# New Compounds of Rhenium: Preparation and Crystal Structures of $Re(CO)_5F{\cdot}ReF_5$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$

By Donald M. Bruce, John H. Holloway, and David R. Russell*
(*Department of Chemistry, The University. Leicester* LE1 7RH)

*Summary* $Re(CO)_5F.ReF_5$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$ have been obtained from the reaction of $ReF_6$ with $Re_2(CO)_{10}$ in anhydrous hydrogen fluoride; the structures of the compounds have been determined by *X*-ray diffraction.

As part of a systematic effort to prepare metal carbonyl fluorides,[1,2] we have studied the reaction of rhenium hexafluoride with rhenium carbonyl in anhydrous hydrogen fluoride.

In a typical reaction 1·08 mmol of $ReF_6$ was condensed stepwise on to 0·75 mmol of $Re_2(CO)_{10}$ in anhydrous hydrogen fluoride to give a green solution from which approximately equal amounts of two solids separated as orange prisms (**1**), and green platelets (**2**), both in high yield. No detectable carbon monoxide evolution occurred and no evidence for $Re_2(CO)_{10}$, $ReF_6$, or $ReF_5$ was obtained.

Compounds (**1**) and (**2**) are highly sensitive to moisture, blackening rapidly on exposure to the atmosphere. Complex, but reproducible i.r. absorptions can be obtained from Nujol mulls in the 2200—1900 $cm^{-1}$ and the 750—500 $cm^{-1}$ regions. Suitable crystals were mounted in a dry box for *X*-ray studies. *Crystal data:* (**1**), $C_5F_6O_5Re_2$, *M* = 626·4.

orange orthorhombic crystals, $a = 22{\cdot}34(5)$, $b = 15{\cdot}51(3)$, $c = 13{\cdot}67(3)$ Å, $U = 4737$ Å$^3$, $Z = 16$, $D_c = 3{\cdot}51$ g cm$^{-3}$, space group *Pbca*. (**2**) $C_6F_{11}O_6Re_3$, $M = 935{\cdot}6$, green *orthorhombic* crystals, $a = 15{\cdot}30(3)$, $b = 13{\cdot}64(3)$, $c = 8{\cdot}16(2)$ Å, $U = 1703$ Å$^3$, $Z = 4$, $D_c = 3{\cdot}65$ g cm$^{-3}$, space group chosen *Pnma*. The data, collected by a Stoe Weissenberg diffractometer using Mo-$K_\alpha$ irradiation (graphite monochromator, $\lambda = 0{\cdot}7107$ Å), and corrected for absorption, consist of 2047 reflections for (**1**) and 763 for (**2**). At the present stage of refinement $R$-values are 0·061 and 0·064, respectively, with anisotropic Re atoms only.

The crystal structure of the orange compound (**1**) contains two almost identical $Re(CO)_5F{\cdot}ReF_5$ molecules in the asymmetric unit. Both rhenium atoms are in approximate octahedral co-ordination and are linked by a bent fluorine bridge. Some details of the molecular geometry are given in the Figure. The chemical interpretation of the molecular structure is not immediately obvious. We prefer the covalent formulation $Re(CO)_5F{\cdot}ReF_5$ to alternatives such as $Re(CO)_5{\cdot}ReF_6$ which implies an unlikely acid-base behaviour for the two components of the adduct, or the ionic formulation $[Re(CO)_5]^+[ReF_6]^-$. Certainly the Re–F(bridging) distances lend little support to any significant contribution from the ionic alternative when allowance is made for the different covalent radii of $Re^I$ and $Re^V$. A covalent formulation is also favoured for the related adduct $[Re(CO)_5Cl]_2SbCl_5$.[3] Other distances are directly comparable with those of the only known metal carbonyl fluoride structure $[Ru(CO)_3F_2]_4$.[2]

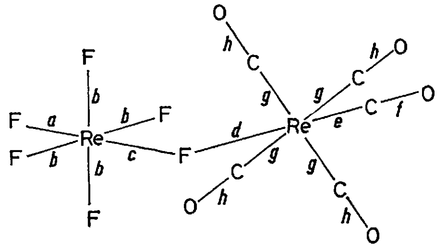

FIGURE. *Molecular geometry of* $Re(CO)_5F{\cdot}ReF_5$. *Average bond lengths* (Å) *with s.d.s, taken from the two non-equivalent molecules:* a = 1·91(3), b = 1·83(3), c = 1·97(2), d = 2·17(4), e = 1·89(3), f = 1·19(4); g = 1·99(4), h = 1·13(3) Å. *The e.s.d.'s of individual bonds are* Re–F 0·03, Re–C 0·05, C–O 0·07. *Average* Re–F–Re *angle* 141°(1).

It is remarkable that an adduct can form between components containing metal atoms in two so dissimilar formal oxidation states. Presumably this is possible as a consequence of the differing stabilising influences of the two ligands, carbon monoxide and fluoride ion, which tend to equalise the net charge on the separate metal atoms by redistribution of $\pi$-electron density.

The green compound (**2**) contains discrete $[Re(CO)_6]^+$ and $[Re_2F_{11}]^-$ ions. Four carbon monoxide groups of the $[Re(CO)_6]^+$ cation lie on a crystallographic mirror plane and the $[Re_2F_{11}]^-$ anion is required to be centrosymmetric, consequently the single fluorine bridge is linear and the two linked $ReF_6$ octahedra are eclipsed. Average bond lengths are, Re–C 2·01(4), C–O 1·13(3), Re–F(terminal) 1·84(2), Re–F(bridge) 2·01(1) Å. In this compound there is no doubt of the ionic formulation. There are no close contacts between fluorine atoms and the rhenium cation (closest contacts of F to the atoms of the cation are, to Re = 4·13 Å, to O = 2·85 Å, to C = 3·19 Å). The $Re(CO)_6^+$ cation is well known, the hexafluoroarsenate being the closest related analogue.[4] The $[Re_2F_{11}]^-$ anion is **a** further example of the series $[M_2F_{11}]^-$ established for a variety of metals.[5] What is again remarkable is the mutual coexistance of $Re^I$ and $Re^V$ in the same lattice.

In a recent study of the reaction of $ReF_6$ with $Re_2(CO)_{10}$ the products were reported[6] to be a dark brown solid, formulated as $Re(CO)_3F_3$, a green solution assumed from its colour to contain $ReF_5$, and carbon monoxide. Our results provide no evidence for any of these compounds but the i.r. and $X$-ray powder data reported for $Re(CO)_3F_3$ closely resemble those we have obtained for $[Re(CO)_6]^+[Re_2F_{11}]^-$.

We thank the S.R.C. and the Royal Society for financial support.

(*Received*, 19*th March* 1973; *Com.* 372.)

---

[1] R. D. W. Kemmitt, R. D. Peacock, and I. L. Wilson, *Chem. Comm.*, 1968, 772.

[2] C. J. Marshall, R. D. Peacock, D. R. Russell, and I. L. Wilson, *Chem. Comm.*, 1970, 1643.

[3] R. B. King, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2119.

[4] E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

[5] See for example, V. M. McCrae, R. D. Peacock, and D. R. Russell, *Chem. Comm.*, 1967, 62; J. H. Holloway and J. G. Knowles, *J. Chem. Soc.* (*A*), 1969, 756; R. D. Peacock, *Adv. Fluorine Chem.*, 1973, **7**, 113.

[6] T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 1972, **11**, 2563.