The Chemistry of Polynuclear Compounds. Part XXVI.[1] Products of the Pyrolysis of Dodecacarbonyl-*triangulo*-triruthenium and -triosmium †

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Pyrolysis of [$Ru_3(CO)_{12}$] in a sealed evacuated tube gives [$Ru_6(CO)_{17}C$] thereby clearly establishing that the ' isolated ' carbon atom is derived from reduction of a CO group. Pyrolysis of [$Os_3(CO)_{12}$] under similar conditions leads to formation of polynuclear osmium carbonyl species based on five to eight osmium atoms, *viz.* [$Os_5(CO)_{16}$], [$Os_5(CO)_{15}C$], [$Os_6(CO)_{18}$], [$Os_7(CO)_{21}$], [$Os_8(CO)_{23}$], and [$Os_8(CO)_{21}C$]. The probable structures of these polynuclear complexes are discussed.

WE have previously shown[2] that thermal decomposition of dodecacarbonyl-*triangulo*-triruthenium, [$Ru_3(CO)_{12}$], in n-octane or n-nonane under reflux leads to formation of the hexanuclear carbido-cluster [$Ru_6(CO)_{17}C$]. This parent carbide, together with the arene-substituted form, [$Ru_6(CO)_{14}C(arene)$] (arene = toluene, *m*-xylene, or mesitylene), is also produced on heating [$Ru_3(CO)_{12}$] in the appropriate arene under reflux for 5 h.[2] More recently, the parent carbide has been isolated in moderate yield from the reaction of [$Ru_3(CO)_{12}$] with di-n-butyl ether [3] or 4,6,7-trimethylazulene.[4] The presence of an isolated carbon atom has been confirmed by single-crystal *X*-ray diffraction studies on both [$Ru_6(CO)_{17}C$] [5] and [$Ru_6(CO)_{14}C(C_6H_3Me_3\text{-}1,3,5)$] [6] but the origin of the carbon atom remained uncertain. In a recent publication by Chini and his co-workers [7] the anion [$Rh_6(CO)_{15}C]^{2-}$ has been identified by single-crystal *X*-ray analysis and apparently the carbide atom is derived from chloroform. This has been confirmed by ^{13}C-labelling experiments. It was, therefore, of some interest to establish the source of the single carbon atom in [$Ru_6(CO)_{17}C$] and it was with this in mind that the work presented here was initiated. An obvious extension of the work was to the pyrolysis of [$Os_3(CO)_{12}$]. We now report that with this carbonyl, and unlike [$Ru_3(CO)_{12}$], pyrolysis leads to formation of polynuclear osmium carbonyls based on Os_5, Os_6, Os_7, and Os_8 units and the new carbidocarbonyl clusters [$Os_5(CO)_{15}C$] and [$Os_8(CO)_{21}C$]. Brief reports [8,9] of this work have been previously given; in this paper we discuss the full preparative details and probable structures of these complexes.

RESULTS AND CONCLUSIONS

Pyrolysis of [$Ru_3(CO)_{12}$].—On heating [$Ru_3(CO)_{12}$] at 150 °C in a sealed tube for 12 h a green solid was obtained; after separation by t.l.c. a low yield (*ca.* 5%) of [$Ru_6(CO)_{17}C$] together with some residual [$Ru_3(CO)_{12}$] were

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† No reprints available.

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obtained. The yields of $[Ru_6(CO)_{17}C]$ increased slightly as the temperature of the reaction was raised to a maximum of 180 °C. Above this temperature total conversion into ruthenium metal was observed. At all temperatures the only carbonyl product which could be isolated was $[Ru_6(CO)_{17}C]$. The formation of the hexanuclear carbide, which was identified on the basis of its mass and i.r. spectra, conclusively shows that the isolated carbon atom arises from reduction of a co-ordinated carbonyl group since the cluster has been produced in the absence of any other source of carbon. In the course of this work, it was found that, contrary to our previous report,[2] small amounts (*ca.* 3%) of $[Ru_6(CO)_{14}C(C_6H_6)]$ could be produced by heating $[Ru_3(CO)_{12}]$ in benzene for at least 3 d. This complex was isolated as an air-stable purple solid by t.l.c. and characterized by the usual spectroscopic methods (Table 1).

TABLE 1

I.r. spectrum, ^1H n.m.r. spectrum, and molecular-ion value (m/e) of $[Ru_6(CO)_{14}C(C_6H_6)]$

I.r. spectrum (cm^{-1}) [a]			
ν(CO)	Co-ordinated benzene	τ [b]	*m/e* [c]
2 076s	2 950	4.44	1 089
2 030s (sh)	2 915		
2 022vs	2 855		
2 003m (sh)	1 098		
1 980m	1 003		
1 970m (sh)			
1 809w, br			

[a] In $CHCl_3$. [b] In $CDCl_3$ with tetramethylsilane as internal standard. [c] There is a difference of only six mass units between the molecular ions of $[Ru_6(CO)_{14}C(C_6H_6)]$ and $[Ru_6(CO)_{17}C]$; this makes the use of an internal standard, such as 1,3,5-tris(perfluoroheptyl)triazine, essential.

The formation of $[Ru_6(CO)_{17}C]$ by reduction of a co-ordinated carbonyl group possibly suggests that the carbide atoms in the polynuclear iron clusters $[Fe_5(CO)_{15}C]$, $[Fe_5(CO)_{14}C]^{2-}$, and $[Fe_6(CO)_{16}C]^{2-}$ might be produced in a similar manner.[10-13] However, our attempts to produce iron carbidocarbonyls, *e.g.* $[Fe_6(CO)_{17}C]$ or $[Fe_5(CO)_{15}C]$, by pyrolysis (90—114 °C) of $[Fe_3(CO)_{12}]$ in sealed evacuated tubes led to formation of $[Fe(CO)_5]$ and metallic iron; the same substances were the products of pyrolysis of $[Fe_3(CO)_{12}]$ in n-octane, n-nonane, mesitylene, *m*-xylene, toluene, or benzene under reflux. When other metal carbonyls were pyrolyzed in the complete absence of solvents using sealed evacuated tubes, carbide clusters were not produced. Thus $[Re_2(CO)_{10}]$ (183—300 °C) gave only rhenium metal, $[Co_4(CO)_{12}]$ (63—100 °C) and $[Rh_4(CO)_{12}]$ (130—170 °C) were converted into the hexanuclear clusters $[Co_6(CO)_{16}]$ and $[Rh_6(CO)_{16}]$, whilst $[Ir_4(CO)_{12}]$ (165—260 °C) was extremely inert and no evidence for higher clusters was found.

Pyrolysis of $[Os_3(CO)_{12}]$.—Pyrolysis of $[Os_3(CO)_{12}]$ in a sealed tube at 210 °C for 12 h gave a dark brown, highly crystalline, solid. After extraction into ethyl acetate followed by separation using t.l.c., a number of air-stable metal carbonyl complexes were obtained. One of these corresponded to a small amount of unchanged $[Os_3(CO)_{12}]$ whilst the remainder were polynuclear carbonyls based on units of five to eight osmium atoms.

The characterization of these new clusters, which presented a considerable problem because of the difficulties encountered in their separation and purification, resulted largely from mass spectroscopic studies. In all cases the spectra obtained were similar to those of other unsubstituted polynuclear carbonyls [14-16] and exhibited intense molecular-ion peaks and peaks corresponding to stepwise loss of carbonyl groups. The isotopic distributions within these peaks were in complete agreement with computed patterns. In keeping with the enhanced stability associated with clusters of second- and third-row transition metals, the cluster unit $[M_n]^+$ (n = 5—8) did not break down further and, more significantly, doubly charged ions were observed in high abundance. The effectiveness of microanalysis in the formulation of these osmium carbonyls is very limited because the analytical values are insufficiently different to clearly distinguish between the clusters (Table 2). In two cases our formulations have been confirmed by single-crystal *X*-ray analysis.[17,18]

TABLE 2

Calculated analytical data (%) for the new osmium clusters

Compound	C	Os
$[Os_5(CO)_{16}]$	13.7	68.0
$[Os_6(CO)_{18}]$	13.1	69.4
$[Os_7(CO)_{21}]$	13.1	69.4
$[Os_8(CO)_{23}]$	12.7	70.2

By far the major product of this reaction at 210 °C was $[Os_6(CO)_{18}]$ (80%) which could be isolated in moderately large quantities and in high purity. Other products were $[Os_5(CO)_{16}]$ (7%), $[Os_7(CO)_{21}]$ (10%), and $[Os_8(CO)_{23}]$ (2%). When the temperature of the pyrolysis was steadily increased to a maximum of 260 °C (when total conversion to osmium metal was observed) the yields of $[Os_7(CO)_{21}]$ and $[Os_8(CO)_{23}]$ improved considerably whilst $[Os_5(CO)_{16}]$ was no longer observed. At these higher temperatures the carbides $[Os_5(CO)_{15}C]$ and $[Os_8(CO)_{21}C]$ were also produced. Thus at 250 °C a typical product analysis was $[Os_6(CO)_{18}]$ (60%), $[Os_7(CO)_{21}]$ (20%), $[Os_8(CO)_{23}]$ (5%), $[Os_8(CO)_{21}C]$ (8%), and $[Os_5(CO)_{15}C]$ (5%). The carbides $[Os_5(CO)_{15}C]$ and $[Os_8(CO)_{21}C]$ were also characterized by their mass spectra which showed strong molecular ions, ions corresponding to stepwise loss of CO groups, and a very intense peak due to the

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$[Os_nC]^+$ ion (n = 5 or 8 respectively). Unlike the cluster $[Fe_5(CO)_{15}C]$ no further fragmentation of these osmium carbido-ions was observed and in general these spectra are very similar to those reported for $[Ru_6(CO)_{17}C]$. A surprising feature of these $[Os_3(CO)_{12}]$ pyrolysis reactions was the absence of $[Os_6(CO)_{17}C]$, a fact which contrasts sharply with the pyrolysis of $[Ru_3(CO)_{12}]$. The synthetic routes employed in this work again indicate that the source of the carbido-carbon is from reduction of a co-ordinated carbonyl group. The formation of carbides is obviously preferred at higher temperatures and this supports our view that under the conditions used they arise from a reaction of type (1). The chemistry of the

$$[Os_8(CO)_{23}] \longrightarrow [Os_8(CO)_{21}C] + CO_2 \qquad (1)$$

' carbon atom ' in these and other carbide systems is under investigation since their ready formation may suggest their potential intermediacy in any high-temperature reaction process.

From these pyrolysis studies it is apparent that the size of the cluster produced increases with temperature and that in the limiting case osmium metal is formed. It is reasonable to assume therefore that the clusters are intermediates in formation of the metal and it is interesting to speculate on their usefulness as catalysts spanning as they do homo- and hetero-geneous systems. Furthermore these clusters contain *ca.* 70% osmium metal, the amount of which increases with cluster size (Table 2) such that in the limiting case it may be convenient to consider very large clusters as the equivalent of adsorption of carbon monoxide onto a metal surface. These polynuclear carbonyls may therefore assimilate some of the chemical reactivity associated with carbon monoxide on an osmium surface.

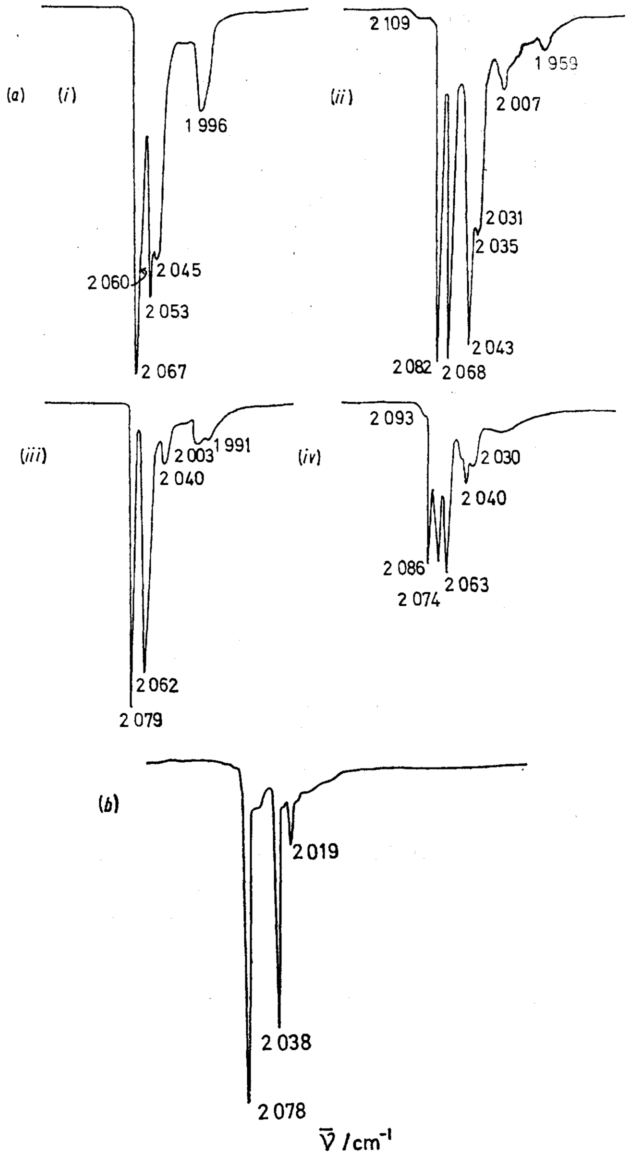
TABLE 3

Colour, i.r. spectra (1 600—2 200 cm^{-1}), and molecular-ion value (m/e) of the products obtained from pyrolysis of $[Os_3(CO)_{12}]$ at various temperatures

Compound	Colour	ν(CO)*/cm^{-1}	m/e
$[Os_5(CO)_{16}]$	pink-red	2 067vs, 2 060m (sh), 2 053s, 2 045s, 1 996m (br)	1 400
$[Os_6(CO)_{18}]$	dark brown	2 109vw, 2 082s, 2 068s, 2 043s, 2 035m, 2 031m (sh), 2 007w, 1 959w	1 646
$[Os_7(CO)_{21}]$	orange	2 079s, 2 062s, br, 2 040w, 2 003w, 1 991w	1 920
$[Os_8(CO)_{23}]$	orange-yellow	2 093w, 2 086s, 2 074s, 2 063s, 2 040m, 2 030w	2 167
$[Os_5(CO)_{15}C]$	yellow	2 078vs, 2 038s, 2 019w	1 384
$[Os_8(CO)_{21}C]$	deep purple	2 093m, 2 080m, 2 074s, 2 049vw, 2 041vw, 2 029w, br, 2 023w, br, 2 010w	2 123

* In cyclohexane. In some cases the spectra have been recalibrated.[8,9]

Probable Structures of the New Clusters.—Some physical data for the four new osmium carbonyl clusters are given in Table 3 whilst the i.r. spectra in the carbonyl-stretching region are given in Figure (*a*). The relative simplicity of these spectra indicates that the symmetry of the molecules is moderately high. In addition, the absence of bands in the region 1 900—1 700 cm^{-1} appears to indicate that bridging carbonyl groups are not present; this possibility cannot be *entirely* excluded since in some cases this type of absorption is known to be very weak and broad.



I.r. spectra (1 600—2 200 cm^{-1}) in cyclohexane: (*a*) the four new polynuclear clusters produced on pyrolysis of $[Os_3(CO)_{12}]$ at 210 °C $[Os_5(CO)_{16}]$(*i*), $[Os_6(CO)_{18}]$ (*ii*), $[Os_7(CO)_{21}]$ (*iii*), and $[Os_8(CO)_{23}]$ (*iv*); (*b*) $[Os_5(CO)_{15}C]$

(*a*) *Each individual metal atom obeying the* 18-*electron rule.* Table 4 predicts the arrangement of metal atoms if each individual metal atom obeyed the 18-electron rule. In the cases of $[Os_5(CO)_{16}]$, $[Os_7(CO)_{21}]$, and $[Os_8(CO)_{23}]$ $\{[Os_8(CO)_{21}C]\}$ it is necessary to invoke bridging carbonyls if each *individual* metal atom obeys the 18-electron rule.

(*b*) *Application of Wade's skeletal electron-counting scheme.* It is apparent from preliminary *X*-ray data on these osmium clusters, that Wade's skeletal electron-counting scheme [19-22] can be applied to some of these polynuclear carbonyls. In this scheme the bonding orbitals of the cluster result from interaction of three atomic orbitals on each metal atom whilst the remaining six orbitals are used for bonding of the ligands to the cluster. The orbitals available for ligand bonding are the first to be filled with electron pairs and those electron pairs which remain are then assigned to cluster bonding (skeletal electron pairs). In terms of a molecular-orbital approach, Wade's scheme suggests that the highest-filled and lowest-empty molecular orbitals are primarily cluster-bonding orbitals whereas the metal–ligand bonding orbitals are at lower energy.

TABLE 4

Compound	Number of valence electrons	Number of metal–metal bonds required for the cluster to obey the 18-electron rule	Number of skeletal electron pairs (S)		Predicted structure	
					a	*b*
$[Os_5(CO)_{15}C]$	74	$\frac{1}{2}(50 - 34) = 8$	7	$(n + 2)$	square-based prism	square-based pyramid
$[Os_5(CO)_{16}]$	72	$\frac{1}{2}(50 - 32) = 9$	6	$(n + 1)$	trigonal bipyramid	trigonal bipyramid
$[Os_6(CO)_{18}]$	84	$\frac{1}{2}(60 - 36) = 12$	6	(n)	regular octahedron	
$[Os_7(CO)_{21}]$	98	$\frac{1}{2}(70 - 42) = 14$	7	(n)	edge-bridged octahedron	
$[Os_8(CO)_{23}]$ $[Os_8(CO)_{21}C]$	110	$\frac{1}{2}(80 - 46) = 17$	7	$(n - 1)$	edge- and face-bridged octahedron or bicapped-trigonal prism	

[a] If the 18-electron rule is obeyed by each metal atom. [b] According to Wade's scheme.

Species with n skeletal atoms adopt *closo* structures if held together by $(n + 1)$ pairs of skeletal electrons, *nido* structures (with one polyhedral corner vacant) if by $(n + 2)$ pairs, and *arachno* structures (two corners vacant) if by $(n + 3)$ pairs. For a transition-metal cluster the total number of skeletal electron pairs (S) is given by formula (2). Table 4 shows the number of

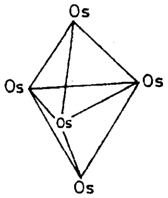
$$S = \tfrac{1}{2}\,(\text{total valence electrons} - 12n) \qquad (2)$$

skeletal electron pairs and the predicted structure for the polynuclear osmium carbonyls described in this paper. It can be seen from this Table that Wade's scheme is not capable of predicting structures for clusters which have n metal atoms and n or $(n - 1)$ skeletal electron pairs. However, the basic stereochemistry of the cluster is established from the number of electron pairs involved in the cluster bonding ($S = 5$, tetrahedron; $S = 6$, trigonal bipyramid; $S = 7$, regular octahedron). Thus we propose that by extending Wade's scheme structures for clusters in which $S = n$ or $(n - 1)$ can be predicted, by taking the basic polyhedra derived from the value of S and, for $S = n$, capping this polyhedra once, whilst for $S = (n - 1)$, capping it twice.

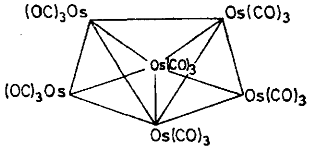
(*c*) *Proposed and observed structures.* (*i*) $[Os_5(CO)_{15}C]$. Both schemes (*a*) and (*b*) predict a square-based pyramidal structure for this pentanuclear carbide. The i.r. spectrum [Figure (*b*)] in the carbonyl region was similar to that of $[Fe_5(CO)_{15}C]$ [10,11] for which a square-based pyramidal structure has been established from *X*-ray studies. Obviously this carbide and the ruthenium analogue are of the same type.

(*ii*) $[Os_5(CO)_{16}]$. *X*-Ray data are not yet available on this cluster but both (*a*) and (*b*) predict a trigonal-prismatic structure, (I). The arrangement of the carbonyl groups is not known, but in order to overcome the observation that (symmetric) bridging carbonyl groups (i.r. spectrum) are apparently not present it is possible that this cluster contains either metal atoms in variable oxidation states similar to that proposed [17] for $[Os_6(CO)_{18}]$ and/or very asymmetric carbonyl bridges. In any case, the complete carbonyl cluster obeys the 18-electron rule.

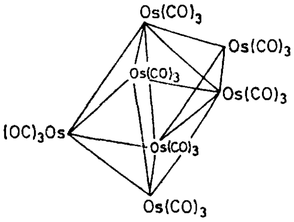
(*iii*) $[Os_6(CO)_{18}]$. Whereas scheme (*a*) may be taken to predict a regular octahedral arrangement of metal atoms with three terminal carbonyl groups bonded to each metal, our extension of Wade's scheme (*b*) predicts a bicapped-tetrahedral structure ($S = 6$; based on a trigonal bipyramid but $S = n = 6$, thus one face is capped with the extra osmium atom). Single-crystal



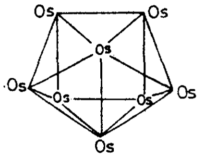
(I)



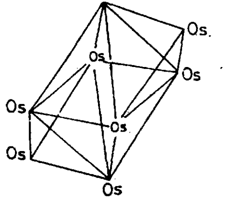
(II)



(III)



(IVa)



(IVb)

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[21] K. Wade, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 563.

[22] K. Wade, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 823.

X-ray diffraction studies on $[Os_6(CO)_{18}]$ have revealed such a novel bicapped-tetrahedral structure (II).[17] Irrespective of how one regards the oxidation states of the individual metal atoms, the complete carbonyl cluster obeys the 18-electron rule.

The only other characterized hexanuclear cluster which has 84 valence electrons is $[Cu_6H_6(PPh_3)_6]$ and this has been shown to possess a regular octahedral structure.[23] In most other six-metal-atom units the regular octahedral arrangement predominates but the 18-electron rule is not obeyed since these clusters have 86 rather than 84 valence electrons. Thus such an octahedral arrangement is observed with $[Co_6(CO)_{16}]$,[24] $[Rh_6(CO)_{16}]$,[25] $[Ru_6(CO)_{18}H_2]$,[26,27] $[Ru_6(CO)_{17}C]$,[5,6] and $[Fe_6(CO)_{16}C]^{2-}$,[13] and is almost certainly present in $[Ir_6(CO)_{16}]$.[28] However the anion $[Rh_6(CO)_{15}C]^{2-}$ was found to have a trigonal prismatic structure but the 90 valence electrons are sufficient to satisfy the 18-electron rule.[7]

(*iv*) $[Os_7(CO)_{21}]$. Scheme (*a*) predicts an edge-bridging octahedral structure whereas (*b*) suggests a monocapped regular octahedral arrangement of metal atoms ($S = 7$; based on a regular octahedron but $S = n = 7$, thus one face is capped). Significantly, $[Os_7(CO)_{21}]$ is isoelectronic with $[Rh_7(CO)_{16}]^{3-}$ which is known to have a monocapped-octahedral arrangement of metal atoms.[29] Preliminary results of *X*-ray diffraction studies [18] on a single crystal of $[Os_7(CO)_{21}]$ indicate that it has a monocapped-octahedral structure, (III), and thus has two electrons in excess of that required to satisfy the 18-electron rule.

(*v*) $[Os_8(CO)_{23}]$. This cluster could similarly be regarded as having two electrons in excess of the 18-electron rule and thus a bicapped regular octahedral arrangement of metal atoms is one possibility, (IVb). This is in agreement with scheme (*b*) [$S = 7$; based on a regular octahedron but $S = (n - 1) = 7$, thus two faces are capped]. An alternative arrangement would be a bicapped-trigonal prism, (IVa), which as a complete cluster would obey the 18-electron rule.

(*vi*) $[Os_8(CO)_{21}C]$. This complex which is isoelectronic with $[Os_8(CO)_{23}]$ can be accommodated readily in both of the structures proposed for the latter by similar placing of a carbon atom at the centre of either the regular octahedron or the trigonal prism.

It appears that Wade's scheme with our extension for $S = n$ and $(n - 1)$ cases can be used to predict reasonable structures for cluster complexes but further *X*-ray crystallography is required before its true value can be determined. It also appears that the strict adherence of most tri- and tetra-nuclear clusters to the 18-electron rule cannot be generally extended to higher clusters. Instead of considering these larger clusters as consisting of individual metal atoms, their bonding, electronic, and structural properties should be interpreted in terms of the complete metal unit. This is becoming apparent from a study of the chemistry of $[Os_6(CO)_{18}]$, $[Os_7(CO)_{21}]$, and various carbonylhydrido-clusters of osmium.[30]

EXPERIMENTAL

The clusters $[Fe_3(CO)_{12}]$,[31] $[Ru_3(CO)_{12}]$,[32] $[Os_3(CO)_{12}]$,[33] $[Co_4(CO)_{12}]$,[34] $[Rh_4(CO)_{12}]$,[35] and $[Ir_4(CO)_{12}]$ [35] were prepared by the literature methods; $[Re_2(CO)_{10}]$ (Strem Chemicals Inc., U.S.A.) was purified by sublimation before use. All reactions were carried out under dry oxygen-free nitrogen unless otherwise stated. I.r. spectra were recorded as solutions in 0.5 mm NaCl cells on a Perkin-Elmer 257 spectrometer with polystyrene as calibrant. Mass spectra were obtained using an A.E.I. M.S. 12 instrument at 70 eV ionizing potential.* ^{1}H N.m.r. spectra were recorded on Perkin-Elmer R12b (60 MHz) and Varian Associates HA 100 or XL 100 spectrometers (100 MHz). Thin-layer chromatography plates were prepared in these laboratories using 20 cm square glass plates coated with a 0.3 mm layer of silica gel/CT (Reeve Angel Scientific, type code S 13 FTLC). Carius-tube pyrolysis was achieved using either a tube furnace (W. E. Heraeus Hanau, type ROKA4/60) or a fan oven (Townson and Mercer Ltd.). All solvents were distilled and degassed before use.

(*Benzene*)*carbidotetradecacarbonylhexaruthenium*, $[Ru_6(CO)_{14}C(C_6H_6)]$.—The complex $[Ru_3(CO)_{12}]$ (0.5 g) was heated in benzene (50 cm^3) under reflux for 3 d. The mixture was then separated by a bulb to bulb distillation to give an orange-brown solid. This was sublimed (100° C, 10^{-2} mmHg) to remove small amounts of $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$ together with any unchanged $[Ru_3(CO)_{12}]$. The remaining complexes, $[Ru_6(CO)_{17}C]$ and $[Ru_6(CO)_{14}C(C_6H_6)]$, were separated by t.l.c. using ethyl acetate–cyclohexane (2 : 3) as eluant. The complex $[Ru_6(CO)_{14}C(C_6H_6)]$ was then recrystallized from n-heptane–benzene as deep purple crystals (13 mg, 3%).

Pyrolysis of Metal Carbonyls.—The carbonyl (0.5 g) was placed in a Carius tube (85 cm^3) which was then evacuated, flamed, sealed, and heated at the required temperature for 12 h. After allowing the contents to cool, the tube was opened and the products extracted into hot ethyl acetate. The solvent was removed *in vacuo* and the mixture separated by t.l.c. using cyclohexane–ethyl acetate as eluant. In the case of $[Ru_3(CO)_{12}]$, the product, $[Ru_6(CO)_{17}C]$, spread very badly on t.l.c. plates and was easily concealed by $[Ru_3(CO)_{12}]$ which, being relatively insoluble in cyclohexane, tails badly. Each of the metal carbonyls, $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Re_2(CO)_{10}]$, $[Co_4(CO)_{12}]$, $[Rh_4(CO)_{12}]$, and

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* 1 eV ≈ 1.6×10^{-19} J, 1 mmHg ≈ 13.6×9.8 Pa.

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$[Ir_4(CO)_{12}]$, was pyrolyzed at least three times over the temperature ranges described earlier.

The pyrolysis of $[Os_3(CO)_{12}]$ was carried out in the range 210—260 °C. A dark brown crystalline mass was obtained which was extracted into boiling ethyl acetate (60 cm^3) and then filtered through Kieselguhr to remove any osmium metal. These extracts were cooled to -20 °C for 24 h; unchanged $[Os_3(CO)_{12}]$ crystallized out and was removed by filtration. The filtrate was reduced in volume (25 cm^3) and, on standing for 2 weeks at -20 °C, dark brown crystals of $[Os_6(CO)_{18}]$ formed which were separated by filtration. Pure samples of this complex were obtained by crystallization from toluene–hexane. After removal of the solid $[Os_6(CO)_{18}]$, the filtrate was reduced in volume (15 cm^3) and left for a further 2 weeks at -20 °C. A small amount of $[Os_6(CO)_{18}]$ was precipitated and after its removal by filtration the resulting filtrate was evaporated to dryness and the remaining mixture separated into its components by t.l.c. The composition of the eluant [ethyl acetate–cyclohexane (1 : 99)] was critical since the R_F values of the components were very similar. The bands (in order of decreasing R_F value) corresponded to: (*a*) $[Os_5(CO)_{16}]$, pink-red; (*b*) $[Os_6(CO)_{18}]$, dark-brown; (*c*) $[Os_7(CO)_{21}]$, orange; (*d*) $[Os_8(CO)_{23}]$, orange-yellow; (*e*) $[Os_5(CO)_{15}C]$, yellow, spreads badly; and (*f*) $[Os_8(CO)_{21}C]$, deep purple. All these clusters tailed quite badly on the silica t.l.c. plates. They were extracted from the silica using ethyl acetate and then rechromatographed to give spectroscopically pure material.

Pyrolysis of $[Os_3(CO)_{12}]$ at 250 °C followed by removal of $[Os_6(CO)_{18}]$ by the method outlined above gave $[Os_7(CO)_{21}]$ as the major t.l.c. product. Alternatively, pyrolysis of $[Os_3(CO)_{12}]$ for 3 d at 210 °C gave $[Os_5(CO)_{16}]$ as a major t.l.c. component. Pyrolysis at 255 °C followed by recrystallization from toluene rather than ethyl acetate gave $[Os_5(CO)_{15}C]$. The carbide $[Os_8(CO)_{21}C]$ was very insoluble in cyclohexane and at the higher pyrolysis temperatures it was isolated as a pure solid by cyclohexane extraction of all other complexes.

These various polynuclear carbonyls were characterized using i.r. and mass-spectral data. Their structures in solid and solution were regarded as being similar since their i.r. spectra in cyclohexane and Nujol mulls were identical. The mass spectra were very clear and intense but because of the high molecular weights certain operating conditions were essential. These were: (*i*) a clean source, (*ii*) a resolving power of 1 part in 2 500, (*iii*) the use of 1,3,5-tris-(perfluoroheptyl)triazine (highest peaks at *m/e* 1 166 and 1 185) as internal calibrant, (*iv*) a source temperature of 150 °C, (*v*) an accelerating voltage adjusted manually between 6 and 3 kV such that the spectrum could just be accommodated onto the full scale. Conditions (*ii*) and (*v*) necessarily led to a reduction in sensitivity, but using moderate multiplier values excellent spectra were always obtained. Whilst the tetra-, penta-, and hexa-nuclear clusters could be easily calibrated using the internal standard (*iii*), hepta- and octa-nuclear clusters gave singularly charged ions which were above the limit of the calibrant (*m/e* 1 185). In these cases the intense doubly charged ions were used whilst $[Os_6(CO)_{18}]$ itself was an excellent standard for such clusters.

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