

Bimetallic Iron–Rhodium Anionic Carbonyl Clusters $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11), $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$, $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$, and $[\text{FeRh}_5(\text{CO})_{16}]^-$

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The syntheses and interconversions of mixed iron–rhodium carbonyl clusters are described; a combination of X-ray analysis and multinuclear n.m.r. measurements allowed the structural characterisation of $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$, $[\text{FeRh}_5(\text{CO})_{16}]^-$, and $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$, which can all be obtained from the unstable cluster, $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11).

Bimetallic carbonyl clusters containing iron are now known with many transition metals.¹ However, whereas $[\text{FeCo}_3(\text{CO})_{12}]^-$ was the first anionic mixed metal cluster to be isolated and characterized,² there have been no reports of the corresponding iron–rhodium carbonyl clusters, although some neutral iron–rhodium carbonyl clusters containing other ligands (*e.g.* C_5H_5 , PPh_3) are known.^{1,3,4} We now report preparative routes for $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11), (1), $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$, (2), $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$, (3), and $[\text{FeRh}_5(\text{CO})_{16}]^-$, (4) (see Scheme 1). The nature of the product depends critically upon the ratio Fe:Rh, the choice of solvent, and atmosphere above the reactants; reactions involving addition of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ are best carried out by stepwise additions with concomitant monitoring of the i.r. spectrum.[†]

It has not yet proved possible to obtain (1) as a pure crystalline solid but the stoichiometry of the reactants and spectroscopic measurements are consistent with the formulation $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11). The i.r. spectrum of (1) shows only terminal carbonyl bands; n.m.r. measurements at -85°C show only one rhodium resonance at $+0.1$ p.p.m.[‡] and the

^{13}C n.m.r. spectrum consists of a singlet at 217.4 p.p.m. due to the iron carbonyls and a doublet at 186.1 p.p.m. [$^1J(\text{Rh}-\text{CO})$ 76.3 Hz] due to the rhodium carbonyls. Unfortunately, ^{13}C n.m.r. spectra of iron–rhodium carbonyl clusters do not give reliable integrations for carbonyls on different metals and the exact value of x for (1) remains undetermined.

Complex (2) has been shown by multinuclear n.m.r. measurements to be isostructural with $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ ⁶ but different from both the solution and solid-state structure of $[\text{Rh}_5(\text{CO})_{15}]^-$.⁷ Direct ^{103}Rh n.m.r. spectra of (2) at -70°C show three resonances in the ratio 2:1:1 at $+59.4$, -241.9 , and -1170.9 p.p.m. due to Rh^A , Rh^B , and Rh^C (Figure 1), respectively and $^{13}\text{C}-\{^{103}\text{Rh}\}$ n.m.r. spectra at -86°C are entirely consistent with the carbonyl distribution shown in Figure 1. The i.r. spectrum[†] and cell constants of $(\text{PPN})_2[\text{FeRh}_4(\text{CO})_{15}]$ [triclinic, $a = 11.447(6)$, $b = 14.096(8)$, $c = 26.050(10)$ Å, $\alpha = 84.05(4)$, $\beta = 83.43$, $\gamma = 82.77(4)^\circ$, $U = 3986$ Å³] are also very similar to those found for $(\text{PPN})_2-[\text{RuIr}_4(\text{CO})_{15}]$ [PPN = $(\text{Ph}_3\text{P})_2\text{N}^+$].⁶ All the carbonyls, except CO^g and CO^h , migrate around the FeRh_4 skeleton at $+65^\circ\text{C}$

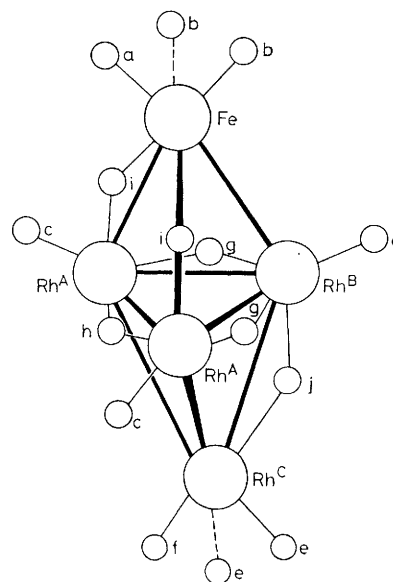
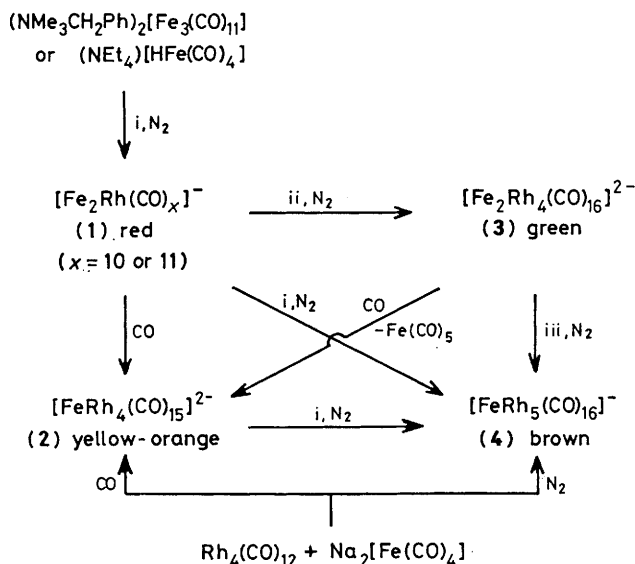


Figure 1. Schematic representation of the structure adopted by $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$.

[†] $\nu(\text{CO})/\text{cm}^{-1}$ for the iron–rhodium carbonyl clusters (1)–(4) in tetrahydrofuran (THF): (1) 2040w, 2000ms, 1980s, 1940m, and 1890w; (2) 2030w, 2005ms, 1970s, 1810s, 1790sh, and 1740s; (3) 2040w, 2005s, 1985ms, 1960m, 1950m, 1900w, 1725ms, and 1710s; (4) 2080w, 2040s, 2005m, 1990m, 1945w, 1790s, and 1765ms.

[‡] 0 p.p.m. = 11.376 MHz at such a magnetic field that the protons in Me_4Si resonate at exactly 360 MHz.

[§] For CO labelling see Figure 1. δ (p.p.m.) 216.3 (CO^a), 217.3 (CO^b), 200.5 [CO^c , $^1J(\text{Rh}-\text{CO})$ 91.5 Hz], 201.3 [CO^d , $^1J(\text{Rh}-\text{CO})$ 91.6 Hz], 200.5 [CO^e , $^1J(\text{Rh}-\text{CO})$ 91.5 Hz], 201.3 [CO^f , $^1J(\text{Rh}-\text{CO})$ 91.6 Hz], 259 [CO^g , $^1J(\text{Rh}-\text{CO})$ 30.5 Hz], 263.5 [CO^h , $^1J(\text{Rh}-\text{CO})$ 36.6 Hz], 253.5 [CO^i , $^1J(\text{Rh}-\text{CO})$ 33.6 Hz], and 250.4 [CO^j , $^1J(\text{Rh}^B-\text{CO})$ 39.7, $^1J(\text{Rh}^C-\text{CO})$ 25.9 Hz].

but, unlike the PtRh₄-group in [PtRh₄(CO)_x]²⁻ (*x* = 12, 14) which can be obtained with the platinum atom in either the equatorial or apical positions,⁸ there is no evidence for rearrangement of the FeRh₄-skeleton.

The structures of (3) and (4) have been established by a combination of X-ray[†] and multinuclear n.m.r. measurements because of metal disorder in the solid state; they are both isostructural with the isoelectronic cluster [Rh₆(CO)₁₆],⁹ and n.m.r. measurements show that (3) contains both *cis*- and *trans*-Fe₂Rh₄ groups (*ca.* 1 : 3, respectively).

Consistent with the increasing iron content, the average metal-metal bond length decreases on going from [Rh₆(CO)₁₆] (2.78 Å)⁹ to (4) (2.750 Å) to (3) (2.727 Å). In both (3) and (4), however, the metal disorder does not significantly affect the carbonyl groups, which show normal thermal parameters and interatomic bond lengths [*d*(M-C_{term}) 1.860, 1.799, *d*(M-C_{face-bridging}) 2.175, 2.139, *d*(C-O_{term}) 1.132, 1.159, and *d*(C-O_{face-bridging}) 1.168, 1.194 Å for (4) and (3), respectively] and the variation of M-C and C-O bond lengths in the series [Rh₆(CO)₁₆], (4), (3) is in keeping with increasing metal-to-carbonyl back-bonding.

At -70 °C the rhodium n.m.r. spectrum of (4) consists of two resonances at -400.6 and -501.7 p.p.m. in the ratio 4 : 1 and ¹³C-¹⁰³Rh } measurements are entirely in accord with the

carbonyl distribution around the FeRh₅-octahedron, being identical to that found in [Rh₆(CO)₁₆].⁹ An identical carbonyl distribution is found for (3) but in this case the ¹⁰³Rh n.m.r. spectrum at -70 °C shows three peaks due to *cis*- (-408.7 and -452.7 p.p.m.) and *trans*-isomers (-408.9 p.p.m.); these assignments were confirmed by ¹³C-¹⁰³Rh } n.m.r. measurements and, although the carbonyls are fluxional at room temperature, there is no evidence for rearrangement of the metallic skeleton.

Thus, the structures of [Fe₂Rh₄(CO)₁₆]²⁻, [FeRh₅(CO)₁₆]⁻, and [Rh₆(CO)₁₆] are very similar whereas the structures of [FeRh₄(CO)₁₅]²⁻ and [Rh₅(CO)₁₅]⁻ are different and this illustrates the present difficulties encountered in predicting arrangements of carbonyls and metals even in closely related transition metal carbonyl clusters.

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[†] Crystal data: [NMe₂CH₂Ph]₂[Fe₂Rh₄(CO)₁₆], (3), C₃₆H₃₂Fe₂N₂O₁₆Rh₄, *M* = 1272.0, monoclinic, space group *P*2/*c*, *a* = 13.219(4), *b* = 9.377(3), *c* = 19.672(4) Å, β = 88.74(3)°, *U* = 2437.9 Å³, *Z* = 2, *D*_c = 1.733 g cm⁻³, μ(Mo-Kα) = 19.4 cm⁻¹. Current *R* 0.058 for 2769 reflections [*6* < 2θ < 50°, *I* ≥ 4σ(*I*)].

[N(PPh₃)₂][FeRh₅(CO)₁₆], (4), C₆₂H₅₀FeNO₁₆P₂Rh₅, *M* = 1557.1, monoclinic, space group *C*2/*c*, *a* = 33.592(3), *b* = 9.721(1), *c* = 33.593(4) Å, β = 94.56(2)°, *U* = 10935 Å³, *Z* = 8, *D*_c = 1.892, *D*_m = 1.89(2) g cm⁻³, μ(Mo-Kα) = 18.2 cm⁻¹. Current *R* 0.045 for 5045 reflections [*6* < 2θ < 50°, *I* > 4σ(*I*)].

Typical e.s.d.'s for both (3) and (4) are Rh-Rh 0.001, Fe-Fe and Rh-C 0.01, and C-O 0.015 Å.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.