Chemistry of the Metal Carbonyls. Part 81.[1] Homonuclear and Heteronuclear Di- and Tri-metal Carbonyl Complexes derived from Dicarbonyl(pentamethylcyclopentadienyl)rhodium; *X*-Ray Crystal Structure of [MnRh(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] †

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Treatment of [Rh(CO)$_2$(η-C$_5$Me$_5$)] with [Mn(CO)$_2$(thf)(η-C$_5$H$_5$)] (thf = tetrahydrofuran) affords [MnRh(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)], the structure of which has been determined by an *X*-ray diffraction study. The crystals are orthorhombic, space group *Pnam* (non-standard setting of *Pnma*, No. 62), in a unit cell with a = 16.851(12), b = 9.338(5), c = 11.566(9) Å, U = 1 820(2) Å^3 at 220 K, and Z = 4. The structure was solved to R 0.057 (R' 0.058) from 1 860 observable independent reflections [$I \geqslant 3.0\sigma(I)$]. The molecule possesses C_s symmetry; one terminal carbonyl ligand on each of the metal atoms, together with the Rh–Mn bond [2.703(2)Å], define the mirror plane. The cyclopentadienyl ligand on the Mn atom is in a *trans* relationship to the pentamethylcyclopentadienyl ligand on the Rh atom and both lie astride (perpendicular to) the mirror plane. The two other carbonyl ligands are terminal to the Mn atom but are strongly semi-bridging to the Rh atom [Mn–C(9) 1.866(7), Rh–C(9) 2.172(7) Å], and define planes which are nearly perpendicular to the mirror plane. A distortion of the Rh–C$_5$ geometry towards a 'diolefin' type attachment is discussed.

Reaction of [Rh(CO)$_2$(η-C$_5$Me$_5$)] with [Fe$_2$(CO)$_9$] in thf affords the compounds [FeRh(μ-CO)$_2$(CO)$_4$(η-C$_5$Me$_5$)] and [Fe$_2$Rh(μ-CO)$_2$(CO)$_7$(η-C$_5$Me$_5$)]. The latter is also formed, together with [FeRh$_2$(μ$_3$-CO)(μ-CO)$_2$(CO)$_3$(η-C$_5$Me$_5$)$_2$], on treatment of [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] with excess [Fe$_2$(CO)$_9$].

The trirhodium complex [Rh$_3$(μ$_3$-CO)(μ-CO)$_2$(η-C$_5$Me$_5$)$_3$] was obtained in high yield by pyrolysis of [Rh(CO)$_2$(η-C$_5$Me$_5$)] and undergoes dynamic behaviour in solution. Protonation of the trirhodium cluster or [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] affords quantitatively the cation [Rh$_3$(μ-H)(μ$_3$-CO)(μ-CO)$_2$(η-C$_5$Me$_5$)$_3$]$^+$ which can be deprotonated with NaOMe in MeOH.

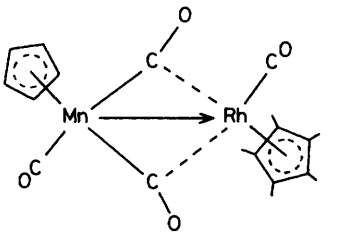
HOFFMANN and co-workers [2] have shown that the as yet unknown molecule [Rh$_2$(μ-CO)$_2$(η-C$_5$H$_5$)$_2$] has valence orbitals similar to those of C$_2$H$_4$. Thus the known anion [Rh$_3$(CO)$_4$(η-C$_5$H$_5$)$_2$]$^-$ can be regarded as a complex of [Rh$_2$(μ-CO)$_2$(η-C$_5$H$_5$)$_2$] and the 14-electron fragment Rh(CO)$_2^-$, just as [Pt(C$_2$H$_4$)L$_2$] is an adduct of C$_2$H$_4$ and the 14-electron species PtL$_2$. In accord with these analogies, it has been shown [3] that the compound prepared by Nutton and Maitlis,[4] [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$], readily reacts with platinum (d^{10}) complexes to afford trimetal clusters [PtRh$_2$(μ-CO)$_2$L$_2$(η-C$_5$Me$_5$)$_2$] (L = PPh$_3$ or CO, or L$_2$ = cyclo-octa-1,5-diene).

During the course of the work on the dirhodiumplatinum compounds it was found that the mononuclear rhodium species [Rh(CO)$_2$(η-C$_5$Me$_5$)], the precursor of [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$], could also be used to prepare compounds with heteronuclear metal–metal bonds. Herein we describe the synthesis of complexes containing rhodium–iron and –manganese bonds. Moreover, during studies on the pyrolysis of [Rh(CO)$_2$(η-C$_5$Me$_5$)] a new trirhodium cluster [Rh$_3$(μ$_3$-CO)(μ-CO)$_2$(η-C$_5$Me$_5$)$_3$] was characterised.

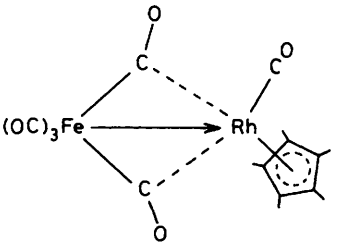
RESULTS AND DISCUSSION

Metal Carbonyl Complexes with Rhodium–Manganese and –Iron Bonds.—Addition of [Rh(CO)$_2$(η-C$_5$Me$_5$)] to a solution of [Mn(CO)$_2$(thf)(η-C$_5$H$_5$)] (thf = tetrahydrofuran) afforded, after several hours at room temperature, a yellow-brown crystalline complex [MnRh(CO)$_4$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (1). The compound was formulated on the basis of microanalysis and mass spectroscopy. In addition to the parent ion (*m/e* 470), the mass spectrum showed ions corresponding to the successive loss of four CO groups, and to the species Rh(CO)(C$_5$Me$_5$) and Mn(CO)$_3$(C$_5$H$_5$).

The i.r. spectrum (hexane), with bands at 1 983, 1 935, 1 818, and 1 807 cm^{-1}, revealed the presence of both terminal and bridging CO ligands. The ^{1}H n.m.r. spectrum showed that η-C$_5$H$_5$ and η-C$_5$Me$_5$ ligands were



(1)



(2)

† Di-μ-carbonyl-1,2-dicarbonyl-2-η^5-cyclopentadienyl-1-η^5-pentamethylcyclopentadienylrhodium–manganese (*Rh*^{1}–*Mn*^{2}).

present. The ^{13}C n.m.r. spectrum had signals for CO ligands at δ 252.2, 227.6, and 188.3 p.p.m. (relative intensity 2 : 1 : 1) with the latter resonance a doublet [J(RhC) 84 Hz], indicating that it was due to a terminal CO on rhodium. The most intense peak at 252.2 p.p.m. was also a doublet, but the relatively low ^{103}Rh–^{13}C coupling (22 Hz) suggested that it was due to a $Mn(\mu\text{-}CO)_2Rh$ group. In contrast the signal at 227.6 p.p.m. was a singlet and, moreover, the chemical shift is close to that observed (δ 225 p.p.m.) in $[Mn(CO)_3(\eta\text{-}C_5H_5)]$ (ref. 5), and thus may be assigned to a terminal MnCO group. Since the spectroscopic properties of (1) did not define the molecular structure unambiguously a single-crystal X-ray diffraction study was undertaken.

The results of this study are summarised in Tables 1 and 2 and the structure of the molecule is shown in Figure 1 with the crystallographic numbering. The molecule is required crystallographically to possess mirror symmetry, the mirror plane being defined by the atoms Mn, Rh, C(4), C(1), C(11), C(7), O(7), C(8), and O(8). Thus, as the carbonyl group C(9)–O(9) is ' terminal ' to the manganese atom and ' semi-bridging ' to the rhodium atom, its mirror-related group C(9′)–O(9′) is necessarily similarly related to the two metal atoms. The 18-electron rule would, therefore, indicate that the Mn–Rh bond be regarded as a donor bond of order one, with the manganese atom as the donor. The effects of any

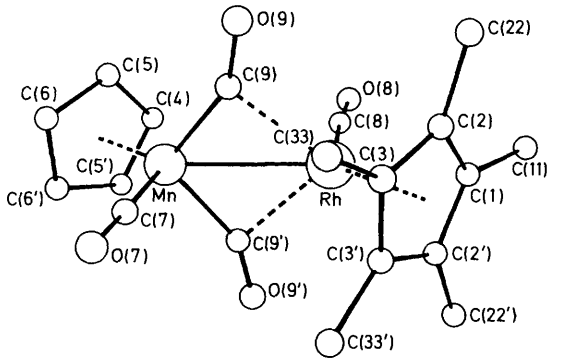


FIGURE 1 Molecular structure of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (1), showing the crystallographic numbering

associated polarity are discussed below. The length of the Mn–Rh bond [2.703(2) Å] is less than that of the only other Mn–Rh bond known to us to have been measured, *viz.* 2.894(5) Å (mean) in the complex $[(CO)_5Mn\text{-}Rh\{\mu\text{-}CNCMe_2CH_2CH_2CMe_2NC\}_4Rh\text{-}Mn(CO)_5]$ and in which the Rh–Rh distance is 2.922(2) Å.[6] The ' semi-bridging ' carbonyls make an interesting study, in that the difference between the two metal–carbon distances is not great [Mn–C(9) 1.866(7), Rh–C(9) 2.172(7) Å] while the distortion from linearity relative to the Mn atom is large [Mn–C(9)–O(9) 153.0(6), Rh–C(9)–O(9) 123.3(5)°]. The planes defined by Mn, Rh, and the two bridging carbonyl ligands are both nearly, but not quite, perpendicular to the molecular mirror plane [interplanar angle 173° with the concave side facing the terminal carbonyl group C(7)–O(7)]. The metal–carbon bond length for the terminal carbonyl ligand on the manganese atom is appreciably shorter than that for the semi-bridging carbonyl, at 1.784(12) Å. The cyclopentadienyl ring and the

TABLE 1

Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (1)

Atom	x	y	z
Rh	0.082 21(4)	0.037 93(7)	0.2500 *
Mn	0.167 49(9)	−0.207 2(2)	0.2500
C(1)	0.034 0(6)	0.257 0(9)	0.2500
C(2)	0.083 6(5)	0.248 5(6)	0.350 9(6)
C(3)	0.160 1(4)	0.225 4(6)	0.312 5(5)
C(11)	−0.052 6(8)	0.289 9(13)	0.2500
C(22)	0.055 9(6)	0.265 0(10)	0.474 9(7)
C(33)	0.234 1(5)	0.216 0(9)	0.387 2(8)
C(4)	0.080 4(10)	−0.377 3(13)	0.2500
C(5)	0.130 5(6)	−0.392 2(8)	0.347 5(10)
C(6)	0.208 7(5)	−0.411 1(7)	0.310 0(7)
C(7)	0.265 4(7)	−0.134 6(12)	0.2500
O(7)	0.329 4(6)	−0.094 6(9)	0.2500
C(8)	−0.014 8(6)	−0.058 9(10)	0.2500
O(8)	−0.075 7(5)	−0.110 2(9)	0.2500
C(9)	0.136 5(4)	−0.100 3(7)	0.378 6(6)
O(9)	0.133 4(4)	−0.077 9(5)	0.478 7(5)

* Those atoms lying in the mirror plane have their z co-ordinates fixed at 0.25.

pentamethylcyclopentadienyl ring are in a *trans* relationship to one another, and the planes of the C_5 rings are parallel within 0.1°, though as often happens[7] the methyl groups of the latter bend back slightly from the plane of the ring, away from the rhodium atom (r.m.s. deviation 0.087 Å). The steric relationships of the various parts of the molecule are clearly seen from the stereopair drawing (Figure 2).* Finally, a subtlety in the bonding of the pentamethylcyclopentadienyl ring to the Rh atom may be noted. Because of the methyl substituents, the atoms of the C_5 ring are much less active thermally than are those of the C_5H_5 ring and so, although the accuracy of the structure determination is not particularly high, evidence of differences in bond lengths will be more apparent for the Rh-C_5Me_5 moiety than for the Mn-C_5H_5. Now, in the C_5Me_5 ring only atoms C(1), C(2), and C(3) are crystallographically distinct [C(1) being in the mirror plane] but the Rh–C distances differ by as much as 0.1 Å, with Rh–C(1) <

* It is illuminating to compare the structure of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ with that[8] of $[CrNi(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$. This latter compound may be considered as a combination of two 17-electron fragments, $Cr(CO)_3(\eta\text{-}C_5H_5)$ and $Ni(CO)(\eta\text{-}C_5H_5)$. With little or no polarity in the metal–metal bond, and with each metal atom retaining one terminal carbonyl ligand, the other two carbonyl groups are only weakly semi-bridging, as evidenced by (*i*) the similarity of the Cr–C(O) terminal and semi-bridging distances [1.84(2) and 1.88(1) Å, respectively], (*ii*) the considerably longer Ni–C(O) semi-bridge distance [2.43(1) Å], (*iii*) the Cr–C–O angle which is more nearly linear at 168°, and (*iv*) i.r. stretching frequencies of 1 910 and 1 890 cm^{-1}. The complex $[CrNi(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ is isoelectronic and also virtually isosteric with $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$. The authors of ref. 8 consider that the molecular geometry in such complexes, including the variation of metal–metal distances and the different folding of the molecular frames along the M–M connection, is determined predominantly by the intramolecular packing of ligands.

TABLE 2

Bond lengths (Å) and angles (°) for the compound [MnRh(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (1) with estimated standard deviations in parentheses

(*i*) Distances

Rh–Mn	2.703(2)	Mn–C(4)	2.162(15)
Rh–C(1)	2.201(9)	Mn–C(5)	2.154(9)
Rh–C(2)	2.287(6)	Mn–C(6)	2.142(7)
Rh–C(3)	2.305(6)	Mn–C(7)	1.784(12)
Rh–C(8)	1.867(10)	Mn–C(9)	1.866(7)
Rh–C(9)	2.172(7)	C(4)–C(5)	1.414(15)
C(1)–C(2)	1.437(9)	C(5)–C(6)	1.399(14)
C(2)–C(3)	1.382(10)	C(6)–C(6′)	1.389(16)
C(3)–C(3′)	1.446(12)	C(7)–O(7)	1.142(15)
C(1)–C(11)	1.491(17)	C(8)–O(8)	1.133(13)
C(2)–C(22)	1.515(11)	C(9)–O(9)	1.178(9)
C(3)–C(33)	1.519(11)		
cp(1)–Rh *	1.932	cp(2)–Mn *	1.789

(*ii*) Angles

Mn–Rh–C(8)	93.2(3)	Rh–Mn–C(7)	99.8(4)
Mn–Rh–C(9)	43.3(2)	Rh–Mn–C(9)	53.0(2)
C(7)–Mn–C(9)	93.1(3)	C(8)–Rh–C(9)	94.7(3)
C(2)–C(1)–C(11)	125.4(4)	C(33)–C(3)–C(3′)	124.7(4)
C(1)–C(2)–C(22)	125.8(7)	C(2)–C(1)–C(2′)	108.6(9)
C(3)–C(2)–C(22)	127.4(7)	C(1)–C(2)–C(3)	106.8(6)
C(2)–C(3)–C(33)	126.3(6)	C(2)–C(3)–C(3′)	108.8(4)
C(5)–C(4)–C(5′)	105.7(14)	Rh–C(8)–O(8)	176.0(9)
C(4)–C(5)–C(6)	109.1(10)	Rh–C(9)–O(9)	123.3(5)
C(5)–C(6)–C(6′)	108.0(6)	Rh–C(9)–Mn	83.7(3)
Mn–C(7)–O(7)	176.8(10)	cp(1)–Rh–Mn *	136.8
Mn–C(9)–O(9)	153.0(6)		
cp(2)–Mn–Rh *	139.3		

* cp(1) is the centroid of the pentamethylcyclopentadienyl ring; cp(2) is the centroid of the cyclopentadienyl ring.

Rh–C(2) < Rh–C(3) (Table 2). Moreover, the ring C–C bond lengths are strongly suggestive of a 'diolefin' distortion of the pentagonal structure, with C(2)–C(3) and C(2′)–C(3′) as the short bonds. The differences here are not as well established, but fit in exactly with the pattern found in a very accurate combined *X*-ray- and

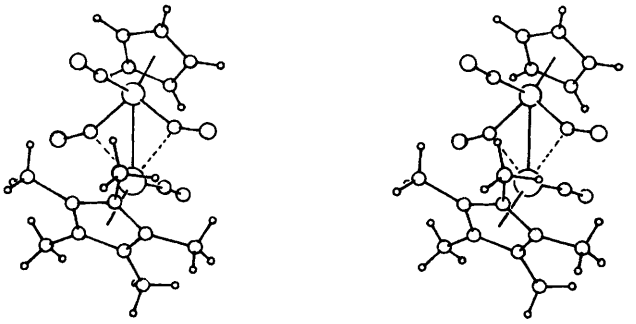


FIGURE 2 Stereoscopic view of the molecular structure of complex (1)

neutron-diffraction study of the *trans* isomer of [Fe$_2$(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)$_2$] at liquid nitrogen temperature.[9]

The structure of (1) established by the *X*-ray diffraction study is in accord with the observed spectroscopic properties discussed earlier. In particular, the i.r. bands at 1 818 and 1 807 cm^{-1} may be ascribed to the semi-bridging CO ligands.

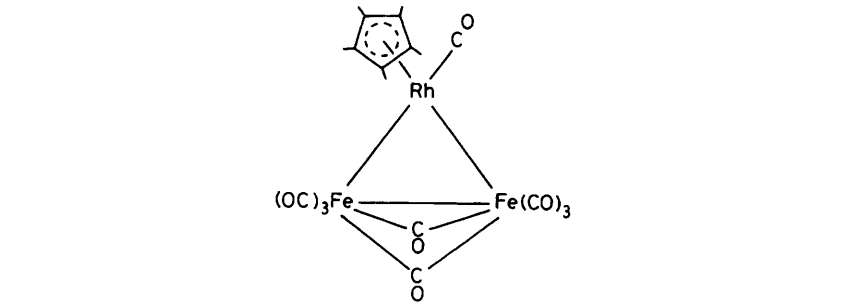
As mentioned above, the metal–metal interaction in (1) can be regarded as arising from donation of an electron pair from the 18-electron species Mn(CO)$_3$(η-C$_5$H$_5$) to the 16-electron group Rh(CO)(η-C$_5$Me$_5$). An analysis of the bonding in Mn(CO)$_3$(η-C$_5$H$_5$) and measurement of the He(I) photoelectron spectra show that the highest occupied molecular orbital (h.o.m.o.) is associated predominantly with the metal.[10] The electron pair in this orbital can be donated to the rhodium atom of the Rh(CO)(η-C$_5$Me$_5$) group, the lowest unoccupied molecular orbital (l.u.m.o.) of the latter[11] being directed towards the manganese. The polar Mn ⟶ Rh σ bond produced would lead to asymmetric CO bridging to mitigate charge imbalance, as proposed by Cotton[12] for [V$_2$(μ-CO)$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$]. In (1) the Rh–μ-CO interaction would result from overlap of the h.o.m.o. of the rhodium fragment with the π^* orbitals of the two CO ligands. Bending of the latter groups will enhance the bonding interaction Rh · · · C while allowing antibonding Rh · · · O to decrease.[13]

Compound (1) is also formed, but in lower yield, from the reaction of [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] and [Mn(CO)$_2$(thf)(η-C$_5$H$_5$)]. An unstable MnRh$_2$ species may be an intermediate in this process. From the reaction between [Co$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] and u.v. irradiated [Mn(CO)$_3$(η-C$_5$H$_4$Me)], Dahl and co-workers[14] have isolated the trimetal cluster [MnCo$_2$(μ-CO)$_3$(μ_3-CO)(η-C$_5$H$_4$Me)(η-C$_5$Me$_5$)$_2$]. The latter is stable, and it is therefore surprising that we did not isolate an analogous MnRh$_2$ compound.

Formation of (1) from [Rh(CO)$_2$(η-C$_5$Me$_5$)] involves CO ligand transfer to manganese. A similar transfer occurs in the synthesis of [CoMn(μ-CO)$_2$(CO)(PMe$_3$)(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)] from [Co(CO)(PMe$_3$)(η-C$_5$H$_5$)] and [Mn(CO)$_2$(thf)(η-C$_5$H$_4$Me)].[15] Interestingly, the cobalt–manganese compound was originally synthesized by reacting [Co(PMe$_3$)$_2$(η-C$_5$H$_5$)] with [Mn(CO)$_3$(η-C$_5$H$_4$Me)], which probably proceeds *via* the 16-electron species Co(PMe$_3$)(η-C$_5$H$_5$) formed by phosphine dissociation.[16] The structure of [CoMn(μ-CO)$_2$(CO)(PMe$_3$)(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)] is likely to be similar to that of (1), when established.[17]

Reaction of [Rh(CO)$_2$(η-C$_5$Me$_5$)] with [Fe$_2$(CO)$_9$] in thf at room temperature affords the compounds [FeRh(μ-CO)$_2$(CO)$_4$(η-C$_5$Me$_5$)] (2) (30%) and [Fe$_2$Rh(μ-CO)$_2$(CO)$_7$(η-C$_5$Me$_5$)] (3) (40%). Treatment of [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] with excess [Fe$_2$(CO)$_9$] in thf affords two trimetal clusters, namely (3) (20%) and [FeRh$_2$(μ_3-CO)(μ-CO)$_2$(CO)$_3$(η-C$_5$Me$_5$)$_2$] (4) (60%). These compounds were characterised by microanalysis, field-desorption mass spectrometry, and i.r. and n.m.r. spectroscopy.

The i.r. spectrum of (2) in the carbonyl region (see Experimental section) had two bands (1 835 and 1 825 cm^{-1}) assignable to asymmetrically bridging CO ligands. The complex is isoelectronic with (1) and we propose a similar structure. The di-ironrhodium compound (3) is analogous to the product [Fe$_2$Rh(μ-CO)$_2$(CO)$_7$(η-C$_5$H$_5$)] obtained[18] by reacting [Fe$_2$(CO)$_9$] with [Rh(CO)$_2$(η-C$_5$H$_5$)]. Both (3) and [Fe$_2$Rh(μ-CO)$_2$(CO)$_7$(η-C$_5$H$_5$)] can be regarded as structurally related to [Fe$_3$(CO)$_{12}$] with the Fe(CO)$_4$ group in the latter replaced by the isolobal Rh(CO)(η-C$_5$R$_5$) (R = Me or H) groups.



(4)

The cluster compound (4) has bands in its i.r. spectrum (see Experimental section) corresponding to the presence in the structure of μ-CO (1 837 and 1 801 cm^{-1}) and μ_3-CO (1 690 cm^{-1}) ligands. The appearance in the ^{13}C n.m.r. spectrum of two broad resonances for the CO groups suggests that site exchange of these ligands occurs on the n.m.r. time-scale. The stoicheiometry of (4) is consistent with the expected addition of $Fe(CO)_4$ to the donor and acceptor orbitals [2] of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. In previous work we have shown [3] that PtL_2 groups, isolobal with $Fe(CO)_4$, react with the dirhodium compound in a similar manner. A dicobaltiron compound $[Co_2Fe(\mu\text{-}CO)_2(\mu_3\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)_2]$ has recently been prepared [14] and its i.r. spectrum is very similar to that of (4), and it is likely that the two compounds have similar structures. On this basis structure (4a) is proposed for the $FeRh_2$ species in the solid state since this geometry has been established for the dicobaltiron compound by *X*-ray diffraction.[14] Related to (4) is the compound $[FeRh_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, prepared in trace quantity by refluxing $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe_2(CO)_9]$ in light petroleum.[18] However, $[FeRh_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ has been assigned a structure similar to (4b) on the basis of its limiting ^{13}C n.m.r. spectrum (−70 °C) which showed a triplet signal [J(RhC) 50 Hz] at δ 234.5 p.p.m. and two equal intensity singlet resonances at 190.0 and 193.3 p.p.m.[19] Since the i.r. spectrum of (4) in the CO region shows more bands than expected for (4a) and, as mentioned above, the ^{13}C n.m.r. spectrum indicates dynamic behaviour, we suggest that in solution there is an equilibrium between (4a) and (4b). In this connection it is interesting that in solution $[Co_2Fe(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_3(\eta\text{-}C_5Me_5)_2]$ exists as a mixture of two isomers, as revealed by ^1H n.m.r. measurements.[14]

In contrast to the earlier study [18] on the products of the reaction of $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe_2(CO)_9]$, in employing $[Rh(CO)_2(\eta^5\text{-}C_5Me_5)]$ we have not observed any tetranuclear Fe_2Rh_2 and Fe_3Rh species. This is probably due to the more sterically demanding $\eta\text{-}C_5Me_5$ ligand. Thus even in $[Fe_3Rh(CO)_{11}(\eta\text{-}C_5H_5)]$ the co-ordination surface of the metal core is so crowded that distortions occur through ligand intramolecular interactions.[20] A similar compound containing $\eta\text{-}C_5Me_5$ could well be unstable.

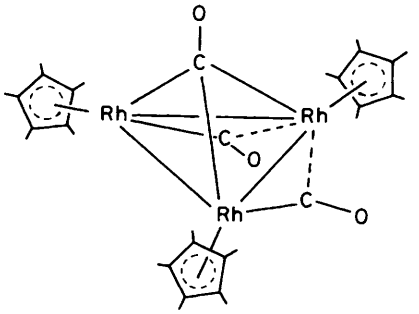
Pentamethylcyclopentadienyl-dirhodium and -trirhodium Complexes.—The compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ was first prepared by heating $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ to 80—85 °C at low pressures (10—20 mmHg *).[4] We have found that treatment of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ with anhydrous Me_3NO in acetone at reflux affords $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ in near quantitative yield. We have also investigated the reaction of the indenyl complex $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ with Me_3NO and find that the trirhodium compound [21] $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_9H_7)_3]$ is formed selectively in acetone at −50 °C.

The reagent Me_3NO has been used previously to obtain from $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ the polynuclear rhodium compounds $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$, $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$, and $[Rh_4(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_4]$.[22] We find that the $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$–$Me_3NO$ system is highly selective, no doubt due to the thermal sensitivity of $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_2]$ and the low solubility of the desired complex $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ in acetone. Herrmann *et al.*[23] have recently reported the synthesis of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ by heating $Me_3NO{\cdot}2H_2O$ with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ in acetone but in addition obtained an oxo-complex $[Rh_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(\eta\text{-}C_5Me_5)_3]$. The latter product probably arises from the use of the trimethylamine oxide as its dihydrate. We have isolated a trirhodium complex in low yield from our system, but this species is

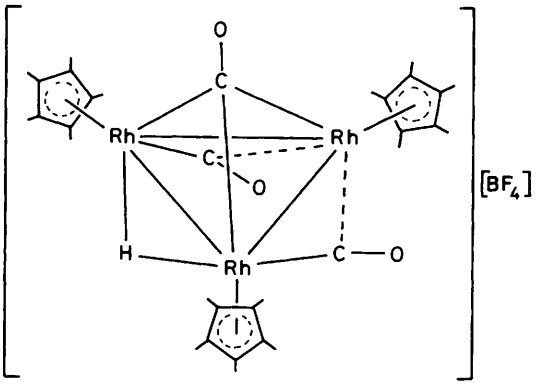
* Throughout this paper: 1 mmHg = (101 325/760) Pa; 1 cal = 4.184 J.

not the oxo-complex, and awaits characterisation by *X*-ray crystallography.

Although formally $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ contains a double Rh=Rh bond a theoretical study [2] on molecules of this type indicates little direct metal–metal bonding, the molecule being mainly held together *via* electron delocalization through the bridging CO ligands. From the ^{13}C n.m.r. spectrum we have measured the chemical shift of the CO ligands at δ 251 p.p.m. with $J(RhC)$ = 55 Hz. This large coupling is consistent with a substantial contribution of the rhodium 5*s* orbitals to the



(5)



(6)

Rh–CO bonds,[24] in accord with strong σ bonding. Moreover, the very low carbonyl stretching frequency (1 732 cm^{-1}) in the i.r. indicates extensive electron delocalization from rhodium into the π^* orbitals of the CO ligands.

In our initial attempts to obtain $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ by pyrolysis of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (80—200 °C, 1—30 mmHg) we isolated (20—60% yield) purple crystals of a compound formulated as $[Rh_3(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ (5). The mass spectrum showed a parent ion. The i.r. spectrum in the solid (Nujol) and in solution showed only three strong bands in the CO stretching region; in hexane at 1 816, 1 777, and 1 655 cm^{-1}. The band at lowest frequency corresponds to a μ_3-CO group, and the two of higher energy to μ-CO ligands.

The ^{13}C n.m.r. spectrum is invariant from −90 to 90 °C, and shows two low-field quartets (relative intensity 1 : 2) assigned to CO groups coupling to three rhodium nuclei. Moreover, only one resonance is observed for the C_5Me_5 groups. These data indicate that the CO ligands are undergoing site exchange, but the mechanism does not equilibrate all three CO groups at room temperature.

The structure assigned for (5) is similar to that established for $[Co_3(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_3]$ and for $[Co_3(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_4Me)(\eta\text{-}C_5Me_5)_2]$ by *X*-ray crystallography.[14,25] Although $[Co_3(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_3]$ has a very similar i.r. spectrum to that of the rhodium analogue (5) when measured in Nujol ($\nu_{max.}$ 1 833, 1 775, and 1 673 cm^{-1}), the i.r. spectrum measured in solution is different and depends on solvent polarity. In contrast to this behaviour, as mentioned above, the spectrum of (5) does not vary between solution and solid state. The spectral properties of the tricobalt compound in solution have been attributed [25] to an equilibrium between isomers, one species with a structure like (5) and the other having a structure in which two of the CO ligands doubly bridge one Co–Co bond while the third cobalt atom carries a terminal CO ligand. The latter structure is adopted by $[Co_3(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_4Me)_3]$ both in solution and in the solid state.[25] This C_s structure is also possessed by one of the two interconvertible isomers of $[Rh_3(CO)_3(\eta\text{-}C_5H_5)_3]$ while the other has a structure $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ with C_{3v} symmetry.[26] Both isomers of $[Rh_3(CO)_3(\eta\text{-}C_5H_5)_3]$ undergo CO site exchange at room temperature.[22,27]

The C_s isomer $[Rh_3(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_3]$ exhibits a quartet for the carbonyl groups in its ^{13}C n.m.r. spectrum at 25 °C, implying that each CO group traverses both faces of the Rh_3 triangle. However, at −120 °C the resonance pattern observed is two quartets [$J(RhC)$ 28 and 31 Hz] of relative intensity 1 : 2. Thus the expected limiting spectrum (doublet for the terminal and a triplet for the bridging CO ligands) was not observed, even at −156 °C. The C_{3v} isomer $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ also exhibits in the ^{13}C n.m.r. spectrum a quartet for the CO groups at 25 °C but at −65 °C the limiting spectrum, a triplet, is reached. The related species $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_9H_7)_3]$ does not undergo dynamic behaviour involving the CO ligands.[21]

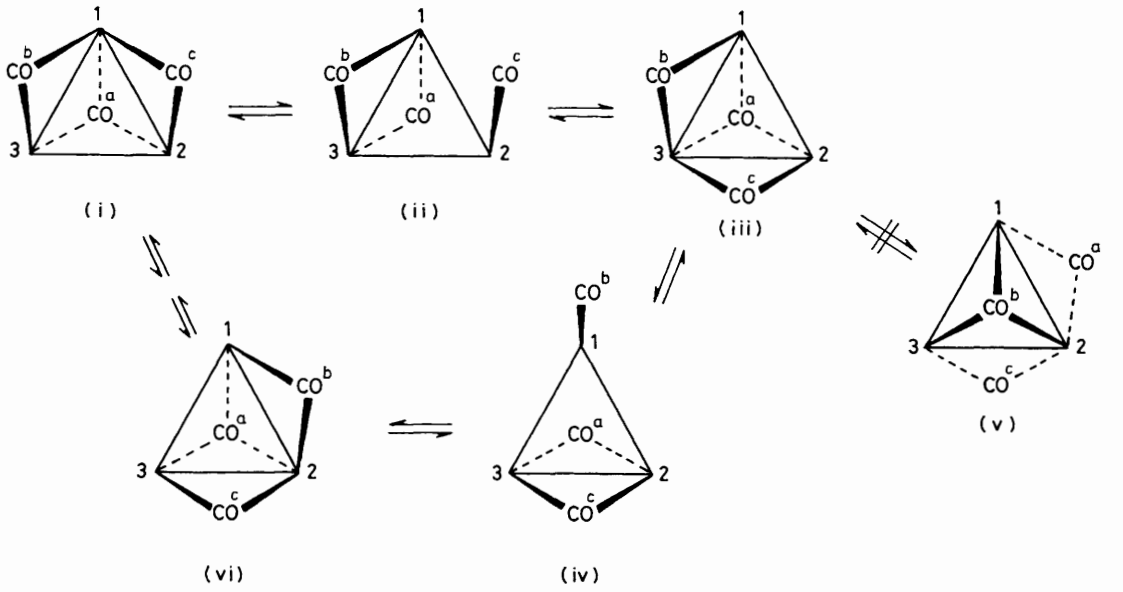
The behaviour of these various trirhodium complexes suggests that the mechanism for CO site exchange for (5) is as shown in the Scheme. The process is similar to that proposed [27] to account for the ^{13}C n.m.r. data for the C_s isomer of $[Rh_3(CO)_3(\eta\text{-}C_5H_5)_3]$, except that for (5) the C_s structure is suggested as the transition state in the rearrangement pathway. Since in (5) the μ-CO groups do not exchange with the μ_3-CO (Scheme, b or c exchanging with a), as evidenced by failure of the two quartets to coalesce even at 90 °C, the edge–face and face–edge movement [Scheme, (iii)→(v)] postulated [27] for $[Rh_3(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_3]$ does not occur with the $\eta\text{-}C_5Me_5$ derivative, probably for steric reasons. Since the ^{13}C n.m.r. spectrum of (5) is not limiting even at −90 °C (*viz.* a triplet or doublet of doublets for the μ-CO groups, and a quartet or doublet of triplets for the μ_3-CO group), the energy of activation for μ-CO site exchange must be

very small. This is consistent with the results [27] for $[Rh_3(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_3]$ where $\Delta G^{\ddagger}$ (−156 °C) ≈4.8 kcal mol^{-1}.

Compound (5) is also formed, albeit slowly, by the reaction of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ in light petroleum or dichloromethane at room temperature. Thus formation of (5) by pyrolysis of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ probably occurs *via* the dirhodium species.

Protonation of (5) with HBF_4 in diethyl ether affords the salt (6) in quantitative yield. The i.r. spectrum (Experimental section) resembles that of (5) in the CO region, except that the bands are shifted by *ca.* 40 cm^{-1} to higher frequency. The ^{1}H n.m.r. spectrum shows two η-C_5Me_5 environments (relative intensity 2 : 1), and a resonance at δ −20.45 p.p.m., appearing as a triplet [J(RhH) 25 Hz], and assignable to an edge bridging hydrido-ligand in accord with the structure proposed for the salt (6). The ^{13}C n.m.r. spectrum was also as expected. There were signals corresponding to two η-C_5Me_5 environments. Two CO resonances (relative intensity 1 : 2) can be assigned to triply-bridging and edge-bridging carbonyl groups, respectively. These signals were a doublet of triplets and a doublet of doublets in accord with the μ_3-CO and μ-CO being asymmetrically bridging. The structure of (6) is related to that established for the cation $[Rh_3(\mu_3\text{-}CH)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_3]^+$ (refs. 28 and 29), but the CO ligands in this species (6) do not site-exchange.

The salt (6) can also be formed by protonation of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Interestingly, protonation of $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ yields $[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ *via* $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]^+$ (ref. 30), and protonation of $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ gives the trirhodium cation $[Rh_3(\mu_3\text{-}CH)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_3]^+$ *via* the dirhodium species $[Rh_2(\mu\text{-}CH_2)(\mu\text{-}H)(CO)_2(\eta\text{-}C_5H_5)_2]^+$ (ref. 28). Unfortunately, we were unable to isolate a dinuclear rhodium intermediate with a μ-H ligand *via* protonation of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Finally, deprotonation of (6) with NaOMe in MeOH affords (5) quantitatively.



SCHEME Possible mechanism for CO site exchange in complex (5)

EXPERIMENTAL

The instrumentation used and the experimental techniques employed were as described earlier.[3] For ^{13}C n.m.r. spectra chemical shifts are in p.p.m. relative to $SiMe_4$, with positive values to high frequency of the reference. Tris(acetylacetonato)chromium(III) was added to reduce relaxation times. Anhydrous Me_3NO was prepared by heating the dihydrate at *ca.* 100 °C *in vacuo*.

Synthesis of Rhodium–Manganese and –Iron complexes.—(*a*) The compound $[Mn(CO)_3(\eta\text{-}C_5H_5)]$ (0.365 g, 1.79 mmol) in thf (50 cm^3) was irradiated with u.v. for 2 h at 0 °C under argon. The solution was then treated with $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.259 g, 0.88 mmol) and the mixture stirred at room temperature for 18 h. Removal of solvent and chromatography afforded unreacted $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Mn(CO)_3(\eta\text{-}C_5H_5)]$ followed by yellow-brown *crystals* of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (1) (0.327 g, 79%), m.p. 158—160 °C (Found: C, 48.7; H, 4.5; *M*, 470. $C_{19}H_{20}MnO_4Rh$ requires C, 48.5; H, 4.3%; *M*, 470); $\nu_{max.}$(CO) at 1 997 (sh), 1 991s, 1 921vs, 1 809w, and 1 788vs cm^{-1} (Nujol); 1 983s, 1 935vs, 1 818w (sh), and 1 807s cm^{-1} (hexane). N.m.r.: ^{1}H ([$^2H_1$]chloroform), δ 1.84 (s, 15 H, C_5Me_5) and 4.62 p.p.m. (s, 5 H, C_5H_5); ^{13}C ([$^2H_2$]dichloromethane–CH_2Cl_2), δ 252.2 [d, 2 C, μ-CO, J(RhC) 22], 227.6 (s, 1 C, MnCO), 188.3 [d, 1 C, RhCO, J(RhC) 84 Hz], 105.0 (C_5Me_5), 86.5 (C_5H_5), and 8.9 p.p.m. (C_5Me_5). Electron-impact (e.i.) mass spectrum *m/e* 470 (*P*), 442 (*P* − CO), 414 (*P* − 2CO), 386 (*P* − 3CO), 358 (*P* − 4CO), 303 [Rh(C_5H_5)(C_5Me_5)], 294 [$Rh(CO)_2(C_5Me_5)$], 266 [Rh(CO)(C_5Me_5)], 238 [$Rh(C_5Me_5)$], 204 [$Mn(CO)_3(C_5H_5)$], 176 [$Mn(CO)_2(C_5H_5)$], 168 [$Rh(C_5H_5)$], 148 [Mn(CO)(C_5H_5)], 120 [Mn(C_5H_5)], and 55 (Mn).

(*b*) The compounds $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.50 g, 0.94

mmol) and $[Fe_2(CO)_9]$ (0.5 g, 1.34 mmol) were stirred in thf (10 cm^3) at room temperature for 24 h. Solvent and $[Fe(CO)_5]$ were removed *in vacuo* and the residue was chromatographed. The first band eluted with light petroleum afforded green *crystals* of $[Fe_2Rh(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5Me_5)]\cdot 0.5\,Et_2O$ (3) (0.100 g, 18%), m.p. >250 °C (decomp.) (Found: C, 39.4; H, 3.0; *M* [field desorption (f.d.)], 602. $C_{19}H_{15}Fe_2O_9Rh\cdot 0.5\,C_4H_{10}O$ requires C, 39.5; H, 3.2%; *M*, 602); $\nu_{max.}$ (CO) at 2 061vs, 2 019vs, 2 005s, 1 997 (sh), 1 965 (sh), 1 957s, 1 845m, and 1 801w cm^{-1} (hexane). Hydrogen-1 n.m.r. ([$^2H_2$]dichloromethane), δ 1.8 p.p.m. (s, Me). Elution with light petroleum–CH_2Cl_2 (19 : 1) afforded purple *crystals* of $[FeRh_2(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_3(\eta\text{-}C_5Me_5)_2]$ (4) (0.395 g, 60%), m.p. 95 °C (decomp.) (Found: C, 44.1; H, 4.5; *M* (f.d.), 700. $C_{26}H_{30}FeO_6Rh_2$ requires C, 44.6; H, 4.3%; *M*, 700); $\nu_{max.}$ (CO) at 2 051w, 2 019vs, 1 993m, 1 971vs, 1 953vs, 1 837s, 1 801m, and 1 690m cm^{-1} (hexane). N.m.r. ([$^2H_2$]-dichloromethane): ^1H, δ 1.72 p.p.m. (s, Me); ^{13}C, δ 229 (br, CO), 219.4 (br, CO), 101.4 (C_5Me_5), and 4.28 p.p.m. (C_5Me_5).

(*c*) The compounds $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.300 g, 1.02 mmol) and $[Fe_2(CO)_9]$ (0.73 g, 2.0 mmol) in thf (10 cm^3) were stirred at room temperature for 16 h. Chromatography, as above, afforded $[Fe_2Rh(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5Me_5)]$ (3) (0.233 g, 38%) and purple *crystals* of $[FeRh(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)]\cdot 0.5Et_2O$ (2) (0.135 g, 29%), m.p. 182 °C (decomp.) (Found: C, 43.6; H, 4.2; *M*(f.d.), 462. $C_{16}H_{15}FeO_6Rh\cdot 0.5\,C_4H_{10}O$ requires C, 43.3; H, 4.0%; *M*, 462); $\nu_{max.}$ (CO) at 2 053vs, 2 017vs, 1 979s, 1 961 (sh), 1 835 (sh), and 1 825s cm^{-1} (hexane). Hydrogen-1 n.m.r. ([$^2H_2$]dichloromethane), δ 1.96 p.p.m. (s, Me).

Synthesis of Di- and Tri-rhodium Complexes.—(*a*) The complex $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (1.0 g, 3.4 mmol) and Me_3NO (0.255 g, 3.4 mmol) in acetone (20 cm^3) were refluxed for 30 min. Solvent was removed *in vacuo* and the residue chromatographed. Traces of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ were eluted with light petroleum. Elution with light petroleum–dichloromethane (1 : 1) gave $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.85 g, 94%), identified by i.r.[4] and by ^{13}C n.m.r. ([$^2H_2$]dichloromethane–CH_2Cl_2), δ 251.5 [t, μ-CO, *J*(RhC) 55 Hz], 100.8 (C_5Me_5), and 8.8 p.p.m. (C_5Me_5).

(*b*) The compound $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (1.1 g, 3.7 mmol) was heated to 200 °C in an evacuated Schlenk tube. Carbon monoxide was removed periodically, but the pressure was maintained at *ca.* 10—20 mmHg to inhibit sublimation. A purple solid residue developed which was chromatographed with light petroleum–dichloromethane (2 : 1) giving $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.10 g, 9%), $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.35 g, 35%), and purple *crystals* of $[Rh_3(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ (5) (0.43 g, 43%), m.p. >250 °C (Found: C, 50.1; H, 6.1; *M* (e.i.), 798. $C_{33}H_{45}O_3Rh_3$ requires C, 49.6; H, 5.7%; *M*, 798); $\nu_{max.}$ (CO) at 1 816vs, 1 777s, and 1 655vs cm^{-1} (hexane). N.m.r. ([$^2H_1$]chloroform): ^1H, δ 1.76 p.p.m. (s, Me); ^{13}C, δ 253.2 [q, 1 C, μ_3-CO, *J*(RhC) 35], 230.2 [q, 2 C, μ-CO, *J*(RhC) 27 Hz], 102.2 (C_5Me_5), and 9.2 p.p.m. (C_5Me_5).

(*c*) *Protonation of compound* (5). To a solution of (5) (0.40 g, 0.50 mmol) in diethyl ether (20 cm^3) was added a slight excess of HBF_4 in diethyl ether. A yellow-brown solid precipitated which was washed with diethyl ether and dried *in vacuo* to give *microcrystals* of $[Rh_3(\mu\text{-}H)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3][BF_4]$ (6) (0.44 g, 100%), m.p. 120 °C (decomp.) (Found: C, 45.5; H, 5.8. $C_{32}H_{46}BF_4O_3Rh_3$ requires C, 44.7; H, 5.2%); $\nu_{max.}$ (CO) at 1 840 vs, 1 806s, and 1 691vs cm^{-1} (Nujol); 1 854vs, 1 817s, and 1 705vs cm^{-1} (CH_2Cl_2). N.m.r. ([$^2H_1$]chloroform): ^1H, δ 1.80 (s, 30 H, C_5Me_5), 1.67 (s, 15 H, C_5Me_5), and −20.45 p.p.m. [t, 1 H, $\overline{Rh(\mu\text{-}H)Rh}$, *J*(RhH) 25 Hz]; ^{13}C, δ 240.2 [d of t, 1 C, μ_3-CO, *J*(RhC) 29 and 31], 225.3 [d of d, 2 C, μ-CO, *J*(RhC) 39 and 43 Hz], 108.9 (s, 5 C, C_5Me_5), 107.3 (s, 10 C, C_5Me_5), 9.5 (s, 10 C, C_5Me_5), and 8.5 p.p.m. (s, 5 C, C_5Me_5).

Crystal Structure Determination of $[MnRh(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (1).—Diffracted intensities were recorded at 220 K to $2\theta = 57°$ from the only suitable crystal that could be found; this was a brown plate-like rhomb of dimensions 0.27 × 0.17 × 0.05 mm. Of the total 2 909 independent reflections measured on a Nicolet *P3m* four-circle diffractometer, 1 860 satisfied the criterion $I \geqslant 3.0\sigma(I)$, and only these were used in the solution and refinement of the structure. The crystal showed no signs of decay (as monitored by two check reflections) during 89 h of exposure to *X*-rays.

Crystal data. $C_{19}H_{20}MnO_4Rh$, $M = 469.8$, Orthorhombic, $a = 16.851(12)$, $b = 9.338(5)$, $c = 11.566(9)$ Å, $U = 1\,820(2)$ $Å^3$ at 220 K, $D_m = 1.71$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 943.9$,* space group *Pnam* (non-standard setting of *Pnma*, no. 62), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 15.8 cm^{-1}.

The structure was solved by vector methods, and by electron-density difference syntheses. Systematic absences indicated an ambiguity in space group symmetry (either $Pna2_1$ or *Pnam*), and although the structure was solved assuming $Pna2_1$, it was evident that the molecular structure so derived itself possessed mirror symmetry. Refinement was therefore completed in the higher symmetry group *Pnam* and led to *R* 0.057 (*R'* 0.058). In this refinement, hydrogen atoms were incorporated at calculated positions (C–H 0.96 Å) with the methyl groups treated as rigid tetrahedral fragments; one common isotropic thermal parameter was used for the hydrogen atoms of each methyl group, and another for those of the cyclopentadienyl group. All other atoms were given anisotropic thermal motion. A weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.000\,62|F_o|^2]$ gave a satisfactory weight analysis. Atomic scattering factors were taken from ref. 31 for hydrogen and from ref. 32 for all other atoms. In the case of Rh and Mn these were corrected for the real and imaginary parts of anomalous dispersion[32] (Rh: $\Delta f'$ −1.287, $\Delta f''$ 0.919; Mn: $\Delta f'$ 0.295, $\Delta f''$ 0.729). All computations were carried out within the laboratory on an 'Eclipse' (Data General) minicomputer with the 'SHELXTL' system of programs.[33] Observed and calculated structure factors, hydrogen atom co-ordinates, and all thermal parameters are given in Supplementary Publication No. SUP 23269 (16 pp.).†

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* This number is not integral because of the allowance for the effects of anomalous dispersion in computing it.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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