A High-pressure Infrared Study of the Stability of Some Ruthenium and Osmium Clusters to CO and H_2 under Pressure

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A high-pressure i.r. study has been made of the stability of some high-nuclearity carbonyl clusters of ruthenium and osmium to carbon monoxide and hydrogen, and of the thermal stabilities of these clusters under an inert atmosphere. In solution, the hexanuclear cluster $[Os_6(CO)_{18}]$ reacts with CO (90 atm, 160 °C, 1 h) to produce the new pentanuclear cluster $[Os_5(CO)_{19}]$ and $[Os(CO)_5]$. In contrast, in the solid state $[Os_6(CO)_{18}]$ adds 2 mol of CO to form $[Os_6(CO)_{20}]$. The pentanuclear carbonyl $[Os_5(CO)_{19}]$ undergoes reaction with CO to give both $[Os_3(CO)_{12}]$ and $[Os_2(CO)_9]$, and with $[Os_2(CO)_9]$ to give $[Os_7(CO)_{21}]$. On heating in an inert atmosphere $[Os_5(CO)_{19}]$ loses CO to generate $[Os_5(CO)_{16}]$. This reaction is reversible. Reaction of $[Os_5(CO)_{16}]$, $[Os_5H_2(CO)_{16}]$, $[Os_6(CO)_{18}]$, or $[Os_6H_2(CO)_{18}]$ with H_2 under moderate pressures and temperatures gives $[Os_4H_4(CO)_{12}]$ and $[OsH_2(CO)_4]$; $[Os_5(CO)_{19}]$ first produces $[Os_5(CO)_{16}]$ and proceeds to the same products. On carbonylation under pressure $[Ru_3(CO)_{12}]$ yields $[Ru(CO)_5]$, and $[Ru_6(CO)_{17}C]$ gives a mixture of $[Ru_5(CO)_{15}C]$ and $[Ru(CO)_5]$. Pyrolysis of $[Ru_6H_2(CO)_{18}]$ under argon at 120 °C gives the hexanuclear carbide $[Ru_6(CO)_{17}C]$ in high yield.

THERE is the view that molecular transition-metal clusters may be reasonable models of metal surfaces, and that studies of their reactions with small substrates may shed light on the interactions which occur on the metal surface.[1] Existing information tends to support this view. The bonding modes adopted by CO, H_2, and small organic molecules on reaction with clusters may be identified with certainty and their relation to those of chemisorbed species may often be inferred from their spectroscopic properties. Reactions involving two or more metal centres are generally different from those observed in monometal systems, and the idea that the mechanisms of heterogeneously catalysed reactions may be understood in terms of the chemistry of monometal systems seems no longer valid.

This approach has led to the view that clusters themselves may function as catalysts for a wide range of chemical processes and may bridge the gap between the heterogeneous and homogeneous fields giving both high selectivity and high reactivity.

A problem exists with the use of clusters in homogeneous catalysis. Although the metal cluster compound is present in solution at the start and at the end of the reaction there is in most cases no evidence that the integrity of the cluster is maintained throughout the reaction. The active catalyst may be a highly unstable monometal species generated under the reaction conditions by the fragmentation of the cluster, or some new cluster showing high activity present in low concentration. The methanation reactions supposedly catalysed by $[Os_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ display very low reaction rates,[2] for example, and, as the metals Os or Ir are active heterogeneous methanation catalysts, a small amount of decomposition of these carbonyl clusters to the metallic state could account for these observations.

Thus, an important consideration in the application of clusters in catalysis is their stability under the conditions of the reaction. To this end we have explored the stability of a number of clusters of ruthenium and osmium to heat and pressures of CO, H_2, and H_2–CO mixtures.

RESULTS AND DISCUSSION

The experiments were conducted in a high-pressure i.r. (h.p.i.r.) cell [3] which allowed constant monitoring of the reaction system and proved invaluable in the identification of reaction intermediates, which might otherwise have been neglected. The results of these experiments are summarised in Table 1 (osmium) and Table 2 (ruthenium). Details of the i.r. spectra of the clusters identified in these studies are given in Table 3 (osmium) and Table 4 (ruthenium).

Osmium Carbonyl Clusters.—Reactions of $[Os_6(CO)_{18}]$ *with* CO. The hexaosmium cluster, $[Os_6(CO)_{18}]$, reacts with carbon monoxide (90 atm,† 160 °C, 1 h) to eliminate $[Os(CO)_5]$ and produce the new pentaosmium cluster $[Os_5(CO)_{19}]$ [4] according to equation (1). Over longer

$$[Os_6(CO)_{18}] \xrightarrow{CO} [Os_5(CO)_{19}] + [Os(CO)_5] \quad (1)$$

periods of time (*ca.* 4 h) further fragmentation occurs to produce $[Os_2(CO)_9]$ and $[Os_3(CO)_{12}]$ [equation (2)]. These

$$[Os_5(CO)_{19}] \xrightarrow{CO} [Os_3(CO)_{12}] + [Os_2(CO)_9] \quad (2)$$

reactions were initially followed by monitoring the i.r. spectra in the h.p.i.r. cell, but the compounds $[Os_5(CO)_{19}]$ and $[Os_3(CO)_{12}]$ were subsequently prepared by routes (1) and (2) in a high-pressure autoclave.

The formation of $[Os(CO)_5]$ and $[Os_2(CO)_9]$ was inferred on the basis of their i.r. spectra (Table 3). Although $[Os_2(CO)_9]$ [5] has been prepared previously it is known to be unstable and certainly under the conditions employed in this work we were not able to isolate and characterise more fully this interesting compound. Further support for the formation of $[Os_2(CO)_9]$ comes from observations made on the reaction of CO with $[Os_5(CO)_{19}]$ over a more limited time span. Treatment of the pentanuclear cluster with CO at 90 atm and 160 °C for 1.5 h generates small amounts of the heptaosmium cluster $[Os_7(CO)_{21}]$, presumably *via* the route shown in equation (3).

$$[Os_5(CO)_{19}] + [Os_2(CO)_9] \rightleftharpoons [Os_7(CO)_{21}] + 7CO \quad (3)$$

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† Throughout this paper: 1 atm = 101 325 Pa.

TABLE 1

Carbonylation and hydrogenation data of some osmium cluster compounds in the h.p.i.r. cell

Cluster	Reaction conditions [a]	Product (%) [b]
$[Os_3(CO)_{12}]$	CO (100), 220, 10	No reaction
	CO–H_2 (90) [c], 200, 4	$[OsH_2(CO)_4]$
$[Os_5(CO)_{16}]$	Ar (1), 200, 5	$[Os_4H_4(CO)_{12}]$
	CO (65), 155, 1	$[Os_5(CO)_{19}]$
	H_2 (60), 180, 2	$[Os_4H_4(CO)_{12}]$ (50) + $[OsH_2(CO)_4]$ (50)
	CO–H_2 (90) [c], 190, 5	$[Os_3(CO)_{12}]$ (40) + $[OsH_2(CO)_4]$ (40) + $[Os_4H_4(CO)_{12}]$
$[Os_5(CO)_{19}]$	Ar (1), 120, 0.25	$[Os_5(CO)_{16}]$
	CO (90), 160, 4	$[Os_3(CO)_{12}]$ (50) + $[Os_2(CO)_9]$ (50)
	H_2 (70), 120, 0.25	$[Os_5(CO)_{16}]$
	CO–H_2 (90) [c], 170, 10	$[Os_3(CO)_{12}]$ (50) + $[Os_2(CO)_9]$ (50)
$[Os_5H_2(CO)_{15}]$	Ar (1), 220, 5	No reaction
	CO (10), 125, fast	$[Os_5H_2(CO)_{16}]$
	H_2 (90), 120, fast	$[Os_4H_4(CO)_{12}]$ (50) + $[OsH_2(CO)_4]$ (50)
	CO–H_2 (90) [c], 80, 3	$[Os_5H_2(CO)_{16}]$ (85) + $[Os_4H_4(CO)_{12}]$ (10)
$[Os_5H_2(CO)_{16}]$	Ar (1), 155, fast	$[Os_5H_2(CO)_{15}]$
	CO (10), 250, 1	$[Os_3(CO)_{12}]$ (*ca.* 95) (octane)
	H_2 (100), 150, 2	$[Os_4H_4(CO)_{12}]$ (50) + $[OsH_2(CO)_4]$ (50)
	CO–H_2 (90) [c], 160, 1.5	$[Os_4H_4(CO)_{12}]$ (50) + $[OsH_2(CO)_4]$ (50)
$[Os_6(CO)_{18}]$	Ar (15), 220, 10	No reaction
	CO (10), 225, 16	$[Os_3(CO)_{12}]$
	CO (90), 160, 1	$[Os_5(CO)_{19}]$ (50) + $[Os(CO)_5]$ (45) + $[Os_3(CO)_{12}]$
	CO (90), 160, 1.5	$[Os_7(CO)_{21}]$ + $[Os_6(CO)_{20}]$ + $[Os_5(CO)_{19}]$ + $[Os_5(CO)_{16}]$ + $[Os_3(CO)_{12}]$ + $[Os_2(CO)_9]$ + $[Os(CO)_5]$
	H_2 (100), 210, 2	$[Os_4H_4(CO)_{12}]$ (80) + $[OsH_2(CO)_4]$ (octane)
	H_2 (10), 130, 18	No reaction (toluene)
	CO–H_2 (90) [c], 160, 1.25	$[Os_3(CO)_{12}]$ (40) + $[OsH_2(CO)_4]$ (50) + $[Os_4H_4(CO)_{12}]$
$[Os_6H_2(CO)_{18}]$	Ar (5), 170, 1	$[Os_6(CO)_{18}]$
	CO (100), 150, 4	$[Os_5H_2(CO)_{16}]$ (45) + $[Os(CO)_5]$ (45) + $[Os_3(CO)_{12}]$ (10)
	H_2 (100), 190, 1.5	$[Os_4H_4(CO)_{12}]$ (80) + $[OsH_2(CO)_4]$
	CO–H_2 (90) [c], 150, 3	$[Os_5H_2(CO)_{16}]$ (45) + $[OsH_2(CO)_4]$ (45) + $[Os_3(CO)_{12}]$ (10)

[a] Given as gas (pressure in atm), temperature (°C), and time (h). [b] Solvent is heptane unless otherwise specified. [c] 35 atm CO + 55 atm H_2.

TABLE 2

Carbonylation and hydrogenation data of some ruthenium clusters in the h.p.i.r. cell

Cluster	Reaction conditions [a]	Product (%) [b]
$[Ru_3(CO)_{12}]$	CO (100), 170, 2	$[Ru(CO)_5]$
$[Ru_4H_2(CO)_{13}]$	CO (100), 50, 0.75	$[Ru_3(CO)_{12}]$ (50) + $[Ru(CO)_5]$ (50)
$[Ru_5(CO)_{15}C]$	Ar (10), 20, 1.5	$[Ru_6(CO)_{17}C]$ (*ca.* 50)
	CO (400), 100, 4	No reaction
	H_2 (15), 100, 4	' $[Ru_5H_2(CO)_{15}C]$ '
$[Ru_6(CO)_{17}C]$	Ar (1), 120, 16	$[Ru_4H_4(CO)_{12}]$ (70)
	CO (10), 120, 2	No reaction
	CO (80), 70, 2	$[Ru_5(CO)_{15}C]$ + $[Ru(CO)_5]$
	H_2 (70), 200, 2	No reaction
	CO–H_2 (90) [c], 90, 3	' $[Ru_5H_2(CO)_{15}C]$ '
$[Ru_6H_2(CO)_{18}]$	Ar (1), 120, fast	$[Ru_6(CO)_{17}C]$
	CO (100), 60, 0.25	$[Ru_3(CO)_{12}]$ (toluene)
	H_2 (100), 75, 0.5	$[Ru_4H_4(CO)_{12}]$
	CO–H_2 (90) [c], 50, fast	$[Ru_3(CO)_{12}]$

[a] Given as gas (pressure in atm), temperature (°C), and time (h). [b] Solvent is heptane unless otherwise specified. [c] 30 atm CO + 60 atm H_2.

Under the conditions employed (*i.e.* CO pressure) the production of $[Os_7(CO)_{21}]$ is expected to be inhibited, in keeping with the observed low yields. However, in a separate experiment a solution of $[Os_5(CO)_{19}]$ and $[Os_2(CO)_9]$ prepared *in situ* was allowed to stand under nitrogen at —40 °C. In this experiment $[Os_7(CO)_{21}]$ was produced, offering some support for the conclusions outlined above. We have further established that the carbonylation of $[Os_7(CO)_{21}]$ to produce $[Os_5(CO)_{19}]$ occurs at 160 °C and 70 atm of CO [equation (4)].

$$[Os_7(CO)_{21}] \xrightarrow{CO} [Os_5(CO)_{19}] + [Os_2(CO)_9] \quad (4)$$

If reaction (1) is stopped after 1 h and the solvent removed, the pentaosmium cluster $[Os_5(CO)_{19}]$ may be separated in yields approaching 80%. Small amounts of $[Os_5(CO)_{16}]$ may also be isolated. These may be safely assumed to be derived from $[Os_5(CO)_{19}]$ by CO loss, equation (5).

$$[Os_5(CO)_{19}] \rightleftharpoons [Os_5(CO)_{16}] + 3CO \quad (5)$$

In agreement, we have found that in boiling octane complete conversion of $[Os_5(CO)_{19}]$ into $[Os_5(CO)_{16}]$ occurs within *ca.* 15 min. This reaction is reversible and

TABLE 3

Infrared spectroscopic data in the ν(CO) region for Os_n (n = 1—6) species

Compound	$\tilde{\nu}$(CO)/cm^{-1} [a]
$[Os(CO)_5]$	2 041w, 2 034s, 1 991vs
$[OsH_2(CO)_4]$	2 067m, 2 055s (sh), 2 047vs, 2 016w
$[Os_2(CO)_9]$	2 080s, 2 038vs, 2 024m, 2 013s, 2 000w, 1 778m
$[Os_3(CO)_{12}]$	2 067s, 2 033s, 2 011m, 1 999m
$[Os_4H_4(CO)_{12}]$	2 084m, 2 066s, 2 059 (sh), 2 019m, 1 995w
$[Os_5(CO)_{16}]$	2 063vs, 2 048s, 2 040s, 1 992w
$[Os_5H_2(CO)_{15}]$	2 075s, 2 067s, 2 047s, 2 036m, 2 027w, 2 013m, 2 004w, 1 994w
$[Os_5H_2(CO)_{16}]$	2 122w, 2 083s, 2 060s, 2 049s, 2 045m (sh), 2 038w, 2 010m
$[Os_5(CO)_{19}]$	2 099m, 2 073s, 2 068w (sh), 2 040s, br, 2 035m (sh), 2 027w (sh), 2 000w, br, 1 980w, br
$[Os_6(CO)_{18}]$	2 104w, 2 074s, 2 061s, 2 036s, 2 030m, 2 026m (sh), 2 000w, 1 954w
$[Os_6H_2(CO)_{18}]$	2 080s, 2 072s, 2 044m, 2 034m, 2 016w, 2 000w
$[Os_6(CO)_{20}]$ [b]	2 103s (sh), 2 092s, 2 064m (sh), 2 035s, br, 2 018s, 1 997s, br, 1 983w, 1 967m, 1 964w (sh), 1 957w, 1 895w
$[Os_7(CO)_{21}]$	2 073s, 2 055br, 2 034w, 1 998w, 1 986w

[a] In hexane solution unless otherwise stated. [b] Nujol mull.

TABLE 4

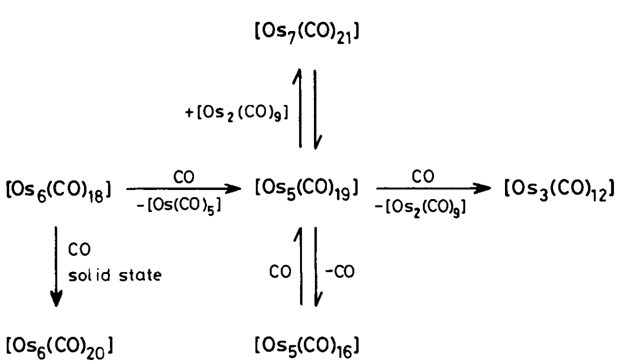
Infrared spectroscopic data in the ν(CO) region for Ru_n (n = 1, 3—6) species

Compound	$\tilde{\nu}$(CO)/cm^{-1} [a]
$[Ru(CO)_5]$	2 035s, 1 999vs
$[Ru_3(CO)_{12}]$	2 059vs, 2 026s, 2 007m
$[Ru_4H_4(CO)_{12}]$	2 079s, 2 064vs, 2 028m, 2 022s, 2 005w
$[Ru_5(CO)_{15}C]$	2 067vs, 2 034s, 2 015m
$[Ru_5H_2(CO)_{15}C]$ [b]	2 079s, 2 070vs, 2 062vs, 2 060vs, 2 048 (sh), 2 044w, 2 033w, 2 027m, 2 020w, 2 014w, 2 007vw, 1 995w
$[Ru_6(CO)_{17}C]$	2 066s, 2 045s, br
$[Ru_6H_2(CO)_{18}]$	2 067 (sh), 2 058s, 2 052s, 2 003w

[a] In hexane. [b] Proposed, not fully characterised.

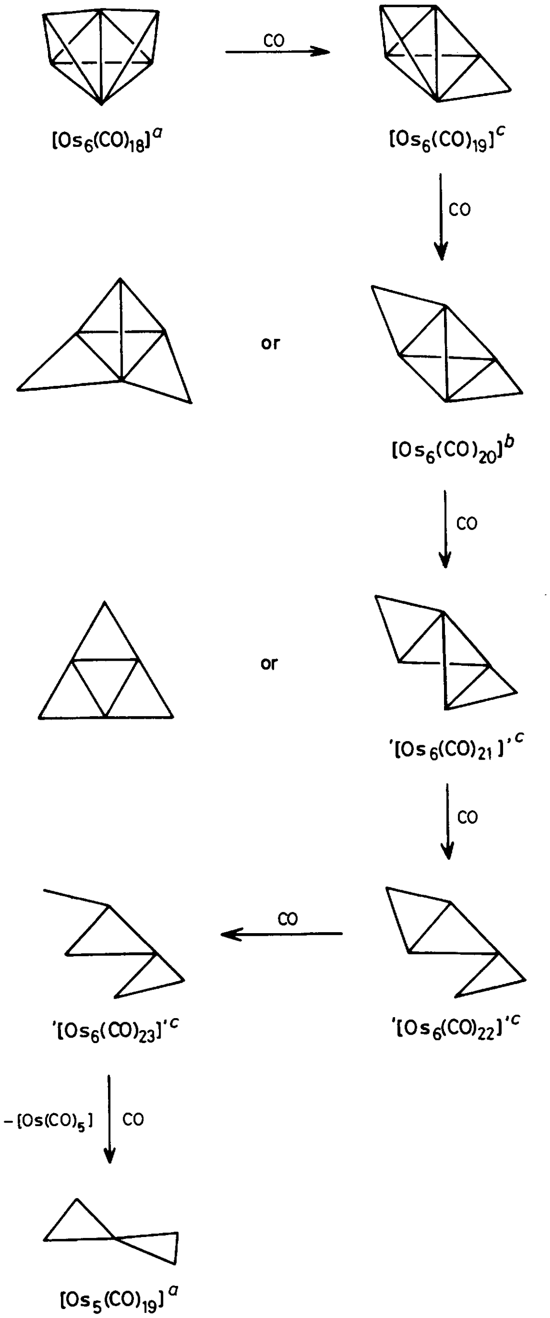
with CO (65 atm, 155 °C), $[Os_5(CO)_{19}]$ is reformed from $[Os_5(CO)_{16}]$ in quantitative amounts.

It is clear from these experiments that under the conditions employed an equilibrium exists between the various osmium carbonyl species. Such an equilibrium is outlined in Scheme 1 and serves to emphasise the sensitivity of these carbonylation reactions to changes in reaction conditions (CO pressure and temperature).



SCHEME 1 The carbonylation of $[Os_6(CO)_{18}]$

The detailed mechanism by which these interconversions occur is difficult to establish. In one possible mechanism the carbonylation of $[Os_6(CO)_{18}]$ may be envisaged as occurring by the sequential addition of three carbonyl ligands, followed by fragmentation, to produce $[Os_5(CO)_{16}]$ and $[Os(CO)_5]$. The pentanuclear cluster $[Os_5(CO)_{16}]$ would then undergo addition of CO to



SCHEME 2 Alternative route to $[Os_5(CO)_{19}]$ from the reaction of CO with $[Os_6(CO)_{18}]$

[a] Isolated and fully characterised. [b] Observed (i.r.) but not fully characterised. [c] Suggested intermediate, not observed.

generate $[Os_5(CO)_{19}]$. Evidence against this reaction scheme is that $[Os_5(CO)_{16}]$ is not observed in the h.p.i.r. spectrum during the initial formation of $[Os_5(CO)_{19}]$.

An alternative route would involve the successive addition of CO to $[Os_6(CO)_{18}]$, sequentially cleaving Os–Os edges of the bicapped tetrahedral unit and eventually, at a stage corresponding to $[Os_6(CO)_{24}]$, $[Os(CO)_5]$ is eliminated. This process is outlined in Scheme 2. Again no direct i.r. evidence has been obtained for the formation of the successive CO addition products corresponding to the compounds $[Os_6(CO)_{18+n}]$ (where $n = 1$—5). However, as reported previously, one of the proposed intermediates, $[Os_6(CO)_{20}]$ ($n = 2$), has been identified as the product of the reaction of $[Os_6(CO)_{18}]$ in the solid state. This new compound was initially observed as a deposit within the i.r. cell during the course of an experimental run and we were subsequently able to show that the reaction of $[Os_6(CO)_{18}]$ (solid) with CO produced $[Os_6(CO)_{20}]$ in almost quantitative amounts. This purple compound was identified on the basis of its mass spectrum which revealed a parent ion $[Os_6(CO)_{20}]^+$ ($m/e = 1\,720$) together with ions corresponding to the stepwise loss of 20 CO groups. The i.r. spectral data for this compound are shown in Table 3. On heating, $[Os_6(CO)_{20}]$ ejects 2 mol of CO (by volume analysis) to regenerate $[Os_6(CO)_{18}]$.[4] Further support for the formation of clusters containing six osmium atoms and higher proportions of CO is not yet available.

Reaction of $[Os_6(CO)_{18}]$ *with hydrogen.* The reaction of $[Os_6(CO)_{18}]$ with H_2 has been explored by following the change of the i.r. spectrum [ν(CO)] as a function of time, temperature, and H_2 pressure. At 100 atm and 210 °C hydrogenation occurs smoothly (2 h); $[OsH_2(CO)_4]$ is eliminated and the tetranuclear cluster $[Os_4H_4(CO)_{12}]$ is produced, along with some minor products which were not identified, equation (6). No pentaosmium intermediate compounds were observed in the course of this reaction and, in keeping with this observation, we have found that the two pentaosmium systems $[Os_5(CO)_{16}]$ and $[Os_5(CO)_{19}]$ both react readily with H_2 to produce the same tetranuclear species $[Os_4H_4(CO)_{12}]$. We have further established that in the reaction with H_2 [equation (7)], $[Os_5(CO)_{19}]$ first undergoes decarbonylation to $[Os_5(CO)_{16}]$ in the same way as when it is heated under argon (see Table 1), the hydrogen acting here as an inert atmosphere. In a series of additional experiments we have further established that under the conditions used in reaction (6) the hydrido-clusters $[Os_6H_2(CO)_{18}]$, $[Os_5H_2(CO)_{15}]$, and $[Os_5H_2(CO)_{16}]$, reactions (9)—(11), also undergo fragmentation to produce $[Os_4H_4(CO)_{12}]$ and $[OsH_2(CO)_4]$. Again some minor products were detected but not identified because of their low yields. Thus, under the conditions employed in reaction (6) the possible reaction intermediates are all known to undergo cleavage to produce the highly stable tetranuclear cluster $[Os_4H_4(CO)_{12}]$. Under less vigorous conditions (*i.e.* 10 atm of H_2), $[Os_6(CO)_{18}]$ does not undergo reaction.

$$[Os_6(CO)_{18}] \longrightarrow [Os_4H_4(CO)_{12}] + [OsH_2(CO)_4] \quad (6)$$

$$[Os_5(CO)_{19}] \xrightarrow[0.25\ h]{H_2,\ 120\ °C} [Os_5(CO)_{16}] + CO \quad (7)$$

$$[Os_5(CO)_{16}] \xrightarrow[2\ h]{180\ °C,\ H_2\ (60\ atm)} [Os_4H_4(CO)_{12}] + [OsH_2(CO)_4] \quad (8)$$

$$[Os_6H_2(CO)_{18}] \xrightarrow[1.5\ h]{H_2\ (100\ atm),\ 190\ °C} [Os_4H_4(CO)_{12}] + [OsH_2(CO)_4] \quad (9)$$

$$[Os_5H_2(CO)_{15}] \xrightarrow[fast]{H_2\ (90\ atm),\ 120\ °C} [Os_4H_4(CO)_{12}] + [OsH_2(CO)_4] \quad (10)$$

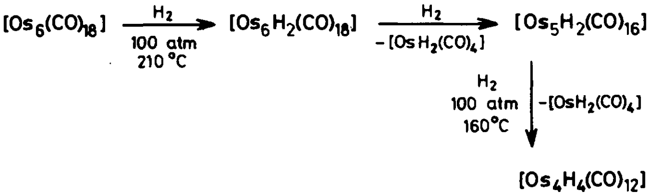
$$[Os_5H_2(CO)_{16}] \xrightarrow[2\ h]{H_2\ (100\ atm),\ 150\ °C} [Os_4H_4(CO)_{12}] + [OsH_2(CO)_4] \quad (11)$$

It is also of interest to note that heating $[Os_6H_2(CO)_{18}]$ and $[Os_5H_2(CO)_{16}]$ in inert atmospheres causes the loss of H_2 [equation (12)] and CO [equation (13)] respectively.

$$[Os_6H_2(CO)_{18}] \xrightarrow[170\ °C]{Ar} [Os_6(CO)_{18}] + H_2 \quad (12)$$

$$[Os_5H_2(CO)_{16}] \xrightarrow[155\ °C]{Ar} [Os_5H_2(CO)_{15}] + CO \quad (13)$$

A reaction sequence similar to that shown in Scheme 3 must therefore also be regarded as reasonable. Throughout, the driving force to reaction appears to be saturation of the cluster to a point such that ejection of the stable $[Os(CO)_5]$ or $[OsH_2(CO)_4]$ molecule occurs.

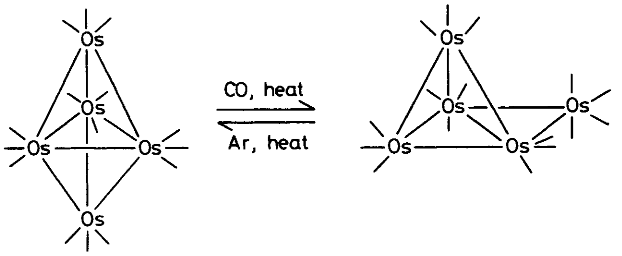


SCHEME 3 Reaction of $[Os_6(CO)_{18}]$ with hydrogen

It should be noted that the loss of CO from $[Os_5H_2(CO)_{16}]$ [equation (13)] effected by heating in an inert atmosphere is reversible; when $[Os_5H_2(CO)_{15}]$ is heated under CO, $[Os_5H_2(CO)_{16}]$ is reformed in quantitative amounts (14).

$$[Os_5H_2(CO)_{15}] \xrightarrow[fast]{CO\ (10\ atm),\ 125\ °C} [Os_5H_2(CO)_{16}] \quad (14)$$

The compound $[Os_5H_2(CO)_{15}]$ is isoelectronic with $[Os_5(CO)_{16}]$, for which a trigonal-bipyramidal structure has been determined[6] and a similar structure for $[Os_5H_2(CO)_{15}]$ is predicted both by Wade theory and the effective atomic number (e.a.n.) rule. Simple addition of CO to $[Os_5H_2(CO)_{15}]$ to give $[Os_5H_2(CO)_{16}]$ results in cleavage of a polyhedral osmium–osmium edge and an opening out of the trigonal-bipyramidal structure to yield the observed edge-bridged tetrahedron[7] (Scheme 4). The fact that this reaction is reversible clearly indicates that a metal–metal bond may readily be broken and reformed and is significant in that the provision of vacant sites for attack is one of the prerequisities for catalytic activity.



$[Os_5H_2(CO)_{15}]$ $[Os_5H_2(CO)_{16}]$

SCHEME 4 Polyhedral edge cleavage on addition of CO to $[Os_5H_2(CO)_{15}]$ (H ligands omitted)

Reaction of $[Os_6(CO)_{18}]$ *with* CO–H_2 *mixtures*. In addition to the experiments discussed above, we have also investigated the reaction of $[Os_6(CO)_{18}]$ with mixtures of CO and H_2. In a typical experiment, $[Os_6(CO)_{18}]$ was heated under a pressure of CO–H_2 (35 and 55 atm) in the h.p.i.r. cell. Reaction occurred according to equation (15) to produce $[Os_4H_4(CO)_{12}]$. The dihydrido-species, $[Os_6H_2(CO)_{18}]$, behaved similarly, forming first $[Os_5H_2(CO)_{16}]$ and ultimately $[Os_4H_4(CO)_{12}]$, equations (16) and (17).

$$[Os_6(CO)_{18}] + H_2 + CO \longrightarrow [Os_4H_4(CO)_{12}] + 2[OsH_2(CO)_4] \quad (15)$$

$$[Os_6H_2(CO)_{18}] + H_2 + CO \longrightarrow [Os_5H_2(CO)_{16}] + [OsH_2(CO)_4] \quad (16)$$

$$[Os_5H_2(CO)_{16}] + H_2 \longrightarrow [Os_4H_4(CO)_{12}] + [OsH_4(CO)_4] \quad (17)$$

Ruthenium Carbonyl Clusters.—The range of available carbonyl clusters of ruthenium is less extensive than that of osmium. In this work we have examined the reactions of $[Ru_3(CO)_{12}]$, $[Ru_4H_2(CO)_{13}]$, $[Ru_6(CO)_{17}C]$, and $[Ru_6H_2(CO)_{18}]$.

Reaction of $[Ru_3(CO)_{12}]$ *with* CO. Treatment of $[Ru_3(CO)_{12}]$ in heptane with carbon monoxide at 100 atm and 170 °C gives quantitative yields of $[Ru(CO)_5]$. This transformation is complete under the conditions within *ca.* 2 h. This observation is in contrast to the chemistry of $[Os_3(CO)_{12}]$, which is stable to CO at 100 atm and 220 °C for periods up to 10 h.

$$[Ru_3(CO)_{12}] \xrightarrow{CO} [Ru(CO)_5] \quad (18)$$

Reaction of $[Ru_4H_2(CO)_{13}]$ *with* CO. When $[Ru_4H_2(CO)_{13}]$ is allowed to react with CO at 100 atm and 50 °C the i.r. spectrum is consistent with the formation of $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$. The fate of the hydrido-ligands is uncertain but they are most probably lost as hydrogen.

$$[Ru_4H_2(CO)_{13}] \xrightarrow{CO} [Ru_3(CO)_{12}] + [Ru(CO)_5] \quad (19)$$

Reaction of $[Ru_6(CO)_{17}C]$ *with* CO. Several years ago we reported[8] the preparation of the hexaruthenium carbido-cluster $[Ru_6(CO)_{17}C]$ directly from $[Ru_3(CO)_{12}]$. We were also able to demonstrate that the carbido-atom originated from C–O bond cleavage and that CO_2 was evolved.

$$2[Ru_3(CO)_{12}] \xrightarrow{\text{heat}} [Ru_6(CO)_{17}C] + 5CO + CO_2 \quad (20)$$

In $[Ru_6(CO)_{17}C]$ the carbon atom is encapsulated by an octahedron of ruthenium atoms and is thus protected from attack by incoming substrates. However, $[Ru_6(CO)_{17}C]$ reacts with CO at 80 atm and 120 °C to produce the pentanuclear cluster $[Ru_5(CO)_{15}C]$ and $[Ru(CO)_5]$ in quantitative amounts, equation (21). Previously, this pentanuclear carbide had been obtained in 1% yield from the reaction of $[Ru_4H_4(CO)_{12}]$ with ethylene.[9] On the basis of *X*-ray analysis it has been shown to be isostructural with $[Fe_5(CO)_{15}C]$ and some preliminary work on this cluster has already been reported.[10]

$$[Ru_6(CO)_{17}C] \xrightarrow{CO} [Ru_5(CO)_{15}C] + [Ru(CO)_5] \quad (21)$$

The only other product of reaction (21) was confirmed as $[Ru(CO)_5]$ on the basis of its physical and spectroscopic properties. The mononuclear species readily converts into $[Ru_3(CO)_{12}]$ and may thereby be used to regenerate $[Ru_6(CO)_{17}C]$.

A surprising feature of $[Ru_5(CO)_{15}C]$ is its reaction to give $[Ru_6(CO)_{17}C]$ on pyrolysis under argon. Yields of the hexanuclear carbide by this route are in the region of 50%.

Pyrolysis of $[Ru_6H_2(CO)_{18}]$. On heating $[Ru_6H_2(CO)_{18}]$ in an inert atmosphere, $[Ru_6(CO)_{17}C]$ is produced and it would appear that the elements of water are lost from the hydrido-carbonyl cluster to give the carbido-cluster [as in equation (22)].

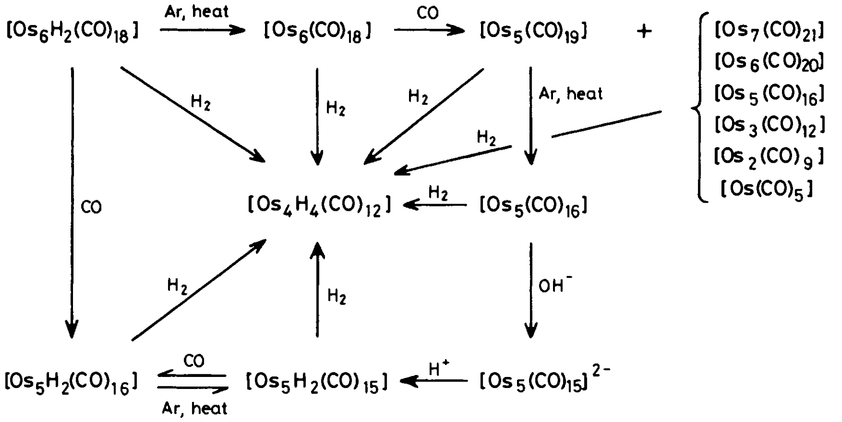
$$[Ru_6H_2(CO)_{18}] \xrightarrow[\text{`}-H_2O\text{'}]{\text{Ar, 120 °C}} [Ru_6(CO)_{17}C] \quad (22)$$

Reaction of $[Ru_5(CO)_{15}C]$ *with* CO. The complex $[Ru_5(CO)_{15}C]$ is exceptionally stable to CO, remaining unchanged after 4 h under 400 atm of CO at 100 °C. Further work is in hand to establish how the cluster is broken down under more vigorous conditions.

Reaction of $[Ru_5(CO)_{15}C]$ *with* H_2. On heating to 100 °C under 15 atm H_2, $[Ru_5(CO)_{15}C]$ reacts over a period of 4 h to give a product which is not as yet fully characterised. On heating to 90 °C under vacuum this product is converted back into $[Ru_5(CO)_{15}C]$, and on the basis of that experiment and its spectroscopic properties we propose that it is the dihydride, $[Ru_5H_2(CO)_{15}]$.

$$[Ru_5(CO)_{15}C] \underset{90\ °C\ \textit{in vacuo}}{\overset{H_2\ (15\ \text{atm}),\ 100\ °C}{\rightleftharpoons}} [Ru_5H_2(CO)_{15}C] \quad (23)$$

Conclusion.—We have seen that there are several routes available for cluster breakdown in reactions with CO and H_2. Reactions with CO tend eventually towards the trinuclear species $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, while in reactions with H_2 (see Scheme 5, for example) the tetranuclear species $[Os_4H_4(CO)_{12}]$, or $[Ru_4H_4(CO)_{12}]$,



Scheme 5 Overall reaction scheme for interactions of osmium cluster compounds with CO or H_2

seems to be the favoured product. As a result of this observation we are making an extensive study of the chemistry of these important hydrido-carbonyl clusters. It should be noted that the products from reactions with mixtures of CO and H_2 are generally not simply the result of a summation of the reaction products from the separate reactions with CO and H_2.

We have demonstrated three types of reaction which may occur when hydrido-carbonyls are heated in inert atmospheres: H_2 loss to give a binary carbonyl [equation (12)]; CO loss to give a new hydrido-carbonyl [equation (13)]; and H_2O loss to give a carbido-carbonyl cluster [equation (22)].

EXPERIMENTAL

The experiments were conducted in a high-pressure i.r. cell (h.p.i.r.) which has been described elsewhere.[3] Before each run the cell was flushed out with fresh heptane. The spectra were recorded under a working pressure of the appropriate gas (CO or H_2) and at the appropriate temperature. Repeated registration of the spectrum allowed the reaction to be followed. Spectra were scanned by a Perkin-Elmer model 237 spectrophotometer. All cluster carbonyls employed were prepared and purified by methods reported in the literature.

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