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Preliminary communication

Synthesis and crystal structure of $[NEt_4]_2[HFe_3Rh(CO)_{12}]$, the first tetranuclear Fe–Rh hydridocarbonyl cluster

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Abstract

The anion $[HFe_3Rh(CO)_{12}]^{2-}$ was obtained by reaction of $[HFe(CO)_4]^-$ with $Rh_2(CO)_4Cl_2$ in refluxing THF. Its solid state structure consists of a tetrahedron of metal atoms with three edge-bridging and nine terminal carbonyl groups. The hydridic ligand bridges a face containing the rhodium atom. $[NEt_4]_2[HFe_3Rh(CO)_{12}]$ crystallizes in the orthorhombic space group *Pnma*, with a 19.983(5) Å, b 15.168(4) Å, c 11.915(2) Å, V 3611(2) Å^3, $Z = 4$, $R = 0.043$, $R_w = 0.054$ for 1680 unique reflections with $I > 3\sigma(I)$.

We have previously made some Fe–Rh mixed metal carbonyl clusters containing 5 or 6 metal atoms and determined their structures by X-ray diffraction [1,2,3], ^{57}Fe Mössbauer spectroscopy [4], and multinuclear NMR studies [2]. In studying the reactivity of such systems, we never observed evidence for the existence of tetranuclear species, which was surprising, since tetranuclear Fe–Rh clusters [5*], possessing different metal arrangements and with ligands other than CO, (i.e. $(\eta^5\text{-}C_5H_5)_2Fe_2Rh_2(CO)_8$ [6], $(\eta^5\text{-}C_5H_5)Fe_3Rh(CO)_{11}$ [7], $[Fe_2Rh_2(CO)_8(\mu\text{-}PPh_2)]$ [8], $[FeRh_3(CO)_8(\mu\text{-}PPh_2)_3]$ [9] and $[Fe_2Rh_2(CO)_8(\mu\text{-}Ph_2PC(=CH_2)PPh_2)_2]$ [10]),

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* Reference number with asterisk indicates a note in the list of references

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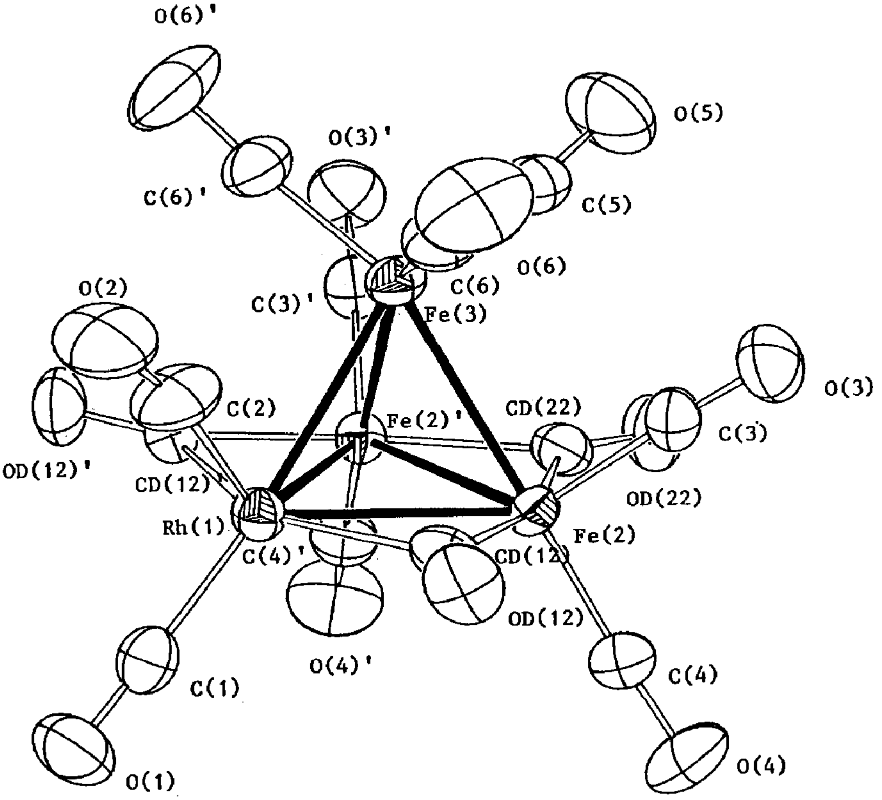

Fig. 1. ORTEP drawing and labelling of atoms for the dianion $[HFe_3Rh(\mu\text{-}CO)_3(CO)_9]^{2-}$. Relevant bond distances are Rh(1)–Fe(2) 2.678(1) Å, Rh(1)–Fe(3) 2.662(1) Å, Fe(2)–Fe(2)′ 2.615(1) Å, Fe(2)–Fe(3) 2.649(1) Å, Rh(1)–$C_{terminal(ave)}$ 1.81 Å, Fe(2)–$C_{terminal(ave)}$ 1.75 Å, Fe(3)–$C_{terminal(ave)}$ 1.76 Å, Rh(1)–CD(12) 2.161(7) Å, Fe(2)–CD(12) 1.925(7) Å, Fe(2)–CD(22) 1.974(8) Å, C–$O_{terminal(avel)}$ 1.15 Å, C–$O_{bridging(ave)}$ 1.18 Å, Typical e.s.d.'s for equivalent interactions are 0.008 for metal–C and 0.010 for C–O.

and also several carbonylic heterometallic compounds with this nuclearity containing both d^8 and d^9 metals, are known (e.g. $[Co_3Fe(CO)_{12}]^-$ [11], $H_2Rh_2Ru_2(CO)_{12}$ [12], $[CoRu_3(CO)_{13}]^-$ [13], $[Ir_3Ru(CO)_{12}]^-$ [14], $H_3Co_3Ru(CO)_{12}$ [15]). Since carbonyl Fe–Rh mixed metal compounds have been shown to be useful precursors of supported bimetallic catalysts which display a very high selectivity for synthesis of ethanol from CO hydrogenation [16] and for hydroformylation of the olefins [17], we reinvestigated the chemistry of these heterometallic derivatives, with the aim of obtaining new compounds with different Fe–Rh ratios.

As previously reported, the reaction of $[HFe(CO)_4]^-$ with $Rh_2(CO)_4Cl_2$ (molar ratio 4/1) in tetrahydrofuran (thf) yields the trinuclear species $[Fe_2Rh(CO)_x]^-$ ($x = 10$ or 11) [1], which is stable at room temperature even in the presence of an excess of $[HFe(CO)_4]^-$. In contrast, refluxing for about 4 h an equimolar mixture of $[HFe(CO)_4]^-$ and $[Fe_2Rh(CO)_x]^-$ in thf gives the new derivative $[HFe_3Rh(CO)_{12}]^{2-}$ in almost quantitative yields. The overall reaction is represented by eq. 1.

$$6[HFe(CO)_4]^- + Rh_2(CO)_4Cl_2 \rightarrow 2[HFe_3Rh(CO)_{12}]^{2-} + 2H_2 + 4CO + 2Cl^- \quad (1)$$

With $(NEt_4)[HFe(CO)_4]$ [18] as starting material the corresponding salt of the mixed metal dianion is obtained. It is insoluble in thf and separates out as a brown oil. It can be recovered by removing the supernatant liquid with a syringe, then washing the residue with methanol and crystallizing it by slow diffusion of 2-propanol into its acetone solutions.

The infrared spectrum of $[HFe_3Rh(CO)_{12}]^{2-}$ (CH_3CN solutions) shows, in the CO stretching region, bands at 2014vw, 1961sh, 1940s, 1895m, 1880sh, 1813w 1737w cm^{-1}. The hydridic nature of this cluster was confirmed by ^1H NMR spectroscopy (δ -18.3 ppm, ^1J(H–Rh) 15.8 Hz, typical values for μ_3-H group in rhodium clusters [19]). The air sensitive dianion is slowly degraded by CO, with formation of $Fe(CO)_5$, $[FeRh_4(CO)_{15}]^{2-}$ and other minor by-products. In the presence of acids it forms the dihydridic derivative, (ν(CO) at 2000vs, 1980vs, 1950m, 1850w, 1810w in thf). The ^1H NMR spectrum of this species at 183 K shows two not well resolved signals at -20.5 and -25 ppm; the signals collapse at 223 K and, at room temperature a sharp doublet (δ -22.7 ppm; J(H–Rh) 7 Hz) is present. All attempts to isolate this new derivative failed since it underwent some decomposition during the work-up.

The $[HFe_3Rh(CO)_{12}]^{2-}$ dianion, of crystallographic $C_s(m)$ symmetry * consists of a tetrahedral metal skeleton bearing nine terminal and three edge bridging carbonyl ligands. Indirect evidence (see later) suggests that the hydride ligand bridges a Fe_2Rh metal face. The crystallographic mirror plane comprises atoms Rh(1), Fe(3), C(1), O(1), C(5), O(5) and relates atoms Fe(2) and Fe(2)′. In terms of the nomenclature usually adopted for other compounds with the same ligand arrangement, such as $Rh_4(CO)_{12}$ [20] and its phosphine substituted derivatives [21], three carbonyls can be seen to be bridging the edges of the "basal" face formed by Rh(1), Fe(2) and Fe(2)′. All these metal atoms carry one "axial" and one "radial" (or "equatorial") terminal CO group. The remaining three carbonyls are bonded to the apical Fe(3) iron atom. Both the metal and ligand arrangements resemble those in the closely related structure of the monoanion $[HFe_3Ni(CO)_{12}]^-$ [22]; in the latter compound the hydride ligand bridges the basal Fe_2Ni triangle, and the radial CO, bonded to the nickel atom, is bent, unsymmetrically bridging the bond between the nickel and the apical iron atoms. In the case of $[HFe_3Rh(CO)_{12}]^{2-}$ the hydrogen atom was not directly located by X-ray analysis, but the ligand stereochemistry strongly suggests that the hydride group bridges the basal metal face, thus the axial CO groups are pushed apart by the presence of the hydride, and are almost colinear with the *trans*-M–M bonds. The average angle Fe(3)–M_{bas}–C_{ax} is in this cluster 175.5°, a value very close to that found for $[HFe_3Ni(CO)_{12}]^-$, and much larger than that observed for $Rh_4(CO)_{12}$ [20] and $Co_4(CO)_{12}$ [23], which show the same ligand arrangement but lack the face bridging ligand. Consistently, space filling models clearly show a large symmetric hole in the carbonyl cover through which the metals of the basal face can be seen, suggesting that the hydride lies on the pseudo three-fold axis of that face. On the other hand, the presence of the hydride does not seem to have a significant lengthening effect on the metal–metal bonds of the basal face, probably because of the concomitant presence on the same edges of bridging

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* *Crystal data.* $C_{28}H_{41}Fe_3N_2O_{12}Rh$, F.W. = 868.09, orthorhombic space group *Pnma* (after refinement), a 19.983(5), b 15.168(4), c 11.915(2) Å, U 3611(2) Å^3, $Z = 4$, D_{calc} 1.596 g/cm^3, μ(Mo-K_α) 16.80 cm^{-1}, $R = 0.043$, $R_w = 0.054$, for 1680 reflections with $I > 3\sigma(I)$.

A table of atomic coordinates and details of bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

carbon monoxide ligands, which usually shorten the metal–metal interactions. As a result the basal bridged Rh(1)–Fe(2) distance (2.678(1) Å) is slightly larger than the unbridged Rh(1)–Fe(3) (2.662(1) Å), but the opposite trend is shown by the Fe–Fe bonds (2.615(1) Å for the basal Fe(2)–Fe(2)′, compared with 2.649(1) Å for the unbridged Fe(2)–Fe(3)).

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