

The Crystal and Molecular Structure of Bis(η -cyclopentadienyl)- μ -[(1,2,5- η :1,4,5- η)-1,2-dimethyl-3-oxo-4,5-bis(trifluoromethyl)-1,4-pentadiene-1,5-diy]dirrhodium (Rh–Rh)

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The structure of bis(η -cyclopentadienyl)- μ -[(1,2,5- η :1,4,5- η)-1,2-dimethyl-3-oxo-4,5-bis(trifluoromethyl)-1,4-pentadiene-1,5-diy]dirrhodium (Rh–Rh), (η -C₅H₅)₂Rh₂{ μ -[(CH₃C₂CH₃)CO(CF₃C₂CF₃)]}, has been determined from 2161 diffractometer data and refined by least squares to $R = 0.041$. The compound is monoclinic, space group $P2_1/n$, with $a = 14.279$ (5), $b = 16.446$ (6), $c = 7.815$ (5) Å, $\beta = 93.15$ (5)°, $Z = 4$. The compound contains a Rh–Rh bond [2.614 (2) Å], and the bridging pentadienone unit is bonded from the terminal C atoms and from the diene π bonds to the two Rh atoms.

Introduction

Compounds containing a pentadienone unit complexed between two metal atoms have been proposed as intermediates in the formation of cyclopentadienone–metal complexes and of free cyclopentadienones (Hubel, 1968). Two different pentadienone–dimetal arrangements are possible (Fig. 1). In (A), one of the metal atoms is σ bonded to both terminal C atoms of the pentadienone unit to form a metallocyclohexadienone ring; the other metal interacts with the π electrons of this ring. (B) contains each metal σ bonded to the terminal C atoms of the pentadienone unit and also interacting with the π electrons from one of the double bonds in the pentadienone. If all substituents R are the same, the two metal atoms are in identical ligand environments in (B), but not in (A).

At least one example of each structure type is known. Investigations of Fe₂(CO)₆(CH₃C₂CH₃)₂CO (Piron, Piret, Meunier-Piret & Van Meerssche, 1969) and Fe₂(CO)₆(C₆H₅C₂C₆H₅)₂CO (Cotton, Hunter & Troup, 1976) indicate that each of these complexes has a molecular structure based on (B). A preliminary report (Davidson, Green, Stone & Welch, 1975) of the structure of (η -C₅H₅)₂Fe₂(CO)(CF₃C₂CF₂)₂CO has revealed the arrangement A.

We have formed the complex (η -C₅H₅)₂Rh₂-(CH₃C₂CH₃)(CF₃C₂CF₃)CO from the reaction between (η -C₅H₅)₂Rh₂(CO)₂(CF₃C₂CF₃) and CH₃C₂CH₃. The spectroscopic data indicate that it probably incorporates a pentadienone ligand. It is unusual because the pentadienone unit is formed from two different alkynes, one incorporating hydrocarbon and the other fluorocarbon substituents.

An investigation of the structure of (η -C₅H₅)₂Rh₂-(CH₃C₂CH₃)(CF₃C₂CF₃)CO was undertaken for several reasons. First, it is becoming increasingly apparent that organo–dimetal complexes are involved in the formation of many organometallic and organic compounds, and a knowledge of the structures of these bimetallic complexes should aid our understanding of the factors affecting their formation and degradation. Second, the substituents attached to the pentadienone unit within the complex are of markedly different electronegativity, and precise structural data might therefore aid our understanding of the influence of substituents on M–C σ - and π -bonding interactions. Finally, the different substituents on the pentadienone unit impose asymmetry on the molecule which precludes the possibility of differentiating between the structural possibilities A and B by NMR and other spectroscopic techniques.

Experimental

(η -C₅H₅)₂Rh₂(CH₃C₂CH₃)(CF₃C₂CF₃)CO was prepared by the treatment of (η -C₅H₅)₂Rh₂(CO)₂-CF₃C₂CF₃ with but-2-yne at 120°C. The compound was purified by thin-layer chromatography with acetone–hexane (3:7) as eluent. Crystallization from hot chloroform gave red crystals. The analysis for C₁₉H₁₆Rh₂F₆O was: calculated C, 39.33; H, 2.78; F, 19.65%; found C, 39.53; H, 2.88; F, 19.4%.

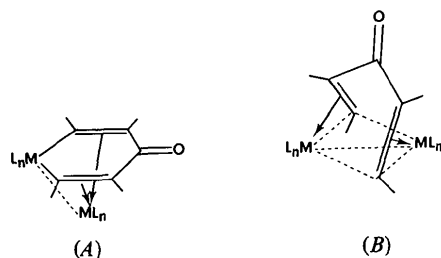


Fig. 1. Possible structures for the complexes $L_n M_2 (RC_2 R)_2 CO$.

Crystal data

$\text{C}_{19}\text{H}_{16}\text{Rh}_2\text{F}_6\text{O}$, $M_r = 580.16$, monoclinic, $a = 14.279$ (5), $b = 16.446$ (6), $c = 7.815$ (5) Å, $\beta = 93.15$ (5)°, $U = 1832.5$ Å³. $D_m = 2.10$ (by flotation in chloroform and 1,1,2,2-tetrabromoethane), $Z = 4$, $D_c = 2.10$ g cm⁻³. $F(000) = 1128$, $\mu = 18.2$ cm⁻¹ for Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Space group $P2_1/n$ from systematic absences: $h0l$, $h + l$ odd; $0k0$, k odd. Cell parameters were determined with a Philips PW 1100 X-ray diffractometer (Gatehouse & Miskin, 1974).

Intensity measurements

Intensities were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. A unique set was collected out of 2θ (Mo $K\alpha$) = 50° by the ω -scan technique at a scan rate of 0.05° s⁻¹ and over a range about the calculated scattering position given by $\pm(1.5 + 0.2 \tan \theta)/2^\circ$.

3218 independent reflexions were measured; 2161 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and only these were used in the subsequent calculations. Three standard reflexions, monitored every 1.5 h, showed no significant variations in intensity.

Data reduction and calculation of standard deviations in the structure factors were performed (Davies, Gatehouse & Murray, 1973). A value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. All reflexions were corrected for Lorentz and polarization effects. No correction for extinction or absorption was applied.

Structure determination and refinement

Solution of the structure was achieved by a combination of Patterson and difference Fourier methods. Scattering factors for Rh, C, F and O were taken from Cromer & Waber (1965). The major programs used were *MONLS*, a modified version of the full-matrix least-squares program of Busing, Martin & Levy (1962); *MONDLS*, a block-diagonal least-squares program based on that of Shiono (1968); and the Fourier summation program of White (1965). Diagrams were drawn by *ORTEP* (Johnson, 1965). All major calculations were performed on the Monash University CDC 3200 computer.

A Patterson synthesis revealed one of the Rh atoms. Refinement by full-matrix least squares, varying scale only, followed by difference syntheses, located the second Rh and all other nonhydrogen atoms. This

Table 1. *Final positional parameters* ($\times 10^3$; x and $y \times 10^5$, $z \times 10^4$ for Rh) and *anisotropic thermal parameters* ($\times 10^3$; $\times 10^4$ for Rh) for individual atoms in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$

Estimated standard deviations are in parentheses. The temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}b^*c^*kl\dots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	36422 (9)	18537 (8)	3045 (2)	255 (6)	245 (6)	222 (6)	12 (6)	18 (5)	-5 (6)
Rh(2)	44333 (9)	27751 (8)	5435 (2)	249 (6)	290 (7)	232 (6)	-1 (6)	3 (5)	-10 (6)
C(1)	380 (1)	67 (1)	174 (2)	56 (12)	34 (11)	36 (11)	2 (9)	3 (10)	-14 (6)
C(2)	307 (1)	111 (1)	86 (12)	48 (12)	44 (12)	38 (11)	4 (10)	-6 (10)	-25 (10)
C(3)	347 (1)	184 (1)	19 (2)	64 (13)	54 (13)	17 (9)	17 (11)	-3 (9)	-15 (10)
C(4)	444 (1)	182 (1)	71 (2)	53 (12)	63 (14)	31 (11)	0 (11)	-18 (10)	-19 (11)
C(5)	466 (1)	110 (1)	165 (2)	51 (12)	41 (12)	32 (11)	14 (10)	7 (9)	-14 (9)
C(6)	526 (1)	391 (1)	599 (3)	40 (11)	37 (12)	66 (14)	-25 (9)	-15 (11)	7 (11)
C(7)	567 (1)	347 (1)	462 (3)	31 (10)	85 (17)	47 (12)	-34 (11)	-6 (10)	2 (13)
C(8)	598 (1)	270 (1)	525 (3)	13 (8)	83 (16)	50 (13)	-8 (10)	4 (9)	-13 (12)
C(9)	576 (1)	266 (1)	705 (3)	30 (10)	68 (15)	50 (13)	-8 (10)	-7 (10)	-2 (12)
C(10)	532 (1)	342 (1)	744 (3)	37 (11)	53 (13)	44 (12)	-17 (10)	-7 (10)	-16 (10)
C(11)	333 (1)	301 (1)	370 (2)	16 (7)	18 (9)	31 (9)	-4 (7)	3 (7)	1 (8)
C(12)	297 (1)	306 (1)	538 (2)	27 (9)	22 (9)	24 (9)	4 (7)	-1 (7)	1 (7)
C(13)	241 (1)	230 (1)	574 (2)	30 (9)	32 (10)	17 (8)	1 (8)	2 (7)	5 (8)
C(14)	294 (1)	154 (1)	540 (2)	34 (9)	25 (9)	27 (9)	1 (8)	3 (8)	8 (8)
C(15)	393 (1)	163 (1)	567 (2)	36 (10)	25 (9)	19 (8)	7 (8)	-2 (8)	-2 (7)
C(16)	453 (1)	92 (1)	631 (2)	53 (12)	30 (11)	36 (11)	16 (9)	-8 (10)	10 (9)
C(17)	241 (1)	75 (1)	556 (3)	60 (13)	28 (11)	54 (13)	-13 (10)	1 (11)	10 (10)
C(18)	263 (1)	381 (1)	624 (3)	50 (12)	30 (11)	42 (11)	7 (9)	7 (10)	2 (9)
C(19)	329 (1)	370 (1)	246 (2)	38 (10)	32 (10)	29 (10)	0 (9)	3 (8)	5 (9)
O	161 (1)	232 (1)	615 (2)	30 (7)	56 (9)	51 (8)	-3 (6)	14 (6)	6 (7)
F(1)	244 (1)	376 (1)	167 (2)	54 (7)	57 (8)	59 (8)	2 (6)	-13 (6)	27 (6)
F(2)	389 (1)	362 (1)	122 (1)	82 (9)	54 (8)	43 (7)	4 (7)	28 (6)	19 (6)
F(3)	347 (1)	444 (1)	314 (1)	96 (9)	25 (6)	50 (7)	-13 (6)	-4 (7)	6 (6)
F(4)	241 (1)	365 (1)	787 (1)	86 (9)	56 (8)	34 (6)	14 (7)	18 (6)	-6 (6)
F(5)	183 (1)	410 (1)	548 (2)	55 (7)	49 (7)	70 (8)	28 (6)	17 (7)	9 (7)
F(6)	322 (1)	442 (1)	635 (2)	73 (8)	28 (6)	74 (9)	-2 (6)	17 (7)	-14 (6)

approximate structure, for which the isotropic temperature factors for Rh, C, F and O were assigned values of 2, 3, 3, and 3 Å², gave $R_1 = 0.175$, where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. Block-diagonal least-squares refinement, varying all atomic positional parameters and isotropic temperature factors, gave $R_1 = 0.055$. Anisotropic thermal parameters were then introduced for all atoms. After block-diagonal least-squares refinement all parameters converged to give $R_1 = 0.041$. The weighted R_2 converged to 0.047,* where $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. A final difference synthesis did not locate the H atoms; there were no major characteristics greater than 0.75 e Å⁻³. Final positional and thermal parameters are in Table 1, with their estimated standard deviations derived from the inverse least-squares matrix. Bond lengths are in Table 2 and angles in Table 3.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32026 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Intramolecular bonding distances (Å) and selected non-bonding distances (Å) in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$

(a) Bonding distances

Rh(1)—Rh(2)	2.614 (2)	Rh(1)—C(1)	2.22 (2)
Rh(1)—C(11)	2.02 (1)	Rh(1)—C(2)	2.22 (2)
Rh(1)—C(14)	2.20 (2)	Rh(1)—C(3)	2.23 (2)
Rh(1)—C(15)	2.10 (2)	Rh(1)—C(4)	2.21 (2)
Rh(2)—C(11)	2.05 (1)	Rh(1)—C(5)	2.24 (2)
Rh(2)—C(12)	2.14 (2)	Rh(2)—C(6)	2.23 (2)
Rh(2)—C(15)	2.03 (2)	Rh(2)—C(7)	2.22 (2)
C(11)—C(12)	1.44 (2)	Rh(2)—C(8)	2.22 (2)
C(12)—C(13)	1.52 (2)	Rh(2)—C(9)	2.23 (2)
C(13)—C(14)	1.49 (2)	Rh(2)—C(10)	2.23 (2)
C(14)—C(15)	1.42 (2)		
C(15)—C(16)	1.52 (2)		
C(14)—C(17)	1.52 (3)	C(1)—C(2)	1.43 (3)
C(12)—C(18)	1.49 (2)	C(2)—C(3)	1.44 (3)
C(11)—C(19)	1.50 (2)	C(3)—C(4)	1.42 (3)
C(13)—O	1.21 (2)	C(4)—C(5)	1.41 (3)
C(19)—F(1)	1.34 (2)	C(5)—C(1)	1.42 (3)
C(19)—F(2)	1.33 (2)	C(6)—C(7)	1.44 (3)
C(19)—F(3)	1.33 (2)	C(7)—C(8)	1.41 (3)
C(18)—F(4)	1.36 (2)	C(8)—C(9)	1.46 (3)
C(18)—F(5)	1.34 (2)	C(9)—C(10)	1.43 (3)
C(18)—F(6)	1.31 (2)	C(10)—C(6)	1.39 (3)

(b) Non-bonding distances

Rh(1) ... C(12)	2.90 (2)	Rh(1) ... C(17)	3.26 (2)
Rh(2) ... C(14)	2.94 (2)	Rh(2) ... C(16)	3.13 (2)
C(11) ... C(15)	2.84 (2)	Rh(2) ... C(18)	3.18 (2)
Rh(1) ... C(19)	3.11 (2)	Rh(2) ... C(19)	3.16 (2)
Rh(1) ... C(18)	4.36 (2)	Rh(2) ... C(17)	4.42 (2)
Rh(1) ... C(16)	3.19 (2)		

Results and discussion

The structure is shown in Fig. 2 and consists of the packing of discrete molecules of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$. There are no unusually short intermolecular contacts. Representations of the molecular structure of the complex are shown in Figs. 3 and 4. Fig. 3 also indicates the labelling of the atoms. Two alternative arrangements of the pentadienone—dimetal system are possible. The observed structure is based on the arrangement *B* (Fig. 1), and is closely related to the structures of the iron complexes $\text{Fe}_2(\text{CO})_6(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{CO}$ and $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2\text{CO}$.

The basic molecular structure consists of a five-carbon-atom ligand bridging two $[(\eta\text{-C}_5\text{H}_5)\text{Rh}]$ moieties. The five-carbon ligand is composed of C(11),

Table 3. Selected intramolecular bond angles (°) in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$

Rh(1)—C(11)—C(12)	113 (1)	C(12)—C(18)—F(4)	111 (1)
Rh(2)—C(11)—C(12)	73 (1)	C(12)—C(18)—F(5)	112 (1)
Rh(1)—C(11)—Rh(2)	80 (1)	C(12)—C(18)—F(6)	116 (2)
Rh(1)—C(11)—C(19)	124 (1)	C(11)—C(19)—F(1)	111 (1)
C(12)—C(11)—C(19)	122 (1)	C(11)—C(19)—F(2)	113 (1)
C(11)—C(12)—C(13)	109 (1)	C(11)—C(19)—F(3)	115 (1)
C(11)—C(12)—C(18)	127 (1)	F(1)—C(19)—F(2)	106 (1)
C(13)—C(12)—C(18)	114 (1)	F(2)—C(19)—F(3)	105 (1)
C(12)—C(13)—C(14)	112 (1)	F(3)—C(19)—F(1)	106 (1)
C(12)—C(13)—O	123 (1)	F(4)—C(18)—F(5)	105 (1)
C(14)—C(13)—O	125 (2)	F(5)—C(18)—F(6)	107 (1)
C(13)—C(14)—C(15)	114 (1)	F(4)—C(18)—F(6)	105 (1)
C(13)—C(14)—C(17)	116 (1)		
C(15)—C(14)—C(17)	125 (2)	C(5)—C(1)—C(2)	110 (2)
C(14)—C(15)—Rh(2)	116 (1)	C(1)—C(2)—C(3)	107 (2)
C(14)—C(15)—Rh(1)	75 (1)	C(2)—C(3)—C(4)	106 (2)
Rh(1)—C(15)—Rh(2)	78 (1)	C(3)—C(4)—C(5)	111 (2)
C(14)—C(15)—C(16)	121 (1)	C(4)—C(5)—C(1)	106 (2)
C(11)—Rh(1)—C(15)	87 (1)	C(7)—C(6)—C(10)	108 (2)
C(11)—Rh(2)—C(15)	88 (1)	C(6)—C(7)—C(8)	109 (2)
		C(7)—C(8)—C(9)	107 (2)
		C(8)—C(9)—C(10)	107 (2)
		C(9)—C(10)—C(6)	109 (2)

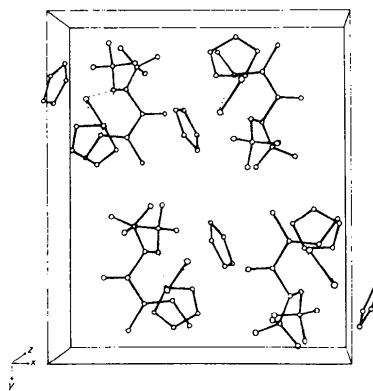


Fig. 2. The molecular packing in the unit cell. The view is down *c*.

C(12), C(13), C(14) and C(15), and consists of two alkene functions defined by C(11)–C(12) and C(14)–C(15) connected by single bonds to C(13). C(13) is bonded to an O atom forming a ketonic carbonyl group. Thus the organic ligand is properly described as a tetra-substituted penta-1,4-dien-3-one. Each alkene function in the ligand interacts with one of the two Rh atoms, presumably by normal alkene–metal π bonding. C(11) and C(15) at the ends of the ligand interact with both Rh atoms.

Perhaps the most interesting feature of the molecular structure is the arrangement of Rh(1), Rh(2), C(11) and C(15). These atoms are not coplanar, and the perpendicular displacements from the weighted least-squares plane through them are given in Table 4. However, the arrangement of the atoms is fairly symmetrical (Fig. 5). The distance of 2.614 (2) Å between the two Rh atoms is somewhat shorter than that found in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$ (Mills & Nice, 1967) or $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ (Dickson, Kirsch & Lloyd, 1975), and is certainly consistent with a Rh–Rh bonding interaction. The C(11)–C(15) distance is 2.84 (2) Å, which is too long for a bonding distance. These two C atoms are held in position by bonding

interactions with both Rh atoms. Each C atom is positioned almost equidistant from both Rh atoms, and consequently each is assumed to interact with both. All four Rh–C distances fall within the range normally observed for Rh–C(sp^2) σ bonds (Churchill, 1970; Ricci & Ibers, 1971; Mague, 1970; Dickson, Kirsch & Lloyd, 1975).

The C(11)–C(12) and C(14)–C(15) distances are 1.44 (2) and 1.42 (2) Å respectively, intermediate between normal double and single C–C lengths. They are very similar to those generally observed for alkenes coordinated to metals. There is no detectable difference in

Table 4. Equations of least-squares planes, and distances of individual atoms (Å) from the planes

X , Y and Z are coordinates in Å referred to an orthogonal system of axes and are related to the fractional coordinates x, y, z in the crystal system by the matrix equation:

$$\begin{bmatrix} 14.279 & 0 & -0.429 \\ 0 & 16.446 & 0 \\ 0 & 0 & 7.803 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

- (i) Plane through C(1), C(2), C(3), C(4), C(5)
 $0.2327X - 0.4807Y - 0.8455Z + 0.4312 = 0$
 Rh(1) –1.863 (1)
- (ii) Plane through C(6), C(7), C(8), C(9), C(10)
 $-0.8796X - 0.3978Y - 0.2608Z - 10.1161 = 0$
 Rh(2) 1.866 (1)
- (iii) Plane through Rh(1), Rh(2), C(11), C(15)
 $0.8883X - 0.0205Y - 0.4588Z - 3.0171 = 0$
 Rh(1) 0.334 (1) C(11) –0.358 (15)
 Rh(2) 0.360 (1) C(15) –0.336 (16)
- (iv) Plane through C(11), C(12), C(13), C(14), C(15)
 $-0.3897X - 0.3658Y - 0.8452Z + 6.4527 = 0$
 C(11) 0.407 (16) C(14) 0.413 (17)
 C(12) –0.502 (16) C(15) –0.358 (16)
 C(13) 0.040 (16) Rh(1) 1.353 (1)
 Rh(2) –1.178 (1)

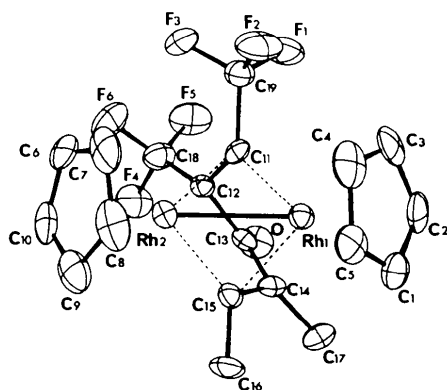


Fig. 3. A drawing of the molecular structure of the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$, with H atoms omitted. The 50% probability ellipsoids are shown. The view is down the ketonic carbonyl bond.

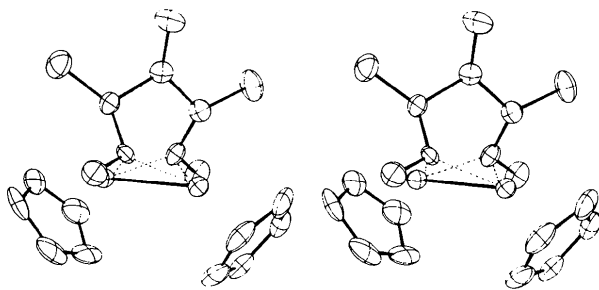


Fig. 4. A stereo view of the pentadienone–dimetal arrangement in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$.

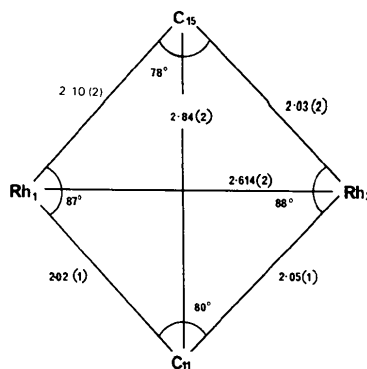


Fig. 5. The symmetrical arrangement of atoms within the Rh(1), Rh(2), C(11), C(15) segment of the molecule.

the coordinated C=C bond distances for the $\text{CH}_3-\overset{\text{C}}{\text{C}}=\overset{\text{C}}{\text{C}}-\text{CH}_3$ and $\text{CF}_3-\overset{\text{C}}{\text{C}}=\overset{\text{C}}{\text{C}}-\text{CF}_3$ parts of the pentadienone ligand. Moreover, the Rh(2)—C(11) and Rh(2)—C(12) distances are only slightly shorter than those for Rh(1)—C(14) and Rh(1)—C(15). Apparently, the nature of the substituents has very little effect on the alkene—Rh π -bonding interactions. One effect of the various Rh—C interactions is to distort the pentadienone unit from planarity. The displacements from the best plane (Table 4) arise principally because each C=C group is tilted towards one of the Rh atoms, presumably to improve the alkene—Rh π -bonding interactions.

The C—O distance of 1.21 (2) Å is normal for a ketonic carbonyl group, and is similar to the carbonyl bond lengths found in many other organometallic compounds, including the cyclopentadienone complex $(\eta\text{-C}_5\text{H}_5)\text{Co}[\text{C}_4(\text{CF}_3)_4\text{CO}]$ (Gerloch & Mason, 1964); the *p*-benzoquinone complex $(\eta\text{-C}_5\text{H}_5)\text{Co}[\text{C}_4(\text{CH}_3)_4(\text{CO})_2] \cdot 2\text{H}_2\text{O}$ (Uchtman & Dahl, 1972); the cycloheptatrienone complex $[\text{C}_6\text{H}_6\text{CO}]\text{Fe}(\text{CO})_3$ (Dodge, 1964); and the pentadienone complex $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2\text{CO}$ (Cotton, Hunter & Troup, 1976).

The bond distances between the pentadienone C atoms and those of the CH_3 and CF_3 substituents, C(11)—C(19), C(12)—C(18), C(14)—C(17), and C(15)—C(16), do not vary significantly and are close to the sum of the covalent radii for sp^2 and sp^3 hybridized C atoms. The average C—C—F and F—C—F angles, 113 and 106° respectively, are close to the theoretical tetrahedral angles.

The cyclopentadienyl C atoms are coplanar (Table 4) and the geometry within the rings is regular within the accuracy of our determination. The Rh to cyclopentadienyl-plane distances are 1.863 (1) and 1.866 (1) Å for Rh(1) and Rh(2) respectively, very similar to those reported for other $(\eta\text{-C}_5\text{H}_5)\text{-Rh}$ complexes.

Complexes of the type $\text{L}_n\text{M}_2(\text{RC}_2\text{R})_2\text{CO}$ have been proposed as intermediates in the formation of both free and metal-complexed cyclopentadienones. The distance between C(11) and C(15) in $(\eta\text{-C}_5\text{H}_5)\text{Rh}_2(\text{CH}_3\text{C}_2\text{CH}_3)(\text{CF}_3\text{C}_2\text{CF}_3)\text{CO}$ is 2.84 Å, and for a C—C σ bond to be formed in the production of a closed cyclopentadienone ring, this distance must be reduced to between 1.5 and 1.4 Å. It seems reasonable to suggest that the new C—C bond could be formed after thermal cleavage of the Rh—C(11) and Rh—C(15) σ bonds. Depending on the relative thermal stabilities of the cyclopentadienone—metal and the metal—metal bonds within the

species formed in this way, the cyclopentadienone ring could remain attached to one metal atom to form a cyclopentadienone complex $(\eta\text{-C}_5\text{H}_5)\text{Rh}[\text{C}_4\text{R}_4\text{CO}]$, or it could dissociate to give the free cyclopentadienone.

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