

Polynuclear Metal Carbonyl Hydrides of Manganese, Ruthenium, and Osmium

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THE detection of hydrogen in some polynuclear carbonyl hydrides has proved difficult. This difficulty has been clearly revealed for $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and related systems.¹ Wilkinson² has used mass spectral data as a method of detecting the presence of hydrogen in the complex $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ but was able only to detect two of the four hydrogens in the complex, presumably because of the instability of the parent ion. We wish to emphasise the value of this method for the detection or confirmation of the presence of hydrogen in polynuclear carbonyl hydrides.

The mass spectra of the known compounds $\text{Mn}(\text{CO})_5\text{H}$, $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ and $\text{H}_3\text{Re}_3(\text{CO})_{12}$, and the new compounds $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ have been examined and fragmentation patterns

established. In all cases the fragmentation pattern involves the loss of both CO groups and H atoms.

With $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ the parent ions are observed. However, it is important to note that this is not always the case and with, for example, $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ the presence of three hydrogen atoms in the molecule has been established only by detailed examination of the fragmentation pattern when ions of the type $\text{H}_3\text{Mn}_3(\text{CO})_n^+$ ($n < 12$) were observed.

During this work a convenient synthesis³ of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ was developed. Reaction of potassium hydroxide with manganese decacarbonyl followed by acidification of the resultant product yields the manganese carbonyl hydride $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ in good yields. Similar treatment

TABLE

*Infrared spectra of hydrido- and deuterio-compounds**

$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	$\text{D}_2\text{Ru}_4(\text{CO})_{13}$	$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	$\text{D}_4\text{Ru}_4(\text{CO})_{12}$	$\text{H}_3\text{Mn}_3(\text{CO})_{12}$	$\text{D}_3\text{Mn}_3(\text{CO})_{12}$
2083(s)	2079(s)	2080(s)	2076(s)	2080(m)	2075(m)
2068(s)	2063(s)	2068(s)	2064(s)	2034(s)	2034(s)
2056(s)	2056(s)	2056(s)	2056(s)	2008(s)	2008(s)
2033(m)	2033(m)	2034(m)	2033(m)	1986(s)	1986(s)
2026(s)	2019(s)	2027(s)	2019(s)		
2008(w)	2003(w)	2008(w)	2004(w)		
1880(w)	1880(w)				

* All spectra in cyclohexane.

of triruthenium dodecacarbonyl yields two *new* hydrido-carbonyls, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$. The former complex has a similar formulation to the hydride recently reported by Wilkinson *et al.*,³ but the n.m.r. spectrum (resonance at τ 18.6) establishes this as a different complex. The complex $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ is similar to the complex $\text{H}_2\text{Fe}_4(\text{CO})_{13}$ first reported by Hieber *et al.*⁴ With both compounds the presence of hydrogen in the molecule was initially established from mass spectral data.

Reaction of sodium borohydride with triosmium dodecacarbonyl yields two complexes, the mass spectra of which indicate the presence of at least

five hydrogen atoms per $\text{Os}_4(\text{CO})_{12}$ unit in one case and at least four hydrogen atoms in the other.

The infrared spectra of the complexes $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ in the region 1800—2100 cm^{-1} is complex (see the Table). Deuteration of these complexes and the manganese complex leads to only minor changes in the infrared, consistent with the presence of a metal-hydrogen-metal bridge of the type first postulated by Wilkinson *et al.*⁵

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¹ W. Fellman, D. K. Huggins, H. D. Kaesz, and J. M. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 4841.² J. W. S. Jamieson, J. V. Kingston, and G. Wilkinson, *Chem. Comm.*, 1966, 569.³ W. Fellman, D. K. Huggins, and H. D. Kaesz, Abstracts of Papers Presented to the VIIIth International Conference on Coordination Chemistry, September 1964.⁴ W. Hieber, J. Sedlmeir, and R. Werner, *Chem. Ber.*, 1957, **90**, 286.⁵ A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.