# Ruthenium–Iron Carbonyls

By D. B. W. YAWNEY and F. G. A. STONE*
(*Department of Inorganic Chemistry, The University, Bristol* 8)

THE dehalogenating and carbonylating properties of pentacarbonyl iron are well known and exemplified by its reactions with tungsten hexachloride affording $W(CO)_6$,[1] and with stannous chloride giving $Sn[Fe(CO)_4]_4$.[2] A possible new synthesis of polynuclear carbonylmetal complexes containing atoms of different transition metals could thus involve reaction between a reactive metal carbonyl, such as $Fe(CO)_5$, and a polynuclear carbonyl halide of another element.

A mixture of pentacarbonyliron and $[Ru(CO)_3Cl_2]_2$[3] was heated at 90—100° under nitrogen for 30 hr. Chromatography afforded five products shown by elemental analysis, and i.r. and mass spectroscopy, to be a new polynuclear hydride $H_2FeRu_3(CO)_{13}$, and the new carbonyls $Fe_2Ru(CO)_{12}$ and $Ru_2Fe(CO)_{12}$, in addition to the well known carbonyls $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$. Formation of orange, crystalline, $H_2FeRu_3(CO)_{13}$ [decomp. above 112°; $^1$H n.m.r., $\tau$ 28·7 s; $\nu_{CO}$ (cyclohexane), 2084 vs, 2072·5 vs, 2063 w, 2041 vs, 2031 m, 2021 w, 1991 m, 1883·8 w and 1845·3 m cm.$^{-1}$], could be due to moisture in the iron carbonyl. The mass spectrum of $H_2FeRu_3(CO)_{13}$ shows a parent ion *m/e* 727, followed by peaks corresponding to the loss of seven CO groups. Only after $[P - 7CO]^+$ are there peaks due to loss of H and CO. The compound $H_2Fe_4(CO)_{13}$ has been known for some time[4] and the structure of the dianion $Fe_4(CO)_{13}{}^{2-}$ established by an *X*-ray crystallographic study.[5] Moreover, $H_2Ru_4(CO)_{13}$ is one of several recently reported polynuclear ruthenium hydrides.[6] Mixed hydrides such as $H_2FeRu_3(CO)_{13}$ are as yet relatively rare,[7] and its isolation suggests the existence of $H_2Fe_2Ru_2(CO)_{13}$ and $H_2Fe_3Ru(CO)_{13}$.

The mass spectrum of purple crystalline $RuFe_2(CO)_{12}$ (decomp. above 125°) shows a parent ion at *m/e* 550 followed by loss of twelve carbonyl groups. The i.r.spectrum in the carbonyl stretching region (cyclohexane) shows bands at 2056·5 s, 2044 vs, 2023 w sh, 2003·5 m br, 1859 vw and 1834 vw cm$^{-1}$. The presence of the bands at 1859 and 1834 cm.$^{-1}$ suggests that the molecular structure of $RuFe_2(CO)_{12}$ is similar to that of $Fe_3(CO)_{12}$,[8] with an $Ru(CO)_4$ group replacing the $Fe(CO)_4$ group. The structure of brown $Ru_2Fe(CO)_{12}$ [$\nu_{CO}$ (cyclohexane), 2067 m, 2042 vs, 2033·5 s, 2011·5 m and 1988·5 cm$^{-1}$; parent ion in mass spectrum at 595] is probably similar to that of $Ru_3(CO)_{12}$,[9] with the metal–metal bonds in the $Ru_2Fe$ cluster unsupported by bridging carbonyl groups. Only two other mixed metal-carbonyl complexes with structures probably involving a triangular metal cluster $M_2M'$ have been described, $[Fe_2M'(CO)_{12}]^-$ ($M' = Mn$ [10] or Re[11]).

A direct reaction between a 2:1 molar ratio of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ in dry petroleum (80—100°) also gives some $H_2FeRu_3(CO)_{13}$ and $Ru_2Fe(CO)_{12}$.

(*Received, April 1st,* 1968; *Com.* 405.)

---

[1] A. N. Nesmeyanov, K. N. Anisimov, E. P. Mikheev, V. L. Volkov, and Z. P. Valueva, *Zhur. neorg. Khim*, 1959, **4**, 249,503.

[2] J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1967, 264.

[3] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. (A)*, 1967, 1238.

[4] W. Hieber, J. Sedlmeir, and R. Werner, *Chem. Ber.*, 1957, **90**, 286.

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

[6] B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Comm.*, 1966, 851.

[7] M. J. Mays and R. N. F. Simpson, *Chem. Comm.*, 1967, 1024.

[8] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821.

[9] E. R. Corey and L. F. Dahl, *J. Amer. Chem. Soc.*, 1961, **83**, 2203; *Inorg. Chem.*, 1962, **1**, 521; E. R. Corey, E. R. de Gil, and L. F. Dahl, to be published.

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

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