A Study of the Reaction of the Series of Neutral Metal Carbonyls $M_3(CO)_{12}$ (M = Fe, Ru, or Os) with the Metal Carbonyl Anions $[M'(CO)_5]^-$ (M' = Mn or Re)

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The reaction of $M_3(CO)_{12}$ (M = Fe, Ru, or Os) with $M'(CO)_5^-$ (M' = Mn or Re) in different solvents and at different temperatures has been studied. The reactions are exceedingly complex and the nature of the products obtained depends critically on the experimental conditions. Isolation of individual anionic species from the complex mixtures formed is difficult, and it has only proved possible to obtain three such species, $Me_4N^+M'Os_2(CO)_{12}^-$ and $Me_4N^+ReRu_3(CO)_{16}^-$ in an analytically pure condition. In addition to these, good evidence has been obtained for the formation of $Et_4N^+HRu_3(CO)_{11}^-$. Acidification of the reaction mixtures obtained under various conditions leads to the formation of neutral hydride-containing species, and these may be separated more readily. Apart from a number of previously characterised products the following new complexes have been prepared in this way: $HM'Os_2(CO)_{12}$, $HM'Os_3(CO)_{16}$, $HReOs_3(CO)_{15}$, $H_3M'Os_3(CO)_{13}$, $H_2Ru_6(CO)_{18}$, $H_2Re_2Ru_2(CO)_{16}$ and $H_2Re_2Ru(CO)_{12}$. From the nature of the products obtained in these reactions it is possible to deduce some of the reaction paths which are probably involved in the formation of polynuclear carbonyl complexes by this route.

THE reduction of binary metal carbonyls with loss of carbon monoxide is a well-established method for the synthesis of polynuclear metal carbonyl anions. Sodium amalgam is the reducing agent most commonly employed and its use generally leads to the formation of mononuclear carbonyl anions, *e.g.* as in the reduction of $Co_2(CO)_8$ to $Co(CO)_4^-$.[1] Other reducing agents may

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[1] S. V. Dighe and M. Orehin, *Inorg. Chem.*, **1962**, **1**, **965**.

also be used, however, and often give reduction products which are different from those obtained with sodium amalgam. Thus reaction of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with alcoholic potassium hydroxide gives respectively $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$,[2] while the reduction of $Co_2(CO)_8$ with alkali metals gives the trinuclear $[Co_3(CO)_{10}]^-$ [3] or the hexanuclear $[Co_6(CO)_{14}]^{4-}$ [4] depending upon the reaction conditions. Sodium borohydride is a frequently used and effective reducing agent leading most often to the formation of hydride-containing species as in the preparation of $[H_6Re_4(CO)_{12}]^{2-}$ from $Re_2(CO)_{10}$.[5] More unusual examples of specific reductions include the use of wet morpholine which reduces $Rh_4(CO)_{12}$ to $[Rh_7(CO)_{16}]^{3-}$.[6]

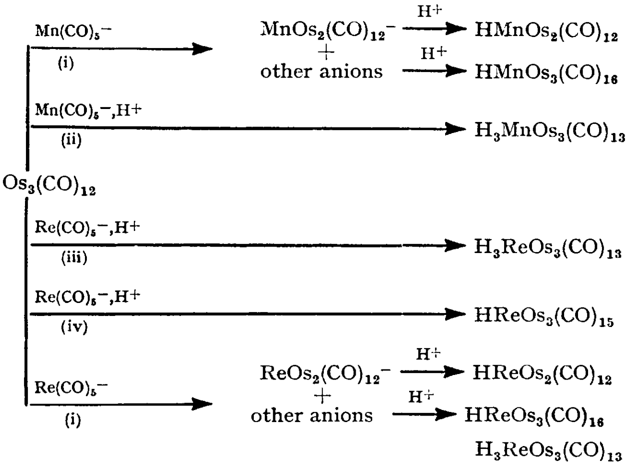
A further class of reducing agents which have been used extensively are the metal carbonyl anions themselves. Although these sometimes react to give mononuclear carbonyl anions [7] this type of reaction more commonly leads to the formation of polynuclear carbonyl anions. These may be homonuclear as in the formation [8] of $[Fe_4(CO)_{13}]^{2-}$ from $Fe(CO)_5$ and $[Fe_3(CO)_{11}]^{2-}$ or, since the metal carbonyl anion used as the reducing agent is frequently incorporated into the product, heteronuclear species may also be obtained, *e.g.* $[MnFe_2(CO)_{12}]^-$,[9] $[MnCr(CO)_{10}]^-$,[10] and $[W_2Ni_3(CO)_{16}]^{2-}$.[11] This type of reaction, however, frequently depends most critically on the reaction conditions and rarely leads to only one product being formed.

In order to investigate further the factors involved in determining the course of these exceedingly complex reduction reactions and in order to extend our synthetic work on polynuclear mixed-metal carbonyl complexes [12] we have studied systematically the reduction of $M_3(CO)_{12}$ (M = Fe, Ru, or Os) with a variety of anionic carbonyl species, and in this paper we present our results using $M'(CO)_5^-$ (M' = Mn or Re). Preliminary accounts of part of this work describing some of the new complexes isolated have already been published.[13,14]

RESULTS AND DISCUSSION

It must be emphasised again that nearly all the reactions described below give rise to complex mixtures of anionic species in solution which are often exceedingly difficult to separate and crystallise in a pure condition. Although we have been successful in isolating certain of these anionic species, generally as their tetramethylammonium salts, in the majority of cases it has proved necessary to acidify the reaction mixtures, forming neutral hydride-containing species which may be more readily separated and characterised. Since it is probable that the majority of the anionic species present in the original reaction mixtures give rise to the corresponding hydride complexes on acidification (*vide infra*) it is therefore possible to obtain information concerning the nature of these anionic species by identification of the hydride complexes.

Reactions of $Os_3(CO)_{12}$ *with* $Mn(CO)_5^-$ *and* $Re(CO)_5^-$.—Most of the complexes isolated from reactions of $Os_3(CO)_{12}$ with manganese and rhenium pentacarbonyl anions are ' mixed-metal ' compounds, showing that the reduction process occurs with incorporation of the manganese or rhenium atoms into the products. In refluxing diglyme a rapid reaction takes place to give a mixture of anionic species from which the complexes $M'Os_2(CO)_{12}^-$ (M' = Mn or Re) may be isolated as their tetramethylammonium salt. On acidification of the mixture, in addition to $HM'Os_2(CO)_{12}$, the complexes $HM'Os_3(CO)_{16}$ and $HReOs_3(CO)_{15}$ were obtained. Using tetrahydrofuran (THF) as the solvent it was also possible to prepare $HReOs_3(CO)_{15}$ and $H_3M'Os_3(CO)_{13}$ as pure compounds. A summary of the reaction conditions required is given in Scheme 1. Some of the properties of these new complexes are now described.



SCHEME 1

Summary of reactions of $Os_3(CO)_{12}$ with $M'(CO)_5^-$; (i), heated under reflux in diglyme for 5 min; (ii) heated under reflux in THF for 65 h; (iii) heated under reflux in THF for 20 h; (iv) heated under reflux in THF for 10 min.

(*a*) $Me_4N^+MnOs_2(CO)_{12}^-$ *and* $Me_4N^+ReOs_2(CO)_{12}^-$.—These air-stable crystalline salts were identified by analysis. Their i.r. spectra in the carbonyl region (Table 2) show seven and eight absorptions respectively, all in the terminal region. The most likely structure for the anions is therefore one of C_{2v} symmetry as in

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[2] W. Hieber and G. Brendel, *Z. anorg. Chem.*, 1957, **289**, 324.

[3] S. A. Fieldhouse, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *Chem. Comm.*, 1970, 181.

[4] R. Chini, V. Albano, and S. Martinengo, *J. Organometallic Chem.*, 1969, **16**, 471.

[5] H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Amer. Chem. Soc.*, 1969, **91**, 1021.

[6] P. Chini and S. Martinengo, *Chem. Comm.*, 1969, 1092.

[7] R. E. Dessy and P. M. Weissmann, *J. Amer. Chem. Soc.*, 1966, **88**, 5129.

[8] W. Hieber and E. H. Schubert, *Z. anorg. Chem.*, 1965, **338**, 32.

[9] U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.

[10] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1818.

[11] J. K. Ruff, R. P. White, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 2159.

[12] J. Knight and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 654.

[13] J. Knight and M. J. Mays, *Chem. Comm.*, 1971, 62.

[14] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Comm.*, 1970, 458.

structure (1). It is analogous to $FeOs_2(CO)_{12}$ [15] and it may be regarded as derived from that of $Os_3(CO)_{12}$ by replacement of an osmium atom by manganese or rhenium. Both the manganese and rhenium salts are readily soluble in acetone, moderately so in methanol and THF but insoluble in ether.

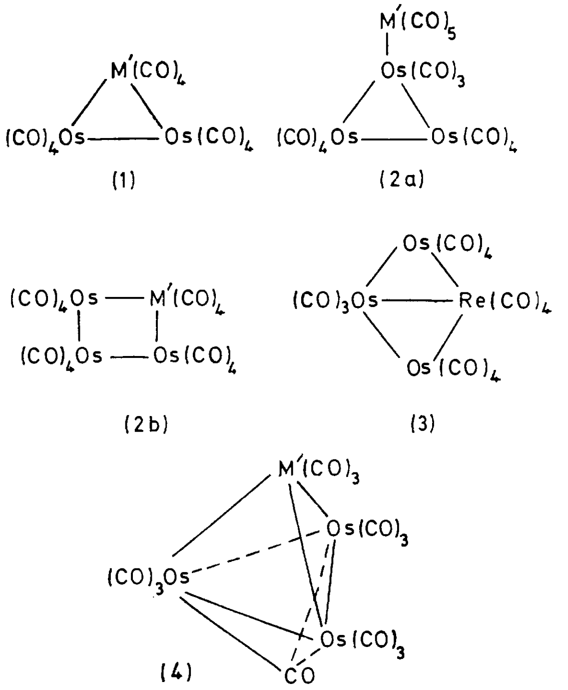
(*b*) $HMnOs_2(CO)_{12}$ *and* $HReOs_2(CO)_{12}$.—Addition of acetone solutions of the salts $Me_4N^+M'Os_2(CO)_{12}^-$ to aqueous phosphoric acid gave precipitates of the hydrides $HM'Os_2(CO)_{12}$. The manganese compound was obtained in sufficient quantity for characterisation both by mass spectroscopy and by analysis; the rhenium complex was characterised by mass spectroscopy only.

Peaks at the *m*/*e* values 776 and 908 attributable to the molecular ions $HMn{}^{192}Os_2(CO)_{12}^+$ and $H{}^{187}Re{}^{192}Os_2(CO)_{12}^+$ respectively were observed together with the ions $HM'Os_2(CO)_n^+$ ($n = 0$—9 for M' = Mn, $n = 0$—11 for M' = Re). For both complexes, loss of hydrogen and oxygen only became significant when the number of remaining carbonyl groups was small, giving rise to fragment ions such as $MnOs_2(CO)^+$ and $HReOs_2(CO)C^+$. Other series of fragment ions to be identified in the spectra of both compounds were $HM'Os_2(CO)_n^{2+}$ and $Os_2(CO)_n^+$.

The i.r. spectra of the hydrides show several carbonyl stretching bands, all in the terminal region, suggesting that the overall molecular symmetry is low. This information is not sufficient, however, for us to be able to propose a site for the hydrogen atom. $HMnOs_2(CO)_{12}$ is sparingly soluble in petroleum and is decomposed by dichloromethane.

(*c*) $HMnOs_3(CO)_{16}$ *and* $HReOs_3(CO)_{16}$.—The anion $MnOs_2(CO)_{12}^-$, although present in the complex mixture resulting from reaction of $Os_3(CO)_{12}$ with $Mn(CO)_5^-$ in boiling diglyme, is evidently not the major product of this reaction. Acidification of the anion mixture gives a moderately good yield of the tetranuclear hydride, $HMnOs_3(CO)_{16}$, and the same complex is also formed on acidification of the products of the reaction of u.v. irradiation of $Os_3(CO)_{12}$ and $Mn(CO)_5^-$. Its formulation is based on mass spectroscopy and chemical analysis. In contrast to the other osmium–manganese hydrides, it is readily soluble in organic solvents, giving intense yellow solutions although it was not sufficiently soluble for it to be possible to detect the presence of hydrogen by n.m.r. spectroscopy.

The mass spectrum of the complex, however, reveals that at least one hydrogen atom is present. A mass multiplet, spanning the *m*/*e* value 1076 and possessing an isotopic pattern in good agreement with that calculated for an ion containing the $MnOs_3$ nucleus was observed. In particular, the component peak at *m*/*e* 1080 had approximately the correct relative intensity expected for the molecular ion, $HMn{}^{192}Os_3(CO)_{16}^+$. Other ions identified in the spectrum were the series $HMnOs_3(CO)_n^+$ ($n = 0$—11), $MnOs_3(CO)_n^+$, $Os_3(CO)_n^+$, and $HMnOs_2(CO)_n^+$. The fact that no fragment ions containing more than one hydrogen atom were identified does not exclude the possibility that more than one hydrogen atom is present in the neutral molecule, since, *e.g.* $H_4Ru_4(CO)_{12}$ gives rise to a mass spectrum in which $H_3Ru_4(CO)_{12}^+$ is the ion of highest *m*/*e* value observed [although $H_4Ru_4(CO)_{12}^+$ could be seen when photoionisation was used].[16] $HMnOs_3(CO)_{16}$, however, contains an average of four carbonyl groups per metal atom, suggesting an 'open' rather than a 'closed tetrahedral' structure. Such open clusters generally obey the 18-electron rule for each individual metal atom,[17] and this is possible for $HMnOs_3(CO)_{16}$ provided that only one hydrogen atom is present.



Possible structures for some polynuclear carbonyl complexes; (1), $M'Os_2(CO)_{12}^-$; (2a) and (2b), $HM'Os_3(CO)_{16}$; (3), $HReOs_3(CO)_{15}$; (4), $H_3M'Os_3(CO)_{13}$; hydride ligands have been omitted

The i.r. spectrum of the complex in solution shows 13 terminal carbonyl stretching vibrations indicating a low molecular symmetry. Structures (2a) and (2b) show two possible structures for the complex (hydrogen atoms omitted). Although no examples of polynuclear carbonyl complexes containing either of these types of metal-atom arrangements have yet been proven by *X*-ray analysis both allow each of the metal atoms to obey the 18-electron rule. Structure (2a) can be regarded as derived from that of osmium carbonyl by replacement of a carbonyl group by the two one-electron ligands H and $Mn(CO)_5$. An *X*-ray determination of the crystal structure of this complex is in progress.*

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* M. R. Churchill *et al.*, to be published.

[15] W. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1970, **23**, C23.

[16] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.

[17] P. Chini, *Inorg. Chim. Acta, Rev.*, 1968, **2**, 31.

The reaction of $Os_3(CO)_{12}$ with $Re(CO)_5^-$ in diglyme at 160° is roughly analogous to that with $Mn(CO)_5^-$ under similar conditions. Acidification of the reaction mixture as before gives a mixture of carbonyl hydride species and separation of the components of the mixture by thin-layer chromatography reveals the presence of an intense yellow band of similar R_f value to $HMnOs_3(CO)_{16}$. Although pure samples of the complex could not be obtained even by repeated application of t.l.c. (usually the most effective method of separation) the mass spectrum indicated that $HReOs_3(CO)_{16}$ was present. The component peak, $H^{187}Re^{192}Os_3(CO)_{16}^+$, in the molecular-ion multiplet had an m/e value of 1212 as expected. Fragment ions formed by loss of carbonyl groups from this ion were also observed together with the series $HReOs_2(CO)_n^+$ ($n = 0$—12). Although the latter ions may have arisen by breakdown of $HReOs_3(CO)_{16}$ in the mass spectrometer, they could also have been formed by thermal decomposition of the complex on the probe of the mass spectrometer prior to ionisation.

(*d*) $HReOs_3(CO)_{15}$.—Acidification of the anion mixture formed after 20 min reflux of osmium carbonyl with rhenium pentacarbonyl anion in THF afforded the hydride $HReOs_3(CO)_{15}$ in low yield. This orange crystalline complex was sparingly soluble in organic solvents and was identified by mass spectroscopy and analysis. The ion multiplet of highest m/e value in the mass spectrum of the complex had an isotopic pattern in agreement with that expected for the $ReOs_3$ combination and the component peak at m/e 1184 could be attributed to the ion $H^{187}Re^{192}Os_3(CO)_{15}^+$. Ions formed from the molecular ion by carbonyl loss and the doubly-charged ions $HReOs_3(CO)_n^{2+}$ were observed but there was no significant abundance of any other metal-containing ion and, in particular, there was no evidence for ions containing more than one hydrogen atom.

The i.r. spectrum of the compound in a KBr pellet (Table 1) indicated that no bridging carbonyl groups were present. Again, application of the 18-electron rule would suggest that the four metal atoms form some open structure rather than a closed tetrahedral cluster core. A polynuclear carbonyl species having the same overall number of electrons in the valence shells of the metal atoms is $Re_4(CO)_{16}^{2-}$.[18] Its molecular structure, as revealed by an *X*-ray determination, consists of a double-triangulated rhenium-atom framework with carbonyl ligands terminally bound to each rhenium atom. It is therefore possible that $HReOs_3(CO)_{15}$ has a structure which is likewise based on a double-triangulated $ReOs_3$ nucleus as in structure (3). Repeated attempts to prepare the manganese analogue of this complex were not successful. Conditions more vigorous than those required to form $HMnOs_3(CO)_{16}$ gave $H_3MnOs_3(CO)_{13}$ (*vide infra*) and no evidence could be obtained for the presence of $HMnOs_3(CO)_{15}$ in even trace quantities on acidification of reaction mixtures obtained under a variety of experimental conditions. This does not, of course, exclude the possibility that $MnOs_3(CO)_{15}^-$ is formed in solution but, if so, either it or the corresponding hydride complex are much more labile than their rhenium analogues.

(*e*) $H_3MnOs_3(CO)_{13}$ *and* $H_3ReOs_3(CO)_{13}$.—These compounds are obtained in moderate yield on acidification of the anion mixture present after prolonged reflux of $Os_3(CO)_{12}$ with $M'(CO)_5^-$ in THF solution. Some $H_3ReOs_3(CO)_{13}$ is also formed on acidification of the anion mixture present after five minutes reflux of $Os_3(CO)_{12}$ with $Re(CO)_5^-$ in diglyme. The complexes were identified by mass spectroscopy and chemical analysis and are air- and thermally stable. Both compounds form small orange crystals which are very sparingly soluble in organic solvents and they can be recrystallised, without decomposition, from concentrating acetone solutions by boiling in air. Their i.r. spectra in KBr pellets (Table 2) show that terminal and bridging carbonyl groups are present in the molecules. Among the examples of polynuclear carbonyls having the $M_4(CO)_{13}$ stoicheiometry are $H_2FeOs_3(CO)_{13}$ [15] and $Fe_4(CO)_{13}^{2-}$.[19] The structure of the latter, determined by *X*-ray crystallography, shows that the metal atoms form a closed tetrahedral arrangement and that one of the carbonyl groups occupies a triply-bridging position below the basal Fe_3 triangle. A likely arrangement of the heavy atoms in $H_3M'Os_3(CO)_{13}$ is therefore as shown in structure (4). The locations of hydrogen atoms in all the hydrides are even less certain than those of the metal atoms and carbonyl groups, and cannot be obtained directly by *X*-ray crystallography. For $H_3M'Os_3(CO)_{13}$, however, two possible sites are (*i*) around the edges of the basal Os_3 triangle or (*ii*) in bridging positions between M′ and Os atoms on the sides of the tetrahedron.

Reactions of $Ru_3(CO)_{12}$ *with* $Mn(CO)_5^-$ *and* $Re(CO)_5^-$.—$Ru_3(CO)_{12}$ is attacked more readily than is $Os_3(CO)_{12}$ by both $Mn(CO)_5^-$ and $Re(CO)_5^-$ and reacts in THF solution even at 20°. The products of reaction are, in general, more labile than in the case of $Os_3(CO)_{12}$. In addition to the known complexes $H_4Ru_4(CO)_{12}$ [16,20] and $H_2Ru_4(CO)_{13}$,[16,20] the new complexes $H_2Ru_6(CO)_{18}$, $H_2Re_2Ru(CO)_{12}$, and $H_2Re_2Ru_2(CO)_{16}$ have been obtained. We have also been able to prepare one further new complex which we have not fully characterised but which, on the evidence presently available, we formulate as $HRu_3(CO)_{11}^-$. The various experimental conditions required for the preparations are summarised in Scheme 2. It is noteworthy that $Ru_3(CO)_{12}$ is attacked by both manganese and rhenium pentacarbonyl anions at 20° in THF, whereas $Os_3(CO)_{12}$ is inert under these conditions. The properties of the new complexes prepared in the above reactions will now be discussed under separate headings as for the osmium complexes.

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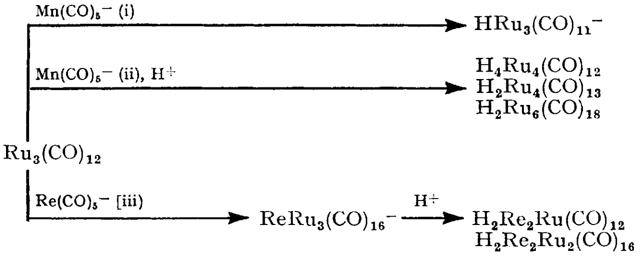
[18] M. R. Churchill and R. Bau, *Inorg. Chem.*, 1968, **7**, 2606.

[19] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.

[20] H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Comm.*, 1971, 477.

(*a*) $Et_4N^+HRu_3(CO)_{11}^-$.—$Ru_3(CO)_{12}$ reacted with $Mn(CO)_5^-$ in THF at 20° to give a deep red solution containing a mixture of products. From this mixture a deep red hydrido-carbonyl anion was isolated as its tetraethylammonium salt, and although consistent analyses could not be obtained, the most probable formulation of the complex is $Et_4N^+HRu_3(CO)_{11}^-$ in the light of the following information. The manganese content of the salt was estimated by decomposition of a weighed amount of the compound with concentrated nitric acid, subsequent oxidation with KIO_4 and comparison of the intensity of the visible absorption spectrum of the $HMnO_4$ produced against that of standard solutions. Only trace quantities of manganese were found to be present. The salt was shown to contain hydrogen bonded directly to the metal atoms from its n.m.r. spectrum. In addition to the resonances due to the protons of the tetraethylammonium cation, a high-field singlet was observed at τ 22·9. Integration of the signals was difficult but the ratio of peak areas obtained was close to that expected for $Et_4N^+HRu_3(CO)_{11}^-$ (8 : 12 : 1). The i.r. spectrum of the salt in solution in the carbonyl region (Table 2) showed that terminal and bridging carbonyl groups were present in the anion and furthermore, the frequencies and relative intensities of the bands were similar to those of the anion $HFe_3(CO)_{11}^-$ in the same solvent. Acidification of the anion gave a red unstable complex which decomposed almost exclusively into $Ru_3(CO)_{12}$ as the only carbonyl-containing product. This may be compared with the behaviour of $HFe_3(CO)_{11}^-$ under similar conditions[2] which gives $Fe_3(CO)_{12}$ on acidification.



SCHEME 2

Summary of reactions of $Ru_3(CO)_{12}$ with $M'(CO)_5^-$; (i) in THF for 28 h at 20°; (ii) heated under reflux in THF for 4 h; (iii) in THF for 20 min at 20°.

TABLE 1

Analytical data

	Found			Required			
Compound	C	H	N	C	H	N	Colour
$Me_4N^+MnOs_2(CO)_{12}^-$	22·5	1·5	1·9	22·7	1·4	1·7	Red
	22·5	1·4	1·6				
$HMnOs_2(CO)_{12}$	18·7			18·7			Orange
$HMnOs_3(CO)_{16}$	18·2			17·9			Yellow
$H_3MnOs_3(CO)_{13}$	15·7			15·7			Red
$Me_4N^+ReOs_2(CO)_{12}^-$	19·8	1·3	1·3	19·9	1·3	1·5	Orange
$HReOs_3(CO)_{15}$	15·2			15·3			Orange
$H_3ReOs_3(CO)_{13}$	13·9			13·9			Orange
$Et_4N^+HRu_3(CO)_{11}^-$	31·6	3·1	1·9	30·7	2·9	1·9	Red
	32·4	3·0	2·3				
$H_2Ru_6(CO)_{18}$	19·5			19·4			Purple
$Me_4N^+ReRu_3(CO)_{16}^-$	23·9	1·3	1·6	23·7	1·2	1·4	Orange
	24·1	1·6	1·4				

TABLE 2

I.r. spectra

Compound	Phase	ν(C–O) cm^{-1}
$Me_4N^+MnOs_2(CO)_{12}^-$	THF	2080w, 2018s, 1981vs, 1943m, 1914m 1897sh, 1887m
$HMnOs_2(CO)_{12}$	n-hexane	2136w, 2081s, 2051vs, 2038vs, 2016m, 2001m, 1993m, 1975m, 1957m, 1951m
$HMnOs_3(CO)_{16}$	n-hexane	2136w, 2093m, 2069s, 2056s, 2031m, 2022m, 2015m, 2006m, 1996m, 1988m,br, 1977m, 1970w
$H_3MnOs_3(CO)_{13}$	KBr	2133m, 2086s, 2055s, 2043sh, 2020sh, 2008s, 1990sh, 1950m, 1830m
$Me_4N^+ReOs_2(CO)_{12}^-$	THF	2085w, 2021s, 2009s, 1990s, 1954w, 1941sh, 1925sh, 1887m
$HReOs_2(CO)_{12}$	n-hexane	2136w, 2086s, 2058sh, 2053vs, 2029m, 2014m, 2000s, 1992m, 1982m, 1967m, 1953m
$HReOs_3(CO)_{15}$	KBr	2131w, 2091s, 2070sh, 2057sh, 2051s, 2018s, 1991sh, 1971sh, 1950m, 1933m
$H_3ReOs_3(CO)_{13}$	KBr	2138s, 2090s, 2063sh, 2030br, 1983s, 1968sh, 1900m
$Et_4N^+HRu_3(CO)_{11}^-$	THF	2072w, 2011s, 1983s, 1949sh, 1898m, 1730vw
$H_2Ru_6(CO)_{18}$	CCl_4	2060s, 2054s, 2008w
$D_2Ru_6(CO)_{18}$	CCl_4	2060s, 2054s, 2007w
$Me_4N^+ReRu_3(CO)_{16}^-$	THF	2009vs, 1982s, 1960brsh, 1932sh, 1891m
$H_2Re_2Ru(CO)_{12}$	n-hexane	2095m, 2091sh, 2070m, 2042s, 2034sh, 2009m, 2001m, 1987m, 1978m, 1956m

No other reaction products could be isolated but when the ionic species in the reaction mixture were extracted into water and then acidified, a dark red precipitate was obtained, the mass spectrum of which exhibited the series of ions $Mn_2Ru(CO)_n^+$ (n = 0—14) and these possessed the expected isotopic pattern for the Mn_2Ru combination. Although no other evidence for the existence of the neutral molecule $Mn_2Ru(CO)_{14}$ could be obtained, since the material decomposed in solution even in the absence of air, other similar molecules such as $Mn_2Fe(CO)_{14}$[21] and $Re_2Fe(CO)_{14}$[22] have been synthesised.

(*b*) $H_2Ru_6(CO)_{18}$.—Heating of the red solution obtained in the reaction of $Ru_3(CO)_{12}$ with $Mn(CO)_5^-$ in THF at room temperature as described above causes decomposition of some, if not all, of the constituents and after refluxing for 3 h in THF a deep brown solution was obtained. Extraction of the mixture of polynuclear carbonyl anions present into water and subsequent acidification gave a mixture of carbonyl hydride species. On extraction of this mixture with petroleum, the known tetranuclear carbonyl hydrides $H_4Ru_4(CO)_{12}$[16,20] and $H_2Ru_4(CO)_{13}$[23] were removed and the solid remaining was shown to contain a new hexanuclear

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[21] E. H. Schubert and R. K. Sheline, *Z. Naturforsch.*, 1965, **20b**, 1306.

[22] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186.

[23] B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1970, 901.

carbonyl hydride, $H_2Ru_6(CO)_{18}$. This purple air-stable crystalline complex was identified by mass spectroscopy and by analysis. It is decomposed by basic solvents and is not sufficiently soluble in any organic solvent in which it is stable for an n.m.r. study to be possible but the presence of two hydrogen atoms was confirmed by carrying out the acidification step using D_3PO_4 in D_2O. The mass spectrum of the corresponding product then showed, using $Rh_6(CO)_{16}$ as calibrant, that the *m/e* value of the molecular ion $D_2Ru_6(CO)_{18}^+$ was two units higher than in the hydride.

The i.r. spectrum of the complex in solution in the carbonyl region is simple, showing only three absorptions, all in the terminal region (Table 2). Little change in the frequencies of the bands is observed in the spectrum of the deuteride. The i.r. spectrum therefore suggests a highly symmetrical structure for the molecule and such a structure has been confirmed by an *X*-ray crystallographic investigation from which it was shown that the six metal atoms define an octahedron, each ruthenium atom bearing three terminal carbonyl groups.[14] It is reasonable to deduce that the two hydride ligands occupy triply-bridging positions either in or above two opposing faces of the octahedron, since the ruthenium–ruthenium distances around two such opposite faces are larger than those around the other four. In addition, the carbonyl groups above these two large faces are spread away from truly axial positions. This new complex is isoelectronic with other known octahedral polynuclear carbonyl complexes such as $Rh_6(CO)_{16}$ [24] and $Ru_6(CO)_{17}C$.[25] For such complexes the 18-electron rule is not obeyed for each individual metal atom and the bonding within the cluster must be considered as a whole. If certain somewhat arbitrary but reasonable assumptions are made as to the number of electrons to be allocated to metal–ligand bonding and to essentially non-bonding orbitals, it can be shown that seven electron-pairs are available for cluster metal–metal bonding.[26] A formal analogy then exists between this complex and $B_6H_6^{2-}$ for which an M.O. treatment also based on the availability of seven bonding electron-pairs has been given.[27]

(*c*) $Me_4N^+ReRu_3(CO)_{16}^-$.—$Ru_3(CO)_{12}$ and $Re(CO)_5^-$ react rapidly in THF at 20° giving a mixture of carbonyl anions from which the mixed anion, $ReRu_3(CO)_{16}^-$, was isolated as its tetramethylammonium salt. The compound crystallises as orange-red, air-stable needles and was identified by chemical analysis. The i.r. spectrum in solution shows many carbonyl absorptions, all in the terminal region, and such a spectrum would be consistent with the complex having either of the two types of structure (2a) or (2b) already proposed for $HMnOs_3(CO)_{16}$ (Figure).

(*d*) $H_2Re_2Ru(CO)_{12}$ *and* $H_2Re_2Ru_2(CO)_{16}$.—Acidification of $Me_4N^+ReRu_3(CO)_{16}^-$ gives a mixture of hydrido-complexes even when the temperature is lowered to 0°. It was possible to separate some of the components of this mixture in trace quantities using thin-layer chromatography and two of these, $H_2Re_2Ru(CO)_{12}$ and $H_2Re_2Ru_2(CO)_{16}$, were identified by mass spectroscopy. The isolation of these two products illustrates the caution that is necessary in deducing which anions are present in reaction mixtures from the nature of the neutral hydride-containing products obtained on acidification of such mixtures.

Reactions of $Fe_3(CO)_{12}$ *with* $Mn(CO)_5^-$ *and* $Re(CO)_5^-$.—Rapid reaction occurred between $Fe_3(CO)_{12}$ and either $Mn(CO)_5^-$ or $Re(CO)_5^-$ in THF at 20°. The products in each case were identified as mixtures of the known polynuclear carbonyl anions of iron [28] and no products formed by insertion of manganese or rhenium atoms into $Fe_3(CO)_{12}$ were observed.

CONCLUSIONS

The most important point to emerge from the present investigation is the critical influence of reaction conditions upon the nature of the products obtained from reactions of the type under study. This suggests that a reinvestigation of many known related reactions using minor variations of reported conditions may lead to entirely different products being obtained. An example from the recent literature which illustrates this point is the effect of temperature on the reaction between $Fe(CO)_5$ and $Mn(CO)_5^-$ in diglyme. At *ca.* 120° $MnFe_2(CO)_{12}^-$ is formed but at *ca.* 160° after slightly shorter reaction periods none of this complex is present and, instead, $Fe_6(CO)_{16}C^{2-}$ may be isolated in good yield.[29]

It is clear that the relative stability of the various types of cluster isolated in this study varies according to the particular metals involved and, for example, $HReOs_3(CO)_{15}$ is clearly much more 'stable' than $HMnOs_3(CO)_{15}$ which we were unable to isolate. This relative stability is, however, as likely to be due to kinetic as to thermodynamic factors. If control is indeed kinetic then the only point which can be made is that, since the greatest range of complexes can be obtained when two third-row metals are involved, the activation-energy barriers for consecutive reactions appear to be highest in this case. This may be associated with the greater metal–metal bond strengths [30] when two third-row metals are involved.

The complexity of the reactions described here precludes any detailed mechanistic study. The nature of the products formed do, however, suggest some reaction paths which may be important. Thus the isolation of the three complexes $HReOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and

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$H_3ReOs_3(CO)_{13}$ after acidification of the products from the reaction of $Os_3(CO)_{12}$ and $Re(CO)_5^-$ suggests a possible mechanism for the formation of a tetrahedral cluster complex. This suggestion is based on the previously discussed assumption that anions corresponding to all of the three hydrides exist in the reaction mixture prior to acidification and that these have structures based on the respective metal-atom frameworks shown. If this is so (2a) could be formed by direct combination of an intermediate, perhaps $Os_3(CO)_{11}$, with $Re(CO)_5^-$. The formation of $ReOs_3(CO)_{15}^-$ and $ReOs_3(CO)_{13}^{3-}$ under more vigorous conditions could then be envisaged to occur by successive metal–metal bond formation and corresponding carbonyl loss. The third stage would, of course, require donation of further electrons to the system, presumably by acceptance from $Re(CO)_5^-$.

The conversion of an 'open' cluster to a 'closed' cluster under similar experimental conditions is not completely unknown. Thus the anion $Re_4(CO)_{16}^{2-}$,[18] which is known to possess a structure analogous to (3) is converted, after further reduction with sodium borohydride, into the hydrido-anion $H_6Re_4(CO)_{12}^{2-}$ [5] which has a 'closed' tetrahedral structure analogous to (4).

EXPERIMENTAL

Analyses were carried out by the Microanalytical Department of the University Chemical Laboratory. Mass spectra were recorded on an AEI MS9 mass spectrometer and n.m.r. spectra on a Varian 100 MHz spectrometer. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer to an accuracy of ± 1 cm^{-1} with carbon monoxide as calibrant.

Reactions were carried out in an atmosphere of dry nitrogen and solvents were degassed before use. Silica gel was used for column or thin-layer chromatographic separations with light petroleum (b.p. 40—60°) or mixtures of light petroleum and benzene as eluants.

$Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ were prepared by literature methods.[29]

The yields of new complexes, where given, represent the quantities of analytically pure material which could be isolated. The total amounts present in the various reaction mixtures were probably in many cases very much in excess of these quoted yields.

$Me_4N^+MnOs_2(CO)_{12}^-$.—$Mn_2(CO)_{10}$ (147 mg) was reduced to the anion by sodium amalgam in dry diglyme (5 ml). The pale green solution obtained was added to solid $Os_3(CO)_{12}$ (374 mg) and the mixture was heated under reflux for 5 min. The deep red solution produced was evaporated to dryness by evacuation at 60° and the solid residue was extracted with methanol–water (1 : 1). The filtered solution was then treated with an excess of an aqueous solution of Me_4NCl and the resulting red-brown precipitate was filtered off. On washing the precipitate with two 25 ml portions of diethyl ether, some components, presumably the tetramethylammonium salts of other carbonyl anions, were completely removed. The red ether-insoluble residue was then dissolved in a minimum quantity of acetone, and the filtered solution was treated dropwise with diethyl ether at 20°. The red-black crystals which were deposited were given further recrystallisations from acetone–ether and methanol to give pure $Me_4N^+MnOs_2(CO)_{12}^-$ (30 mg).

$Me_4N^+ReOs_2(CO)_{12}^-$.—A suspension of $Re_2(CO)_{10}$ (650 mg) in dry diglyme (7 ml) was shaken with excess of sodium amalgam to give a deep yellow solution of $NaRe(CO)_5$. This was added to solid $Os_3(CO)_{12}$ (900 mg) and the mixture was heated under reflux for 5 min, after which time a deep red solution was obtained. The solvent was removed at 60° *in vacuo* and some $Re_2(CO)_{10}$ sublimed out of the mixture. The residue was extracted with methanol–water (1 : 1) as before giving a deep red solution and leaving a white solid which was shown to consist mainly of $Re_2(CO)_{10}$ by i.r. spectroscopy. The red solution was treated with excess of Me_4NCl and the red-brown precipitate was filtered off. Washing of the precipitate with two 40 ml portions of diethyl ether caused the complete removal of the tetramethylammonium salts of other carbonyl anions and this solution was evaporated to dryness [see under $HReOs_3(CO)_{16}$]. The solid remaining after removal of the other carbonyl species with ether was dissolved in hot methanol, filtered and then concentrated to small volume. Slow cooling of the solution to $-10°$ then led to the separation of pure $Me_4N^+ReOs_2(CO)_{12}^-$ as small orange crystals (10 mg).

$HMnOs_2(CO)_{12}$.—Pure $Me_4N^+MnOs_2(CO)_{12}^-$ (10 mg) in acetone (1 ml) was added to an excess of dilute aqueous phosphoric acid solution. The yellow precipitate which formed was coagulated by blowing carbon monoxide through the solution and then filtered off and washed with water. The dried solid was dissolved in a large volume of petroleum (b.p. 40—60°) and the solution was filtered and reduced to small volume. Slow cooling to $-10°$ gave the pure product as orange-red crystals (5 mg).

$HReOs_2(CO)_{12}$.—Pure $Me_4N^+ ReOs_2(CO)_{12}^-$ (4 mg) was dissolved in acetone (1 ml) and the solution was added to an excess of dilute aqueous phosphoric acid. The pale yellow precipitate obtained was coagulated by passing carbon monoxide through the solution and it was then filtered off and washed with water. The amount of the compound available was insufficient for analysis but it was identified as $HReOs_2(CO)_{12}$ by mass spectroscopy (1 mg).

$HMnOs_3(CO)_{16}$.—A solution of $NaMn(CO)_5$ was prepared by reducing $Mn_2(CO)_{10}$ (110 mg) in dry diglyme (20 ml) with sodium amalgam. This solution was added to solid $Os_3(CO)_{12}$ (400 mg) and the mixture was refluxed for 3 min, when all the osmium carbonyl had dissolved to give a red solution. After removal of solvent by evacuation, the black residue was extracted with methanol–water (1 : 1). The filtered solution was acidified with 85% H_3PO_4 and a dark-coloured oil was produced. Extraction of this with a large volume of petroleum (b.p. 30—40°) gave an intense yellow solution from which, on concentration, a yellow solid was deposited.

Recrystallisation of this from a small volume of dichloromethane gave pure $HMnOs_3(CO)_{16}$ as yellow-bronze crystals (120 mg).

$HReOs_3(CO)_{16}$.—The ether-soluble extract of the tetramethylammonium salts obtained in the preparation of $Me_4N^+ReOs_2(CO)_{12}^-$ was dissolved in acetone–water and acidified with phosphoric acid. The yellow precipitate produced was filtered and washed with water, then dried by evacuation. A broad separation of the constituents was achieved by extraction with dichloromethane, in which some of the complexes were soluble. The filtered solution was concentrated and then portions of it were evaporated on to t.l.c. plates. Subsequent elution with petroleum indicated the presence of the following bands: purple $H_2Os_3(CO)_{10}$, unidentified yellow and orange bands in trace amounts, and then an intense yellow band. The mass spectrum of the material obtained from this band showed that it contained $HReOs_3(CO)_{16}$, although not in a pure condition.

The dichloromethane-insoluble residue mentioned above was shown to consist mainly of $H_3ReOs_3(CO)_{13}$ by mass spectroscopy.

$HReOs_3(CO)_{15}$.—A suspension of $Os_3(CO)_{12}$ (151 mg) in THF (50 ml) was treated with a solution of $NaRe(CO)_5$ [prepared by reducing 300 mg $Re_2(CO)_{10}$ in THF (7 ml) with sodium amalgam]. The mixture was refluxed for 10 min after which time the $Os_3(CO)_{12}$ had disappeared and a deep red solution had formed. Solvent was removed *in vacuo* and the residue was extracted with water. The filtered aqueous solution was acidified with H_3PO_4 giving an orange precipitate. A preliminary extraction of the solid with petroleum then removed other neutral carbonyl species [including $HRe_3(CO)_{14}$ which was identified by i.r. spectroscopy]. The orange residue was dissolved in hot acetone, filtered and then concentrated to small volume. Small orange crystals of pure $HReOs_3(CO)_{15}$ were deposited after gradual cooling of the solution to 20°.

$H_3MnOs_3(CO)_{13}$.—$Mn_2(CO)_{10}$ (186 mg) was converted to the anion by sodium amalgam reduction in THF (8 ml). The solution was added to one of $Os_3(CO)_{12}$ (600 mg) in THF (150 ml) and the mixture was refluxed for 65 h, then pumped dry. The solid residue was extracted with water and the filtered aqueous solution was acidified with phosphoric acid. The deep yellow precipitate which formed was filtered off and washed with methanol (200 ml). The remaining solid was taken up in a large volume of hot acetone and the filtered solution was concentrated by boiling to small volume. On cooling the solution gradually to room temperature, small scarlet crystals of the pure product were obtained (20 mg).

$H_3ReOs_3(CO)_{13}$.—$Re_2(CO)_{10}$ (293 mg) was reduced to the anion in THF (8 ml) using sodium amalgam. The solution was added to solid $Os_3(CO)_{12}$ (271 mg) and the mixture was refluxed for 20 h. The dark brown solution was pumped dry and the residue extracted into water, filtered and acidified with H_3PO_4. The yellow-brown precipitate thus obtained was washed with small portions of acetone until the filtrates were almost colourless and the solid remaining was taken up in hot acetone. This solution was then filtered and concentrated to small volume when orange-red crystals of the pure product were obtained (50 mg).

$Et_4N^+HRu_3(CO)_{11}^-$.—A solution of $NaMn(CO)_5$ was prepared by reducing $Mn_2(CO)_{10}$ (389 mg) in THF (5 ml) with an excess of sodium amalgam. The solution was added to one of $Ru_3(CO)_{12}$ (644 mg) in THF (100 ml) and the mixture was allowed to stand at 20° for 28 h, then pumped dry at ambient temperature. The black crystalline residue was extracted into water and the filtered aqueous solution was treated with an excess of Et_4NCl, giving a deep red precipitate. This was dried by evacuation and then dissolved in a small quantity of dichloromethane. Petroleum (b.p. 30—40°) was added dropwise to the red solution until precipitation just occurred and then centrifuging and slow cooling to $-15°$ caused the deposition of small red-black crystals of the product. Although this preparation was attempted many times, the product, if isolated at all, did not analyse consistently well, despite the fact that its i.r. spectra in the carbonyl region were entirely reproducible. It is probable that the solution from which the final product came contained many other metal carbonyl species.

$H_2Ru_6(CO)_{18}$.—$Mn_2(CO)_{10}$ (254 mg) was reduced to the anion in THF (8 ml) and the solution was added to one of $Ru_3(CO)_{12}$ (831 mg) in THF (50 ml). After 4 h reflux, the initial dark red colour of the reaction mixture had changed to dark brown and then heating was discontinued and solvent removed. The red-brown solution obtained on extraction of the residue into water was filtered and then acidified with H_3PO_4, giving a deep brown precipitate. This was filtered off, washed, and then extracted with petroleum until the initially red washings had become colourless. The trace quantity of solid remaining was dissolved in dichloromethane, filtered and concentrated when purple-black crystals of the product were obtained. Recrystallisation from CH_2Cl_2 gave pure $H_2Ru_6(CO)_{18}$ (30 mg).

The other petrol-soluble compounds in the acidfied product were found to be $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ by i.r. spectroscopy.

$Me_4N^+ReRu_3(CO)_{16}^-$.—A solution of $NaRe(CO)_5$ was prepared by reducing $Re_2(CO)_{10}$ (136 mg) in THF (8 ml) with sodium amalgam. The solution was added to solid $Ru_3(CO)_{12}$ (426 mg) and the mixture was shaken vigorously for 20 min when all the $Ru_3(CO)_{12}$ had dissolved. After pumping dry, the residue was extracted with water and the filtered aqueous solution was treated with an excess of Me_4NCl giving a red-brown precipitate. Extraction of the solid with dichloromethane gave a deep red-brown solution and left an orange solid which is only sparingly soluble in this solvent. The solid was filtered off, dissolved in a minimum quantity of acetone, and water added until precipitation just occurred. The filtered solution was then left for some of the acetone to evaporate and orange-red needle crystals of the product were obtained. Pure Me_4N^+-$ReRu_3(CO)_{16}^-$ resulted when the crude product was recrystallised from acetone–diethyl ether (50 mg).

$H_2Re_2Ru_2(CO)_{16}$ *and* $H_2Re_2Ru(CO)_{12}$.—$Me_4N^+ReRu_3$-$(CO)_{16}$ (30 mg) in acetone (1 ml) was acidified with H_3PO_4 and a yellow precipitate was formed. This was filtered off, washed, dried and then separated into components by t.l.c., with petroleum as eluant. Bands were observed as follows: $H_4Ru_4(CO)_{12}$ (pale yellow), β-$H_2Ru_4(CO)_{13}$ (red), $H_2Re_2Ru_2(CO)_{16}$ (intense yellow, identified by mass spectroscopy), an orange band, and finally a trace quantity of a green band. The R_f values of these bands were so similar that no further progress could be made.

Acidification of the anion mixture after refluxing Ru_3-$(CO)_{12}$ with $Re(CO)_5^-$ gave essentially the same mixture of hydrides but the relative amounts of the known tetranuclear ruthenium hydrides were increased.

Heating of $H_2Re_2Ru_2(CO)_{16}$ in petroleum gave a trinuclear hydride $H_2Re_2Ru(CO)_{12}$ which was isolated in trace quantities as pale yellow needle crystals. The complex was identified by mass spectroscopy.

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