New Polynuclear Carbonyl Hydride Complexes Containing Osmium with Manganese or Rhenium

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Summary The preparation of some new polynuclear carbonyl hydride complexes containing osmium with manganese or rhenium is reported.

RECENT interest in the synthesis and mechanism of formation[2,3] of polynuclear carbonyl complexes prompts us to report the synthesis of four new types of "mixed metal" polynuclear carbonyl hydrides, $HMOs_2(CO)_{12}$, $HMOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and $H_3MOs_3(CO)_{13}$ (M = Mn or Re).

These complexes were prepared by acidification of the products of the reaction of $Os_3(CO)_{12}$ with $M(CO)_5^-$ under various conditions and have been identified by m.s. and chemical analysis. Although the reaction solutions prior to acidification contained complex mixtures of polynuclear carbonyl anions, the only species which we could isolate (as their Me_4N^+ salts) were the anions $MOs_2(CO)_{12}^-$. These latter compounds, which were identified by chemical analysis, gave the neutral hydrides $HMOs_2(CO)_{12}$ on acidification.

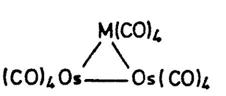
Whilst unequivocal determination of the structures of all the carbonyl hydride complexes awaits the results of *X*-ray analyses,[4] the noble-gas rule allows us to suggest possible structures for the four compounds (Figure). We cannot make a choice between structures (**2a**) and (**2b**) for $HMOs_3(CO)_{16}$. Molecules possessing the types of metal atom framework shown in (**3**) and (**4**) are not completely unknown in polynuclear carbonyl chemistry. Thus the anion $Re_4(CO)_{16}^{2-}$, for which a similar double-triangular structure to that shown in (**3**) has been found by *X*-ray analysis,[5] has the same overall number of electrons in the valence shells of the metal atoms as does $HReOs_3(CO)_{15}$. Also, among the examples of polynuclear carbonyls possessing the $M_4(CO)_{13}$ unit, are $Fe_4(CO)_{13}^{2-}$,[6] the structure of which is analogous to (**4**) and $H_2FeOs_3(CO)_{13}$[7] which is isoelectronic with $H_3MnOs_3(CO)_{13}$. The positions of the hydrogen atoms in all the new clusters are uncertain.

Progressively more severe conditions are required to produce the reaction mixtures from which $HReOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and $H_3ReOs_3(CO)_{13}$ may best be obtained after acidification, and, if it is assumed that anions corresponding to these three types of hydride complex exist in the reaction mixture prior to acidification [as shown for $HMOs_2(CO)_{12}$], then the isolation of the hydrides suggests a possible mechanism for the reaction. Thus the "closed" tetrahedral anions $MOs_3(CO)_{13}^{3-}$ could be formed *via* the intermediate species $MOs_3(CO)_{16}^-$ and $MOs_3(CO)_{15}^-$ with successive metal–metal bond formation and consequent loss of carbonyl ligands, although the formation of $MOs_3(CO)_{13}^{3-}$ from $MOs_3(CO)_{15}^-$ must also involve an additional reduction step.

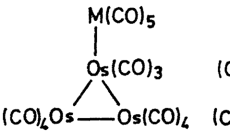
New complexes and their i.r. spectra in the carbonyl region

Compound	Phase	ν(C–O) (cm⁻¹)
$Me_4N^+MnOs_2(CO)_{12}^-$	THF	2080w, 2018s, 1981vs, 1943m, 1914m, 1897sh, and 1887m
$HMnOs_2(CO)_{12}$	n-Hexane	2135w, 2081s, 2051vs, 2038vs, 2016m, 2001m, 1993m, 1975m, 1957m and 1951m
$HMnOs_3(CO)_{16}$	n-Hexane	2136w, 2093m, 2069s, 2056s, 2031m, 2022m, 2015m, 2006m, 1996m, 1988mbr, 1977m, and 1970w
$H_3MnOs_3(CO)_{13}$	KBr	2133m, 2086s, 2055s, 2043sh, 2020sh, 2008s, 1990sh, 1950m, and 1830m
$Me_4N^+ReOs_2(CO)_{12}^-$	THF	2085w, 2021s, 2009s, 1990s, 1954m, 1941sh, 1925sh, and 1887m
$HReOs_2(CO)_{12}$	n-Hexane	2136w, 2086s, 2058sh, 2053vs, 2029m, 2014m, 2000s, 1992m, 1982m, 1967m, and 1953m
$HReOs_3(CO)_{16}$[a]		
$HReOs_3(CO)_{15}$	KBr	2131w, 2091s, 2070sh, 2057sh, 2051s, 2018s, 1991sh, 1971sh, 1950m, and 1933m
$H_3ReOs_3(CO)_{13}$	KBr	2138s, 2090s, 2063sh, 2030br, 1983s, 1968sh, and 1900m

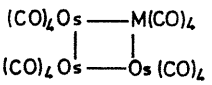
[a] Not obtained pure. Characterised by its mass spectrum in which the molecular ion is observed.



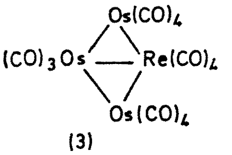
(1)



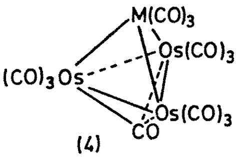
2a



2b



(3)



(4)

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