X-Ray Crystallographic Determination of the Structure of $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$—a Complex with an Unexpected Distribution of Ligands Around a Tetrahedral Cluster of Metal Atoms

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Summary The molecular structure of $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$ has been determined by single-crystal *X*-ray diffraction techniques.

THE reaction of $[(\pi\text{-}C_5H_5)Rh(CO)_2]$ and $Fe_2(CO)_9$ has been shown[1] to give rise to an interesting series of trinuclear and tetranuclear mixed metal cluster complexes. One of these, $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$, shows an i.r. spectrum with five terminal and two bridging carbonyl stretches, and a ^{57}Fe Mössbauer spectrum which suggests two different iron environments [1] Since no unambiguous structure could be assigned to this molecule, we have subjected the compound to a single-crystal *X*-ray diffraction study.

Crystal data: $C_{18}H_{10}O_8Fe_2Rh_2$, $M = 671{\cdot}78$, orthorhombic, $a = 17{\cdot}979(15)$, $b = 12{\cdot}079(12)$, $c = 9{\cdot}386(8)$ Å, $U = 2038{\cdot}3$ Å^3, $D_m = 2{\cdot}11$, $D_c = 2{\cdot}188$ gcm^{-3}, $Z = 4$, space group *Pnma* (D^{16}_{2h}, No. 62).

Diffraction data to $\sin\theta = 0{\cdot}38$ (Mo-K_α radiation) were collected on a Supper-Pace "Buerger Automated Diffractometer" and were corrected for absorption ($\mu = 30{\cdot}15$ cm^{-1}). The structure was solved by Patterson, Fourier, and least-squares refinement techniques. All non-hydrogen atoms have been located, the present discrepancy index being $R = 7{\cdot}90\%$ for the 627 independent non-zero reflections.

As shown in Figure 1, the molecule has precise (*i.e.*, crystallographically-dictated) C_s symmetry, with the

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molecular mirror plane passing through Fe(1), Fe(2), C(1), O(1), C(3), O(3), C(4), O(4), C(6), O(6). Distances within the tetrahedral metal atom cluster are: Fe(1)–Fe(2) = 2·539(7), Fe(1)–Rh = Fe(1)–Rh′ = 2·570(5), Fe(2)–Rh = Fe(2)–Rh′ = 2·589(5), and Rh–Rh′ = 2·648(4) Å. Ligands are distributed among metal centres in the following way: one π-C_5H_5 ligand is associated with each rhodium atom, and a carbonyl group bridges the two rhodium atoms [Rh–C(1) = Rh′–C(1) = 1·96(4) Å]; two carbonyl groups [C(3)–O(3) and C(4)–O(4)] are attached terminally to Fe(2) and three to Fe(1). The remaining two carbonyl ligands [C(2)–O(2) and the symmetry-related C(2′)–O(2′)] are involved in asymmetric bridge systems in which Fe(2)–C(2) = 1·79(4) and Rh · · · C(2) = 2·18(3) Å.‡ The Fe(1) · · · C(2) distance of 2·81(4) Å is essentially non-bonding.

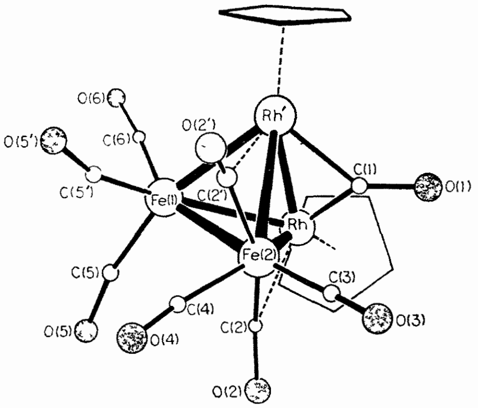
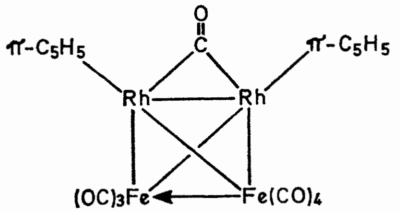


FIGURE 1. *The molecular structure of* $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$. *Atoms lying in and below the molecular mirror plane are numbered normally. Atoms lying above the mirror plane are numbered with a prime.*

It is pertinent to note that similarly asymmetric M–(CO)–M bridges have previously been reported for $[Fe_4(CO)_{13}{}^{2-}]$,[2] a species isoelectronic with the unknown (and, apparently, sterically unattainable[2]) $Fe_4(CO)_{14}$, which, along with the present $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$ and with $[(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}]$[1] (presently under crystallographic investigation in our laboratories), is a member of the $[(\pi\text{-}C_5H_5)_{4-n}Rh_{4-n}Fe_n(CO)_{3n+2}]$ series.

Polynuclear transition-metal carbonyl complexes are customarily treated within the framework of the valence-bond method, with the object of showing that each metal atom achieves the appropriate noble-gas configuration. Tetrahedral metal carbonyl clusters are generally consistent with the "noble-gas rule," having 60 outer valence electrons associated with the metal atoms (18 per atom, 12 electrons being shared in metal–metal bonds). In $[(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8]$, however, while the 60-electron total is achieved, no classical valence-bond description of the observed molecular geometry is consistent with the assignment of 18 outer valence electrons to each metal atom. [(I) (Figure 2)



(I)

FIGURE 2

which ignores rhodium participation in the asymmetric Fe–(CO) · · · Rh bridges, is perhaps the closest approach.] Similar observations apply to the azulene complex $[Me_3C_{10}H_5Ru_4(CO)_9]$[3,4] and to $[Fe_4(CO)_{13}{}^{2-}]$.[2] The tetranuclear metal carbonyl clusters are therefore better treated by a molecular-orbital method; Kettle[5,6] has presented a qualitative scheme. It should be emphasized, however, that violations of the "noble-gas rule" observed in tetrahedral metal clusters usually seem to arise from stereochemical and spacial requirements of the surrounding ligands.

The weakness of the valence-bond approach is further shown by the full range of octahedral metal carbonyl cluster complexes {*e.g.*, $Co_6(CO)_{16}$,[7] $[Co_6(CO)_{15}{}^{2-}]$,[8] $[Co_6(CO)_{14}{}^{4-}]$,[9] $[Ni_2Co_4(CO)_{14}{}^{2-}]$,[10] $Rh_6(CO)_{16}$,[11] $[Rh_6(CO)_{14}{}^{4-}]$,[12] $[Rh_{12}(CO)_{30}{}^{2-}]$,[13] $Ru_6(CO)_{17}C$,[14] $[(\text{arene})Ru_6(CO)_{14}C]$,[15] $[H_2Ru_6(CO)_{18}]$[16]}, each of which has a metal skeleton which is associated with two electrons in excess of the number predicted on the basis of the "noble-gas rule." The sole heptanuclear cluster complex, $[Rh_7(CO)_{16}{}^{3-}]$,[17] also has this two-electron excess.

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‡ We believe that this is the first reported complex in which a carbonyl ligand forms a bridge from a first-row to a second- (or third-) row transition metal: *cf.* E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1969, **23**, 325, especially p. 331, lines 4—6.

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