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THE FORMATION, STRUCTURE, AND DECARBONYLATION OF $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2\{\mu\text{-}\eta^1,\eta^1\text{-}C(O)C_2(CF_3)_2\}$

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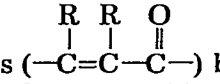
Summary

The complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$ is obtained, together with the known *cis*- and *trans*-isomers of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$, when the intractable products formed from $[Rh(CO)_2Cl]_2$ and $CF_3C{\equiv}CCF_3$ at 25° C are treated with $(C_5H_5)Tl$. An X-ray diffraction study on crystals of the tricarbonyl complex has established that it contains two terminal carbonyls in *trans*-arrangement, and a 1-ene-3-one unit, $C(CF_3){=}C(CF_3)C(O)$, which bridges the metal—metal bond. NMR data for solutions of the complex have been interpreted in terms of an equilibrium between the solid state species (II) and an isomer (III) which has two bridging carbonyls. The proportion of III in the equilibrium mixture increases as the temperature is lowered. Coupling constant data indicate that there is rapid carbonyl scrambling in II, even at —100° C. Decarbonylation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$ is achieved at 25° C by treatment with Me_3NO; this reaction produces *cis*- and *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2$-$(CF_3C_2CF_3)$ plus $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CF_3C_2CF_3)$.

There is growing interest [1,2] in the possibility that binuclear metal complexes may play a key role in many metal-mediated organic syntheses. Recently, Knox et al. reported [3,4] the structures of some dimetallocycles in which 1-ene-3-one groups ( $-\overset{R}{\overset{|}{C}}=\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-$) bridge metal—metal bonds. These bridging groups are formed under mild conditions by condensation of an alkyne with a carbonyl group at the dinuclear metal centre. Spectroscopic data reveal that the complexes are fluxional in solution, and that fluxionality involves facile C—C bond breaking in some complexes. Thus, the formation and

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properties of these complexes establish that a dimetal centre can provide a suitable base for facile C—C bond formation and cleavage.

In our studies of the reaction of alkynes with carbonylrhodium compounds, we have isolated and characterized another binuclear complex which incorporates the 1-ene-3-one bridging group. We report our structural characterization of the dirhodium compound, which establishes that the nature of the bridge bond differs from that for the diruthenium [3] and ditungsten [4] complexes studied by Knox. We also show that the fluxional behavior of the dirhodium complex in solution does not involve changes in the ene-one bridging group. Finally, we discuss a reaction of the dirhodium complex in which there is facile breaking of a C—C bond within the bridging group.

Formation and characterization of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$

In a previous study [5], we obtained a solvated fluorocarbon-rhodium complex of approximate formula $[RhCl(CO)_{2 \text{ or } 3}(C_4F_6)]_n$ from the reaction between $[Rh(CO)_2Cl]_2$ and hexafluorobut-2-yne at 80—120° C. Treatment of the complex with cyclopentadienylthallium gave the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2Rh_2(CF_3C_2CF_3)_2$ in low yield. Repetition of the reaction between $[Rh(CO)_2Cl]_2$ and hexafluorobut-2-yne at room temperature, and subsequent treatment of the intractable products with cyclopentadienylthallium, has given three major products. Two of these have been characterized as the *trans*- and *cis*-isomers of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$. A detailed discussion of the spectroscopic properties of these species is reported elsewhere [6], and the structure of the *trans*-isomer has been determined by single crystal X-ray diffraction [7]. The third product is an orange crystalline solid of formula $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$.

The parent ion is exceedingly weak in the mass spectrum of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$, but peaks corresponding to the fragmentation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ are clearly observed. The infrared spectrum shows bands at 2010, 1860, and 1630 cm^{-1} which can be assigned to terminal, bridging, and ketonic carbonyls, respectively. These assignments were confirmed by preparation of a sample using ^{13}CO-enriched $[Rh(CO)_2Cl]_2$. In addition to the bands listed above, bands were observed at 1963, 1819, and 1597 cm^{-1} (Fig. 1), in good agreement with values (1965, 1819, and 1594) calculated using a simple conversion factor based on reduced masses of ^{12}CO and ^{13}CO. Additional weak bands are observed at 1922, 1882, and 1827 cm^{-1} in the carbonyl region for the ^{13}CO-enriched sample, and the origin of these bands is not clear. Two weak bands at 1589 and 1572 cm^{-1} may be associated with the C—C double bond. The infrared data are consistent with a structure I which incorporates one terminal and one bridging carbonyl and a metallocyclobutenone. Alternatively, the isomers II and III could co-exist in both the solid and solution phases.

The ^1H NMR spectrum of the complex exhibits a broad singlet at δ 5.64 ppm in $CDCl_3$, but in acetone-d_6 this separates into two resonances at δ 5.91(s) and 5.76(d) ppm (J(Rh—H) 0.6 Hz). These resonances show small shifts of position with temperature (δ 5.91 and 5.76 ppm at 28° C shift to δ 6.17 and 6.00 ppm at —93° C). The ^{19}F spectrum ($CDCl_3$) consists of two quartets at δ 53.26 and 59.27 ppm with $J(F—F')$ ~14 Hz. This coupling constant is larger

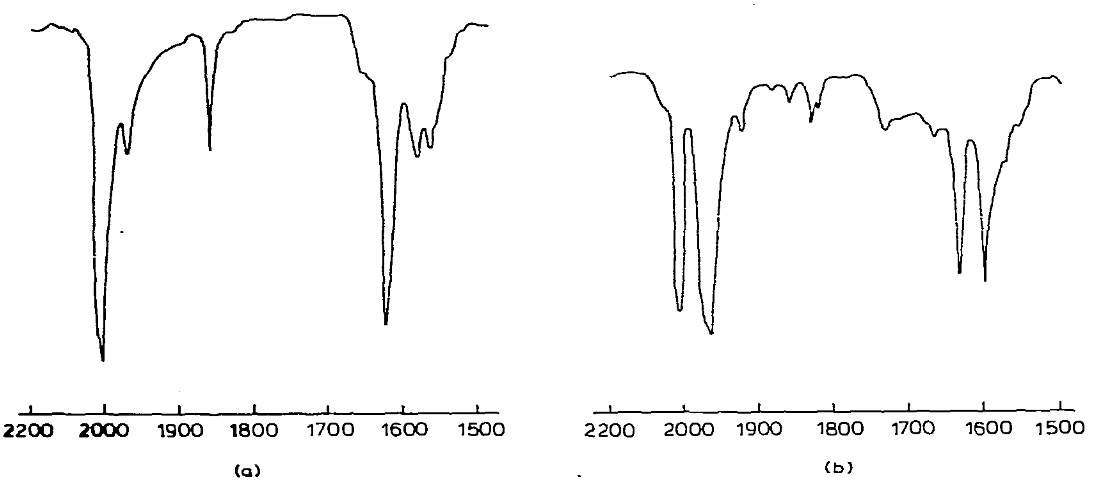
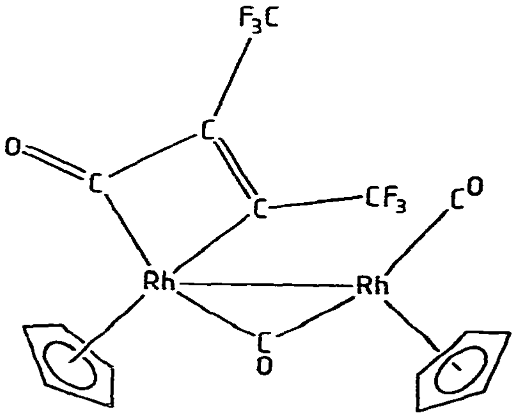


Fig. 1. Infrared spectrum in the carbonyl region (2100—1600 cm^{-1}) for $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$: (a) KBr disk, (b) ^{13}CO-enriched sample, KBr disk.

than the values reported for CF_3-substituted metallocyclobutenones and analogous four-membered heterocycles [8—11]. The resonance at lower field shows further unresolved coupling and is therefore assigned to the CF_3 group on the carbon atom adjacent to a rhodium. The magnitude of the F—F coupling indicates that the CF_3 groups are in a *cis*-arrangement. The ^{13}C spectrum of a ^{13}CO-enriched sample reveals, in addition to the resonances for two inequivalent $(\eta\text{-}C_5H_5)$ groups, two multiplets which show large shifts of position with temperature. The resonance at lower field is a doublet with *J*(Rh—C) 28 Hz. The second resonance has the appearance of a 1/2/1 triplet, but at higher resolution the central peak is split, indicating that this resonance is a doublet of doublets with *J*(Rh—C) ~40 Hz and *J*(Rh'—C) ~38 Hz. When the relaxation agent $Cr(acac)_3$ is added to the solutions, integration of the spectrum indicates relative intensities of 1/2 for the carbonyl multiplets. The position of the doublet changes from 213.7 ppm at 37°C to 219.3 ppm at —95°C. For the doublet of doublets, the chemical shift changes from 197.4 ppm at 37°C to 209.3 ppm at —95°C. There is no significant change in the profile of either peak over this temperature range. This variation in chemical shift with temperature is unusual, but similar behavior has been reported [12] for the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(PMe_2Ph)$, where the terminal and bridging carbonyls were found to be exchanging at the lowest temperature studied (—104°C), and the average resonance moved downfield 7 ppm on cooling from 25 to —104°C.

The room temperature ^{13}C data for $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$ are consistent with a rapid one-for-one two centre exchange of terminal and bridging carbonyls in I (cf. $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2L$, L = PMe_2Ph or $P(OPh)_3$ [12,13]), or alternatively, with rapid scrambling of the terminal carbonyls in II via the bridged species III (cf. $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ [6]). Uncertainty about how to interpret the spectroscopic data prompted us to determine the solid state structure of the complex by single crystal X-ray diffraction.



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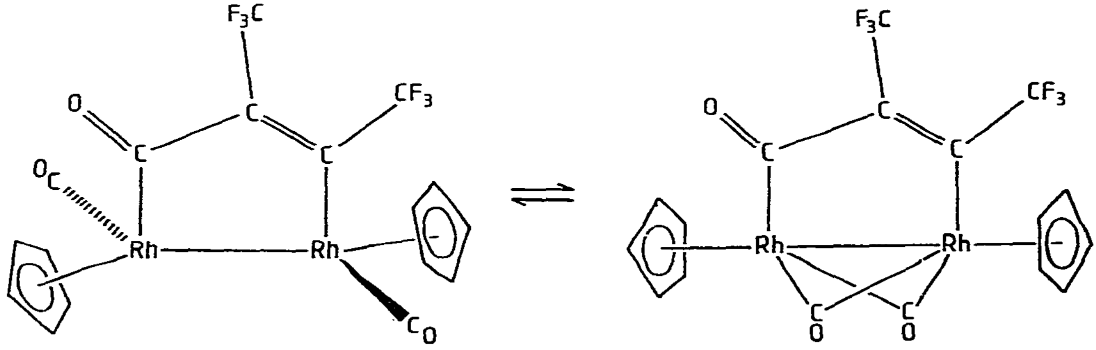


II

III

Crystal and molecular structure of the complex

A representative tabular crystal (0.025 × 0.138 × 0.138 mm) was selected and mounted on a quartz fibre. All data were collected on a Philips PW 1100 diffractometer with Mo-K_α radiation (λ 0.7107 Å).

Crystal data

$C_{17}H_{10}F_6O_3Rh_2$, M 581.88, monoclinic, a 8.276(6), b 14.776(7), c 14.753(7) Å, β 101.85(5)°, U 1765.64 Å^3. D_m 2.19(3), D_c ($Z = 4$) 2.189 g cm^{-3}, $F(000)$ 1096, systematic absences $h0l$ l odd, $0k0$ k odd, space group $P2_1/c$ (C_{2h}^5), μ 17.6 cm^{-1} for Mo-K_α radiation.

Intensity measurements and structure solution

5503 unique reflections were collected by the $\theta/2\theta$ scan technique with a scan range of ±0.70° from the calculated Bragg scattering angle (with an allowance for dispersion) at a rate of 0.05° sec^{-1}. The 5503 reflections were reduced to 2937 with $I \geqslant 3\sigma(I)$ in a manner described previously [14]. Three approximately axial reflections, monitored every 1.5 h, showed no systematic variation in intensity.

The atomic scattering factors [15] for Rh, C, F and O were corrected for

FINAL POSITIONAL AND THERMAL PARAMETERS (Estimated standard deviations are in parentheses)

(a) Atoms with anisotropic thermal parameters ($\times 10^3$, *Rh* $\times 10^4$)

The anisotropic thermal parameter is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	1573(1)	1761(1)	1928(1)	310(2)	252(2)	294(2)	40(2)	−3(2)	−9(2)
Rh(2)	2658(1)	3121(1)	1009(1)	323(1)	250(2)	330(2)	28(2)	6(2)	−63(2)
O(1)	38(8)	3324(4)	2731(4)	90(4)	63(3)	84(4)	−13(3)	43(4)	15(3)
O(2)	2966(7)	1668(4)	−363(3)	71(4)	62(3)	54(3)	−16(3)	15(3)	−3(3)
O(3)	−397(7)	3975(3)	195(6)	79(4)	33(3)	196(8)	30(4)	−53(5)	6(3)
F(1)	−3320(5)	1246(4)	581(4)	28(2)	145(5)	134(5)	56(4)	−13(3)	−20(3)
F(2)	−1463(7)	307(3)	448(4)	99(4)	55(3)	131(5)	−17(3)	2(4)	−34(3)
F(3)	−1728(6)	752(2)	1776(4)	78(3)	130(5)	85(4)	51(3)	10(3)	−48(3)
F(4)	−2613(5)	1660(3)	−970(3)	70(3)	72(3)	71(3)	−18(3)	−26(3)	−4(2)
F(5)	−1807(6)	2953(3)	−1274(4)	67(3)	105(4)	53(3)	33(3)	0(2)	98(3)
F(6)	−3592(5)	2835(4)	434(3)	37(2)	118(4)	83(3)	8(3)	1(2)	33(2)

(b) Atoms with isotropic thermal parameters ($\times 10^3$)

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
C(1)	−506(7)	1769(4)	889(4)	32(1)	C(10)′	4008(52)	941(30)	2019(32)	58(11)
C(2)	−816(7)	2418(4)	245(4)	34(1)	C(11)′	2552(49)	410(21)	1722(23)	39(8)
C(3)	253(8)	3246(4)	389(5)	44(2)	C(12′)	1720(30)	338(17)	2503(23)	26(7)
C(4)	−1738(9)	1023(5)	912(5)	56(2)	C(13)	3302(14)	4586(6)	915(8)	37(2)
C(5)	−2199(8)	2462(5)	−589(5)	45(2)	H(13)	2650	4956	320	
C(6)	656(9)	2741(5)	2421(5)	48(2)	C(14)	2936(14)	4409(7)	1817(9)	46(3)
C(7)	2829(8)	2200(4)	190(4)	39(1)	H(14)	1825	4584	2053	
C(8)	3317(14)	1207(6)	3187(7)	41(3)	C(15)	4220(14)	3793(7)	2306(7)	44(3)
H(8)[a]	3671	1670	3761		H(15)	4261	3441	2952	
C(9)	1932(12)	606(7)	2951(8)	42(3)	C(16)	5307(13)	3601(7)	1703(9)	41(3)
H(9)	1034	474	3372		H(16)	6218	3068	1836	
C(10)	1947(11)	244(6)	2035(8)	38(2)	C(17)	4745(15)	4073(7)	861(8)	37(3)
H(10)	1181	−295	1688		H(17)	5209	4000	231	
C(11)	3303(13)	625(6)	1727(6)	36(2)	C(13′)	2919(30)	4616(16)	1324(25)	33(6)
H(11)	3658	467	1080		C(14′)	3457(31)	4146(16)	2148(17)	29(6)
C(12)	4160(11)	1207(6)	2425(8)	35(2)	C(15′)	4905(40)	3684(18)	2052(22)	37(7)
H(12)	5072	1725	2406		C(16′)	5217(47)	3812(27)	1265(34)	66(10)
C(8′)[b]	2589(53)	946(27)	3204(26)	52(10)	C(17′)	4147(50)	4320(23)	826(21)	49(8)
C(9′)	3847(41)	1217(19)	2865(28)	34(7)					

[a] Hydrogen atoms are numbered according to the carbons to which they are bonded. Their thermal parameters are equal to 73(11). [b] Atom numbers in alternate configuration of Cp rings.

anomalous dispersion with values taken from Cromer and Liberman [16]. All calculations were carried out on the Monash University B 6700 computer, the major program being that of Sheldrick [17].

The structure was solved by conventional Patterson and Fourier methods. The cyclopentadienyl rings exist in two orientations, and the proportion of each ring was determined by allowing the relative occupancies to be refined. The refined proportions were 0.77/0.23 and 0.74/0.26 for the C_5H_5 rings attached to Rh(1) and Rh(2), respectively.

A total of twelve low angle reflections were severely affected by extinction and were omitted from the refinement. The oxygen and fluorine atoms had large thermal vibrations and were refined anisotropically in final refinement cycles; the rhodium atoms were also refined anisotropically. A correction for absorption was applied. The final R factors were $R_1 = 0.0403$ and $R_2 = 0.0394$ where $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ and $R_2 = [\omega(|F_0| - |F_c|)^2/\Sigma |F_0|^2]^{1/2}$, and individual reflections were assigned weights equal to $1/\sigma^2(F)$. Final positional and thermal parameters are given in Table 1.

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

Discussion of the structure

The structure consists of a (η-C_5H_5)Rh(CO) dimer with a 1-ene-3-one bridging unit which is σ-bonded along the Rh—Rh bond; this forms a distorted five-membered ring. A terminal carbonyl is bound to each rhodium, and these carbonyls are mutually *trans* (Fig. 2). Apart from the staggered configuration of the cyclopentadienyl groups, the geometry about each rhodium atom is similar to that in *trans*-(η-C_5H_5)$_2$Rh$_2$(CO)$_2$($CF_3C_2CF_3$) [7].

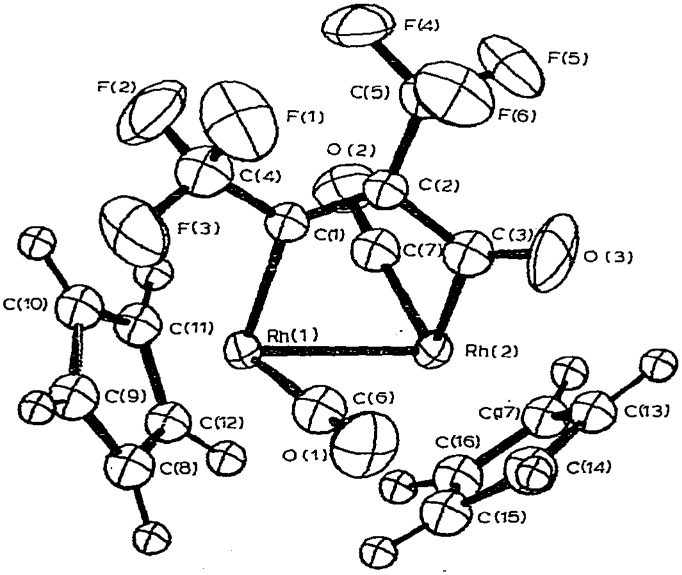


Fig. 2. Molecular structure of the complex (η-C_5H_5)$_2$Rh$_2$(CO)$_3$($CF_3C_2CF_3$). The cyclopentadienyl groups are shown in their predominant orientation. The 50% probability ellipsoids are shown, 30% for hydrogen.

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) (Estimated standard deviations are in parentheses)

Rh(1)—C(1)	2.056(5)	C(8')—C(9')	1.307(52)
Rh(1)—C(6)	1.852(7)	C(9')—C(10')	1.346(52)
Rh(1)—Rh(2)	2.680(1)	C(10')—C(11')	1.429(49)
Rh(2)—C(3)	2.021(6)	C(11')—C(12')	1.462(44)
Rh(2)—C(7)	1.845(6)	C(12')—C(8')	1.446(44)
C(1)—C(2)	1.336(5)	C(13')—C(14')	1.392(36)
C(1)—C(4)	1.506(9)	C(14')—C(15')	1.411(39)
C(2)—C(3)	1.499(8)	C(15')—C(16')	1.255(50)
C(2)—C(5)	1.500(8)	C(16')—C(17')	1.237(48)
C(3)—O(3)	1.213(8)	C(17')—C(13')	1.440(43)
C(4)—F(1)	1.341(8)		
C(4)—F(2)	1.306(9)	C(1)—Rh(1)—Rh(2)	86.2(2)
C(4)—F(3)	1.335(8)	C(1)—Rh(1)—C(6)	86.6(3)
C(5)—F(4)	1.327(7)	Rh(1)—C(1)—C(2)	122.9(4)
C(5)—F(5)	1.336(8)	Rh(1)—C(1)—C(4)	116.5(4)
C(5)—F(6)	1.339(8)	C(4)—C(1)—C(2)	120.6(5)
C(6)—O(1)	1.144(8)	C(1)—C(2)—C(3)	117.6(5)
C(7)—O(2)	1.155(7)	C(1)—C(2)—C(5)	128.1(5)
C(8)—C(9)	1.435(13)	C(3)—C(2)—C(5)	114.1(5)
C(9)—C(10)	1.456(13)	C(2)—C(3)—Rh(2)	119.2(4)
C(10)—C(11)	1.411(13)	C(2)—C(3)—O(3)	118.2(6)
C(11)—C(12)	1.415(12)	O(3)—C(3)—Rh(2)	122.4(5)
C(12)—C(8)	1.441(13)	C(3)—Rh(2)—Rh(1)	84.1(2)
C(13)—C(14)	1.448(13)	C(3)—Rh(2)—C(7)	88.4(3)
C(14)—C(15)	1.471(14)	Rh(1)—C(6)—O(1)	177.3(7)
C(15)—C(16)	1.419(15)	Rh(2)—C(7)—O(2)	175.3(6)
C(16)—C(17)	1.417(15)		
C(17)—C(13)	1.430(13)		

The interatomic bond lengths and angles are given in Table 2. The average Rh—C(C_5H_5) bond length of 2.269 Å (2.263 Å for Rh—C') is somewhat longer than that observed for either (η-C_5H_5)$_2$Rh$_2$(CO)$_2$($CF_3C_2CF_3$) or (η-C_5H_5)$_2$Rh$_2$(CO)($CF_3C_2CF_3$) with values of 2.25 and 2.266 Å, respectively [7,8]. Consequently the average perpendicular distances between the planes containing the cyclopentadienyl rings and their rhodium atoms are greater; 1.90 and 1.88 Å compared to 1.912 Å (1.936 Å for Rh—C') for this work (Table 3). The (F_3C)-C=C(CF_3) distance of 1.336(5) Å is also significantly longer than the value of 1.269(14) Å observed for (η-C_5H_5)$_2$Rh$_2$(CO)$_2$($CF_3C_2CF_3$) [7]. The distance observed in the present study is normal for a localized C=C double bond. Apart from these notable exceptions, the bond lengths and angles are well within the range observed for similar structures.

The carbon atom, C(3), is displaced by 0.523(7) Å out of the mean plane through the atoms Rh(1), Rh(2), C(1) and C(2) (Table 3). The oxygen, O(3), which is attached to C(3) exhibits a very large thermal vibration. It is possible that the displacement of C(3) is the result of a slight strain in the Rh(2)Rh(1)-C(1)C(2)C(3) ring. We note that the CF_3 substituent that is attached to C(2) is displaced towards C(3)—O(3) and this could contribute to the strain. The unusual thermal vibration of O(3) could be due to a small disorder effect in the location of this atom and this may possibly be related to the occurrence of the two orientations of the adjacent C_5H_5 ring. A search for short non-binding interactions that could affect the position of the O(3) atom has revealed no

TABLE 3

EQUATIONS OF MEAN PLANES AND DEVIATIONS (Å) OF INDIVIDUAL ATOMS FROM PLANES

Estimated standard deviations are in parentheses

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z by the matrix equation:

$$\begin{pmatrix} 8.275 & 0 & -3.029531 \\ 0 & 14.776 & 0 \\ 0 & 0 & 14.438592 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Plane 1:	C(8), C(9), C(10), C(11), C(12)			
	$(-0.4973)x + (0.7624)y + (-0.4142)z - (-1.4330) = 0$			
	C(8)	0.01(1)	C(11)	0.01(1)
	C(9)	0.01(1)	C(12)	0.01(1)
	C(10)	−0.01(1)	Rh(1)	1.907(1)
Plane 2:	C(13), C(14), C(15), C(16), C(17)			
	$(-0.5022)x + (-0.7821)y + (-0.3690)z - (-7.0124) = 0$			
	C(13)	−0.01(1)	C(16)	0.0(1)
	C(14)	0.01(1)	C(17)	0.01(1)
	C(15)	−0.01(1)	Rh(2)	1.917(1)
Plane 3:	C(8′), C(9′), C(10′), C(11′), C(12′)			
	$(-0.4713)x + (0.7902)y + (-0.3917)z + (-1.2899) = 0$			
	C(8′)	0.03(4)	C(11′)	0.05(3)
	C(9′)	0.0(3)	C(12′)	−0.05(2)
	C(10′)	−0.03(4)	Rh(1)	1.917(1)
Plane 4:	C(13′), C(14′), C(15′), C(16′), C(17′)			
	$(-0.4980)x + (-0.7900)y + (-0.3575)z - (-7.0623) = 0$			
	C(13′)	−0.01(3)	C(16′)	0.0(4)
	C(14′)	0.01(3)	C(17′)	0.01(4)
	C(15′)	−0.01(3)	Rh(2)	1.955(1)
Plane 5:	C(1), C(2), Rh(1), Rh(2)			
	$(0.5174)x + (-0.6437)y + (-0.5638)z - (-2.8333) = 0$			
	C(1)	0.072(6)	Rh(2)	0.022(1)
	C(2)	−0.054(6)	C(3)	−0.523(7)
	Rh(1)	−0.040(1)	O(2)	−1.307(6)

near neighbours. The closest atoms are a F atom of the adjacent CF_3 group (F···O, 2.701(8) Å) and a hydrogen atom attached to a C_5H_5 group of an adjacent molecule (H···O, 2.442(6) Å).

An illustration of the unit cell contents is shown in Fig. 3. There are no unusual intermolecular contacts observed for this structure.

Rationalization of the spectroscopic results

The observation of structure II for crystals of the complex allows a more definitive interpretation of most of the spectroscopic results. We suggest the following.

In solution at room temperature, isomers II and III exist in equilibrium, and the carbonyls in II scramble rapidly between the alternative rhodium sites via the bridged carbonyl species III. At low temperature (−93° C), rapid carbonyl scrambling is maintained but the equilibrium II $\rightleftharpoons$ III is shifted in favor of III. The NMR data provide strong support for this interpretation. In the carbonyl

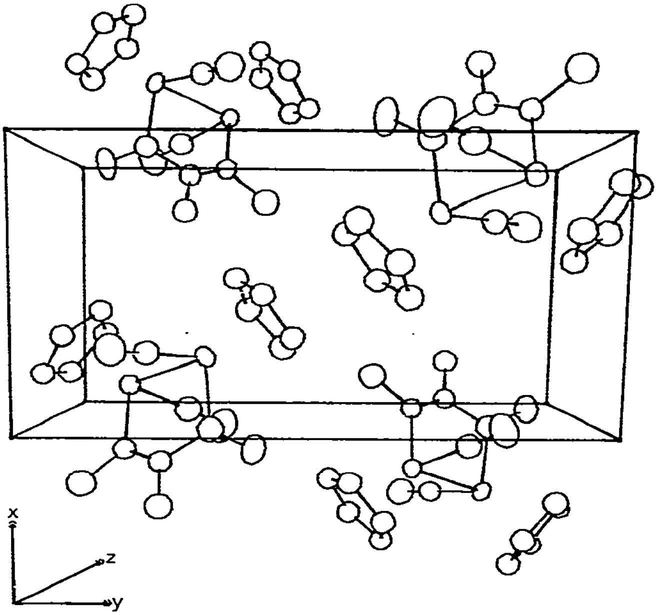


Fig. 3. Unit cell contents of (η-C_5H_5)$_2$$Rh_2(CO)_3$($CF_3C_2CF_3$). Fluorine and hydrogen atoms have been omitted. The cyclopentadienyl groups are shown in their predominant orientation.

region of the ^{13}C spectrum, the observed doublet of doublets (J 40 Hz, J' 38 Hz) is expected for II with rapid CO exchange, and for isolated III. For II without rapid CO scrambling, J(Rh—C) would be expected to be approximately 80 Hz (cf. J(Rh—C) 83, 85, and 79 Hz for (η-C_5H_5)$_2$$Rh_2(CO)_3$ (IV), (η-C_5H_5)$_2$$Rh_2(CO)_2${P(OPh)$_3$} (V) [12,13], and ($\eta$-$C_5H_5$)$_2$$Rh_2(CO)_2$($CF_3C_2CF_3$) (VI) [6] at the slow-exchange limit). The chemical shift (δ 197.4 ppm) of this resonance is between the normal ranges for terminal carbonyls (cf. $\delta(CO_t)$ at 191.8, 190.4, and 190.8 ppm for IV, V, and VI) and bridging carbonyls (cf. $\delta(CO_{br})$ at 231.8, 239.4 and 205.1 ppm for IV, V, and (η-C_5H_5)$_2$$Rh_2$($\mu$-CO)($CF_3C_2CF_3$), respectively). At low temperature, there is no change in the coupling pattern but the chemical shift is displaced towards the bridging carbonyl region (δ(CO) 197.4 ppm at 37°C to 209.4 ppm at −95°C). Thus, the solid state structure II appears to be less favored in solution at low temperature. The observation that the C_5H_5 resonances in the ^1H spectra are also temperature dependent (5.91 and 5.76 ppm at 28°C → 6.17 and 6.00 ppm at −93°C) is consistent with these views.

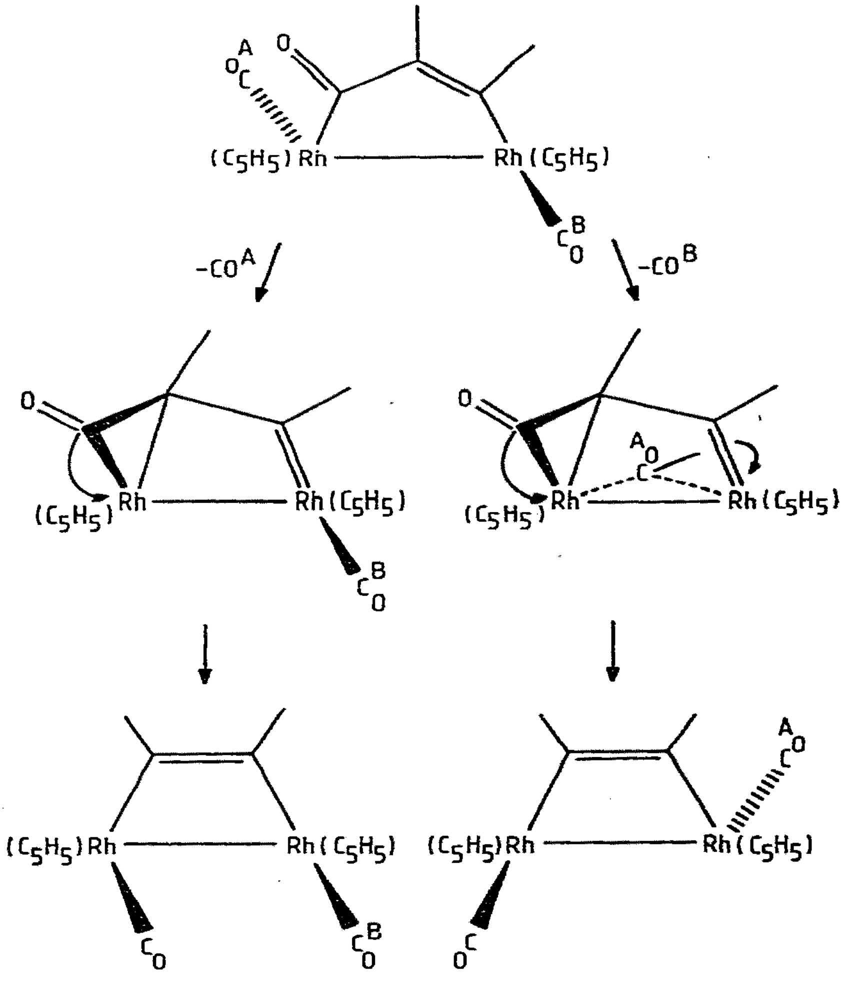
There is no evidence for involvement of the acyl-carbonyl in the fluxional process. Thus, the ^{13}C resonance for this group remains as a doublet (J(Rh—C) 28 Hz) throughout the temperature range studied. Again, there is a drift in the chemical shift as the temperature is lowered (δ 213.7 ppm at 37°C → 219.3 ppm at −95°C).

We remain somewhat confused by the infrared results where a bridging carbonyl is indicated for both solution and solid phases. We do note that the relative intensity of the band at 1860 cm^{-1} varies somewhat from sample to sample, and we have checked that it is indeed present in the spectra of samples which are crystallographically identical to that used in the crystal structure determination. Perhaps the barrier to interconversion between II and III is so low that II is converted to a mixture of II and III even by grinding in the process of preparing a KBr disk or a Nujol mull.

Decarbonylation of the complex

We have shown previously that $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is decarbonylated upon treatment with Me_3NO to give the monocarbonyl species $(\eta\text{-}C_5H_5)_2\text{-}Rh_2(\mu\text{-}CO)(CF_3C_2CF_3)$. Decarbonylation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2\{(CF_3C_2CF_3)\text{-}(CO)\}$ can also be achieved with Me_3NO in acetone at room temperature. The products of this reaction are *cis*- and *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (total yield ~60%) and $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (yield ~40%). Presumably,

SCHEME 1



these products are formed according to the reaction sequence:

$$\begin{tikzcd}
(\eta\text{-}C_5H_5)_2Rh_2(CO)_2\{(CF_3C_2CF_3)CO\} \arrow[r, "Me_3NO"] & (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{(CF_3C_2CF_3)CO\} \arrow[d] \\
 & (\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3) \arrow[d, "Me_3NO"'] \\
 & (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CF_3C_2CF_3)
\end{tikzcd}$$

Rearrangement of the acyl-intermediate $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{(CF_3C_2CF_3)CO\}$ to $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ involves a particularly facile cleavage of a C—C bond within the bridging unit.

Scheme 1 outlines a pathway for the decarbonylation and subsequent rearrangement reaction. It can be seen that the formation of *cis*- or *trans*-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ depends upon which of CO^A or CO^B is removed initially. As reported in an earlier study [6], the *cis*-dicarbonyl complex transforms to the *trans*-isomer in solution with a half-life of about 12 h at room temperature. The decarbonylation reaction is not reversible, at least under mild conditions. Thus, $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is recovered unchanged when CO is bubbled through solutions of the complex at room temperature.

Experimental

(a) General

Tetracarbonyldi-μ-chlorodirhodium, $[Rh(CO)_2Cl]_2$, was prepared [19] from $RhCl_3 \cdot 3\ H_2O$ and CO at 105°C. Hexafluorobut-2-yne was obtained from Bristol Organics Ltd., and trimethylamine-*N*-oxide dehydrate from Ega-Chemie; anhydrous Me_3NO was produced by heating to 100°C under vacuum. Hydrocarbon solvents were dried over sodium wire before use.

Thin layer chromatography was carried out on 20 by 20 cm plates with 1/1 silica gel G-HF_{254} mixture as adsorbent.

Infrared spectra were recorded with a Perkin—Elmer 521 spectrometer. A Bruker WH-90 spectrometer was used to obtain the nuclear magnetic resonance spectra; the ^1H magnetic resonance spectra are reported as δ values, the ^{19}F chemical shifts are reported upfield from trichlorofluoromethane internal reference, and the ^{13}C chemical shifts are downfield from tetramethylsilane. Mass spectra were recorded with a V.G. Micromass 7070-F spectrometer. Microanalyses (C, H and F) were performed by the Australian Microanalytical Service, Melbourne.

(b) Preparation of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2\{(CF_3C_2CF_3)CO\}$ and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$

Tetracarbonyldi-μ-chlorodirhodium (0.295 g), hexafluorobut-2-yne (1.7 g, mole ratio 1/14) and benzene (10 ml) were kept at 20°C for 108 h in a Carius tube. Excess alkyne was removed. A yellow solid (0.380 g) was collected by filtration and was washed with benzene.

The yellow solid (0.308 g) and cyclopentadienylthallium (0.364 g, mol ratio Cl/Tl $\approx$ 1/1.2) in hexane (20 ml) were stirred at 20°C for 1 h. The reaction mixture was filtered and the residue was washed with dichloromethane. The filtrate was concentrated and chromatographed by TLC with hexane/dichloromethane (1/1) as eluent. This separated three orange bands from some minor products.

The first orange band gave *trans*-(η-C_5H_5)$_2$$Rh_2(CO)_2(CF_3C_2CF_3)$ (0.109 g), which was identified spectroscopically [6]. The second band yielded orange crystals of *cis*-(η-C_5H_5)$_2$$Rh_2(CO)_2(CF_3C_2CF_3)$ (0.107 g) m.p. 146°C (Found: C, 34.8; H, 2.0; F, 20.6. $C_{16}H_{10}F_6O_2Rh_2$ calcd.: C, 34.7; H, 1.8; F, 20.6%). Infrared absorption (KBr): ν(CO) at 2002vs and 1966s, ν(C=C) at 1642m cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, 28°C): δ 5.59(s) ppm. ^{19}F NMR spectrum ($CDCl_3$, 28°C): δ 55.12(m) ppm. ^{13}C NMR spectrum (CD_2Cl_2, 30°C): δ 190.4 (d, *J*(Rh—C) 78.7 Hz, CO) and 90.1 ppm (s, C_5H_5). Mass spectrum: 554 (<1%, *M*), 526 (28%, $M - CO$), 233 (100%, $C_{10}H_{10}Rh^+$).

The third band gave orange crystals of (η-C_5H_5)$_2$$Rh_2(CO)_2\{(CF_3C_2CF_3)CO\}$ (0.020 g) m.p. 149°C (dec.). (Found: C, 35.8; H, 1.7; F, 19.5. $C_{17}H_{10}O_3F_6Rh_2$ calcd.: C, 35.1; H, 1.7; F, 19.6%). Infrared absorption (KBr): ν(CO) at 2020(sh), 2008vs, 1859m and 1628vs cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, 24°C): δ 5.64 (s, br) ppm. (Acetone-d_6; 28°C); δ 5.91(s) and 5.76(s) ppm. ^{19}F NMR spectrum ($CDCl_3$, 23°C): δ 53.3 (q, *J*(F—F) 13.7 Hz, 3 F) and 59.3 ppm (q, *J*(F—F) 13.7 Hz, 3 F). ^{13}C NMR spectrum (acetone-d_6, 28°C): δ 214.6 (d, *J*(Rh—C) 28.0 Hz), 199.3 (dd, *J*(Rh—C) 38.2 and *J*(Rh'—C) 40.4 Hz), 96.0(s) and 93.1 ppm (s). Mass spectrum: 554 (<1%, $M - CO$), 526 (26%, $M - 2$ CO), 498 (3%, $M - 3$ CO), 233 (100%, $C_{10}H_{10}Rh^+$).

(c) Reaction of (η-C_5H_5)$_2$$Rh_2(CO)_2\{(CF_3C_2CF_3)CO\}$ with Me_3NO

(η-C_5H_5)$_2$$Rh_2(CO)_2\{(CF_3C_2CF_3)CO\}$ (0.037 g) and Me_3NO (0.009 g, mol ratio 1/1.9) in acetone (2 ml) were stirred at 20°C for 2 h. Evaporation of the solvent, and chromatography of the residue by TLC with hexane/dichloromethane (1/1) as eluent separated three main bands from a number of minor bands. Further chromatography of the three main bands on a short alumina column yielded (η-C_5H_5)$_2$$Rh_2(CO)(CF_3C_2CF_3)$ (0.013 g, 39%), *trans*-(η-C_5H_5)$_2$-$Rh_2(CO)_2(CF_3C_2CF_3)$ (0.012 g, 34%) and *cis*-(η-C_5H_5)$_2$$Rh_2(CO)_2(CF_3C_2CF_3)$ (0.009 g, 25%). All products were identified spectroscopically.

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