

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 synthesis and chemical behaviour of the new 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 $[\text{FeRh}_5(\text{CO})_{16}]^-$ are reported. Low-temperature multinuclear n.m.r. studies (^{13}C , $^{13}\text{C}\{-^{103}\text{Rh}\}$, and ^{103}Rh) on the penta- and hexa-nuclear clusters allow their structures in solution to be unambiguously established and their fluxional behaviour has been investigated through variable-temperature measurements. None shows rearrangement of the metal polyhedron.

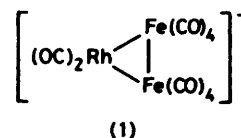
Bimetallic carbonyl clusters containing iron are now known for most of the transition metals (Cr, Mo, W, Mn, Ru, Os, Co, Rh, Ni, Pd, and Pt).^{1,2} However, whereas $[\text{FeCo}_3(\text{CO})_{12}]^-$ was the first anionic mixed-metal carbonyl cluster to be isolated and characterised³ there has been only one recent report of an anionic iron–rhodium carbonyl cluster,² although some neutral iron–rhodium carbonyl clusters containing other ligands (e.g. C_3H_5 or PPh_2) are known.^{4,5} Our interest in this class of compounds led us to investigate this area of chemistry and we now report preparative routes for the synthesis of $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ 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); their chemical behaviour and variable-temperature multinuclear magnetic resonance spectra (^{13}C , $^{13}\text{C}\{-^{103}\text{Rh}\}$, and ^{103}Rh) are also reported. A preliminary report of this work has already appeared.⁶

Results

Synthesis and Behaviour of Iron–Rhodium Anionic Carbonyl Clusters.—All the bimetallic anionic carbonyl clusters described above have been synthesized *via* redox condensations involving an iron anionic carbonyl substrate {e.g. $[\text{FeH}(\text{CO})_4]^-$, $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ } and a rhodium substrate in a higher oxidation state {e.g. $[\text{Rh}_4(\text{CO})_{12}]$, $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$, or RhCl_3 }. This allowed us to test a wide range of combinations and, as a result, we have been able to synthesise clusters with an Fe:Rh ratio ranging from 2:1 to 2:10. However, it should be noted that the nature of the product critically depends, not only on the ratio of Fe:Rh, but also on the atmosphere (N_2 or CO) above the reactants.

Infrared spectra show that $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11) (1) is the first formed product on reaction of (a) $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ with either $[\text{FeH}(\text{CO})_4]^-$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$; (b) RhCl_3 with $[\text{Fe}_3(\text{CO})_{11}]^{2-}$; (c) $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ with a large excess of $[\text{Fe}(\text{CO})_5]$. However, the synthesis of (1) is best carried out by the slow addition of a tetrahydrofuran (thf) solution of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ to a solution

of $[\text{FeH}(\text{CO})_4]^-$ in thf under nitrogen atmosphere with concomitant monitoring of the i.r. spectrum of the solution until the band at 1880 cm^{-1} due to $[\text{FeH}(\text{CO})_4]^-$ has disappeared. Despite the ease with which this red compound can be obtained from a variety of substrates, it has not yet proved possible to obtain (1) as a pure crystalline solid due to decomposition upon attempted isolation. However, there are complete coincidences in both relative intensities and positions of carbonyl absorption bands in the i.r. spectra of compounds resulting from grossly different synthetic routes and this suggests that this spectrum is attributable to a unique species in solution rather than a mixture. However, the i.r. spectrum of (1) [Figure 1(a) and Table 1] is unusual for iron–rhodium carbonyl clusters since only terminal carbonyl bands are observed. The stoichiometry of the reactants is consistent with a Fe:Rh ratio of 2:1 for (1) and the simple ^{13}C and ^{103}Rh n.m.r. spectra of (1) at low temperatures (see later) suggest a simple structure based on a Fe_2Rh group. Unfortunately, the ^{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 $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ remains presently undetermined. However, we prefer a value of $x = 10$ or 11 . If $x = 11$, then (1) would be isoelectronic with $[\text{Fe}_3(\text{CO})_{12}]$ whereas $x = 10$ seems more in keeping with the stoichiometry of the reactants involved in the formation of (1). In this last case, the formulation of (1)



would be as shown above. This could be rationalised using the isolobal relationship in which $[\text{Rh}(\text{CO})_2]^+$ reacts with $[\text{Fe}_2(\text{CO})_8]^{2-}$ in a similar way to that found in the reaction of $[\text{Fe}_2(\text{CO})_8]^{2-}$ with CH_2I_2 to give $[\text{Fe}_2(\text{CO})_8(\mu\text{-CH}_2)]^-$.⁷

Under a nitrogen atmosphere, solutions of (1) are stable for several days but precipitation or crystallization by slow diffusion techniques always resulted in disproportionation [equation (i)]. As a result, crystals of the hexanuclear cluster, $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3), are invariably obtained when attempting to isolate (1) under a nitrogen atmosphere, whereas under a carbon monoxide atmosphere the pentanuclear cluster,

† 1,1,2,2,2,2,3,3,3,3-Decacarbonyl-triangulo-rhodiumdiferate(1-), 1,2,2,3,3,4,4,4,4,5,5-hexa- μ -carbonyl-1,1,1,2,3,4,5,5,5-nona-carbonyl-cyclo-tetrahodiumdiferate(2-)(3 Fe-Rh)(6 Rh-Rh), and 1,2,3,1,4,5,2,5,6,3,4,6-tetra- μ_3 -carbonyl-dodecacarbonyl-octahydro-tetrahodiumdiferate(2-) and -pentarhodiumdiferate(1-) respectively.

Table 1. Infrared data for mixed iron-rhodium carbonyl clusters

| Compound | Colour | Solvent | $\nu(\text{CO})/\text{cm}^{-1}$ | |
|--|---------------|------------------------|--|---------------|
| | | | terminal | face-bridging |
| $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{Fe}_2\text{Rh}(\text{CO})_x]$ ($x = 10$ or 11) | Red | thf | 2 001s, 1 985vs, 1 948ms, 1 890m | |
| $[\text{N}(\text{PPh}_3)_2]_2[\text{FeRh}_4(\text{CO})_{15}]$ | Yellow-orange | thf | 2 033w, 1 998s, 1 964vs, 1 813ms, 1 746m | |
| $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]$ | Green | CH_3CN | 2 048w, 2 005vs, 1 986s, 1 961m, 1 948m, 1 904w, 1 728 (sh), 1 710ms | |
| $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{FeRh}_5(\text{CO})_{16}]$ | Brown | thf | 2 081w, 2 037vs, 2 007m, 1 986m, 1 942w, 1 782ms, 1 761m | |

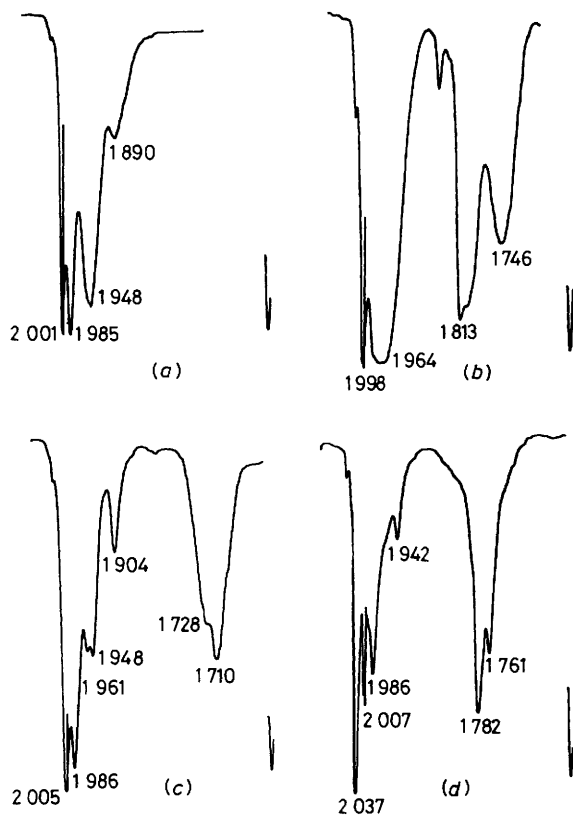
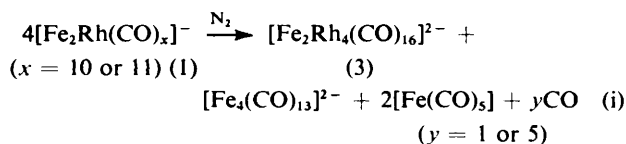


Figure 1. Infrared spectra [$\nu(\text{CO})/\text{cm}^{-1}$] of (a) $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{Fe}_2\text{Rh}(\text{CO})_x]$ ($x = 10$ or 11) (1), in thf; (b) $[\text{N}(\text{PPh}_3)_2]_2[\text{FeRh}_4(\text{CO})_{15}]$ (2), in thf; (c) $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]$ (3), in acetonitrile; and (d) $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{FeRh}_5(\text{CO})_{16}]$ (4), in thf

$[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2), is formed together with other by-products.

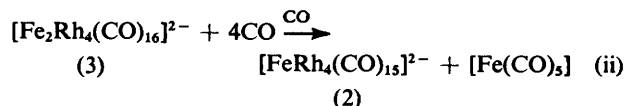


Equation (i) provides the best route for the synthesis of (3), which has been shown by X-ray analysis⁶ to be isostructural with $[\text{Rh}_6(\text{CO})_{16}]$.⁸ Complex (3) has been isolated as a green crystalline solid with a variety of tetrasubstituted ammonium and phosphonium salts in yields up to 50–60%.

The i.r. spectrum of (3) [Figure 1(c)] is very similar to (1) in the terminal carbonyl region but additionally has intense absorptions in the face-bridging carbonyl region.

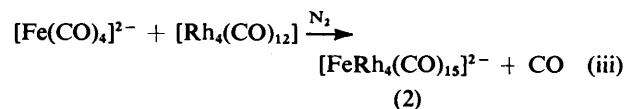
Complex (3), like (1), reacts under carbon monoxide according to equation (ii). The dark green solution of (3) turns

yellow-orange over a period of 1 h and a reasonably pure sample of (2) can be obtained by removing the solvent and $[\text{Fe}(\text{CO})_5]$ *in vacuo*.

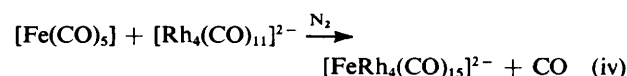


The reverse reaction to that described in equation (ii) could, in principle, provide an alternative synthesis of (3), since (2) is readily available from many different routes. However, this method produces further reaction, which results in the formation of (1) when working in thf at 50 °C in the presence of excess $[\text{Fe}(\text{CO})_5]$, and, as a result, has not been further investigated.

The pentanuclear cluster, (2), has also been prepared directly by addition of solid $[\text{Rh}_4(\text{CO})_{12}]$ to a suspension of $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot n\text{thf}$ in anhydrous thf under a nitrogen atmosphere [equation (iii)]. In this case, some $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ is

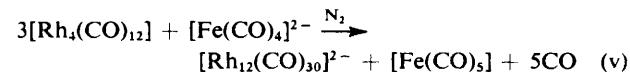


often obtained as a by-product but, because of the high solubility of most salts of (2) in thf and the low solubility of the corresponding salt of $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ in thf, separation is easily effected. Additionally, (2) can be prepared as shown in equation (iv), but the difficult preparation of $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ ⁹

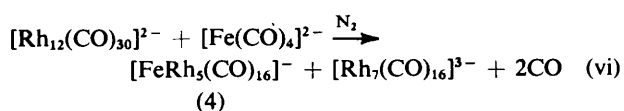


makes this route unattractive. The $[\text{NMe}_4]^+$ and $[\text{N}(\text{PPh}_3)_2]^+$ salts of (2) have been obtained as yellow-orange crystals and the i.r. spectrum [Figure 1(b)] is coincident with that previously reported for the isoelectronic cluster, $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$; ¹⁰ the $[\text{N}(\text{PPh}_3)_2]^+$ salts of both (2) and $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ have also been shown to be isomorphous.⁶ Unambiguous evidence that (2) is isostructural with $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ ¹⁰ has been obtained by low-temperature multinuclear n.m.r. measurements (see below).

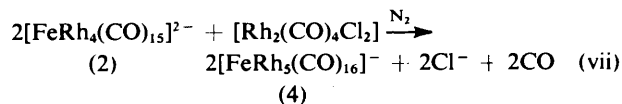
It should be noted that reaction (iii) follows a completely different course when making the reverse addition of reagents. Thus, on adding a solution of $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot n\text{thf}$ in thf to a stirred solution of $[\text{Rh}_4(\text{CO})_{12}]$ in thf under a nitrogen atmosphere reaction (v) results. Further addition of $[\text{Fe}(\text{CO})_4]^{2-}$



results in the formation of the brown hexanuclear cluster $[\text{FeRh}_5(\text{CO})_{16}]^-$ (4), according to equation (vi). However, (4)



is best obtained *via* a two-step synthesis, which involves the formation of (2) [equation (iii)], followed by further reaction with $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ as shown in equation (vii). Complex (4),



rather than the expected cluster, $[\text{Fe}_2\text{Rh}_4\text{H}(\text{CO})_{16}]^-$, is also formed in good yield on reaction of phosphoric acid in acetonitrile with (3). However, despite the gross rearrangement implied in this reaction, there is no i.r. evidence for any other by-products except $[\text{Fe}(\text{CO})_5]$.

Complex (4) has also been obtained on reaction of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ with an excess of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$. I.r. spectra show the intermediate formation of (1) which is then apparently transformed directly into (4) at a mol ratio between the two reactants of *ca.* 1 : 2.

Because of the several syntheses presently available for (4), it has been crystallised with a variety of counter ions $\{[\text{NMe}_4]^+, [\text{NEt}_4]^+, [\text{NMe}_3(\text{CH}_2\text{Ph})]^+, [\text{PPh}_4]^+, \text{or } [\text{N}(\text{PPh}_3)_2]^+\}$ usually from dichloromethane-*n*-heptane. X-Ray analysis of $[\text{N}(\text{PPh}_3)_2][\text{FeRh}_5(\text{CO})_{16}]$ shows the anion to be isostructural with $[\text{Rh}_6(\text{CO})_{16}]^8$ and $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3);⁶ in agreement, the i.r. spectrum shows strong bands due to both terminal and face-bridging carbonyls [Figure 1(d) and Table 1].

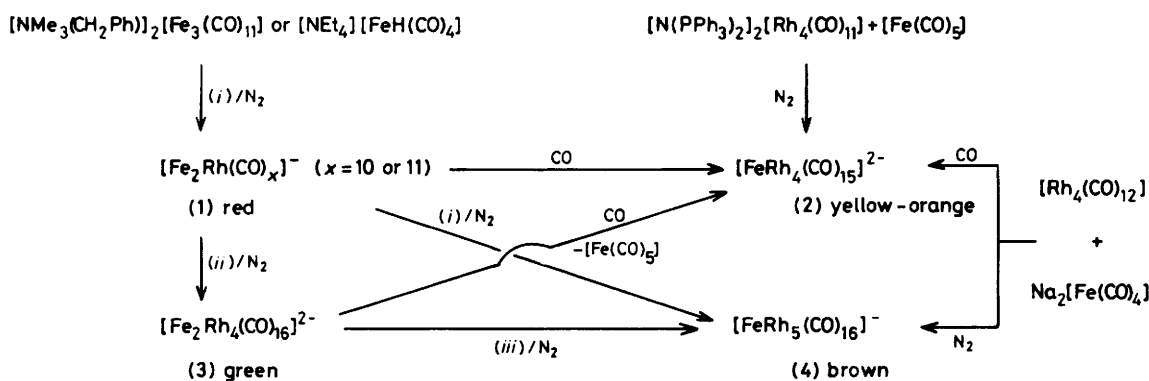
The stability of (4) is much greater than the other anionic iron-rhodium clusters and is more akin to the stability of $[\text{Rh}_6(\text{CO})_{16}]$. Thus, it is very stable towards aerial oxidation and can be recovered unchanged after prolonged standing in air both as a solid or in solution. It is also stable towards protonation.

rhodium carbonyls, which was confirmed by ^{13}C -(^{103}Rh) n.m.r. measurements.

The relative integration of iron-rhodium carbonyls (9 : 2) is higher than expected (8 : 2) but no variation in relative intensities was observed on varying either T_R (repetition time) from 0.5 to 5.0 s or the concentration of relaxing reagent, $[\text{Cr}(\text{acac})_3]$ (acac = acetylacetonate), over a significant range. Related problems have been encountered with other mixed iron-rhodium carbonyl clusters and may stem from the method of preparation which involves the reaction between iron and rhodium carbonyls with only the rhodium carbonyl being enriched with ^{13}C . It becomes impossible to monitor the reaction by i.r. if both reagents are enriched with ^{13}C . However, in view of the simple n.m.r. spectra, the absence of high-field resonances in the ^1H n.m.r. spectrum and the stoichiometry of the reactions involved in the formation of (1), we prefer to formulate (1) as a trinuclear cluster, $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ with $x = 10$ or 11. The value of $x = 10$ seems more in keeping with the ^{13}C n.m.r. integration since if $x = 11$ then the expected ratio of carbonyl resonances on Fe : Rh would be 8 : 3 which is very different from that found (14 : 3).

The ^{13}C n.m.r. spectrum of (1) at room temperature consists of a broad resonance at *ca.* 214 p.p.m. due to an intermediate rate of exchange of all the carbonyls. The position of this resonance is also more in keeping with the mean value calculated for $x = 10$ (211.1 p.p.m.) than for $x = 11$ (208.9 p.p.m.).

It should be noted that we have no evidence for resolution of the axial-equatorial iron carbonyls in (1) either at room or low temperature and we therefore conclude that they are coincident in the ^{13}C n.m.r. spectrum. This is not unreasonable since, although the axial-equatorial iron carbonyls in $[\text{Fe}_3\text{Pt}_3(\text{CO})_{15}]^{2-}$ ¹¹ undergo exchange at room temperature as evidenced by the time-averaged value of $^2J(\text{Pt}-\text{CO}) = 49.0$ Hz, $\delta(\text{CO})$ 216.3 p.p.m., they are resolved at -83°C [$\delta(\text{CO}_{ax})$ 216.1 p.p.m., $^2J(\text{Pt}-\text{CO}_{ax}) = 11.0$ Hz; $\delta(\text{CO}_{eq})$ 215.4 p.p.m., $^2J(\text{Pt}-\text{CO}_{eq}) = 89.4$ Hz] but they have very similar chemical shifts.



Scheme. (i) + $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ in thf; (ii) + Pr^1OH ; (iii) + H_3PO_4 in CH_3CN

The various preparative routes to compounds (1)–(4) are summarised in the Scheme together with their interconversions.

N.M.R. Studies and Fluxional Behaviour of Anionic Iron-Rhodium Carbonyl Clusters.— $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ ($x = 10$ or 11) (1). Rhodium-103 n.m.r. measurements on (1) at -85°C show only one resonance at +0.1 p.p.m. and the ^{13}C n.m.r. spectrum of (1) (12% ^{13}C) at the same temperature consists of a singlet at 217.4 p.p.m. due to the iron carbonyls and a doublet at 186.1 p.p.m. [$^1J(^{103}\text{Rh}-^{13}\text{C}) = 76.3$ Hz] due to the

It should also be noted that $\delta(^{103}\text{Rh})$ for (1) is in a region normally associated with rhodium +1 oxidation states¹² and is thus consistent with the formal addition of $[\text{Rh}(\text{CO})_2]^+$ to $[\text{Fe}_2(\text{CO})_8]^{2-}$ discussed earlier.

$[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2). Direct ^{103}Rh n.m.r. measurements on (2) in thf at -70°C show three rhodium resonances at +59.4, -241.9, and -1 170.9 p.p.m. in the ratio 2 : 1 : 1 due to the Rh_A , Rh_B , and Rh_C respectively (Figure 2). As found in $[\text{Rh}_5(\text{CO})_{15}]^-$, the apical rhodium resonance, Rh_C , in (2) is at significantly lower frequency than the equatorial rhodium

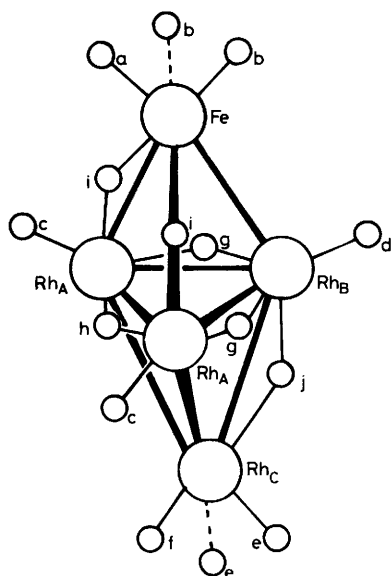


Figure 2. Schematic representation of the structure adopted by $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2)

resonances, Rh_A and Rh_B . The ^{13}C - $\{^{103}\text{Rh}\}$ n.m.r. spectra at -86°C (Figure 3) are entirely consistent with the carbonyl distribution shown in Figure 2, which is isostructural with $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ ¹⁰ but different from $[\text{Rh}_5(\text{CO})_{15}]^-$ both in solution and in the solid state.¹³

On increasing the temperature, two different carbonyl migrations are found for (2). The lowest energy process involves only the apical terminal carbonyls and equatorial-apical edge-bridging carbonyls in exchange and resembles a rocking motion on the upper and lower half of the trigonal bipyramidal metal skeleton [Figure 4(a)]. Consistent with this mechanism is the fact that the resonance due to C^bO broadens faster than the resonance due to C^aO . At higher temperatures all the carbonyls, except C^aO and C^bO , become involved in intra-exchange [Figure 4(a) and (b)]. At $+65^\circ\text{C}$, the equatorial edge-bridging carbonyl resonance is a sharp triplet due to both C^aO and C^bO as well as Rh_A and Rh_B becoming equivalent through migration of the other carbonyls, which give rise to a broad resonance at 218.5 p.p.m. The position of this resonance is similar to the calculated mean chemical shift for the exchanging carbonyls (217.7 p.p.m.) and suggests that the carbonyls spend approximately equal time on each of the rhodium and iron atoms. However, unlike the PtRh_4 group which can be obtained with the platinum atom in either the equatorial, in $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$, or apical, in $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$, positions,¹⁴ there is no evidence for rearrangement of the FeRh_4 skeleton. It should also be noted that the equatorial edge-bridging carbonyls seem to present a particularly stable situation and remain static in (2), $[\text{Rh}_5(\text{CO})_{15}]^-$, and $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$; in the latter cluster, the terminal carbonyl group on the equatorial platinum atom also remains stationary and this could be due to the strong $\text{Pt}-\text{CO}$ bond.

$[\text{FeRh}_5(\text{CO})_{16}]^-$ (4). Complex (4) is isostructural with $[\text{Rh}_6(\text{CO})_{16}]^8$ and is represented schematically in Figure 5. Consistent with this, the ^{103}Rh n.m.r. spectrum of (4) in $[\text{D}_6]\text{acetone}$ at -70°C shows two resonances in the ratio 4:1 at -400.6 and -501.7 p.p.m. due to Rh_A and Rh_B respectively. Consideration of the symmetry of the carbonyl skeleton in Figure 5 shows there to be two types of face-bridging carbonyls, C^aO and C^bO , in the ratio 2:2 and four types of terminal carbonyls, C^aO , C^bO , C^cO , and C^dO ,

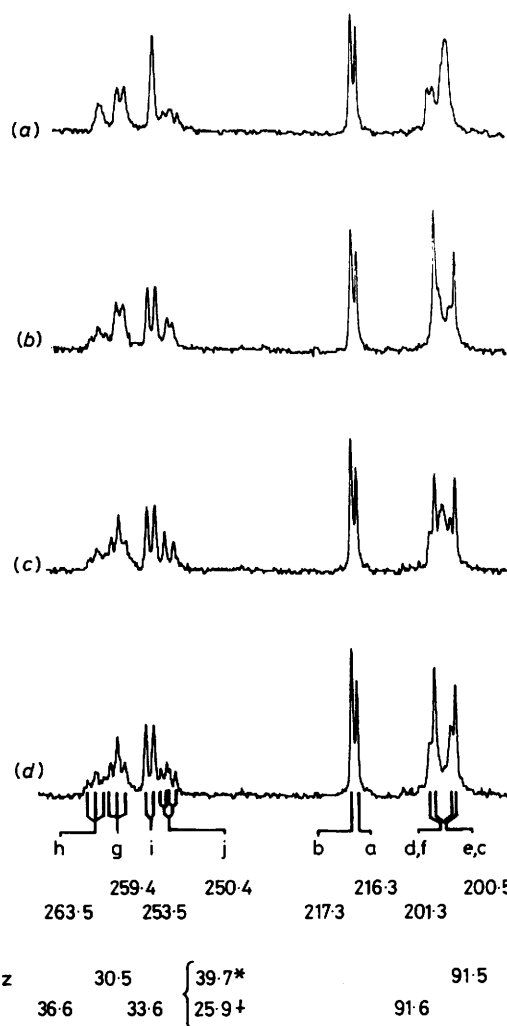


Figure 3. ^{13}C - $\{^{103}\text{Rh}\}$ N.m.r. spectra of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2), in thf under CO (30% ^{13}C) at -86°C . (a) Decoupling at 3.160 176 MHz [$\delta(^{103}\text{Rh}_A) + 59.4$ p.p.m.], (b) decoupling at 3.159 247 MHz [$\delta(^{103}\text{Rh}_B) - 241.9$ p.p.m.], (c) decoupling at 3.156 311 MHz [$\delta(^{103}\text{Rh}_C) - 1170.9$ p.p.m.], and (d) non-decoupled spectrum. For $\delta(^{103}\text{Rh})$ 0 p.p.m. = 3.16 MHz at such a magnetic field that the protons in SiMe_4 resonate at 100 MHz. * $^1J(\text{Rh}_B-\text{CO})$. [†] $^1J(\text{Rh}_C-\text{CO})$

in the ratio 2:4:4:2 respectively. The ^{13}C n.m.r. spectrum of (4) (ca. 25% ^{13}C) in thf at -90°C is entirely consistent with this carbonyl distribution, which has been confirmed by ^{13}C - $\{^{103}\text{Rh}\}$ measurements (Figure 6). In keeping with previous observations, resonances of carbonyl groups associated with iron occur at considerably lower field than rhodium carbonyl resonances. Thus, the resonance due to C^aO occurs at 256.8 p.p.m. as a triplet [$^1J(^{103}\text{Rh}_A-^{13}\text{C}^a\text{O}) = 12.2$ Hz] and collapses to a singlet on decoupling Rh_A whereas the other set of face-bridging carbonyls, C^bO , occurs at higher field, 233.5 p.p.m., and collapses to a doublet on decoupling Rh_A [$^1J(^{103}\text{Rh}_B-^{13}\text{C}^b\text{O}) = 21.4$ Hz] and a triplet on decoupling Rh_B [$^1J(^{103}\text{Rh}_A-^{13}\text{C}^b\text{O}) = 25.9$ Hz] (Figure 6). Similarly, the terminal iron carbonyls, C^cO , are at lower field than the rhodium carbonyls which can be assigned from their relative intensities and from ^{13}C - $\{^{103}\text{Rh}\}$ measurements.

In keeping with the increased metal to carbonyl back-bonding in $[\text{FeRh}_5(\text{CO})_{16}]^-$ compared to $[\text{Rh}_6(\text{CO})_{16}]^8$, $\delta(^{13}\text{C})$ for the carbonyls associated with rhodium are at

Table 2. ^{13}C and ^{103}Rh n.m.r. data for $[\text{Rh}_{6-x}\text{Fe}_x(\text{CO})_{16}]^{x-}$ ($x = 0-2$)

| | $[\text{Rh}_6(\text{CO})_{16}]^0$ ^a | $[\text{FeRh}_5(\text{CO})_{16}]^{-1}$ ^a | <i>trans</i> - $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ ^a | <i>cis</i> - $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ ^a |
|---|--|---|--|--|
| $\delta(^{13}\text{C})/\text{p.p.m.}^b$ | | | | |
| C ^o | 180.1 (70.2) | 211.0 | 212.4 | |
| C ^o | 180.1 (70.2) | 186.8 (70.2) ^c | 189.7 (73.2) | |
| C ^o | 180.1 (70.2) | 186.1 (67.1) ^c | 189.7 (73.2) | |
| C ^o | 180.1 (70.2) | 184.7 (70.2) | 212.4 | |
| C ^o | 231.5 (24.4) | 256.8 (12.2) | 260.8 (19.8) | |
| C ^o | 231.5 (24.4) | 233.5 (25.9) ^d 21.4 ^e | 260.8 (19.8) | |
| $T/^\circ\text{C}$ | +60 | -70 | -90 | |
| Solvent | CDCl_3 | $[\text{H}_2]\text{thf}$ | $[\text{H}_2]\text{Acetone}$ | $[\text{H}_2]\text{Acetone}$ |
| $\delta(^{103}\text{Rh}_A)/\text{p.p.m.}^f$ | -426 (60) | -400.6 (-70) | -408.9 (-70) | { -408.7 (-70) |
| $\delta(^{103}\text{Rh}_B)/\text{p.p.m.}^f$ | -426 (60) | -501.7 (-70) | | { -452.7 (-70) |

^a For assignment see Figure 5; for $[\text{Rh}_6(\text{CO})_{16}]$ M = Rh, for *trans*- $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ Rh_B = Fe. ^b Values of $^1J(^{103}\text{Rh}-^{13}\text{C})$ in Hz are given in parentheses unless otherwise stated. ^c Assignment could be reversed. ^d $^1J(^{103}\text{Rh}_A-^{13}\text{C})$. ^e $^1J(^{103}\text{Rh}_B-^{13}\text{C})$. ^f 11.376 MHz = 0 p.p.m. at such a magnetic field that the protons in SiMe_4 resonate at exactly 360 MHz. Values of $T/^\circ\text{C}$ are given in parentheses.

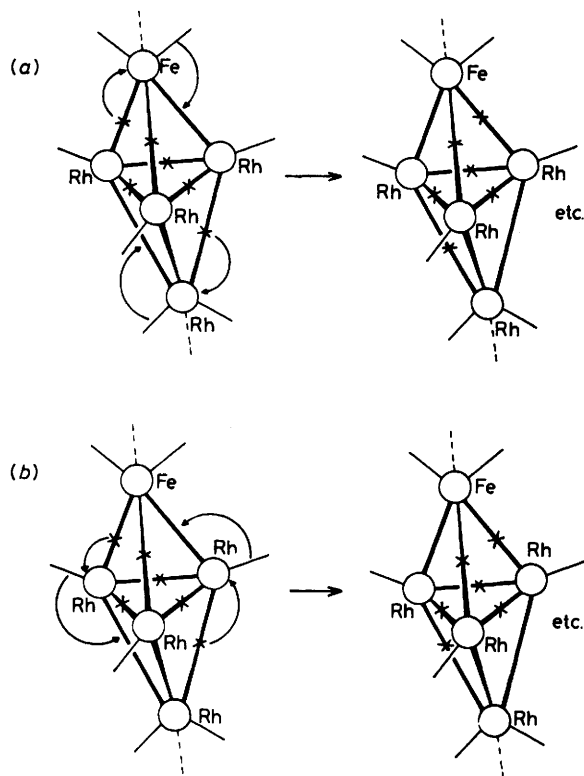


Figure 4. Schematic representation of the carbonyl migration pathways found for $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2) (see text)

lower field in (4) than in $[\text{Rh}_6(\text{CO})_{16}]$ ¹⁵ (Table 2). It is also worth noting that both compounds have similar values of $^1J(^{103}\text{Rh}-^{13}\text{C})$ except for the face-bridging carbonyl, C^o; in this case, C^o appears to be more strongly bonded to iron since $^1J(^{103}\text{Rh}_A-^{13}\text{C}^o)$ in (4) is 12.2 Hz compared to 24.4 Hz in $[\text{Rh}_6(\text{CO})_{16}]$.¹⁵ This could be consistent with partial localisation of the anionic charge on the iron atom which would be expected to result in the bridging carbonyls, C^o, becoming more strongly bonded to iron than to Rh_A.

At room temperature, (4) did not exhibit carbonyl fluxionality, and is thus similar to the behaviour of $[\text{Rh}_6(\text{CO})_{16}]$.¹⁵

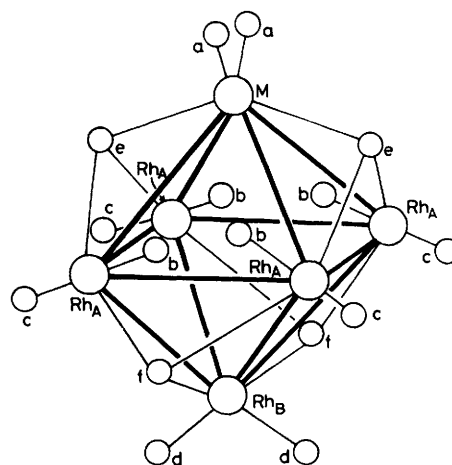


Figure 5. Schematic representation of the structure of $[\text{FeRh}_5(\text{CO})_{16}]^{2-}$ (4) (M = Fe)

$[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3). The structure of (3) is similar to (4) and $[\text{Rh}_6(\text{CO})_{16}]$ but is found in solution to be a mixture of *trans*- and *cis*- Fe_2Rh_4 groups in the ratio *ca.* 3 : 1. Thus, the ^{103}Rh n.m.r. spectra both at -70 and $+25^\circ\text{C}$, show three peaks due to the *trans* (-408.9 p.p.m. at -70°C) and *cis* isomers (-408.7 and -452.7 p.p.m. at -70°C).

For the *trans* isomer, the iron carbonyls are all equivalent and appear as a singlet at 212.4 p.p.m., the terminal rhodium carbonyls are all equivalent and appear as a doublet at 189.7 p.p.m. [$^1J(^{103}\text{Rh}-^{13}\text{C}) = 73.2$ Hz] and the face-bridging carbonyls are equivalent and appear as a triplet at 260.8 p.p.m. [$^1J(^{103}\text{Rh}-^{13}\text{C}) = 19.8$ Hz]; all the carbonyl resonances coupled to rhodium collapse to singlets on rhodium decoupling.

For the *cis* isomer of (3), the carbonyl distribution is similar to the *trans* isomer but there are now many more inequivalences and this, coupled with the lower abundance of this isomer, has prevented us obtaining a complete ^{13}C n.m.r. assignment.

Discussion

During the present work we failed to obtain even spectroscopic evidence for the existence of $[\text{FeRh}_3(\text{CO})_{12}]^{-}$, which

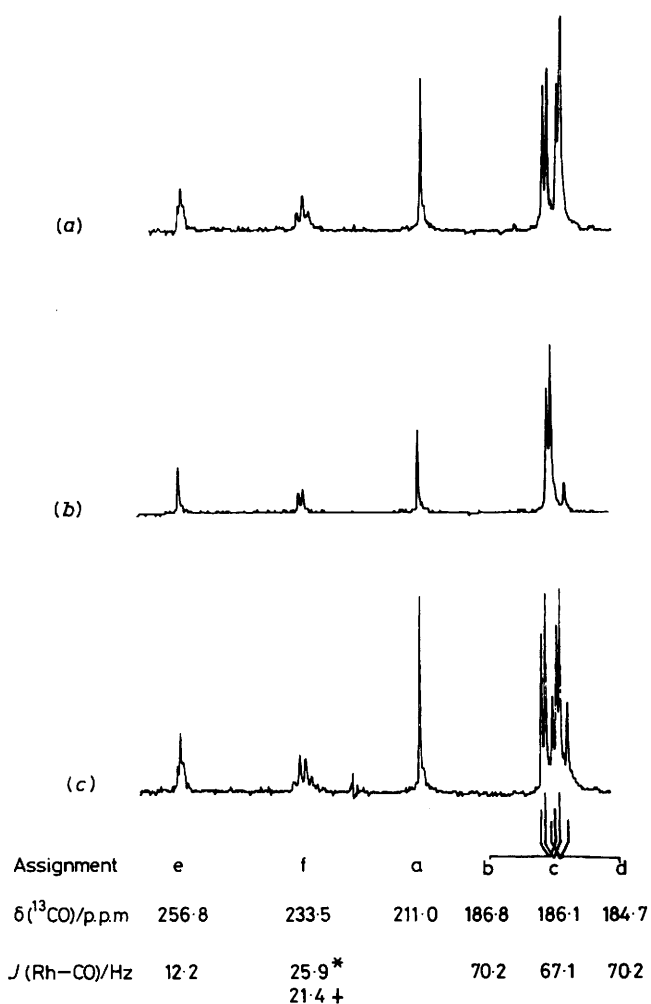


Figure 6. $^{13}\text{C}\{-^{103}\text{Rh}\}$ N.M.R. spectra of $[\text{N}(\text{PPh}_3)_2][\text{FeRh}_5(\text{CO})_{16}]$ (4) (ca. 25% ^{13}C) in thf at -90°C . (a) Decoupling at 3.158 369 MHz [$\delta(^{103}\text{Rh}_\text{B}) - 516.0$ p.p.m.], (b) decoupling at 3.159 689 MHz [$\delta(^{103}\text{Rh}_\text{A}) - 414.9$ p.p.m.], (c) non-decoupled spectrum. The assignment of b and c could be reversed. * $^1J(\text{Rh}_\text{A}-\text{CO})$. † $^1J(\text{Rh}_\text{B}-\text{CO})$.

would be isoelectronic with $[\text{Rh}_4(\text{CO})_{12}]$ and related to the first bimetallic anionic cluster, namely $[\text{FeCo}_3(\text{CO})_{12}]^-$.³ This is probably due to the instability of tetranuclear anionic rhodium clusters towards condensation to hexanuclear species. Thus, although $[\text{Rh}_4(\text{CO})_{11}(\text{CO}_2\text{R})]^-$ ($\text{R} = \text{alkyl}$) and $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ have been isolated and characterised,^{9,16} there is no evidence for the existence of an extensive series of compounds of formula $[\text{Rh}_4(\text{CO})_{11}\text{X}]^-$ ($\text{X} = \text{anionic ligand}$), as in the case of $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$, reactions devised to synthesize such species always resulted in the formation of hexanuclear derivatives.¹⁷

The penta- and hexa-nuclear iron-rhodium carbonyls described above are isoelectronic with the corresponding homometallic rhodium carbonyl clusters, $[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{Rh}_6(\text{CO})_{16}]$, and whereas the hexanuclear clusters, $[\text{Rh}_6(\text{CO})_{16}]$, $[\text{FeRh}_3(\text{CO})_{16}]^-$ (4), and $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3), are isostructural, the pentanuclear clusters, $[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2), are not. This exemplifies the present difficulties encountered in trying to predict carbonyl arrangements in metal clusters and is related to the different structures adopted by the following closely related pairs of isoelectronic clusters containing the same number of carbonyls: $[\text{M}_4-$

$(\text{CO})_{12}]$ ($\text{M} = \text{Co}$ or Rh)¹⁸ and $[\text{Ir}_4(\text{CO})_{12}]$,¹⁹ $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ ¹⁵ and $[\text{Ir}_6(\text{CO})_{15}]^{2-}$,²⁰ $[\text{Rh}_6(\text{CO})_{16}]$ ⁸ and $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$.²¹

Because of a variety of different interconnected factors, similar difficulties are presently encountered in predicting metal occupancies of different sites in heterometallic clusters. For $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2), optimisation of metal-metal bond strength would suggest that iron should occupy an apical site. Additionally, some localisation of the anionic charge would be expected on iron. For effective charge dissipation, iron should be associated with more carbonyls than rhodium and this is more easily accomplished if iron is in an apical site. Additional stabilisation of the weak iron-rhodium bonds occurs through two $\text{Fe}-\text{Rh}_{\text{eq}}$ edges becoming carbonyl bridged whereas only one of the stronger $\text{Rh}_{\text{ap}}-\text{Rh}_{\text{eq}}$ is edge-bridged (Figure 2). It is worth pointing out that for $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$, and presumably $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$, the five carbonyls on the unique apical atom, Ru or Fe, form a regular square-based pyramid about the apical metal atom and the non-bridged ruthenium-iridium bond completes a regular octahedron. An exactly similar arrangement is found for $[\text{Rh}_5(\text{CO})_{14}\text{I}]^{2-}$,²² with the $\text{M}(\text{CO})_5$ group in $[\text{MM}'(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Fe}$, $\text{M}' = \text{Rh}$; $\text{M} = \text{Ru}$, $\text{M}' = \text{Ir}$) being replaced by the electron-rich iodide-substituted rhodium group, $\text{Rh}(\text{CO})\text{I}$. The other apical group in either $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ or $[\text{Rh}_5(\text{CO})_{14}\text{I}]^{2-}$ [$\text{Ir}(\text{CO})_4$ and $\text{Rh}(\text{CO})_4$ respectively] also form, together with the two non-bridged apical-equatorial metal-metal bonds, an approximate octahedron.

Slight changes in polarisation within the metallic skeleton are sufficient to alter significantly the instantaneous structure and also the carbonyl fluxionality.²³ However, in all the iso-electronic clusters, $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$, $[\text{Rh}_5(\text{CO})_{15}]^-$, and $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ presently investigated, although different migratory behaviour is found for the carbonyls, the equatorial edge-bridging carbonyls always stay fixed. This seems to be a particular stable configuration and probably results from these three equatorial bridging carbonyls being coplanar with the equatorial Rh_3 triangle. A similar stereochemistry is found in $[\text{Pt}_3\text{M}(\text{CO})_{6n}]^{2-}$ ($n = 2, 3$, or 4),²⁴ $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$,²⁵ and in nickel clusters,²⁶ which are stereochemically rigid, whereas when the carbonyls are not in the same plane as the M_3 triangle (e.g. $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ ²⁷) carbonyl migration readily occurs.

An increasing reactivity is found with increasing iron content and this is probably associated with a decrease in thermodynamic stability due to the increased number of iron-iron bonds.

Experimental

All reactions were carried out in purified solvents under either an atmosphere of nitrogen or carbon monoxide. Infrared spectra were recorded on a Perkin-Elmer 683 grating spectrophotometer using calcium fluoride cells. Iron and rhodium analyses were carried out by atomic absorption using an AA-5 Varian Techtron spectrophotometer. Tetrasubstituted ammonium or phosphonium cations were analysed by precipitation as tetraphenylborate salts. Carbon monoxide was determined as described previously.²⁸

The ^{13}C , $^{13}\text{C}\{-^{103}\text{Rh}\}$, and ^{103}Rh n.m.r. spectra were recorded on JEOL PS-100 and Bruker WH 360 MHz spectrometers as described previously.²⁹

Literature methods were used to synthesise $[\text{Fe}(\text{CO})_4]^{2-}$,³⁰ $[\text{Fe}(\text{CO})_4\text{H}]^-$,³¹ $[\text{Fe}_3(\text{CO})_{11}]^{2-}$,³² $[\text{Rh}_4(\text{CO})_{12}]$,³³ and $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$.³⁴

^{13}C -enriched samples of the iron-rhodium clusters were obtained by starting from pre-enriched (ca. 60% ^{13}C) $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$, except for $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ which was directly exchanged with ^{13}C using standard vacuum-line techniques.

Synthesis of $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ (1) from $[\text{FeH}(\text{CO})_4]^-$ and $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$.—The complex $[\text{NET}_4][\text{FeH}(\text{CO})_4]$ (1.63 g, 5.46 mmol) was dissolved in thf (15 cm³) in a two-necked, round-bottom flask equipped with a microburette. A solution of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (0.61 g, 1.56 mmol) in thf (20 cm³) was added dropwise with stirring. The i.r. spectrum of the resulting dark red solution is shown in Figure 1(a). All attempts to isolate (1) as a crystalline solid have so far failed but the product has been used directly for subsequent reactions and n.m.r. measurements.

Synthesis of $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ (1) from $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ and $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$.—The complex $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_3(\text{CO})_{11}]$ (1.05 g, 1.35 mmol) was dissolved in anhydrous thf (25 cm³) and treated as above with $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (0.48 g, 1.25 mmol) in thf (15 cm³). The i.r. spectrum of the resulting dark red solution showed that apart from the presence of trace amounts of $[\text{FeRh}_5(\text{CO})_{16}]^-$, the solution usually contained essentially pure (1).

Similar results have been obtained on reacting $[\text{NET}_4]_2[\text{Fe}_2(\text{CO})_8]$ or $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_4(\text{CO})_{13}]$ with $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ in a 1 : 0.5 and 1 : 0.7 mol ratio respectively.

Synthesis of $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2) from $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Fe}(\text{CO})_4]^{2-}$.—The complex $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot n\text{thf}$ (0.3 g) was suspended in anhydrous thf (25 cm³) and solid $[\text{Rh}_4(\text{CO})_{12}]$ (0.5 g) added with stirring under an atmosphere of CO. The resulting yellow-green solution was filtered and evaporated *in vacuo*. The residue was dissolved in water (30 cm³) under CO and the mixture of anionic compounds present in solution was precipitated by addition of tetramethylammonium chloride. The resulting precipitate was filtered off and dried *in vacuo*; extraction of the residue with thf gave an orange solution containing fairly pure $[\text{NMe}_4]_2[\text{FeRh}_4(\text{CO})_{15}]$ (2), leaving a green residue of $[\text{NMe}_4]_3[\text{Rh}_7(\text{CO})_{16}]$.

Recrystallization by slow diffusion of cyclohexane into a thf solution of (2) under CO gave pure crystals of $[\text{NMe}_4]_2[\text{FeRh}_4(\text{CO})_{15}]\cdot n\text{thf}$, yield 0.6 g.

The corresponding $[\text{N}(\text{PPh}_3)_2]^+$ salt of (2) was obtained similarly by dissolving the crude product, obtained in the above reaction, in methanol, instead of water, followed by precipitation, under CO, with excess $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ and water. The resulting precipitate was recrystallized as above (Found: $[\text{N}(\text{PPh}_3)_2]^+$, 50.60; Fe, 2.55; Rh, 19.15% {mol ratio $[\text{N}(\text{PPh}_3)_2]^+ : \text{Fe} : \text{Rh} = 2.07 : 1.0 : 4.19$ }. Calc. for $[\text{N}(\text{PPh}_3)_2]_2[\text{FeRh}_4(\text{CO})_{15}]\cdot 2\text{thf}$: $[\text{N}(\text{PPh}_3)_2]^+$, 51.05; Fe, 2.65; Rh, 19.55% { $[\text{N}(\text{PPh}_3)_2]^+ : \text{Fe} : \text{Rh} = 2 : 1 : 4$ }).

Synthesis of $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2) from $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3).—The complex $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]$ (0.5 g) was dissolved in acetone (30 cm³) and stirred under an atmosphere of CO (25 °C, 10⁵ Pa). Over 1 h the green solution became yellow-orange; this solution was then evaporated to dryness to eliminate $[\text{Fe}(\text{CO})_5]$. The residue is very soluble in most polar solvents and recrystallization as above gave pure crystals of (2).

Synthesis of $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3) from $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ and $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$.—To $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_3(\text{CO})_{11}]$ (1.75 g) in thf (25 cm³) was added a thf solution (30 cm³) containing $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (0.82 g). The resulting dark red solution was filtered and evaporated to dryness. The residue was dissolved in methanol (60 cm³), precipitated by addition of excess benzyltrimethylammonium chloride and water, filtered off and dried *in vacuo*. Extraction with thf removed any unreacted $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$, which was initially present but is essentially transformed into (3) on evacuation, and other by-products. The residue of crude $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4$

$(\text{CO})_{16}]$ was dissolved in acetone and recrystallized by slow diffusion with Pr'OH. Further product can be obtained by subjecting the above thf solution obtained on extraction to slow diffusion with Pr'OH. The overall yield of (3) is ca. 50% based on rhodium (Found: $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, 23.10; Fe, 8.40; Rh, 32.05% {mol ratio $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+ : \text{Fe} : \text{Rh} = 1.0 : 0.98 : 2.02$ }. Calc. for $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]$: $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, 23.60; Fe, 8.80; Rh, 32.30% { $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+ : \text{Fe} : \text{Rh} = 1 : 1 : 2$ }).

The corresponding $[\text{NET}_4]^+$ salt of (3) was obtained similarly.

Synthesis of $[\text{FeRh}_5(\text{CO})_{16}]^-$ (4) from $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ via $[\text{Fe}_2\text{Rh}(\text{CO})_x]^-$ (1).—To a stirred solution of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_3(\text{CO})_{11}]$ (0.503 g) in thf (15 cm³) was slowly added $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (0.507 g) in thf (20 cm³). The resulting brown solution was filtered and then evaporated to dryness. The crude residue was dissolved in methanol (50 cm³), precipitated by addition of excess $[\text{NMe}_3(\text{CH}_2\text{Ph})]\text{Cl}$ and water, filtered off and dried *in vacuo*. The brown solid was extracted with dichloromethane, which was then subjected to slow diffusion with heptane, to give brown crystals of $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{FeRh}_5(\text{CO})_{16}]$ (4) (yield 0.35 g, 57%).

Synthesis of $[\text{FeRh}_5(\text{CO})_{16}]^-$ (4) from $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (2).—A solution of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (0.09 g, 0.23 mmol) in thf (5 cm³) was added to a stirred solution of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeRh}_4(\text{CO})_{15}]$ (0.85 g, 0.43 mmol) under nitrogen. The resulting brown solution was evaporated to dryness. The residue was washed with n-hexane (2 × 20 cm³), suspended in methanol (30 cm³) and precipitation completed by addition of excess $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ and water. The dark solid was filtered off, dried *in vacuo* and recrystallized by slow diffusion from dichloromethane–heptane (ca. 1 : 10) in ca. 80% yield.

Synthesis of $[\text{FeRh}_5(\text{CO})_{16}]^-$ (4) from $[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]^{2-}$ (3).—To a stirred solution of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{Fe}_2\text{Rh}_4(\text{CO})_{16}]$ (0.5 g) in acetonitrile (25 cm³) was added phosphoric acid (48%, ca. 1 cm³). The initial green solution turned brown over 1 h when the solution was evaporated to dryness and the residue dissolved in methanol. Addition of excess $[\text{NMe}_3(\text{CH}_2\text{Ph})]\text{Cl}$ and water to this solution caused precipitation of $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{FeRh}_5(\text{CO})_{16}]$ which was purified as described above (Found: $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, 12.90; Fe, 4.60; Rh, 43.85% {mol ratio $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+ : \text{Fe} : \text{Rh} = 1 : 0.96 : 4.95$ }. Calc. for $[\text{NMe}_3(\text{CH}_2\text{Ph})][\text{FeRh}_5(\text{CO})_{16}]$: $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, 12.85; Fe, 4.80; Rh, 44.05% { $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+ : \text{Fe} : \text{Rh} = 1 : 1 : 5$ }).

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