

**THE ADDITION OF METAL NUCLEOPHILES  $(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})\text{L}$  TO THE DIRHODIUM COMPLEX  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ ; CRYSTAL STRUCTURE OF  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$**

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**Summary**

The complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  are obtained by addition of  $(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{M} = \text{Co}$  or  $\text{Rh}$ ) to the binuclear complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ . The reactions occur slowly at room temperature in hydrocarbon solvents. Spectroscopic data reveal that the trinuclear complexes contain three different types of carbonyl group: terminal, edge-bridging, and acyl. The molecular geometry of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  has been established by X-ray diffraction. There is a V-shaped arrangement of the three rhodium atoms. Within the  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  unit the CO has become terminal and the  $\text{CF}_3\text{C}_2\text{CF}_3$  has twisted to sit askew the Rh–Rh bond. The two Rh–CO bonds of  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  have added to this binuclear unit in different ways. One gives the new Rh–Rh bond which is bridged unsymmetrically by the carbonyl. The other has undergone a 1,2-addition to the coordinated  $\text{CF}_3\text{C}_2\text{CF}_3$  moiety; this gives a four-membered metallacyclic ring incorporating an acyl carbonyl. Two isomers of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  can be isolated. Spectroscopic data indicate that the minor isomer is structurally analogous to  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  but that the major isomer has a different but, as yet, undetermined structure. The cobalt complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{Co}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  are structurally analogous to  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ . The following products are obtained when the tertiary phosphine complexes  $(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})(\text{PR}'_3)$  are added to  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ ;  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ ,  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{PR}'_3)(\text{CF}_3\text{C}_2\text{CF}_3)$ . Thus, this metal nucleophile adds as the separate components  $[(\eta\text{-C}_5\text{R}_5)\text{Rh}]$ ,  $[\text{CO}]$ , and  $[\text{PR}'_3]$ . The major product obtained when  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  is treated with  $(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2$  is  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ .

**Introduction**

The considerable current interest in the formation and properties of metal clusters is prompted by several considerations. One is the belief that large metal clusters may

be suitable models for metal surfaces; ligands of the type CO or  $\text{RC}\equiv\text{CR}$  on these clusters may mimic the behaviour of chemisorbed species on the metal surface [1,2]. Another is the expectation that mixed metal clusters may be important in stoichiometric and catalytic reactions [3–9]; particular substrates may be activated selectively at the different metal sites.

One method of forming metal clusters, including mixed metal systems, involves the addition of metal nucleophiles to coordinatively unsaturated metal complexes [7–9]. Our recent investigations [10–15] with the complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  establish that it readily adds a range of nucleophiles. Consequently, we decided to treat this complex with some basic metal complexes. In this paper, we describe the addition of  $d^8$ -metal complexes of the type  $(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})\text{L}$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{M} = \text{Co}$  or  $\text{Rh}$ ;  $\text{L} = \text{CO}$  or  $\text{PR}'_3$ ).

## Results and discussion

### *Addition of the dicarbonyl complexes $(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2$*

Each of the complexes  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ,  $(\eta\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$ ,  $(\eta\text{-C}_5\text{H}_5)\text{-Rh}(\text{CO})_2$  and  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  adds to  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  in pentane or hexane at room temperature. The reactions are slow, and the reaction mixtures must be left for 2–7 days. The addition products  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{-Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  are isolated as brown or green solids, and the yields vary from ca. 20% (for addition of  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  over 7 days) to ca. 65% (+  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ , 7 days). Two isomers of the complex  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3\text{-}(\text{CF}_3\text{C}_2\text{CF}_3)$  were separated by chromatography.

The complexes obtained from  $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  are not particularly stable. The  $\text{Rh}_2\text{Co}$  complex decomposes slowly in the solid state, and satisfactory elemental analyses could not be obtained for this species. Although the  $\text{Rh}_3$  complex was stable as a solid, it decomposed slowly in solution under anaerobic conditions. For instance, recovery of the  $\text{Rh}_3$  complex was only 40% after 6 days in chloroform. Two decomposition pathways are indicated by the products isolated from the aged chloroform solution. The formation of  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  is consistent with some dissociation of the addition product; decarbonylation of the addition product is indicated by the formation of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ . Since the same compounds are obtained as by-products in the initial addition reactions, it seems likely that the decomposition reactions occur also in alkane solvents.

Greater stability was observed for the addition products obtained from  $(\eta\text{-C}_5\text{Me}_5)\text{M}(\text{CO})_2$  in solution over several days. Presumably, this is due to the electron-donating properties of the  $\text{C}_5\text{Me}_5$  ligand which increases the metal basicity.

Differences in the relative stabilities of these compounds are revealed also in the mass spectral data. Parent ions are observed for the complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  ( $\text{M} = \text{Co}$  and  $\text{Rh}$ ), but not for the compounds  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ . For these latter species, the peak of highest mass corresponds to  $[\text{M} - \text{CO}]$  for  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  (minor isomer),  $[\text{M} - 2\text{CO}]$  for  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_2\text{Co}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  and  $[\text{M} - (\text{C}_5\text{H}_5)\text{Rh}(\text{CO})_2]$  for  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  (major isomer). These mass spectral results again reflect the two decomposition pathways, namely dissociation of  $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  and decarbonylation.

TABLE 1

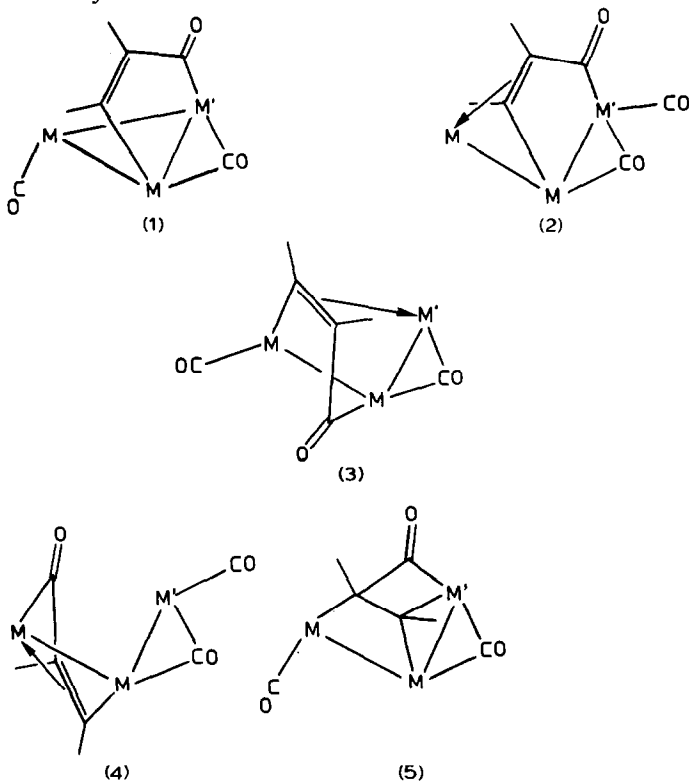
INFRARED RESULTS ( $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ) FOR THE COMPLEXES  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{-M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  (KBr disk)

$(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{M-}$	$\text{CO}_t$	$\text{CO}_{br}$	$\text{CO}_{acyl}$
$(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3$			
major isomer	1995	1811	1624
minor isomer	2010	1821	1698
$(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3$	1993	1792	1694
$(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_2\text{Co}$	2011	1813	1700
$(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_2\text{Co}$	1995	1786	1696

Treatment of  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  with the binuclear complex  $(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2$  also results in the formation of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ . The yield is 55% after 3 weeks. Although the other products of the reaction have not been fully characterized, there is no evidence for a tetranuclear addition product.

*Spectroscopic properties of the complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ , ( $R = \text{H}, \text{Me}; M = \text{Co}, \text{Rh}$ )*

Infrared data for the various complexes is summarized in Table 1. It is clear that the addition products have three different types of carbonyl group; terminal, edge-bridging, and acyl. Each of the possible structures 1–5 has this diversity of carbonyls.



Replacement of the ligand  $C_5H_5$  by  $C_5Me_5$  in metal carbonyl complexes is known to have a marked effect on the carbonyl stretching frequencies. This is illustrated by comparing the infrared spectra of pairs of compounds such as  $(\eta-C_5H_5)Rh(CO)_2$  ( $\nu(CO)$  at 2051, 1987  $cm^{-1}$ ) [16] and  $(\eta-C_5Me_5)Rh(CO)_2$  (2004, 1950) [17], or  $(\eta-C_5H_5)_2Co_2(\mu-CO)_2$  (1790) [18] and  $(\eta-C_5Me_5)_2Co_2(CO)_2$  (1756) [19]. Inspection of the data in Table 1 reveals greater variation in  $\nu(CO)$  for the bridging carbonyl than for the other types of carbonyl. This seems to be consistent with a structure in which the bridging carbonyl spans a  $(\eta-C_5R_5)M-Rh(\eta-C_5H_5)$  rather than a  $(\eta-C_5H_5)Rh-Rh(\eta-C_5H_5)$  bond.

Infrared results for the addition products obtained from  $^{13}C$ -enriched reactants are of interest. When  $(\eta-C_5H_5)Rh(^{13}CO)_2$  is added to  $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ , the label appears to be evenly distributed between all three carbonyl sites. Although the addition of  $(\eta-C_5Me_5)Rh(CO)_2$  to  $(\eta-C_5H_5)_2Rh_2(\mu-^{13}CO)(\mu-CF_3C_2CF_3)$  also gives a product in which the label is distributed over the three sites, there does seem to be more enrichment of the terminal carbonyl. Although these data imply some mobility of the carbonyl groups within the structure, the  $^{13}C$  NMR results provide no evidence of rapid carbonyl scrambling.

The room temperature  $^{13}C$  NMR spectra for each of the  $Rh_3$  complexes show individual resonances for the three different types of carbonyl group. The chemical shifts for the terminal and edge-bridging carbonyls are observed near 190 ppm (doublet, with  $J(Rh-C)$  ca. 80 Hz) and 220 ppm (doublet of doublets with each  $J(Rh-C)$  ca. 45 Hz), respectively. For the acyl carbonyl, a doublet is observed at 194 or 212 ppm. Variable temperature spectra could not be recorded because heat increased the rate of decomposition of the complexes. The sensitivity of  $\delta(CO-acyl)$  to the change from  $(\eta-C_5H_5)_3Rh_3$  to  $(\eta-C_5H_5)_2(\eta-C_5Me_5)Rh_3$  may indicate that this carbonyl is attached directly to  $(\eta-C_5Me_5)Rh$  in the latter complex.

The  $^{13}C$  NMR spectrum of  $(\eta-C_5H_5)_2(\eta-C_5Me_5)Rh_2Co(CO)_3(CF_3C_2CF_3)$  is illuminating because the carbon atoms attached to Co show no coupling to the metal. For this complex, the carbonyl signals are observed at  $\delta$  238.2 (doublet with  $J(Rh-C)$  42 Hz), 217.2 (singlet) and 189.4 (doublet, with  $J(Rh-C)$  80 Hz) for the bridging, acyl and terminal carbonyls respectively. The observed multiplicities indicate that the edge-bridging carbonyl spans a  $Rh-Co$  bond, the acyl carbonyl is attached to Co, and the terminal carbonyl is bound to a Rh atom. These data are consistent with the arrangements **1** and **4** where  $M' = Co$ .

Other signals are observed in the  $^{13}C$  NMR spectra of these complexes. The best total spectrum was obtained for  $(\eta-C_5H_5)_2(\eta-C_5Me_5)Rh_2Co(CO)_3(CF_3C_2CF_3)$ , and the peak positions and assignments are given in the experimental section.

The  $^1H$  and  $^{19}F$  NMR spectra of most of the complexes are unremarkable. The results for  $(\eta-C_5H_5)_2(\eta-C_5Me_5)Rh_3(CO)_3(CF_3C_2CF_3)$  are typical. Thus, different environments for the three cyclopentadienyl rings are revealed in the  $^1H$  spectrum, and the  $^{19}F$  spectrum shows a quartet near 53 ppm and a quartet of doublets near 60 ppm. The F-F coupling constant of 12 Hz is consistent with a *cis*-arrangement of the two  $CF_3$  groups, and the additional coupling in the high field resonance is attributed to Rh-F coupling. This high field resonance is assigned to a  $CF_3$  group on a C atom which is attached to both the acyl-CO and rhodium. This additional coupling in the high field multiplet is not observed in the analogous  $Rh_2Co$  complex, indicating that  $J(Rh-C)$  is much smaller for this system.

Some different spectroscopic features are observed with the major isomer of

$(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ . In the infrared spectrum,  $\nu(\text{CO})$  for the acyl carbonyl is some  $75\text{ cm}^{-1}$  lower than for all the other complexes. Moreover, both  $\text{CF}_3$  resonances in the  $^{19}\text{F}$  NMR spectrum are at lower field than for the other complexes. These observations will be considered further after discussion of the structure of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ .

*Crystal and molecular structure of the complex  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$*

Consideration of the cumulative spectroscopic results does not lead to a definite decision about the structure of the trinuclear complexes. Consequently, the crystal and molecular structure of one of the complexes,  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ , was determined by single crystal X-ray diffraction. A representative prismatic crystal ( $0.094 \times 0.106 \times 0.275$  mm) was selected and mounted on a quartz fibre. All data were collected on a Philips PW1100 diffractometer with  $\text{Mo-K}_\alpha$  radiation ( $\lambda$  0.7107 Å).

*Crystal data.*  $\text{C}_{27}\text{H}_{25}\text{F}_6\text{O}_3\text{Rh}_3$ ,  $M$  820.22, monoclinic,  $a$  11.168(8),  $b$  15.456(10),  $c$  15.876(10) Å,  $\beta$  100.59(6)°,  $U$  2693.7 Å<sup>3</sup>.  $D_m$  2.02(3),  $D_c$  2.02 g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000)$  1479.9, systematic absences  $h0l$   $l$  odd,  $0k0$   $k$  odd, space group  $P2_1/c$  ( $C_2^5h$ ),  $\mu$  18.2 cm<sup>-1</sup> for  $\text{Mo-K}_\alpha$  radiation.

*Intensity measurements and structure solution*

7844 unique data were collected between  $3^\circ \leq \theta \leq 30^\circ$  by the  $\omega$  scan technique with a scan range of  $\pm 0.75^\circ$  in  $\theta$  from the calculated Bragg scattering angle (with an allowance for dispersion) at a rate of  $0.05^\circ \text{ sec}^{-1}$ . Intensity data were processed as described earlier [20], 3527 data were considered to be observed [ $I \geq 3\sigma(I)$ ]. Three standard reflections monitored every 3 h showed no significant variation of intensity over the data collection period.

The atomic scattering factors for neutral atoms were taken from ref. 21 and were corrected for anomalous dispersion by using values from ref. 21. All calculations were performed on a Monash University DEC/VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick [22]. A numerical absorption correction was applied to the data.

The structure was solved by conventional Patterson and Fourier methods. Full matrix least-squares refinement of all positional atom coordinates and thermal parameters (anisotropic for Rh) reduced  $R_1$  to 0.067 and  $R_2$  to 0.064 where  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2 = \sum w^{1/2} (||F_o| - |F_c||) / \sum w^{1/2} |F_o|$ , and individual reflections were assigned weights equal to  $1/\sigma^2(F)$ . Final positional are given in Table 2.

A list of thermal parameters and observed and calculated structure factors may be obtained from the authors.

*Discussion of the structure*

The molecular structure is shown in Fig. 1 and it is helpful to view it in two parts. The first is based on the dimetallacyclic unit  $\text{Rh}(2)\text{-C}(4)\text{-C}(5)\text{-Rh}(3)$ . The geometry here is similar to that found [23] for the complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  and proposed [10] for the related complexes  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\text{L}(\text{CF}_3\text{C}_2\text{CF}_3)$ . The other incorporates the  $\text{Rh}(1)\text{-C}(3)\text{-C}(4)\text{-C}(5)\text{-Rh}(3)$  unit which is formed by two concerted addition reactions. In one, the  $\text{Rh}(1)\text{-C}(1)\text{O}(1)$  bond of  $(\eta\text{-$

TABLE 2

FINAL POSITIONAL PARAMETERS ( $\times 10^4$ ) (Estimated standard deviations are in parentheses).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Rh(1)	1649(1)	-96(1)	2902(1)	C(30)	861(13)	-1272(9)	3567(9)
Rh(2)	3379(1)	986(1)	1213(1)	C(31)	1621(14)	-788(9)	4179(10)
Rh(3)	2487(1)	-565(1)	1523(1)	C(32)	1161(15)	81(11)	4176(11)
C(1)	1010(12)	83(8)	1642(8)	C(33)	66(15)	114(11)	3535(11)
C(2)	4831(16)	416(11)	1231(11)	C(34)	-110(13)	-710(9)	3182(9)
C(3)	2325(12)	1101(8)	2771(8)	C(301)	1027(15)	-2248(11)	3420(11)
C(4)	3517(10)	859(7)	2579(7)	C(311)	2707(17)	-1124(12)	4839(12)
C(5)	3395(10)	-103(7)	2678(7)	C(321)	1668(20)	790(14)	4822(14)
C(6)	4606(14)	1383(10)	3067(10)	C(331)	-785(20)	896(13)	3303(14)
C(7)	4388(13)	-654(9)	3168(9)	C(341)	-1195(16)	-1031(12)	2455(12)
C(10)	2836(14)	2394(11)	1023(10)	O(1)	66(9)	308(6)	1236(7)
C(11)	1734(15)	1833(11)	814(11)	O(2)	5768(12)	118(8)	1206(9)
C(12)	1867(15)	1310(10)	101(11)	O(3)	1929(9)	1803(7)	2918(7)
C(13)	3005(14)	1531(10)	-126(10)	F(1)	5678(9)	1091(6)	3000(6)
C(14)	3644(15)	2203(10)	473(11)	F(2)	4553(9)	1421(6)	3901(7)
C(20)	2734(13)	-2024(9)	1470(10)	F(3)	4507(9)	2215(7)	2801(7)
C(21)	3606(14)	-1615(10)	1054(10)	F(4)	4837(8)	-335(5)	3947(6)
C(22)	2949(16)	-1152(11)	321(11)	F(5)	4076(7)	-1465(5)	3267(5)
C(23)	1705(16)	-1264(11)	306(11)	F(6)	5379(9)	-698(6)	2784(6)
C(24)	1548(14)	-1792(10)	991(10)				

$C_5Me_5Rh(CO)_2$  adds to Rh(3) of  $(\eta-C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ ; this gives a V-shaped arrangement of the three rhodium atoms in which an edge-bridging carbonyl spans the Rh(1)–Rh(3) bond. In the second, there is addition of the Rh(1)–C(3)O(3) bond from  $(\eta-C_5Me_5)Rh(CO)_2$  to the C(4)=C(5) double bond of

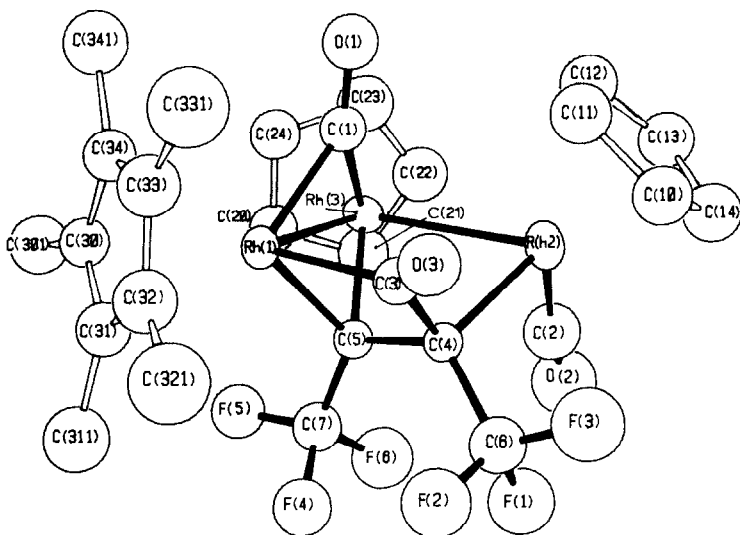


Fig. 1. Molecular structure of the complex  $(\eta-C_5H_5)_2(\eta-C_5Me_5)Rh_3(CO)(\mu-CO)\{\mu-C(O)C_2(CF_3)_2\}_2$ ; 50% thermal ellipsoids are shown for the non-hydrogen atoms, together with the atom labelling scheme.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) (Estimated standard deviations are in parentheses.)

Rh(1)–Rh(2)	3.953(1)	Rh(2)–C(10)	2.265(16)
Rh(1)–Rh(3)	2.636(1)	Rh(2)–C(11)	2.251(17)
Rh(2)–Rh(3)	2.676(1)	Rh(2)–C(12)	2.263(16)
		Rh(2)–C(13)	2.254(16)
C(1)–Rh(1)	2.015(13)	Rh(2)–C(14)	2.266(16)
C(1)–Rh(3)	1.968(13)		
C(1)–O(1)	1.183(14)	C(20)–C(21)	1.421(20)
		C(20)–C(24)	1.446(20)
C(2)–Rh(2)	1.841(18)	C(21)–C(22)	1.446(21)
C(2)–O(2)	1.150(18)	C(22)–C(23)	1.396(22)
		C(23)–C(24)	1.396(21)
C(3)–Rh(1)	2.023(13)		
C(3)–Rh(2)	2.93(1)	Rh(3)–C(20)	2.275(14)
C(3)–Rh(3)	> 3	Rh(3)–C(21)	2.256(15)
C(3)–O(3)	1.210(14)	Rh(3)–C(22)	2.256(17)
C(3)–C(4)	1.468(17)	Rh(3)–C(23)	2.245(18)
		Rh(3)–C(24)	2.255(15)
C(4)–Rh(2)	2.154(12)		
C(4)–C(5)	1.503(16)	C(30)–C(31)	1.386(19)
C(4)–C(6)	1.546(18)	C(30)–C(34)	1.435(18)
		C(30)–C(301)	1.544(20)
C(5)–Rh(1)	2.045(11)	C(31)–C(32)	1.439(21)
C(5)–Rh(3)	2.054(11)	C(31)–C(311)	1.539(23)
C(5)–C(7)	1.498(17)	C(32)–C(33)	1.441(22)
		C(32)–C(321)	1.536(25)
C(6)–F(1)	1.302(16)	C(33)–C(34)	1.391(20)
C(6)–F(2)	1.338(17)	C(33)–C(331)	1.540(24)
C(6)–F(3)	1.351(16)	C(34)–C(341)	1.592(22)
C(7)–F(4)	1.341(16)		
C(7)–F(5)	1.320(15)	Rh(1)–C(30)	2.352(14)
C(7)–F(6)	1.378(16)	Rh(1)–C(31)	2.298(15)
		Rh(1)–C(32)	2.208(17)
C(10)–C(11)	1.492(21)	Rh(1)–C(33)	2.213(17)
C(10)–C(14)	1.397(21)	Rh(1)–C(34)	2.297(14)
C(11)–C(12)	1.420(22)	O(1)–Rh(1)	2.965(10)
C(12)–C(13)	1.426(21)	O(1)–Rh(3)	2.982(10)
C(13)–C(14)	1.498(21)		
Rh(1)–Rh(3)–Rh(2)	96.2(0)	Rh(2)–C(2)–O(2)	174.3(1.6)
Rh(3)–Rh(1)–C(1)	47.8(4)		
Rh(3)–Rh(1)–C(3)	88.3(4)	Rh(1)–C(3)–O(3)	130.1(1.0)
Rh(3)–Rh(1)–C(5)	50.1(3)	Rh(1)–C(3)–C(4)	99.1(0.8)
C(3)–Rh(1)–C(5)	66.5(5)	C(4)–C(3)–O(3)	130.2(1.2)
		C(3)–C(4)–C(5)	97.3(0.9)
Rh(3)–Rh(2)–C(2)	109.0(5)	C(3)–C(4)–C(6)	115.0(1.1)
Rh(3)–Rh(2)–C(4)	72.2(3)	C(3)–C(4)–Rh(2)	106.7(0.8)
C(2)–Rh(2)–C(4)	92.3(6)	C(5)–C(4)–C(6)	122.9(1.1)
		C(5)–C(4)–Rh(2)	101.8(0.7)
Rh(1)–Rh(3)–C(1)	49.3(4)	C(6)–C(4)–Rh(2)	111.1(0.8)
Rh(1)–Rh(3)–C(5)	49.8(3)		
Rh(2)–Rh(3)–C(5)	73.3(3)	C(4)–C(5)–C(7)	122.9(1.0)
		C(4)–C(5)–Rh(1)	96.9(0.7)
Rh(1)–C(1)–Rh(3)	82.9(5)	C(4)–C(5)–Rh(3)	106.9(0.8)
Rh(1)–C(1)–O(1)	134.3(1.1)	Rh(1)–C(5)–C(7)	123.4(0.9)
Rh(3)–C(1)–O(1)	140.9(1.1)	Rh(3)–C(5)–C(8)	117.6(0.9)
		Rh(1)–C(5)–Rh(3)	80.1(0.4)

$(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  to form a four-membered metallacyclic ring. The complete structural core has four cyclic systems, two with four atoms and two with three. Overall, there has been *trans*-addition of  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  to  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  to give the arrangement represented in 4.

The interatomic bond distances and angles are given in Table 3. The Rh(1)–Rh(3) and Rh(2)–Rh(3) distances of 2.636(1) and 2.676(1) Å are as expected for Rh–Rh single bonds. The slightly shorter distance incorporates the rhodium atom that is linked to the  $\text{C}_5\text{Me}_5$  ring. The very long distance of almost 4 Å between Rh(1) and Rh(2) indicates clearly that there is no bonding interaction between these metals. A bridging carbonyl lies along the Rh(1)–Rh(3) bond. There is some asymmetry in the bridge bonding, with C(1) being closer to Rh(3) and O(1) closer to Rh(1). The bond angles around C(1) also reflect this asymmetry.

The C(4)–C(5) bond lies askew the Rh(2)–Rh(3) bond, with C(4) attached to Rh(2) and C(5) to Rh(3). The deviations from the best fit plane through these four atoms are considerable (see Table 4, Plane 1), and the angle between the Rh(2)–Rh(3) and C(4)–C(5) vectors is 18.4(6)°. The Rh–C bond distances are 2.154(12) and 2.054(11) Å, respectively; they span the Rh–C  $\sigma$ -bond distance of 2.08 Å [24] for the complex  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{CF}_2\text{CF}_3)\text{I}$ . The C(4)–C(5) distance of 1.503(16) is slightly shorter than the 'normal'  $\text{C}(\text{sp}^3)$  single bond length. Trifluoromethyl groups are attached to the carbon atoms C(4) and C(5). Although there is some scatter of the C–F bond distances and F–C–F bond angles, this is common for  $\text{CF}_3$  groups in organometallic compounds.

The metallacyclic ring obtained by adding Rh(1)–C(3)O(3) along C(5)–C(4) is fairly symmetrical. The Rh(1)–C(3) and Rh(1)–C(5) distances are 2.023(13) and 2.045(11) Å, respectively, and the C(3)–C(4) and C(4)–C(5) distances are 1.468(17) and 1.503(16) Å. There are only small deviations of the atoms from the plane through Rh(1), C(3), C(4), C(5) and O(3) (see Table 4, Plane 2). The dihedral angle between planes 1 and 2 is 98.7°.

The bond distances of the three cyclopentadienyl rings are compared in Fig. 2. Rings (a) and (b) are the  $\text{C}_5\text{H}_5$  groups which are attached to Rh(2) and Rh(3), respectively, while ring (c) is the  $\text{C}_5\text{Me}_5$  ligand which is attached to Rh(1).

Ring (b) is the most symmetrical of the three rings. The ring carbon atoms are coplanar (maximum deviation 0.007 Å; see Plane 4, Table 4), and the C–C distances vary between 1.40 and 1.45 Å. Some slight tilting of this ring with respect to the vector from Rh to the mid point of the plane is indicated by the Rh–C distances. Thus, Rh(3)–C(23) seems to be shorter (2.245(18) Å) and Rh(3)–C(20) is significantly longer (2.275(14) Å) than the other Rh–C distances (2.255–2.256 Å).

There is evidence for localized bonding within ring (a). Thus, there is one short (C(10)–C(14) 1.40 Å), two intermediate (C(11)–C(12) 1.42, C(12)–C(13) 1.43 Å), and two long (C(10)–C(11) 1.49, C(13)–C(14) 1.50 Å) bonds. Further, the bonds from Rh to C(11) and C(13) seem to be shorter than those to the other ring carbons. These parameters are consistent with localization of the  $\pi$ -electron density as shown in Fig. 2 (a). This type of bonding has been recognized previously; perhaps the best example is provided by the ethylene complex  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{PPh}_3)(\text{C}_2\text{H}_4)$  [25].

A contribution from another type of localized bonding is indicated in ring (c). Here, two of the bonds are shorter (C(30)–C(31) and C(33)–C(34) 1.39 Å) than the other three (C(31)–C(32), C(32)–C(33) and C(34)–C(30) 1.44 Å). In other examples of this type of localization (e.g.  $(\eta\text{-C}_5\text{Ph}_4\text{Cl})\text{Rh}(\text{C}_2\text{H}_4)_2$  [26],  $(\eta\text{-C}_5\text{Cl}_5)\text{Rh}(1,5\text{-COD})$



TABLE 4

EQUATIONS OF MEAN PLANES AND DEVIATIONS (Å) OF INDIVIDUAL ATOMS FROM PLANES (Estimated standard deviations are in parentheses)

( $x$ ,  $y$ ,  $z$  are orthogonal coordinates with respect to  $abc^*$ )

Plane 1:	Rh(2), Rh(3), C(4), C(5)		
	$(0.9346)x + (-0.3519)y + (-0.0520)z - (2.4672) = 0$		
	Rh(2)	0.094(11)	C(4) -0.176(11)
	Rh(3)	-0.102(10)	C(5) 0.184(11)
Plane 2:	Rh(1), C(3), C(4), C(5), O(3)		
	$(-0.2151)x + (0.0024)y + (-0.9766)z - (-4.6599) = 0$		
	Rh(1)	0.023(10)	C(5) -0.069(11)
	C(3)	0.056(13)	O(3) -0.061(11)
	C(4)	0.050(11)	
Plane 3:	C(10), C(11), C(12), C(13), C(14)		
	$(-0.3340)x + (0.7075)y + (-0.6228)z - (0.6521) = 0$		
	C(10)	0.013(16)	C(13) 0.012(16)
	C(11)	-0.006(17)	C(14) -0.016(16)
	C(12)	-0.004(16)	
Plane 4:	C(20), C(21), C(22), C(23), C(24)		
	$(0.1192)x + (-0.8107)y + (-0.5731)z - (1.5309) = 0$		
	C(20)	0.004(15)	C(23) -0.005(17)
	C(21)	-0.006(16)	C(24) 0.001(15)
	C(22)	0.007(17)	
Plane 5:	C(30), C(31), C(32), C(33), C(34)		
	$(0.6752)x + (0.2597)y + (-0.6904)z - (-4.4147) = 0$		
	C(30)	0.008(14)	C(301) -0.073(17)
	C(31)	-0.005(15)	C(311) -0.162(19)
	C(32)	0.000(17)	C(321) -0.160(22)
	C(33)	0.005(17)	C(331) -0.027(22)
	C(34)	0.008(14)	C(341) -0.029(18)

[27] and  $(\eta\text{-C}_5\text{Me}_5)\text{RhCl}(\eta^3\text{-MeHCCHCHMe})$  [28]) the carbon atom which is equivalent to C(32) is bent towards the metal. Although this is not found in the present case, the Rh(1)–C(32) bond is significantly shorter than the other Rh–C bonds except for that to the adjacent carbon C(33). As is usual with  $\text{C}_5\text{Me}_5\text{-M}$  systems, all methyl groups are displaced away from the metal (see Plane 5, Table 4).

*Possible structure of the major isomer of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$*

As mentioned previously, the spectroscopic properties of the major isomer of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  differ in some respects from those of the other

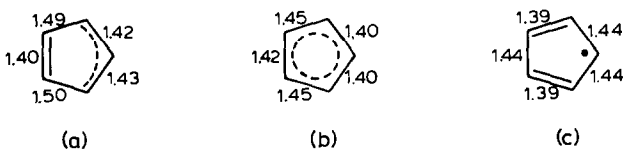
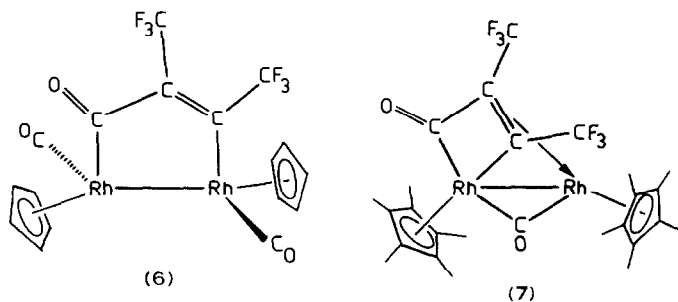


Fig. 2. Bond distances ( $\pm 0.02$  Å) and proposed  $\pi$ -electron distribution, for the three cyclopentadienyl rings.

compounds in the series. In the infrared spectra, for instance,  $\nu(\text{CO-acyl})$  is at  $1624 \text{ cm}^{-1}$  for this compound but near  $1700 \text{ cm}^{-1}$  for all the other compounds. Another major difference is observed in the  $^{19}\text{F}$  NMR spectrum. For this compound, the  $\text{CF}_3$  resonances are observed at 41.2(q) and 55.3(q), whereas these resonances are at 51–53(q) and ca. 60(q or qd) for the other complexes. More subtle differences are found in the chemical shift and coupling constant data for the acyl-C in the  $^{13}\text{C}$  NMR spectra. For this compound,  $\delta$  is 212.0 ppm and  $J$  31 Hz; for the other compounds, the chemical shifts are in the range 194–203 ppm and  $J$  is 25 Hz. It is possible, then, that the structure of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  (major isomer) differs from that determined for  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  and indicated for the other complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_2\text{M}(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ , including  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  (minor isomer). The possible structures 1 to 3 should be considered.

The complexes  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2\{\text{C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (**6**) [29] and  $(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})\{\text{C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (**7**) [30] are suitable models for the types of bridge bonding shown in structures 1 and 2–4, respectively. Table 5 makes comparisons of selected spectroscopic properties for these model compounds and the two



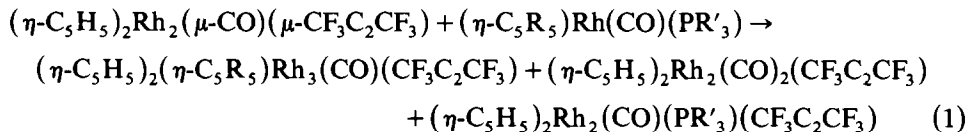
complexes  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{R}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ). It is clear that the acyl carbonyl in  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  is like that in **6** but unlike that in **7** and  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ . However, the environment of one of the  $\text{CF}_3$  groups in  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  is most unusual and remains unexplained. We have found [30] a similar low field chemical shift ( $\delta$  39.2 and 55.8 ppm) for one of the  $\text{CF}_3$  resonances in the complex  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\text{C}(\text{NPr}^1)\text{C}_2(\text{CF}_3)_2\}$ . Attempts to grow crystals of  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  that are suitable for X-ray structure determination were not successful; the crystals did not diffract.

TABLE 5

	$\nu(\text{CO-acyl})$	$\delta(\text{CF}_3)$	$\delta(\text{CO-acyl}),$ ( $J(\text{Rh-C})$ )
$(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$ major isomer	1624	41.2, 55.3	212.0 (31)
$(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$	1693	53.3, 59.5	202.7 (25)
$(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2\{\text{C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$	1630	53.3, 59.3	213.7 (28)
$(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})\{\text{C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$	1717(sh) 1698s	54.8, 59.3	not obtained

*Addition of the tertiary phosphine complexes  $(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})(\text{PR}'_3)$*

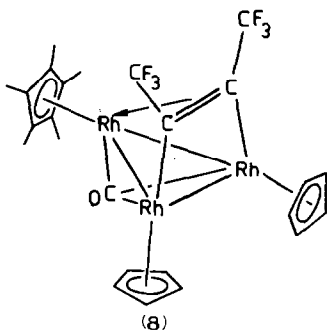
The products obtained from reactions between  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  and  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$ ,  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})(\text{PMePh}_2)$  or  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})\{\text{P}(\text{OMe})_3\}$  are shown in equation 1.



The reactions are slow at room temperature; the addition of  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$ , for example, is only 50% complete after 3 weeks. Formation of the particular products obtained can be viewed in terms of the separate additions of the components  $[(\eta\text{-C}_5\text{R}_5)\text{Rh}]$ ,  $[\text{CO}]$ , and  $[\text{PR}'_3]$  to the dinuclear rhodium complex.

Knowledge of the structure of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  helps to some extent in rationalizing the course of this reaction. In the addition of  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ , one carbonyl becomes edge-bridging and the other becomes the acyl carbonyl in a four-membered metallacyclic ring. The tertiary phosphine in  $(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})(\text{PR}'_3)$  cannot assume either of these roles, and hence a different reaction pathway must be followed. Presumably, the initial nucleophilic attack of  $(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})(\text{PR}'_3)$  on one rhodium of  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  is followed by formation of a  $\text{Rh}_3$  (triangular cluster with elimination of  $\text{CO}$  and  $\text{PR}'_3$ ). As shown previously, the latter two ligands can combine independently with  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$ .

Of the products formed in this reaction, only  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  is a new compound. This trinuclear complex can also be prepared by the decarbonylation of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)$  with  $\text{Me}_3\text{NO}$  in refluxing acetone. Several closely related species of formula  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{RC}_2\text{R})$  ( $\text{R} = \text{Ph}, \text{C}_6\text{F}_5, \text{Me}$  or  $\text{CF}_3$ ) have been obtained previously [32,33], and two different structures are possible for these complexes. In one, the carbonyl is face bridging; in the other, there is an edge bridging carbonyl [34]. The two structure types are readily distinguished spectroscopically [33]. Spectroscopic results for the new complex  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  are consistent with a face-bridging structure **8**. Thus, the infrared spectrum shows a carbonyl absorption at 1693 ( $\text{CH}_2\text{Cl}_2$ ) or 1711 ( $\text{MeCN}$ ), and the  $^{13}\text{C}$  NMR spectrum shows the carbonyl resonance at  $\delta$  239.0 ppm as a triplet ( $J(\text{Rh}-\text{C})$  42 Hz)



of doublets ( $J(\text{Rh}'-\text{C})$  25 Hz). The difference in the magnitude of the coupling constants may indicate that the  $\text{CO}$  group is closer to each of the two  $(\eta\text{-C}_5\text{H}_5)\text{Rh}$

units than to  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}$ . The corresponding resonance in  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  was observed [33] as a quartet ( $J$  37 Hz) at  $\delta$  234.3 ppm.

## Experimental

### (a) General

The rhodium complexes  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  [10],  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  [35],  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$  [36],  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  [37],  $(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2$  [38],  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})\{\text{P}(\text{OMe})_3\}$  [39] and  $(\eta\text{-C}_5\text{Me}_5)\text{-Rh}(\text{CO})(\text{PMePh}_2)$  [40] and the cobalt complex  $(\eta\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$  [19] were prepared by published procedures.  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  was obtained from Strem Chemicals.

All solvents were purified by standard procedures and stored over Linde 4A molecular sieves. X4 refers to petroleum fraction (b.p. range 30–60°C).

Reactions were generally performed in evacuated Pyrex Carius tubes (ca. 100 ml capacity) fitted with Quickfit Rotaflon Teflon taps. Column chromatography was carried out in glass columns under a nitrogen atmosphere; the dry packing method was used, and the adsorbent was deactivated (10% water) alumina. Thin-layer chromatography was carried out on 20 by 20 cm plates with a 1/1 silica gel G-HF<sub>254</sub> mixture as adsorbent.

Microanalyses (C, H, F) were performed by the Australian Microanalytical Service, Melbourne.

Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer; the reported peaks are taken from the carbonyl region (2100–1600  $\text{cm}^{-1}$ ). Mass spectra (70 eV) were obtained with a V.G. Micromass 7070-F spectrometer. Bruker WH90 and AM300 NMR spectrometers were used to record the nuclear magnetic resonance spectra. The  $^1\text{H}$  magnetic resonance spectra were measured at 90 MHz and are reported as  $\delta$  values; the  $^{19}\text{F}$  chemical shifts were measured at 84.66 MHz and are reported in ppm upfield from  $\text{CCl}_3\text{F}$  internal reference;  $^{13}\text{C}$  chemical shifts were measured at 75.47 MHz and are reported as  $\delta$  values downfield from tetramethylsilane.

### (b) Formation of $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$

A solution containing  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  (0.215 g) and  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  (0.100 g, mol ratio 1/1.1) in hexane (5 ml) was kept at 20°C for 1 week. During this time, brown-black crystals were deposited. The contents of the tube were dissolved in chloroform and the solution was chromatographed by TLC with hexane/dichloromethane (1/1) as eluent; seven colored bands were developed.

Compounds in the first three bands were identified as  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$  (small amount), *trans*- $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (0.070 g, 31%) and  $(\eta\text{-C}_5\text{H}_5)_2\text{-Rh}_2(\text{CO})_3$  (<1 mg). The fourth band was initially dull green in color, but it decomposed on the plate leaving a broad purple band. The latter was combined with the fifth band which was also purple; further TLC of this combined fraction revealed the presence of only one compound,  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  (0.079 g, 28%).

The sixth band gave a dark tan solid, probable formula  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.010 g, 3%) m.p. 138°C (dec.). Mass spectrum: 722 (<1%,  $M - \text{CO}$ ), 694 (5%,  $M - 2\text{CO}$ ), 666 (4%,  $M - 3\text{CO}$ ), 526 (30%,  $\text{C}_{15}\text{H}_{10}\text{F}_6\text{ORh}_2^+$ ),

233 (100%,  $C_{10}H_{10}Rh^+$ ). Infrared absorption (KBr):  $\nu(CO)$  at 2010vs, 1821vs, 1698vs, 1674s  $cm^{-1}$ ; with a sample prepared from  $^{13}CO$  enriched  $(\eta-C_5H_5)Rh(CO)_2$ , additional bands were observed at 1963, 1778 and 1650  $cm^{-1}$ .  $^1H$  NMR spectrum ( $CDCl_3$ , 27°C):  $\delta$  5.64 (s, 5H,  $C_5H_5$ ), 5.50 (d, 5H,  $J(Rh-H)$  1.1 Hz,  $C_5H_5$ ), 5.33 ppm (s, 5H,  $C_5H_5$ ).  $^{19}F$  NMR spectrum ( $CDCl_3$ , 27°C):  $\delta$  52.3 (q, 3F,  $J(F-F)$  12 Hz,  $CF_3$ ), 59.9 ppm (qd, 3F,  $J(F-F)$  12 and  $J(Rh-F)$  3 Hz,  $CF_3$ ).  $^{13}C$  NMR spectrum ( $CDCl_3$ , 39°C):  $\delta$  219.8 (dd,  $J(Rh-C)$  47 and  $J(Rh'-C)$  44 Hz,  $\mu-CO$ ), 193.8 (d,  $J(Rh-C)$  25 Hz, acyl-CO), 189.6 (d,  $J(Rh-C)$  79 Hz, CO), 93.9 (d,  $J(Rh-C)$  2 Hz,  $C_5H_5$ ), 92.0 (d,  $J(Rh-C)$  2 Hz,  $C_5H_5$ ), and 91.9 ppm (d,  $J(Rh-C)$  2Hz,  $C_5H_5$ ).

This complex slowly decomposes in chloroform solution. TLC of a solution that had been kept for 4 days separated a number of colored bands; the three major ones were identified as *trans*- $(\eta-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ ,  $(\eta-C_5H_5)_3Rh_3-(CO)(CF_3C_2CF_3)$  and unchanged  $(\eta-C_5H_5)_3Rh_3(CO)(\mu-CO)\{\mu-C(O)C_2(CF_3)_2\}$  (70% recovery).

The seventh band from the original chromatogram yielded brown-black crystals of  $(\eta-C_5H_5)_3Rh_3(CO)(\mu-CO)\{\mu-C(O)C_2(CF_3)_2\}$  (0.052 g, 17%) m.p. 130°C (dec.) (Found: C, 36.0; H, 2.1; F, 15.3.  $C_{22}H_{15}F_6O_3Rh_3$  calcd.: C, 35.2; H, 2.0; F, 15.2%). Infrared absorption (KBr):  $\nu(CO)$  at 1995vs, 1811vs, 1624vs  $cm^{-1}$ ; with a sample prepared from  $^{13}CO$  enriched  $(\eta-C_5H_5)Rh(CO)_2$ , additional  $\nu(CO)$  absorptions were observed at 1951, 1779 and 1590  $cm^{-1}$ .  $^1H$  NMR spectrum ( $CDCl_3$ , 27°C):  $\delta$  5.64 (s, 5H,  $C_5H_5$ ), 5.55 (s, 5H,  $C_5H_5$ ), 5.35 ppm (s, 5H,  $C_5H_5$ ).  $^{19}F$  NMR spectrum ( $CDCl_3$ , 27°C):  $\delta$  41.2 (q, 3F,  $J(F-F)$  12.5 Hz,  $CF_3$ ), 55.3 ppm (q, 3F,  $J(F-F)$  12.5 Hz,  $CF_3$ ).  $^{13}C$  NMR ( $CDCl_3$ , 39°C):  $\delta$  220.3 (t,  $J(Rh-C)$  44 Hz,  $\mu-CO$ ), 212.0 (d,  $J(Rh-C)$  31 Hz, acyl-CO), 190.7 (d,  $J(Rh-C)$  81 Hz, CO), 95.6 (d,  $J(Rh-C)$  2 Hz,  $C_5H_5$ ), 92.4 (d,  $J(Rh-C)$  2 Hz,  $C_5H_5$ ), 90.4 ppm (s,  $C_5H_5$ ). Mass spectrum: 526 (10%,  $M - C_5H_5Rh(CO)_2$ ), 233 (100%,  $C_{10}H_{10}Rh^+$ ). TLC of a 6-day old solution of this complex separated small amounts of  $(\eta-C_5H_5)Rh(CO)_2$ ,  $(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$ ,  $(\eta-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$  and  $(\eta-C_5H_5)_3Rh_3-(CO)(CF_3C_2CF_3)$  from unchanged  $(\eta-C_5H_5)_3Rh_3(CO)(\mu-CO)\{\mu-C(O)C_2(CF_3)_2\}$  (40% recovery).

(c) Formation of  $(\eta-C_5H_5)_3Rh_3Co(CO)(\mu-CO)\{\mu-C(O)C_2(CF_3)_2\}$

$(\eta-C_5H_5)_2Rh_2(\mu-CO)(\mu-CF_3C_2CF_3)$  (0.092 g) and  $(\eta-C_5H_5)Co(CO)_2$  (0.20 g, mol ratio 1/6.3) in hexane (8 ml) were kept at 20°C for 42 h. The tube contents were extracted with chloroform, and solvent and excess  $(\eta-C_5H_5)Co(CO)_2$  were removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed by TLC with  $CH_2Cl_2$  as eluent. This separated three minor bands which were rejected from three major bands.

The first band was yellow and contained  $(\eta-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$  (0.012 g, 12%).

The second band gave a dark green solid, probable formula  $(\eta-C_5H_5)_3Rh_2Co(CO)_n(CF_3C_2CF_3)$  with  $n = 1, 2$  or 3, (0.008 g) m.p. 166°C. Infrared absorption (KBr):  $\nu(CO)$  at 1834vs, 1829vs, 1708vs  $cm^{-1}$ .  $^1H$  NMR spectrum ( $CDCl_3$ , 29°C):  $\delta$  5.36 (s, 10H,  $C_5H_5$ ), 4.88 ppm (s, 5H,  $C_5H_5$ ).  $^{19}F$  NMR spectrum ( $CDCl_3$ , 28°C):  $\delta$  51.6 ppm (s). Mass spectrum: 650 (48%,  $M$  ( $n = 1$ )), 622 (46%,  $M - CO$ ), 233 (100%,  $C_{10}H_{10}Rh^+$ ).

The third band was brown-green and gave green crystals, probable formula

$(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_2\text{Co}(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.052 g, 42%) m.p. 110°C. The sample deteriorated before it could be analyzed. Infrared absorption (KBr):  $\nu(\text{CO})$  at 2011 vs, 1813 vs, 1700 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  5.66 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.25 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.03 ppm (s, 5H,  $\text{C}_5\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  51.0 (poorly resolved multiplet, 3F,  $\text{CF}_3$ ), 60.9 ppm (poorly resolved multiplet, 3F,  $\text{CF}_3$ ). Mass spectrum: 650 (5%,  $M - 2\text{CO}$ ), 622 (7%,  $M - 3\text{CO}$ ), 526 (18%,  $M - \text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ ), 233 (100%,  $\text{C}_{10}\text{H}_{10}\text{Rh}^+$ ). TLC of a 24 h old solution of this complex separated nine bands; the major band contained unchanged complex (25% recovery).

(d) *Formation of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$*

$(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  (0.27 g) and  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  (0.15 g, mol ratio 1/1) in pentane (8 ml) were kept at 20°C for 1 week. Chromatography on a deactivated alumina column with X4 as eluent separated  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\text{-}(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (0.035 g, 13%) from a green band.

The latter yielded dark green crystals of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.357 g, 85%) m.p. 168°C. (Found: C, 39.7; H, 3.2; F, 14.1.  $\text{C}_{27}\text{H}_{25}\text{O}_3\text{F}_6\text{Rh}_3$  calcd.: C, 39.5; H, 3.1; F, 13.9%). Infrared absorption (KBr):  $\nu(\text{CO})$  at 1993vs, 1792s, 1693m  $\text{cm}^{-1}$ ; in  $\text{CHCl}_3$ ,  $\nu(\text{CO})$  at 2012vs, 1813s, 1795s, 1690m, 1673m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  5.54 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.27 (s, 5H,  $\text{C}_5\text{H}_5$ ), 1.83 ppm (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  53.3 (q, 3F,  $J(\text{F-F})$  12 Hz,  $\text{CF}_3$ ), 59.5 ppm (qd, 3F,  $J(\text{F-F})$  12 and  $J(\text{Rh-F})$  3 Hz,  $\text{CF}_3$ ).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ,  $\text{Cr}(\text{acac})_3$  added, 28°C):  $\delta$  224.5 (t,  $J(\text{Rh-C})$  41 Hz,  $\mu\text{-CO}$ ), 202.7 (d,  $J(\text{Rh-C})$  25 Hz, acyl-CO), 190.0 (d,  $J(\text{Rh-C})$  81 Hz, CO), 104.3 (d,  $J(\text{Rh-C})$  5 Hz,  $\text{C}_5\text{Me}_5$ ), 92.0 (d,  $J(\text{Rh-C})$  3 Hz,  $\text{C}_5\text{H}_5$ ), 91.2 (d,  $J(\text{Rh-C})$  3 Hz,  $\text{C}_5\text{H}_5$ ), and 9.0 ppm (s,  $\text{C}_5\text{Me}_5$ ). Mass spectrum: 820 (< 1%,  $M$ ), 792 (< 1%,  $M - \text{CO}$ ), 764 (1%,  $M - 2\text{CO}$ ), 736 (1%,  $M - 3\text{CO}$ ), 233 (100%,  $\text{C}_{10}\text{H}_{10}\text{Rh}^+$ ).

(e) *Decarbonylation of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  with  $\text{Me}_3\text{NO}$*

$(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.10 g, 0.12 mmol) and  $\text{Me}_3\text{NO}$  (0.018 g, 0.24 mmol) in acetone (60 ml) were heated at 56°C for 2 h. The initial brown-green solution turned deep-purple. Removal of solvent under reduced pressure and chromatography on a deactivated alumina column with X4 as eluent separated unchanged  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.01 g, 10%) from a purple band.

The latter gave purple-black crystals of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  (0.084 g, 90%) m.p. 225°C. (Found: C, 39.5; H, 3.6; F, 15.0.  $\text{C}_{25}\text{H}_{25}\text{F}_6\text{ORh}_3$  calcd.: C, 39.3; H, 3.3; F, 14.9%). Infrared absorption:  $\nu(\text{CO})$  at 1693vs (in  $\text{CH}_2\text{Cl}_2$ ) or at 1711vs  $\text{cm}^{-1}$  (in MeCN).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  5.25 (s, 10H,  $\text{C}_5\text{H}_5$ ), 1.83 (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  52.2 ppm (s,  $\text{CF}_3$ ).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 28°C):  $\delta$  239.0 (dt,  $J(\text{Rh-C})$  25 and  $J(\text{Rh'-C})$  42Hz,  $\mu_3\text{-CO}$ ), 102.7 (d,  $J(\text{Rh-C})$  6 Hz,  $\text{C}_5\text{Me}_5$ ) 89.1 (s,  $\text{C}_5\text{H}_5$ ), 9.7 ppm (s,  $\text{C}_5\text{Me}_5$ ). Mass spectrum: 764 (45%,  $M$ ), 736 (60%,  $M - \text{CO}$ ), 303 (100%,  $\text{C}_{15}\text{H}_{20}\text{Rh}^+$ ), 233 (100%,  $\text{C}_{10}\text{H}_{10}\text{Rh}^+$ ).

In the absence of  $\text{Me}_3\text{NO}$ , there was no thermal decomposition of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  in toluene below ca. 65°C. Work up of a solution that had been kept at 93°C for 30 min separated  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$  (8%),

$(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (8%) and  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{-C}_2\text{CF}_3)$  (26%) from unchanged starting complex (30% recovery).

(f) *Formation of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_2\text{Co}(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$*

$(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  (0.17 g) and  $(\eta\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$  (0.32 g, mol ratio 1/4) in hexane (10 ml) were kept at 25°C for 1 week. Chromatography on a column of deactivated alumina with X4/CHCl<sub>3</sub> (5/2) as eluent separated  $(\eta\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$  (0.10 g, 33%) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (0.045 g, 26%) from a green band.

Removal of solvent from the latter yielded dark green crystals of  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_2\text{Co}(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2(\text{CF}_3)_2\}$  (0.091 g, 37%) m.p. 156°C (Found: C, 41.7; H, 3.5; F, 14.4. C<sub>27</sub>H<sub>25</sub>CoF<sub>6</sub>O<sub>3</sub>Rh<sub>2</sub> calcd.: C, 41.8; H, 3.3; F, 14.7%). Infrared absorption: (KBr),  $\nu(\text{CO})$  at 1995vs, 1786 vs, 1696s; (CHCl<sub>3</sub>),  $\nu(\text{CO})$  at 2012vs, 1804vs, 1784s, 1694 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 28°C):  $\delta$  5.61 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.21 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 1.68 ppm (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>19</sup>F NMR spectrum (CDCl<sub>3</sub>, 28°C):  $\delta$  51.5 (q, 3F, *J*(F-F) 13 Hz, CF<sub>3</sub>), 60.1 ppm (q, 3F, *J*(F-F) 13 Hz, CF<sub>3</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, Cr(acac)<sub>3</sub>, added, 28°C):  $\delta$  238.2 (d, *J*(Rh-C) 42 Hz,  $\mu\text{-CO}$ ), 217.2 (s, acyl-CO), 189.4 (d, *J*(Rh-C) 80 Hz, CO), 129.9 (q, *J*(F-C) 274 Hz, CF<sub>3</sub>), 125.7 (q, *J*(F-C) 279 Hz, CF<sub>3</sub>), 101.2 (s, C<sub>5</sub>Me<sub>5</sub>), 92.3 (d, *J*(Rh-C) 3 Hz, C<sub>5</sub>H<sub>5</sub>), 91.6 (d, *J*(Rh-C) 3 Hz, C<sub>5</sub>H<sub>5</sub>), 8.8 (s, CH<sub>3</sub>). Mass spectrum: 776 (1%, *M*), 748 (4%, *M* - CO), 720 (15%, *M* - 2CO), 692 (17%, *M* - 3CO), 233 (100%, C<sub>10</sub>H<sub>10</sub>Rh<sup>+</sup>).

(g) *Treatment of  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  with  $(\eta\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})\text{L}$*

(i)  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$ . The reactants (1/1 mol ratio) in pentane were kept at 25°C for three weeks. Chromatography on deactivated alumina with X4/CH<sub>2</sub>Cl<sub>2</sub> as eluent separated: unchanged  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  (46%);  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (12%);  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{PPh}_3)(\text{CF}_3\text{C}_2\text{CF}_3)$  (11%); unchanged  $(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$  (54%) and  $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  (26%).

(ii)  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})(\text{PMePh}_2)$ . The reactants (1/1 mol ratio) in pentane were kept at 25°C for five weeks. Chromatography on deactivated alumina with X4/CH<sub>2</sub>Cl<sub>2</sub> as eluent separated:  $(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  (39%);  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (22%) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{PMePh}_2)(\text{CF}_3\text{-C}_2\text{CF}_3)$  (23%).

(iii)  $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})\{\text{P}(\text{OMe})_3\}$ . The reactants (1/1 mol ratio) in pentane were kept at 25°C for 3 weeks. Chromatography on deactivated alumina with X4 as eluent separated:  $(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_3(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$  (42%);  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  (29%) and  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{CF}_3\text{C}_2\text{CF}_3)$  (28%).

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