New Rhenium–Iron Polynuclear Carbonyls

By G. O. EVANS, J. P. HARGADEN, and R. K. SHELINE
(*Department of Chemistry, Florida State University, Tallahassee, Florida* 32306)

CURRENT intensive interest in theoretical and structural aspects of metal–metal bonded compounds prompts us to report the synthesis of two new trinuclear metal carbonyls.

The irradiation (G. E. AH-6 lamp) of an n-hexane solution 0·005M in both $Fe(CO)_5$ and $Re_2(CO)_{10}$ for 1 hr. was found to yield $Re_2Fe(CO)_{14}$ (I) and the anion $[ReFe_2(CO)_{12}]^-$ (II). (I), a stable yellow solid (m.p. 163° decomp.), was isolated by means of silica gel chromatography followed by fractional sublimation of $Re_2(CO)_{10}$ from the product. The molecular formula was determined by a complete elemental analysis and molecular-weight determination. Compound (II) was then produced in higher yields by the irradiation of a diethyl ether solution 0·007M in both $Re_2(CO)_{10}$ and $Fe(CO)_5$ and precipitated as its tetraethylammonium salt. It was purified by recrystallization from ethanol and characterized by a complete elemental analysis.

Preliminary structural studies have been limited to the infrared spectra in the carbonyl stretching region. The simplicity of the spectrum of (I) in the terminal CO region (2097m, 2034m 2022s), 1982m cm.$^{-1}$; n-hexane solution) and the absence of bridging CO stretching bands strongly suggests the very symmetrical linear structure $(CO)_5Re{\cdot}Fe(CO)_4{\cdot}Re(CO)_5$ (D_{4h} point group) for which four infrared-active CO vibrations would be predicted. We have previously reported[1] an analogous compound, $Mn_2Fe(CO)_{14}$ (2067m, 2019s, 1987m cm.$^{-1}$; n-hexane solution). The CO infrared spectrum of the tetraethylammonium salt of (II) in tetrahydrofuran (2075w, 2006m, 1991s, 1946m, 1903w, 1814w, 1785w cm.$^{-1}$) is extremely similar to that reported earlier for $[NEt_4]^+[MnFe_2(CO)_{12}]^-$ (2063, 1999, 1990, 1972, 1944, 1903, 1827, 1785 cm.$^{-1}$; tetrahydrofuran solution) prepared by other methods,[2] and strongly suggests an identical C_{2v} molecular symmetry. The structure may be thought of as being derived from that of $Fe_3(CO)_{12}$,[3] by replacing the $Fe(CO)_4$ group by $Re(CO)_4^-$.

Detailed structural investigations of (I) and (II) are now being carried out to establish their exact stereochemical configurations.

(*Received, November 14th,* 1966; *Com.* 886.)

---

[1] E. H. Schubert and R. K. Sheline, *Z. Naturforsch.*, 1965, **20b**, 1306.
[2] U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.
[3] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821.