Bifunctional Activation of a Carbonyl Group in the Pentanuclear Carbido-clusters $[Os_5C(CO)_{15}]$ and $[Os_5C(CO)_{15}I_2]$ by Alcohols: *X*-Ray Analysis of $[Os_5C(CO)_{14}(CO_2Et)H]$ and $[Os_5C(CO)_{14}(CO_2Me)I]$ †,‡

Brian F. G. Johnson, Jack Lewis,* William J. H. Nelson, J. Nichola Nicholls, and Maria D. Vargas
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Dario Braga, Kim Henrick, and Mary McPartlin
School of Chemistry, The Polytechnic of North London, London N7 8DB

The clusters $[Os_5C(CO)_{15}]$ (1) and $[Os_5C(CO)_{15}I_2]$ (2) react with alcohols (ROH) under mild conditions to give derivatives of the type $[Os_5C(CO)_{14}(CO_2R)H]$ (3) and $[Os_5C(CO)_{14}(CO_2R)I]$ (4) respectively. *X*-Ray analysis has confirmed that in both cases the alkoxy-group has attacked a carbonyl ligand in the parent compound to form a C,O-bonded μ-CO_2R group. In contrast, when the species $[Os_5C(CO)_{15}I(X)]$ [X = H or Au(PPh_3)] are heated under reflux in alcohols the complexes $[Os_5C(CO)_{15-n}I(X)]$ [*n* = 1 or 2, X = H; *n* = 1, X = Au(PPh_3)] are formed, as had previously been found for the analogous ruthenium compounds. Crystals of $[Os_5C(CO)_{14}(CO_2Et)H]$ (3; R = Et) are monoclinic, space group $P2_1/n$, with *a* = 15.665(3), *b* = 16.761(3), *c* = 10.198(2) Å, β = 90.4(1)°, and *Z* = 4; refinement of atomic parameters using 3 461 absorption-corrected data converged at *R* 0.0386. The complex $[Os_5C(CO)_{14}(CO_2Me)I]$ (4; R = Me) crystallises in the orthorhombic space group $Pna2_1$ with *a* = 17.019(3), *b* = 10.063(3), *c* = 15.810(3) Å, and *Z* = 4; refinement of atomic parameters using 2 460 absorption-corrected data converged at *R* 0.0487.

We have recently reported that new high-nuclearity cluster species $[Os_8(CO)_{22}H]^-$ and $[Os_9(CO)_{21}\{CHC(CH_3)CH\}]^-$ are obtained when $[Os_3(CO)_{12}]$ is heated under reflux in Bu^{t}OH.[1,2] As an extension of this work we have investigated the reactions of the pentanuclear carbido-cluster $[Os_5C(CO)_{15}]$ (1) and its di-iodo-derivative $[Os_5C(CO)_{15}I_2]$ (2) with alcohols. The reactions of the analogous ruthenium compounds have been reported previously.[3]

Results and Discussion

When $[Os_5C(CO)_{15}]$ (1) is heated under reflux with alcohol (ROH), compounds formulated as $Os_5C(CO)_{15}H(OR)$ on the basis of n.m.r. and mass spectrometric data (Table 1) are obtained in good yield. However, the similarity of their i.r. spectra to that[4] of $[Os_5C(CO)_{14}H(NC_5H_4)]$ indicated that these compounds were the result of alkoxy attack on a carbonyl ligand and should be formulated as $[Os_5C(CO)_{14}(CO_2R)H]$. This was confirmed by an *X*-ray analysis of the EtOH derivative, (3), which has the structure shown in Figures 1 and 2. Selected bond distances and angles for (3) are given in Table 2.

$$\underset{(1)}{[Os_5C(CO)_{15}]} \xrightarrow{\text{ROH, reflux}} \underset{(3;\ R\ =\ Et)}{[Os_5C(CO)_{14}(CO_2R)H]} \quad \text{(i)}$$

Table 1. Spectroscopic data for the complexes

Compound	$\tilde{\nu}$(CO)/cm^{-1} [a]	*m/z* [b]
(1) $[Os_5C(CO)_{15}]$	2 095w, 2 073vs, 2 033s, 2 015w	1 392
(2) $[Os_5C(CO)_{15}I_2]$	2 112w, 2 080s, 2 070vs, 2 026m	1 646
(3) $[Os_5C(CO)_{14}(CO_2Et)H]$ [c]	2 109w, 2 081vs, 2 061vs, 2 056(sh), 2 028s, 1 984m, 1 970w	1 438
(4) $[Os_5C(CO)_{14}(CO_2Me)I]$ [d]	2 106w, 2 077s, 2 063vs, 2 059(sh), 2 026s, 2 019m, 2 006m, 1 998w, 1 977w	1 423
(5) $[Os_5C(CO)_{15}H(I)]$	2 121w, 2 088s, 2 075s(sh), 2 070vs, 2 055w(sh), 2 021m,br, 1 991w	1 520
$[Os_5C(CO)_{14}H(I)]$	2 083s, 2 074w, 2 067vs, 2 058m, 2 040s, 2 023m, 2 020(sh), 2 009w, 2 000w	1 492
$[Os_5C(CO)_{13}H(I)]$	2 105m, 2 071s, 2 058vs, 2 051s, 2 037m, 2 028w, 2 019w, 2 010m, 1 993w	1 464
(6) $[Os_5\{Au(PPh_3)\}C(CO)_{15}I]$	2 105w, 2 076m, 2 066vs, 2 045s, 2 006m, 1 980w, 1 968w	
$[Os_5\{Au(PPh_3)\}C(CO)_{14}I]$ [e]	2 100w, 2 067m, 2 058vs, 2 046m, 2 025w, 2 006w, 1 999vw, 1 989vw	

[a] In CH_2Cl_2. Full details of the i.r. spectroscopic characterisation of these complexes will be reported elsewhere. [b] Based on ^{192}Os. [c] Proton n.m.r. in $CDCl_3$: δ 6.25 (q, CH_2), 8.95 (t, CH_3), and 34.68 (s, OsH). [d] Proton n.m.r. in CD_2Cl_2: δ 7.09 (s, CH_3). [e] In hexane.

In compound (3) the metal core has the 'bridged-butterfly' or *arachno*-pentagonal-bipyramidal geometry expected for M_5 clusters with eight skeletal electron pairs (*S* = 8).[5,6] The carbonyl ligands are all terminal with Os–C–O angles in the range 174—179°. Osmium atoms Os(1), Os(2), Os(3), and Os(5) are each attached to three carbonyl ligands, and two are co-ordinated to Os(4). The two equatorial atoms Os(4) and Os(5) are spanned by a μ-CO_2Et group; the Os(4) ··· Os(5) distance is 3.604 Å, 0.494 Å shorter than the corresponding unbridged distance on the other side of the molecule

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† Preliminary report: 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.

‡ μ_5-Carbido-1,1,1,2,2,2,3,3,3,4,4,5,5,5-tetradecacarbonyl-2,4-μ-ethoxycarbonyl-*C*(Os^4)*O*(Os^2)-3,4-μ-hydrido-*cyclo*-pentaosmium-(7 *Os–Os*) and μ_5-carbido-1,1,1,2,2,2,3,3,3,4,4,5,5,5-tetradecacarbonyl-3,4-μ-iodo-2,4-μ-methoxycarbonyl-*C*(Os^4)*O*(Os^2)-*cyclo*-pentaosmium(6 *Os–Os*).

Supplementary data available (No. SUP 23924, 51 pp.): thermal parameters, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

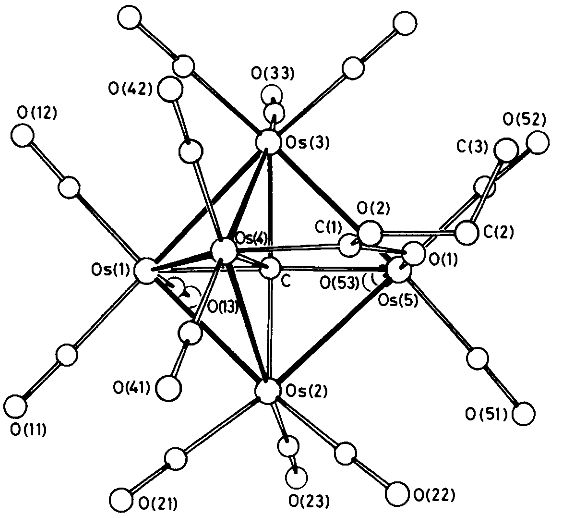


Figure 1. Molecular structure of $[Os_5C(CO)_{14}(CO_2Et)H]$ (3). The carbon atoms of the carbonyl ligands have the same numbers as the oxygens to which they are attached

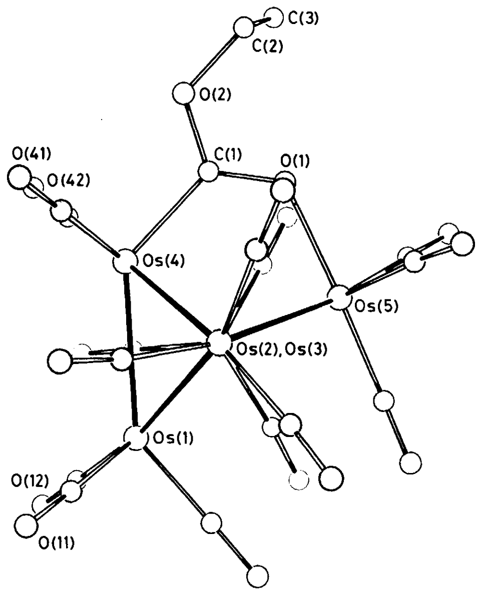


Figure 2. Molecular structure of $[Os_5C(CO)_{14}(CO_2Et)H]$ (3) viewed onto the equatorial plane formed by Os(1), Os(4), and Os(5)

Table 2. Selected bond lengths (Å) and angles (°) for complexes (3) and (4)

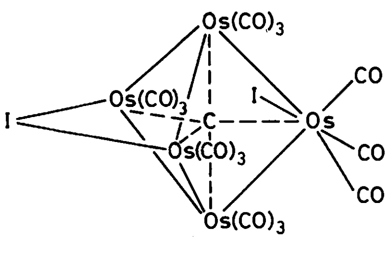
	(3)	(4)
Os(1)–Os(2)	2.889(1)	2.906(2)
Os(1)–Os(3)	2.885(1)	2.922(2)
Os(1)–Os(4)	2.921(1)	
Os(2)–Os(4)	2.857(1)	2.916(2)
Os(2)–Os(5)	2.916(1)	2.915(2)
Os(3)–Os(4)	2.865(1)	2.927(3)
Os(3)–Os(5)	2.931(1)	2.905(2)
Os(1)–I		2.834(4)
Os(4)–I		2.833(3)
Os(4)–C(1)	2.028(15)	2.02(4)
Os(5)–O(1)	2.118(12)	2.17(3)
Os–Carbido C	1.959—2.112(16)	1.88—2.21(3)
Os–Carbonyl C	1.884—1.971(17)	1.84—1.96(5)
Carbonyl C–O	1.103—1.172(23)	1.05—1.22(6)
C(1)–O(1)	1.283(20)	1.29(5)
C(1)–O(2)	1.344(2)	1.28(5)
C(2)–O(2)	1.473(23)	1.56(6)
C(2)–C(3)	1.35(4)	
C(2)–O(2)–C(1)	120(1)	122(4)
O(2)–C(1)–Os(4)	120(1)	121(3)
O(2)–C(1)–O(1)	116(1)	119(4)
C(1)–O(1)–Os(5)	124(1)	128(3)
O(1)–C(1)–Os(4)	124(1)	120(3)
Os(1)–I–Os(4)		76.6(1)
Os(1)–Os(4)–C(1)	134.1(5)	
O(1)–Os(5)–C(53)	176.4(6)	176(1)
I–Os(4)–C(1)		178(1)
Os–C–O (carbonyl)	174—179(2)	166—179(5)

[Os(1) ··· Os(5) 4.101 Å]. The overall structure is very similar to that of $[Os_5C(CO)_{14}H(\mu\text{-}NC_5H_4)]$ in which an ortho-metallated pyridine ligand also spans equatorial Os atoms giving an Os(4) ··· Os(5) distance of 3.626 Å.[4] It may be inferred from the characteristic displacement of the carbonyl ligands[7] associated with the 'hinge' bond Os(1)–Os(4) (Figure 2, *cis* Os–Os–CO angles 111.7—117.1°) that the H ligand is bridging these two atoms.

Bridging CO_2R ligands have also been found in clusters of the type $[Os_3(CO)_{10}(CO_2R)H]$,[8] prepared in low yield by acidification of the anionic mixture formed on reaction of $[Os_3(CO)_{12}]$ with alkoxides dissolved in their corresponding alcohol as solvent. In this reaction anionic intermediates of the type $[Os_3(CO)_{11}(\sigma\text{-}CO_2R)]^-$ are formed which readily give the bridged derivatives *via* loss of a CO group.[8] Formation of compound (3) in the present work may also be viewed as the result of initial nucleophilic attack by an alkoxide group on the carbon atom of a CO ligand, followed by a bending across of the carbonyl oxygen atom to donate two electrons to an adjacent Os atom. However, in this case this process results in the cleavage of an Os–Os bond instead of the ejection of a CO group.

The attack of the alkoxy-group of ROH at a carbonyl ligand in (1) to give (3) may be contrasted with the better known reactions of the clusters $[M_5C(CO)_{15}]$ (M = Ru or Os) with molecules of the type XY [X = H, $Au(PPh_3)$, Br, or I; Y = Cl, Br, or I]. Adducts of the form $[M_5C(CO)_{15}(\mu\text{-}X)Y]$ are produced having a bridged-butterfly configuration of metal atoms in which the X ligand spans the butterfly 'hinge' bond, and the halide atom, Y, is attached terminally to the metal that spans the 'wing-tips' of the butterfly.[3,9] However, a reaction more similar to the formation of (3) is that of $[AuMe(PPh_3)]$ with $[Ru_5C(CO)_{15}]$ in which attack of methyl occurs at a CO group also to produce the complex $[Ru_5\{Au(PPh_3)\}C(CO)_{14}(\mu\text{-}COMe)]$.[10] This has a structure closely related to that of (3), but with the gold group instead of hydrogen spanning the 'hinge' of the bridged butterfly M_5 arrangement. Treatment of $[M_5C(CO)_{15}]$ (M = Ru or Os) with stronger nucleophiles, such as $[OH]^-$, results in expulsion of CO as CO_2, leading to the formation of the dianions $[M_5C(CO)_{14}]^{2-}$.[11]

Compounds containing a similar bridging CO_2R ligand, $[Os_5C(CO)_{14}(CO_2R)I]$, are formed under even milder conditions. When MeOH was added as a solvent to $[Os_5C(CO)_{15}I_2]$ (2), in an attempt to obtain crystals suitable for *X*-ray analysis, the orange-yellow solid immediately dissolved to give a pale yellow solution. Removal of the solvent gave a pale yellow microcrystalline solid which was shown to be $[Os_5C(CO)_{14}(CO_2Me)I]$ (4), from i.r. and mass spectroscopic data (Table 1), and a full single-crystal *X*-ray analysis. A comparison of the i.r. spectrum of $[Os_5C(CO)_{15}I_2]$ (2) with those of the structurally characterised[8] derivatives $[M_5C(CO)_{15}H(X)]$



(2)

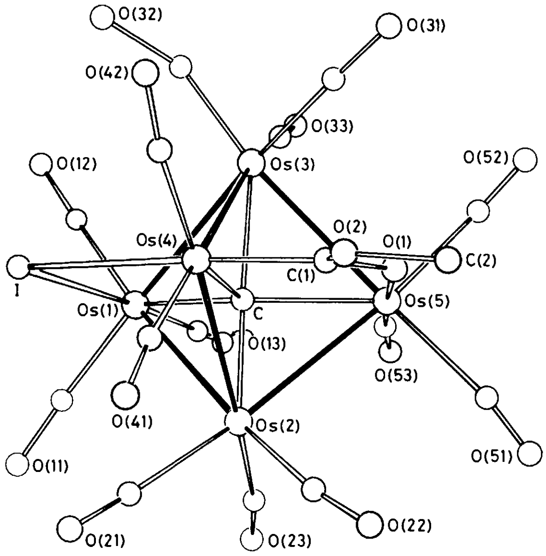


Figure 3. Molecular structure of $[Os_5C(CO)_{14}(CO_2Me)I]$ (4)

$$\begin{array}{lcl}[Os_5C(CO)_{15}I_2] & \xrightarrow{ROH,\ r.t.} & [Os_5C(CO)_{14}(CO_2R)I] \quad (ii)\\ (2) & & (4;\ R = Me)\end{array}$$

indicates that (2) may have the structure shown. The MeOH derivative (4) has a related structure to that proposed for (2). It is also similar to that in (3) but with the 'hinge' bond broken [Os(1) · · · Os(4) 3.512(3) Å] by the presence of the μ-I ligand which contributes two more electrons than the μ-H ligand in (3). The overall structure of (4) is shown in Figure 3 and selected bond lengths and angles are given in Table 2.

The metal geometry in compound (4) may be described as a distorted trigonal bipyramid with three very long, non-bonded Os · · · Os distances in the equatorial plane, or alternatively as a *hypho*-hexagonal bipyramid (Figure 4) the geometry expected from Wade theory for pentanuclear clusters with $S = 9$.[5] As in (3), atoms Os(1), Os(2), Os(3), and Os(5) are each attached to three terminal carbonyl ligands, and two terminal CO groups are co-ordinated to Os(4); the Os–C–O angles are in the range 166—179°.

The bonding mode of the CO_2Me ligand in compound (4) is very similar to that observed in (3). The C(1)–O(1) distances in these complexes [1.283(20) Å in (3) and 1.29(5) Å in (4)] are longer than the C–O distances of the carbonyl ligands, consistent with the decrease in bond order produced by the alkoxy attachment to the C atom. Although the bifunctional activation of CO, in which both the C and O atoms are co-ordinated, is thought to aid the three primary modes of CO reduction recognised at present,[12] few specific models of intermediates of this type in the conversion of carbon monoxide into (ultimately) separate C and O atoms on a metal surface have been found in clusters with more than four metal atoms.

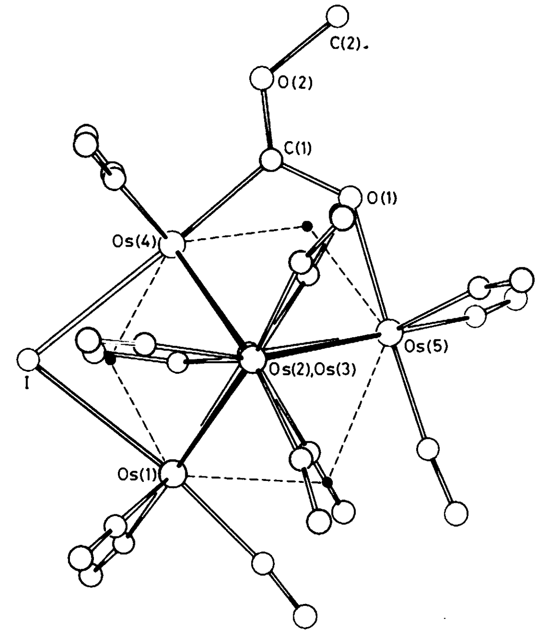


Figure 4. Molecular structure of $[Os_5C(CO)_{14}(CO_2Me)I]$ (4) viewed onto the equatorial plane formed by Os(1), Os(4), and Os(5), showing the relationship to a *hypho*-hexagonal bipyramid. Important non-bonded distances are Os(1) · · · Os(4) 3.512(3), Os(1) · · · Os(5) 3.985(2), and Os(4) · · · Os(5) 3.625(2) Å

The formation of compound (4) may also be viewed as initial attack by an alkoxy-group on the carbon atom of a CO ligand in (2), but in this case the oxygen atom replaces the terminal iodide present in (2) which is eliminated as HI. Conversion of $[M_5C(CO)_{15}]$ (M = Ru or Os), which has a square-pyramidal metal skeleton ($S = 7$), into derivatives of the type $[M_5C(CO)_{15}L]$, in which the metal atoms adopt a bridged-butterfly arrangement, is a very facile process.[5,13] It seems therefore that the halogen atoms in compound (2) are responsible for the easier formation of the μ-CO_2R group in (4), and the activation of the CO group in (2) towards alkoxy attack is not simply a consequence of the 'preformed' metal geometry.

As an extension of this work, the reactivity of the complexes $[Os_5C(CO)_{15}I(X)]$ [X = H (5) or $Au(PPh_3)$ (6)] with alcohols was investigated. On heating these complexes under reflux in EtOH, CO ejection occurs rather than the formation of a μ-CO_2R ligand, and the species $[Os_5C(CO)_{15-n}I(X)]$ are formed. From these results it may be concluded that the two

$$\begin{array}{lcl}[Os_5C(CO)_{15}I(X)] & \xrightarrow{ROH,\ reflux} & Os_5C(CO)_{15-n}I(X) + nCO \quad (iii)\\ (5)\ X = H & & n = 1 \text{ or } 2,\ X = H\\ (6)\ X = Au(PPh_3) & & n = 1,\ X = Au(PPh_3)\end{array}$$

reactions which the CO ligand in $[Os_5C(CO)_{15}I(X)]$ [X = I, H, or $Au(PPh_3)$] can undergo are competitive processes and of these attack of 'RO^-' at the carbon atom of the carbonyl group seems to be favoured by the presence of the μ-I three-electron donor atom.

The carbido-atom appears to play an important role in determining the structures adopted by these carbido-clusters as the number of cluster valence electrons is increased. The differences in geometry between *nido*-octahedral ($S = 7$), *arachno*-pentagonal bipyramidal ($S = 8$), and *hypho*-hexagonal bipyramidal ($S = 9$) may be regarded as resulting from breaking of Os–Os bonds in such a way that an approximately linear Os–C–Os axis is always maintained with the other three Os atoms swinging round it in the equatorial plane. Effectively the metal core may be regarded as having a trigonal-bipyramidal geometry of differing degrees of distortion. This contrasts with the behaviour usually observed on addition of electrons to species without carbido-atoms, *i.e.* stepwise fission of metal–metal bonds leading to several possible arrangements of metal atoms.[14] In compounds (3) and (4) the CO_2C unit lies in the equatorial Os(1),Os(4),Os(5),C(carbido) plane and it is interesting that in similar Os_5C derivatives substitution or addition of ligands occurs primarily in this plane.[4,13,15]

Reaction of compound (3) with H_2 or CO [160 °C, 50 atm (*ca.* 5.07×10^6 Pa), 3 h] leads to removal of the alkoxy-group and, on the basis of mass spectroscopic evidence, formation of the known dihydride $[Os_5C(CO)_{15}H_2]$.[11] In the reaction with CO it is thought that some disproportionation of the starting material occurs to provide the extra H ligands required to form the dihydride. A second known cluster, $[Os_5C(CO)_{16}]$,[11] was also isolated from the reaction of (3) with CO and was identified by i.r. and mass spectroscopy. The alkoxy-group also appears to be removed by concentrated H_2SO_4 in CH_2Cl_2; a cationic species is formed which we believe to be $[Os_5C(CO)_{15}H]^+$ from a comparison of its i.r. spectrum [ν(CO) in CH_2Cl_2 at 2 125vw, 2 099m, 2 084ms, 2 077s, 2 062w, 2 035(sh), 2 031m, and 2 008vw cm^{-1}] with that of the ions $[M_5C(CO)_{15}H]^+$ (M = Ru or Os), formed by protonation of the parent carbonyl carbido-species.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas as calibrant (central position 2 143 cm^{-1}), and n.m.r. spectra were obtained on a Varian CFT20 spectrometer. Thin-layer chromatography plates (Merck) consisted of 20 × 20 mm glass plates coated with a 0.25-mm layer of silica gel.

Preparation of $[Os_5C(CO)_{14}(CO_2R)H]$.—The complex $[Os_5C(CO)_{15}]$ (1) (40 mg) was heated under reflux in MeOH, EtOH, or Bu^{t}OH (20 cm^3). A slow colour change from orange to pale yellow was observed; the reaction was monitored by i.r. spectroscopy and was complete after 17, 6, and 2 h respectively. Evaporation of the solvents followed by crystallisation from CH_2Cl_2–ROH by slow evaporation at 0 °C gave light yellow crystals of $[Os_5C(CO)_{14}(CO_2R)H]$. Yields of recrystallised product varied from 60 to 80%. Spectroscopic data for these compounds are given in Table 1.

Synthesis of $[Os_5C(CO)_{15}I_2]$.—Slow addition of 1 equivalent of I_2 in CH_2Cl_2 to a solution of $[Os_5C(CO)_{15}]$ (10 mg) in CH_2Cl_2 (5 cm^3) gave $[Os_5C(CO)_{15}I_2]$ (2) as the only product. Evaporation of the solvent gave (2) in quantitative yield (Table 1).

Reaction of $[Os_5C(CO)_{15}I_2]$ *with* MeOH.—When MeOH (3 cm^3) was added to $[Os_5C(CO)_{15}I_2]$ (2) (15 mg) in an attempt to obtain crystals of *X*-ray quality using this solvent, the solid immediately dissolved to give a pale yellow solution. Reduction of the volume of the solution by one quarter gave a light yellow powder identified as $[Os_5C(CO)_{14}(CO_2Me)I]$ (4) on the basis of i.r., n.m.r., and mass spectroscopy (Table 1). Yields of product recrystallised (from CH_2Cl_2) varied from 80 to 90%.

Preparation of $[Os_5C(CO)_{15}H(I)]$.—Hydrogen iodide, prepared from iodine and tetrahydronaphthalene,[16] was bubbled through a warm (60 °C) solution of $[Os_5C(CO)_{15}]$ (20 mg) in hexane (20 cm^3) for 2 h. A change in colour of the solution occurred from orange to yellow. The solvent was evaporated and the compound purified by t.l.c. using CH_2Cl_2–hexane (1 : 1) as eluant. The product, $[Os_5C(CO)_{15}H(I)]$ (5), was crystallised in 60% yield from CH_2Cl_2–hexane and characterised by i.r. and mass spectroscopy (Table 1).

Preparation of $[Os_5\{Au(PPh_3)\}C(CO)_{15}I]$.—Addition of 1 equivalent of $[AuI(PPh_3)]$ to $[Os_5C(CO)_{15}]$ (15 mg) in CH_2Cl_2 (5 cm^3) gave, after 1 h, $[Os_5\{Au(PPh_3)\}C(CO)_{15}I]$ (6). Evaporation of the solvent followed by crystallisation from CH_2Cl_2–hexane gave orange crystals of the pure compound in quantitative yield; these were characterised by i.r. spectroscopy (Table 1) and microanalysis (Found: C, 22.0; H, 1.1; P, 1.8. Calc. for $C_{34}H_{15}AuIO_{15}Os_5P$: C, 22.2; H, 0.8; P, 1.7%).

Reaction of $[Os_5C(CO)_{15}H(I)]$ *with* EtOH.—The complex $[Os_5C(CO)_{15}H(I)]$ (5) (10 mg) was heated under reflux in EtOH (10 cm^3) for 6 h. The reaction was monitored by i.r. spectroscopy; after 2 h the main product was $[Os_5C(CO)_{14}H(I)]$ and after 4 h it was $[Os_5C(CO)_{13}H(I)]$. The solvent was evaporated, the yellow solid taken up in CH_2Cl_2, and the solution was filtered. Attempts to crystallise the compound by slow-evaporation techniques from CH_2Cl_2–hexane failed: it decomposed after 24 h at room temperature. Spectroscopic data for the complexes $[Os_5C(CO)_{15-n}H(I)]$ (n = 1 or 2) are given in Table 1.

Reaction of $[Os_5\{Au(PPh_3)\}C(CO)_{15}I]$ *with* EtOH.—The complex $[Os_5\{Au(PPh_3)\}C(CO)_{15}I]$ (15 mg) was heated under reflux in EtOH (10 cm^3) for 1 h; i.r. spectroscopy showed that $[Os_5\{Au(PPh_3)\}C(CO)_{14}I]$ was the only product of the reaction at this stage. This was recrystallised from CH_2Cl_2–hexane and characterised by i.r. spectroscopy (Table 1) and microanalysis (Found: C, 21.5; H, 0.9. Calc. for $C_{33}H_{15}AuIO_{14}Os_5P$: C, 21.8; H, 0.8%).

Crystallography.—*Crystal data.* (3) $C_{18}H_6O_{16}Os_5$, M = 1 429.24, monoclinic, space group $P2_1/n$, a = 15.665(3), b = 16.761(3), c = 10.198(2) Å, β = 90.4(1)°, U = 2 677.53 Å^3, Z = 4, D_c = 3.544 g cm^{-3}, $F(000)$ = 2 488, μ(Mo-K_α) = 227.90 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å.

(4) $C_{17}H_3IO_{16}Os_5$, M = 1 541.11, orthorhombic, space group $Pna2_1$, a = 17.019(3), b = 10.063(3), c = 15.810(3) Å, U = 2 707.66 Å^3, Z = 4, D_c = 3.779 g cm^{-3}, $F(000)$ = 2 700, μ(Mo-K_α) = 236.08 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å.

The methods of data collection, data processing, and absorption correction used for compounds (3) and (4) were similar to those described previously.[17] The crystals selected for data collection had dimensions 0.34 × 0.16 × 0.13 mm for (3) and 0.23 × 0.12 × 0.09 mm for (4). A scan width of 0.80° was used to collect data in the range θ 3—25.0° for both crystals. 427 Azimuthal scan data for (3) and 361 for (4) were used in absorption correction, and relative transmission factors varied from 1.00 to 0.35 for (3) and 1.00 to 0.78 for (4). Equivalent reflections were averaged to give 3 461 and 2 460 data with $I/\sigma(I) > 3.0$ for (3) and (4) respectively.

Structure solution and refinement.[18] For both compounds (3) and (4) the positions of the five osmium atoms were found from respective Patterson syntheses. The remaining non-hydrogen atoms were found from subsequent Fourier difference syntheses. Blocked full-matrix refinement of the atomic positional and thermal parameters converged at final R and R' values of 0.0386 and 0.0377 for (3) and 0.0487 and 0.0474

Table 3. Fractional atomic co-ordinates for [$Os_5C(CO)_{14}(CO_2Et)H$] (3)

Atom	x	y	z	Atom	x	y	z
Os(1)	0.195 37(4)	0.177 11(4)	−0.257 42(6)	C(32)	0.118 7(14)	0.005 6(11)	−0.115 3(20)
Os(2)	0.302 51(4)	0.273 04(4)	−0.088 02(6)	O(32)	0.111 7(10)	−0.054 3(8)	−0.169 5(17)
Os(3)	0.130 11(4)	0.103 00(4)	−0.023 22(6)	C(33)	0.015 1(13)	0.137 2(10)	−0.049 6(15)
Os(4)	0.310 63(4)	0.103 26(4)	−0.066 48(6)	O(33)	−0.053 9(9)	0.154 8(10)	−0.075 3(15)
Os(5)	0.188 97(4)	0.240 26(4)	0.130 91(6)	C(41)	0.429 4(15)	0.109 0(12)	−0.101 3(22)
C	0.217 0(10)	0.190 4(8)	−0.054 1(16)	O(41)	0.502 1(12)	0.115 7(12)	−0.125 2(22)
C(11)	0.252 3(12)	0.218 9(11)	−0.405 4(17)	C(42)	0.310 8(10)	−0.009 0(11)	−0.057 8(17)
O(11)	0.286 2(11)	0.242 2(10)	−0.500 0(12)	O(42)	0.313 2(11)	−0.077 8(9)	−0.050 6(17)
C(12)	0.135 2(15)	0.099 3(12)	−0.357 9(18)	C(51)	0.239 4(14)	0.328 7(11)	0.223 5(20)
O(12)	0.099 1(11)	0.052 1(9)	−0.419 7(15)	O(51)	0.267 2(11)	0.384 0(9)	0.275 3(15)
C(13)	0.109 4(13)	0.256 6(10)	−0.273 2(16)	C(52)	0.123 0(11)	0.208 2(10)	0.286 1(16)
O(13)	0.056 0(10)	0.303 4(9)	−0.282 6(17)	O(52)	0.087 6(9)	0.194 2(9)	0.376 4(13)
C(21)	0.383 6(12)	0.273 8(11)	−0.226 3(18)	C(53)	0.097 9(13)	0.302 7(11)	0.063 1(17)
O(21)	0.437 2(9)	0.270 9(8)	−0.303 3(13)	O(53)	0.044 6(10)	0.338 9(9)	0.022 1(15)
C(22)	0.386 8(13)	0.305 1(11)	0.036 2(19)	C(1)	0.328 4(12)	0.115 0(10)	0.129 7(15)
O(22)	0.437 2(10)	0.325 6(10)	0.113 0(15)	C(2)	0.401 8(17)	0.081 5(14)	0.333 9(18)
C(23)	0.255 9(13)	0.375 0(11)	−0.115 8(18)	C(3)	0.346 8(28)	0.039 9(19)	0.409 0(28)
O(23)	0.226 9(11)	0.435 7(8)	−0.137 9(15)	O(1)	0.286 8(8)	0.164 1(7)	0.201 7(12)
C(31)	0.115 2(12)	0.051 9(11)	0.143 6(20)	O(2)	0.387 8(9)	0.071 0(7)	0.192 1(13)
O(31)	0.106 9(11)	0.021 2(9)	0.241 1(15)				

Table 4. Fractional atomic co-ordinates for [$Os_5C(CO)_{14}(CO_2Me)I$] (4)

Atom	x	y	z	Atom	x	y	z
Os(1)	0.228 71(9)	0.204 63(17)	0.306 43(14)	O(22)	−0.058 7(21)	0.033 5(39)	0.233 9(24)
Os(2)	0.086 22(9)	0.146 06(16)	0.130 60(13)	C(23)	0.035 1(24)	0.293 7(40)	0.081 9(26)
Os(3)	0.222 52(9)	−0.075 04(16)	−0.012 74(13)	O(23)	0.014 7(22)	0.384 2(37)	0.051 8(23)
Os(4)	0.195 32(9)	−0.068 59(16)	0.170 00(12)	C(31)	0.209 1(30)	−0.263 5(54)	−0.029 0(32)
Os(5)	0.052 84(9)	−0.050 42(17)	0.000 00	O(31)	0.194 7(20)	−0.373 9(34)	−0.037 0(20)
I	0.315 1(2)	0.126 1(3)	0.181 3(2)	C(32)	0.335 1(34)	−0.099 3(53)	−0.000 6(38)
C	0.154 1(21)	0.034 4(33)	0.069 1(20)	O(32)	0.402 7(24)	−0.117 1(39)	0.009 0(26)
C(1)	0.106 7(25)	−0.201 4(42)	0.162 9(27)	C(33)	0.225 7(24)	−0.037 2(42)	−0.127 5(26)
C(2)	0.024 8(33)	−0.386 7(54)	0.219 0(34)	O(33)	0.227 6(23)	−0.006 8(41)	−0.196 5(25)
O(1)	0.058 9(18)	−0.198 2(29)	0.099 5(18)	C(41)	0.177 4(27)	−0.052 8(46)	0.291 6(27)
O(2)	0.095 6(20)	−0.288 1(34)	0.220 8(20)	O(41)	0.158 2(24)	−0.035 5(40)	0.360 0(24)
C(11)	0.226 4(25)	0.373 4(42)	0.087 9(28)	C(42)	0.268 8(27)	−0.200 5(45)	0.192 5(28)
O(11)	0.222 5(19)	0.472 1(34)	0.123 7(21)	O(42)	0.316 9(23)	−0.287 6(37)	0.195 3(24)
C(12)	0.325 2(22)	0.216 0(38)	−0.022 9(23)	C(51)	−0.059 8(20)	−0.050 0(34)	0.027 6(20)
O(12)	0.384 4(25)	0.221 0(41)	−0.060 2(26)	O(51)	−0.127 3(23)	−0.039 8(38)	0.042 1(24)
C(13)	0.179 2(31)	0.261 9(54)	−0.060 6(33)	C(52)	0.039 8(30)	−0.184 7(52)	−0.088 8(31)
O(13)	0 154 7(23)	0.323 2(38)	−0.117 5(24)	O(52)	0.036 3(23)	−0.274 1(40)	−0.132 1(25)
C(21)	0.118 2(30)	0.240 1(52)	0.233 6(32)	C(53)	0.039 4(22)	0.079 5(38)	−0.088 0(24)
O(21)	0.132 9(23)	0.291 1(38)	0.297 4(24)	O(53)	0.028 0(22)	0.151 4(38)	−0.134 3(22)
C(22)	−0.001 4(28)	0.080 1(47)	0.198 5(28)				

for (4).[17] Anisotropic thermal parameters were assigned to the Os and I atoms of (4) and to all the non-hydrogen atoms of (3) in the final cycles of refinement.

The final atomic co-ordinates for the anions in compounds (3) and (4) are listed in Tables 3 and 4 respectively.

Acknowledgements

We thank the S.E.R.C. (D. B. and J. N. N.), I.C.I. (W. J. H. N.), and C.N.Pq (Brazil) (M. D. V.) for financial support and Dr. J. Puga for running the n.m.r. spectra.

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Received 19*th September* 1983; *Paper* 3/1644