rather large (see Fig. 3). For this reason an attempt was made to refine the structure in the noncentrosymmetric space group $P6_3$. Isotropic least-squares refinement converged with positional and isotropic thermal parameters equivalent within error to those obtained in the similar refinement in the centrosymmetric space group, except for atoms H(1*A*), H(1*B*), and H(2) on the ethyl sulfate group. However, attempts to continue refinement with anisotropic thermal parameters were unsuccessful, in that the temperature factors for the S atom and atom H(1*A*) became non-positive definite. It is our feeling that the true space group is $P6_3/m$, and that the large ellipsoids for the ethyl sulfate hydrogens are due to extreme thermal motion. It is possible that the H atoms are disordered, in which case a lowering of the local symmetry of the Y site is not completely ruled out. However, since the $Y(OH_2)_9^{3+}$ moiety still conformed, within error, to C_{3h} site symmetry when refinement was attempted in the $P6_3$ space group, it is likely that the possible perturbation of the crystal-field levels of Yb^{3+} (which partially substitutes Y in the crystals used in a spin refrigerator) would be extremely small.

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The Crystal and Molecular Structure of μ-Carbonyl-bis(η-cyclopentadienyl)-μ-η-(hexafluoro-2-butyne)-dirhodium(*Rh–Rh*)

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(*Received* 8 *May* 1979; *accepted* 20 *June* 1979)

Abstract

The structure of $Rh_2(C_4F_6)(C_5H_5)_2(CO)$, $C_{15}H_{10}F_6ORh_2$, has been determined from 4084 diffractometer data and refined to $R = 0.043$. The compound is triclinic, space group $P\bar{1}$, with $a = 8.907\ (4)$, $b = 9.534\ (2)$, $c = 10.269\ (5)$ Å, $\alpha = 90.57\ (4)$, $\beta = 106.35\ (4)$, $\gamma = 92.56\ (3)°$, $Z = 2$. The hexafluoro-2-butyne ligand is *cis* bent and lies perpendicular to and 1·41 Å above the Rh–Rh bond. The coordinated C≡C

0567-7408/79/102321-05$01.00

distance is 1·363 (8) Å and the Rh–Rh length is 2·651 (1) Å. The CO group is symmetrically bridging, and an approximate mirror plane passes through this group and the four C and two F atoms of the alkyne. The CO group is 0·43 Å closer to one alkyne C than the other. The two $(C_5H_5)Rh$ units are in an eclipsed orientation.

Introduction

The structure of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ has been described (Dickson, Johnson, Kirsch & Lloyd, 1977). In that complex, the alkyne is σ-bonded to and coplanar with the two metal atoms (Fig. 1*a*). Removal of one carbonyl from $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ can be achieved by treatment with trimethylamine oxide (Dickson & Pain, 1979). Spectroscopic data indicate that the alkyne in the decarbonylation product, $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, may be π-bonded to the two Rh atoms, with the C≡C unit positioned normal to and above the Rh–Rh bond (Fig. 1*b*). We have confirmed this change in alkyne bonding mode by an X-ray structure determination of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$.

Experimental

Blue-green dichroic crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ were prepared from $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and Me_3NO in acetone (Dickson & Pain, 1979). Well-formed prisms were obtained from *n*-pentane at 243 K, and a crystal 0·22 × 0·21 × 0·15 mm was mounted on a Lindemann-glass fibre.

Crystal data

$C_{15}H_{10}F_6ORh_2$, M_r = 526·04, triclinic, $P\bar{1}$, a = 8·907 (4), b = 9·534 (2), c = 10·269 (5) Å, α = 90·57 (4), β = 106·35 (4), γ = 92·56 (3)°, U = 835·7 Å^3. D_m = 2·06 (by flotation in aqueous K_2HgI_4), Z = 2, D_c = 2·09 Mg m^{-3}, $F(000)$ = 503·99, μ = 1·845 mm^{-1} for Mo $K\alpha$ radiation (λ = 0·7107 Å). Weissenberg photographs revealed the crystal symmetry. Cell parameters were determined by a least-squares fit of 2θ values measured for 25 strong reflexions.

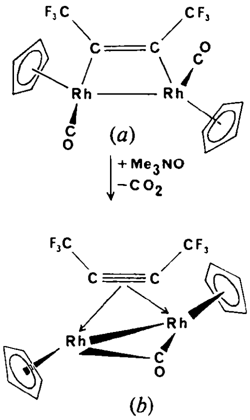

Fig. 1. Conversion of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ by treatment with Me_3NO.

Intensity measurements

Intensities were collected on a Rigaku-AFC four-circle diffractometer with Mo $K\alpha$ radiation (graphite crystal monochromator). Data to a 2θ maximum of 60° were recorded by an ω–2θ scan over a range about the calculated scattering position given by $\pm(1\cdot2 + 0\cdot5\tan\theta)/2°$; stationary background counts of 10 s were made at both ends of the scan. 4084 of the non-equivalent terms measured obeyed the condition $|F_o| > 2\sigma|F_o|$ and were used in subsequent calculations. Three standard reflexions, measured every 50 reflexions, showed no significant intensity variation. The intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption.

Structure determination and refinement

Scattering factors for C, Rh, F and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections, f' and f'', were made for all atoms (Cromer & Liberman, 1970).

The structure was solved by the heavy-atom method. The Rh atoms were located from the vector map, and a subsequent difference synthesis revealed the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters yielded $R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot223$. After refinement with anisotropic thermal parameters for the Rh atoms, R_1 was reduced to 0·075. Final refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0\cdot043$ and $R_2 = 0\cdot052$, where $R_2 = [\sum w^{1/2}(||F_o| - |F_c||)/\sum w^{1/2}|F_o|]$. Although some H atoms were located on the final difference map, others were not significantly above the residual maxima of 0·6 e Å^{-3} and we chose to neglect all H atoms.

All major calculations were performed on the La Trobe University DEC-10 computer. The refinements were made with *SHELX* 76 (Sheldrick, 1976), the function minimized being $\sum w(|F_o| - |F_c|)^2$ with the terms weighted according to $w = n/(\sigma^2|F_o| + m \times 10^{-2}|F_o|^2)$ for which n and m were 1·18 and 0·38, respectively.

Final positional parameters are listed in Table 1.* Bond lengths are in Table 2 and bond angles in Table 3.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34555 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* (×10⁴, ×10⁵ *for* Rh)

E.s.d.'s are in parentheses.

	x	*y*	*z*
Rh(1)	22417 (4)	31529 (4)	43550 (3)
Rh(2)	22171 (4)	31552 (4)	17671 (3)
C(1)	1930 (6)	4695 (5)	3005 (5)
C(2)	631 (6)	2204 (5)	2666 (5)
C(3)	2010 (7)	1545 (5)	3002 (5)
C(4)	2499 (11)	81 (7)	3069 (8)
C(5)	−1043 (7)	1809 (6)	2270 (7)
C(6)	3057 (10)	2149 (7)	6377 (6)
C(7)	4244 (7)	3148 (7)	6320 (6)
C(8)	3532 (9)	4477 (7)	6138 (6)
C(9)	1939 (9)	4279 (9)	6164 (6)
C(10)	1656 (8)	2835 (9)	6275 (6)
C(11)	3148 (20)	2224 (11)	167 (11)
C(12)	1685 (13)	2699 (16)	−412 (7)
C(13)	1810 (13)	4141 (15)	−232 (9)
C(14)	3300 (13)	4551 (10)	545 (8)
C(15)	4164 (9)	3342 (15)	769 (8)
O	1710 (6)	5901 (4)	2971 (5)
F(1)	1906 (9)	−620 (5)	1921 (6)
F(2)	2034 (9)	−620 (5)	4008 (6)
F(3)	4010 (8)	9 (6)	3360 (8)
F(4)	−1493 (7)	1089 (8)	1115 (7)
F(5)	−1467 (7)	1037 (9)	3155 (7)
F(6)	−1925 (5)	2863 (6)	2066 (8)

Table 2. *Intramolecular bonding distances* (Å) *and selected non-bonding distances* (Å)

(*a*) Bonding distances

Rh(1)–Rh(2)	2·651 (1)	C(2)–C(5)	1·462 (8)
Rh(1)–C(1)	2·005 (5)	C(3)–C(4)	1·477 (8)
Rh(2)–C(1)	2·005 (5)	C(4)–F(1)	1·310 (9)
Rh(1)–C(2)	2·082 (5)	C(4)–F(2)	1·327 (10)
Rh(2)–C(2)	2·075 (5)	C(4)–F(3)	1·299 (11)
Rh(1)–C(3)	2·023 (5)	C(5)–F(4)	1·316 (8)
Rh(2)–C(3)	2·036 (5)	C(5)–F(5)	1·301 (8)
Rh(1)–C(6)	2·238 (6)	C(5)–F(6)	1·286 (9)
Rh(1)–C(7)	2·286 (6)	C(6)–C(7)	1·405 (10)
Rh(1)–C(8)	2·215 (6)	C(7)–C(8)	1·432 (10)
Rh(1)–C(9)	2·224 (6)	C(8)–C(9)	1·431 (11)
Rh(1)–C(10)	2·197 (6)	C(9)–C(10)	1·400 (12)
Rh(2)–C(11)	2·232 (8)	C(10)–C(6)	1·413 (11)
Rh(2)–C(12)	2·188 (7)	C(11)–C(12)	1·372 (18)
Rh(2)–C(13)	2·209 (7)	C(12)–C(13)	1·381 (17)
Rh(2)–C(14)	2·208 (7)	C(13)–C(14)	1·379 (15)
Rh(2)–C(15)	2·251 (7)	C(14)–C(15)	1·399 (15)
C(1)–O	1·173 (7)	C(15)–C(11)	1·387 (16)
C(2)–C(3)	1·363 (8)		

(*b*) Non-bonding distances

Rh(1)···O	2·986 (4)	Rh(2)···C(5)	3·297 (7)
Rh(2)···O	2·990 (4)	C(1)···C(2)	2·571 (7)
Rh(1)···C(4)	3·245 (7)	C(1)···C(3)	3·008 (7)
Rh(2)···C(4)	3·224 (7)	C(2)···C(4)	2·639 (10)
Rh(1)···C(5)	3·297 (7)	C(3)···C(5)	2·634 (9)

Some mean planes and deviations are presented in Table 4. The diagrams were prepared with *ORTEP* (Johnson, 1965).

Table 3. *Selected angles* (°)

(*a*) Intramolecular bond angles

Rh(1)–C(1)–Rh(1)	82·8 (2)	C(2)–C(5)–F(5)	113·4 (6)
Rh(1)–C(1)–O	138·3 (4)	C(2)–C(5)–F(6)	113·8 (5)
Rh(2)–C(1)–O	138·9 (4)	F(1)–C(4)–F(2)	106·5 (8)
C(1)–Rh(1)–Rh(2)	48·6 (2)	F(1)–C(4)–F(3)	106·6 (8)
C(1)–Rh(2)–Rh(1)	48·6 (2)	F(2)–C(4)–F(3)	107·3 (7)
C(2)–Rh(1)–Rh(2)	50·3 (1)	F(4)–C(5)–F(5)	106·0 (7)
C(2)–Rh(2)–Rh(1)	50·5 (1)	F(4)–C(5)–F(6)	104·0 (7)
C(3)–Rh(1)–Rh(2)	49·4 (2)	F(5)–C(5)–F(6)	106·5 (8)
C(3)–Rh(2)–Rh(1)	49·0 (1)	C(6)–C(7)–C(8)	106·2 (7)
C(2)–Rh(1)–C(3)	38·7 (2)	C(7)–C(8)–C(9)	108·8 (7)
C(2)–Rh(2)–C(3)	38·7 (2)	C(8)–C(9)–C(10)	106·8 (7)
C(3)–C(2)–C(5)	137·6 (5)	C(9)–C(10)–C(6)	108·8 (7)
C(2)–C(3)–C(4)	136·7 (6)	C(10)–C(6)–C(7)	109·3 (7)
C(5)–C(2)–Rh(1)	136·3 (4)	C(11)–C(12)–C(13)	106·5 (1·0)
C(5)–C(2)–Rh(2)	136·9 (4)	C(12)–C(13)–C(14)	109·8 (9)
C(4)–C(3)–Rh(1)	135·4 (5)	C(13)–C(14)–C(15)	106·9 (9)
C(4)–C(3)–Rh(2)	132·5 (5)	C(14)–C(15)–C(11)	107·0 (9)
C(3)–C(4)–F(1)	112·5 (6)	C(15)–C(11)–C(12)	109·6 (1·0)
C(3)–C(4)–F(2)	111·2 (7)		
C(3)–C(4)–F(3)	112·4 (7)		
C(2)–C(5)–F(4)	112·5 (6)		

(*b*) Vector-plane angles

Rh(1)–Rh(2)–C(1)–O C(1)–O–C(2)–C(3)–C(4)–C(5)	89·9 (2)
Rh(1)–Rh(2)–C(2) C(1)–O–C(2)–C(3)–C(4)–C(5)	89·8 (2)
Rh(1)–Rh(2)–C(3) C(1)–O–C(2)–C(3)–C(4)–C(5)	89·8 (2)

Results and discussion

The crystal structure shown in Fig. 2 consists of the packing of discrete molecules with no unusually short intermolecular contacts. Views of the molecule, with the atom labelling, are presented in Figs. 3 and 4. The molecule consists of two eclipsed η^5-cyclopentadienylrhodium units bridged by an η^2-alkyne and a symmetrically bridging carbonyl group. An approximate mirror plane passes through O, C(1), C(2), C(3), C(4), C(5), F(3) and F(6). The distance of 2·651 Å between the two Rh atoms is shorter (Dickson, Johnson, Kirsch & Lloyd, 1977) than in $(C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ [2·682 (1) Å], but is within the range 2·51 to 2·85 Å found for Rh–Rh single-bond lengths in a number of multinuclear Rh compounds (Trinh-Toan, Broach, Gardner, Rausch & Dahl, 1977). The two Rh atoms are coplanar with the C and O of the bridging carbonyl and the Rh–C–Rh angle is 82·8 (2)°. The Rh–C (carbonyl) and C–O distances of 2·005 (5) and 1·173 (7) Å respectively are similar to those reported (Trinh-Toan, Broach, Gardner, Rausch & Dahl, 1977) for other multinuclear Rh compounds.

The coordinated hexafluoro-2-butyne is *cis* bent and lies perpendicular to (Table 3*b*) and above (1·41 Å) the

Table 4. *Equations of the mean planes and deviations (Å) of atoms from these planes*

Each plane is represented by an equation of the type $AX + BY + CZ - D = 0$, with X,Y,Z expressed in Å, referred to orthogonal coordinates.*

Plane 1: Rh(1), Rh(2), C(1), O
$-0{\cdot}9393X - 0{\cdot}2085Y - 0{\cdot}2726Z + 2{\cdot}3403 = 0$

Plane 2: C(1), O, C(2), C(3), C(4), C(5)
$0{\cdot}2710X + 0{\cdot}0266Y - 0{\cdot}9622Z + 2{\cdot}5579 = 0$

Plane 3: C(6), C(7), C(8), C(9), C(10)
$0{\cdot}0223X - 0{\cdot}1018Y - 0{\cdot}9946Z + 6{\cdot}4271 = 0$

Plane 4: C(11), C(12), C(13), C(14), C(15)
$0{\cdot}5065X + 0{\cdot}1465Y - 0{\cdot}8497Z - 1{\cdot}5075 = 0$

Plane 1		Plane 2	
Rh(1)	−0·0011 (4)	C(1)	0·0024 (49)
Rh(2)	−0·0011 (4)	O	0·0016 (48)
C(1)	0·0049 (52)	C(2)	0·0028 (48)
O	−0·0028 (54)	C(3)	−0·0185 (50)
		C(4)	0·0114 (79)
		C(5)	0·0040 (66)

Plane 3		Plane 4	
C(6)	0·0034 (58)	C(11)	0·0099 (134)
C(7)	−0·0144 (54)	C(12)	−0·0223 (89)
C(8)	0·0199 (58)	C(13)	0·0263 (97)
C(9)	−0·0180 (60)	C(14)	−0·0199 (94)
C(10)	0·0091 (57)	C(15)	0·0060 (81)
Rh(1)	1·88 (1)	Rh(2)	1·87 (1)

* Conversion from triclinic to orthogonal coordinates is given by:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & cP \\ 0 & 0 & cQ \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

where $P = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$, $Q = (1 - \cos^2\beta - P^2)^{1/2}$.

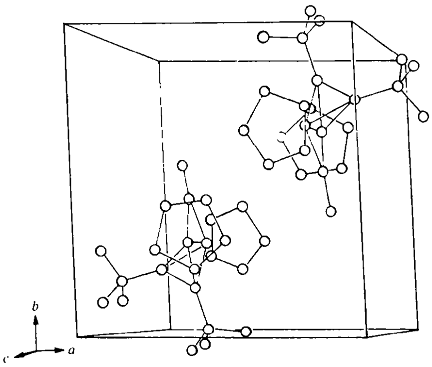

Fig. 2. The molecular packing in the unit cell. The view is along **c**.

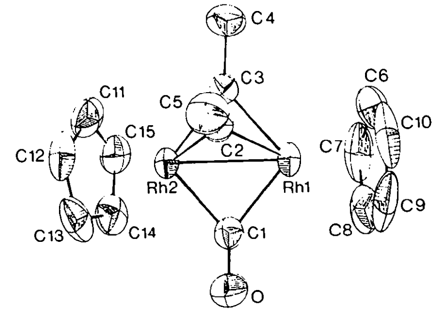

Fig. 3. The molecular structure of the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, with H and F atoms omitted. The 50% probability ellipsoids are shown.

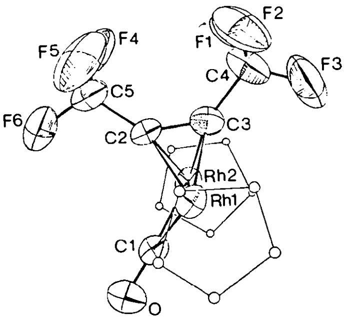

Fig. 4. An alternative view of the molecule showing the orientations of the bridging alkyne and carbonyl groups. For clarity, the cyclopentadienyl C atoms are put in idealized positions.

Rh—Rh bond. Thus, removal of a carbonyl from $(C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ has indeed resulted in a 90° rotation of the alkyne unit. There is a significant difference between the two pairs of Rh—C(alkyne) bond lengths. Thus, Rh(1)—C(2) and Rh(2)—C(2) are 2·082 (5) and 2·075 (5) Å respectively (mean 2·078 Å) whereas Rh(1)—C(3) and Rh(2)—C(3) are 2·023 (5) and 2·036 (5) Å respectively (mean 2·029 Å). This unsymmetrical alkyne–dirhodium bonding can be attributed to the non-equivalent nature of the two alkyne C atoms; C(2) is much closer to the carbonyl group (Fig. 3 and Table 2*b*). The C(2)—C(3) length of 1·363 (8) Å is within the range 1·28–1·39 Å observed for other μ_2-η^2-alkyne-bridged binuclear compounds (Muetterties, Pretzer, Thomas, Beier, Thorn, Day & Anderson, 1978), and is 0·09 Å longer than the μ_2-η^1-alkyne distance in $(C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (Dickson, Johnson, Kirsch & Lloyd, 1977). The lengthening of the C—C bond indicates some reduction in bond order, and this is consistent with the observed decrease of ν(C—C) from 1642 to 1592 cm^{-1} in the infrared spectra of $(C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, respectively. The average C—C—CF_3 angle of 137·1 (6) is similar to the corresponding angle in related alkyne–dimetal complexes, including 141·3 for $Rh_2(PF_3)_4(PPh_3)_2(PhC_2Ph)$ (Bennett, Johnson, Robertson, Turney & Whimp, 1976) and 134·2 (6)° for $(C_5H_5)_2Mo_2(CO)_4(EtC_2Et)$ (Bailey, Chisholm, Cotton & Rankel, 1978). The corresponding angle in $(C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is 128·5 (1·0)° which is closer to the normal olefinic angle of 120°.

The CF_3 substituents were refined without constraints and do not have ideal tetrahedral geometry. The average C—C—F and F—C—F angles are 112·8 and 106·1°, respectively. Comparable values are found for CF_3 groups in other structures which have been refined in a similar way (Gerloch & Mason, 1964; Dickson, Gatehouse & Johnson, 1977; Smart, Browning, Green, Laguna, Spencer & Stone, 1977). It has been suggested (Churchill & Mason, 1966) that the use of ellipsoids for the atoms of CF_3 groups is not adequate to represent their thermal motion and that, in addition, the error associated with the position of the C atom is largely responsible for the deviation of the observed angles from the tetrahedral angle of 109°.

The cyclopentadienyl groups are planar with an average Rh—C distance of 2·226 Å. The perpendicular distance between the ring planes and the Rh atoms of 1·88 (1) Å is similar to values reported previously (Dickson, Johnson, Kirsch & Lloyd, 1977; Trinh-Toan, Broach, Gardner, Rausch & Dahl, 1977). The geometry of the cyclopentadienyl groups is not regular, with C—C distances ranging from 1·37 to 1·43 Å. The average distances for the individual rings are 1·384 and 1·416 Å, and this difference may result from restrictions imposed by molecular stereochemistry and crystal packing on the thermal motion of the rings (Bryan & Greene, 1970; Bryan, Greene, Newlands & Field, 1970).

If the Rh—Rh bond is ignored, the overall coordination geometry about each Rh atom can be fitted to an octahedron, with the cyclopentadienyl group parallel to the ($\bar{1}1\bar{1}$) face, the Rh–C(O) vector in the [010] direction and the Rh–*alk* vector (where *alk* represents the midpoint of the alkyne C≡C bond) in the [101] direction. Within this model the *Cp*—Rh—*alk* angle (where *Cp* represents the centroid of the cyclopentadienyl plane) is 145° which is close to the calculated 144·7°. Similarly, the *Cp*—Rh—C(carbonyl) angle of 126° agrees well with the calculated 125·3°. Miller & Stephens (1975) have studied the geometry of the *Cp*–Fe–*L* group in a series of bridged binuclear Fe compounds and were able to fit regular octahedra to a large number of the structures.

$(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ readily adds a range of small molecules (Dickson & Pain, 1979). This high reactivity may be due to the exposed nature of the CO [nearest non-bonded atom, C(2), with C···C = 2·571 Å], the Rh—Rh bond, and one C atom of the alkyne ligand [nearest non-bonded atom, F(3), with C···F = 2·308 Å] (Fig. 4).

We thank the Australian Government for an Australian Postgraduate Research Award (to GNP), and the Australian Research Grants Committee for financial support of this work.

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