The Reductive Activation of $[M_5C(CO)_{15}]$ (M = Ru or Os) and Subsequent Reactions of the Dianion $[Os_5C(CO)_{14}]^{2-}$, Carbonylation of $[M_5C(CO)_{15}]$ (M = Ru or Os), and the Crystal Structures of $[Os_5C(CO)_{16}]$, $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$, and $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ †

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High pressure infrared (h.p.i.r.) studies indicate that the cluster $[Ru_5C(CO)_{15}]$ (1) adds carbon monoxide under relatively mild conditions (20 °C, 80 atm) to give $[Ru_5C(CO)_{16}]$ (2), while under more forcing conditions (90 °C, 80 atm) the cluster (2) reverts back to (1). The osmium analogue, $[Os_5C(CO)_{15}]$ (3), gives $[Os_5C(CO)_{16}]$ (4) at 70 °C and 50 atm but may be obtained in quantitative yield from an autoclave reaction in the absence of solvent. Complex (4) crystallises in space group $P\bar{1}$ with $a = 10.017(3)$, $b = 15.823(5)$, $c = 16.507(8)$ Å, $\alpha = 96.78(3)$, $\beta = 103.20(3)$, $\gamma = 93.41(2)$°, and $Z = 4$. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked full-matrix least squares to $R = 0.073$ for 6 120 reflections. The five Os atoms define a ' bridged-butterfly ' configuration with a carbide at the centre. There are four terminal carbonyl groups bound to the bridging metal atom and three to each of the other four metal atoms. A h.p.i.r. study of the reaction of (4) with H_2 has shown that at a pressure of 75 atm and at temperatures around 90 °C the cluster $[Os_5H_2(C)(CO)_{15}]$ (5) is produced. The electrochemical or chemical reduction of $[M_5C(CO)_{15}]$ [M = Ru (1) or Os (3)] produces the corresponding dianion $[M_5C(CO)_{14}]^{2-}$ [M = Ru (6) or Os (7)]. An *X*-ray analysis of the $[N(PPh_3)_2]^+$ salt of (7) shows that the square-pyramidal Os_5C core geometry of (3) is retained. One of the Os–Os bonds in the basal plane is symmetrically bridged by a carbonyl group. The remaining 13 carbonyl ligands are co-ordinated terminally, two each to the carbonyl-bridged metal atoms, and three each to the other three metal atoms. The salt crystallises in space group $P\bar{1}$ with $a = 13.244(6)$, $b = 14.648(9)$, $c = 21.963(14)$ Å, $\alpha = 86.78(5)$, $\beta = 85.54(5)$, $\gamma = 81.22(5)$°, and $Z = 2$. The structure was solved using the same techniques as for (4) and refined by blocked-cascade least squares to $R = 0.065$ for 5 780 observed diffractometer data. The dianion (7) reacts with two equivalents of $[Au(PPh_3)Cl]$ to give the neutral complex $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10) which has also been characterised crystallographically. In (10) the Os_5C core shows significant distortions from square-pyramidal geometry. Two opposite Os(basal)–Os(apical) bonds are bridged by the Au atoms of the $Au(PPh_3)$ ligands and these two bonds are significantly longer than the other two unbridged Os(basal)–Os(apical) bonds. Two carbonyl groups are bonded terminally to the apical Os atom, and three each to the four basal Os atoms. This complex crystallises in space group $P2_1/c$ with $a = 20.307(4)$, $b = 9.843(2)$, $c = 27.980(6)$ Å, $\beta = 100.53(2)$°, and $Z = 4$. The structure was solved and refined as for (7) to $R = 0.060$ for 7 013 observed diffractometer data.

The pentanuclear cluster complexes $[M_5C(CO)_{15}]$ (M = Ru or Os) react with two-electron donor ligands to give adducts of the form $[M_5C(CO)_{15}L]$ [L = NCMe,[1] I^-,[2] or pyridine (py)[3]]. In certain cases this addition may be reversible and the reversibility involves a change in metal geometry. When acetonitrile adds to $[Ru_5C(CO)_{15}]$ an Ru–Ru bond in the square-based pyramidal metal framework is broken and the cluster opens out to give the bridged ' butterfly ' configuration. The acetonitrile ligand co-ordinates to the bridging Ru atom in this complex but upon subsequent loss of the ligand the metal–metal bond reforms and the cluster reverts to the square-based pyramidal metal geometry. Although the carbide in these clusters plays no direct role in the adduct formation it does donate four electrons to the cluster without occupying co-ordination sites on the periphery which might, by steric constraints, prevent reformation of the metal–metal bonds. In fact the carbide may be considered to hold the cluster together while the rearrangement of the metal framework occurs. The presence of a carbide has been shown to facilitate the formation of mixed-metal clusters from homonuclear metal carbido-species.[4]

The successful reduction reaction of $[Fe_5C(CO)_{15}]$ to $[Fe_5C(CO)_{14}]^{2-}$,[5] coupled with the reversible adduct formation for the pentanuclear ruthenium and osmium systems,[1-3] has led us to investigate the reductive chemistry of the $[M_5C(CO)_{15}]$ (M = Ru or Os) complexes and the reversible reactions of these neutral species; the addition of two electrons to the square-pyramidal carbido-clusters might lead to dianion formation with a net reduction of the metal framework. Any consequent activation *via* metal–metal or metal–carbonyl bond breaking would be expected to lead to a change in either the geometry of the M_5 polyhedron or in the ligand distribution around the cluster core. Such a reductive activation with respect to ligand substitution has been achieved recently by the addition of sodium–benzophenone to a series of tri- and

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† μ_5-Carbido-μ-tetracarbonylosmio-*cyclo*-tetrakis(tricarbonylosmium)(*7Os–Os*), bis[bis(triphenylphosphine)iminium] μ_5-carbido-2,3-μ-carbonyl-1,1,1,2,2,3,3,4,4,4,5,5,5-tridecacarbonyl-*cyclo*-pentaosmate(2−)(*8Os–Os*), and μ_5-carbido-1,1,2,2,2,3,3,3,4,-4,4,5,5,5-tetradecacarbonyl-1,2;1,4-bis[μ-(triphenylphosphine)-aurio]-*cyclo*-pentaosmium(*8Os–Os*, *4Au–Os*).

Supplementary data available (No. SUP 23690, 133 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Selected bond parameters (lengths in Å, angles in degrees) for $[Os_5C(CO)_{16}]$ (4)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Os(1)–Os(2)	2.915(2)	2.910(2)	Os(2)–C(1)	2.11(3)	2.13(2)
Os(1)–Os(3)	2.900(1)	2.901(2)	Os(3)–C(1)	2.13(2)	2.12(2)
Os(1)–Os(5)	2.916(1)	2.915(1)	Os(4)–C(1)	2.00(2)	2.03(2)
Os(2)–Os(3)	2.757(1)	2.746(1)	Os(5)–C(1)	2.15(2)	2.16(2)
Os(2)–Os(4)	2.912(1)	2.915(1)	Os(5)–C(51)	1.94(3)	1.93(2)
Os(3)–Os(4)	2.910(2)	2.917(1)	Os(5)–C(52)	1.88(3)	1.90(3)
Os(4)–Os(5)	2.917(1)	2.917(2)	Os(5)–C(53)	1.90(3)	1.85(3)
Os(1)–C(1)	1.96(2)	1.93(2)	Os(5)–C(54)	1.91(2)	1.95(2)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Os(3)–Os(1)–Os(2)	56.6(1)	56.4(1)	Os(4)–Os(5)–Os(1)	85.5(1)	85.4(1)
Os(5)–Os(1)–Os(2)	86.2(1)	87.3(1)	Os(2)–C(1)–Os(1)	91.3(9)	91.7(8)
Os(5)–Os(1)–Os(3)	88.0(1)	87.4(1)	Os(3)–C(1)–Os(1)	90.1(10)	91.6(8)
Os(3)–Os(2)–Os(1)	61.4(1)	61.6(1)	Os(3)–C(1)–Os(2)	81.0(8)	80.7(8)
Os(4)–Os(2)–Os(1)	85.6(1)	85.5(1)	Os(4)–C(1)–Os(1)	178.4(16)	178.8(13)
Os(4)–Os(2)–Os(3)	61.7(1)	61.9(1)	Os(4)–C(1)–Os(2)	90.2(11)	89.1(9)
Os(2)–Os(3)–Os(1)	62.0(1)	62.0(1)	Os(4)–C(1)–Os(3)	89.5(8)	89.4(10)
Os(4)–Os(3)–Os(1)	85.9(1)	85.7(1)	Os(5)–C(1)–Os(1)	90.1(9)	90.7(10)
Os(4)–Os(3)–Os(2)	61.8(1)	61.9(1)	Os(5)–C(1)–Os(2)	138.1(12)	139.3(9)
Os(3)–Os(4)–Os(2)	56.5(1)	56.2(1)	Os(5)–C(1)–Os(3)	141.0(14)	139.9(8)
Os(5)–Os(4)–Os(2)	86.2(1)	87.2(1)	Os(5)–C(1)–Os(4)	89.2(9)	88.1(7)
Os(5)–Os(4)–Os(3)	87.8(1)	87.1(1)			

tetra-nuclear cluster complexes,[6] while an oxidative activation of $[Os_4H_3(CO)_{12}]^-$ to give, *via* Os–Os bond cleavage, the corresponding tetranuclear ' butterfly ' cation $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ has been observed.[7]

Results and Discussion

The treatment of a solution of $[Ru_5C(CO)_{15}]$ (1) in heptane with carbon monoxide at 400 atm and 100 °C for several hours leads to the recovery of (1) unchanged. This result demonstrates the exceptional stability to degradation by carbon monoxide afforded to the cluster by the presence of the carbon atom within the metal framework.

A high-pressure infrared (h.p.i.r.) study of compound (1) under 80 atm pressure of CO and at lower temperatures, however, leads to the observation that under less forcing conditions a reaction occurs between the carbido-cluster and carbon monoxide. A reaction time of 4 h led to the formation of an equilibrium mixture containing 30% of (1) and 70% of a new cluster (2). On further heating the proportions of the mixture changed as (2) was gradually converted back into (1), until, at 90 °C, the bands in the i.r. spectrum due to (2) had completely disappeared, leaving just those due to (1). In a repeat experiment the reaction was stopped at the point when the mixture contained 70% of (2). However, when the pressure was released rapid conversion of (2) into (1) was observed. This explains why (2) would not have been isolated from the experiment at 400 atm.

The reaction of $[Os_5C(CO)_{15}]$ (3) with CO was also studied using the h.p.i.r. cell, at 50 atm. After 1 h at 70 °C an equilibrium mixture of 30% (3) and 70% of a new cluster (4) was produced. The proportions of these compounds did not change with time. However, as the temperature was increased (3) was regenerated, this reaction being complete at about 150 °C. In this case when the reaction was stopped at 70 °C and cooling was followed by depressurisation, a solution was obtained which still contained a mixture of (3) and (4). Quantitative yields of (4) were obtained by carrying out the reaction of (3) with CO in an autoclave, in the absence of solvent. Final purification was achieved by t.l.c. in 30% $CHCl_3$–hexane. In the absence of CO (1 atm N_2), (4) was converted smoothly back into (3) on heating, in heptane solution, at 70 °C. The reaction was complete after 5 h. Orange-yellow crystals of (4) were obtained by recrystallisation from CH_2Cl_2–hexane.

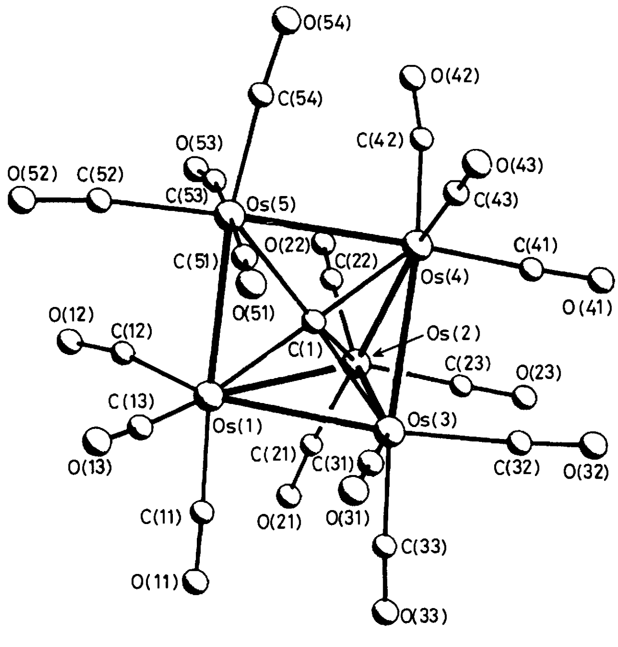


Figure 1. The molecular structure of $[Os_5C(CO)_{16}]$

A single-crystal *X*-ray analysis of compound (4) showed it to consist of discrete molecules of $[Os_5C(CO)_{16}]$ separated by normal van der Waals distances. The asymmetric unit contains two independent but structurally equivalent molecules. The molecular geometry of one molecule is ilustrated in Figure 1 while selected bond lengths and angles are presented in Table 1. The five Os atoms define a bridged ' butterfly ' metal framework with a carbide atom at the centre of the cluster, bonded to all five metal atoms (Figure 2). All sixteen carbonyl groups are terminally co-ordinated, four to the bridging Os(5) atom, and three each to the other four Os atoms.

The overall molecular geometry of $[Os_5C(CO)_{16}]$ (4) closely resembles the related ruthenium-acetonitrile adduct $[Ru_5C(CO)_{15}(NCMe)]$.[1] The same trends in the metal-metal distances are followed, with the Os(2)-Os(3) ' hinge ' bond being the shortest and the Os(wing-tip)-Os(hinge) bonds similar in length to the Os(wing-tip)-Os(bridge) bonds. The dihedral angle between the Os(1)Os(2)Os(3) and the Os(2)Os(3)Os(4) planes, 101.2(4)° for molecule 1 and 101.8(4)° for molecule 2, is the same as the equivalent angle of 101(1)° in the ruthenium complex. The Ru-C(carbide) distances in the Ru_5 cluster [Ru(hinge)-C 2.08(2), Ru(wing-tip)-C 1.97(2), and Ru-(bridge)-C 2.16(2) Å] also show the same trends as in (4). Although the estimated standard deviations on the Os-C-(carbonyl) distances are rather high to make an accurate assessment of the bonding, the trend is that the bond distances for the two axial carbonyls associated with Os(5) are longer than the equatorial, in keeping with the expected back-bonding capabilities for two *trans* carbonyls. The average Os-C(carbonyl) distance for the other four metal atoms is 1.87(2) Å.

There are a number of other pentanuclear osmium carbido-clusters which also exhibit the carbide-centred, bridged ' butterfly ' metal frameworks.[2,8] The metal—metal distances in these compounds show some variations due to the nature of the ligands surrounding the cluster core. However, all these complexes including $[Os_5C(CO)_{16}]$ (4), which are 76-electron systems, may not only be considered to have bridged ' butterfly ' geometries but can also be considered to have *arachno*-pentagonal-bipyramidal geometries, based on the 72-electron parent complex $[Os_5(CO)_{16}]$,[9] and derived by the breaking of two metal-metal bonds. A theoretical intermediate between the structures of $[Os_5(CO)_{16}]$ and $[Os_5C(CO)_{16}]$ would be a *nido*-octahedron, or a square-based pyramid, as observed in $[Os_5C(CO)_{15}]$,[2] in which only one bond from the parent trigonal bipyramid is broken. The geometry of compound (4) is related to that of $[Os_5(CO)_{16}]$ [9] in that one of the equatorial Os atoms is co-ordinated to four terminal carbonyl groups and in (4) this Os atom is moved away from the others, and the two equatorial Os-Os bonds to it broken. The third equatorial bond in $[Os_5(CO)_{16}]$, at 2.748(4) Å, is similar to the Os(2)-Os(3) ' hinge ' bond in (4). It is interesting that the carbide formally acts as a four-electron donor, and the inclusion of a carbide in the $[Os_5(CO)_{16}]$ structure adds two electron pairs concomitant with the breaking of two metal-metal bonds. The carbide exerts no steric influence on the periphery of the cluster, so four electrons have been added formally without the requirement of additional external ligands which would cause unfavourable steric congestion. In this way the carbide stabilises the cluster.

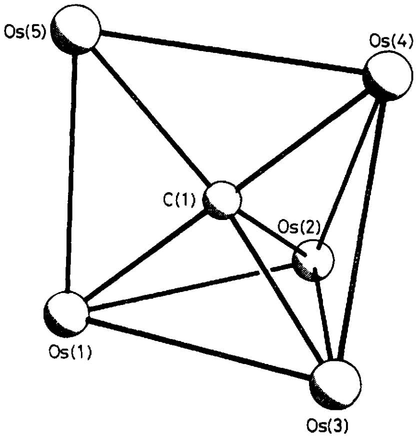
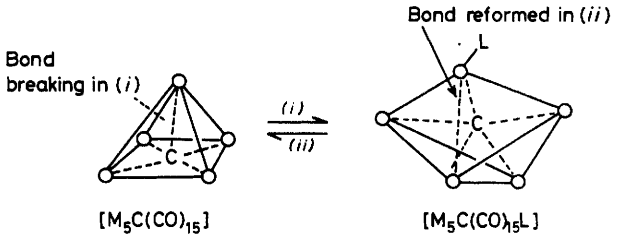


Figure 2. The cluster core in $[Os_5C(CO)_{16}]$

Because of the similarity in the ν(CO) i.r. stretching frequencies of compounds (2) and (4), and because of their similar behaviour in the carbonylation experiments, it is assumed that (2) is $[Ru_5C(CO)_{16}]$ and has a similar structure to (4), and to $[Ru_5C(CO)_{15}(NCMe)]$.[1] In the case of $[Ru_5C(CO)_{16}]$ the acetonitrile group is simply replaced by a carbonyl group. In the same way as the acetonitrile group may be removed from $[Ru_5C(CO)_{15}(NCMe)]$ under vacuum or in solution, to reform $[Ru_5C(CO)_{15}]$, so may a carbonyl group be lost from (2) to reform the same parent cluster (Scheme 1).

An h.p.i.r. study of the stability of $[Os_5C(CO)_{16}]$ (4) to



Scheme 1. L = MeCN or CO. (*i*) +L; (*ii*) heat

Table 2. Infrared carbonyl stretching bands (cm^{-1})

Complex	
(1) $[Ru_5C(CO)_{15}]$ [a]	2 067vs, 2 034s, 2 015m
(6) $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ [b]	2 033w, 1 975s, 1 964 (sh), 1 919w, 1 753w
(2) $[Ru_5C(CO)_{16}]$ [a]	2 077m, 2 057s, 2 028m
(3) $[Os_5C(CO)_{15}]$ [a]	2 073vs, 2 034s, 2 017m
(4) $[Os_5C(CO)_{16}]$ [a]	2 083w, 2 079m, 2 071w, 2 062s, 2 034w, 2 028m, 2 007w, 1 983w, 1 978w, 1 964w
(7) $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ [b]	2 040w, 2 015w, 1 991s, 1 975vs, 1 968vs, 1 945s, 1 926w, 1 720w
(8) $[N(PPh_3)_2][Os_5H(C)(CO)_n]$ (n = 14 or 15)	2 088w, 2 058m, 2 040vs, 2 020s, 2 008 (sh), 2 002s, 1 978m (sh), 1 966m, 1 937w
(5) $[Os_5H_2(C)(CO)_{15}]$ [a]	2 084m, 2 075s, 2 065vs, 2 057w, 2 037w, 2 024s, 2 004w, 1 997 (sh), 1 992w
(10) $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$	2 087w, 2 053vs, 2 038m (sh), 2 004s, 1 994m (sh), 1 966w, 1 938w, 1 905w

[a] In hexane. [b] In CH_2Cl_2.

Table 3. Selected bond parameters (lengths in Å, angles in degrees) for $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$

Os(1)–Os(2)	2.768(2)	Os(1)–C(1)	2.06(2)
Os(1)–Os(4)	2.921(2)	Os(2)–C(1)	2.04(2)
Os(1)–Os(5)	2.913(2)	Os(3)–C(1)	2.03(2)
Os(2)–Os(3)	2.917(2)	Os(4)–C(1)	2.05(2)
Os(2)–Os(5)	2.897(3)	Os(5)–C(1)	2.22(2)
Os(3)–Os(4)	2.904(2)	Os(1)–C(13)	2.05(3)
Os(3)–Os(5)	2.817(3)	Os(2)–C(13)	2.06(3)
Os(4)–Os(5)	2.813(2)	C(13)–O(13)	1.23(3)
Os(2)–Os(1)–Os(4)	91.3(1)	Os(1)–Os(2)–Os(3)	91.4(1)
Os(2)–Os(1)–Os(5)	61.3(1)	Os(1)–Os(2)–Os(5)	61.8(1)
Os(4)–Os(1)–Os(5)	57.7(1)	Os(3)–Os(2)–Os(5)	58.0(1)
Os(2)–Os(3)–Os(4)	88.7(1)	Os(1)–Os(4)–Os(3)	88.6(1)
Os(2)–Os(3)–Os(5)	60.7(1)	Os(1)–Os(4)–Os(5)	61.0(1)
Os(4)–Os(3)–Os(5)	58.9(1)	Os(3)–Os(4)–Os(5)	59.0(1)
Os(1)–Os(5)–Os(3)	90.5(1)	Os(1)–C(1)–Os(2)	84.9(7)
Os(2)–Os(5)–Os(3)	61.4(1)	Os(1)–C(1)–Os(3)	168.5(11)
Os(1)–Os(5)–Os(4)	61.3(1)	Os(2)–C(1)–Os(2)	91.6(8)
Os(2)–Os(5)–Os(4)	90.9(1)	Os(1)–C(1)–Os(4)	90.4(8)
Os(3)–Os(5)–Os(4)	62.1(1)	Os(2)–C(1)–Os(4)	167.4(12)
Os(1)–C(13)–Os(2)	84.8(10)	Os(3)–C(1)–Os(4)	90.7(8)
Os(1)–C(13)–O(13)	139.7(21)	Os(1)–C(1)–Os(5)	85.8(8)
Os(2)–C(13)–O(13)	135.6(20)	Os(2)–C(1)–Os(5)	85.7(7)
		Os(3)–C(1)–Os(5)	83.0(7)
		Os(4)–C(1)–Os(5)	82.3(7)

hydrogen, under pressure, was carried out. A heptane solution of the cluster was heated under 75 atm pressure of H_2. Gradual heating to 70 °C resulted only in the regeneration of $[Os_5C(CO)_{15}]$, which as the temperature was increased to 90 °C began to react to give the new cluster $[Os_5H_2(C)(CO)_{15}]$ (5) (see below).

Cyclic voltammetry at platinum electrodes of $[M_5C(CO)_{15}]$ [M = Ru (1) or Os (3)] in dichloromethane containing 0.1 mol l^{-1} $[NBu^n_4][BF_4]$ as base electrolyte shows two-electron irreversible reductions at −1.78 V (M = Ru) and −1.50 V (M = Os) respectively *vs.* an Ag–$AgNO_3$ reference electrode at a scan rate of 1 V s^{-1} at 25 °C. Quantitative reduction of the $[M_5C(CO)_{15}]$ clusters in CH_2Cl_2 by controlled-potential electrolysis at the above voltages under a constant stream of argon gas leads to the reduction of the pentanuclear complexes with concomitant change of colour from red to orange (M = Ru) or orange to yellow (M = Os). In addition to the bands due to terminal carbonyl ligands, the solution i.r. spectra of the dianions $[M_5C(CO)_{14}]^{2-}$ (6) and (7) (in CH_2Cl_2) show an absorption band at 1 753 cm^{-1} (M = Ru) or 1 720 cm^{-1} (M = Os) indicating the presence of bridging carbonyls in these species (Table 2). No e.s.r.-active intermediates could be detected during the formation of the dianionic species at room temperature.

The same products may also be prepared by the chemical reduction of $[M_5C(CO)_{15}]$ [M = Ru (1) or Os (3)] with sodium–potassium alloy in tetrahydrofuran, with KOH in methanol, or with Na_2CO_3 in methanol. These routes to the dianion were preferred to the electrochemical reduction as preparative methods, since isolation of the dianions from electrochemical solutions is hindered by the presence of an excess of base electrolyte. Yellow crystals, in the form of rectangular blocks, of the $[N(PPh_3)_2]^+$ salt of the $[Os_5C(CO)_{14}]^{2-}$ dianion (7) were obtained by recrystallisation from CH_2Cl_2–MeOH, and a single-crystal *X*-ray analysis was undertaken. The structure consists of discrete $[N(PPh_3)_2]^+$ cations and $[Os_5C(CO)_{14}]^{2-}$ anions without any abnormally short interactions between them. Selected bond lengths and interbond angles are presented in Table 3. The geometry of $[Os_5C(CO)_{14}]^{2-}$ is shown in Figure 3 which includes the atom-numbering scheme employed.

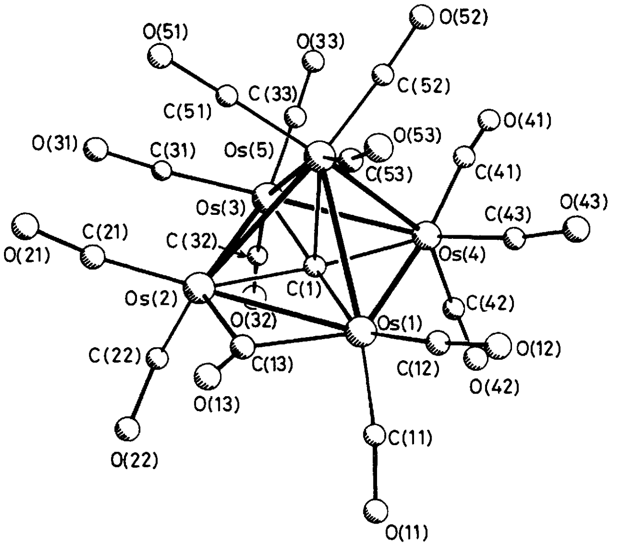


Figure 3. The molecular geometry of the $[Os_5C(CO)_{14}]^{2-}$ dianion

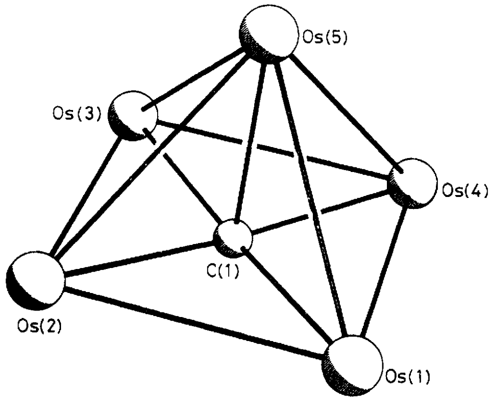


Figure 4. The Os_5C core in $[Os_5C(CO)_{14}]^{2-}$

The five Os atoms in the dianion define a distorted square-based pyramid. The carbido-carbon atom lies 0.21 Å below the square base (Figure 4). One carbonyl ligand symmetrically bridges a basal Os–Os bond, an uncommon occurrence in higher osmium cluster chemistry where only a few compounds containing bridging carbonyls have been crystallographically characterised. The remaining 13 carbonyl ligands are terminally bonded to the metal atoms. The two basal Os atoms which are involved with the bridging carbonyl group each have two terminal carbonyls bonded to them, while the apical and the two other basal Os atoms are each co-ordinated to three terminal carbonyl groups. A similar overall geometry has been observed for the $[Fe_4RhC(CO)_{14}]^-$ anion.[4]

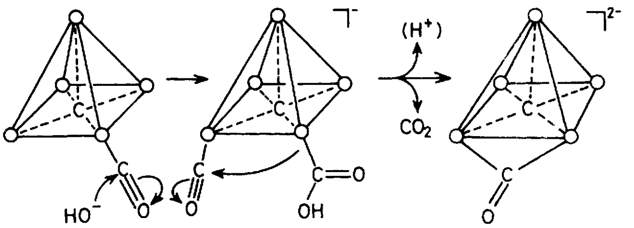
The Os–Os distances in the dianion show a greater variation than those in the neutral complex $[Os_5C(CO)_{15}]$ (3)[2] which has the same Os_5C core geometry. In the neutral complex the average Os(basal)–Os(basal) bond length is 2.88(2) Å and the average Os(basal)–Os(apical) bond length is 2.85(3) Å. In the dianion the four Os(basal)–Os(apical) bonds may be split into two groups. The Os(1)–Os(5) and Os(2)–Os(5) bonds, where the Os(1) and Os(2) atoms are associated with the bridging carbonyl group, are significantly longer [mean 2.905(3) Å] than the Os(3)–Os(5) and Os(4)–Os(5) bonds [mean 2.815(2) Å], such that the apical metal atom Os(5) does not lie over the centre of the Os_4 base. In the basal plane the opposite edges Os(1)–Os(4) and Os(2)–Os(3) are equivalent [mean 2.919(2) Å] and are only marginally longer than the Os(3)–Os(4) bond [2.904(2) Å]. The fourth metal–metal bond in the basal plane, Os(1)–Os(2), is *ca.* 0.15 Å shorter at 2.768(2) Å. The presence of a bridging carbonyl group across a metal–metal bond has a bond-shortening effect because the highest occupied molecular orbital involved is bonding both with respect to metal–metal and metal–ligand interactions.[10] Presumably the other variations in Os–Os distances compensate for the electron imbalance in the metal framework and the accommodation of the 2− charge.

The carbido-atom C(1) lies under the centre of the Os_4 basal plane and the average Os–C(1) distance of 2.05(2) Å is not significantly different from the value of 2.06(4) Å in $[Os_5C(CO)_{15}]$.[2]

The average Os–C(13) bond length of 2.05(2) Å for the metal atoms bridged by the carbonyl C(13)O(13) lies within the range 2.00(3)—2.22(3) Å found for the bridging carbonyl in the $[Os_4H(CO)_{13}]^-$ anion,[11] and the angle Os(1)–C(13)–Os(2) is the same as the value of 84.8(11)° in the Os_4 monoanion. The Os–C–O angles at carbon for the 13 terminal carbonyl ligands do not deviate significantly from linearity [average 176(2)°]. The orientation of the carbonyl groups is such that they are staggered with respect to the metal–metal bonds in such a way that if only the metal–metal and metal–carbonyl bonds were considered the metal atoms would exhibit distorted octahedral co-ordination geometry, except for Os(5) which is seven-co-ordinate. In this way each Os–Os bond has at least one carbonyl group in a pseudo-*trans* position and the average Os–Os–*trans*-C(carbonyl) angle is 155(6)°. The largest deviations from this ligand arrangement are caused by the steric influence of the bridging carbonyl group. The two carbonyl groups closest to the Os_4 basal plane which are adjacent to the Os(1)–Os(2) bridged bond are bent back with an average Os–Os–C(carbonyl) angle of 143(2)°. The rather high estimated standard deviations on the terminal Os–C(carbonyl) and C–O bond lengths make a detailed analysis of the bonding difficult but the average distances of 1.89(7) and 1.14(7) Å are similar to those in a number of other Os_5 clusters.[9,12] The arrangement of the carbonyl ligands is probably the most efficient way of packing 14 ligands around a square-based pyramid of metal atoms, and also reduces the electron imbalance in the system with the presence of the bridging carbonyl. The dianion is formally a 74-electron system and the geometry observed is that predicted by Wade's rules.[13]

The geometry and dimensions of the two $[N(PPh_3)_2]^+$ cations are similar to those in a number of other crystal structures where the cluster anion is electronically counterbalanced by this cation.[14]

Although the best method of preparation of the anions $[M_5C(CO)_{14}]^{2-}$ [M = Ru (6) or Os (7)] is by the reaction of $[M_5C(CO)_{15}]$ with Na_2CO_3–MeOH, there is some doubt as to the mechanism of this reaction. It was thought that the reaction might occur *via* MeO^- attack at a CO ligand, but the reaction of $[Ru_5C(CO)_{15}]$ with NaOMe in MeOH failed to give $[Ru_5C(CO)_{14}]^{2-}$. However, trace amounts of hydroxide in the Na_2CO_3–MeOH mixture would be sufficient to effect the reduction, which could then proceed *via* the mechanism illustrated in Scheme 2.



Scheme 2.

These results indicate that activation of a metal–carbonyl bond occurs on reduction of the pentanuclear carbido-clusters $[M_5C(CO)_{15}]$. This is in direct contrast to the reaction of these complexes with two-electron donor ligands, when metal–metal bond cleavage occurs to give products with *arachno*-pentagonal-bipyramidal structures. We have recently demonstrated an example of attack at the carbon atom of a cluster-bound carbonyl group in the reaction of $[Os_5C(CO)_{15}]$ with alcohols to give $[Os_5H(C)(CO)_{14}(COOR)]$.[15] In the present work, the reaction appears to have proceeded a step further with expulsion of the carbonyl group on reduction.

The i.r. spectra in the carbonyl region for $[M_5C(CO)_{14}]^{2-}$ [M = Ru (6) or Os (7)] (Table 2) are similar to that reported [5] for $[Fe_5C(CO)_{14}]^{2-}$, the chemistry of which has been studied in some detail.[4] It is assumed that all three cluster dianions adopt the same overall geometry of a square-based pyramid of metal atoms with one edge-bridging carbonyl group. The structures of these $[M_5C(CO)_{14}]^{2-}$ dianions (M = Fe, Ru, or Os) are therefore analogous to the isoelectronic $[Fe_4RhC(CO)_{14}]^-$ monoanion.[4]

The complexes $[M_5C(CO)_{14}]^{2-}$ [M = Ru (6) or Os (7)] show irreversible oxidation waves in dichloromethane at +0.15 V (M = Ru) and +0.35 V (M = Os) *vs.* an Ag–$AgNO_3$ electrode. Quantitative oxidation of these complexes at a platinum gauze in dichloromethane yields $[M_5C(CO)_{15}]$ in low yield with significant decomposition products. The reformation of $[M_5C(CO)_{15}]$ in these redox reactions is attributed to scavenging of carbon monoxide by the electron-deficient '$[M_5C(CO)_{14}]$'.

Protonation of $[Os_5C(CO)_{14}]^{2-}$ with concentrated H_2SO_4 gives a dark brown, neutral product, which may be formulated as $[Os_5H_2(C)(CO)_{15}]$ on the basis of mass spectroscopy (Table 2). It is proposed that, on protonation of the dianion, disproportionation occurs, resulting in the production of this pentadecacarbonyl species and other as yet uncharacterised products.

The dihydride $[Os_5H_2(C)(CO)_{15}]$ is also obtained upon direct reaction of $[Os_5C(CO)_{15}]$ or $[Os_5H(C)(CO)_{14}(COOR)]$ [15] with hydrogen at 50 atm pressure and 120 or 175 °C, respectively, or by the route outlined below.

Reduction of $[Os_5C(CO)_{15}]$ with $[X][BH_4]$ {X = $[N(PPh_3)_2]^+$ or $[NEt_4]^+$} gives a monoanionic, monohydridic species formulated as $[Os_5H(C)(CO)_n]^-$ (8) (n = 14 and 15) on the basis of ^1H n.m.r. and i.r. spectroscopy (Table 2). Protonation of this anion again yields $[Os_5H_2(C)(CO)_{15}]$, and indeed the monohydride was detected as an intermediate in the protonation of $[Os_5C(CO)_{14}]^{2-}$ to give the dihydride. If n = 15 it would be expected that the structure of the monohydride would be analogous to that of $[Os_5C(CO)_{15}I]^-$,[2] with the terminal iodine atom on the bridging Os atom of the bridged butterfly structure replaced by a hydrogen. If, however, reduction by $[BH_4]^-$ has resulted in the concomitant loss of a carbonyl group it would be expected that the structure of $[Os_5H(C)(CO)_{14}]^-$ would be more closely related to that of $[Os_5C(CO)_{14}]^{2-}$ with, perhaps, one edge-bridging hydride.

The cluster $[Os_5H_2(C)(CO)_{15}]$ is stable under conditions of 80 atm of CO at 150 °C for 3 h. No product was detected at any stage during the h.p.i.r. study.

The dianion $[Os_5C(CO)_{14}]^{2-}$ reacts with one equivalent of $[Au(PPh_3)Cl]$, in the presence of $Tl[PF_6]$ (which removes Cl^- from the reaction mixture), to give an orange monoanion which could not be isolated in a pure state. Attempts to purify

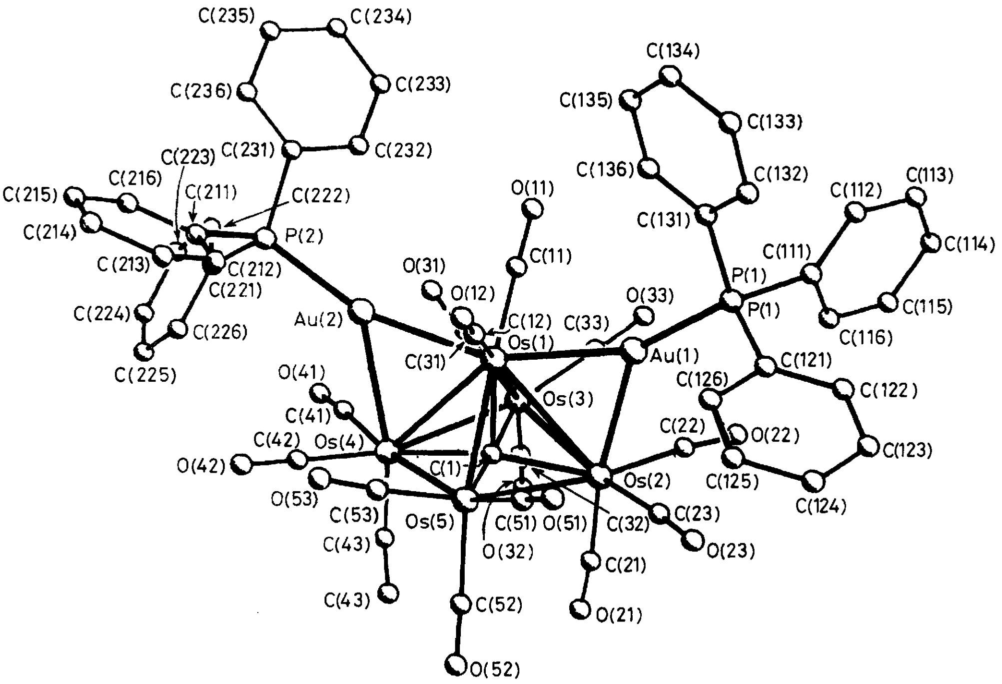


Figure 5. The molecular structure of $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$

Table 4. Selected bond parameters (lengths in Å, angles in degrees) for $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$

Os(1)–Os(2)	3.019(1)	Au(1)–Os(1)	2.694(1)
Os(1)–Os(3)	2.793(1)	Au(1)–Os(2)	2.855(1)
Os(1)–Os(4)	3.038(1)	Au(2)–Os(1)	2.662(1)
Os(1)–Os(5)	2.796(1)	Au(2)–Os(4)	2.873(1)
Os(2)–Os(3)	2.912(1)	Au(1)–P(1)	2.293(5)
Os(2)–Os(5)	2.897(1)	Au(2)–P(2)	2.295(5)
Os(3)–Os(4)	2.894(1)	Os(1)–C(1)	2.038(14)
Os(4)–Os(5)	2.892(1)	Os(2)–C(1)	2.072(17)
Os(4)–C(1)	2.019(17)	Os(3)–C(1)	2.026(18)
Os(5)–C(1)	2.056(18)		
Os(2)–Os(1)–Os(3)	60.0(1)	Os(1)–Au(1)–Os(2)	65.8(1)
Os(2)–Os(1)–Os(4)	84.5(1)	Os(1)–Au(1)–P(1)	153.5(1)
Os(2)–Os(1)–Os(5)	59.6(1)	Os(2)–Au(1)–P(1)	139.8(1)
Os(3)–Os(1)–Os(4)	59.3(1)	Os(1)–Au(2)–Os(4)	66.5(1)
Os(3)–Os(1)–Os(5)	93.6(1)	Os(1)–Au(2)–P(2)	162.2(1)
Os(4)–Os(1)–Os(5)	59.3(1)	Os(4)–Au(2)–P(2)	130.9(1)
Os(1)–Os(2)–Os(3)	56.2(1)	Os(1)–C(1)–Os(2)	94.5(7)
Os(1)–Os(2)–Os(5)	56.4(1)	Os(1)–C(1)–Os(3)	86.8(6)
Os(3)–Os(2)–Os(5)	89.1(1)	Os(1)–C(1)–Os(4)	97.0(6)
Os(1)–Os(3)–Os(2)	63.9(1)	Os(1)–C(1)–Os(5)	86.1(6)
Os(1)–Os(3)–Os(4)	64.5(1)	Os(2)–C(1)–Os(3)	90.5(7)
Os(2)–Os(3)–Os(4)	89.0(1)	Os(2)–C(1)–Os(4)	168.5(8)
Os(1)–Os(4)–Os(3)	56.1(1)	Os(2)–C(1)–Os(5)	89.1(7)
Os(1)–Os(4)–Os(5)	56.2(1)	Os(3)–C(1)–Os(4)	91.4(7)
Os(3)–Os(4)–Os(5)	89.5(1)	Os(3)–C(1)–Os(5)	172.9(8)
Os(1)–Os(5)–Os(2)	64.0(1)	Os(4)–C(1)–Os(5)	90.4(7)
Os(1)–Os(5)–Os(4)	64.5(1)		
Os(2)–Os(5)–Os(4)	89.4(1)		

it by crystallisation from the reaction mixture, or by t.l.c., led to a disproportionation to $[Os_5C(CO)_{14}]^{2-}$ and a neutral, red solid. However, the i.r. spectrum is consistent with the formulation of a monoanion such as $[Os_5C(CO)_{14}\{Au(PPh_3)\}]^-$ (9). The neutral, red solid could also be obtained directly by the reaction of $[Os_5C(CO)_{14}]^{2-}$ with two equivalents of $[Au(PPh_3)Cl]$. It was purified by t.l.c. using CH_2Cl_2–hexane (1 : 1) and initially characterised as $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10) on the basis of microanalysis and spectroscopic techniques. In order to obtain the full molecular geometry a single-crystal *X*-ray analysis was undertaken.

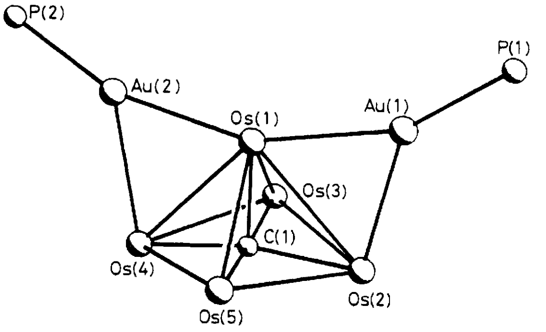


Figure 6. The core geometry in $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$

The molecular geometry of $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10) is shown in Figure 5 while selected bond parameters are listed in Table 4. There are no abnormally short contacts between the molecules in the solid state. As in the $[Os_5C(CO)_{14}]^{2-}$ dianion, the five Os atoms and the carbide carbon define a square-based pyramid. However, the two Au atoms from the Au(PPh$_3$) groups asymmetrically bridge two opposite Os (basal)–Os(apical) bonds. These two bridged bonds are *ca.* 0.23 Å longer [mean 3.029(5) Å] than the two unbridged bonds [mean 2.795(2) Å]. This has the effect of distorting the square-based pyramid (Figure 6) and the carbide, instead of lying beneath the Os$_4$ basal plane as in $[Os_5C(CO)_{15}]$[2] and $[Os_5C(CO)_{14}]^{2-}$, actually lies 0.04(2) Å above the mean plane of the four basal Os atoms, within the square pyramid; the four basal Os atoms show individual deviations of ±0.16 Å from this plane. The two unbridged Os(basal)–Os(apical) bond distances are shorter than the equivalent distances in [Os$_5$C-

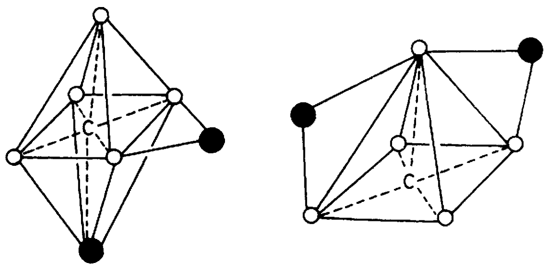
Table 5. Crystal data and refinement parameters for $[Os_5C(CO)_{16}]$ (4), $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ (7), and $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10)

	(4)	(7)	(10)
Formula	$C_{171}O_6Os_5$	$C_{87}H_{60}N_2O_{14}Os_5P_4$	$C_{51}H_{30}Au_2O_{14}Os_5P_2$
M	1 411.17	2 208.25	2 273.63
Crystal habit	Rectangular block	Rectangular block	Plate
Colour	Orange	Orange	Red
Crystal dimensions (mm)	0.34 × 0.27 × 0.24	0.41 × 0.27 × 0.23	0.49 × 0.37 × 0.11
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	10.017(3)	13.244(6)	20.307(4)
b/Å	15.823(5)	14.648(9)	9.843(2)
c/Å	16.507(8)	21.963(14)	27.980(6)
α/°	96.78(3)	86.78(5)	90.0
β/°	103.20(3)	85.54(5)	100.53(2)
γ/°	93.41(2)	81.22(5)	90.0
U/Å^3	2 519.3(2.5)	4 193.8(3.0)	5 498.5(3.0)
D_c/g cm^{-3}	3.72	1.75	2.75
Z	4	2	4
F(000)	2 440	2 324	4 064
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
μ(Mo-K_α)/cm^{-1}	251.99	76.61	169.07
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	Stoe
Mode of data collection	ω—2θ scan	ω—2θ scan	ω—θ scan
2θ limits/°	$3 < 2\theta < 50$	$3 < 2\theta < 50$	$5 < 2\theta < 50$
Reflections measured	7 874	8 453	10 618
Reflections used in refinement	6 120	5 780	7 013
n in $\vert F > n\sigma(F)\vert$	$n = 5$	$n = 3$	$n = 5$
Weighting scheme	$8.029/\vert\sigma^2(F) + 0.0015F^2\vert$	$\vert\sigma^2(F) + 0.002F^2\vert^{-1}$	$\vert\sigma^2(F) + 0.0018F^2\vert^{-1}$
Method of absorption correction	Pseudo-ellipsoid model	Pseudo-ellipsoid model	Numerical
No. of absorption scan data	402	403	—
Transmission factors min.	0.107	0.482	0.010
max.	1.000	0.921	0.161
Method of least-squares refinement	Blocked full matrix	Blocked cascade	Blocked cascade
R	0.073	0.065	0.060
R' $\vert\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\vert F_o\vert\vert$	0.071	0.066	0.063

Features common to all three data sets included the use of Mo-K_α radiation (λ = 0.710 69 Å); D_m = not measured.

$(CO)_{15}]$ [2] [mean 2.85(3) Å] and the shorter pair of Os(basal)–Os(apical) bonds in $[Os_5C(CO)_{14}]^{2-}$ [mean 2.815(2) Å]. The four Os(basal)–Os(basal) distances [mean 2.899(4) Å] in $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10) are similar in length to the average value of 2.88(2) Å in $[Os_5C(CO)_{15}]$ [2] and to the average value for the non-carbonyl bridged bonds of 2.912(4) Å in the dianion (7). The five Os–C(carbide) distances are not significantly different, and average 2.04(2) Å, similar to the values of 2.06(4) Å in $[Os_5C(CO)_{15}]$ [2] and 2.05(2) Å in $[Os_5C(CO)_{14}]^{2-}$.

There is evidence to suggest that a $Au(PPh_3)$ unit bonds to clusters in a similar manner to a hydride.[16] Certainly both ligands formally donate one electron to the cluster, and in the case of the former the Au atom is considered to be in the +1 oxidation state and it is an *sp*-hybridized orbital which interacts with the cluster. Hydride ligands are known to cause a lengthening of unsupported metal–metal bonds,[17] and $Au(PPh_3)$ appears to exert a similar effect.[18] In $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ the Os–Au distances are similar to the range [2.745(2)—2.803(2) Å] observed in $[Os_4Au(\mu\text{-}H)(CO)_{13}(PEt_3)]$ and $[Os_4Au(\mu\text{-}H)_3(CO)_{12}(PEt_3)]$.[18] In compound (10) the shorter Au–Os bond is associated with the apical Os(1) metal atom which is formally nine-co-ordinate; the other four Os atoms are seven- or eight-co-ordinate. It is probably better to consider the mode or bonding of the $Au(PPh_3)$ unit to the Os–Os bond as a three-centre delocalised bond involving the two Os and the Au atom. The P(1) and P(2) atoms lie only 0.22 and 0.14 Å out of the Os(1)Os(2)Au(1) and Os(1)Os(4)Au(2) planes, respectively, indicating that a projection of the Au–P vectors would intersect with the cluster along the bridged Os–Os edges. The bond parameters within the $Au(PPh_3)$ ligands are similar to those in a number of other OsAu clusters.[18,19] In view of the overall structure it appears that it is the influence of the gold phosphine ligands which causes the observed distortions in the metal framework, since there is little difference in the other bond parameters between $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ and $[Os_5C(CO)_{15}]$ or $[Os_5C(CO)_{14}]^{2-}$. It is probable that the structure of $[Os_5H_2(C)(CO)_{14}]$ is similar to that of (10) with the hydrides occupying similar sites to the $Au(PPh_3)$ groups.



$[Fe_5C(CO)_{14}\{Au(PPh_3)\}_2]$ $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$

Figure 7. The different core geometries of the clusters $[M_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (M = Fe or Os)

The 14 carbonyl groups are all terminally co-ordinated to the cluster, two to the apical metal atom, Os(1), and three each to the other four Os atoms. The average Os–C–O angle is 176(2)°, and the average Os–C and C–O distances are 1.89(3) and 1.15(3) Å, respectively.

Table 6. Atom co-ordinates (× 10^4) for compound (4)

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	10 117(1)	2 913(1)	6 400(1)
Os(2)	9 283(1)	3 622(1)	7 902(1)
Os(3)	10 164(1)	4 732(1)	6 924(1)
Os(4)	12 081(1)	4 438(1)	8 457(1)
Os(5)	12 873(1)	2 973(1)	7 484(1)
Os(6)	15 177(1)	8 973(1)	6 392(1)
Os(7)	14 236(1)	7 796(1)	7 414(1)
Os(8)	14 601(1)	9 509(1)	8 010(1)
Os(9)	16 746(1)	8 436(1)	8 678(1)
Os(10)	17 976(1)	8 771(1)	7 295(1)
C(1)	11 072(24)	3 663(13)	7 428(17)
C(2)	15 922(21)	8 714(11)	7 508(15)
C(11)	8 332(25)	2 996(16)	5 771(18)
O(11)	7 317(23)	2 992(12)	5 252(16)
C(12)	9 880(28)	1 729(12)	6 434(20)
O(12)	9 569(25)	1 001(12)	6 411(17)
C(13)	10 898(30)	2 890(16)	5 471(18)
O(13)	11 393(28)	2 927(15)	4 898(17)
C(21)	7 519(29)	3 169(18)	7 320(23)
O(21)	6 427(28)	2 835(17)	6 982(20)
C(22)	9 486(33)	2 855(18)	8 678(19)
O(22)	9 550(30)	2 430(16)	9 217(18)
C(23)	8 604(33)	4 451(17)	8 543(21)
O(23)	8 089(24)	4 975(13)	8 895(16)
C(31)	11 108(30)	5 092(16)	6 166(18)
O(31)	11 589(30)	5 283(16)	5 623(18)
C(32)	10 233(30)	5 838(11)	7 428(20)
O(32)	10 310(23)	6 565(11)	7 685(15)
C(33)	8 310(22)	4 789(15)	6 321(18)
O(33)	7 170(22)	4 833(13)	5 961(16)
C(41)	11 474(29)	5 337(15)	9 083(19)
O(41)	11 086(27)	5 891(14)	9 479(17)
C(42)	12 797(29)	3 992(16)	9 448(17)
O(42)	13 286(26)	3 636(15)	10 011(16)
C(43)	13 705(22)	5 090(14)	8 445(19)
O(43)	14 720(21)	5 470(13)	8 404(17)
C(51)	13 502(30)	3 745(16)	6 790(19)
O(51)	13 950(24)	4 168(13)	6 362(16)
C(52)	13 282(29)	2 027(13)	6 805(17)
O(52)	13 470(23)	1 413(11)	6 391(14)
C(53)	12 224(27)	2 178(14)	8 109(18)
O(53)	11 748(23)	1 670(13)	8 448(15)
C(54)	14 606(23)	3 149(14)	8 290(17)
O(54)	15 678(22)	3 280(13)	8 769(16)
C(61)	15 754(32)	10 029(14)	6 102(23)
O(61)	16 175(23)	10 694(12)	5 974(16)
C(62)	15 429(27)	8 233(14)	5 457(15)
O(62)	15 646(24)	7 739(13)	4 927(14)
C(63)	13 353(26)	9 071(17)	5 848(20)
O(63)	12 247(25)	9 160(14)	5 463(18)
C(71)	13 627(31)	7 338(17)	8 258(18)
O(71)	13 249(27)	7 093(15)	8 816(17)
C(72)	12 418(26)	7 753(17)	6 746(20)
O(72)	11 280(25)	7 714(14)	6 352(18)
C(73)	14 598(29)	6 748(13)	6 866(19)
O(73)	14 835(27)	6 073(13)	6 592(18)
C(81)	15 399(28)	10 624(13)	8 231(21)
O(81)	15 914(25)	11 323(12)	8 331(18)
C(82)	12 870(24)	9 798(18)	7 493(22)
O(82)	11 754(23)	9 969(13)	7 211(16)
C(83)	14 009(31)	9 497(16)	8 988(17)
O(83)	13 625(26)	9 432(13)	9 597(16)
C(91)	15 918(35)	8 256(19)	9 601(20)
O(91)	15 435(27)	8 079(14)	10 147(17)
C(92)	17 826(29)	7 518(14)	8 836(25)
O(92)	18 296(30)	6 858(10)	8 819(23)
C(93)	17 985(37)	9 197(19)	9 503(14)
O(93)	18 875(41)	9 678(23)	9 952(19)
C(101)	18 229(32)	9 977(13)	7 706(21)
O(101)	18 496(26)	10 698(13)	7 985(17)
C(102)	18 599(31)	8 957(16)	6 322(15)
O(102)	18 877(22)	9 081(12)	5 693(14)
C(103)	19 668(26)	8 641(16)	7 981(20)
O(103)	20 759(26)	8 547(15)	8 382(18)
C(104)	17 642(30)	7 550(12)	6 906(19)
O(104)	17 511(22)	6 837(11)	6 594(15)

Similar reactions have been reported between $[Fe_5C(CO)_{14}]^{2-}$ and $[Au(PR_3)Cl]$ (R = Ph or Et),[20] and the complexes $[Fe_5C(CO)_{14}\{Au(PR_3)\}]^-$ and $[Fe_5C(CO)_{14}\{Au(PR_3)\}_2]$ observed. However, the geometry of $[Fe_5C(CO)_{14}\{Au(PEt_3)\}_2]$ is in marked contrast to that of $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$.[20] In the former the Fe_5 core is a square-based pyramid with the carbide lying in the basal plane, but one $Au(PEt_3)$ bridges one of the basal Fe–Fe edges; the other three basal edges are bridged by carbonyl groups. The second $Au(PEt_3)$ group μ_4-caps the basal plane and interacts with the carbide to give a distorted Fe_5Au octahedron. The reason for this difference in structure between the iron and osmium analogues is not clear at present but it is probable that electronic rather than steric factors are of importance. The different core geometries of the two clusters $[M_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (M = Fe or Os) may be compared by reference to Figure 7.

Experimental

All reactions were carried out under nitrogen using dry, distilled solvents. Thin-layer chromatography (t.l.c.) and subsequent procedures were carried out in air. Autoclave reactions were carried out in a Roth laboratory autoclave of capacity 100 cm^3. The autoclave was charged, sealed, and purged of any air by pressurising to *ca.* 50 atm with the reaction gas and then venting to the atmosphere, twice, before filling to the required pressure. The compounds $[Ru_5C(CO)_{15}]$[1] and $[Os_5C(CO)_{15}]$[15] were prepared by literature methods.

Synthesis of $[Os_5C(CO)_{16}]$.—The preparation of $[Os_5C(CO)_{15}]$ *via* the pyrolysis of $[Os_3(CO)_{12}]$ rarely yields the carbido-cluster in high purity, the main contaminant being $[Os_6(CO)_{18}]$. The synthesis of $[Os_5C(CO)_{16}]$, then, is also the preferred method of purification of $[Os_5C(CO)_{15}]$ {which is regenerated on heating $[Os_5C(CO)_{16}]$ in solution}, the $[Os_6(CO)_{18}]$ being converted into the insoluble complex $[Os_6(CO)_{20}]$. In a typical experiment 200 mg of the $[Os_5C(CO)_{15}]$–$[Os_6(CO)_{18}]$ mixture were placed in an autoclave and treated, in the absence of solvent, with CO (50 atm) for 16 h at 165 °C. The autoclave was cooled, the pressure was released, and the solid was extracted with CH_2Cl_2 (100 cm^3) to give a dark blue solid, identified by its i.r. spectrum (Nujol mull) as $[Os_6(CO)_{20}]$, and an orange-yellow solution. The CH_2Cl_2 extracts were evaporated to dryness and the solid was further purified by t.l.c. in 30% $CHCl_3$–hexane. The t.l.c. plate showed the presence of several low-yield products and one strong yellow band, which was collected and found to be $[Os_5C(CO)_{16}]$ (yield 80 mg). Recrystallisation from CH_2Cl_2–hexane yielded *X*-ray-quality crystals of $[Os_5C(CO)_{16}]$.

Conversion of $[Os_5C(CO)_{16}]$ *into* $[Os_5C(CO)_{15}]$ (3).—The compound $[Os_5C(CO)_{16}]$ was heated in refluxing heptane for

Table 7. Atom co-ordinates ($\times$ 10^4) for compound (7)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	4 110(1)	3 219(1)	8 012(1)
Os(2)	4 266(1)	2 247(1)	6 955(1)
Os(3)	4 863(1)	502(1)	7 633(1)
Os(4)	4 723(1)	1 523(1)	8 740(1)
Os(5)	5 992(1)	1 967(1)	7 713(1)
C(1)	4 347(15)	1 826(14)	7 854(9)
C(11)	2 754(23)	3 657(19)	8 185(13)
O(11)	1 875(14)	3 931(12)	8 257(9)
C(12)	4 480(19)	4 243(18)	8 369(12)
O(12)	4 739(16)	4 861(13)	8 596(9)
C(13)	4 121(19)	3 637(18)	7 107(12)
O(13)	4 072(16)	4 353(11)	6 784(7)
C(21)	4 859(27)	2 280(24)	6 125(18)
O(21)	5 221(19)	2 321(17)	5 642(8)
C(22)	3 061(24)	2 206(21)	6 744(14)
O(22)	2 109(16)	2 264(16)	6 595(11)
C(31)	5 211(21)	202(19)	6 783(14)
O(31)	5 372(18)	−10(14)	6 311(9)
C(32)	3 635(23)	−43(20)	7 756(13)
O(32)	2 917(17)	−407(16)	7 816(12)
C(33)	5 843(24)	−491(23)	7 932(14)
O(33)	6 454(19)	−1 058(14)	8 070(12)
C(41)	5 528(20)	425(19)	9 166(13)
O(41)	5 880(16)	−122(13)	9 422(10)
C(42)	3 510(24)	1 431(19)	9 144(14)
O(42)	2 733(17)	1 368(15)	9 424(11)
C(43)	5 136(20)	2 467(18)	9 216(12)
O(43)	5 429(13)	2 984(11)	9 474(7)
C(51)	6 684(21)	1 673(18)	6 938(13)
O(51)	7 143(15)	1 462(16)	6 495(10)
C(52)	7 013(22)	1 252(20)	8 211(13)
O(52)	7 577(15)	849(16)	8 490(9)
C(53)	6 349(20)	3 137(19)	7 746(12)
O(53)	6 708(16)	3 827(13)	7 758(12)
N(1)	9 081(15)	3 503(13)	716(9)
P(1)	8 243(5)	3 448(4)	235(3)
C(101)	7 283(10)	2 736(10)	472(7)
C(102)	7 407(10)	1 824(10)	294(7)
C(103)	6 693(10)	1 251(10)	505(7)
C(104)	5 853(10)	1 591(10)	895(7)
C(105)	5 728(10)	2 503(10)	1 073(7)
C(106)	6 443(10)	3 076(10)	861(7)
C(111)	7 592(9)	4 601(10)	81(7)
C(112)	8 033(9)	5 353(10)	239(7)
C(113)	7 576(9)	6 252(10)	91(7)
C(114)	6 677(9)	6 399(10)	−215(7)
C(115)	6 235(9)	5 648(10)	−373(7)
C(116)	6 693(9)	4 749(10)	−225(7)
C(121)	8 899(11)	3 006(11)	−473(7)
C(122)	9 967(11)	2 854(11)	−532(7)
C(123)	10 478(11)	2 584(11)	−1 088(7)
C(124)	9 921(11)	2 466(11)	−1 584(7)
C(125)	8 853(11)	2 619(11)	−1 524(7)
C(126)	8 342(11)	2 888(11)	−969(7)
P(2)	9 535(5)	2 888(4)	1 269(3)
C(201)	10 667(12)	3 331(8)	1 438(7)
C(202)	11 466(12)	2 782(8)	1 723(7)
C(203)	12 301(12)	3 171(8)	1 883(7)
C(204)	12 337(12)	4 110(8)	1 757(7)
C(205)	11 538(12)	4 660(8)	1 472(7)
C(206)	10 704(12)	4 270(8)	1 312(7)
C(211)	9 847(11)	1 690(10)	1 121(7)
C(212)	10 769(11)	1 372(10)	796(7)
C(213)	10 983(11)	453(10)	632(7)
C(214)	10 274(11)	−148(10)	793(7)
C(215)	9 353(11)	170(10)	1 118(7)
C(216)	9 139(11)	1 089(10)	1 282(7)
C(221)	8 700(12)	3 038(10)	1 953(8)
C(222)	8 851(12)	2 437(10)	2 464(8)
C(223)	8 253(12)	2 616(10)	3 008(8)
C(224)	7 505(12)	3 396(10)	3 040(8)
C(225)	7 354(12)	3 997(10)	2 529(8)
C(226)	7 951(12)	3 818(10)	1 985(8)
N(2)	1 543(21)	2 535(15)	3 856(10)
P(3)	1 094(6)	1 734(5)	4 229(3)
C(301)	653(13)	1 015(13)	3 682(8)
C(302)	1 251(13)	879(13)	3 134(8)
C(303)	984(13)	308(13)	2 704(8)
C(304)	118(13)	−126(13)	2 822(8)
C(305)	−481(13)	9(13)	3 370(8)
C(306)	−213(13)	580(13)	3 800(8)
C(311)	1 993(13)	963(12)	4 664(8)
C(312)	2 125(13)	8(12)	4 610(8)
C(313)	2 851(13)	−563(12)	4 941(8)
C(314)	3 445(13)	−177(12)	5 326(8)
C(315)	3 313(13)	779(12)	5 380(8)
C(316)	2 587(13)	1 349(12)	5 048(8)
C(321)	14(15)	2 134(12)	4 732(7)
C(322)	−720(15)	2 840(12)	4 517(7)
C(323)	−1 590(15)	3 153(12)	4 891(7)
C(324)	−1 726(15)	2 761(12)	5 480(7)
C(325)	−992(15)	2 055(12)	5 695(7)
C(326)	−122(15)	1 741(12)	5 321(7)
P(4)	2 026(6)	3 461(5)	3 859(3)
C(401)	1 243(14)	4 368(10)	3 479(9)
C(402)	487(14)	4 139(10)	3 133(9)
C(403)	−152(14)	4 833(10)	2 828(9)
C(404)	−34(14)	5 757(10)	2 870(9)
C(405)	722(14)	5 987(10)	3 217(9)
C(406)	1 360(14)	5 293(10)	3 521(9)
C(411)	2 202(11)	3 824(13)	4 609(8)
C(412)	3 164(11)	3 841(13)	4 821(8)
C(413)	3 244(11)	4 129(13)	5 408(8)
C(414)	2 361(11)	4 401(13)	5 782(8)
C(415)	1 399(11)	4 384(13)	5 570(8)
C(416)	1 319(11)	4 096(13)	4 983(8)
C(421)	3 260(14)	3 278(10)	3 440(8)
C(422)	3 651(14)	4 009(10)	3 116(8)
C(423)	4 590(14)	3 848(10)	2 776(8)
C(424)	5 139(14)	2 957(10)	2 760(8)
C(425)	4 748(14)	2 226(10)	3 084(8)
C(426)	3 809(14)	2 386(10)	3 424(8)

30 min, after which the solution i.r. spectrum indicated the presence of pure $[Os_5C(CO)_{15}]$ (3).

Reduction of $[Ru_5C(CO)_{15}]$.—*Method* (*a*). Nitrogen was bubbled through a suspension of Na_2CO_3 (40 mg) in methanol (15 cm^3) for 0.25 h. The compound $[Ru_5C(CO)_{15}]$ (10 mg, 0.11 mol) was added and the mixture stirred for 0.25 h. As the red carbido-cluster dissolved an orange solution of $[Ru_5C(CO)_{14}]^{2-}$ was formed. Filtration, followed by addition of $[N(PPh_3)_2]Cl$ (13 mg, 0.023 mmol) to the filtrate and partial evaporation of the solvent by N_2 flow yielded orange microcrystals of $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ (6) (Found: C, 51.45; H, 3.25; N, 1.85. Calc.: C, 52.6; H, 3.00; N, 1.40%).

Method (*b*). The compound $[Ru_5C(CO)_{15}]$ (22 mg, 0.023 mmol) was added to tetrahydrofuran (thf) (30 cm^3). Three drops of Na/K alloy were added and the mixture stirred for 2 h. Filtration of the reaction mixture followed by addition of $[N(PPh_3)_2]Cl$ (27 mg, 0.047 mmol) to the orange filtrate and evaporation of the solvent gave an orange solid $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$.

Preparation of $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10).—Addition of

Table 8. Atom co-ordinates (× 10^4) for compound (10)

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	7 379(1)	963(1)	2 266(1)
Os(2)	5 969(1)	1 866(1)	2 305(1)
Os(3)	6 293(1)	−658(1)	1 857(1)
Os(4)	6 890(1)	915(1)	1 173(1)
Os(5)	6 849(1)	3 299(1)	1 771(1)
Au(1)	7 031(1)	1 595(1)	3 123(1)
Au(2)	8 173(1)	13(1)	1 684(1)
P(1)	7 260(3)	2 082(5)	3 938(2)
P(2)	9 043(2)	−1 029(4)	1 409(2)
C(1)	6 520(7)	1 325(18)	1 780(6)
C(11)	7 721(9)	−557(17)	2 624(7)
O(11)	7 950(9)	−1 489(14)	2 872(7)
C(12)	8 096(10)	2 150(19)	2 518(7)
O(12)	8 531(8)	2 872(15)	2 673(7)
C(21)	5 207(10)	2 195(19)	1 832(7)
O(21)	4 768(8)	2 359(18)	1 517(6)
C(22)	5 515(11)	871(21)	2 729(9)
O(22)	5 207(8)	322(17)	2 988(7)
C(23)	5 881(10)	3 448(18)	2 685(7)
O(23)	5 827(9)	4 436(16)	2 886(6)
C(31)	6 832(9)	−2 170(18)	1 715(7)
O(31)	7 148(8)	−2 996(13)	1 625(8)
C(32)	5 483(13)	−1 215(25)	1 444(10)
O(32)	4 998(10)	−1 493(28)	1 193(11)
C(33)	6 159(12)	−1 579(23)	2 410(9)
O(33)	6 088(12)	−2 173(19)	2 763(9)
C(41)	6 997(12)	−762(24)	852(10)
O(41)	6 987(10)	−1 728(16)	629(7)
C(42)	7 503(11)	1 734(21)	831(9)
O(42)	7 892(9)	2 280(17)	638(7)
C(43)	6 151(15)	1 407(28)	730(11)
O(43)	5 647(11)	1 773(26)	480(8)
C(51)	7 052(9)	4 566(19)	2 297(7)
O(51)	7 205(9)	5 299(14)	2 595(6)
C(52)	6 198(10)	4 450(19)	1 378(8)
O(52)	5 834(8)	5 139(16)	1 142(7)
C(53)	7 586(10)	3 959(20)	1 529(8)
O(53)	8 079(10)	4 345(17)	1 394(8)
C(111)	6 820(6)	1 054(14)	4 323(5)
C(112)	7 116(6)	686(14)	4 795(5)
C(113)	6 751(6)	−51(14)	5 083(5)
C(114)	6 089(6)	−420(14)	4 900(5)
C(115)	5 793(6)	−51(14)	4 428(5)
C(116)	6 159(6)	686(14)	4 139(5)
C(121)	7 072(8)	3 859(14)	4 038(5)
C(122)	6 652(8)	4 253(14)	4 355(5)
C(123)	6 493(8)	5 621(14)	4 397(5)
C(124)	6 755(8)	6 596(14)	4 122(5)
C(125)	7 175(8)	6 201(14)	3 804(5)
C(126)	7 334(8)	4 833(14)	3 762(5)
C(131)	8 140(6)	1 896(12)	4 208(5)
C(132)	8 410(6)	2 676(12)	4 613(5)
C(133)	9 079(6)	2 510(12)	4 833(5)
C(134)	9 478(6)	1 564(12)	4 648(5)
C(135)	9 209(6)	784(12)	4 243(5)
C(136)	8 540(6)	950(12)	4 023(5)
C(211)	9 707(7)	116(13)	1 309(5)
C(212)	9 727(7)	1 413(13)	1 512(5)
C(213)	10 247(7)	2 301(13)	1 464(5)
C(214)	10 746(7)	1 891(13)	1 212(5)
C(215)	10 725(7)	594(13)	1 009(5)
C(216)	10 206(7)	−293(13)	1 057(5)
C(221)	8 803(7)	−1 851(12)	816(5)
C(222)	8 810(7)	−3 259(12)	761(5)
C(223)	8 575(7)	−3 841(12)	307(5)
C(224)	8 333(7)	−3 014(12)	−91(5)
C(225)	8 327(7)	−1 606(12)	−36(5)
C(226)	8 562(7)	−1 024(12)	417(5)
C(231)	9 401(6)	−2 423(14)	1 794(6)
C(232)	8 969(6)	−3 034(14)	2 064(6)
C(233)	9 168(6)	−4 204(14)	2 334(6)
C(234)	9 799(6)	−4 763(14)	2 333(6)
C(235)	10 231(6)	−4 152(14)	2 063(6)
C(236)	10 032(6)	−2 982(14)	1 793(6)

$[Au(PPh_3)Cl]$ (6 mg) and $Tl[PF_6]$ (5 mg) to $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ (15 mg) in CH_2Cl_2 (8 cm^3) led to a gradual change in the colour of the solution (5 min) from yellow to red when the reaction was complete. T.l.c. of the solution using CH_2Cl_2–hexane (1 : 1) as eluant gave pure $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (10) which was crystallised from CH_2Cl_2–hexane by slow evaporation at 0 °C (Found: C, 26.7; H, 1.4; P, 2.8. Calc.: C, 26.8; H, 1.3; P, 2.7%).

Reduction of $[Os_5C(CO)_{15}]$.—*Method* (*a*). Nitrogen was bubbled through a stirred suspension of Na_2CO_3 (150 mg) in methanol (60 cm^3) for 0.25 h. The compound $[Os_5C(CO)_{15}]$ (50 mg, 0.36 mmol) was added and the mixture stirred for 2.5 h. As the orange solid dissolved a yellow solution of $[Os_5C(CO)_{14}]^{2-}$ was produced. Filtration, followed by the addition of $[N(PPh_3)_2]Cl$ (42 mg, 0.073 mmol) and evaporation to a volume of 10 cm^3, gave a yellow microcrystalline solid, $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ (7) (yield 66 mg, 75%).

Method (*b*). The salt $[NEt_4][BH_4]$ (62.5 mg) was added to $[Os_5C(CO)_{15}]$ (100 mg), in CH_2Cl_2 (18 cm^3). The mixture was stirred for 0.5 h, and excess of $[NEt_4][BH_4]$ removed by washing with water (3 × 18 cm^3); the CH_2Cl_2 solution was dried over $MgSO_4$. Filtration of the mixture followed by evaporation of the solvent gave $[NEt_4][Os_5H(C)(CO)_n]$ (8) (n = 14 or 15) as a yellow powder which was subsequently recrystallised from CH_2Cl_2–hexane (1 : 2) (yield 62.8 mg, 57%).

Preparation of $[Os_5H_2(C)(CO)_{15}]$ (5).—*Method* (*a*). Addition of three drops of concentrated H_2SO_4 (A.R. grade) to a solution of $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ (15 mg) in CH_2Cl_2 (10 cm^3) gave a brown solution of the dihydride.

Method (*b*). Reaction of $[Os_5C(CO)_{15}]$ (20 mg) with H_2 (50 atm) in heptane (50 cm^3) in an autoclave (130 °C, 2 h) gave a yellow solution having the same i.r. spectrum as the product from method (*a*).

Molecular Structure Determinations of $[Os_5C(CO)_{16}]$, $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$, *and* $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$.—Suitable single crystals of the three compounds were mounted either in Lindemann tubes or on the end of glass fibres with epoxy-resin adhesive, and unit-cell dimensions and space groups determined *via* Weissenberg (Cu) *X*-ray photography.

The crystals were transferred to a four-circle diffractometer and the intensity data recorded using the parameters displayed in Table 5. The accurate cell parameters were derived from the angular measurements of a number of reflections in the range $15 < 2\theta < 25°$. On the Syntex diffractometer a 96-step scan was employed, and the scan rate varied from 3.0 to 29.3° min^{-1} depending on the intensity obtained from a 1-s prescan; reflections with intensities below 9 counts s^{-1} were not remeasured. On the Stoe four-circle diffractometer a 24-step scan was employed, with a step width of 0.04°, and a step time which was varied between 0.5 and 3.0 s depending upon the intensity measured in a 0.5-s prescan. Three standard reflections were measured at regular intervals throughout the data collections and showed no significant variations.

Each of the three data sets were profile fitted.[21] Empirical absorption corrections were applied to the $[Os_5C(CO)_{16}]$ and $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ data sets using a pseudo-ellipsoid model and azimuthal scan data. A numerical absorption correction was applied to the $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ data set; the crystal was bounded by the planes {100}, {010}, and {001}. Lorentz polarisation corrections were also applied.

In each structure solution the unique Os atom positions were derived from multisolution Σ_2 sign expansion and the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. In the appropriate structures the H atoms on the phenyl rings were placed in idealised positions (C–H 1.08 Å and C–C–H 120°) and a common isotropic thermal parameter assigned. The phenyl groups were constrained to be regular hexagons (C–C 1.395 Å and C–C–C 120°) and refined as rigid bodies. In the $[Os_5C(CO)_{16}]$ structure, the carbonyl C–O distances were constrained to be 1.170(1) Å. The structures were refined until convergence was reached, with the Os atoms assigned anisotropic thermal parameters for $[Os_5C(CO)_{16}]$, the Os, N, P, and carbonyl O atoms assigned anisotropic thermal parameters for $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$, and the Os, Au, P, carbide C, and carbonyl O atoms assigned anisotropic thermal parameters for $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$.

Complex neutral atom scattering factors [22] were employed throughout all three structure solutions and refinements. All computations were performed on the University of Cambridge IBM 370/165 computer using programs written by Professor G. M. Sheldrick. The molecular plots were drawn using the PLUTO package written by Dr. W. D. S. Motherwell. The final atomic co-ordinates for the non-hydrogen atoms for $[Os_5C(CO)_{16}]$, $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$, and $[Os_5C(CO)_{14}\{Au(PPh_3)\}_2]$ are listed in Tables 6, 7, and 8, respectively.

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References

1 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. McPartlin, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 277.

2 P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 564.

3 W. J. H. Nelson, unpublished work.

4 M. Tachikawa, A. C. Sievert, E. L. Muetterties, M. R. Thompson, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1980, **102**, 1725.

5 C. G. Cooke and M. J. Mays, *J. Organomet. Chem.*, 1969, **16**, 471.

6 M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Reiger, and M. S. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442.

7 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, P. R. Raithby, M. Schröder, and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1982, 610.

8 A. G. Orpen and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1992; J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *ibid.*, p. 1994; P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 2099.

9 B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1977, **33**, 173.

10 M. Bernard, *Inorg. Chem.*, 1979, **18**, 2782.

11 P. A. Dawson, B. F. G. Johnson, J. Lewis, D. A. Kaner, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 961.

12 J. J. Guy and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1725.

13 K. Wade, *Chem. Br.*, 1975, **11**, 177.

14 M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1976, 883; A. V. Rivera, G. M. Sheldrick, and M. B. Hursthouse, *Acta Crystallogr., Sect. B*, 1978, **34**, 3376; P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224.

15 D. Braga, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, J. N. Nicholls, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1982, 966.

16 J. W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103**, 7648.

17 M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.

18 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314.

19 B. F. G. Johnson, D. A. Kaner, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **215**, C33.

20 B. F. G. Johnson, D. A. Kaner, J. Lewis, and M. J. Rosales, *J. Organomet. Chem.*, 1982, **238**, C73.

21 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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