The Chemistry of Polynuclear Compounds. Part 29.[1] Products of the Reaction of Triruthenium and Triosmium Dodecacarbonyls with Water

By **Colin R. Eady**, **Brian F. G. Johnson**, and **Jack Lewis**,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The reaction of triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$, with water leads to the formation of the tetranuclear hydrides α-$[Ru_4(CO)_{12}H_4]$ and α-$[Ru_4(CO)_{13}H_2]$. The significance of this reaction to the possible activation of alkanes is discussed. The corresponding reaction of $[Os_3(CO)_{12}]$ leads to the isolation of clusters based on three, four, five, six, and seven metal atoms, *viz.* $[Os_3(CO)_{10}H(OH)]$, $[Os_4(CO)_{13}H_2]$, $[Os_4(CO)_{12}H_4]$, $[Os_5(CO)_{16}H_2]$, $[Os_5(CO)_{15}H_2]$, $[Os_6(CO)_{18}H_2]$, and $[Os_7C(CO)_{19}H_2]$. The probable structures of these polynuclear osmium carbonyls are discussed and compared with those of the previously characterized osmium cluster carbonyls.

SEVERAL years ago workers in this group [2] observed that triruthenium dodecacarbonyl when heated under reflux in n-octane or n-nonane gave the carbido-complex $[Ru_6C(CO)_{17}]$ and, more significantly, small amounts of tetranuclear hydrides α-$[Ru_4(CO)_{13}H_2]$ and α-$[Ru_4(CO)_{12}H_4]$.[3,4] Although these products were readily separated and characterized, the nature and course of the reaction remained uncertain. The formation of these hydrido-clusters was taken to indicate the possible activation of the alkanes by a simple and direct method in which the metal carbonyl was involved in a process of hydrogen abstraction. Although a similar reaction has been observed, resulting in the formation of $[FeRu_3(CO)_{13}H_2]$ from $[Fe(CO)_5]$ and $[Ru_3(CO)_{12}]$ in light petroleum, a systematic and detailed examination was not made.[5] A number of examples exist in the literature [6-10] which would support this possible alkane activation by metal complexes. Hodges and his co-workers reported the first example of the activation of saturated hydrocarbons by transition-metal complexes. Furthermore, the complex $[Cr(CO)_5(S)]$ (S = alkane solvent) was suggested as the first observable flash-photolysis product of $[Cr(CO)_6]$ in hydrocarbon glasses at 77 K.[11] More recently, Cotton [12,13] has shown convincingly by *X*-ray crystallographic work that alkyl groups attached to boron can be activated by transition metals. There is, therefore, a precedent which suggests that the reaction of refluxing n-octane with $[Ru_3(CO)_{12}]$, in which Kaesz [14] observed a 70% yield of $[Ru_4(CO)_{12}H_4]$, could be a genuine alkane-activation process. It was with this in mind that the work presented here was initiated.

Having established that the source of hydrogen atoms in the tetranuclear ruthenium hydrides was not from the alkane but rather from trace amounts of water, an obvious extension of this work was to a study of the reaction of $[Os_3(CO)_{12}]$ with water. We now report that with this carbonyl, and in contrast to $[Ru_3(CO)_{12}]$, reaction with water leads to hydrido-clusters based on Os_3, Os_4, Os_5, Os_6, and Os_7 units. Some aspects of this work have been previously reported;[15] in this paper we discuss the full preparative details, the probable structures of these new osmium clusters, and possible mechanisms for their formation.

RESULTS AND DISCUSSION

(1) *Reaction of* $[Ru_3(CO)_{12}]$ *with Alkanes.*—(*a*) *Variability of yields.* When $[Ru_3(CO)_{12}]$ was heated under reflux in pure n-octane for various lengths of time (10—60 h) low yields (*ca.* 2%) of the tetranuclear hydrides, α-$[Ru_4(CO)_{13}H_4]$ and α-$[Ru_4(CO)_{12}H_4]$ were produced together with the carbidocarbonyl $[Ru_6C(CO)_{17}]$ (20%). The yields of these tetranuclear hydrides were variable and independent of the reaction times employed. Low yields of the metal hydrides would necessarily lead to a low yield of any organic product, *e.g.* octenes, hexadecane, or dioctyl ketone, which would be difficult to detect by conventional techniques. This problem was overcome by carrying out all subsequent reactions in sealed evacuated Carius tubes and recycling the solvent at least five times. This should lead to a steady increase in the concentration of any organic products.

(*b*) *Recycling of the organic solvents.* When $[Ru_3(CO)_{12}]$ and n-octane were subjected to this recycling procedure small yields of the tetranuclear hydrides were obtained after each cycle. Gas–liquid chromatography (g.l.c.) of the n-octane after five cycles revealed no new organic compounds, whilst thin-layer chromatography (t.l.c.) on the five solid residues did not display any new organic or organoruthenium species, *e.g.* complexes involving C_8 units. The possibility, however, that the organoruthenium species may have decomposed on silica could not be ruled out. The reaction of *cis*-oct-2-ene

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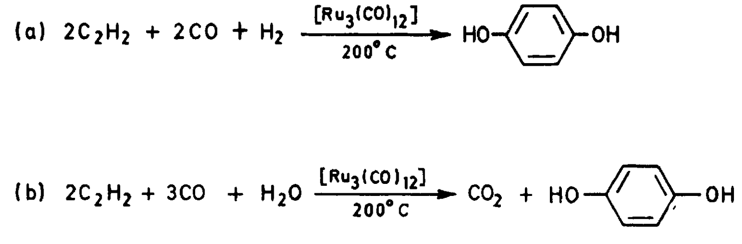
with $[Ru_3(CO)_{12}]$, which gave only trace amounts of the tetranuclear hydrides, was used to eliminate octenes as a possible source of these species, particularly since g.l.c. revealed them as a very small but slowly decreasing impurity in the n-octane.

Similarly, the reactions of $[Ru_3(CO)_{12}]$ with very pure (*i*) n-heptane, (*ii*) n-nonane,[2] (*iii*) cyclohexane, (*iv*) di-n-butyl ether,[4] (*v*) benzene, (*vi*) toluene,[2] (*vii*) mesitylene,[2] or (*viii*) xylene [2] in a recycling fashion identical to that used for n-octane gave small yields (*ca.* 2%) of the tetranuclear hydrides, but g.l.c. and t.l.c. once again revealed no new compounds.

(*c*) *Addition of water.* Parts (*a*) and (*b*) suggest that hydride formation is not the result of hydrogen abstraction from alkanes or other organic solvents. It can be shown that only trace amounts (10 μl) of water are necessary to convert the trinuclear metal carbonyl (*ca.* 0.5 g) into the hydrides. The use of water or ethanol as a hydrogen source in industrial catalysis is well established (*e.g.* see Scheme 1).[16] When a few microlitres of distilled water were added to the reaction of $[Ru_3(CO)_{12}]$ with n-octane, the yields of hydrides, particularly α-$[Ru_4(CO)_{12}H_4]$, increased considerably. When D_2O rather than H_2O was used the mass spectra of the hydrides conclusively showed total deuterium incorporation.



SCHEME 1

(*d*) *The use of totally deuteriated solvents.* The reaction of refluxing alkanes with $[Ru_3(CO)_{12}]$ was repeated using deuterioheptane or deuteriocyclohexane (99.9% ^2H);* the mass spectra of the hydrides after the third cycle did not show α-$[Ru_4(CO)_{12}D_4]$ and α-$[Ru_4(CO)_{13}D_2]$ but rather α-$[Ru_4(CO)_{12}H_4]$ and α-$[Ru_4(CO)_{13}H_2]$. These results clearly indicate that $[Ru_3(CO)_{12}]$ does not activate alkanes under the conditions used and that the hydrides come from trace amounts of water. In agreement with this proposal, moderately good yields (40%) of α-$[Ru_4(CO)_{12}H_4]$ were obtained by the direct reaction of $[Ru_3(CO)_{12}]$ with water in a sealed tube at 135 °C, the pure tetranuclear hydride being isolated.

One anomalous reaction was that of $[Ru_3(CO)_{12}]$ with deuteriobenzene, because after recycling three times using sealed Carius tubes the small yields of the hydrides, when analysed by mass spectroscopy, showed total deuteriation. It may well be that the hydrides were initially produced from trace amounts of water; however, the co-ordination of benzene to metal carbonyl clusters by σ as well as π bonds is well established,[17-19] and this could provide a route for H–D exchange. Indeed, the new compound $[Ru_6C(CO)_{14}]\cdot C_6H_6$ was isolated from this reaction.[20] Further evidence for the tetranuclear hydrides exchanging with deuteriobenzene is provided by the work of Parshall [21] who showed that transition-metal hydrides catalyse the exchange of aromatic hydrogen atoms with deuterium gas.

The studies presented here in section (1) indicate that great care must be taken in work involving the metal carbonyls of iron, ruthenium, and osmium [see section (2)]. A large number of publications have appeared in which $[Ru_3(CO)_{12}]$ has been treated with complex organic molecules and it is possible that some of these involve α-$[Ru_4(CO)_{12}H_4]$ rather than the trinuclear metal carbonyl (Scheme 2).

(i) [5] $[Fe(CO)_5] + [Ru_3(CO)_{12}] \xrightarrow{\text{light petroleum}} [FeRu_3(CO)_{13}H_2]$ Variable yield

(ii) [22] $[Ru_3(CO)_{12}] + S \xrightarrow[\text{no solvent}]{\text{CO pressure}} [Ru_3(CO)_9H_2(S)]$ Trace amounts

(iii) [23] $[Mn_2(CO)_{12}] \xrightarrow[h\nu]{\text{acetone}} [Mn_3(CO)_{12}H_2]^-$ Yield not reported

(iv) [24] $RNO_2 + [Fe(CO)_5] \xrightarrow[\text{120—132 °C}]{\text{diglyme}} \underset{4\text{—}14\%}{RNHCHO} + \underset{7\text{—}18\%}{(RNH)_2CO}$

(v) [14b] $[Os_3(CO)_{12}] + D_2 \xrightarrow[\text{120 °C}]{\text{octane}}$

$$\underset{9\%}{[Os_3(CO)_{10}D_2]} + \underset{42\%}{[Os_3(CO)_{10}(H)D]} + \underset{49\%}{[Os_3(CO)_{10}H_2]}$$

SCHEME 2 Some examples of reactions in which the hydrogen source may be water

(2) *Reaction of* $[Os_3(CO)_{12}]$ *with Water.*—When $[Os_3(CO)_{12}]$ was heated at 230 °C with small amounts of water in a sealed evacuated Carius tube a dark brown mixture was obtained which, after extraction into ethyl acetate followed by separation using t.l.c., was shown to

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* Kindly provided by Professor E. L. Muetterties.

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consist of a mixture of polynuclear osmium species. Certain of these were found to be identical to those obtained[20,25] directly from the pyrolysis of $[Os_3(CO)_{12}]$ whilst others, *viz.* $[Os_3(CO)_{10}H(OH)]$, $[Os_4(CO)_{13}H_2]$, and $[Os_4(CO)_{12}H_4]$ have been previously isolated either as by-products formed during the preparation of $[Os_3(CO)_{12}]$ or from the reaction of $[Os_3(CO)_{12}]$ with base or sodium tetrahydroborate.[26] However, in addition and more significantly, the four carbonyl-hydrido-species, $[Os_5(CO)_{15}H_2]$, $[Os_5(CO)_{16}H_2]$, $[Os_6(CO)_{18}H_2]$, and $[Os_7C(CO)_{19}H_2]$ were identified (Figure 1 and Table 1).

TABLE 1

Hydride chemical shifts (τ), i.r. spectra (1 600—2 200 cm^{-1}), and molecular-ion value (M^+) of the products isolated from the pyrolysis of $[Os_3(CO)_{12}]$ with water: a comparison with some ruthenium analogues

Complex	ν(CO) [a]		Chemical shift [b]	M^+
$[Os_3(CO)_{10}H(OH)]$ [c]	2 114vw 2 077s 2 064m 2 027vs	2 025m (sh) 2 005m 1 992w	22.58	870
$[Os_4(CO)_{13}H_2]$ [d,e]	2 085s 2 068s 2 059s	2 021m, br 2 005w 1 860vw, br	31.23	1 128
α-$[Ru_4(CO)_{13}H_2]$ [d]	2 080vs 2 069vs 2 055vs 2 033m	2 022s 2 004w 1 871w, br	28.50	772 [f]
$[Os_4(CO)_{12}H_4]$ [e]	2 092m 2 074s 2 065m (sh)	2 026s 2 002w	30.35	1 102
α-$[Ru_4(CO)_{12}H_4]$ [d]	2 077s 2 062vs 2 026m (sh)	2 021s 2 004w	27.65	746
$[Os_5(CO)_{16}H_2]$	2 126w 2 088s 2 066s 2 053s	2 045m (sh) 2 038w 2 013m	30.55	1 402
$[Os_5(CO)_{15}H_2]$	2 079s 2 070s 2 051s 2 040m	2 030w 2 018w 2 007w 1 998w	31.10 [g]	1 374
$[Os_6(CO)_{18}H_2]$	2 084s 2 078s	2 049m 2 042m	22.23 31.80	1 648
$[Ru_6(CO)_{18}H_2]$ [h]	2 060s 2 054s	2 008m		1 114
$[Os_7C(CO)_{19}H_2]$	2 085s 2 071s, br	2 042m 2 032w	23.13 [g] 32.45	1 878

[a] In cyclohexane unless otherwise stated. [b] In CD_2Cl_2 (internal standard). [c] In agreement with ref. 27. [d] In n-heptane. [e] Our spectrum of $[Os_4(CO)_{12}H_4]$, despite contrary reports,[14b] corresponds within reasonable calibration differences with that presented in ref. 35 but as with $[Os_4(CO)_{14}H_2]$ it does not agree with those of ref. 26. Such a calibration difference exists between spectra of $[Os_4(CO)_{12}H_4]$ presented in refs. 14*a* and 14*b*. [f] The isomeric nature of $[Ru_4(CO)_{13}H_2]$ and $[Ru_4(CO)_{12}H_4]$ together with their spectroscopic data are discussed in ref. 1. Under our operating conditions, $[Ru_4(CO)_{12}H_4]$ showed an isotope pattern centred at *m/e* **746** but different from a computed molecular-ion pattern, thus indicating some decomposition of the cluster under ionization.[3,4] The complex $[Ru_4(CO)_{13}H_2]$ showed an intense molecular ion. [g] Tentative or indirect assignment. [h] In CCl_4.

The characterization of these new polynuclear hydrides followed directly from the use of ^1H Fourier-transform n.m.r. and mass-spectroscopic studies. Thus under electron impact all the hydrides showed intense molecular ions together with ions corresponding to the stepwise loss of carbonyl groups. The isotopic distributions within these peaks were in complete agreement with computed patterns. Intense doubly charged ions were observed in each case. The mass spectra of $[Os_5(CO)_{16}H_2]$ and $[Os_6(CO)_{18}H_2]$ were substantially different to those[21,26] of $[Os_5(CO)_{16}]$ and $[Os_6(CO)_{18}]$ and the use of an internal calibrant confirmed the presence of two hydride ligands. In each case ejection of H does not occur until after several carbonyl groups have been removed. The fragmentation patterns may be represented by Scheme 3. This mass-spectroscopic information suggests that the H ligands occupy bridging positions in the cluster. Supporting evidence comes from the ^1H Fourier-transform n.m.r. spectra which exhibited signals in the high-field region at chemical-shift values greater than τ 20. This is consistent with, but by no means definitive, for bridging rather than terminal hydrides. In the case of the pentanuclear hydrides $[Os_5(CO)_{15}H_2]$ (τ 31.10) and $[Os_5(CO)_{16}H_2]$ (τ 30.55) the sharp singlets did not broaden on cooling to −70 °C. This suggests that the hydride ligands are in similar if not identical environments. This contrasts with the ^1H n.m.r. spectra of $[Os_6(CO)_{18}H_2]$ which shows two separate hydride resonances (τ 22.23 and 31.80) of equal intensity.[27] The complex $[Os_7C(CO)_{19}H_2]$ appears to show two similar hydride resonances (τ 23.13 and 32.45) of equal intensity.

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The ^1H Fourier-transform n.m.r. spectra and i.r. spectra [ν(CO)] of the tetranuclear osmium hydrides $[Os_4(CO)_{13}H_2]$ (τ 31.23) and $[Os_4(CO)_{12}H_4]$ (τ 30.35) were similar to those of the corresponding α-ruthenium species and it can therefore be assumed that they are isostructural (based on a tetrahedron of metal atoms).[28,29]

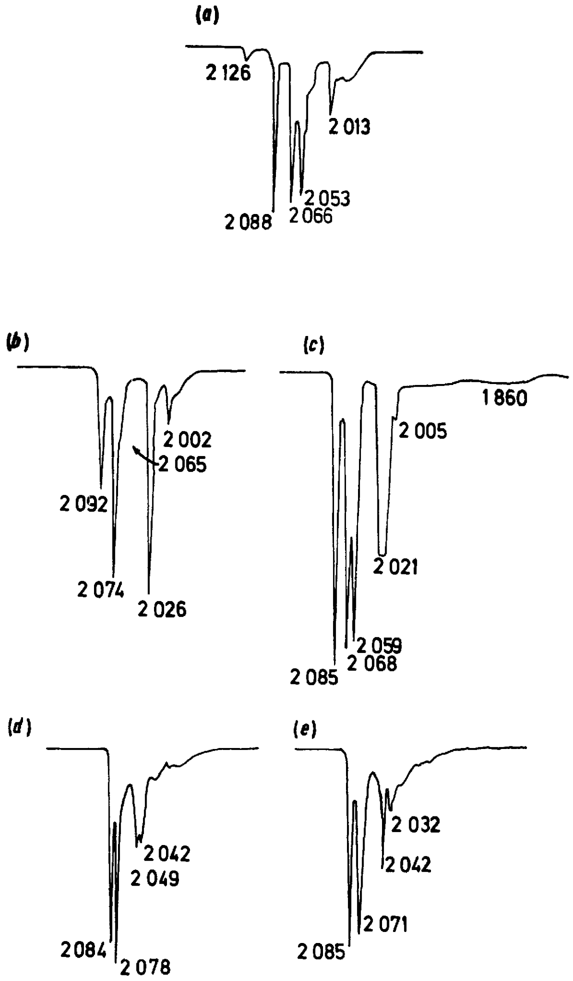

FIGURE 1 Infrared spectra in the carbonyl-stretching region of some of the products isolated from the reaction of $[Os_3(CO)_{12}]$ with water: (*a*) $[Os_5(CO)_{16}H_2]$; (*b*) $[Os_4(CO)_{12}H_4]$; (*c*) $[Os_4(CO)_{13}H_2]$; (*d*) $[Os_6(CO)_{18}H_2]$; and (*e*) $[Os_7C(CO)_{19}H_2]$

The i.r. spectra in the carbonyl-stretching region of the new osmium clusters (Figure 1) are reasonably simple and this indicates that the symmetry of the molecules is relatively high. The absence of bands in the 1 600—1 900 cm^{-1} region suggests that bridging carbonyls are absent. This possibility cannot be entirely excluded since in certain cases, *e.g.* $[Os_4(CO)_{13}H_2]$, bridging carbonyl absorptions were broad and very weak (Figure 1).

(3) *Possible Structures of the Four New Polynuclear Carbonyl Hydrides.*—In a previous publication [20] we discussed the structures of $[Os_5(CO)_{16}]$, $[Os_6(CO)_{18}]$, $[Os_7(CO)_{21}]$, $[Os_8(CO)_{23}]$, $[Os_5C(CO)_{15}]$, and $[Os_8C(CO)_{21}]$ in terms of the 18-electron rule and an extended version of Wade's skeletal electron-counting scheme. In some cases, *e.g.* $[Os_5C(CO)_{15}]$, both the skeletal electron-counting scheme and the 18-electron rule correctly predict the structure whereas in other cases, *e.g.* $[Os_7(CO)_{21}]$, the skeletal electron-counting scheme predicts the correct structure, *viz.* a monocapped octahedral arrangement of osmium atoms whereas the 18-electron rule does not. The structures of $[Os_5(CO)_{15}H_2]$, $[Os_5(CO)_{16}H_2]$, $[Os_6(CO)_{18}H_2]$, and $[Os_7C(CO)_{19}H_2]$ may be discussed in similar terms (Table 2) and clearly a number of distinct series of polynuclear osmium carbonyls based on *S* (the number of skeletal electron pairs) are emerging, each member of a particular series differing by an $Os(CO)_2$ fragment. This fragment cannot contribute electron pairs to the skeletal bonding and thus *S* is constant within that particular series.

$$\begin{tikzcd}
\text{(a) } [Os_5(CO)_{15}H_2]^+ \arrow[r, "-4\,CO"] & {[Os_5(CO)_{11}H_2]^+} \arrow[r, "-2H-CO"] & {[Os_5(CO)_{10}]^+} \arrow[d, "-10\,CO"] \\
& & {[Os_5]^+ \text{ (intense)}} \\
\text{(b) } [Os_5(CO)_{16}H_2]^+ \arrow[r, "-5\,CO"] & {[Os_5(CO)_{11}H_2]^+} \arrow[r, "-2H-CO"] & {[Os_5(CO)_{10}]^+} \arrow[d, "-10\,CO"] \\
& & {[Os_5]^+ \text{ (intense)}} \\
\text{(c) } [Os_6(CO)_{18}H_2]^+ \arrow[r, "-5\,CO"] & {[Os_6(CO)_{13}H_2]^+} \arrow[r, "-2H-CO"] & {[Os_6(CO)_{12}]^+} \arrow[d, "-12\,CO"] \\
& & {[Os_6]^+ \text{ (intense)}} \\
\text{(d) } [Os_7C(CO)_{19}H_2]^+ \arrow[r, "-6\,CO"] & {[Os_7C(CO)_{13}H_2]^+} \arrow[r, "-2H-2CO"] & {[Os_7C(CO)_{11}]^+} \arrow[d, "-11\,CO"] \\
& & {[Os_7C]^+ \text{ (very intense)}}
\end{tikzcd}$$

SCHEME 3

(*a*) $[Os_5(CO)_{15}H_2]$. This cluster is isoelectronic with $[Os_5(CO)_{16}]$ for which a trigonal-bipyramidal structure was predicted.[20] Both the 18-electron rule and the skeletal electron-counting scheme predict such a trigonal-bipyramidal arrangement of metal atoms for $[Os_5(CO)_{15}H_2]$ [Table 2 and Figure 2(*a*)].

(*b*) $[Os_5(CO)_{16}H_2]$. This cluster is isoelectronic with $[Os_5C(CO)_{15}]$ for which a square-based pyramidal structure is expected.[20] Both electron-counting schemes predict such a metal atom unit for $[Os_5(CO)_{16}H_2]$ [Table 2 and Figure 2(*b*)]. An alternative arrangement which obeys the 18-electron rule but which violates the skeletal electron-counting rule is shown in Figure 2(*c*).

(*c*) $[Os_7C(CO)_{19}H_2]$. This heptanuclear cluster represents, to our knowledge, the first example of a polynuclear carbido-hydride. Possible structures are necessarily tentative since Wade's scheme predicts a *closo* structure based on a pentagonal bipyramid [Figure 2(*d*)].

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A strict adherence to the 18-electron rule would require 13 metal–metal bonds, and thus a monocapped trigonal-prismatic structure related to $[Rh_6C(CO)_{15}]^{2-}$ (ref. 30) could be one possibility [Figure 2(*e*)].

TABLE 2

Complex	Number of skeletal electron pairs (S); n = number of metal atoms	Predicted structure according to Wade's scheme	Number of metal–metal bonds required for the cluster to obey the 18-electron rule
$[Os_4(CO)_{13}H_2]$ $\{[Os_4(CO)_{12}H_4]\}$	6; $n + 2$	Tetrahedron	6
$[Os_5(CO)_{15}H_2]$	6; $n + 1$	Trigonal bipyramid	9
$[Os_5(CO)_{16}H_2]$	7; $n + 2$	Square-based pyramid	8
$[Os_6(CO)_{18}H_2]$	7; $n + 1$	Regular octahedron	11
$[Os_7C(CO)_{19}H_2]$	8; $n + 1$	Pentagonal bipyramid	13

(4) *Some Points of Interest.*—It appears that osmium shows an unusual ability to form polynuclear carbonyl clusters. These clusters appear to fall into a number of series the members of which show a steady and systematic increase in cluster size. Thus we have been able to characterize $[Os_5(CO)_{16}]$ and $[Os_5(CO)_{16}H_2]$, $[Os_6(CO)_{18}]$ and $[Os_6(CO)_{18}H_2]$, and $[Os_7(CO)_{21}]$ and $[Os_7C(CO)_{19}H_2]$. It has been suggested that there are some similarities between boranes and metal carbonyl clusters.[31,32] The products isolated from the pyrolysis of $[Os_3(CO)_{12}]$ in the presence and absence of water are in agreement with these proposals since each emerging series of osmium carbonyls formally differ, like certain of the boranes, by two electrons. Furthermore, the pyrolysis of B_2H_6 leads to the formation of higher members of these borane series, the structures of which can be accommodated by Wade's skeletal electron-counting scheme. A comprehensive treatment of these trends, which will be given in a later paper, must await the results of X-ray structural studies currently in progress.

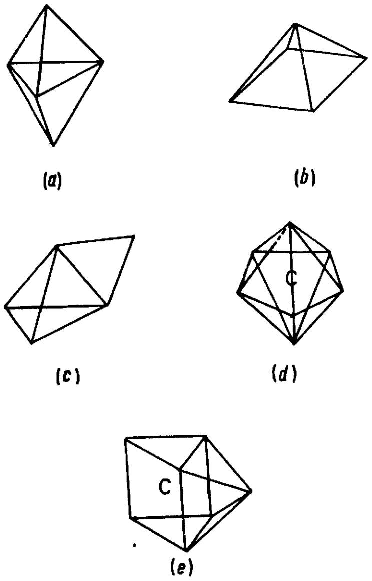

FIGURE 2 Some possible structures for $[Os_5(CO)_{15}H_2]$, $[Os_5(CO)_{16}H_2]$ (*b*) and (*c*), and $[Os_7C(CO)_{19}H_2]$ (*d*) and (*e*). The arrangement of the ligands is not shown

The structures of the simpler polynuclear carbonyls have often been successfully rationalized in terms of the 18-electron rule. This rule has however become difficult to interpret as a result of the realization that most of the known regular octahedral six-metal atom clusters have 86 rather than 84 valence electrons. The structures of the products resulting from the pyrolysis of $[Os_3(CO)_{12}]$ in the presence and absence of water provide an example of the necessity to consider the osmium atoms as complete metal units rather than as individual metal atoms. Wade's skeletal electron-counting scheme is a theoretical progression towards this necessity. This theory does suffer one major limitation. It provides no method of deciding the particular arrangement of carbonyl or hydride ligands, although reasonable deductions can often be made after the metal skeleton has been established. The significant feature of Wade's scheme is that it is suggesting that the highest-filled and lowest-empty molecular orbitals are primarily involved in cluster bonding whilst the metal–ligand orbitals are at much lower energy. Because different series of osmium carbonyls can be characterized, each differing by two electrons, the highest-filled {*e.g.* $[Os_6(CO)_{18}]^{2-}$} or lowest empty {*e.g.* $[Os_6(CO)_{18}]$} molecular orbital may be either nonbonding or weakly bonding or antibonding with regard to the metal–metal skeleton. Thus one can understand why interest is developing in the ability of polynuclear metal clusters to act as electron sinks and why their electronic properties are of some interest.

With carbides it is always assumed that the carbide atom is situated at the centre of the polyhedra and thus Wade's scheme leads to their classification into two distinct types: (*a*) carbides having *closo* structures, *e.g.* $[Ru_6C(CO)_{17}]$, in which the carbon atom lies inside the metal polyhedron; (*b*) carbides having *nido* or *arachno* structures, *e.g.* $[Os_5C(CO)_{15}]$, in which the carbon atom is exposed. This classification will obviously be reflected in the chemistry of the carbon atoms in these different types of carbides.

In the same way that the clusters $[Os_5(CO)_{16}]$, $[Os_6(CO)_{18}]$, $[Os_7(CO)_{21}]$, and $[Os_8(CO)_{23}]$ could be regarded as the equivalent of adsorption of carbon monoxide on to an osmium surface, so could these carbonyl hydrides {*e.g.* $[Os_6(CO)_{18}H_2]$ and $[Os_5(CO)_{16}H_2]$ which contain *ca.* 0.1% hydrogen} be regarded as the equivalent of CO and hydrogen adsorption.

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[30] V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.

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(5) *Possible Mechanisms of Formation of the Polynuclear Carbonyls under Pyrolysis Conditions.*—The mechanism of formation of the polynuclear metal carbonyls under pyrolysis conditions is of some interest. When $[Mn_2(CO)_{10}]$, $[ReMn(CO)_{10}]$, or $[Re_2(CO)_{10}]$ are photolysed in the presence of $[Fe(CO)_5]$, the linear trinuclear molecules $M(CO)_5{-}Fe(CO)_4{-}M'(CO)_5$ are produced in which an $Fe(CO)_4$ unit inserts into the metal–metal bond of the binuclear carbonyl.[33] Similarly, the pyrolysis of $[Ru_3(CO)_{12}]$ and $[Re_2(CO)_{10}]$ in a sealed evacuated Carius tube at 150 °C gave an orange solid. T.l.c. (cyclohexane as eluant) revealed a number of complexes, two of which were characterized by mass spectroscopy as $Re(CO)_5{-}Ru(CO)_4{-}Re(CO)_5$ and $Re(CO)_5{-}Ru(CO)_4{-}Ru(CO)_4{-}Re(CO)_5$. The former was isolated as a yellow solid which gave an i.r. spectrum [ν(CO)] similar (Figure 3) to that of the corresponding iron clusters, but which was unstable to light, decomposing over a period of 5 min to give an uncharacterized carbonyl species. The osmium analogues have been prepared using similar pyrolysis techniques at temperatures ranging from 205 to 250 °C.[34]

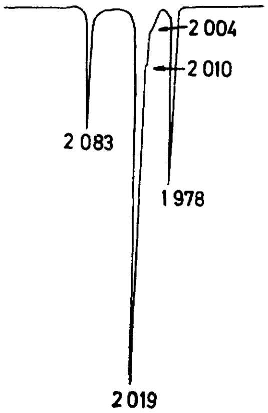

FIGURE 3 Infrared spectrum of n-heptane in the carbonyl-stretching region (1 600—2 200 cm^{-1}) of $Re(CO)_5{-}Ru(CO)_4{-}Re(CO)_5$, a yellow solid of *m/e* 866

It appears from these mixed-metal studies that under the pyrolysis conditions used the diradical $M(CO)_4$ species (M = Os or Ru) is important and that the combination of one or more of these species with the parent carbonyl leads to higher clusters, the driving force being the formation of strong and energetically favourable metal–metal bonds. The formation of the hydrido-clusters is possibly the result of a similar interaction between $M(CO)_4H_2$ and $M(CO)_4$ units, the initial product being $M_4(CO)_{12}H_4$. In the case of osmium this tetranuclear cluster reacts further since the pyrolysis of $[Os_4(CO)_{12}H_4]$ in sealed evacuated Carius tubes at 230 °C leads to the formation of $[Os_5(CO)_{15}H_2]$, $[Os_5(CO)_{16}H_2]$, $[Os_6(CO)_{18}H_2]$, and $[Os_7C(CO)_{19}H_2]$. A similar mechanism has been proposed for the formation of $[Os(CO)_4H_2]$,$[Os_2(CO)_8H_2]$, $[Os_3(CO)_{10}H_2]$, $[Os_3(CO)_{12}]$, and $[Os_4(CO)_{16}H_2]$ when $[Os_3(CO)_{12}H_2]$ is pyrolysed at 120 °C.[35] Furthermore, heating an n-heptane solution of $[Os(CO)_4H_2]$ at 100 °C produces pure $[Os_4(CO)_{12}H_4]$.[35] This proposed reaction path is similar to that reported for the reaction of $[Ru_3(CO)_{12}]$ with halogens (X_2); *cis*-$[Ru(CO)_4X_2]$ is produced initially and this then polymerizes to $[Ru_2(CO)_6X_4]$, $[Ru_3(CO)_{12}X_6]$, and $[\{Ru(CO)_2X_2\}_n]$.[36] The intermediacy of $[Os_4(CO)_{12}H_4]$ in the production of the larger hydrido-osmium clusters would perhaps suggest an analogous chemistry for α-$[Ru_4(CO)_{12}H_4]$. However, preliminary experiments on the pyrolysis of α-$[Ru_4(CO)_{12}H_4]$ at 155 °C led to the formation of $[Ru_6C(CO)_{17}]$ and ruthenium metal, whilst the sole product from the reaction of $[Ru_3(CO)_{12}]$ with water was α-$[Ru_4(CO)_{12}H_4]$.

In the case of pyrolysis of $[M_3(CO)_{12}]$ (M = Ru or Os) with water the mechanism propounded in the previous paragraph is incomplete since the possible formation of $[M(CO)_4H_2]$ from water needs to be understood. The use of water as a hydrogen source has already been exemplified in section (1) (Scheme 1). This could be the result of the equilibrium (1). Although the amount of hydrogen produced under pyrolysis conditions may be small, it can be calculated [section (1)] that only trace amounts of hydrogen would be necessary to completely convert the trinuclear metal carbonyls into hydrides by the Kaesz route.[14] Indeed, CO_2 was found to be a product of these sealed-tube water–metal carbonyl pyrolysis reactions.

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \qquad (1)$$

EXPERIMENTAL

The complexes $[Ru_3(CO)_{12}]$ [37] and $[Os_3(CO)_{12}]$ [26] were prepared by the literature methods, whilst $[Re_2(CO)_{10}]$ was purchased from Strem Chemicals Inc. and purified by sublimation before use. Alkanes were purified by stirring over concentrated sulphuric acid for 24 h, treating with sodium hydrogencarbonate solution and water, degassing with nitrogen, and then distilling over calcium hydride through a Vigreux column. The arenes were purified by initially passing them down an alumina column (removal of sulphur) and then fractionally distilling them over calcium hydride under a stream of nitrogen. Di-n-butyl ether was fractionated over potassium hydroxide pellets. Deuteriated solvents [deuterioheptane (5 g), deuteriocyclohexane (2 g), and deuteriobenzene (10 g)] were used as received from Merck, Sharp, and Dohm. The purity of these various solvents was analysed by g.l.c. (LAC 1R 296 stationary phase, 70 °C). All the other solvents were distilled and degassed before use.

All the manipulations were made under dry oxygen-free nitrogen unless otherwise stated. Infrared spectra were recorded on 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 instru-

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ment operating at 70 eV ionizing potential.* Hydrogen-1 n.m.r. spectra were recorded at 100 MHz on Varian Associates HA 100 or XL 100 spectrometers. G.l.c. was carried out on a Perkin-Elmer F11 FI machine using 0.125-in diameter columns. T.l.c. plates were prepared in these laboratories using 20-cm square glass plates coated with a 0.3-mm layer of Reeve Angel Scientific silica gel/CT (type code S 13FTLC). Carius-tube pyrolysis was achieved using either a W.E. Heraeus Hanau tube furnace (type ROKA4/60) or a Townson and Mercer Ltd. fan oven.

A Typical Reaction of an Alkane, Arene, or Ether with $[Ru_3(CO)_{12}]$.— This is best illustrated by the n-octane reaction. The complex $[Ru_3(CO)_{12}]$ (250 mg) was pumped and flamed under high vacuum (10^{-3} mmHg) for 6 h in a Carius tube (85 cm^3) and then n-octane (10 cm^3) was added to the carbonyl and the mixture degassed three times (by freezing, pumping, and thawing). The Carius tube was sealed under high vacuum, heated for the required length of time (10—60 h), and then opened and the volatile species analysed by g.l.c. (OV 1 or Porapak Q columns). The liquid was distilled off under high vacuum from the deep red reaction mixture directly on to more dry $[Ru_3(CO)_{12}]$ contained in another flamed Carius tube. After five cycles this distillate was analysed under high-sensitivity conditions by g.l.c. [squalane, OV 1, SE 30, LAC IR 296, and 1,2,3-tris(2-cyanoethoxy)propane columns]. The residues of the reactions were analysed by t.l.c. (cyclohexane as eluant) and were found to contain three components: (*a*) $[Ru_3(CO)_{12}]$–α-$[Ru_4(CO)_{12}H_4]$; (*b*) α-$[Ru_4(CO)_{13}H_2]$, and (*c*) $[Ru_6C(CO)_{17}]$. The formation of the tetranuclear metal carbonyl hydrides was confirmed by i.r. [ν(CO)] and mass spectroscopy (source temperature 90 °C, internal calibrant perfluorotributylamine) [14b] (see footnote *f*, Table 1).

The reactions using deuteriated solvents were carried out in an identical manner to that described above, except that proportionally smaller amounts of $[Ru_3(CO)_{12}]$ were used.

Preparation of α-$[Ru_4(CO)_{12}H_4]$ *by Reaction of* $[Ru_3(CO)_{12}]$ *with Water*.—The complex $[Ru_3(CO)_{12}]$ (100 mg) was heated in a sealed evacuated Carius tube with distilled water (5 cm^3) for 24 h at 135 °C. The resulting dark brown liquid was extracted with hot cyclohexane leaving a black tarry residue. After drying the orange extracts over magnesium sulphate, the cyclohexane was removed *in vacuo* to leave a yellow solid, the i.r. spectrum [ν(CO)] of which showed pure α-$[Ru_4(CO)_{12}H_4]$ (36 mg, 40%). The use of D_2O rather than water gave pure α-$[Ru_4(CO)_{12}D_4]$.

Pyrolysis of $[Os_3(CO)_{12}]$ *with Water*.—The complex $[Os_3(CO)_{12}]$ (500 mg) was placed in a Carius tube (85 cm^3) with distilled water (20 μl) and the tube sealed under high vacuum and then heated at 230 °C for 12 h. The resulting dark brown mixture was extracted into boiling ethyl acetate (60 cm^3) and these extracts were filtered through Kieselguhr in order to remove osmium metal. Cooling of this solution to -20 °C over a period of 24 h gave $[Os_4(CO)_{12}H_4]$ {or in some reactions, $[Os_4(CO)_{12}H_4]$–$[Os_3(CO)_{12}]$ mixtures} as a yellow crystalline solid (70 mg, 15%). The mixture was filtered, the filtrate reduced in volume (20 cm^3), and then this solution was allowed to stand at -20 °C for 2 weeks. The complex $[Os_6(CO)_{18}]$ which slowly crystallized out over this period was removed by filtration and the resulting filtrate was evaporated to dryness. This residue was separated into its air-stable 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*) $[Os_4(CO)_{12}H_4]$ (yellow); (*b*) $[Os_4(CO)_{13}H_4]$ (yellow-orange); (*c*) $[Os_5(CO)_{16}]$ (pink-red); (*d*) $[Os_6(CO)_{18}]$ (dark brown); (*e*) $[Os_6(CO)_{18}H_2]$ (orange-brown); (*f*) $[Os_7C(CO)_{19}H_2]$ (green); (*g*) $[Os_7(CO)_{21}]$ (orange); (*h*) $[Os_8(CO)_{23}]$ (orange-yellow); (*i*) $[Os_5(CO)_{16}H_2]$ (green-yellow); (*j*) $[Os_3(CO)_{10}H(OH)]$ (yellow); and (*k*) $[Os_8C(CO)_{21}]$ (deep purple). The hexa- and hepta-nuclear clusters $[Os_6(CO)_{18}H_2]$ and $[Os_7C(CO)_{19}H_2]$ were not completely separated under the conditions used and in some cases the tailing of $[Os_6(CO)_{18}]$ obliterated the bands due to these two carbonyl hydrides. The various clusters were extracted from the silica using ethyl acetate and then rechromatographed to give the pure clusters in amounts sufficient for spectroscopic studies. Apart from $[Os_4(CO)_{12}H_4]$, the yields of the carbonylhydrides were low (2% each).

The complex $[Os_5(CO)_{15}H_2]$ could not be isolated pure from this pyrolysis reaction. It was characterized indirectly by the existence of a sharp hydride resonance (τ 31.10) in the ^{1}H Fourier-transform n.m.r. spectrum of the total product mixture. The action of base on $[Os_6(CO)_{18}]$ followed by acidification led to a product giving a similar hydride resonance and which under mass-spectroscopic conditions produced an intense spectrum corresponding to a molecular formula $[Os_5(CO)_{15}H_2]$.

These various hydrido-clusters were characterized by i.r., ^{1}H n.m.r., and mass spectral data. The mass spectra were intense and readily obtained if those conditions previously described were adhered to.[20] Hydrogen-1 Fourier-transform n.m.r. spectra were recorded using CD_2Cl_2 as solvent and internal standard (τ 4.65). Operating conditions were: (*a*) range, τ 0—50; (*b*) transients, 2 000; (*c*) acquisition time, 0.4 s; (*d*) pulse width, 30 μs. The use of dichloromethane as n.m.r. solvent was not the ideal since it reacted slowly over a period of 24 h with some of the hydrido-clusters, yet it was one of the few solvents in which the clusters were sufficiently soluble for n.m.r. studies.

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 mmHg $\approx 13.6 \times 9.8$ Pa.