12)
Os(1)–C(12)	1.907(14)	C(12)–O(12)	1.151(17)
Os(1)–C(13)	1.899(10)	C(13)–O(13)	1.170(12)
Os(2)–C(21)	1.906(9)	C(21)–O(21)	1.169(12)
Os(2)–C(22)	1.922(12)	C(22)–O(22)	1.152(16)
Os(2)–C(23)	1.932(11)	C(23)–O(23)	1.103(14)
Os(3)–C(31)	1.932(12)	C(31)–O(31)	1.144(14)
Os(3)–C(32)	1.854(10)	C(32)–O(32)	1.142(12)
Os(3)–C(33)	1.947(13)	C(33)–O(33)	1.114(16)
(*ii*) Tricyclohexylphosphine			
Pt–P	2.372(2)		
P–C(41)	1.846(12)	P–C(51)	1.859(9)
C(41)–C(42)	1.546(13)	C(51)–C(52)	1.558(17)
C(42)–C(43)	1.541(18)	C(52)–C(53)	1.510(15)
C(43)–C(44)	1.496(17)	C(53)–C(54)	1.532(16)
C(44)–C(45)	1.553(16)	C(54)–C(55)	1.524(20)
C(45)–C(46)	1.509(18)	C(55)–C(56)	1.525(14)
C(46)–C(41)	1.546(14)	C(56)–C(51)	1.547(13)
P–C(61)	1.863(9)		
C(61)–C(62)	1.544(15)	C(64)–C(65)	1.519(16)
C(62)–C(63)	1.525(14)	C(65)–C(66)	1.554(13)
C(63)–C(64)	1.534(18)	C(66)–C(61)	1.541(16)
(*b*) Angles			
(*i*) Metal tetrahedron			
Os(1)–Pt–Os(2)	58.82(3)	Pt–Os(2)–Os(1)	61.87(3)
Os(1)–Pt–Os(3)	57.54(4)	Pt–Os(2)–Os(3)	61.00(3)
Os(2)–Pt–Os(3)	59.45(5)	Os(1)–Os(2)–Os(3)	59.01(5)
Pt–Os(1)–Os(2)	59.31(4)	Pt–Os(3)–Os(1)	61.79(2)
Pt–Os(1)–Os(3)	60.68(5)	Pt–Os(3)–Os(2)	59.55(5)
Os(2)–Os(1)–Os(3)	60.71(3)	Os(1)–Os(3)–Os(2)	60.28(2)
(*ii*) Carbonyls		(*iii*) Tricyclohexylphosphine	
Os(2)–Pt–C(01)	86.2(3)	Pt–P–C(41)	109.0(3)
Os(3)–Pt–C(01)	88.8(3)	Pt–P–C(51)	118.6(3)
Os(2)–Os(1)–C(11)	89.6(4)	Pt–P–C(61)	112.6(3)
Os(3)–Os(1)–C(11)	86.4(3)	C(41)–P–C(51)	107.0(4)
Pt–Os(1)–C(12)	109.5(3)	C(41)–P–C(61)	105.4(5)
Os(3)–Os(1)–C(12)	105.3(3)	C(51)–P–C(61)	103.3(4)
Pt–Os(1)–C(13)	108.1(3)	C(46)–C(41)–C(42)	110.5(8)
Os(2)–Os(1)–C(13)	99.2(3)	C(41)–C(42)–C(43)	108.3(9)
Pt–Os(2)–C(21)	86.3(3)	C(42)–C(43)–C(44)	113.5(9)
Os(1)–Os(2)–C(21)	87.4(4)	C(43)–C(44)–C(45)	109.1(10)
Pt–Os(2)–C(22)	103.9(3)	C(44)–C(45)–C(46)	112.2(10)
Os(3)–Os(2)–C(22)	112.0(3)	C(45)–C(46)–C(41)	111.2(8)
Os(1)–Os(2)–C(23)	99.6(4)	C(56)–C(51)–C(52)	110.9(9)
Os(3)–Os(2)–C(23)	112.0(3)	C(51)–C(52)–C(53)	110.6(10)
Pt–Os(3)–C(31)	96.0(3)	C(52)–C(53)–C(54)	112.8(9)
Os(2)–Os(3)–C(31)	110.0(4)	C(53)–C(54)–C(55)	108.2(10)
Os(1)–Os(3)–C(32)	105.6(3)	C(54)–C(55)–C(56)	112.1(10)
Os(2)–Os(3)–C(32)	115.6(4)	C(55)–C(56)–C(51)	111.4(8)
Pt–Os(3)–C(33)	89.2(3)	C(66)–C(61)–C(62)	108.5(7)
Os(1)–Os(3)–C(33)	80.8(3)	C(61)–C(62)–C(63)	109.2(8)
Pt–C(01)–O(01)	179.3(9)	C(62)–C(63)–C(64)	113.0(10)
Os(1)–C(11)–O(11)	178.7(9)	C(63)–C(64)–C(65)	109.3(8)
Os(1)–C(12)–O(12)	177.3(9)	C(64)–C(65)–C(66)	110.4(8)
Os(1)–C(13)–O(13)	175.9(9)	C(65)–C(66)–C(61)	111.2(9)
Os(2)–C(21)–O(21)	179.8(8)		
Os(2)–C(22)–O(22)	176.8(10)		
Os(2)–C(23)–O(23)	178.5(10)		
Os(3)–C(31)–O(31)	174.0(10)		
Os(3)–C(32)–O(32)	174.7(11)		
Os(3)–C(33)–O(33)	175.9(8)		

* Hydrido-ligand positions calculated.

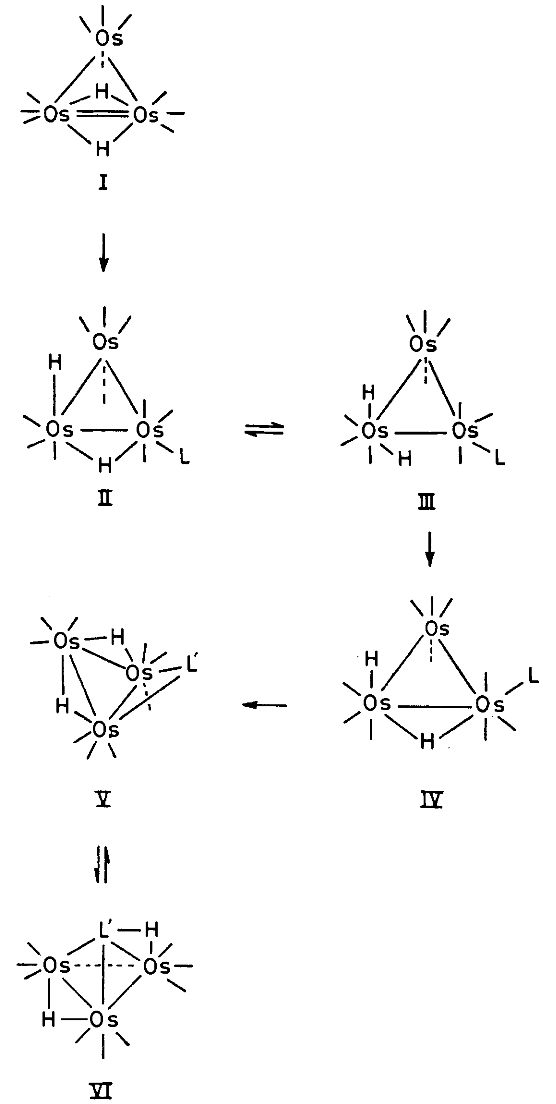
but having two platinum atoms per molecule adopt ' butterfly ' type structures. Evidently introduction of a platinum atom into a heteronuclear cluster such as (1)—(3), $[Co_2Pt_2(CO)_8(PPh_3)_2]$, or $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ causes them to behave structurally as if they contained an extra electron pair for each platinum atom. This behaviour can be partly understood if account is taken of the fact that platinum in its compounds often does not adopt a rare-gas electron configuration, so that in compounds (1)—(3) only five electron pairs are needed for the $Pt(CO)(PR_3)$ groups to bond the ligands and fill the ' non-bonding ' orbitals whereas according to Wade's[35] precepts six pairs are necessary.

The n.m.r. spectra of compounds (1)—(3) are consistent with the existence in solutions of structures similar to that established for (1) in the solid state. Since the hydrido-ligands bridge opposite edges of the cluster the exchange process observed between the two sites could involve either terminal or face-bridging intermediates, or more probably the ' butterfly ' structure discussed below. Recently Schilling and Hoffmann[37] have reported an extended Hückel calculation on the hypothetical dianion $[Fe_3Pt(CO)_{10}(PH_3)]^{2-}$ with specific reference to our compounds (1)—(3). It was concluded that the barrier to rotation of $Pt(CO)(PR_3)$ fragments around the metal triangle would be very low (*ca.* 25 kJ mol^{-1}), although it was suggested that bulky phosphine groups and bridging hydrido-ligands might affect this value. It was mentioned above that for (3) the hydrido-ligand-exchange process has a barrier of *ca.* 58 kJ mol^{-1}, which is considerably higher than the estimated[37] rotational barrier. Moreover, assuming that one H ligand remains bonded to platinum, since we observe ^{195}Pt coupling, then rapid ' spinning ' of the $Pt(H)(CO)(PR_3)$ moiety about the triosmium framework would not render the two hydrido-ligands equivalent. However, it is possible that any rapid rotation of the platinum moiety is such a low-energy process that it is not observed in the ^1H n.m.r. spectrum, and only some higher energy transformation can be detected. A variable-temperature ^{13}C n.m.r. spectrum on an enriched sample may shed light on the mechanisms involved.

As mentioned above, establishment of the structure of (1) revealed that CO ligand transfer had occurred in the reactions between $[Pt(C_2H_4)_2(PR_3)]$ [$PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3, or $PBu^t{}_2Me$] and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ which prompts the question as to whether this transfer takes place before or after the platinum–osmium bonds form. If the former process occurs species $Pt(CO)(PR_3)$ would be the expected intermediates and these would rapidly trimerise to afford the very stable complexes $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$,[26] unless the $Pt(CO)(PR_3)$ monomers react more rapidly with the Os_3 cluster, which seems unlikely. Thus the observation in several independent syntheses of (1)—(3) that no $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ compounds are formed suggests that a Pt–Os bond is generated prior to CO migration to platinum.

An attractive proposed mechanism for the formation of (1)—(3) can be based on the known chemistry of

$[Os_3(\mu\text{-}H)_2(CO)_{10}]$ in relation to its reactions with two-electron donor ligands (CO, PR_3, $AsMe_2Ph$, CNMe, or NCPh).[11,12] Thus the triphenylphosphine adduct of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has been shown [38] to have the structure II (L = PPh_3) depicted in the Scheme, and it is possible that a $Pt(PR_3)$ moiety, derived from $[Pt(C_2H_4)_2(PR_3)]$, attacks the unsaturated triosmium cluster in a similar manner. Moreover, examination of the variable-temperature ^1H n.m.r. spectrum of the complexes $[Os_3(\mu\text{-}H)_2(CO)_{10}L]$ (L = CO, CNMe, PMe_2Ph, or $AsMe_2Ph$) revealed exchange of terminal and bridge hydride sites for which an intermediate of structure III was postulated.[12] The transformation III into IV has precedent in the fluxional behaviour of $[Os_3(CO)_{12}]$.[39] Alternative possibilities are that either the intermediate IV is formed in the initial attack of $Pt(PR_3)$ on I, or that addition of $Pt(PR_3)$ to I occurs at an axial position on the osmium atom. It has recently been found that in $[Os_3H(\mu\text{-}H)(CO)_{10}(CNBu^t)]$ the $CNBu^t$ is in the axial position.[40] Transfer of a CO from the $Os(CO)_4$ group in IV (or its axially substituted isomer) to the platinum and formation of a Os–Pt bond could generate the ' butterfly ' structure V, not uncommonly found in tetrametal structures. Collapse of V into VI with migration of one of the bridging hydrides would produce the final products. It is interesting to speculate that the hydrido-exchange process observed for compounds (1)—(3), and discussed above, might occur *via* V as an intermediate, the latter forming by slipping the $Pt(CO)PR_3$ group over an Os–Os bond, with hydrido-ligand migration as shown. This alternative structure has been mentioned elsewhere.[37]



SCHEME L = $Pt(PR_3)$; L′ = $Pt(CO)(PR_3)$; CO groups are omitted for clarity

The interaction of Pt^0 species with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ is probably related to two other types of reaction. Thus, $[Re(CO)_5]^-$ reacts with $[Os_3(CO)_{12}]$, followed by protonation, to give the tetrahedral structure $[Os_3Re(\mu\text{-}H)_3(CO)_{13}]$,[41] while $[Ru(CO)_4]^{2-}$ similarly produces $[Os_3Ru(\mu\text{-}H)_4(CO)_{12}]$.[42] The first step in these reactions is thought to be addition of the carbonylmetallate to a single Os atom of $[Os_3(CO)_{12}]$ with displacement of CO. It is proposed [41,42] that the second step involves a ' butterfly ' arrangement of the metal atoms followed by formation of the closed tetrahedral structure. The second analogy concerns the addition of Pt^0 species to the edge of a *nido*-carbaborane having B(μ-H)B bonds in the face.[43] In this case formation of a *closo* structure necessitates pyrolysis and loss of hydrogen. The incipient similarity of B(μ-H)B and Os(μ-H)Os was mentioned earlier.[21]

Finally it should be pointed out that several other heteronuclear metal cluster complexes containing the Os_3 group have been reported since our initial communication.[22] The compound $[CoOs_3(\mu\text{-}H)_3(CO)_{12}]$ has been obtained by heating $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Co_4(CO)_{12}]$ under reflux.[44] The more forcing conditions and the tetranuclear nature of the cobalt species used in the preparation suggests that the reaction is not related to those described herein. However, Shapley and co-workers [45] in a study of the complex $[Os_3(CO)_{10}(NCMe)_2]$ have prepared two tetrahedral triosmiumtungsten compounds $[Os_3W(\mu\text{-}H)(CO)_{12}(\eta\text{-}C_5H_5)]$ and $[Os_3W(\mu\text{-}H)_3(CO)_{11}(\eta\text{-}C_5H_5)]$ by refluxing the acetonitriletriosmium complex with excess of $[WH(CO)_3(\eta\text{-}C_5H_5)]$. The complex $[Os_3(CO)_{10}(NCMe)_2]$ behaves as a source of ' $Os_3(CO)_{10}$ '. Similarly, $[ReH(CO)_5]$ reacts with the acetonitriletriosmium complex to give $[Os_3Re(\mu\text{-}H)(CO)_{15}]$, $[Os_3Re(\mu\text{-}H)(CO)_{16}]$, and $[Os_3Re_2(\mu\text{-}H)_2(CO)_{20}]$.[46] However, these molecules have structures in which $Re(CO)_5$ groups form σ bonds with one osmium of the Os_3 triangle.[47]

EXPERIMENTAL

Nuclear magnetic resonance spectra (^1H, hydrogen-1 decoupled ^{13}C and ^{31}P) were recorded on JEOL PFT and PS 100 spectrometers, with ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.) and ^{31}P shifts relative to H_3PO_4 (external) taken as positive to low frequency (high field). Unless otherwise stated, data are of room-temperature measurements in [$^2H_1$]chloroform. Infrared spectra were measured in cyclohexane and obtained with Perkin-Elmer 257 and 457 spectrophotometers. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. The complexes $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ [48] and $[Pt(C_2H_4)_2(PR_3)]$ [17] were made by the methods described previously.

Synthesis of the Platinumtriosmium Complexes.—(*a*) To a stirred solution of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.85 g, 1.0 mmol) in light petroleum (100 cm^3) was added a solution of $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.54 g, 1.0 mmol) in the same solvent (20 cm^3). The colour changed from purple to green as stirring continued (0.5 h). Volatile material was removed *in vacuo*, and the residue was dissolved in light petroleum and chromatographed on alumina. Removal of solvent gave black *crystals* of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (1) (0.32 g, 25%), from diethyl ether, m.p. 176—178 °C (decomp.) (Found: C, 25.4; H, 2.8. $C_{28}H_{35}O_{10}Os_3PPt$ requires C, 25.3; H, 2.7%); $\nu_{max.}$ (CO) at 2 075m, 2 043s, 2 017s, 1 985m, 1 973m, 1 959w, and 1 943m cm^{-1}. N.m.r.: ^{1}H, τ 8.25—8.75 (m, br, 33 H, C_6H_{11}), 16.93 [s, 1 H, Os(μ-H)Os], and 18.44 [s, 1 H, Os(μ-H)Pt, *J*(PtH) 583 Hz]; ^{31}P, δ −74.8 p.p.m. [s, *J*(PtP) 2 503 Hz]; ^{31}P (selectively decoupled), δ −74.8 p.p.m. [d, *J*(PH) 11, *J*(PtP) 2 502 Hz].

(*b*). In a similar fashion $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.85 g, 1.0 mmol) was treated with $[Pt(C_2H_4)_2(PPh_3)]$ (0.51 g, 1.0 mmol) in light petroleum (60 cm^3). Removal of solvent, and crystallisation of crude product from diethyl ether at −20 °C gave black *crystals* of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$ (2) (0.8 g, 61%), m.p. 141—145 °C (decomp.) (Found: C, 25.7; H, 1.2. $C_{28}H_{17}O_{10}Os_3PPt$ requires C, 25.7; H, 1.3%); $\nu_{max.}$ (CO) at 2 079m, 2 053(sh), 2 045s, 2 029vw, 2 019s, 1 989s, 1 975m, 1 963w, and 1 947w cm^{-1}. N.m.r.: ^{1}H (−60 °C), τ 2.6 (m, 15 H, Ph), 16.16 [s, 1 H, Os(μ-H)Os, *J*(PtH) 8], and 17.52 [d, 1 H, Os(μ-H)Pt, *J*(PH) 16, *J*(PtH) 590 Hz]; ^{31}P, δ −54.8 p.p.m. [s, *J*(PtP) 2 609 Hz]; ^{31}P (selectively decoupled), δ −54.8 p.p.m. [d, *J*(PH) 7, *J*(PtP) 2 610 Hz].

(*c*). In a similar manner, $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (0.85 g, 1.0 mmol) and a freshly prepared solution of $[Pt(C_2H_4)_2(PBu^t{}_2Me)]$ (1 mmol) were stirred for 0.5 h. Removal of solvent *in vacuo*, followed by crystallisation of the residue from diethyl ether gave black *microcrystals* of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PBu^t{}_2Me)]$ (3) (0.9 g, 74%), washed with light petroleum and dried *in vacuo*, m.p. 158—162 °C (Found: C, 18.8; H, 2.0. $C_{19}H_{23}O_{10}Os_3PPt$ requires C, 18.9; H, 1.9%); $\nu_{max.}$ (CO) at 2 077m, 2 043s, 2 019s, 1 987m, 1 975m, 1 963w, and 1 947m cm^{-1}. N.m.r.: ^{1}H (−20 °C), τ 7.98 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 30], 8.82 [d, 18 H, Bu^t, *J*(PH) 14], 16.83 [s, 1 H, Os(μ-H)Os], and 18.21 [d, 1 H, Os(μ-H)Pt, *J*(PH) 15, *J*(PtH) 577 Hz]; ^{31}P, δ −77.8 p.p.m. [s, *J*(PtP) 2 532 Hz]; ^{13}C {−70 °C, $[Cr(C_5H_8O_2)_3]$ added}, δ 193.0 [s, *J*(PtC) 30], 185.0, 181.8, 176.9 and 170.1 (m, CO), 35.2 [d, Me, *J*(PC) 20], 28.3 [s, $C(CH_3)_3$], and 9.6 [d, *C*Me$_3$, *J*(PC) 26 Hz]. See also Figure 1.

Crystal-structure Determination of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$.—The complex crystallises as intensely dark green (nearly black) prisms. Diffracted intensities were collected at 200 K from a crystal of dimensions 0.14 × 0.20 × 0.21 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[49] Of the total 6 586 independent reflections for $2.9 < 2\theta < 60.0°$, 5 737 satisfied the criterion $I \geqslant 2.58\sigma(I)$, and only these were used in the solution and refinement of the structure. Three reflections were used to monitor the stability of the measurements ($2\,\bar{1}\,0$, $0\,0\,2$, and $\bar{1}\,2\,0$) and these were remeasured every 40 reflections. No significant variation was observed. The intensities were corrected for Lorentz, polarisation, and *X*-ray absorption effects.[50]

Crystal data. $C_{28}H_{35}O_{10}Os_3PPt$, $M = 1\,328.2$, Monoclinic, $a = 11.822(4)$, $b = 16.584(5)$, $c = 17.763(9)$ Å, $\beta = 108.10(4)°$, $D_m = 2.55$, $Z = 4$, $D_c = 2.67$ g cm^{-3}, $U = 3\,310$ Å^3, $F(000) = 2\,416$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 166.6 cm^{-1}.

The structure was solved by heavy-atom methods; the allocation of Os ($Z = 76$) and Pt ($Z = 78$) among the four heavy-atom positions was achieved by refinement of thermal parameters and confirmed subsequently by the configuration of the molecule, in that the phosphine ligand was already known, from the ^{31}P n.m.r. spectrum, to be bonded to the platinum atom. All non-hydrogen atoms were located by successive electron-density difference syntheses; both their positional and anisotropic thermal parameters were refined by blocked-matrix least squares. The hydrogen atoms of the cyclohexyl groups appeared on the final-difference maps with maxima *ca.* 0.8 e Å^{-3} but were nevertheless incorporated at calculated positions and were not refined. At the suspected locations of the bridging hydride ligands, deduced from the molecular stereochemistry (see earlier), peaks *ca.* 1.3 e Å^{-3} were evident The validity of the locations of these peaks was further borne out by potential energy calculations with the program HYDEX.[33] Weights were applied according to the scheme $w^{-1} = \sigma^2(F_o)$, where $\sigma(F_o)$ is the estimated error in the observed structure amplitude based on counting statistics only. The refinement converged to *R* 0.035 (*R'* 0.038) with a mean shift-to-error ratio in the last cycle of 0.1. Atomic scattering factors were taken from ref. 51 for hydrogen and from ref. 52 for all other atoms. In the case of Os, Pt, and P these were corrected for the real and imaginary parts of anomalous dispersion.[53] All computational work was carried out at the University of London Computer Centre with the '*X*-Ray' system of programs.[50] Observed and calculated structure factors, all thermal parameters, and all hydrogen atom co-ordinates are listed in Supplementary Publication No. SUP 22892 (29 pp.).*

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

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