Chemistry of the Unsaturated Cluster Compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$; *X*-Ray Crystal Structures of $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$, $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$, and $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\text{-}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (Two Isomers)†

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Reactions of the unsaturated cluster compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ with hydrogen and with diazomethane have been investigated, and the structures of the products determined by *X*-ray diffraction. The structure of the previously prepared carbon monoxide adduct $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ has also been established. The latter species, which is formed in a readily reversed reaction, has a 'butterfly' arrangement of the metal atoms with the platinum atom at a wing-tip position. One hydrido-ligand bridges the Os–Os vector of the body of the butterfly, and the other an Os–Pt edge. The latter is *cis* to the $P(cyclo\text{-}C_6H_{11})_3$ group on the platinum, which also carries a CO ligand. The osmium atom at the other wing-tip is ligated by four CO groups, and the remaining two Os are each terminally bonded to three carbonyls. The hydrogen adduct $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ is also formed reversibly but in contrast with the product from carbon monoxide has a *closo*-tetrahedral metal core. The hydrido-ligands occupy edge-bridging sites on the cluster framework, with two bridging Os–Pt vectors [*cis* to the $P(cyclo\text{-}C_6H_{11})_3$ ligand on platinum] and two bridging Os–Os vectors. Thus the M_4 tetrahedron has D_{2d} symmetry with two short unbridged edges and four longer bridged edges. Diazomethane readily adds to $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ to give the complex $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)\text{-}(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ which exists as an equilibrium mixture of two isomeric forms (orange-yellow and red crystals). Both species have a *closo* distorted tetrahedral geometry for the metal atoms, with the methylene group bridging an Os–Os edge cisoid to the $P(cyclo\text{-}C_6H_{11})_3$ ligand on the platinum in the orange-yellow form and transoid to the phosphine group in the red isomer. The relative positions of the hydrido-ligands also differ. In the orange-yellow form they bridge the remaining two Os–Os edges, while although not located directly in the red isomer, being assigned on potential-energy grounds, they bridge an Os–Os edge and the Os–Pt edge *cis* to the $P(cyclo\text{-}C_6H_{11})_3$ ligand. N.m.r. studies reveal that the two isomers maintain these solid-state structures in solution. The mechanism of formation of the two isomers is discussed in the context of the orange-yellow form being the kinetically controlled product, which after several days in solution establishes a 1 : 4 equilibrium with the red form.

Some years ago the synthesis of the platinumtriosmium cluster compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ [$PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3, or PBu^t_2Me] was reported.[1a] An *X*-ray diffraction study on the complex containing the tricyclohexylphosphine ligand showed that the four metal atoms adopt an essentially tetrahedral structure, even though the cluster contains 58 rather than 60 c.v.e.s (cluster valence electrons). There are thus five electron pairs for skeletal bonding and the compounds are 'unsaturated,' a property suggesting that reactions would occur with other molecules able to contribute two electrons to produce 60 c.v.e. species. Indeed, the green complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**1a**) reacts reversibly with carbon monoxide but whether the core metal atoms in the yellow adduct $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**2**) adopt a closed tetrahedral or an open butterfly structure was not established.[1b] However, the compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ (**3**), obtained by treating $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$ (**1b**) with PPh_3, has a butterfly arrangement of its Os_3Pt core, with the platinum atom occupying a wing-tip position, the structure being established by *X*-ray crystallography.

These observations prompted us to examine in more detail the chemistry of complex (**1a**). The results described herein involve establishment of the molecular structure of the CO adduct (**2**), and studies on reactions of the platinumtriosmium cluster with hydrogen and with diazomethane. Whereas the chemistry of trinuclear metal complexes has been extensively investigated,[2] including that of the synthetically useful species $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[3] much less is known about the reactivity patterns of tetranuclear metal compounds, especially those species involving two different transition elements, such as (**1a**). The latter species is of particular interest since it contains an element (Os) which in its carbonyl complexes of low metal nuclearity generally follows the 18-electron rule, and a metal (Pt) which commonly is satisfied with 16 electrons in its valence shell. A preliminary account has been given[4] of the results described in this paper.

Results and Discussion

The synthesis of (**2**) (Scheme 1), its ready reversion to (**1a**) by purging solutions of the complex with nitrogen, and its

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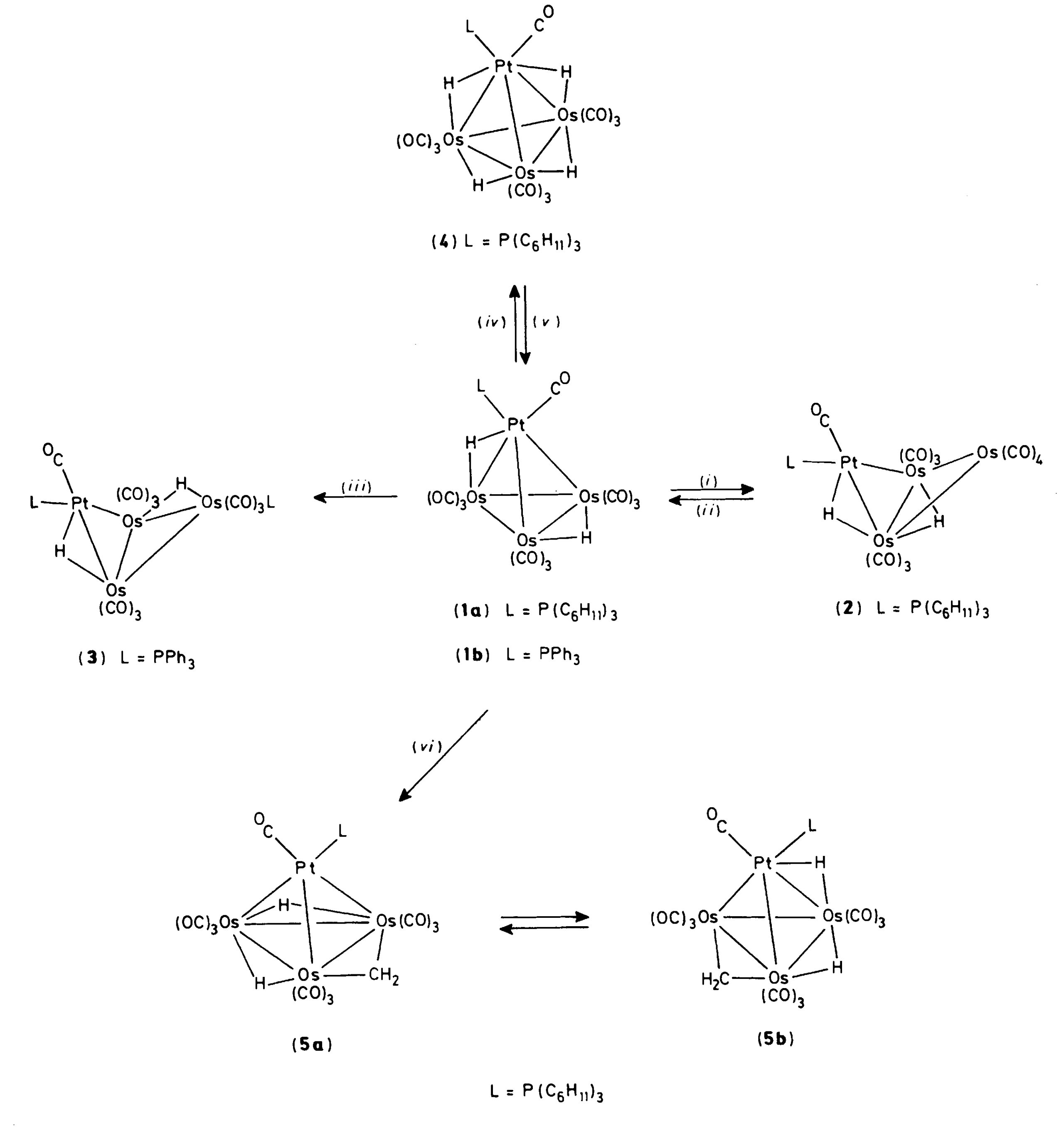
† 1,2,2,2,3,3,3-Heptacarbonyl-1,2;2,3-di-μ-hydrido-2,3-μ-tetracarbonylosmio-1-tricyclohexylphosphine-*triangulo*-platinumdiosmium, 1,2,2,2,3,3,3,4,4,4-decarbonyl-1,2;1,3:2,4;3,4-tetra-μ-hydrido-1-tricyclohexylphosphine-*tetrahedro*-platinumtriosmium, 1,2,2,2,3,3,3,4,4,4-decacarbonyl-2,3;2,4- and 1,2,2,2,3,3,3,4,4,4-decarbonyl-1,2;2,3-di-μ-hydrido-3,4-μ-methylene-1-tricyclohexylphosphine-*tetrahedro*-platinumtriosmium.

Supplementary data available (No. SUP 54075, 10 pp.): thermal parameters, H-atom co-ordinates for (**2**), (**4**), (**5a**), and (**5b**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Scheme. 1. (*i*) $+CO$; (*ii*) N_2 purge, $-CO$; (*iii*) $+PPh_3$; (*iv*) $+H_2$; (*v*) N_2 purge, $-H_2$; (*vi*) $+CH_2N_2$

spectroscopic properties have been previously reported.[1b] However, in the early work it had not been possible to grow single crystals of quality good enough for an *X*-ray diffraction study. In the work reported herein a suitable crystal of (**2**) was obtained by slow evaporation of a dichloromethane solution under a CO atmosphere. The molecular geometry is illustrated in Figure 1, and the essential structural parameters are given in Table 1. For complex (**2**), and for the other species studied by *X*-ray diffraction and reported herein, angles and distances within the cyclohexyl rings have been omitted since they have the usual values within experimental uncertainties.

The structure of complex (**2**) may be derived from that of (**1a**) in a formal sense by addition of CO to one of the osmium atoms participating in the unusually short hydrido-bridged Os–Os bond present in (**1a**)[1a] [*i.e.* Os(2) in Figure 1], and cleavage of the bond between this osmium and the platinum. In addition, the hydrido-ligand bound to Os(2) migrates to a site bridging the remaining two osmium atoms [Os(1) and Os(3)]. Thus the metal atoms of this 60 c.v.e. complex adopt a 'butterfly' geometry with a non-bonding separation Os(2)···Pt of 3.775(1) Å. A very similar geometry has been observed for the closely related complex (**3**),[1b] which, as mentioned above, is formed by addition of PPh_3 to the 58 c.v.e. species (**1b**). The butterfly geometry of (**2**), however, differs in detail from that in (**3**), thus in the latter complex the Pt···Os non-bonded distance is 3.530(1) Å, and the dihedral angle between the $PtOs_2$

Table 1. Selected interatomic distances (Å) and bond angles (°) for the complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**2**), with estimated standard deviations (e.s.d.s) in parentheses

P–Pt	2.346(4)	P–C(111)	1.883(17)	Os(2)–C(1)	1.903(20)	Os(2)–C(2)	1.943(35)
P–C(121)	1.848(20)	P–C(131)	1.828(16)	Os(2)–C(3)	1.901(26)	Os(2)–C(4)	1.935(18)
Os(1)–Pt	2.729(1)	Os(1)–Os(3)	2.869(1)	Os(1)–C(1)	1.200(24)	O(2)–C(2)	1.134(40)
Os(1)–Os(2)	2.877(1)	Os(1)–C(8)	1.909(17)	O(3)–C(3)	1.157(31)	O(4)–C(4)	1.148(22)
Os(1)–C(9)	1.885(18)	Os(1)–C(10)	1.908(25)	O(5)–C(5)	1.204(23)	O(6)–C(6)	1.050(27)
Pt–Os(3)	2.914(1)	Pt–C(11)	1.852(22)	O(7)–C(7)	1.090(29)	O(8)–C(8)	1.166(23)
Os(3)–Os(2)	2.882(1)	Os(3)–C(5)	1.842(18)	O(9)–C(9)	1.150(23)	O(10)–C(10)	1.122(33)
Os(3)–C(6)	1.953(21)	Os(3)–C(7)	1.902(21)	O(11)–C(11)	1.157(28)		

Os(1)–H(1)–Os(3)	101.4	Pt–H(2)–Os(3)	104.2	Pt–Os(3)–Os(2)	81.3(1)	H(1)–Os(3)–C(5)	81.9
Pt–P–C(111)	116.3(6)	Pt–P–C(121)	112.9(5)	H(2)–Os(3)–C(5)	164.0	Os(1)–Os(3)–C(5)	103.1(7)
C(111)–P–C(121)	103.9(8)	Pt–P–C(131)	109.1(5)	Pt–Os(3)–C(5)	158.2(7)	Os(2)–Os(3)–C(5)	94.8(7)
C(111)–P–C(131)	107.9(7)	C(121)–P–C(131)	106.2(8)	H(1)–Os(3)–C(6)	173.8	H(2)–Os(3)–C(6)	73.2
H(1)–Os(1)–Pt	82.2	H(1)–Os(1)–Os(3)	39.4	Os(1)–Os(3)–C(6)	141.7(7)	Pt–Os(3)–C(6)	108.5(5)
Pt–Os(1)–Os(3)	62.7(1)	H(1)–Os(1)–Os(2)	94.5	Os(2)–Os(3)–C(6)	84.1(7)	C(5)–Os(3)–C(6)	92.3(9)
Pt–Os(1)–Os(2)	84.6(1)	Os(3)–Os(1)–Os(2)	60.2(1)	H(1)–Os(3)–C(7)	84.8	H(2)–Os(3)–C(7)	83.9
H(1)–Os(1)–C(8)	87.0	Pt–Os(1)–C(8)	168.4(8)	Os(1)–Os(3)–C(7)	116.5(7)	Pt–Os(3)–C(7)	92.1(6)
Os(3)–Os(1)–C(8)	106.1(7)	Os(2)–Os(1)–C(8)	92.1(5)	Os(2)–Os(3)–C(7)	173.4(6)	C(5)–Os(3)–C(7)	91.5(9)
H(1)–Os(1)–C(9)	83.3	Pt–Os(1)–C(9)	88.0(6)	C(6)–Os(3)–C(7)	97.6(10)	Os(1)–Os(2)–Os(3)	59.7(1)
Os(3)–Os(1)–C(9)	115.0(8)	Os(2)–Os(1)–C(9)	172.5(7)	Os(1)–Os(2)–C(1)	88.8(6)	Os(3)–Os(2)–C(1)	92.7(7)
C(8)–Os(1)–C(9)	94.9(8)	H(1)–Os(1)–C(10)	177.0	Os(1)–Os(2)–C(2)	95.3(6)	Os(3)–Os(2)–C(2)	154.7(6)
Pt–Os(1)–C(10)	96.4(5)	Os(3)–Os(1)–C(10)	142.0(6)	C(1)–Os(2)–C(2)	90.4(10)	Os(1)–Os(2)–C(3)	161.9(9)
Os(2)–Os(1)–C(10)	88.0(6)	C(8)–Os(1)–C(10)	94.6(9)	Os(3)–Os(2)–C(3)	102.2(10)	C(1)–Os(2)–C(3)	91.0(9)
C(9)–Os(1)–C(10)	94.0(10)	H(2)–Pt–P	80.0	C(2)–Os(2)–C(3)	102.8(11)	Os(1)–Os(2)–C(4)	87.4(6)
H(2)–Pt–Os(1)	97.5	P–Pt–Os(1)	173.3(1)	Os(3)–Os(2)–C(4)	84.5(6)	C(1)–Os(2)–C(4)	176.0(8)
H(2)–Pt–Os(3)	38.0	P–Pt–Os(3)	115.1(1)	C(2)–Os(2)–C(4)	91.0(9)	C(3)–Os(2)–C(4)	92.4(9)
Os(1)–Pt–Os(3)	61.0(1)	H(2)–Pt–C(11)	171.1	Os(2)–C(1)–O(1)	171.2(16)	Os(2)–C(2)–O(2)	176.6(16)
P–Pt–C(11)	101.7(5)	Os(1)–Pt–C(11)	81.8(5)	Os(2)–C(3)–O(3)	177.9(15)	Os(2)–C(4)–O(4)	173.9(20)
Os(3)–Pt–C(11)	142.7(5)	H(1)–Os(3)–H(2)	112.8	Os(3)–C(5)–O(5)	178.2(23)	Os(3)–C(6)–O(6)	173.0(20)
H(1)–Os(3)–Os(1)	39.2	H(2)–Os(3)–Os(1)	92.6	Os(3)–C(7)–O(7)	177.7(20)	Os(1)–C(8)–O(8)	173.5(22)
H(1)–Os(3)–Pt	77.0	H(2)–Os(3)–Pt	37.7	Os(1)–C(9)–O(9)	176.6(17)	Os(1)–C(10)–O(10)	178.4(17)
Os(1)–Os(3)–Pt	56.3(1)	H(1)–Os(3)–Os(2)	94.1	Pt–C(11)–O(11)	174.6(16)		
H(2)–Os(3)–Os(2)	90.5	Os(1)–Os(3)–Os(2)	60(1)				

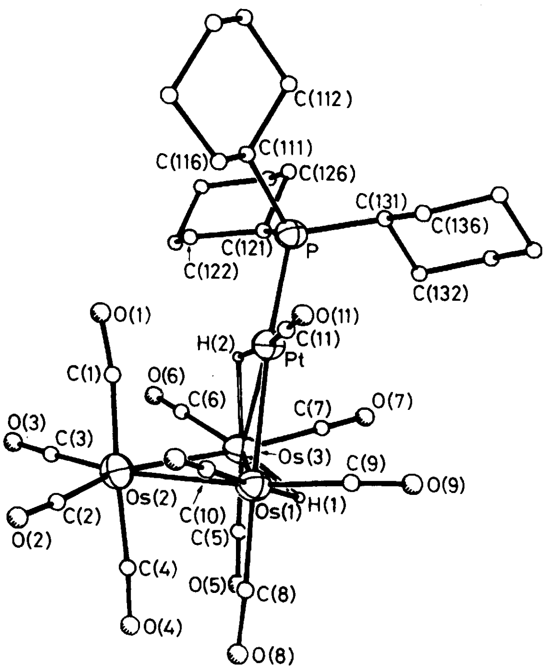


Figure 1. Molecular structure of the complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**2**), showing the crystallographic numbering sequence

and Os_3 planes is 88.4°, compared with 100.0° in (**2**). Moreover, in complex (**2**) the second μ-H ligand bridges the 'hinge' Os–Os bond, whereas in (**3**) this ligand bridges a wing tip to hinge Os–Os vector which is *cis* to the PPh_3 group on the wing-tip osmium atom.

The structural study on complex (**2**) is important in establishing that the equilibrium (**1a**) + CO $\rightleftharpoons$ (**2**) is accompanied by metal-metal bond breakage and bond formation within the two clusters. Reversible uptake of carbon monoxide has been observed with other metal cluster systems including the species $[Rh_{12}(CO)_{30}]^{2-}$,[5] $[Fe_2Mn(\mu_3\text{-}PPh)(CO)_8(\eta\text{-}C_5H_5)]$,[6] $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[7] $[Os_5(\mu\text{-}H)(\mu\text{-}NC_6H_4NPh)(CO)_{13}]$,[8] and $[Os_5(CO)_{19}]$,[9] and others [6,10] have pointed out the possible importance of tetrahedral $\rightleftharpoons$ butterfly metal-core rearrangements in catalysis, particularly the water gas shift reaction. In this context the ability of a metal cluster to react with hydrogen is important. Consequently, the reaction of (**1a**) with hydrogen was studied.

Compound (**1a**) did not react with hydrogen at an appreciable rate at room temperature. However, a diethyl ether solution pressurised under hydrogen at 200 atm and heated to 50 °C afforded a yellow solution containing yellow crystals of the tetrahydrido-complex (**4**) in *ca.* 90% yield. On standing at ambient temperatures, yellow solutions of (**4**) rapidly revert to the green colour of (**1a**), and a nitrogen purge leads to recovery of the latter in 70—80% yield (Scheme 1). The reaction of complex (**1a**) with H_2 thus parallels the reaction with CO in being reversible. Reversible uptake of hydrogen by a cluster is a rare phenomenon,[11] and under conditions for reactions with CO and H_2 to occur cluster fragmentation is often observed.[9] Compound (**1a**) appears to be the first well authenticated example of a cluster species showing reversible reactivity towards both CO and H_2.

In the i.r. spectrum, complex (**4**) shows several bands in the CO stretching region between 2 095 and 1 934 cm^{-1}, but it is difficult to measure a spectrum which does not show peaks due

Table 2. Selected interatomic distances (Å) and bond angles (°) for the complex $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**4**), with e.s.d.s in parentheses

Os(1)–Pt(4)	2.723(4)	Os(1)–Os(2)	3.003(4)	Os(7)–Os(6)	2.862(3)	Os(7)–Os(5)	2.979(4)
Os(1)–Os(3)	2.973(4)	Os(1)–C(1)	1.867(47)	Os(7)–Pt(8)	2.939(4)	Os(7)–C(47)	1.874(45)
Os(1)–C(2)	1.902(39)	Os(1)–C(3)	1.963(36)	Os(7)–C(48)	1.897(33)	Os(7)–C(49)	1.965(38)
Pt(4)–Os(2)	3.015(4)	Pt(4)–Os(3)	2.930(4)	Os(6)–Os(5)	2.993(4)	Os(6)–Pt(8)	3.003(4)
Pt(4)–P(1)	2.386(11)	Pt(4)–C(10)	1.788(46)	Os(6)–C(44)	1.851(43)	Os(6)–C(45)	1.941(42)
Os(2)–Os(3)	2.871(3)	Os(2)–C(4)	1.953(49)	Os(6)–C(46)	1.936(31)	Os(5)–Pt(8)	2.710(4)
Os(2)–C(5)	1.891(46)	Os(2)–C(6)	1.874(41)	Os(5)–C(41)	1.917(48)	Os(5)–C(42)	1.888(34)
Os(3)–C(7)	1.869(47)	Os(3)–C(8)	1.918(48)	Os(5)–C(43)	1.923(36)	Pt(8)–P(2)	2.360(10)
Os(3)–C(9)	1.864(48)	P(1)–C(11)	1.866(40)	Pt(8)–C(50)	1.802(43)	P(2)–C(51)	1.908(34)
P(1)–C(17)	1.856(41)	P(1)–C(23)	1.850(35)	P(2)–C(57)	1.846(33)	P(2)–C(63)	1.817(32)
C(1)–O(1)	1.195(64)	C(2)–O(2)	1.143(51)	C(41)–O(41)	1.124(59)	C(42)–O(42)	1.152(43)
C(3)–O(3)	1.064(45)	C(4)–O(4)	1.139(59)	C(43)–O(43)	1.125(44)	C(44)–O(44)	1.244(56)
C(5)–O(5)	1.196(57)	C(6)–O(6)	1.218(47)	C(45)–O(45)	1.109(55)	C(46)–O(46)	1.126(36)
C(7)–O(7)	1.161(58)	C(8)–O(8)	1.154(60)	C(47)–O(47)	1.178(55)	C(48)–O(48)	1.168(44)
C(9)–O(9)	1.178(56)	C(10)–O(10)	1.260(59)	C(49)–O(49)	1.102(44)	C(50)–O(50)	1.204(53)

Pt(4)–Os(1)–Os(2)	63.3(1)	Pt(4)–Os(1)–Os(3)	61.7(1)	Os(3)–C(8)–O(8)	176.8(34)	Os(3)–C(9)–O(9)	179.5(61)
Os(2)–Os(1)–Os(3)	57.4(1)	Pt(4)–Os(1)–H(1)	89.2	Pt(4)–C(10)–O(10)	166.9(35)	H(6)–Os(7)–H(8)	96.6
Os(2)–Os(1)–H(1)	33.4	Os(3)–Os(1)–H(1)	87.5	H(6)–Os(7)–Os(6)	88.7	H(8)–Os(7)–Os(6)	95.5
Pt(4)–Os(1)–H(2)	90.1	Os(2)–Os(1)–H(2)	86.1	H(6)–Os(7)–Os(5)	34.1	H(8)–Os(7)–Os(5)	79.3
Os(3)–Os(1)–H(2)	34.2	H(1)–Os(1)–H(2)	107.7	Os(6)–Os(7)–Os(5)	61.6(1)	H(6)–Os(7)–Pt(8)	84.3
Pt(4)–Os(1)–C(1)	166.6(14)	Os(2)–Os(1)–C(1)	105.7(13)	H(8)–Os(7)–Pt(8)	35.2	Os(6)–Os(7)–Pt(8)	62.3(1)
Os(3)–Os(1)–C(1)	106.4(12)	H(1)–Os(1)–C(1)	83.9(12)	Os(5)–Os(7)–Pt(8)	54.5(1)	H(6)–Os(7)–C(47)	80.3
H(2)–Os(1)–C(1)	81.2(11)	Pt(4)–Os(1)–C(2)	87.4(14)	H(8)–Os(7)–C(47)	175.7	Os(6)–Os(7)–C(47)	87.4(10)
Os(2)–Os(1)–C(2)	146.8(14)	Os(3)–Os(1)–C(2)	96.0(12)	Os(5)–Os(7)–C(47)	99.3(13)	Pt(8)–Os(7)–C(47)	146.3(11)
H(1)–Os(1)–C(2)	173.3(11)	H(2)–Os(1)–C(2)	78.1(11)	H(6)–Os(7)–C(48)	173.9	H(8)–Os(7)–C(48)	86.4
C(1)–Os(1)–C(2)	100.5(18)	Pt(4)–Os(1)–C(3)	95.6(13)	Os(6)–Os(7)–C(48)	96.3(8)	Os(5)–Os(7)–C(48)	152.0(8)
Os(2)–Os(1)–C(3)	103.9(11)	Os(3)–Os(1)–C(3)	154.7(12)	Pt(8)–Os(7)–C(48)	101.1(9)	C(47)–Os(7)–C(48)	96.5(17)
H(1)–Os(1)–C(3)	80.8(11)	H(2)–Os(1)–C(3)	169.9(12)	H(6)–Os(7)–C(49)	80.5	H(8)–Os(7)–C(49)	79.1
C(1)–Os(1)–C(3)	94.6(17)	C(2)–Os(1)–C(3)	93.7(16)	Os(6)–Os(7)–C(49)	167.2(13)	Os(5)–Os(7)–C(49)	105.8(14)
Os(1)–Pt(4)–Os(2)	62.9(1)	Os(1)–Pt(4)–Os(3)	63.3(1)	Pt(8)–Os(7)–C(49)	109.4(14)	C(47)–Os(7)–C(49)	97.5(18)
Os(2)–Pt(4)–Os(3)	57.7(1)	Os(1)–Pt(4)–P(1)	172.4(2)	C(48)–Os(7)–C(49)	94.9(16)	H(5)–Os(6)–H(7)	96.3
Os(2)–Pt(4)–P(1)	120.8(2)	Os(3)–Pt(4)–P(1)	112.1(2)	H(5)–Os(6)–Os(7)	94.0	H(7)–Os(6)–Os(7)	83.4
Os(1)–Pt(4)–H(3)	91.6	Os(2)–Pt(4)–H(3)	33.2	H(5)–Os(6)–Os(5)	33.8	H(7)–Os(6)–Os(5)	85.0
Os(3)–Pt(4)–H(3)	84.3	P(1)–Pt(4)–H(3)	94.1	Os(7)–Os(6)–Os(5)	61.1(1)	H(5)–Os(6)–Pt(8)	75.3
Os(1)–Pt(4)–H(4)	90.2	Os(2)–Pt(4)–H(4)	89.8	H(7)–Os(6)–Pt(8)	33.4	Os(7)–Os(6)–Pt(8)	60.1(1)
Os(3)–Pt(4)–H(4)	35.5	P(1)–Pt(4)–H(4)	83.3	Os(5)–Os(6)–Pt(8)	53.7(1)	H(5)–Os(6)–C(44)	80.7
H(3)–Pt(4)–H(4)	107.0(1)	Os(1)–Pt(4)–C(10)	88.4(16)	H(7)–Os(6)–C(44)	176.2	Os(7)–Os(6)–C(44)	94.3(10)
Os(2)–Pt(4)–C(10)	126.3(14)	Os(3)–Pt(4)–C(10)	146.6(15)	Os(5)–Os(6)–C(44)	91.2(13)	Pt(8)–Os(6)–C(44)	142.8(12)
P(1)–Pt(4)–C(10)	93.8(17)	H(3)–Pt(4)–C(10)	115.5(12)	H(5)–Os(6)–C(45)	174.8	H(7)–Os(6)–C(45)	87.3
H(4)–Pt(4)–C(10)	137.5(12)	Os(1)–Os(2)–Pt(4)	53.8(1)	Os(7)–Os(6)–C(45)	90.2(9)	Os(5)–Os(6)–C(45)	150.9(9)
Os(1)–Os(2)–Os(3)	60.8(4)	Pt(4)–Os(2)–Os(3)	59.7(1)	Pt(8)–Os(6)–C(45)	109.6(12)	C(44)–Os(6)–C(45)	95.9(18)
Os(1)–Os(2)–H(1)	33.5	Pt(4)–Os(2)–H(1)	80.3	H(5)–Os(6)–C(46)	86.7	H(7)–Os(6)–C(46)	84.5
Os(3)–Os(2)–H(1)	90.8	Os(1)–Os(2)–H(3)	82.8	Os(7)–Os(6)–C(46)	168.0(12)	Os(5)–Os(6)–C(46)	117.2(12)
Pt(4)–Os(2)–H(3)	33.1	Os(3)–Os(2)–H(3)	86.0	Pt(8)–Os(6)–C(46)	108.7(11)	C(44)–Os(6)–C(46)	97.6(16)
H(1)–Os(2)–H(3)	99.5	Os(1)–Os(2)–C(4)	97.3(14)	C(45)–Os(6)–C(46)	89.9(15)	H(5)–Os(5)–H(6)	111.6
Pt(4)–Os(2)–C(4)	144.8(12)	Os(3)–Os(2)–C(4)	90.1(11)	H(5)–Os(5)–Os(7)	90.2	H(6)–Os(5)–Os(7)	34.1
H(1)–Os(2)–C(4)	82.9	H(3)–Os(2)–C(4)	175.4	H(5)–Os(5)–Os(6)	33.8	H(6)–Os(5)–Os(6)	84.6
Os(1)–Os(2)–C(5)	150.5(11)	Pt(4)–Os(2)–C(5)	105.0(14)	Os(7)–Os(5)–Os(6)	57.3(1)	H(5)–Os(5)–Pt(8)	83.6
Os(3)–Os(2)–C(5)	91.6(10)	H(1)–Os(2)–C(5)	174.6	H(6)–Os(5)–Pt(8)	91.4	Os(7)–Os(5)–Pt(8)	62.0(1)
H(3)–Os(2)–C(5)	85.5	C(4)–Os(2)–C(5)	92.3(20)	Os(6)–Os(5)–Pt(8)	63.3(1)	H(5)–Os(5)–C(41)	89.5
Os(1)–Os(2)–C(6)	112.9(17)	Pt(4)–Os(2)–C(6)	110.4(16)	H(6)–Os(5)–C(41)	79.3	Os(7)–Os(5)–C(41)	105.5(13)
Os(3)–Os(2)–C(6)	169.9(16)	H(1)–Os(2)–C(6)	85.6	Os(6)–Os(5)–C(41)	104.5(13)	Pt(8)–Os(5)–C(41)	165.6(13)
H(3)–Os(2)–C(6)	85.3	C(4)–Os(2)–C(6)	98.8(20)	H(5)–Os(5)–C(42)	78.2	H(6)–Os(5)–C(42)	168.3
C(5)–Os(2)–C(6)	92.9(10)	Os(1)–Os(3)–Pt(4)	54.9(1)	Os(7)–Os(5)–C(42)	156.6(13)	Os(6)–Os(5)–C(42)	106.8(11)
Os(1)–Os(3)–Os(2)	61.8(1)	Pt(4)–Os(3)–Os(2)	62.6(1)	Pt(8)–Os(5)–C(42)	96.2(13)	C(41)–Os(5)–C(42)	94.8(17)
Os(1)–Os(3)–H(2)	34.4	Pt(4)–Os(3)–H(2)	83.8	H(5)–Os(5)–C(43)	165.8	H(6)–Os(5)–C(43)	80.0
Os(2)–Os(3)–H(2)	90.4	Os(1)–Os(3)–H(4)	82.3	Os(7)–Os(5)–C(43)	96.1(12)	Os(6)–Os(5)–C(43)	147.2(13)
Pt(4)–Os(3)–H(4)	35.2	Os(2)–Os(3)–H(4)	94.3	Pt(8)–Os(5)–C(43)	88.1(14)	C(41)–Os(5)–C(43)	100.9(18)
H(2)–Os(3)–H(4)	98.8	Os(1)–Os(3)–C(7)	101.1(14)	C(42)–Os(5)–C(43)	91.3(15)	H(7)–Pt(8)–H(8)	105.4
Pt(4)–Os(3)–C(7)	150.7(12)	Os(2)–Os(3)–C(7)	92.2(11)	H(7)–Pt(8)–Os(7)	81.3	H(8)–Pt(8)–Os(7)	35.3
H(2)–Os(3)–C(7)	81.4	H(4)–Os(3)–C(7)	173.5	H(7)–Pt(8)–Os(6)	33.6	H(8)–Pt(8)–Os(6)	91.0
Os(1)–Os(3)–C(8)	146.6(11)	Pt(4)–Os(3)–C(8)	93.4(13)	Os(7)–Pt(8)–Os(6)	57.6(1)	H(7)–Pt(8)–Os(5)	94.1
Os(2)–Os(3)–C(8)	89.2(11)	H(2)–Os(3)–C(8)	177.2	H(8)–Pt(8)–Os(5)	87.4	Os(7)–Pt(8)–Os(5)	63.5(1)
H(4)–Os(3)–C(8)	84.0	C(7)–Os(3)–C(8)	95.9(10)	Os(6)–Pt(8)–Os(5)	62.9(1)	H(7)–Pt(8)–P(2)	88.7
Os(1)–Os(3)–C(9)	114.4(19)	Pt(4)–Os(3)–C(9)	110.1(18)	H(8)–Pt(8)–P(2)	88.7	Os(7)–Pt(8)–P(2)	113.8(2)
Os(2)–Os(3)–C(9)	172.7(17)	H(2)–Os(3)–C(9)	88.4	Os(6)–Pt(8)–P(2)	119.0(2)	Os(5)–Pt(8)–P(2)	175.7(2)
H(4)–Os(3)–C(9)	78.8	C(7)–Os(3)–C(9)	94.7(21)	H(7)–Pt(8)–C(50)	121.2	H(8)–Pt(8)–C(50)	133.4
C(8)–Os(3)–C(9)	92.4(22)	Pt(4)–P(1)–C(11)	110.5(15)	Os(7)–Pt(8)–C(50)	145.5(14)	Os(6)–Pt(8)–C(50)	126.7(13)
Pt(4)–P(1)–C(17)	115.2(14)	C(11)–P(1)–C(17)	110.0(18)	Os(5)–Pt(8)–C(50)	87.4(15)	P(2)–Pt(8)–C(50)	93.9(15)
Pt(4)–P(1)–C(23)	108.2(15)	C(11)–P(1)–C(23)	103.8(18)	Pt(8)–P(2)–C(51)	115.0(11)	Pt(8)–P(2)–C(57)	110.1(12)

Table 2 (*continued*)

C(17)–P(1)–C(23)	108.4(18)	Os(1)–H(1)–Os(2)	113.1	C(51)–P(2)–C(57)	109.2(15)	Pt(8)–P(2)–C(63)	111.1(14)
Os(1)–H(2)–Os(3)	111.4	Pt(4)–H(3)–Os(2)	113.8	C(51)–P(2)–C(63)	105.3(15)	C(57)–P(2)–C(63)	105.6(16)
Pt(4)–H(4)–Os(3)	109.2	Os(6)–H(5)–Os(5)	112.4	Os(5)–C(41)–O(41)	176.3(41)	Os(5)–C(42)–O(42)	179.3(37)
Os(7)–H(6)–Os(5)	111.8	Os(6)–H(7)–Pt(8)	113.0	Os(5)–C(43)–O(43)	171.9(31)	Os(6)–C(44)–O(44)	172.1(29)
Os(7)–H(8)–Pt(8)	109.5	Os(1)–C(1)–O(1)	178.0(35)	Os(6)–C(45)–O(45)	172.3(32)	Os(6)–C(46)–O(46)	174.9(36)
Os(1)–C(2)–O(2)	176.5(31)	Os(1)–C(3)–O(3)	177.1(32)	Os(7)–C(47)–O(47)	177.3(29)	Os(7)–C(48)–O(48)	178.7(21)
Os(2)–C(4)–O(4)	175.4(41)	Os(2)–C(5)–O(5)	172.3(40)	Os(7)–C(49)–O(49)	172.9(41)	Pt(8)–C(50)–O(50)	175.7(25)
Os(2)–C(6)–O(6)	177.2(49)	Os(3)–C(7)–O(7)	177.1(34)				

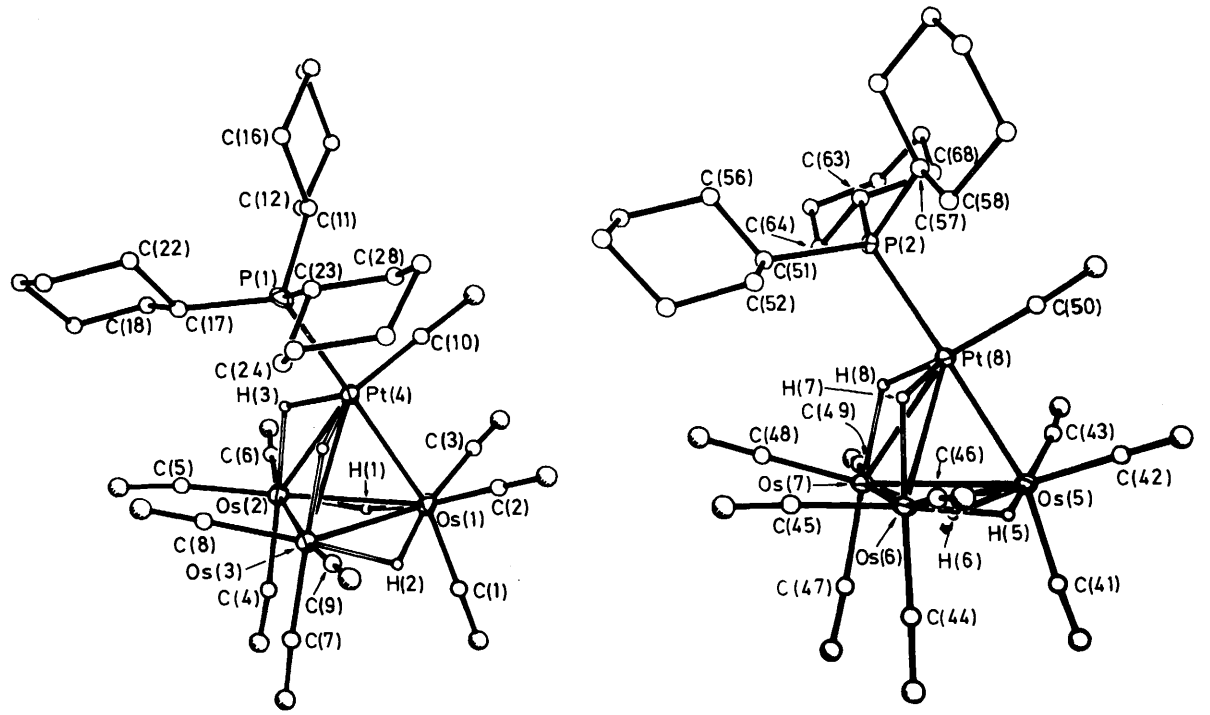


Figure 2. Molecular structure of the complex $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**4**), showing the two crystallographically independent molecules and the atom numbering scheme

to (**1a**). The ^1H n.m.r. spectrum, measured at −80 °C to avoid hydrogen dissociation, showed the expected resonance for the cyclohexyl groups (relative intensity 33 H) and signals for the hydrido-ligands at δ −15.50 (2 H) and −20.77 p.p.m. (2 H). The peak at −15.50 p.p.m. had ^{195}Pt satellites [J(PtH) 570 Hz], indicating the presence of a Os(μ-H)Pt group in (**4**) while the resonance at −20.77 with no $^{195}Pt–^1H$ coupling must be due to an Os(μ-H)Os group. In the ^1H n.m.r. spectrum of complex (**1a**) the hydrido-ligands resonate at δ −6.93 and −8.44 [J(PtH) 583 Hz],[1a] allowing a ready distinction from the data for (**4**), so that the presence of the latter in a mixture can be readily identified.

In order to establish the structure of complex (**4**) in the solid state an X-ray diffraction study was carried out. There are two crystallographically independent molecules and both are shown in Figure 2, with the interatomic separations and angles listed in Table 2. It will be seen immediately that addition of hydrogen to (**1a**) to give (**4**) has had a much less drastic effect on the geometry of the Os_3Pt core atoms than in the reaction of CO to give (**2**). In complex (**4**) the *closo*-tetrahedral structure is retained, and although the hydrido-ligands were not located directly they occupy bridging sites on the cluster framework, two bridging Os–Pt vectors [*cis* to the $P(cyclo\text{-}C_6H_{11})_3$ ligand on platinum] and two bridging Os–Os vectors, as inferred from the metal–metal separations and potential-energy calculations.[12] The 60 c.v.e. homonuclear clusters $[M_4(\mu\text{-}H)_4(CO)_{12}]$ (M = Ru[13] or Os[14]) have a similar pattern of hydrido-bridges such that the M_4 tetrahedra have D_{2d} symmetry with two short unbridged edges and four longer bridged edges.

Following the results obtained with CO and H_2, the addition of a CH_2 group, *via* CH_2N_2, to complex (**1a**) was investigated. A variety of unsaturated organotransition-metal complexes readily add diazoalkanes.[2] For example, it has been shown[15] that $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, an unsaturated 46 c.v.e. species, reacts readily with diazomethane to give $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ which in solution exists in tautomeric equilibrium with $[Os_3(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_{10}]$. In view of the unsaturated nature of (**1a**) it seemed likely that it also would react with CH_2N_2. Dropwise addition of a diethyl ether solution of diazomethane to a tetrahydrofuran solution of complex (**1a**) at *ca.* −10 °C led to a rapid colour change from green to orange. Column chromatography on alumina resulted in the elution of a single band from which a mixture of orange-yellow and red crystals was obtained. Microanalysis, and a field-desorption mass spectrum which showed a molecular ion, suggested that the orange and red crystals were isomers of a compound $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**5**). Moreover, n.m.r. studies (discussed below) established that the initially formed product was the orange-yellow form (**5a**) which was

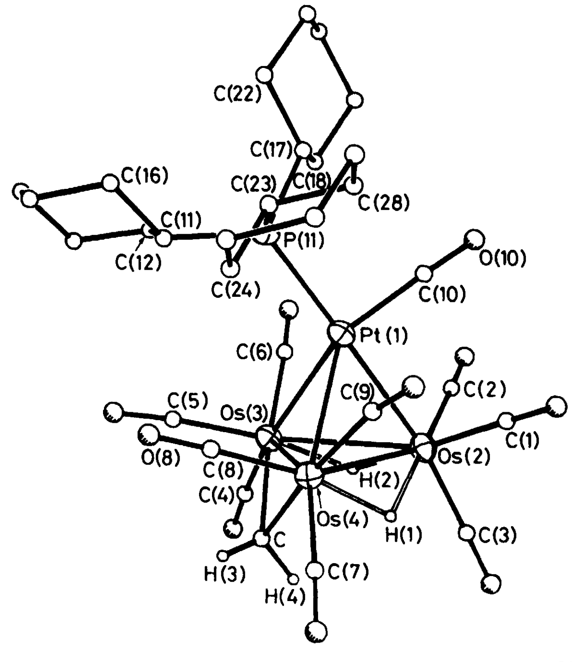


Figure 3. Molecular structure of the complex $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ (**5a**) (yellow isomer), showing the crystallographic numbering sequence

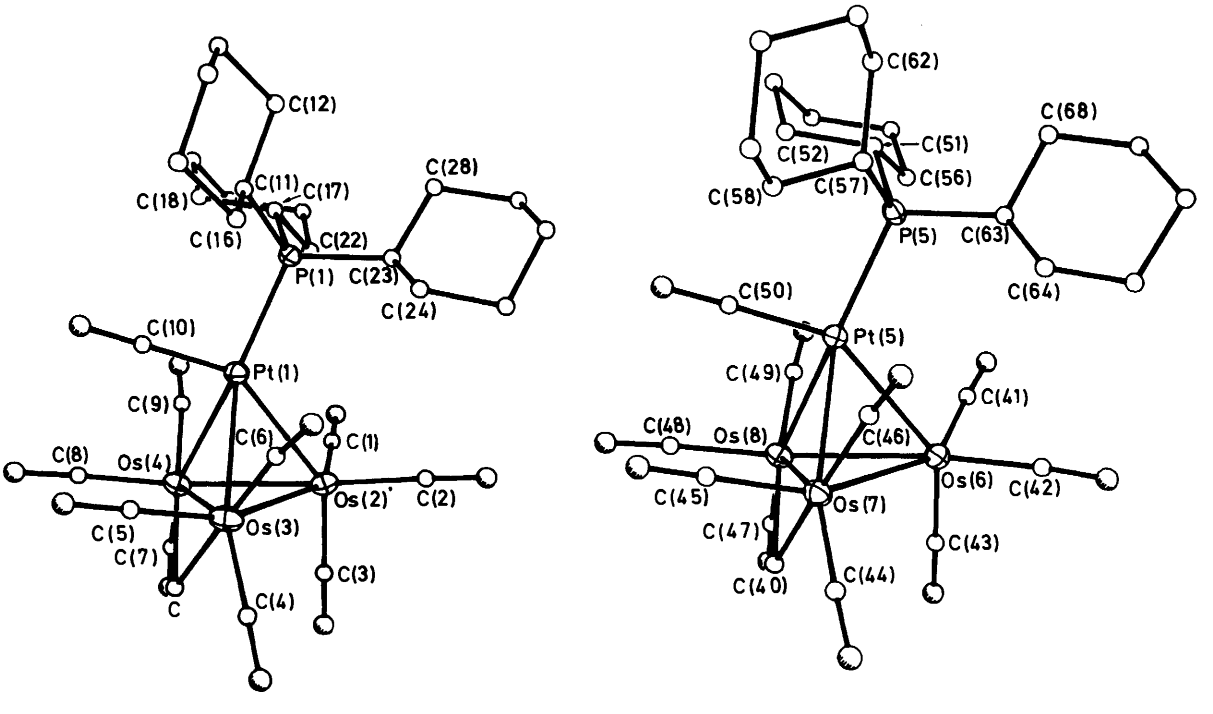


Figure 4. Molecular structure of the complex $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ (**5b**) (red isomer), showing the two crystallographically independent molecules and the atom numbering sequence

subsequently converted into the red isomer (**5b**), so that after several days the mixture in solution is approximately 1:4 in favour of (**5b**) (Scheme 1). Fortunately, the crystals could be separated by hand, and both types were of sufficient quality for *X*-ray diffraction studies (Figures 3 and 4 and Tables 3 and 4).

It will be seen that these 60 c.v.e. species retain the *closo* 'tetrahedral' geometry of their 58 c.v.e. parent (**1a**). The structure of (**5b**) may be derived formally from that of (**1a**) by insertion of a methylene moiety into the hydrido-bridged Os–Os bond and migration of that hydride ligand to another Os–Os edge (see Figure 4 which shows the geometries of the two crystallographically unique molecules). Thus the hydrido-ligands, not located directly but assigned on potential-energy grounds,[12] bridge the Pt(a)–Os(2) [Pt(5)–Os(6)] and Os(2)–Os(3) [Os(6)–Os(7)] edges of the cluster. The structure of (**5b**) may be formally derived from (**5a**) by rotation of the $Pt(CO)\{P(cyclo-C_6H_{11})_3\}$ group about an axis through the platinum and approximately normal to the Os_3 plane, with concomitant migration of a hydrogen bridging an Os–Os vector to an Os–Pt edge. Thus (**5a**) has approximate mirror symmetry in the solid state (Figure 3), and in solution also, as determined by n.m.r. studies (Table 5).

The n.m.r. measurements were carried out on solutions containing mixtures of the two isomers, but assignment of resonances was readily made on the basis of relative band intensities. The peaks due to the initially formed product (**5a**) gradually decreased in intensity as the thermodynamically favoured (**5b**) formed in increasing amount. The $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ data are in accord with the presence of $Pt(CO)\{P(cyclo-C_6H_{11})_3\}$ fragments in both isomers. The assignments in Table 5 were made by selective ^1H-decoupling experiments. Thus the singlet resonance at δ 10.8 p.p.m. becomes a triplet in the selectively decoupled ^{31}P spectrum, due to coupling with two equivalent μ-H ligands, and the singlet at 65.2 p.p.m. becomes a doublet being coupled only to one μ-H group. The former signal is thus ascribed to complex (**5a**) and the latter to (**5b**). The doublet signals in the $^{195}Pt-\{^1H\}$ spectra can then be assigned to each isomer by correlating the *J*(PPt) values with those associated with the resonances in the $^{31}P-\{^1H\}$ spectra. The ^1H n.m.r. spectra are revealing, and the data are in accord with the structures found by *X*-ray

Table 3. Selected interatomic distances (Å) and bond angles (°) for the complex [$Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}$] (**5a**)

Pt(1)–Os(2)	2.730(1)	Pt(1)–Os(3)	2.814(1)	Os(4)–C(7)	1.893(9)	Os(4)–C(8)	1.889(13)
Pt(1)–Os(4)	2.826(1)	Pt(1)–P(1)	2.380(3)	Os(4)–C(9)	1.983(10)	P(1)–C(11)	1.861(12)
Pt(1)–C(10)	1.858(11)	Os(2)–Os(3)	2.954(1)	P(1)–C(17)	1.885(9)	P(1)–C(23)	1.855(9)
Os(2)–Os(4)	2.941(1)	Os(2)–H(1)	1.99(11)	H(3)–C	0.85(12)	H(4)–C	1.05(13)
Os(2)–H(2)	1.72(12)	Os(2)–C(1)	1.929(10)	C(10)–O(10)	1.130(14)	C(1)–O(1)	1.121(13)
Os(2)–C(2)	1.937(10)	Os(2)–C(3)	1.898(13)	C(2)–O(2)	1.117(12)	C(3)–O(3)	1.133(16)
Os(3)–Os(4)	2.826(1)	Os(3)–H(2)	1.76(13)	C(4)–O(4)	1.135(12)	C(5)–O(5)	1.147(16)
Os(3)–C	2.143(8)	Os(3)–C(4)	1.902(9)	C(6)–O(6)	1.121(10)	C(7)–O(7)	1.145(11)
Os(3)–C(5)	1.884(12)	Os(3)–C(6)	1.974(8)	C(8)–O(8)	1.140(16)	C(9)–O(9)	1.120(12)
Os(4)–H(1)	1.71(16)	Os(4)–C	2.118(8)				

Os(1)–Pt(1)–Os(3)	64.4(1)	Os(2)–Pt(1)–Os(4)	63.9(1)	Os(2)–Os(3)–C(6)	91.1(3)	Os(4)–Os(3)–C(6)	128.9(2)
Os(3)–Pt(1)–Os(4)	60.1(1)	Os(2)–Pt(1)–P(1)	178.1(1)	H(2)–Os(3)–C(6)	92(4)	C–Os(3)–C(6)	174.6(4)
Os(3)–Pt(1)–P(1)	113.8(1)	Os(4)–Pt(1)–P(1)	115.0(1)	C(4)–Os(3)–C(6)	97.5(4)	C(5)–Os(3)–C(6)	95.2(4)
Os(2)–Pt(1)–C(10)	89.2(4)	Os(3)–Pt(1)–C(10)	140.0(3)	Pt(1)–Os(4)–Os(2)	56.5(1)	Pt(1)–Os(4)–Os(3)	59.7(1)
Os(4)–Pt(1)–C(10)	135.6(3)	P(1)–Pt(1)–C(10)	92.6(4)	Os(2)–Os(4)–Os(3)	61.6(1)	Pt(1)–Os(4)–H(1)	95(4)
Pt(1)–Os(2)–Os(3)	59.2(1)	Pt(1)–Os(2)–Os(4)	59.6(1)	Os(1)–Os(4)–H(1)	41(4)	Os(3)–Os(4)–H(1)	91(4)
Os(3)–Os(2)–Os(4)	57.3(1)	Pt(1)–Os(2)–H(1)	92(4)	Pt(1)–Os(4)–C	108.4(2)	Os(2)–Os(4)–C	84.2(3)
Os(3)–Os(2)–H(1)	82(4)	Os(4)–Os(2)–H(1)	34(5)	Os(3)–Os(4)–C	48.8(2)	H(1)–Os(4)–C	83(4)
Pt(1)–Os(2)–H(2)	89(5)	Os(3)–Os(2)–H(2)	32(5)	Pt(1)–Os(4)–C(7)	161.8(3)	Os(2)–Os(4)–C(7)	117.8(4)
Os(4)–Os(2)–H(2)	82(5)	H(1)–Os(2)–H(2)	93(5)	Os(3)–Os(4)–C(7)	135.7(3)	H(1)–Os(4)–C(7)	77(4)
Pt(1)–Os(2)–C(1)	90.6(4)	Os(3)–Os(2)–C(1)	147.4(4)	C–Os(4)–C(7)	87.1(4)	Pt(1)–Os(4)–C(8)	95.7(3)
Os(4)–Os(2)–C(1)	98.4(4)	H(1)–Os(2)–C(1)	87(4)	Os(2)–Os(4)–C(8)	147.6(3)	Os(3)–Os(4)–C(8)	91.2(3)
H(2)–Os(2)–C(1)	179(5)	Pt(1)–Os(2)–C(2)	89.1(4)	H(1)–Os(4)–C(8)	169(4)	C–Os(4)–C(8)	90.6(4)
Os(3)–Os(2)–C(2)	97.0(4)	Os(4)–Os(2)–C(2)	146.2(4)	C(7)–Os(4)–C(8)	93.8(5)	Pt(1)–Os(4)–C(9)	67.9(3)
H(1)–Os(2)–C(2)	178(4)	H(2)–Os(2)–C(2)	85(4)	Os(2)–Os(4)–C(9)	87.2(3)	Os(C)–Os(4)–C(9)	127.5(3)
C(1)–Os(2)–C(2)	94.2(4)	Pt(1)–Os(2)–C(3)	171.7(4)	H(1)–Os(4)–C(9)	89(4)	C–Os(4)–C(9)	171.3(5)
Os(3)–Os(2)–C(3)	114.7(4)	Os(4)–Os(2)–C(3)	112.7(4)	C(7)–Os(4)–C(9)	95.4(4)	C(8)–Os(4)–C(9)	97.6(5)
H(1)–Os(2)–C(3)	82(4)	H(2)–Os(2)–C(3)	87(5)	Pt(1)–P(1)–C(11)	119.8(3)	Pt(1)–P(1)–C(17)	107.0(4)
C(1)–Os(2)–C(3)	94.0(5)	C(2)–Os(2)–C(3)	97.4(5)	C(11)–P(1)–C(17)	109.9(4)	Pt(1)–P(1)–C(23)	113.9(4)
Pt(1)–Os(3)–Os(2)	56.4(1)	Pt(1)–Os(3)–Os(4)	60.1(1)	C(11)–P(1)–C(23)	102.7(5)	C(17)–P(1)–C(23)	102.3(4)
Os(2)–Os(3)–Os(4)	61.1(1)	Pt(1)–Os(3)–H(2)	85(4)	Os(2)–H(1)–Os(4)	105(6)	Os(2)–H(2)–Os(3)	116(7)
Os(2)–Os(3)–H(2)	32(4)	Os(4)–Os(3)–H(2)	85(4)	Os(3)–C–Os(4)	83.1(3)	Os(3)–C–H(3)	125(9)
Pt(1)–Os(3)–C	108.0(2)	Os(2)–Os(3)–C	83.5(3)	Os(4)–C–H(3)	102(8)	Os(3)–C–H(4)	113(6)
Os(4)–Os(3)–C	48.1(2)	H(2)–Os(3)–C	84(4)	Os(4)–C–H(4)	117(6)	H(3)–C–H(4)	112(10)
Pt(1)–Os(3)–C(4)	161.2(3)	Os(2)–Os(3)–C(4)	113.3(4)	Pt(1)–C(10)–O(10)	176.8(10)	Os(2)–C(1)–O(1)	178.0(9)
Os(4)–Os(3)–C(4)	131.9(3)	H(2)–Os(3)–C(4)	82(4)	Os(2)–C(2)–O(2)	177.5(10)	Os(2)–C(3)–O(3)	178.3(12)
C–Os(3)–C(4)	84.6(4)	Pt(1)–Os(3)–C(5)	101.7(3)	Os(3)–C(4)–O(4)	175.6(9)	Os(3)–C(5)–O(5)	174.7(8)
Os(2)–Os(3)–C(5)	152.9(3)	Os(4)–Os(3)–C(5)	95.1(3)	Os(3)–C(6)–O(6)	170.4(8)	Os(4)–C(7)–O(7)	177.3(10)
H(2)–Os(3)–C(5)	172(4)	C–Os(3)–C(5)	89.7(4)	Os(4)–C(8)–O(8)	177.3(8)	Os(4)–C(9)–O(9)	166.7(8)
C(4)–Os(3)–C(5)	92.0(5)	Pt(1)–Os(3)–C(6)	68.7(2)				

diffraction. The more symmetrical (**5a**) exhibits one high-field signal for the hydrido-ligands (δ −20.94 p.p.m.), in accord with the approximate mirror symmetry mentioned above. This resonance is a doublet of triplets showing the expected couplings (^{31}P, ^{1}H, and ^{195}Pt). The small (18 Hz) ^{1}H–^{195}Pt coupling is in accord with there being no direct hydride–platinum bond, and the coupling to the two μ-CH_2 protons (*ca.* 2.5 Hz) is apparently equal. The unsymmetrical isomer (**5b**) gives rise to two high-field ^{1}H resonances at δ −13.57 and −21.73 p.p.m., the former showing a ^{195}Pt–^{1}H coupling of the magnitude (557 Hz) expected for an Os(μ-H)Pt group.[1] Measurement of the ^{1}H n.m.r. spectra at temperatures up to 100 °C shows that (**5b**) undergoes dynamic behaviour in solution with line broadening, but the limiting spectrum was not obtained, and under these conditions (**5a**) decomposed. Evidently hydrido-ligand site exchange in complex (**5b**) is a higher-energy process than in the precursor (**1a**).[1a]

As mentioned, the initially formed species in the reaction of (**1a**) with diazomethane is (**5a**), and other experiments showed that the compound [$Os_3(\mu-H)_2(\mu-CH_2)(CO)_{10}$] when treated with [$Pt(C_2H_4)_2\{P(cyclo-C_6H_{11})_3\}$] also afforded the same isomeric mixture of (**5a**) and (**5b**). In order to establish the mechanism of formation of these species from (**1a**), deuterium-labelling studies were undertaken involving preparing the isomeric mixture from (**1a**) and CD_2N_2, and from [$Os_3Pt(\mu-D)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}$] and CH_2N_2. The ^{1}H and ^{2}H n.m.r. spectra of the product mixtures were then examined. In these experiments, which were repeated to ensure constant data, the partially deuteriated and freshly prepared solutions of (**5a**) $\rightleftharpoons$ (**5b**) were filtered through a glass sinter to remove traces of insoluble impurity prior to n.m.r. analysis. The solutions were not chromatographed since this promotes the transformation of complex (**5a**) into (**5b**).

In all the reactions studied, the spectra observed confirmed the initial formation of complex (**5a**) and its subsequent isomerisation to the equilibrium mixture of (**5a**) and (**5b**). Moreover, the distribution of ^{1}H and ^{2}H isotopes between the methylene and hydride sites of (**5a**) gave useful mechanistic information. These distributions could be independently determined by careful integration of both ^{1}H and ^{2}H n.m.r. spectra. In preparations from CD_2N_2 and complex (**1a**), *ca.* 30% of the ^{2}H nuclei in the CD_2N_2 were transferred to hydride sites in (**5a**); on isomerisation of (**5a**) to the equilibrium mixture of (**5a**) and (**5b**) this $^{1}H/^{2}H$ distribution remained unchanged. Similarly, in preparations from CH_2N_2 and deuteriated (**1a**) 29% of the ^{1}H nuclei in the CH_2N_2 were transferred to hydride sites in (**5a**), and the distribution was unchanged on isomerisation, except in two experiments where a gradual

Table 4. Selected interatomic distances (Å) and bond angles (°) for the complex $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ (**5b**)

Pt(1)–Os(2)	2.869(1)	Pt(1)–Os(3)	2.853(1)	Pt(5)–Os(7)	2.854(1)	Pt(5)–Os(6)	2.865(1)
Pt(1)–Os(4)	2.789(1)	Pt(1)–P(1)	2.347(4)	Pt(5)–Os(8)	2.765(1)	Pt(5)–P(5)	2.341(4)
Pt(1)–C(10)	1.816(19)	Os(2)–Os(3)	2.973(1)	Pt(5)–C(50)	1.847(15)	Os(7)–Os(6)	2.976(1)
Os(2)–Os(4)	2.802(1)	Os(2)–C(1)	1.900(15)	Os(7)–Os(8)	2.865(1)	Os(7)–C(40)	2.087(20)
Os(2)–C(2)	1.935(19)	Os(2)–C(3)	1.917(18)	Os(7)–C(46)	1.977(18)	Os(7)–C(45)	1.893(17)
Os(3)–Os(4)	2.866(1)	Os(3)–C	2.159(19)	Os(7)–C(44)	1.856(16)	Os(6)–Os(8)	2.814(1)
Os(3)–C(4)	1.886(17)	Os(3)–C(5)	1.854(23)	Os(6)–C(42)	1.938(18)	Os(6)–C(41)	1.867(20)
Os(3)–C(6)	1.909(19)	Os(4)–C	2.125(17)	Os(6)–C(43)	1.900(19)	Os(8)–C(40)	2.193(18)
Os(4)–C(7)	1.866(19)	Os(2)–C(8)	1.886(24)	Os(8)–C(49)	1.909(19)	Os(8)–C(47)	1.887(20)
Os(4)–C(9)	1.952(16)	P(1)–C(11)	1.866(16)	Os(8)–C(48)	1.929(16)	P(5)–C(51)	1.838(16)
P(1)–C(17)	1.840(15)	P(1)–C(23)	1.831(17)	P(5)–C(57)	1.851(17)	P(5)–C(63)	1.847(15)
C(10)–O(10)	1.188(25)	C(1)–O(1)	1.143(25)	C(50)–O(50)	1.170(19)	C(46)–O(46)	1.115(23)
C(2)–O(2)	1.132(20)	C(3)–O(3)	1.117(25)	C(45)–O(45)	1.123(22)	C(44)–O(44)	1.166(21)
C(4)–O(4)	1.142(22)	C(5)–O(5)	1.205(23)	C(42)–O(42)	1.132(23)	C(41)–O(41)	1.114(26)
C(6)–O(6)	1.190(31)	C(7)–O(7)	1.175(25)	C(43)–O(43)	1.170(25)	C(49)–O(49)	1.175(25)
C(8)–O(8)	1.183(24)	C(9)–O(9)	1.112(20)	C(47)–O(47)	1.137(26)	C(48)–O(48)	1.126(21)

Os(2)–Pt(1)–Os(3)	62.6(1)	Os(2)–Pt(1)–Os(4)	59.3(1)	Os(7)–Pt(5)–Os(6)	62.7(1)	Os(7)–Pt(5)–Os(8)	61.3(1)
Os(3)–Pt(1)–Os(4)	61.0(1)	Os(2)–Pt(1)–P(1)	116.3(1)	Os(6)–Pt(5)–Os(8)	59.9(1)	Os(7)–Pt(5)–P(5)	138.3(1)
Os(3)–Pt(1)–P(1)	144.5(1)	Os(4)–Pt(1)–P(1)	152.5(1)	Os(6)–Pt(5)–P(5)	116.8(1)	Os(8)–Pt(5)–P(5)	158.8(1)
Os(2)–Pt(1)–C(10)	146.4(6)	Os(3)–Pt(1)–C(10)	94.6(5)	Os(7)–Pt(5)–C(50)	98.3(5)	Os(6)–Pt(5)–C(50)	143.9(5)
Os(4)–Pt(1)–C(10)	88.5(6)	P(1)–Pt(1)–C(10)	96.7(6)	Os(8)–Pt(5)–C(50)	84.1(5)	P(5)–Pt(5)–C(50)	97.9(5)
Pt(1)–Os(2)–Os(3)	58.4(1)	Pt(1)–Os(2)–Os(4)	58.9(1)	Pt(5)–Os(7)–Os(6)	58.8(1)	Pt(5)–Os(7)–Os(8)	57.8(1)
Os(3)–Os(2)–Os(4)	59.4(1)	Pt(1)–Os(2)–C(1)	97.0(4)	Os(6)–Os(7)–Os(8)	57.6(1)	Pt(5)–Os(7)–C(40)	107.4(5)
Os(3)–Os(2)–C(1)	147.2(5)	Os(4)–Os(2)–C(1)	90.0(5)	Os(6)–Os(7)–C(40)	81.6(5)	Os(8)–Os(7)–C(40)	49.6(5)
Pt(1)–Os(2)–C(2)	113.0(5)	Os(3)–Os(2)–C(2)	111.7(5)	Pt(5)–Os(7)–C(46)	68.4(5)	Os(6)–Os(7)–C(46)	93.1(5)
Os(4)–Os(2)–C(2)	169.8(5)	C(1)–Os(2)–C(2)	97.4(7)	Os(8)–Os(7)–C(46)	126.2(5)	C(40)–Os(7)–C(46)	174.5(7)
Pt(1)–Os(2)–C(3)	145.8(6)	Os(3)–Os(2)–C(3)	100.0(6)	Pt(5)–Os(7)–C(45)	95.5(5)	Os(6)–Os(7)–C(45)	148.9(6)
Os(4)–Os(2)–C(3)	87.7(6)	C(1)–Os(2)–C(3)	89.5(7)	Os(8)–Os(7)–C(45)	94.9(6)	C(40)–Os(7)–C(45)	91.1(8)
C(2)–Os(2)–C(3)	99.2(8)	Pt(1)–Os(3)–Os(2)	59.0(1)	C(46)–Os(7)–C(45)	92.9(8)	Pt(5)–Os(7)–C(44)	160.8(5)
Pt(1)–Os(3)–Os(4)	58.4(1)	Os(2)–Os(3)–Os(4)	57.3(1)	Os(6)–Os(7)–C(44)	117.1(5)	Os(8)–Os(7)–C(44)	138.5(6)
Pt(1)–Os(3)–C	108.3(4)	Os(2)–Os(3)–C	82.4(5)	C(40)–Os(7)–C(44)	89.7(7)	C(46)–Os(7)–C(44)	93.9(7)
Os(4)–Os(3)–C	49.9(4)	Pt(1)–Os(3)–C(4)	163.8(7)	C(45)–Os(7)–C(44)	92.9(7)	Pt(5)–Os(6)–Os(7)	58.5(1)
Os(2)–Os(3)–C(4)	113.8(6)	Os(4)–Os(3)–C(4)	132.3(6)	Pt(5)–Os(6)–Os(8)	58.3(1)	Os(7)–Os(6)–Os(8)	59.3(1)
C–Os(3)–C(4)	83.7(7)	Pt(1)–Os(3)–C(5)	98.4(6)	Pt(5)–Os(6)–C(42)	118.3(6)	Os(7)–Os(6)–C(42)	107.8(6)
Os(2)–Os(3)–C(5)	151.6(6)	Os(4)–Os(3)–C(5)	97.2(6)	Os(8)–Os(6)–C(42)	166.9(6)	Pt(5)–Os(6)–C(41)	92.9(5)
C–Os(3)–C(5)	90.1(9)	C(4)–Os(3)–C(5)	92.3(9)	Os(7)–Os(6)–C(41)	149.8(5)	Os(8)–Os(6)–C(41)	99.0(5)
Pt(1)–Os(3)–C(6)	73.3(5)	Os(2)–Os(3)–C(6)	97.9(6)	C(42)–Os(6)–C(41)	93.8(8)	Pt(5)–Os(6)–C(43)	141.3(8)
Os(4)–Os(3)–C(6)	131.6(5)	C–Os(3)–C(6)	178.3(6)	Os(7)–Os(6)–C(43)	104.4(5)	Os(8)–Os(6)–C(43)	83.1(5)
C(4)–Os(3)–C(6)	94.7(8)	C(5)–Os(3)–C(6)	90.5(9)	C(42)–Os(6)–C(43)	99.5(8)	C(41)–Os(6)–C(43)	92.2(8)
Pt(1)–Os(4)–Os(2)	61.8(1)	Pt(1)–Os(4)–Os(3)	60.7(1)	Pt(5)–Os(8)–Os(7)	60.9(1)	Pt(5)–Os(8)–Os(6)	61.8(1)
Os(2)–Os(4)–Os(3)	63.3(1)	Pt(1)–Os(4)–C	108.8(5)	Os(7)–Os(8)–Os(6)	63.2(1)	Pt(5)–Os(8)–C(40)	107.3(5)
Os(2)–Os(4)–C	85.6(5)	Os(3)–Os(4)–C	48.2(5)	Os(7)–Os(8)–C(40)	46.4(5)	Os(6)–Os(8)–C(40)	83.8(5)
Pt(1)–Os(4)–C(7)	158.1(7)	Os(2)–Os(4)–C(7)	100.1(7)	Pt(5)–Os(8)–C(49)	73.8(6)	Os(7)–Os(8)–C(49)	134.3(6)
Os(3)–Os(4)–C(7)	124.6(6)	C–Os(4)–C(7)	79.9(7)	Os(6)–Os(8)–C(49)	91.4(5)	C(40)–Os(8)–C(49)	137.3(7)
Pt(1)–Os(4)–C(8)	102.8(6)	Os(2)–Os(4)–C(8)	160.4(6)	Pt(5)–Os(8)–C(47)	162.6(5)	Os(7)–Os(8)–C(47)	125.5(6)
Os(3)–Os(4)–C(8)	99.2(6)	C–Os(4)–C(8)	88.7(8)	Os(6)–Os(8)–C(47)	104.9(5)	C(40)–Os(8)–C(47)	80.9(8)
C(7)–Os(4)–C(8)	97.3(9)	Pt(1)–Os(4)–C(9)	74.3(5)	C(49)–Os(8)–C(47)	96.4(8)	Pt(5)–Os(8)–C(48)	102.3(5)
Os(2)–Os(4)–C(9)	93.0(6)	Os(3)–Os(4)–C(9)	134.7(5)	Os(7)–Os(8)–C(48)	98.2(6)	Os(6)–Os(8)–C(48)	159.4(6)
C–Os(4)–C(9)	175.2(6)	C(7)–Os(4)–C(9)	95.9(8)	C(40)–Os(8)–C(48)	89.2(7)	C(49)–Os(8)–C(48)	96.7(7)
C(8)–Os(4)–C(9)	94.2(8)	Pt(1)–P(1)–C(11)	112.1(6)	C(47)–Os(8)–C(48)	93.0(8)	Pt(5)–P(5)–C(51)	111.9(5)
Pt(1)–P(1)–C(17)	111.4(6)	C(11)–P(1)–C(17)	102.7(7)	Pt(5)–P(5)–C(57)	112.5(5)	C(51)–P(5)–C(57)	109.8(7)
Pt(1)–P(1)–C(23)	113.5(5)	C(11)–P(1)–C(23)	111.3(8)	Pt(5)–P(5)–C(63)	112.9(5)	C(51)–P(5)–C(63)	102.3(7)
C(17)–P(1)–C(23)	105.2(7)	Os(3)–C–Os(4)	81.9(6)	C(57)–P(5)–C(63)	106.7(8)	Os(7)–C(40)–Os(8)	84.0(6)
Pt(1)–C(10)–O(10)	179.5(17)	Os(2)–C(1)–O(1)	176.9(14)	Pt(5)–C(50)–O(50)	178.4(12)	Os(7)–C(46)–O(46)	171.8(14)
Os(2)–C(2)–O(2)	177.8(14)	Os(2)–C(3)–O(3)	177.5(17)	Os(7)–C(45)–O(45)	177.0(19)	Os(7)–C(44)–O(44)	176.7(15)
Os(3)–C(4)–O(4)	176.3(16)	Os(3)–C(5)–O(5)	174.7(19)	Os(6)–C(42)–O(42)	174.6(18)	Os(6)–C(41)–O(41)	177.1(18)
Os(3)–C(6)–O(6)	170.9(15)	Os(4)–C(7)–O(7)	177.4(18)	Os(6)–C(43)–O(43)	178.8(17)	Os(8)–C(49)–O(49)	169.6(17)
Os(4)–C(8)–O(8)	176.8(18)	Os(4)–C(9)–O(9)	170.2(15)	Os(8)–C(47)–O(47)	177.7(17)	Os(8)–C(48)–O(48)	177.6(14)

equilibration of ^1H and ^2H nuclei between the two sites was observed, possibly caused by solvent impurities.

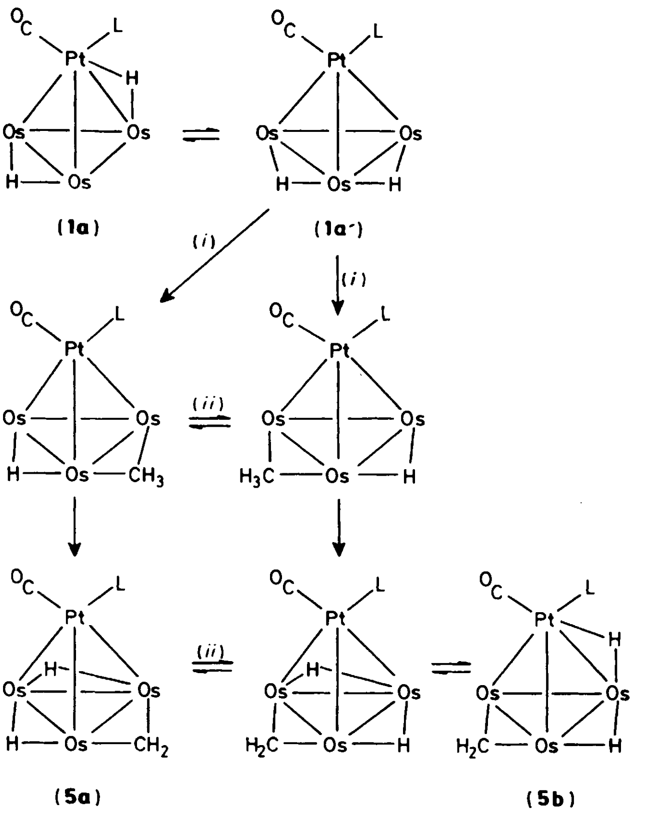
The proportion of nuclei transferred between methylene and hydride sites during the formation of complex (**5a**) is significantly different from 50%, the proportion which would be expected if ^1H and ^2H nuclei were scrambled statistically between the two sites. Furthermore, the similarity in the proportions transferred, irrespective of whether CH_2N_2 or CD_2N_2 was used for the preparation, shows that there is no establishment of an equilibrium where one isotope prefers one of the two possible sites.

The closeness of the proportion of nuclei transferred to 33% suggests the involvement of a species in which the two ^1H or ^2H nuclei of the CH_2N_2 or CD_2N_2 are scrambled with one of the two hydride ligands of complex (**1a**). Possible species in which this scrambling might occur are shown in Scheme 2, where

Table 5. N.m.r. data[a] for the two isomers of $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$

Isomer	$^{31}P-\{^1H\}$[b]	$^{195}Pt-\{^1H\}$[c]	^1H
(5a)	10.8 [s, *J*(PtP) 2 513]	1 045 [d, *J*(PPt) 2 513]	6.40 [d of d of t, 1 H, CH_2, *J*(HH) 6 and 2.5, *J*(PH) 2], 6.32 [d of t, 1 H, CH_2, *J*(HH) 6 and 2.5], 2.0—1.3 (m, 33 H, C_6H_{11}), −20.94 [d of t, 2 H, Os(μ-H)Os, *J*(PH) 5, *J*(HH) 2.5, *J*(PtH) 18]
(5b)	65.2 [s, *J*(PtP) 2 661]	172 [d, *J*(PPt) 2 661]	7.46 [d, 1 H, CH_2, *J*(HH) 5], 6.96 [d of d, 1 H, CH_2, *J*(HH) 6 and 2], 2.0—1.3 (m, 33 H, C_6H_{11}), −13.57 [d, 1 H, Os(μ-H)Pt, *J*(PH) 10, *J*(PtH) 557], −21.73 [s, Os(μ-H)Os, *J*(PtH) 20]

[a] Chemical shifts δ in p.p.m., coupling constants *J* in Hz; spectra measured in $[^2H_1]$chloroform at ambient temperatures. [b] Chemical shifts positive to high frequency of 85% H_3PO_4 (external). [c] Chemical shifts to high frequency of $\Xi(^{195}Pt)$ 21.4 MHz.



Scheme 2. L = cyclo-$P(C_6H_{11})_3$; CO ligands omitted for clarity. (*i*) CH_2N_2; (*ii*) rotation of $Pt(CO)\{P(C_6H_{11})_3\}$ fragment about an axis essentially perpendicular to the Os_3 plane

(**1a′**),* an isomer of (**1a**), reacts with CH_2N_2 to form intermediates containing a bridging CH_3 group, precedent for which exists in the work of Shapley and co-workers.[15] In the deuteriation experiments this methyl group would be either CDH_2 or CHD_2. A statistical transfer of any of the three ^1H or ^2H nuclei of this methyl group to an Os(μ-H)Os group would result in a transfer of one third of the nuclei from the CH_2N_2 or CD_2N_2 to the hydride sites of complex (**5a**), close to the values of 29 and 30% observed. A preferential transfer of, say, ^1H to the hydride site would increase the proportion of ^1H nuclei transferred for CH_2N_2, and decrease the proportion of ^2H nuclei transferred from CD_2N_2. The similarity of the values obtained indicates that the transfer observed is dominated by statistical factors. Establishment of an equilibrium distribution of ^1H and ^2H nuclei between the two sites in complex (**5a**) [or (**5b**)] is prevented by this mechanism if the formation of (**5a**) from the methyl-bridged intermediate is irreversible. This is unlike the situation with the compound $[Os_3(\mu-H)_2(\mu-CH_2)(CO)_{10}]$[15] in which a preferential distribution of ^2H nuclei in the methylene sites is achieved by a rapid, reversible isomerisation to the methyl-bridged isomer $[Os_3(\mu-H)(\mu-CH_3)(CO)_{10}]$. The absence of any scrambling of ^1H and ^2H nuclei between hydride and methylene sites during isomerisation of (**5a**) to (**5b**) suggests that bridging methyl groups cannot be involved in the isomerisation, which therefore probably occurs *via* rotation of the $Pt(CO)(PR_3)$ fragment with respect to the Os_3 triangle, and transfer of a bridging hydride ligand from an Os–Os edge to an Os–Pt edge, as shown in Scheme 2. This Scheme shows a sequential isomerisation *via* an unobserved isomeric intermediate. We have, however, no evidence to prove either the sequence of the two steps, or that the two steps are not concerted.

Having carried out *X*-ray diffraction studies on the four closely related molecules it is interesting to make some general structural comparisons. Noteworthy is the co-ordination geometry of the individual metal atoms. These geometries are best described by ignoring the metal–metal connectivities in Figures 1—4 which are hydrido- or methylene-bridged, and by treating the metal atoms as being ligated only by bridging and terminal ligands, and by the unbridged metal–metal bonds. Viewed in this way, in all four structures the osmium atoms are essentially octahedrally co-ordinated, the platinum atoms of (**4**), (**5a**), and (**5b**) are trigonally bipyramidally ligated, and the platinum atom in (**2**) is in a square-planar environment. Of course the deviations of relevant angles from idealised values for these co-ordination geometries are large, particularly since the M–M–M (M = Os or Pt) angles are *ca.* 60°, except for those involving the 'hinge' osmium atoms of (**2**). These distortions are particularly pronounced for the platinum atoms of complexes (**5a**) and (**5b**), where the Os(3)–Pt(1)–Os(4) angle (*ca.* 60°) is one of the equatorial angles at the trigonal-bipyramidal platinum. This distortion in the two isomers is accompanied by a close approach of certain carbonyl-ligand carbon atoms, as noted below. This analysis of the cluster geometries in terms of the co-ordination of individual metal atoms emphasises the ability of platinum to act as either a 16-electron square-planar centre in complex (**2**) or an 18-electron trigonal-bipyramidal centre in (**4**), (**5a**), and (**5b**), with a consequent change in the number of formal metal–metal bonds. This variability in co-ordination geometry is of course characteristic of mononuclear platinum chemistry, and also typical of mononuclear platinum metal centres involved in homogeneous catalytic processes. That such behaviour persists in cluster chemistry may be of importance in designing clusters of potential catalytic utility.

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* Isomer (**1a′**) is derived from (**1a**) by migration of a hydrido-ligand and rotation of the $Pt(CO)\{P(cyclo-C_6H_{11})_3\}$ group about an axis through the platinum and the midpoint of the Os_3 triangle. Variable-temperature ^1H n.m.r. studies[1a] reveal that the hydrido-ligands in (**1a**) undergo site exchange in solution, and this may occur *via* an intermediate (**1a′**). Schilling and Hoffmann[16] consider that the barrier for such a rotation would be small.

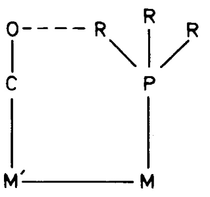
The relief of the electronic unsaturation of complex (**1a**) upon co-ordination of a two-electron ligand [or two one-electron ligands in the formation of (**4**)] is accompanied by a general increase in Os–Os separations in keeping with the unsaturation in (**1a**), discussed previously.[1a] Thus the average lengths of the Os–Os vectors not hydrido-bridged in (**1a**), (**2**), (**4**), (**5a**), and (**5b**) are 2.759, 2.880, 2.867, 2.826, and 2.837 Å [estimated standard deviations (e.s.d.s) *ca.* 0.002 Å]. Similarly, the mean hydrido-bridged Os–Os distances are, respectively 2.789, 2.869, 2.987, 2.947, and 2.975 Å (e.s.d.s *ca.* 0.002 Å) for these species,* distances typical of a range of *closo-* and butterfly homo- and hetero-nuclear tetrametal clusters, *e.g.* [$Os_4(\mu-H)_3(\mu-I)(CO)_{12}$],[17] [$IrOs_3(\mu-Cl)(\mu-H)_2(CO)_{12}$],[18] and [$Os_4(\mu-H)_4(CO)_{12}$].[14] In common with other structures in which the four metal atoms adopt a butterfly configuration, *e.g.* [$Os_4(\mu-H)_3(\mu-I)(CO)_{12}$],[17] the hydrido-bridged 'hinge' Os–Os vector in (**2**) is shorter than the hydrido-bridged Os–Os vectors in (**4**), (**5a**), and (**5b**). There is considerable variation in the unbridged Os–Pt distances among the structures, with the shortest in (**4**) and in (**5a**) lying along the axis of the platinum atom's 'trigonal bipyramid,' 2.717(4) and 2.730(1) Å, respectively. These values may be compared with the Os(1)–Pt distance [2.729(1) Å] in (**2**), where the platinum is in an essentially square-planar environment. Other unbridged Os–Pt distances for complexes (**5a**) and (**5b**) are in the range 2.777(2)—2.854(2) Å, and these may be compared with the Os–Pt separations of 2.791(1) and 2.832(1) Å in (**1a**).[1a] The lengths of the hydrido-bridged Os–Pt vectors likewise show considerable variation, averaging 2.863(1), 2.914(1), 2.972(4), and 2.867(2) Å for (**1a**), (**2**), (**4**), and (**5b**), respectively. It appears that in the set of four 60 c.v.e. clusters (**2**), (**4**), (**5a**), and (**5b**) it is the electronic requirement of the 'extra' ligand(s) for a bridging site (H or CH_2), or not (CO), that is in some way connected with the adoption of a *closo*-tetrahedral or a *nido*-butterfly geometry.

In both complexes (**5a**) and (**5b**) the methylene ligands occupy sites bridging two osmium atoms; whether for kinetic or thermodynamic reasons, in neither is an Os–Pt edge bridged by a methylene ligand. As noted elsewhere,[18] alkylidene ligands show a marked preference for bridging geometry, in contrast to CO for which the terminal mode of bonding is preferred here, as well as in most other clusters of osmium. In (**5a**) and (**5b**) the Os–μ-CH_2 distances are similar to those in the trinuclear cluster [$Os_3(\mu-H)_2(\mu-CH_2)(CO)_{10}$],[15] and the methylene groups symmetrically bridge the osmium atoms with mean Os–μ-C distances of 2.131(8) and 2.16(2) Å in (**5a**) and (**5b**), respectively. The Os–μ-C–Os angles [83.1(3) (**5a**) and 83.0(6)° (**5b**)] are acute, and in the range observed for alkylidene groups bridging metal–metal bonds in many di- and poly-nuclear metal complexes. In complex (**5a**) the orientation of the CH_2 ligand is approximately orthogonal to the metal–metal vector, in accord with theoretical and experimental findings on similar systems.[19] In (**5b**) the methylene hydrogens were not detected crystallographically.

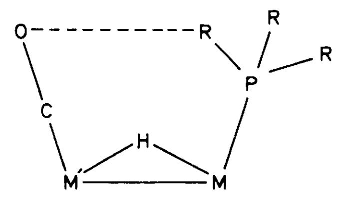
In complexes (**2**), (**4**), (**5a**), and (**5b**) all the CO groups are terminal, and essentially linear. The most marked deviations from linearity of the M–C–O systems occur for osmium-bound CO ligands which interact weakly with the platinum atom: *viz.* for (**2**), Pt $\cdots$ C(1) 2.99(2); for (**5a**), Pt(1) $\cdots$ C(6) 2.790(8) and Pt(1) $\cdots$ C(9) 2.777(9); and for (**5b**), Pt(1) $\cdots$ C(6) 2.88 (2) and Pt(1) $\cdots$ C(9) 2.91(2) Å. The Os–C–O angles for these ligands are, respectively, 171.2(16), 170.4(8), 166.7(8), 171.4(14), and 169.9(15)°. There are no short Pt $\cdots$ C(O) contacts in (**4**).

Hydride positions for complexes (**2**), (**4**), and (**5b**) were calculated,[12] and only in (**5a**) could they be confirmed by refinement against diffraction data without positional restraints. As mentioned above, in the four molecules these ligands occupy bridging sites across both Os–Pt and Os–Os edges. Clearly the energetic distinction between isomers with Os(μ-H)Pt or Os(μ-H)Os sites, and between various Os(μ-H)Os sites, is small. Thus complexes (**5a**) and (**5b**) show such tautomerism, and (**2**) has the 'hinge' Os–Os vector bridged by hydride, rather than a wing tip to hinge vector as in (**3**).[1b]

It is notable that in all structures where hydrido-ligands are attached to a platinum atom they lie *cis* to the phosphine ligand. This is true also for (**1a**) and for the cation [$PtRh_2(\mu-H)(\mu-CO)_2(CO)(PPh_3)(\eta-C_5Me_5)_2$]$^+$.[20] This stereochemical preference may be related to the relief of inter-ligand steric pressure to be gained by placing the relatively small hydrido-ligand adjacent to the large P(cyclo-C_6H_{11})$_3$ group. The consequent opening of the M–M′–L angles (L = CO or PR_3; M, M′ = metal atoms bridged by the hydride) would reduce the repulsive, non-bonded, interactions between carbonyl ligands and the neighbouring phosphine substituents [see (**A**) and (**B**) below]. Clearly the hydride ligand would not interact strongly with these substituents. Placing a hydride ligand in a site not *cis* to PR_3 would raise the steric pressure on the PR_3 ligand as a result of increased M′–M–C(O) angles elsewhere in the molecule.



(A)



(B)

In the four structures other features of ligand geometry are unremarkable, mean distances and angles being of the usual dimensions. Thus for (**2**), (**4**), (**5a**), and (**5b**), respectively, Pt–C distances are 1.85(2), 1.80(5), 1.858(11), and 1.83(2) Å, mean Os–C(O) separations are 1.908(10), 1.905(9), 1.921(12), and 1.903(8) Å, and mean Pt–P bond lengths are 2.346(4), 2.378(10), 2.380(3), and 2.344(10) Å. The most significant deviations from these mean values occur for the carbonyl ligands in complexes (**5a**) and (**5b**) distorted by contact with the platinum atom (see above); these show marginally increased Os–C distances.

Experimental

All reactions were carried out under oxygen-free nitrogen, using Schlenk-tube techniques. Solvents were dried prior to use. Light petroleum was that fraction of b.p. 40—60 °C. The compound [$Os_3Pt(\mu-H)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}$] was prepared as previously described.[1a] The n.m.r. measurements were made with JEOL FX 90Q and FX 200 instruments, and i.r. spectra were recorded with a Nicolet FT spectrophotometer.

Reaction of [$Os_3Pt(\mu-H)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}$] (**1a**) *with Hydrogen.*—A diethyl ether (20 cm^3) solution of complex (**1a**) (0.13 g, 0.10 mmol) in a glass tube (50 cm^3) placed in a stainless-steel autoclave (100 cm^3) was pressurised with hydrogen (200 atm), and heated at 50 °C for 30 h. The pressure was then released and the glass container removed. The latter contained a pale yellow solution and yellow *crystals* of [$Os_3Pt(\mu-H)_4(CO)_{10}\{P(cyclo-C_6H_{11})_3\}$] (**4**) which were recovered by decanting the solvent: $\nu_{max.}$(CO) at 2 095m, 2 086m, 2 070m, 2 056vs, 2 047s, 2 024vs, 2 013s, 1 992s, 1 979s, 1 944w, and 1 934w cm^{-1} (Et_2O); ^1H n.m.r. (in [$^2H_2$]dichloromethane

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* In the discussion here and elsewhere of the structures of (**4**) and (**5b**), values are averaged over the two crystallographically independent molecules.

Table 6. Data for crystal structure analyses *

	(2)	**(4)**	**(5a)**	**(5b)**
Molecular Formula	$C_{29}H_{35}O_{11}Os_3PPt$	$C_{28}H_{37}O_{10}Os_3PPt$	$C_{29}H_{37}O_{10}Os_3PPt$	$C_{29}H_{37}O_{10}Os_3PPt$
M	1 356.3	1 330.3	1 342.3	1 342.3
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic
Crystal colour and habit	Yellow prism	Yellow, irregular	Yellow prism	Red needle
Space group	$P\bar{1}$	*Pccn*	$P\bar{1}$	$P2_1/c$
a/Å	10.158(5)	20.848(11)	12.244(5)	18.708(4)
b/Å	15.097(7)	36.254(26)	9.533(4)	16.664(3)
c/Å	12.007(5)	18.350(9)	16.239(6)	22.875(5)
α/°	94.06(3)	90	77.00(3)	90
β/°	86.66(4)	90	72.79(3)	101.82(2)
γ/°	105.26(4)	90	75.84(3)	90
U/Å^3	1 770(1)	13 870(14)	1 731(1)	6 890(2)
Z	2	16	2	8
D_c/g cm^{-3}	2.54	2.55	2.57	2.55
F(000)	1 236	9 689	1 224	4 896
μ(Mo-K_α)/cm^{-1}	148.25	151.4	149.8	148.6
T/K	295	210	220	220
Method	θ—2θ	ω(Wyckoff)	θ—2θ	θ—2θ
2θ range/°	$3 \leqslant 2\theta \leqslant 50$	$4 \leqslant 2\theta \leqslant 45$	$3 \leqslant 2\theta \leqslant 60$	$3 \leqslant 2\theta \leqslant 60$
Transmission coefficient range	0.017—0.005	0.056—0.008	0.058—0.018	0.119—0.045
No. of azimuthal scan data used	247	238	306	397
Approx. crystal size (mm)	diameter 0.41	0.1 × 0.3 × 0.4	0.32 × 0.26 × 0.39	0.11 × 0.20 × 0.20
No. of data collected	3 971	9 189	7 911	10 901
No. of unique data	3 763	9 062	7 192	10 363
No. of observed data (N_o)	3 652	5 559	6 859	8 755
Criterion for observed, n [$I \geqslant n\sigma(I)$]	2.5	2	3	3
Refinement				
Solution method	Direct	Direct	Patterson	Direct
Anisotropic atoms	Os, Pt, P, C, O	Os, Pt, P	Os, Pt, P, C, O	Os, Pt, P
Isotropic atoms	H	C, O, H	H	C, O, H
H atoms refined	None	None	CH_2, μ-H	None
No. of parameters refined (N_v)	406	395	409	405
Final R	0.048	0.081	0.037	0.047
R'	0.047	0.076	0.039	0.046
g	0.0015	0.001	0.0003	0.0012
S	1.41	1.58	1.93	
Largest final electron-density	+2.3	+5.2	+4.1	+2.1
difference features (e Å^{-3})	−1.8	−3.9	−2.2	−1.8
Shift/e.s.d. in last cycles of refinement:				
maximum	0.074	0.085	0.058	0.101
average	0.007	0.012	0.003	0.008

* Features common to all determinations: λ(Mo-K_α) 0.710 69 Å; *P3m* diffractometer; $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}F_o$; $w = 1/[\sigma_c^2(F_o) + gF_o^2]$, $\sigma_c(F_o)$ = e.s.d. in F_o from counting statistics; $S = [\Sigma w(F_o - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

at −80 °C), δ 2.0—1.3 (m, 33 H, C_6H_{11}), −15.5 [s, 2 H, Os(μ-H)Pt, J(PtH) 570 Hz], and −20.77 p.p.m. [s, 2 H, Os(μ-H)Os]. Further product was obtained by cooling the recovered solution to *ca.* −20 °C in a Schlenk tube, and evaporating by using a stream of hydrogen gas. In this manner a combined yield of 0.12 g (90%) of complex (**4**) was obtained.

Reaction of Complex (**1a**) *with Diazomethane*.—A deep green tetrahydrofuran (20 cm^3) solution of complex (**1a**) (0.20 g, 0.15 mmol) was treated dropwise at *ca.* −10 °C with a diethyl ether solution (5—10 cm^3) of diazomethane generated from an Aldrich Diazald Chemical Co. kit. The orange solution obtained was evaporated *in vacuo*, and the residue extracted with light petroleum. Chromatography on alumina (3 × 10 cm column), eluting with light petroleum–dichloromethane (4:1), afforded a single orange eluate. Removal of solvent gave orange and red *crystals* of [$Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}$] (0.195 g, 96%) (Found: C, 25.7; H, 2.6. $C_{29}H_{37}O_{10}Os_3PPt$ requires C, 25.9; H, 2.7%); $\nu_{max.}$(CO) at 2 084w, 2 081w, 2 054s, 2 044s, 2 025s, 2 008 (sh), 2 005w, 1 996 (sh), 1 978m, 1 966w, 1 957w, 1 950w, and 1 941w cm^{-1} (light petroleum). N.m.r. data for the individual isomers are given in Table 5, and were measured from equilibrium mixtures.

Crystal Structure Determinations and Refinements.—Crystals of complex (**2**) were grown from a CH_2Cl_2 solution by slow evaporation under an atmosphere of CO, those of (**4**) by cooling a saturated Et_2O solution obtained from the autoclave (see above). Crystals of (**5a**) and (**5b**) were obtained by evaporation of CH_2Cl_2–light petroleum (1:4) solutions containing the isomeric mixture. Details of the data-collection procedures, structure solution and refinement are given in Table 6. Data were collected for a unique volume of reciprocal space on single crystals mounted under N_2 in thin-walled glass capillaries using graphite monochromated X-radiation. For complexes (**4**), (**5a**), and (**5b**) the temperature of the crystal was maintained by use of a locally modified LT-1 attachment to the Nicolet *P3m* diffractometer. In each case absorption corrections were

Table 7. Atomic positional (fractional co-ordinates) parameters (× 10^4)

(*a*) $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
P	−1 666(5)	6 283(3)	2 894(3)	C(9)	2 096(26)	8 715(12)	5 192(15)
Os(1)	2 492(1)	8 926(1)	3 665(1)	C(10)	3 864(24)	8 267(12)	3 529(17)
Pt	344(1)	7 452(1)	3 190(1)	C(11)	1 348(21)	6 857(11)	3 967(17)
Os(3)	302(1)	9 252(1)	2 488(1)	C(111)	−1 441(18)	5 139(10)	2 310(15)
Os(2)	2 764(1)	9 072(1)	1 282(1)	C(112)	−2 580(24)	4 290(11)	2 675(15)
O(1)	1 751(18)	6 963(9)	845(11)	C(113)	−2 403(27)	3 406(15)	2 051(26)
O(2)	5 709(19)	8 882(12)	1 040(19)	C(114)	−1 039(28)	3 306(15)	2 123(25)
O(3)	2 100(26)	9 239(12)	1 132(13)	C(115)	78(26)	4 128(13)	1 746(24)
O(4)	3 861(19)	11 165(9)	1 724(14)	C(116)	−97(22)	4 991(13)	2 412(18)
O(5)	1 039(21)	11 343(10)	2 485(17)	C(121)	−2 782(19)	6 582(12)	1 901(14)
O(6)	−908(17)	9 079(9)	240(12)	C(122)	−2 149(21)	6 693(12)	737(13)
O(7)	−2 302(19)	9 236(11)	3 797(18)	C(123)	−3 024(23)	758(14)	−7(14)
O(8)	4 616(18)	10 770(10)	4 086(15)	C(124)	−4 466(22)	6 435(15)	−42(19)
O(9)	1 856(23)	8 631(10)	6 133(11)	C(125)	−5 117(24)	6 296(14)	1 075(17)
O(10)	4 676(19)	7 885(12)	3 424(16)	C(126)	−4 262(22)	5 944(13)	1 849(17)
O(11)	1 880(16)	6 455(10)	4 487(13)	C(131)	−2 662(18)	6 097(11)	4 214(13)
C(1)	2 114(24)	7 769(14)	1 105(15)	C(132)	−3 112(22)	6 971(12)	4 651(14)
C(2)	4 639(34)	8 979(14)	1 146(17)	C(133)	−4 011(25)	6 801(16)	5 672(17)
C(3)	2 366(31)	9 193(17)	−219(20)	C(134)	−3 326(27)	6 411(17)	6 608(16)
C(4)	3 380(20)	10 390(13)	1 569(16)	C(135)	−2 916(25)	5 577(14)	6 146(16)
C(5)	739(21)	10 516(12)	2 470(19)	C(136)	−1 971(26)	5 771(15)	5 143(17)
C(6)	−452(24)	9 096(12)	1 006(17)	H(1)	1 121	9 528	3 858
C(7)	−1 346(21)	9 231(12)	3 335(19)	H(2)	−491	8 007	2 228
C(8)	3 751(24)	10 099(12)	3 925(15)				

(*b*) $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**4**)

Os(1)	5 918(1)	1 254(1)	−205(1)	P(2)	1 674(5)	1 486(3)	7 245(5)
Pt(4)	7 206(1)	1 363(1)	−86(1)	C(41)	4 919(23)	1 072(12)	7 431(19)
Os(2)	6 686(1)	632(1)	432(1)	O(41)	5 428(17)	970(9)	7 431(14)
Os(3)	6 785(1)	786(1)	−1 098(1)	C(42)	4 243(20)	1 625(10)	8 168(16)
P(1)	8 334(5)	1 468(3)	−153(5)	O(42)	4 349(14)	1 834(8)	8 625(12)
C(1)	5 091(23)	1 068(12)	−338(18)	C(43)	4 160(22)	1 651(11)	6 687(18)
O(1)	4 561(21)	947(11)	−400(16)	O(43)	4 181(16)	1 840(8)	6 201(12)
C(2)	5 903(22)	1 661(11)	−861(18)	C(44)	3 935(21)	369(11)	8 127(18)
O(2)	5 871(19)	1 914(10)	−1 232(15)	O(44)	4 366(18)	137(10)	8 235(15)
C(3)	5 688(21)	1 557(11)	643(18)	C(45)	2 592(21)	314(11)	8 005(17)
O(3)	5 549(16)	1 729(8)	1 085(13)	O(45)	2 248(18)	88(10)	7 887(14)
C(4)	6 074(24)	238(13)	227(19)	C(46)	3 088(19)	723(11)	9 126(16)
O(4)	5 740(17)	−7(9)	139(14)	O(46)	3 043(13)	741(7)	9 736(10)
O(5)	7 784(17)	65(9)	363(13)	C(47)	3 833(22)	355(12)	6 525(19)
C(5)	7 391(22)	305(12)	392(18)	O(47)	4 160(16)	90(9)	6 508(14)
C(6)	6 655(28)	620(15)	1 452(22)	C(48)	2 516(16)	497(9)	6 351(14)
O(6)	6 635(15)	628(8)	2 115(12)	O(48)	2 044(15)	335(8)	6 224(12)
C(7)	6 240(24)	395(12)	−1 339(19)	C(49)	3 408(24)	915(13)	5 517(20)
O(7)	5 882(18)	164(10)	−1 497(15)	O(49)	3 475(14)	964(7)	4 930(12)
C(8)	7 563(23)	503(13)	−1 129(19)	C(50)	2 940(23)	1 854(12)	7 686(19)
O(8)	8 035(18)	340(9)	−1 180(15)	O(50)	3 020(15)	2 172(8)	7 850(12)
C(9)	6 888(20)	945(16)	−2 057(25)	C(51)	1 167(16)	1 048(9)	7 236(14)
O(9)	6 956(16)	1 044(9)	−2 664(14)	C(52)	1 121(20)	866(10)	7 948(16)
C(10)	7 041(25)	1 805(13)	303(19)	C(53)	800(18)	499(10)	7 899(16)
O(10)	6 969(19)	2 143(10)	440(15)	C(54)	128(25)	522(14)	7 567(20)
C(11)	8 585(22)	1 815(2)	543(18)	C(55)	183(26)	714(13)	6 813(20)
C(12)	8 395(22)	1 720(11)	1 303(17)	C(56)	540(19)	1 090(10)	6 884(16)
C(13)	8 529(20)	2 031(11)	1 828(17)	C(57)	1 378(18)	1 797(10)	7 966(15)
C(14)	9 232(25)	2 188(14)	1 714(20)	C(58)	1 579(21)	1 683(11)	8 723(16)
C(15)	9 406(24)	2 276(12)	978(18)	C(59)	495(24)	2 200(12)	8 478(18)
C(16)	9 265(24)	1 975(13)	429(20)	C(60)	1 394(21)	1 987(11)	9 269(18)
C(17)	8 841(20)	1 049(11)	−81(18)	C(61)	698(22)	2 084(12)	9 243(18)
C(18)	8 844(20)	853(10)	630(16)	C(62)	655(21)	1 909(11)	7 920(18)
C(19)	9 146(26)	498(14)	650(22)	C(63)	1 497(20)	1 717(10)	6 390(16)
C(20)	9 845(24)	514(13)	333(19)	C(64)	1 679(20)	1 481(10)	5 711(15)
C(21)	9 885(25)	709(12)	−392(18)	C(65)	1 476(22)	1 675(11)	5 017(19)
C(22)	9 505(27)	1 081(15)	−303(23)	C(66)	1 741(22)	2 056(11)	4 964(18)
C(23)	8 510(22)	1 697(11)	−1 031(18)	C(67)	1 594(25)	2 293(12)	5 627(18)
C(24)	8 408(24)	1 426(12)	−1 698(18)	C(68)	1 786(22)	2 098(11)	6 322(17)
C(25)	8 676(21)	1 593(11)	−2 414(16)	H(1)	5 969	907	493
C(26)	8 323(29)	1 948(14)	−2 532(22)	H(2)	6 036	1 030	−1 072
C(27)	8 354(24)	2 333(12)	−1 833(18)	H(3)	7 279	989	552
C(28)	8 172(25)	2 046(13)	−1 179(19)	H(4)	7 321	1 172	−977

Table 7 (*continued*)

(*b*) $[\mathrm{Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$ (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(7)	3 282(1)	763(1)	6 536(1)	H(5)	3 885	1 018	8 235
Os(6)	3 248(1)	691(1)	8 088(1)	H(6)	4 041	995	6 622
Os(5)	4 072(1)	1 278(1)	7 426(1)	H(7)	2 612	1 027	8 018
Pt(8)	2 787(1)	1 390(1)	7 381(1)	H(8)	2 794	1 173	6 501

(*c*) $[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$ (**5a**)

Pt(1)	2 123(1)	2 858(1)	2 208(1)	C(9)	419(9)	2 087(13)	3 698(7)
Os(2)	238(1)	3 257(1)	1 553(1)	O(9)	453(7)	929(8)	4 050(5)
Os(3)	1 146(1)	5 792(1)	1 662(1)	C(11)	4 164(9)	4 249(10)	2 943(7)
Os(4)	−27(1)	4 189(1)	3 220(1)	C(12)	4 763(9)	5 148(11)	2 058(7)
P(1)	3 754(2)	2 594(3)	2 782(2)	C(13)	5 002(11)	6 571(12)	2 171(8)
C	−528(8)	6 318(10)	2 546(6)	C(14)	5 695(11)	6 318(13)	2 850(9)
C(10)	2 697(9)	1 091(11)	1 786(7)	C(15)	5 109(10)	5 465(13)	3 704(8)
O(10)	3 022(9)	45(9)	1 499(6)	C(16)	4 992(9)	4 005(12)	3 594(8)
C(1)	99(10)	1 236(11)	1 995(8)	C(17)	5 017(8)	1 525(10)	2 078(7)
O(1)	−10(9)	76(9)	2 268(7)	C(18)	5 240(10)	2 120(12)	1 090(7)
C(2)	1 285(10)	2 852(12)	441(7)	C(19)	6 162(12)	1 027(14)	575(9)
O(2)	1 891(9)	2 671(10)	−208(5)	C(20)	7 272(12)	680(15)	840(10)
C(3)	−1 170(10)	3 755(13)	1 195(7)	C(21)	7 075(11)	82(14)	1 812(10)
O(3)	−2 022(8)	4 073(10)	997(6)	C(22)	6 167(9)	1 143(13)	2 360(8)
C(4)	628(9)	7 547(11)	939(7)	C(23)	3 644(9)	1 414(11)	3 869(7)
O(4)	248(8)	8 585(9)	535(6)	C(24)	2 690(9)	2 130(12)	4 598(7)
C(5)	1 775(9)	6 807(10)	2 226(6)	C(25)	2 701(12)	1 193(13)	5 491(7)
O(5)	2 072(7)	7 458(8)	2 606(6)	C(26)	2 537(13)	−351(14)	5 517(8)
C(6)	2 638(9)	5 145(10)	833(6)	C(27)	3 435(11)	−1 052(12)	4 794(8)
O(6)	3 458(6)	4 968(8)	300(6)	C(28)	3 441(10)	−138(11)	3 897(7)
C(7)	−1 535(9)	4 457(12)	3 990(7)	H(1)	−856(101)	3 724(126)	2 677(74)
O(7)	−2 449(7)	4 677(10)	4 447(6)	H(2)	380(101)	5 054(125)	1 154(76)
C(8)	627(9)	4 966(12)	3 896(7)	H(3)	−679(97)	6 842(116)	2 939(71)
O(8)	1 008(7)	5 489(9)	4 287(5)	H(4)	−1 216(92)	6 483(113)	2 255(69)

(*d*) $[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$ (**5b**)

Pt(1)	3 973(1)	7 933(1)	3 661(1)	Pt(5)	537(1)	2 006(1)	3 381(1)
Os(2)	5 017(1)	6 854(1)	4 343(1)	Os(7)	−449(1)	860(1)	2 731(1)
Os(3)	4 433(1)	8 249(1)	4 907(1)	Os(6)	1 080(1)	414(1)	3 283(1)
Os(4)	3 561(1)	6 875(1)	4 477(1)	Os(8)	781(1)	1 459(1)	2 297(1)
P(1)	4 157(3)	8 269(8)	2 706(2)	P(5)	786(3)	2 589(3)	4 332(2)
C	4 006(11)	7 315(11)	5 392(8)	C(40)	−83(11)	591(11)	1 951(8)
C(10)	3 097(11)	8 430(10)	3 596(8)	C(50)	183(10)	2 910(10)	2 951(7)
O(10)	2 524(10)	8 754(9)	3 558(7)	O(50)	−47(8)	3 471(7)	2 666(6)
C(1)	4 810(10)	5 958(9)	3 822(7)	C(46)	−697(10)	1 114(10)	3 509(8)
O(1)	4 677(8)	5 444(8)	3 487(6)	O(46)	−901(8)	1 194(7)	3 931(6)
C(2)	6 004(10)	7 044(10)	4 239(8)	C(45)	−1 114(11)	1 627(11)	2 321(9)
O(2)	6 589(9)	7 137(9)	4 193(7)	O(45)	−1 488(9)	2 088(9)	2 061(7)
C(3)	5 221(11)	6 163(11)	5 011(9)	C(44)	−1 124(10)	31(10)	2 565(8)
O(3)	5 349(8)	5 740(8)	5 413(6)	O(44)	−1 519(9)	−514(9)	2 462(7)
C(4)	4 988(11)	8 518(11)	5 666(9)	C(42)	1 017(11)	−340(11)	3 922(8)
O(4)	5 318(10)	8 641(10)	6 136(8)	O(42)	1 047(9)	−825(9)	4 269(7)
C(5)	3 673(13)	8 920(13)	5 001(10)	C(41)	2 044(12)	717(11)	3 594(9)
O(5)	3 145(11)	9 301(11)	5 059(8)	O(41)	2 616(10)	885(10)	3 802(8)
C(6)	4 835(11)	9 079(11)	4 498(9)	C(43)	1 368(11)	−292(11)	2 722(9)
O(6)	5 140(9)	9 625(9)	4 319(7)	O(43)	1 550(9)	−716(9)	2 372(7)
C(7)	3 543(12)	5 928(12)	4 908(9)	C(49)	1 600(12)	2 116(11)	2 629(9)
O(7)	3 545(9)	5 343(9)	5 196(7)	O(49)	2 162(9)	2 443(9)	2 785(7)
C(8)	2 637(18)	7 268(13)	4 547(10)	C(47)	1 206(10)	965(10)	1 709(8)
O(8)	2 053(10)	7 481(10)	4 605(8)	O(47)	1 485(9)	670(9)	1 367(7)
C(9)	3 204(10)	6 400(10)	3 691(8)	C(48)	275(10)	2 247(10)	1 746(8)
O(9)	2 947(8)	6 058(8)	3 284(6)	O(48)	−30(9)	2 686(9)	1 411(7)
C(11)	3 714(10)	9 241(9)	2 435(7)	C(51)	1 514(9)	3 346(9)	4 407(7)
C(12)	3 784(11)	9 487(11)	1 784(8)	C(52)	1 325(9)	4 050(9)	3 951(7)
C(13)	3 267(12)	10 213(11)	1 588(9)	C(53)	1 930(10)	4 660(10)	4 017(8)
C(14)	3 451(12)	10 898(11)	2 037(8)	C(54)	2 636(10)	4 256(10)	3 947(8)
C(15)	3 411(12)	10 665(12)	2 660(9)	C(55)	2 839(11)	3 585(11)	4 387(9)
C(16)	3 905(11)	9 930(11)	2 861(9)	C(56)	2 218(10)	2 976(10)	4 339(8)
C(17)	3 701(10)	7 552(9)	2 139(7)	C(57)	−36(9)	3 034(9)	4 536(7)
C(18)	2 882(11)	7 519(11)	2 067(9)	C(58)	−628(10)	3 325(10)	4 017(8)
C(19)	2 525(12)	6 942(11)	1 577(9)	C(59)	−1 312(12)	3 568(11)	4 213(9)
C(20)	2 845(11)	6 107(12)	1 689(10)	C(60)	−1 190(11)	4 219(11)	4 712(8)
C(21)	3 694(12)	6 127(12)	1 753(9)	C(61)	−569(11)	3 939(12)	5 238(9)

Table 7 (*continued*)

(*d*) $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(\text{cyclo-}C_6H_{11})_3\}]$ **(5b)**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(22)	4 029(11)	6 697(10)	2 256(8)	C(62)	115(11)	3 696(11)	5 024(9)
C(23)	5 119(9)	8 255(9)	2 648(7)	C(63)	1 165(10)	1 868(9)	4 929(7)
C(24)	5 565(11)	8 897(11)	3 038(9)	C(64)	627(11)	1 183(11)	4 998(9)
C(25)	6 380(12)	8 776(12)	3 089(9)	C(65)	1 007(13)	534(12)	5 392(9)
C(26)	6 524(12)	8 806(11)	2 446(9)	C(66)	1 326(12)	863(12)	6 037(9)
C(27)	6 119(12)	8 163(12)	2 045(10)	C(67)	1 843(11)	1 575(11)	5 978(8)
C(28)	5 293(11)	8 274(11)	2 022(8)	C(68)	1 473(11)	2 222(10)	5 541(8)

applied based on a six-parameter fit to azimuthal scan data collected at room temperature.

The structures were refined to convergence by blocked-cascade full-matrix least squares. Cyclohexyl-group hydrogen atoms were incorporated into the final refined model at idealised geometries with C–H 0.96 Å and tetrahedral geometry for carbon atoms. Hydride-hydrogen atoms were placed at calculated positions[12] (with metal–hydrogen distance *ca.* 1.85 Å) for complexes **(2)** and **(4)**, and hydride and methylene hydrogens allowed to refine without positional constraints in **(5a)**. Hydrogen-atom thermal parameters were fixed at values *ca.* 1.2 times those of their carbon atoms, except in the case of **(5b)** where they were assigned refined common thermal parameters [final value 0.044(1) Å^2]. Final electron-density difference syntheses showed no features of chemical significance, the largest peaks and troughs being within *ca.* 1 Å of the metal atoms. Analyses of the variations of the sum of $w\Delta^2$ [$\Delta = (F_o - |F_c|)$] according to $|F_o|$ and sin θ indicated that the weighting schemes used were appropriate. The resultant positional co-ordinates for the atoms, other than the cyclohexyl-group hydrogens, are given in Table 7. All atoms were assigned complex neutral atom scattering factors taken from ref. 21. All calculations were carried out on a Nicolet R3m/E structure-determination facility using programs of the SHELXTL package.[22]

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