Synthesis of Tetra- and Penta-nuclear Platinum–Osmium Carbido-cluster Complexes from Non-carbido-precursors: *X*-Ray Structural Studies on $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$, $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$, and $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ *

Louis J. Farrugia, Anthony D. Miles, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The reaction between the compounds $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ in toluene at 80 °C affords two cluster complexes, one containing a single platinum atom $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(C_6H_{11})_3\}]$ (**1**), and the other two platinum atoms, $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**2**). Both have been characterised by single-crystal *X*-ray diffraction studies. Compound (**1**) contains a triangle of osmium atoms [Os–Os 2.828(1)—2.906(1) Å], with the Pt atom bonded to one osmium [Os(2)–Pt 2.764(1) Å]. The carbido-carbon atom is irregularly bonded [1.90(2)—2.21(2) Å] to all four metal atoms. Each osmium atom is ligated by three terminal carbonyl ligands, whilst the platinum atom is bonded to a terminal carbonyl group and a $P(cyclo\text{-}C_6H_{11})_3$ moiety. Two hydrido-ligands bridge the Os(1)–Os(3) and Os(1)–Os(2) vectors. Compound (**2**) contains a square-planar arrangement comprising two osmium and two platinum atoms with the third osmium atom [Os(3)] bridging the Os(1)–Os(2) edge. The angle between the planes Os(1)Os(2)Pt(1)Pt(2) and Os(1)Os(2)Os(3) is 76.4°. The carbido-carbon atom is approximately equidistant [2.065(11)—2.120(10) Å] from all five metal atoms, and the metal–metal separations are Os–Os 2.855(1)—2.917(1), Os–Pt 2.929(1)—2.935(1), and Pt(1)–Pt(2) 2.716(1) Å. Each osmium atom carries three terminal carbonyl ligands, whilst the platinum atoms are symmetrically bridged by a carbonyl ligand, and each is ligated by a $P(cyclo\text{-}C_6H_{11})_3$ group. The two hydrido-ligands bridge equivalent edges [Os(1)–Os(3) and Os(2)–Os(3)]. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) are all consistent with the structures established in the solid state. Treatment of $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ with $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ in toluene at ambient temperatures affords a pentanuclear metal complex $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**3**), the structure of which was again determined by single-crystal *X*-ray diffraction. Two platinum and two osmium atoms are arranged in a 'buckled' square with the third osmium atom [Os(3)] metal–metal bonded only to Os(1). As in (**2**), the carbido–metal distances are approximately equal [2.075(22)—2.144(20) Å]. Moreover, the metal–metal distances Os–Os [2.813(1)—2.853(1) Å] and Os–Pt [2.891(1)—2.941(1) Å] are rather similar to those in (**2**) but the Pt–Pt distance [2.668(1) Å] is noticeably shorter. In (**3**) each osmium atom carries three terminal carbonyl ligands, while a single carbonyl group asymmetrically bridges the two platinum atoms [Pt–μ-CO 2.032(23) and 1.968(20) Å]. Each platinum bears a $P(cyclo\text{-}C_6H_{11})_3$ group, with the hydrido-ligand bridging the shorter of the two Pt–Os edges [Pt(1)–Os(1)]. The n.m.r. spectra are consistent with the structure established in the solid state though some dynamic behaviour is evident.

The labile complexes $[Pt(C_2H_4)_2(PR_3)]$ (R = alkyl or aryl) are useful building blocks in the synthesis of heteronuclear metal cluster compounds by virtue of their ability to react with either electronically unsaturated or saturated metal–carbonyl complexes.[1] The products contain 'carbene-like' $Pt(CO)(PR_3)$ fragments,[2] and examples of these syntheses include $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[3] $[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PBu^t{}_2Me)_2]$ from $[W\{=C(OMe)Ph\}(CO)_5]$,[4] and $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ from $[N(PPh_3)_2][Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]$.[5] In this paper we describe reactions between the complex $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$[6] and $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$,[7] and between the platinum compound and $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$.[8] The study involving $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ was prompted by a wish to prepare an Os_3Pt cluster compound containing a metal-bridging CH fragment. There is currently considerable interest in polynuclear metal complexes containing bridging methylidyne groups on account of the putative intermediacy of such species in metal surface chemistry. Thus the conversion of metal–carbido-groups into bridging methylene, presumably *via* CH fragments, is thought to be a key step in the reduction of CO.[9–11]

Several homonuclear trimetal complexes have been reported with capping CH fragments in which the C–H vector is perpendicular to the trimetal plane, *e.g.* $[Co_3(\mu_3\text{-}CH)(CO)_9]$,[12] $[M_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9]$ (M = Ru[13] or Os[14]), $[Fe_3(\mu_3\text{-}CH)(CO)_{10}]^-$,[15] $[Rh_3(\mu_3\text{-}CH)(CO)_2(\eta\text{-}C_5H_5)_3]^+$,[16,17] and $[Rh_3(\mu_3\text{-}CH)_2(\eta\text{-}C_5H_5)_3]^+$.[18] For reaction with $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$, however, the compound $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$[7] is of more interest, since the methylidyne

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* μ_4-Carbido-1,2,2,2,3,3,3,4,4,4-decarbonyl-2,3;3,4-di-μ-hydrido-1-(tricyclohexylphosphine)-*cyclo*-platinumtriosmium(3 *Os–Os*)(*Pt–Os*), μ_5-carbido-1,2-μ-carbonyl-3,3,3,4,4,4,5,5,5-nonacarbonyl-3,4;4,5-di-μ-hydrido-1,2-bis(tricyclohexylphosphine)-*cyclo*-diplatinumtriosmium (3 *Os–Os*)(2 *Pt–Os*)(*Pt–Pt*), and μ_5-carbido-1,2-μ-carbonyl-3,3,3,4,4,4,5,5,5-nonacarbonyl-2,3-μ-hydrido-4,5-μ-methoxo-1,2-bis-(tricyclohexylphosphine)-*cyclo*-diplatinumtriosmium(2 *Pt–Os*)(2 *Os–Os*)(*Pt–Pt*) respectively.

Supplementary data available (No. SUP 56311, 13 pp.): H-atom co-ordinates, thermal parameters, remaining bond angles for (1)—(3). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

group adopts an unusual bonding mode, symmetrically bridging two osmium atoms and interacting with a third in such a manner as to imply a two-electron donation from an $Os(CO)_4$ centre to the CH group. In contrast, there is an agostic[19] C–H···metal interaction in the tetrairon complex $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$[20] with the CH ligand acting as a two-electron donor to an adjacent unsaturated iron centre. There seemed no reason why one or other of these kinds of CH–metal interactions might not be found in a methylidyne-bridged heteronuclear cluster of osmium and platinum. In practice, the reaction between $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ and $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ did not afford a product containing a μ_4-CH group but instead yielded two carbido-cluster complexes. For reasons discussed below, this result led to a study of the reaction between the platinum compound and the methoxymethylidynetriosmium complex $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$.

Results and Discussion

The reaction between $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ was carried out in toluene at 80 °C for 12 h, since initial experiments revealed that only a slow reaction occurred at ambient temperatures. After chromatography of the products on alumina, moderate yields of a yellow solid were obtained. A $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum revealed this solid to be a mixture of two complexes, one containing one $Pt\{P(cyclo\text{-}C_6H_{11})_3\}$ unit, the other containing two chemically equivalent $Pt\{P(cyclo\text{-}C_6H_{11})_3\}$ units. Fractional crystallisation of the mixture from light petroleum gave analytically and spectroscopically pure samples of two cluster complexes: $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(C_6H_{11})_3\}]$ (**1**) and $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**2**). Compound (**1**) displayed a singlet at 34.1 p.p.m. in its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, the magnitude of the $^{195}Pt\text{–}^{31}P$ coupling (3 530 Hz) indicating the presence of a direct phosphorus–platinum bond.[3] The ^1H n.m.r. spectrum showed two high-field signals at δ −18.43 and −21.52, indicating the presence of two inequivalent hydrido-ligands. Some fluxional behaviour is evident since the signals were broad at ambient temperatures and sharp at −40 °C, whilst the small couplings to ^{195}Pt (35 and 13 Hz, respectively) indicated the absence of a direct Pt–H bond.

Interestingly, a deshielded resonance observed in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**1**) at δ 304.3 p.p.m. [J(Pt–C) 780 Hz] could be ascribed either to a μ-*C*H ligand or to a μ-carbido-group. To date, $^{13}C\text{-}\{^1H\}$ n.m.r. data on these systems are rather sparse but the μ-CH ligand resonates at δ 335 in $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$,[20] at δ 303.6 in $[Rh_3(\mu_3\text{-}CH)(CO)_2(\eta\text{-}C_5H_5)_3]^+$,[17] at δ 262.4 in $[Fe_3(\mu_3\text{-}CH)(CO)_{10}]^-$,[15] and at δ 219 in $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$.[7] Carbido-carbon resonances are invariably very deshielded,[21,22] in the range 486—264 p.p.m., with δ 486.0 for $[Fe_5(\mu_5\text{-}C)(CO)_{15}]$ representing the largest ^{13}C shift reported[21] for a diamagnetic organometallic compound. The signal at δ 304.3 for (**1**) is towards the high-field end of the above range, and in view of the presence of the two hydrido-ligands, indicated by the ^1H n.m.r. spectrum, and the diamagnetism of (**1**) it seemed highly likely that this resonance was due to a carbido-carbon. The *X*-ray diffraction results for (**1**) (see later) support this hypothesis.

For complex (**2**), the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum displayed a singlet at δ 32.7 p.p.m. with coupling patterns to ^{195}Pt nuclei consistent[5,23] with the presence of a $(cyclo\text{-}C_6H_{11})_3\text{P–Pt–Pt–P}(cyclo\text{-}C_6H_{11})_3$ unit with chemically equivalent ^{31}P nuclei [J(PtP) 4 840 and 267 Hz]. One signal was observed for hydrido-ligands in the ^1H n.m.r. spectrum at δ −20.67 [J(PtH) 12 Hz]. A low-field resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at 322.2 p.p.m. was a triplet with ^{195}Pt satellite peaks [J(PC) 49, J(PtC) 318 Hz] consistent with a carbido-ligand coupled to the two sets of equivalent ^{31}P and ^{195}Pt nuclei. In addition to the observation of several terminal carbonyl stretches in the i.r. spectrum, a low frequency band at 1 786 cm^{-1} indicated the presence of a bridging carbonyl ligand, which was also evidenced by a signal at 215.1 p.p.m. [J(PtC) 1 153 Hz] in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum.

In order to establish the structures of compounds (**1**) and (**2**), and to confirm the presence of carbido-ligands, single-crystal *X*-ray diffraction studies were carried out on both complexes. The molecular structure of (**1**) is shown in Figure 1, and a stereoview in Figure 2. Corresponding views of (**2**) are shown in Figures 3

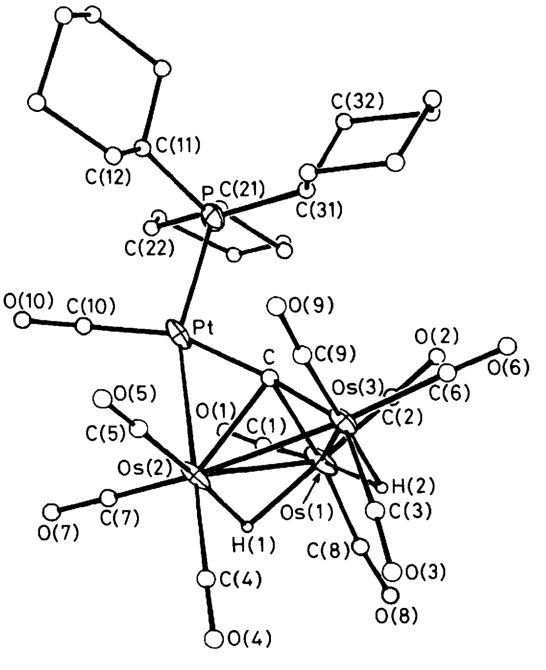

Figure 1. The molecular structure of $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ (**1**), showing the crystallographic numbering

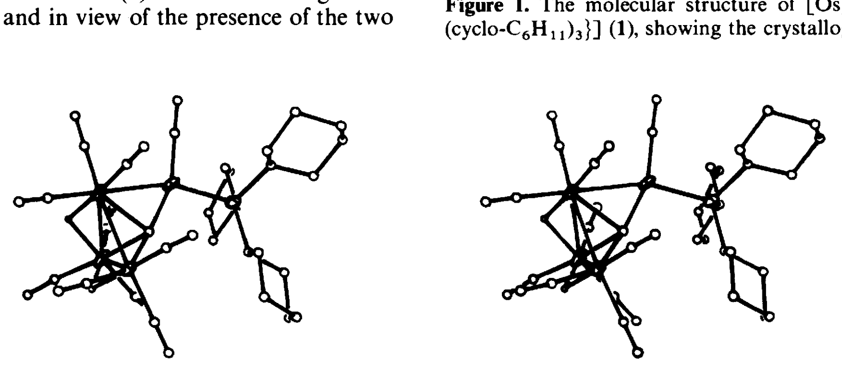

Figure 2. Stereoscopic view of (**1**)

and 4. The results of the structure determinations are summarised in Tables 1 and 2.

Complex (**1**) contains a triangle of osmium atoms [Os–Os separations 2.828(1)—2.906(1) Å] with the platinum bonded to only one of the osmium atoms [Os(2)–Pt 2.764(1) Å]. The Os(2)–Pt vector is inclined at 75.2° to the Os_3 plane. The carbido-carbon atom caps the triosmium face, somewhat asymmetrically (though high e.s.d.s prevent meaningful comparisons), and is also bonded to the platinum atom. The rather 'open' metal framework can be rationalised in terms of the 62 c.v.e. (cluster valence electrons) of the complex. The co-ordination around the platinum is nearly planar, with the greatest deviation from the mean plane defined by P, C(10), Os(2), Pt, and C being 0.12 Å for the carbido-ligand; this situation being consistent with a 16-electron configuration at the metal centre. In many platinum-containing cluster complexes, structures are observed which appear to be electron deficient. Thus in $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$[23] the 'butterfly' arrangement of the Os_3Pt core is associated with 60 c.v.e., rather than the more usual 62. With one atom of Pt present in complex (**1**) we may expect this 62 c.v.e. cluster to have a similar metal framework to that of a 64 c.v.e. compound, *i.e.* a species possessing one extra electron pair. Indeed the complex anion $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$ with 64 c.v.e. has the same metal arrangement[24] as observed in (**1**).

It is convenient to view the metal framework in (**1**) as derived from a 'butterfly' arrangement with the Os(1)–Pt bond broken. Of the two non-bonding Os–Pt distances (Table 1), Os(1)–Pt is the shortest, 3.486(1) *vs.* 3.834(1) Å. Thus Os(1) and Os(2) may be viewed as 'hinge' atoms, and Os(3) and Pt as 'wingtip' atoms. The co-ordination mode of the carbido-carbon may be then compared with that observed for the isoelectronic 62 c.v.e. 'butterfly' cluster compounds $[Fe_4(\mu_4\text{-}C)(CO)_{13}]$,[25] $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$,[26] and $[Fe_4(\mu\text{-}H)(\mu_4\text{-}C)(CO)_{12}]^-$.[27] The major differences are due to the distortion away from a 'butterfly' configuration in (**1**). This is reflected in the Pt–C–Os(3) angle of of 151(1)°, as compared with the nearly collinear 'wingtip'–carbido–'wingtip' arrangements found in the tetrairon complexes.[25–27] Interestingly, the pseudo-'hinge' atom to carbide distances in (**1**) [2.21(2) and 2.16(2) Å] are noticeably longer than the pseudo-'wingtip' to carbide separations [2.05(2) and 1.90(2) Å]. This trend is also consistently observed in the aforementioned tetrairon carbido-complexes,[25–27] as well as for the Fe–N separations in $[Fe_4(\mu_4\text{-}N)(CO)_{12}]^-$,[28] and this is in agreement with the view that (**1**) is derived from a 'butterfly' arrangement. In a recent theoretical study[29] these structural features of tetrairon carbide 'butterfly' clusters have been explained in terms of the metal–carbide bonding. Computed overlap populations for the carbide to 'wingtip-iron' orbitals are considerably greater than for the carbide to 'hinge-iron' orbitals, due in the main to the extensive σ overlap between the carbido-carbon p_y and cluster b_2 orbitals. Optimisation of this σ overlap, as well as important π interactions, tends to favour a collinear 'wingtip'–carbido–'wingtip' configuration with substantially stronger 'wingtip-iron' to carbide than 'hinge-iron' to carbide bonding. Intuitively one might expect that similar σ and π interactions in complex (**1**) would be reduced due to the observed deviation from linearity in Pt–C–Os(3) [151(1)°]. One must be aware, however, that the $Fe_4(\mu_4\text{-}C)$ model of Harris and Bradley[29] may not be realistically applicable to the $Os_3Pt(\mu_4\text{-}C)$ system present in (**1**) due to substantial differences in the orbital energies (H_{ii}), especially for the platinum atom.

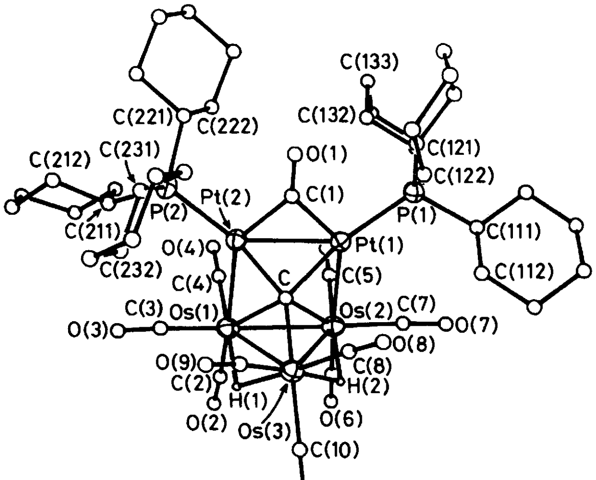

Figure 3. The molecular structure of $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ (**2**), showing the crystallographic numbering

In general, the carbido-ligand has been shown to be sterically undemanding with co-ordination numbers of four, five, six, and eight having been observed in both regular and irregular geometries.[21] Evidence also exists for reactive three-co-ordinate carbido-intermediates.[15,26] In complex (**1**) the co-ordination mode of the carbido-ligand is irregular, and presumably the bonding in this system may only be elucidated by detailed molecular orbital (m.o.) studies.[30]

Complex (**1**) is an example of a tetranuclear mixed-metal carbido-cluster involving the platinum metals, and the rather 'open' metal framework suggests that the carbido-carbon may be sterically accessible and hence reactive. To date reactivity of the carbido-ligand has only been demonstrated in tetrairon systems,[21,27,31] and this reactivity has been the focus of two recent m.o. studies by Harris and Bradley[29] and by Hoffmann and co-workers.[30] The two studies agree essentially that the h.o.m.o. and l.u.m.o. of $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ have little if any carbon character, and thus attack by non-oxidising nucleophiles is likely to take place at the 'hinge' iron atoms rather than at the carbido-atom. Interestingly, the charge on the carbon atom is calculated[29] to be −0.6 e, in line with the view[21] that the

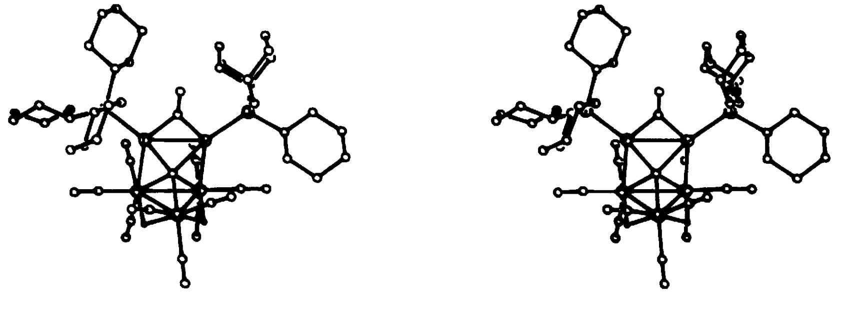

Figure 4. Stereoscopic view of (**2**)

Table 1. Selected internuclear distances (Å) and angles (°) for the complex $[Os_3Pt(\mu-H)_2(\mu_4-C)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ (**1**)

Pt–Os(1)	3.486(1)	Os(1)–C	2.16(2)
Pt–Os(2)	2.764(1)	Os(2)–C	2.21(2)
Pt–Os(3)	3.834(1)	Os(3)–C	2.05(2)
Os(1)–Os(2)	2.906(1)	Pt–C	1.90(2)
Os(1)–Os(3)	2.864(1)	Pt–P	2.297(6)
Os(2)–Os(3)	2.828(1)	Pt–C(10)	1.84(2)
Mean Os–C(CO)	1.88	Mean P–C	1.835
Mean C–O	1.16	Mean C–C	1.514
Pt–Os(2)–Os(1)	75.8(1)	Os(1)–Os(3)–C(3)	114.4(9)
Os(2)–Pt–C(10)	108.1(7)	Os(3)–Os(1)–C(8)	121(1)
Os(2)–Pt–C	52.8(6)	Os(2)–Os(1)–C(8)	117(1)
P–Pt–C	104.0(6)	Os(1)–Os(2)–C(4)	106.9(7)
P–Pt–C(10)	95.5(8)	Os(2)–Os(3)–C(9)	94.2(8)
Pt–C–Os(3)	151(1)	Os(3)–Os(2)–C(5)	92.5(8)
Os(2)–C–Os(3)	82.9(7)	Os(2)–Os(1)–C(1)	96(1)
Os(1)–C–Os(3)	85.5(7)	Pt–C(10)–O(10)	179(2)
Os(1)–C–Os(2)	83.1(7)	Mean Os–C–O	175.7

Table 2. Selected internuclear distances (Å) and angles (°) for the complex $[Os_3Pt_2(\mu-H)_2(\mu_5-C)(\mu-CO)(CO)_9\{P(cyclo-C_6H_{11})_3\}_2]$ (**2**)

Os(1)–Os(2)	2.855(1)	Os(1)–C	2.087(9)
Os(1)–Os(3)	2.916(1)	Os(2)–C	2.120(10)
Os(2)–Os(3)	2.917(1)	Os(3)–C	2.110(11)
Os(1)–Pt(2)	2.929(1)	Pt(1)–C	2.101(9)
Os(2)–Pt(1)	2.935(1)	Pt(2)–C	2.065(11)
Os(3)–Pt(2)	3.693(1)	Pt(1)–P(1)	2.287(3)
Os(3)–Pt(1)	3.628(1)	Pt(2)–P(2)	2.290(3)
Pt(1)–Pt(2)	2.716(1)	Mean Os–C(CO)	1.919
Pt(1)–C(1)	1.990(13)	Mean C–O (terminal)	1.15
Pt(2)–C(1)	1.968(11)	Mean C–C	1.526
C(1)–O(1)	1.207(15)	Mean P–C	1.862
Os(1)–Pt(2)–Pt(1)	92.0(1)	Os(1)–C–Os(3)	88.0(4)
Os(1)–Os(2)–Pt(1)	89.1(1)	Os(1)–C–Pt(2)	89.7(4)
Os(2)–Pt(1)–Pt(2)	90.7(1)	Pt(2)–C–Pt(1)	81.4(4)
Os(2)–Os(1)–Pt(2)	88.1(1)	Pt(1)–C–Os(2)	88.1(4)
Os(1)–Os(2)–Os(3)	60.7(1)	Os(2)–C–Os(3)	87.2(4)
Os(2)–Os(1)–Os(3)	60.7(1)	Pt(2)–C(1)–O(1)	137.4(10)
Os(1)–Os(3)–Os(2)	58.6(1)	Pt(1)–C(1)–O(1)	135.7(10)
Os(2)–Os(3)–C(8)	97.9(5)	Os(1)–Os(3)–C(9)	94.6(4)
Os(2)–Os(3)–C(10)	116.6(3)	Os(3)–Os(3)–C(10)	120.6(3)
Os(3)–Os(2)–C(7)	108.4(5)	Os(3)–Os(1)–C(3)	106.5(4)
Os(3)–Os(2)–C(6)	108.0(4)	Os(3)–Os(1)–C(2)	108.2(4)
Mean *cis*-Os–Os–C	93.8		

low-field shifts observed in the ^{13}C n.m.r. spectra of carbido-metal complexes cannot be ascribed to deshielding due to a positive charge at carbon. In addition to the above electronic barriers to reactivity, the apparent exposure of the carbido-ligand in complex (**1**) as seen in Figure 1 is deceptive. A space-filled view of (**1**) (Figure 5), where each atom is drawn with van der Waals radii, reveals considerable steric hindrance to attack at the carbon atom.

The hydrido-ligand positions in (**1**) were determined from potential energy minimisation calculations[32] and are consistent with the ^1H n.m.r. data in that distinct Os(μ-H)Os sites are present. As is usually observed, the hydrido-bridged edges Os(1)–Os(3) [2.864(1) Å] and Os(1)–Os(2) [2.906(1) Å] are longer than the unbridged edge Os(2)–Os(3) [2.828(1) Å].

In the compound $[Os_3Pt_2(\mu-H)_2(\mu_5-C)(\mu-CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**2**) (Figure 3) the metal framework can be viewed as derived from a square pyramid with two platinum–osmium bonds having been broken, since Pt(1)–Os(3) [3.628(1) Å] and Pt(2)–Os(3) [3.693(1) Å] are too long to be considered bonding.

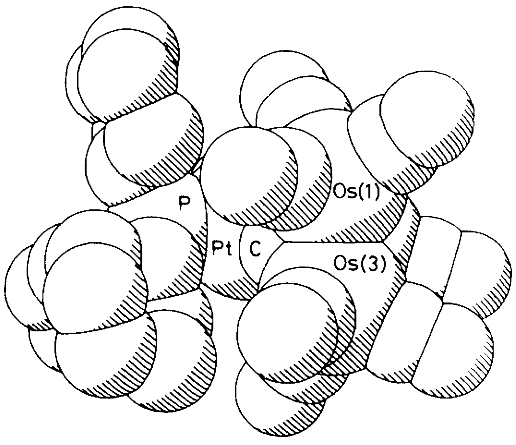

Figure 5. Space-filling diagram of complex (**1**) emphasising the protection of the carbido-ligand by the bulky ligands

The angle between the planes defined by the metal atom triangle Os(1)Os(2)Os(3) and the square Os(1)Os(2)Pt(1)Pt(2) is 76.4°. Each osmium atom carries three terminal carbonyl ligands with a bridging carbonyl group between the platinum atoms. Complex (**2**) has an approximate molecular, though not crystallographically defined, mirror plane through C(1), O(1), C, Os(3), C(10), and O(10). Thus the platinum nuclei are equivalent, as are the phosphorus and hydrido-ligands; as was indicated by the n.m.r. evidence discussed above. The hydrido-positions[32] are in accord with the observed Os–Os separations [Os(1)–Os(2) 2.855(1), Os(1)–Os(3) 2.916(1), and Os(2)–Os(3) 2.917(1) Å], the usual lengthening for the presence of hydride being observed. The two Os–Pt bonding distances are closely similar [Os(1)–Pt(2) 2.929(1), Os(2)–Pt(1) 2.935(1) Å] reflecting the pseudo mirror symmetry of the molecule, which is also observable in the Pt(1)–C(1) [1.990(13) Å] and Pt(2)–C(1) [1.968(11) Å] distances.

The co-ordination mode of the carbide ligand is shown clearly in Figure 3. In contrast with the related pentanuclear osmium cluster $[Os_5(\mu_5-C)(CO)_{15}]$[33] where the carbido-atom is displaced 0.12 Å out of the basal plane away from the apical osmium atom, in (**2**) there is a 0.54 Å displacement towards the apical Os(3), out of the mean plane defined by Os(1), Os(2), Pt(1), and Pt(2). This is in line with the retention of essentially equal carbide bonding distances to all five metal atoms in (**2**), whilst at the same time moving the apical metal Os(3) away from the two platinum atoms and formally breaking these Os(3)–Pt bonds. The range of metal–carbide separations in (**2**) is 2.065(11)—2.120(10) Å with the mean distance (2.09 Å) only slightly longer than that found in $[Os_5(\mu_5-C)(CO)_{15}]$ (2.06 Å).[33]

There is a close conceptual and structural relationship between the 74 c.v.e. cluster $[Os_5(\mu_5-C)(CO)_{15}]$,[33] the 76 c.v.e. species $[Os_5I(\mu_5-C)(CO)_{15}]^-$,[33] $[Os_5(\mu-H)(\mu_5-C)(CO)_{14}\{OP(OMe)_2\}]$,[34] $[Os_5(\mu-H)(\mu_5-C)(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}]$,[35] and $[Os_5(\mu-H)(\mu_5-C)(CO)_{13}\{OP(OMe)OP(OMe)_2\}]$,[36] and complex (**2**), the last being a 74 c.v.e. compound. Using previously elaborated arguments, with two platinum atoms present we might expect (**2**) to have structural similarities to a complex containing two extra electron pairs, *i.e.* a 78 c.v.e. species. The compound $[Os_5I(\mu_5-C)(CO)_{15}]^-$ (76 c.v.e.) has a structure described[33] as an *arachno* pentagonal bipyramid, though it may also be viewed as derived from the square-pyramidal structure of the parent 74 c.v.e. complex $[Os_5(\mu_5-C)(CO)_{15}]$ by scission of one of the apical–basal bonds. A distortion of the square base is clearly required in order to provide three bonding and one non-bonding apical–basal interactions, and such a distortion is visible in $[Os_5I(\mu_5\text{-}C)(CO)_{15}]^-$ and indeed all the 76 c.v.e. Os_5 cluster complexes mentioned above.[33–36] Addition of a further two electrons, giving a 78 c.v.e. species, might be expected to furnish a structure based on the square pyramid, this time with two non-bonding apical–basal interactions. If the bonds are broken to two adjacent basal atoms then there is no required distortion of the square base. The structure of complex (**2**) is fully in accord with this view, since angles within the square Os(1)–Os(2)–Pt(1)–Pt(2) range from 88.1(1) to 92.0(1)°, with the greatest deviation of any metal atom from the mean plane being 0.035 Å. The differing sizes of Os and Pt may account for these minor deviations from strict square planarity. Interestingly the 78 c.v.e. complex $[Os_5(CO)_{19}]$ reported by Lewis and co-workers[37] has a 'bow-tie' structure, which can be thought to arise from a square-pyramidal structure by scission of two non-adjacent basal–basal interactions, rather than the two adjacent apical–basal bonds affected in the structure of (**2**).

The bridging CO ligand in (**2**) has a normal symmetric geometry with a slightly lengthened CO vector [C(1)–O(1) 1.207(15) Å] over the averaged terminal CO bond (1.15 Å). The terminal carbonyl ligands in both complexes (**1**) and (**2**) are essentially linear, and the tricyclohexylphosphine groups display the usual geometry.

The mechanism of formation of the carbido-complexes (**1**) and (**2**) from the methylidyne cluster $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ poses some interesting questions, especially in the light of recent observations. As mentioned in the Introduction, the methylidyne group in $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$ adopts a different bonding mode to the μ_3-CH group in $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$. This is reflected in different chemical behaviour, thus in the tetrairon compound the CH group is acidic, and spin-saturation n.m.r. studies reveal hydrogen exchange between the Fe(μ-H)C and Fe(μ-H)Fe sites.[31] We have observed that treatment of $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$ with $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$ results in deprotonation of the former to give $[Fe_4(\mu\text{-}H)(\mu_4\text{-}C)(CO)_{12}]^-$. Although in $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ the CH group is not acidic it is perhaps not too improbable to postulate transfer of hydrogen from the methylidyne ligand to a metal–metal cluster edge during the synthesis of the complexes (**1**) and (**2**) using the reagent $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$. However, some recent results suggest that a different pathway should be considered. Shapley *et al.*[38] have reported the ready thermal conversion of $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ into the tautomeric ketenylidene complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ with some indication of reversibility. Moreover, the tri-iron ketenylidene complex anion $[Fe_3(\mu_3\text{-}CCO)(CO)_9]^{2-}$ has been recently shown[39] to react with the species $[M(CO)_3(NCMe)_3]$ (M = Mo or W), $[Mn(CO)_5(NCMe)]^+$, and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to give, respectively, the carbido-tetranuclear metal clusters $[Fe_3M(\mu_4\text{-}C)(CO)_{13}]^{2-}$, $[Fe_3Mn(\mu_4\text{-}C)(CO)_{13}]^-$, and $[Fe_3Rh(\mu_4\text{-}C)(CO)_{12}]^-$. Thus in the reaction of $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ with $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$ at 80 °C to give (**1**) and (**2**), the possibility exists that the products are formed *via* the intermediacy of the ketenylidene complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ rather than directly from $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$. In order to investigate this possibility, a solution of the latter alone was treated under the same conditions as gave rise to (**1**) and (**2**), *i.e.* heating at 80 °C in toluene for 12 h. Substantial, though not total, conversion to the ketenylidene complex was observed by examining the ^1H n.m.r. spectrum of the mixture. Subsequently a reaction of equimolar solutions of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ and $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$ at ambient temperatures was found to give readily a mixture of (**1**) and (**2**). It was not found possible to prevent the formation of the diplatinum species (**2**), even when a 1:1 molar ratio was used in the reactions. These results tend strongly to suggest, though not prove, that it is the complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ which is the reactive intermediate. Parallel reaction pathways involving both the ketenylidene complex and $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$, however, remain a distinct possibility in the synthesis of (**1**) and (**2**).

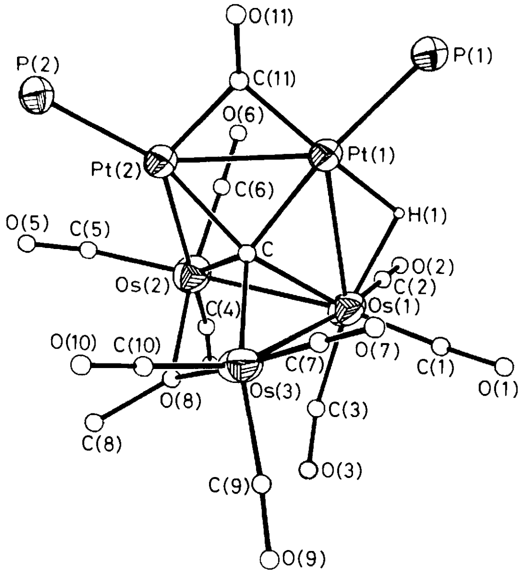

Figure 6. The molecular structure of $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(\text{cyclo-}C_6H_{11})_3\}_2]$ (**3**), showing the crystallographic numbering but with the cyclohexyl groups omitted for clarity

The synthesis of compounds (**1**) and (**2**) was repeated several times and during some experiments it was noticed that another complex, (**3**), was formed. This yellow compound showed a band in its i.r. spectrum at 1 794 cm^{-1}, as well as terminal carbonyl stretches in the range 2 071—1 960 cm^{-1}. Compound (**2**) has a Pt(μ-CO)Pt bridging carbonyl stretching frequency at 1 786 cm^{-1} and a rather similar fragment was suspected in the new complex. A $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum revealed a coupling pattern indicative[5] of two inequivalent phosphine ligands each bonded to inequivalent platinum atoms. In complex (**2**) the P and Pt nuclei are equivalent. In addition to the expected signals due to the cyclo-C_6H_{11} groups, the ^1H n.m.r. spectrum of (**3**) also displayed a doublet of doublets at δ −13.24; the coupling patterns indicating a hydrido-ligand coupled to two inequivalent pairs of phosphorus and platinum nuclei. Moreover, the magnitude of the larger ^{195}Pt coupling (656 Hz) indicated that a direct Pt–H bond was present in the molecule. Furthermore, a signal at δ 3.42, with an integrated intensity three times that of the high-field signal was not easily assignable to any expected ligand. Finally the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of this new complex was revealing. In addition to a low-field signal at 217.3 p.p.m. [*J*(PtC) 1 125 and 1 062 Hz] ascribable to a Pt(μ-CO)Pt unit and peaks due to osmium-bonded carbonyl ligands (185.8, 182.1, 176.5, and 175.6 p.p.m.), a doublet of doublets was observed at 385.3 p.p.m. in the region corresponding to a carbido-resonance. The spectroscopic data thus indicated that (**3**) was a complex somewhat similar to (**2**), but with some asymmetry rendering the two platinum atoms inequivalent. A single-crystal *X*-ray diffraction study was carried out on this complex, which was thus characterised as $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$. A view of (**3**) is given in Figure 6 with a stereoview in Figure 7. Selected bond distances and angles are given in Table 3.

The complex contains a pentanuclear Os_3Pt_2 core with unusual geometry involving a rather 'buckled' square arrangement of two Pt and two Os atoms with a third Os atom [Os(3)]

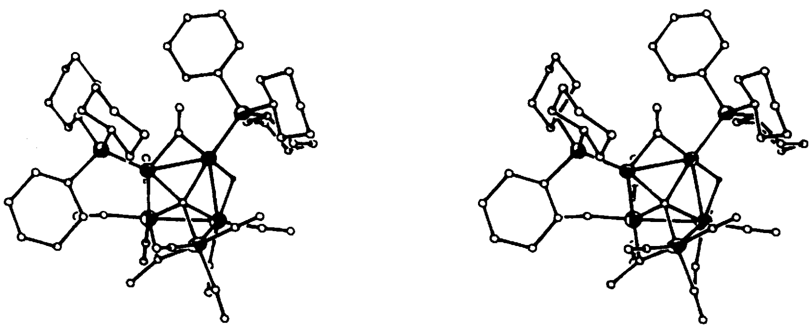

Figure 7. Stereoscopic view of (**3**)

Table 3. Selected internuclear distances (Å) and angles (°) for the complex $[Os_3Pt_2(\mu-H)(\mu_5-C)(\mu-OMe)(\mu-CO)(CO)_9\{P(cyclo-C_6H_{11})_3\}_2]$ (**3**)

Pt(1)–Pt(2)	2.668(1)	Pt(1)–P(1)	2.313(5)
Pt(1)–Os(1)	2.891(1)	Pt(2)–P(2)	2.265(6)
Pt(2)–Os(2)	2.941(1)	Pt(1)–C	2.078(19)
Os(1)–Os(2)	2.853(1)	Pt(2)–C	2.083(22)
Os(1)–Os(3)	2.813(1)	Os(1)–C	2.144(20)
Os(2)–Os(3)	3.328(1)	Os(2)–C	2.077(18)
Os(2)–O(8)	2.115(14)	Os(3)–C	2.075(22)
Os(3)–O(8)	2.104(12)	Pt(1)–C(11)	2.032(23)
C(8)–O(8)	1.46(3)	Pt(2)–C(11)	1.968(20)
Mean C–O (terminal)	1.14	C(11)–O(11)	1.18(3)
Mean Os–C(CO)	1.915	Mean P–C	1.85
		Mean C–C(C_6H_{11})	1.52

Pt(2)–Pt(1)–Os(1)	96.8(1)	Pt(1)–Os(1)–Os(2)	80.0(1)
Pt(1)–Pt(2)–Os(2)	82.2(1)	Os(2)–Os(1)–Os(3)	71.9(1)
Pt(1)–Os(1)–Os(3)	80.8(1)	Pt(2)–Os(2)–Os(1)	91.7(1)
Pt(1)–C(11)–Pt(2)	83.6(8)	Pt(1)–C(11)–O(11)	137.7(16)
Pt(2)–C(11)–O(11)	138.7(17)	Os(2)–O(8)–Os(3)	104.1(5)
Os(2)–O(8)–C(8)	122.3(16)	Os(3)–O(8)–C(8)	124.2(13)
Pt(1)–C–Pt(2)	79.6(7)	Pt(2)–C–Os(2)	89.8(8)
Pt(1)–C–Os(1)	86.4(7)	Os(1)–C–Os(2)	85.0(7)
Os(1)–C–Os(3)	83.6(8)	Pt(2)–C–Os(1)	158.5(11)
Os(2)–C–Pt(1)	125.5(10)	Os(2)–C–Os(3)	106.6(9)
H(1)–Pt(1)–P(1)	85.8(2)	Os(3)–C–Pt(1)	125.7(9)
H(1)–Pt(1)–C	86.4(6)	C(11)–Pt(1)–P(1)	92.5(6)
P(2)–Pt(2)–Os(2)	126.4(1)	C–Pt(1)–C(11)	95.3(8)
P(2)–Pt(2)–C	161.6(5)	P(2)–Pt(2)–C(11)	98.8(7)
C(5)–Os(2)–Os(1)	169.5(7)	P(2)–Pt(2)–Pt(1)	147.4(1)
C(4)–Os(2)–Pt(2)	170.4(11)	Os(2)–Os(1)–C(1)	167.4(7)
O(8)–Os(2)–C(6)	171.8(8)	Os(3)–Os(1)–C(2)	162.5(8)
O(8)–Os(3)–C(7)	172.3(7)	H(1)–Os(1)–C(3)	166.6(7)
C(9)–Os(3)–C	155.0(10)	Os(1)–Os(3)–C(10)	159.2(8)
Pt(1)–Os(1)–C(2)	103.5(8)	Os(2)–Os(1)–C(1)	167.4(7)
Os(2)–Os(1)–C(2)	91.8(8)	Pt(1)–Os(1)–C(1)	100.1(8)
Mean Os–C–O	175		

bonded to only Os(1) in the square [Os(1)–Os(3) 2.813(1), Os(2)–Os(3) 3.328(1) Å]. Atom Os(2) lies 1.16 Å below the plane defined by Pt(1)–Pt(2)–Os(1), with Os(3) 2.10 Å above this plane. This is in contrast with the square arrangement found in (**2**) where the greatest deviation from the mean plane of the four metal atoms is 0.035 Å. The arrangement of metal atoms in complex (**3**) can be thought to arise formally from that in (**2**) by the breaking of the Os(3)–Os(1) bond in the latter. The effect can easily be seen in the widening of the corresponding Os–C–Os angles bridging this vector. In (**3**), Os(3)–C–Os(2) is 106.6(9)°, whilst in (**2**), Os(3)–C–Os(1) is 88.0(4)°.

As a result of the distortion in (**3**), engendered by the absence of a direct Os(2)–Os(3) bond, Pt(1) and Pt(2) are clearly inequivalent, as was indicated by the n.m.r. evidence. A methoxy ligand [O(8)C(8), hydrogen atoms not included] bridges the Os(2)–Os(3) vector, and this group accounts for the resonance observed at δ 3.42 in the ^1H n.m.r. spectrum. In the initial stages of the structural refinement this bridging ligand was assumed to be a carbonyl group, but it became clear both from the values of the thermal parameters and from bond lengths and angles within the fragment that this was not the case. Confirmation of this feature as a bridging methoxy ligand was provided by the partially decoupled ^{13}C n.m.r. spectrum where a signal at δ 74.8 was observed as a quartet [*J*(CH) 141 Hz], in the expected region for OMe.

The geometry of the Os(μ-OMe)Os moiety in (**3**) is similar to that found in $[Os_3(\mu-OMe)_2(CO)_{10}]$.[40] Thus the μ-O–Os distance in (**3**) (av. 2.110 Å) may be compared with the corresponding average distance in $[Os_3(\mu-OMe)_2(CO)_{10}]$ (2.085 Å). The non-bonding Os–Os distance in the latter is somewhat shorter than in (**3**) [3.078(3) *vs.* 3.328(1) Å] with a corresponding more acute Os–O–Os angle [av. 95.5° *vs.* Os(2)–O(8)–Os(3) 104.1° in (**3**)]. The average O–Me distance in $[Os_3(\mu-OMe)_2(CO)_{10}]$ (1.43 Å) compares well with that observed in (**3**) (1.46 Å). In the more accurate structural study on $[Os_3(\mu-H)(\mu-OMe)(CO)_{10}]$[41] geometrical parameters are again comparable, having allowed for the nominal single Os–Os bond present in the Os(μ-OMe)Os fragment. Thus the Os–Os separation is 2.812(10) Å with Os–O–Os 83.9(2)° more acute than found in either (**3**) or $[Os_3(\mu-OMe)_2(CO)_{10}]$. The average Os–O distance is 2.102(9) Å and this bond distance and the O–Me separation [1.456(16) Å] compare well with those found in (**3**).

The carbido-ligand in (**3**) is essentially equidistant from all five metal atoms [distances in the range 2.075(22)—2.144(20) Å]. The co-ordination about the carbon atom approximates to distorted trigonal bipyramidal, as can be seen from the metal–carbide–metal angles in Table 3. Thus Pt(2)–C–Os(1) is 158.5 rather than 180°, with the mean plane Pt(2)–C–Os(1) inclined at 89.5° to the mean plane defined by Pt(1)–Os(2)–Os(3)–C. The environment about the carbide atom in (**3**) is generally similar to that observed in (**2**), making allowances for the distortions due to the scission of the Os(2)–Os(3) bond in (**3**).

The bridging carbonyl ligand [C(11)O(11)] is slightly more asymmetric in (**3**) than in (**2**), with Pt(1)–C(11) 2.032(23) Å and Pt(2)–C(11) 1.968(20) Å. Interestingly, the Pt(1)–Pt(2) distance in (**3**) [2.668(1) Å] is significantly shorter than that observed in (**2**) [2.716(1) Å], there being no obvious rationale for this. Potential energy minimisation calculations[32] indicate that the hydrido-ligand in (**3**) is located on the Os(1)–Pt(1) edge, in accord with the ^1H n.m.r. spectrum. Unusually, however, this hydride bridged vector [2.891(1) Å] is shorter than the unbridged Pt–Os bond [Pt(2)–Os(2) 2.941(1) Å]. Although the hydride atom was not located directly, the circumstantial evidence is strong. A Pt(μ-H)Os moiety was expected from the

^{1}H n.m.r. spectrum (see above). The disposition of carbonyl ligands around Os(1) shows the expected 'bending back', always observed due to the steric requirements of the hydride ligand. Thus the angles Pt(1)–Os(1)–C(2) [103.5(8)°] and Pt(1)–Os(1)–C(1) [100.1(8)°] are significantly greater than 90°, as compared with other *cis* metal–Os–C angles. In addition, the six atoms [C(4), C(5), C(6), O(8), Os(1), and Pt(2)] co-ordinating Os(2) (ignoring C) show little distortion from an octahedral disposition (see Table 3), strongly indicating that the hydrido-ligand does not bridge the Os(2)–Pt(2) edge. The terminal carbonyl ligands on the osmium atoms are essentially linear (av. Os–C–O 175°). The P(cyclo-C_6H_{11})$_3$ ligands display the usual geometry, and are not shown in Figure 6 in order to display the more significant structural features of the cluster more clearly.

The source of the μ-OMe group in complex (**3**) was traced to the presence of [Os_3(μ-H)(μ-COMe)(CO)$_{10}$][8] as an impurity in the starting material [Os_3(μ-H)(μ$_3$-CH)(CO)$_{10}$]. The μ-COMe-containing species is an intermediate in the preparation of the latter and some of this precursor may be reformed in the final stage of this synthesis.[7] A pure sample of [Os_3(μ-H)(μ-COMe)(CO)$_{10}$] was treated with [Pt(C_2H_4)$_2${P(cyclo-C_6H_{11})$_3$}] in toluene and gave, after stirring at ambient temperatures, complex (**3**) as the only isolable product.

It would seem reasonable to postulate that the source of the carbide group in (**3**) is the μ-COMe ligand in [Os_3(μ-H)(μ-COMe)(CO)$_{10}$], with C–O bond cleavage giving rise to the fragments μ-C and μ-OMe. In the reaction of [Os_3(μ-H)$_2$(μ$_3$-CCO)(CO)$_9$], which afforded (**1**) and (**2**), and also in the reactions of [Fe_3(μ$_3$-CCO)(CO)$_9$]$^{2-}$ reported by Shriver and co-workers,[39] attack by a transition metal nucleophile results in conversion of the μ-CX ligand (in this case X = CO) to a μ-C group. Also, as discussed above, the possibility remains that the μ-CH ligand in [Os_3(μ-H)(μ$_3$-CH)(CO)$_{10}$] gives rise to the carbido-complexes (**1**) and (**2**). In all these cases the starting ligand μ-CX has a group X, either CO, OMe, or H, which is well known to act as a bridging ligand across metal–metal bonds. Under the attack of a metal nucleophile low-energy pathways may be available for the transformation of μ-CX groups into μ-C ligands *via* the intermediacy of C–X–metal bridges. In this context it is interesting to note the molecular structure of the

Table 4. Data for crystal-structure analyses

Compound	(1)	(2)	(3)
Formulae	$C_{29}H_{35}O_{10}Os_3PPt$	$C_{47}H_{68}O_{10}Os_3P_2Pt_2$	$C_{48}H_{70}O_{11}Os_3P_2Pt_2$
M	1 339.6	1 814.6	1 845.8
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	17.103(8)	12.328(3)	10.242(5)
b/Å	17.061(9)	12.375(2)	20.65(1)
c/Å	12.222(7)	18.802(3)	26.94(2)
α/°		101.95(1)	
β/°	95.87(4)	85.27(2)	101.55(2)
γ/°		79.83(2)	
U/Å^3	3 548(2)	2 742(1)	5 584(6)
Z	4	2	4
D_c/g cm^{-3}	2.52	2.20	2.19
F(000)	2 416	1 688	3 376
μ(Mo-K_α)/cm^{-1}	147.9	121.8	119.6
T/K	200	295	295
Method	θ—2θ	ω(Wyckoff)	θ—2θ
2θ range/°	$3 \leqslant 2\theta \leqslant 55$	$3 \leqslant 2\theta \leqslant 50$	$3 \leqslant 2\theta \leqslant 45$
Transmission coefficient range	0.18—0.05	0.39—0.05	0.54—0.08
Approx. crystal size (mm)	0.70 × 0.35 × 0.20	0.47 × 0.31 × 0.075	0.30 × 0.25 × 0.05
Crystal faces		⟨1 0 0⟩, ⟨0 0 1⟩, ⟨0 $\bar{1}$ 1⟩, ⟨0 1 1⟩	⟨1 0 0⟩, ⟨0 1 0⟩, ⟨0 0 1⟩
No. of unique reflections	5 936	7 337	4 854
No. of observed data (N_o)	5 198	5 562	4 171
Criterion for observed [$I \geqslant n\sigma(I)$]	$n = 2.5$	$n = 2.5$	$n = 2.0$
Anisotropic atoms	Os, Pt, P	C, O, Os, P, Pt	C, O, Os, P, Pt
Isotropic atoms	C, O, H	C(1), H	C(C_6H_{11}), H
No. of parameters refined (N_v)	202	572	416
R	0.072	0.036	0.054
R'	0.080	0.035	0.053
g	0.0008	0.000 27	0.000 47
S	2.560	1.281	1.364
Largest final electron-density difference features (e Å^{-3})	+4.1	+2.1	+1.28
	−3.5	−1.4	−1.70
Shift-e.s.d. in last cycles of refinement			
maximum	0.007	0.022	0.101
average	0.001	0.005	0.029

• Features common to all determinations: λ(Mo-K_α) = 0.710 69 Å; Nicolet *P*3*m* diffractometer; $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}F_o$; $w = 1/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F_o)$ = e.s.d. in F_o from counting statistics; $S = [\Sigma w(F_o - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

Table 5. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated standard deviations in parentheses for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	1 530(1)	3 617(1)	4 617(1)	O(2)	3 851(11)	2 006(11)	6 103(16)
Os(1)	2 780(1)	3 237(1)	6 992(1)	O(3)	4 174(14)	5 781(14)	7 414(20)
Os(2)	1 903(1)	4 649(1)	6 335(1)	O(4)	2 368(11)	5 886(12)	8 089(17)
Os(3)	3 483(1)	4 490(1)	5 878(1)	O(5)	1 588(11)	5 872(12)	4 564(16)
P	1 781(3)	2 818(3)	3 181(5)	O(6)	5 035(9)	3 793(8)	5 387(12)
C(11)	1 250(13)	3 172(11)	1 903(17)	O(7)	162(12)	4 492(12)	6 719(18)
C(12)	1 279(14)	4 043(13)	1 744(19)	O(8)	3 275(16)	2 921(17)	9 406(26)
C(13)	694(17)	4 328(16)	770(23)	O(9)	3 286(12)	5 452(11)	3 788(17)
C(14)	890(18)	3 860(17)	−298(24)	O(10)	−227(11)	3 646(11)	4 046(16)
C(15)	857(17)	3 039(17)	−148(24)	C(10)	455(14)	3 632(14)	4 277(20)
C(16)	1 425(12)	2 757(11)	856(16)	C(21)	1 497(14)	1 814(14)	3 324(21)
C	2 536(11)	3 786(11)	5 397(16)	C(22)	610(14)	1 709(14)	3 461(22)
C(1)	1 892(19)	2 565(19)	6 934(28)	C(23)	369(20)	853(19)	3 556(29)
C(2)	3 419(14)	2 488(13)	6 457(18)	C(24)	1 059(16)	455(16)	4 467(24)
C(3)	3 942(17)	5 288(16)	6 823(24)	C(25)	1 705(22)	541(21)	4 398(34)
C(4)	2 196(14)	5 441(14)	7 463(20)	C(26)	2 018(19)	1 411(17)	4 252(27)
C(5)	1 689(14)	5 384(13)	5 228(20)	C(31)	2 861(16)	2 815(16)	2 993(25)
C(6)	4 457(12)	4 029(12)	5 558(17)	C(32)	3 164(16)	2 141(17)	2 270(24)
C(7)	869(15)	4 536(14)	6 579(22)	C(33)	4 117(15)	2 204(15)	2 349(22)
C(8)	3 041(20)	3 075(19)	8 507(29)	C(34)	4 338(26)	2 868(24)	2 023(38)
C(9)	3 353(14)	5 099(13)	4 623(20)	C(35)	4 078(21)	3 650(22)	2 629(32)
O(1)	1 332(14)	2 219(14)	6 760(21)	C(36)	3 157(15)	3 536(15)	2 602(22)

complex $[Fe_4(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}COMe)(CO)_{12}]$ in which the OMe group lies over the open face of the Fe_4 'butterfly' core, thereby functioning as a five-electron donor in this 62 c.v.e. cluster.[42,43] The tilted bonding mode of the COMe group in this compound provides a model for the transfer of an OMe group from a μ_3-COMe ligand to the edge of a cluster, as observed in the synthesis of (**3**) from $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$, described above. Relevant to this discussion is the rearrangement of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ into $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ for which an intermediate has been postulated containing Ru(μ-CO)C and Ru(μ-H)C groups.[44] Many factors are doubtless important in these reactions, including the degree of asymmetry in bonding of the μ_3-CX group to the metal triangle.[45]

Interestingly, although $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ reacts with $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ to yield (**3**), in contrast the compound $[Pt(C_2H_4)_2(PPh_3)]$ reacts with $[Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ to give as the product $[Fe_3Pt(\mu_3\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)]$, a species in which the integrity of the COMe group has been maintained, albeit with change from a μ to a μ_3 bonding mode. No mixed-metal cluster complex was isolated from the reaction between $[Pt(C_2H_4)_2(PPh_3)]$ and $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$.[46] The mechanism of formation of (**3**) remains obscure, but it is interesting that no cluster complex containing only one platinum atom could be isolated.

In conclusion, we have demonstrated the facile synthesis of heteronuclear metal carbido-cluster complexes from non-carbido-precursors; results which may have general significance.

Experimental

All manipulations were carried out under a dry oxygen-free nitrogen atmosphere using freshly distilled dry solvents. Light petroleum refers to that fraction of b.p. 40—60 °C. N.m.r. measurements were made with JEOL JNM-FX 90Q and FX 200 instruments. Chemical shifts are in p.p.m. to high frequency of $SiMe_4$ for $^{13}C\text{-}\{^1H\}$, and to high frequency of 85% H_3PO_4 (external) for $^{31}P\text{-}\{^1H\}$; coupling constants are in Hz. I.r. spectra were recorded in hexane solutions on a Nicolet MX 10 FT spectrophotometer. The compounds $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$,[7] $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$,[8] $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$,[47] and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$,[7] were prepared by methods given elsewhere.

Reaction between $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ *and* $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$.—A mixture of $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ (0.86 g, 1.0 mmol) and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.53 g, 1.0 mmol) in toluene (60 cm^3) was heated to 80 °C for 12 h in an evacuated Schlenk tube fitted with a high-pressure stopcock. Removal of solvent *in vacuo*, followed by extraction with light petroleum and chromatography of the extracts on alumina, using the same solvent as eluant, gave several bands. The first bright yellow band afforded a yellow solid (*ca.* 0.51 g) containing two complexes inseparable by column chromatography. Small amounts of each complex were separated, however, by fractional crystallisation from light petroleum to give bright yellow *crystals* of $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(C_6H_{11})_3\}]$ (**1**) and $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**2**). Insufficient material from the other bands did not allow characterisation of these very minor products.

For $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(C_6H_{11})_3\}]$ (**1**) (Found: C, 26.4; H, 2.8. $C_{29}H_{35}O_{10}Os_3PPt$ requires C, 26.0; H, 2.6%); $\nu_{max.}$(CO) at 2 089m, 2 064vs, 2 045vs, 2 018s, 2 008s, 2 001s, 1 986m, and 1 966m cm^{-1}. N.m.r.: ^1H ($CDCl_3$ at −40 °C), δ −21.52 [s, 1 H, Os(μ-H)Os, *J*(PtH) 13], −18.43 [s, 1 H, Os(μ-H)Os, *J*(PtH) 35], and 1.34—1.91 (m, 33 H, C_6H_{11}); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$ at −40 °C), δ 304.3 [μ_4-C, *J*(PtC) 780], 189.2 [d, PtCO, *J*(PC) 9, *J*(PtC) 1 174], 177.7, 176.5, 174.9, 172.0, 170.8, 168.8, 164.9, 163.0, 162.0 (OsCO), and 37.7—25.9 (m, C_6H_{11}); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2 at 25 °C), δ 34.1 [s, *J*(PtP) 3 530].

For $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**2**) (Found: C, 31.2; H, 4.0. $C_{47}H_{68}O_{10}Os_3P_2Pt_2$ requires C, 31.1; H, 3.8%); $\nu_{max.}$(CO) at 2 085m, 2 062vs, 2 033s, 2 008vs, 2 003s, 1 972w, 1 960m, and 1 786w br cm^{-1}. N.m.r. ($CDCl_3$ at 25 °C): ^1H, δ −20.67 [s, 2 H, Os(μ-H)Os, *J*(PtH) 12] and 0.95—2.47 (m, 66 H, C_6H_{11}); $^{13}C\text{-}\{^1H\}$, δ 322.2 [t, μ_5-C, *J*(PC) 49, *J*(PtC) 318], 215.1 [Pt(μ-CO)Pt, *J*(PtC) 1 153 Hz], 177.3—162.1 (OsCO), and 38.2—26.1 (m, C_6H_{11}); $^{31}P\text{-}\{^1H\}$, δ 32.7 [s, *J*(PtP) 4 840 and 267, *J*(PtPt) 2 056, *J*(PP) 10].

Table 6. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated standard deviations in parentheses for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	2 952(1)	3 803(1)	2 056(1)	C(115)	−534(14)	7 467(14)	1 397(10)
Pt(2)	4 377(1)	2 266(1)	2 548(1)	C(116)	−350(11)	6 591(12)	1 870(8)
Os(1)	5 947(1)	1 789(1)	1 213(1)	C(121)	521(11)	5 242(11)	3 189(6)
Os(2)	4 400(1)	3 317(1)	662(1)	C(122)	1 065(14)	6 158(12)	3 615(6)
Os(3)	5 780(1)	4 208(1)	1 737(1)	C(123)	728(17)	6 312(17)	4 431(8)
P(1)	1 147(3)	4 746(3)	2 212(2)	C(124)	−538(18)	6 535(16)	4 628(8)
P(2)	4 481(3)	1 182(3)	3 400(2)	C(125)	−1 045(14)	5 649(16)	4 174(7)
C	4 648(8)	3 112(8)	1 732(5)	C(126)	−755(12)	5 488(14)	3 369(7)
C(1)	2 942(11)	3 255(10)	2 979(6)	C(131)	223(10)	3 780(10)	1 821(6)
C(2)	6 925(11)	1 307(10)	306(6)	C(132)	369(14)	2 769(13)	2 161(8)
C(3)	6 907(12)	1 069(12)	1 802(7)	C(133)	−386(15)	1 938(14)	1 873(9)
C(4)	5 167(11)	590(10)	1 000(6)	C(134)	−120(17)	1 543(14)	1 054(11)
C(5)	3 498(11)	2 223(11)	375(7)	C(135)	−265(14)	2 538(13)	701(7)
C(6)	5 237(10)	2 985(11)	−287(6)	C(136)	460(14)	3 419(12)	985(7)
C(7)	3 350(14)	4 538(14)	508(7)	C(211)	5 511(11)	−162(11)	3 116(6)
C(8)	4 725(14)	5 553(13)	2 238(8)	C(212)	5 944(12)	−766(11)	3 716(6)
C(9)	6 354(11)	4 083(10)	2 627(8)	C(213)	6 919(12)	−1 705(11)	3 393(7)
C(10)	6 931(11)	4 967(10)	1 387(6)	C(214)	6 626(12)	−2 575(11)	2 766(7)
O(1)	2 296(9)	3 409(9)	3 525(4)	C(215)	6 149(13)	−1 994(11)	2 200(7)
O(2)	7 527(9)	962(9)	−240(5)	C(216)	5 188(12)	−1 036(11)	2 511(7)
O(3)	7 531(8)	638(10)	2 122(6)	C(221)	3 112(11)	882(11)	3 691(6)
O(7)	2 748(10)	5 278(10)	358(5)	C(222)	2 448(12)	492(12)	3 050(7)
O(5)	3 002(9)	1 547(9)	161(6)	C(223)	1 257(13)	499(15)	3 343(9)
O(6)	5 721(9)	2 779(9)	−865(5)	C(224)	1 241(15)	−254(16)	3 890(11)
O(4)	4 702(9)	−138(8)	864(4)	C(225)	1 862(14)	119(13)	4 520(8)
O(8)	4 162(9)	6 373(9)	2 547(6)	C(226)	3 067(11)	131(11)	4 248(7)
O(9)	6 784(10)	4 054(9)	3 160(5)	C(231)	4 948(10)	1 872(9)	4 258(6)
O(10)	7 586(8)	5 371(9)	1 156(5)	C(232)	6 132(14)	2 094(14)	4 109(8)
C(111)	840(11)	5 961(11)	1 760(7)	C(233)	6 591(14)	2 562(13)	4 794(9)
C(112)	1 633(12)	6 787(10)	1 923(7)	C(234)	5 807(18)	3 632(14)	5 225(9)
C(113)	1 460(13)	7 709(12)	1 480(8)	C(235)	4 611(17)	3 466(13)	5 385(7)
C(114)	254(15)	8 282(12)	1 546(9)	C(236)	4 163(13)	2 988(10)	4 682(7)

Table 7. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated standard deviations in parentheses for (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	5 268(1)	3 015(1)	1 294(1)	C(114)	9 902(27)	4 118(11)	441(12)
Pt(2)	4 295(1)	2 201(1)	541(1)	C(115)	9 216(23)	4 750(10)	595(10)
Os(1)	4 932(1)	2 171(1)	2 115(1)	C(116)	8 576(22)	4 614(10)	1 029(10)
Os(2)	5 047(1)	1 232(1)	1 348(1)	C(121)	5 468(21)	4 711(9)	1 356(9)
Os(3)	2 373(1)	2 062(1)	1 503(1)	C(122)	5 033(25)	5 000(11)	821(10)
P(1)	6 504(6)	3 960(3)	1 394(3)	C(123)	4 244(25)	5 597(11)	823(11)
P(2)	3 855(6)	2 008(2)	−303(2)	C(124)	3 027(27)	5 454(12)	1 027(12)
O(1)	4 094(23)	3 178(9)	2 825(8)	C(125)	3 281(28)	5 124(12)	1 537(12)
O(2)	7 784(18)	1 839(10)	2 659(9)	C(126)	4 214(23)	4 547(11)	1 520(11)
O(3)	3 795(18)	1 076(7)	2 645(7)	C(131)	7 682(23)	4 045(10)	2 004(10)
O(4)	6 087(29)	144(11)	2 110(10)	C(132)	8 662(25)	3 476(11)	2 109(11)
O(5)	4 733(19)	343(7)	446(7)	C(133)	9 623(31)	3 503(15)	2 602(13)
O(6)	7 807(18)	1 609(10)	1 235(8)	C(134)	8 891(39)	3 534(17)	3 028(17)
O(7)	1 783(18)	3 495(8)	1 640(8)	C(135)	8 114(36)	4 152(17)	2 970(16)
O(8)	3 080(12)	1 111(6)	1 463(6)	C(136)	6 990(29)	4 104(14)	2 438(12)
O(9)	517(20)	1 644(13)	2 213(8)	C(211)	3 043(21)	1 209(9)	−458(9)
O(10)	197(16)	1 983(8)	536(7)	C(212)	1 842(22)	1 130(10)	−184(10)
O(11)	4 774(17)	3 539(7)	229(6)	C(213)	1 329(30)	427(13)	−232(12)
C	4 226(20)	2 155(9)	1 310(8)	C(214)	966(27)	226(12)	−796(11)
C(1)	4 441(23)	2 792(13)	2 572(10)	C(215)	2 016(28)	380(12)	−1 075(13)
C(2)	6 722(25)	1 986(12)	2 452(11)	C(216)	2 489(24)	1 081(10)	−1 033(10)
C(3)	4 212(24)	1 445(12)	2 411(9)	C(221)	2 898(22)	2 681(9)	−656(9)
C(4)	5 775(29)	551(13)	1 821(15)	C(222)	2 644(26)	2 676(11)	−1 240(11)
C(5)	4 853(26)	683(11)	758(11)	C(223)	2 031(27)	3 304(12)	−1 473(13)
C(6)	6 777(23)	1 457(10)	1 289(11)	C(224)	768(27)	3 453(12)	−1 320(11)
C(7)	1 976(21)	2 945(11)	1 579(9)	C(225)	958(25)	3 441(11)	−727(10)
C(8)	2 247(31)	564(12)	1 253(12)	C(226)	1 600(21)	2 807(9)	−489(9)
C(9)	1 145(31)	1 834(14)	1 947(11)	C(231)	5 333(21)	1 917(9)	−604(9)
C(10)	1 021(24)	1 999(10)	906(9)	C(232)	6 295(20)	1 397(9)	−365(9)
C(11)	4 782(19)	3 122(10)	529(9)	C(233)	7 414(25)	1 294(11)	−634(12)
C(111)	7 524(20)	4 071(9)	900(9)	C(234)	8 130(26)	1 929(11)	−687(12)
C(112)	8 194(22)	3 443(9)	759(9)	C(235)	7 231(25)	2 462(12)	−905(11)
C(113)	8 838(22)	3 591(10)	320(9)	C(236)	6 089(19)	2 533(9)	−611(9)

Reaction between $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ *and* $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$.—A toluene (15 cm^3) solution of $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.12 g, 0.23 mmol) and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9]$ (0.098 g, 0.11 mmol) was stirred for 1 h at room temperature. Removal of solvent *in vacuo*, followed by treatment of the residue with light petroleum and chromatography on an alumina column, gave a mixture of (**1**) and (**2**) (70 mg). From a $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum the yields of these species were 6% and 30%, respectively, based on osmium.

Reaction between $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ *and* $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$.—A mixture of the compounds $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.18 g, 0.33 mmol) and $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ (0.15 g, 0.17 mmol) was stirred in toluene (20 cm^3) for 1.5 h. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum and chromatographed on an alumina column. A yellow eluate was evaporated to give, after crystallisation from dichloromethane–hexane (1:2), yellow-orange *crystals* of $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(C_6H_{11})_3\}_2]$ (**3**) (0.15 g, 48%) (Found: C, 31.3; H, 4.1. $C_{48}H_{70}O_{11}Os_3P_2Pt_2$ requires C, 31.2; H, 3.8%); $\nu_{max.}$(CO) at 2 071m, 2 044s, 2 029m, 1 996m, 1 978w, 1 968w, 1 960m, and 1 794w br cm^{-1}. N.m.r.: ^1H ($CDCl_3$ at −40 °C), δ −13.24 [d of d, 1 H, Os(μ-H)Pt, ^2J(PH) 14, ^3J(PH) 4.5, ^1J(PtH) 656, ^2J(PtH) 68], 1.28—2.59 (m, 66 H, C_6H_{11}), and 3.42 (s, 3 H, OMe); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$ at 25 °C), δ 385.3 [d of d, μ_5-C, *J*(PC) 43 and 39], 217.3 [Pt(μ-CO)Pt, *J*(PtC) 1 125 and 1 062], 185.8 [OsCO, *J*(PtC) 37], 182.1 [OsCO, *J*(PtC) 24], 176.5, 175.6 (OsCO), 34.7—26.3 (m, C_6H_{11}), with OMe signal hidden by solvent peaks; ^{13}C (partially decoupled) in CD_2Cl_2, δ 217.5 [d, Pt(μ-CO)Pt, *J*(CH) 15], and 74.8 [q, OMe, *J*(CH) 141]; $^{31}P\text{-}\{^1H\}$ ($CDCl_3$ at 25 °C), δ 42.5 (P^a) and 22.1 (P^b) [AMXY pattern, with $^3J(P^aP^b)$ 9.8, $J(P^aPt^a)$ 5 483, $J(P^bPt^b)$ 3 667, $^2J(P^aPt^b)$ 341.8, $^2J(P^bPt^a)$ 275.9, $J(Pt^aPt^b)$ 2 093, as determined by spectral simulation].

Crystal-structure Determinations and Refinements.—Details of the data-collection procedures, structure solution, and refinement are given in Table 4. Check reflections [(**1**), $\bar{7}\,\bar{3}\,0$, $5\,\bar{9}\,1$, $\bar{2}\,8\,1$; (**2**), $0\,\bar{3}\,7$, $0\,\bar{2}\,\bar{6}$, $\bar{2}\,\bar{6}\,7$; (**3**) $4\,10\,\bar{1}$, $6\,6\,\bar{3}$] were measured every 50 reflections for (**1**) and (**2**), and every 100 for (**3**). In each case corrections were made for Lorentz, polarisation, and *X*-ray absorption effects. For (**1**), the absorption correction was empirical, but due to the high value of the linear adsorption coefficient (μ = 147.9 cm^{-1}) this procedure was not entirely satisfactory, though a significant improvement in standard deviations was observed. This is reflected in the large residuals (*ca.* 4.1 e $Å^{-3}$) close to the metal atoms. There were no residuals, however, of any chemical significance. For complexes (**2**) and (**3**) an analytical absorption correction was computed.[48] All structures were solved by direct methods with refinement by blocked-cascade full-matrix least-squares. For (**1**) some disorder was observed in the cyclohexyl rings as evidenced by abnormal bond lengths. However, no meaningful disordered model could be applied, and only the major component was included in the final calculations. 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 and were assigned fixed thermal parameters 1.2 times those of their carbon atoms. Hydrido-hydrogen atoms were placed at calculated positions[32] (with metal–hydrogen distance *ca.* 1.85 Å). Scattering factors were from ref. 49, and all computations were carried out on a Nicolet *R3m*/E structure-determination facility, using programs of the SHELXTL package.[48] Atom co-ordinates are listed in Tables 5—7.

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