

Preliminary communication

BIMETALLIC IRON–RHODIUM CARBONYL CLUSTERS: SYNTHESIS AND X-RAY STRUCTURE OF THE NOVEL $[\text{Fe}_3\text{Rh}_3(\text{CO})_{17}]^{3-}$ TRI-ANION

ALESSANDRO CERIOTTI, ROBERTO DELLA PERGOLA, GIULIANO LONGONI*,

Dipartimento di Chimica Inorganica e Metallorganica e Centro del CNR, via Venezian 21, 20133 Milano (Italy)

BRIAN T. HEATON,

Department of Inorganic, Physical and Industrial Chemistry, Liverpool L69 3BX (Great Britain)

FRANCESCO DEMARTIN and MARIO MANASSERO*

Istituto di Chimica Strutturistica Inorganica, via Venezian 21, 20133 Milano (Italy)

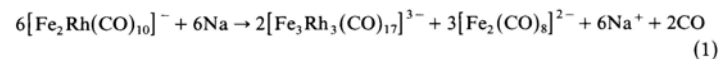
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Summary

The synthesis and the structure of the novel tri-anion, $[\text{Fe}_3\text{Rh}_3(\text{CO})_{17}]^{3-}$, is reported: the metal framework of this 88 valence electron bimetallic cluster is unusual, and consists of an Fe_2Rh_3 trigonal bipyramid with iron and rhodium atoms in apical sites and a dangling Fe atom attached to the apical Rh.

We have previously reported a series of bimetallic iron–rhodium anionic carbonyl clusters [1,2]. Two of them, namely $[\text{FeRh}_5(\text{CO})_{16}]^-$ and $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$, have structures identical to that of $\text{Rh}_6(\text{CO})_{16}$ [3], and thus form members of a series with the general formula $[\text{Fe}_x\text{Rh}_{6-x}(\text{CO})_{12}(\mu_3\text{-CO})_4]^{x-}$ ($x = 0, 1, 2$). Within this series the increase in negative charge with increasing iron content leads to a decreased stability, and it was therefore of interest to ascertain the maximum value of x and examine the structure of the resulting cluster.

As a possible synthetic route to $[\text{Fe}_x\text{Rh}_{6-x}(\text{CO})_{16}]^{x-}$ with $x > 2$, we initially investigated the condensation of $[\text{Fe}_2\text{Rh}(\text{CO})_{10}]^-$ [1,2] with either $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ or $[\text{Fe}_2(\text{CO})_8]^{2-}$; analytical and spectroscopic data suggested that one of the products of these reactions could belong to the above series with $x = 3$. However, X-ray structural analysis of the Fe_3Rh_3 -tri-anion shows it to have an additional carbonyl group, i.e. to be $[\text{Fe}_3\text{Rh}_3(\text{CO})_{10}(\mu_2\text{-CO})_7]^{3-}$ (1), and to also adopt an unusual metal arrangement. 1 can be more selectively obtained by reduction of $[\text{Fe}_2\text{Rh}(\text{CO})_{10}]^-$ with one equivalent of sodium according to eq. 1.



When the above reaction is carried out with $[\text{NEt}_4][\text{Fe}_2\text{Rh}(\text{CO})_{10}]$ in THF a fairly pure solution of $\text{Na}_3[\text{Fe}_3\text{Rh}_3(\text{CO})_{17}]$ is obtained owing to almost quantitative precipitation of $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$. Several tetrasubstituted ammonium (NMe_4^+ , NEt_4^+ , $\text{NMe}_3\text{CH}_2\text{Ph}^+$) and phosphonium (PPh_4^+) salts of **1** have been isolated in the solid state with yields of up to 80% (based on rhodium) by metathesis with the corresponding halides in methanol and/or water. They are soluble in acetone and acetonitrile and sparingly soluble in THF, alcohol, and non-polar solvents. Crystals of $[\text{NMe}_3\text{CH}_2\text{Ph}]_3[\text{Fe}_3\text{Rh}_3(\text{CO})_{17}] \cdot (\text{CH}_3)_2\text{CO}$, suitable for X-ray analysis, were obtained by recrystallization from acetone/isopropanol ($\nu(\text{CO})$ in CH_3CN : 2003w, 1967s, 1929vs, 1898sh, 1820sh, 1794ms and 1766ms cm^{-1}).

Crystal data. $\text{C}_{50}\text{H}_{54}\text{N}_3\text{O}_{18}\text{Fe}_3\text{Rh}_3$: $M = 1461.3$, monoclinic, space group $P2_1/c$ (No. 14): a 11.691(2), b 19.121(4), c 26.212(4) Å; β 98.79(2)°; V 5791(3) Å³, D_c 1.676 g cm^{-3} for $Z = 4$. The structure was solved by standard Patterson and Fourier methods and refined by least squares to the current $R = 0.059$ and $R_w = 0.074$ on the basis of 4672 absorption and decay corrected reflections having $I > 3\sigma(I)$.

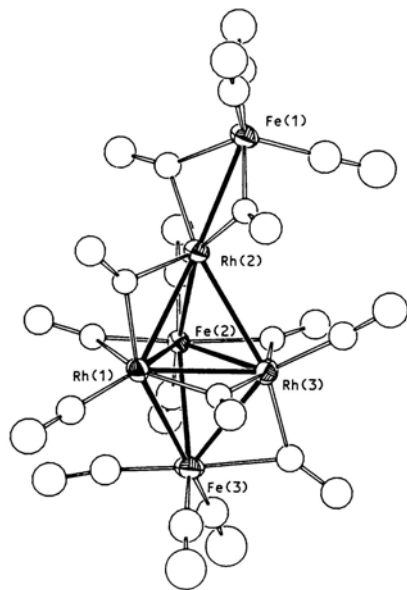


Fig. 1. ORTEP drawing of the $[\text{Fe}_3\text{Rh}_3(\text{CO})_{10}(\mu_2\text{-CO})_7]^{3-}$ tri-anion. Most relevant bond parameters (Å): Rh(1)–Rh(2) 2.771, Rh(1)–Rh(3) 2.682, Rh(2)–Rh(3) 2.869, Rh(1)–Fe(2) 2.714, Rh(1)–Fe(3) 2.802, Rh(2)–Fe(1) 2.575, Rh(2)–Fe(2) 2.819, Rh(3)–Fe(2) 2.673, Rh(3)–Fe(3) 2.716, Fe(2)–Fe(3) 2.770. Average Fe–C, 1.727, Fe–C_b, 1.967, Rh–C, 1.821, Rh–C_b, 1.996, C–O_i, 1.178, C–O_b, 1.190. Typical esd's on single distances are: Rh–Rh 0.001, Rh–Fe 0.002, Fe–Fe 0.002, Rh–C 0.01, Fe–C 0.01 and C–O 0.01.

An ORTEP drawing of **1** is given in Fig. 1 and the most significant molecular parameters are given in the legend. The metal framework consists of a Fe_2Rh_3 trigonal bipyramid with the apical positions essentially occupied by iron and rhodium atoms, vide infra, and the apical rhodium is attached to a unique, dangling, $\text{Fe}(\text{CO})_3$ group via two bridging carbonyls. If each topological M–M interaction in **1** is regarded as a $2c-2e$ bond, the 88 valence electron cluster is electron precise. Only one other example, viz. $\text{RuCo}_3(\text{CO})_{12}[\mu_3\text{-HgCo}(\text{CO})_4]$ [4], of such a metal skeleton has previously been reported, although an isomeric version of such a skeleton was observed recently in $[\text{Os}_6\text{H}_2(\text{CO})_{19}]$ [5].

It is also of interest to speculate as to why the present framework does not undergo conversion into either the octahedral cluster $[\text{Fe}_3\text{Rh}_3(\text{CO})_{12}(\mu_3\text{-CO})_4]^{3-}$, by loss of a carbonyl group, or a raft-like structure, such as those exemplified by $[\text{Fe}_3\text{Pt}_3(\text{CO})_{15}]^{n-}$ ($n = 1, 2$) [6] or $\text{Os}_6(\text{CO})_{21-x}\text{L}_x$ ($\text{L} = \text{P}(\text{OMe})_3, \text{MeCN}$; $x = 1-6$) [7], by gaining a carbonyl group. The most probable reason seems to be the high free negative charge per metal atom, which requires a greater number of the more π -acid-bridging carbonyls [8] than can be stereochemically accommodated on either an octahedral or raft-like metal arrangement. Thus the carbonyl stereochemistry of **1** consists of ten terminal and seven edge-bridging carbonyl groups; of the latter set, that spanning the Fe(2)–Rh(1) edge is grossly unsymmetrical (Fe(2)–C 1.856 and Rh(1)–C 2.300 Å).

As previously found for $[\text{Fe}_x\text{Rh}_{6-x}(\text{CO})_{16}]^{x-}$ ($x = 1, 2$) [1,2], a certain degree of disorder of Fe and Rh metal atoms within the Fe_2Rh_3 trigonal bipyramid is also apparent in solid $[\text{Fe}_3\text{Rh}_3(\text{CO})_{10}(\mu_2\text{-CO})_7]^{3-}$. Only a simplified labelling scheme is shown in Fig. 1 but, in fact, the equatorial Fe(2) site contains a refined rhodium fraction of ca. 0.11 and the corresponding 0.11 fraction of iron is probably randomly distributed over the three rhodium sites. This metal disorder, however, does not affect the carbonyl stereochemistry, and both the carbon and oxygen atoms show normal thermal parameters.

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