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THE REACTION OF HEXAFLUOROBUT-2-YNE WITH $[\text{Rh}(\text{Me}_3\text{CCOCHCOCCMe}_3)(\text{CO})_2]$:
 THE X-RAY CRYSTAL STRUCTURE OF A COMPLEX CONTAINING AN ALKYNE
 CO-ORDINATED PARALLEL TO A RHODIUM-RHODIUM BOND.

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Summary

Hexafluorobut-2-yne reacts with $[\text{Rh}(\text{dpm})(\text{CO})_2]$, (dpm = dipivaloyl-methanato) to give the complex, $[\text{Rh}_2(\text{dpm} \cdot \text{C}_4\text{F}_6)_2(\text{C}_4\text{F}_6)(\text{CO})_2]$, in which there is an alkyne molecule co-ordinated parallel to a rhodium-rhodium bond. Crystals of the complex, $[\text{Rh}_2(\text{dpm} \cdot \text{C}_4\text{F}_6)_2(\text{C}_4\text{F}_6)(\text{CO})_2]$ are triclinic, space group \underline{PT} with $\underline{a} = 15.34$, $\underline{b} = 18.50$, $\underline{c} = 16.01\text{\AA}$, $\alpha = 83.9$, $\beta = 99.2$, $\gamma = 89.5$, $z = 4$. The alkyne bridges the metal atoms to give a dirhodacyclobutene ring, the carbon-carbon bond is inclined by 15° to the rhodium-rhodium bond. Mean bond lengths are Rh-Rh 2.684, Rh-O 2.30, 2.19 and 2.10, Rh-C(carbonyl) 1.78 and Rh-C(CF₃)C(CF₃) 2.11\AA. The η^4 -hexakistrifluoromethylbenzene complex, $[\text{Rh}(\text{dpm} \cdot \text{C}_4\text{F}_6)(\text{C}_6(\text{CF}_3)_6)]$ is formed from C₄F₆ and $[\text{Rh}(\text{dpm})(\text{CO})_2]$ at 110°C. The reactions described show similarities to the reaction of hexafluorobut-2-yne with $[\text{RhCp}(\text{CO})_2]$, (cp= η^5 -C₅H₅).

Introduction

We have recently investigated the reactions of hexafluorobut-2-yne (C_4F_6) with various rhodium(I)- β -ketoenolate-alkene systems^{1,2} and have observed that this highly electrophilic alkyne commonly adds 1,4 across the β -ketoenolatorhodium ring. Subsequent studies have further shown that a range of alkynes will add 1,4 across a six-membered 2,4-pentane-diiminatocobalt ring of the macrocyclic cobalt(II) complex $[Co(C_{22}H_{22}N_4)]$.³ 1,4 addition across a β -ketoenolatometalla ring system produces a tridentate ligand having a formal negative charge. Reaction of C_4F_6 with $[Rh(dpm)(CO)_2]$ might therefore produce a five-co-ordinate complex similar to $[RhCp(CO)_2]$. Reactions of disubstituted alkynes with the latter compound have been studied extensively, and a number of complexes, thought to be intermediates in the trimerisation of alkynes have been isolated.⁴⁻¹⁰

Experimental

M.p.'s were determined on a Reichert hot-stage apparatus and are uncorrected. I.r. spectra (Nujol mulls) were recorded on Perkin-Elmer models 225 and 457 spectrometers. 1H n.m.r. and ^{19}F n.m.r. (relative to α,α,α -trifluorotoluene) were recorded on Varian Associates T60 and DA60 spectrometers respectively. $[Rh(dpm)(CO)_2]$ was prepared by passage of carbon monoxide through a solution of $[Rh(dpm)(1.5-COD)]$ in diethyl ether solution and purified by vacuum sublimation.

$\nu(CO)$, 2011, 2080 cm^{-1} . (Found: C, 45.4, H, 5.5. $C_{13}H_{19}O_4Rh$ requires C, 45.6, H, 5.6%).

Reaction of hexafluorobut-2-yne with dipivaloylmethanotodicarbonylrhodium(I) -

(a) At room temperature. A solution of dipivaloylmethanotodicarbonylrhodium(I), (0.70g, 2.04 mmol), in diethyl ether was introduced into a Carius tube (150 cm^3). An excess of hexafluorobut-2-yne (2.0 cm^3) was condensed ($-196^\circ C$) into the tube. After shaking for 24 h at room temperature, the tube was opened and volatile

material removed. The residue was recrystallised from dichloromethane/methanol solutions to give yellow crystals of the complex (1) (1.90g, 82%), m.p. 183° (decomp.). (Found C, 38.7; H, 3.2; F, 30.2; M(acetone) 1101. $C_{36}H_{38}F_{18}O_6Rh_2$ requires C, 38.3; H, 3.3; F, 30.0%; M, 1114. ν (terminal CO) 2089s, 2003s; ν (C=O) 1679s, 1660s; ν (C=C) 1587w, 1580w, 1639m, cm^{-1} . The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed signals at δ - 12.19 (3F, multiplet), -11.45 (3F, q, broad, J_{FF} 16 Hz), -9.07 (3F, q, J_{FF} 13 Hz), -7.63 (3F, q, J_{FF} 16 Hz), -6.85 (3F, q, J_{FF} 15 Hz) and -6.58 (3F, multiplet), p.p.m.

(b) At 110°C. A solution of $[Rh(dpm)(CO)_2]$ (0.20g, 0.59mmol) in diethyl ether was introduced into a Carius tube (150 cm^3). An excess of hexafluorobut-2-yne (1 cm^3) was condensed (-196°C) into the tube. After shaking for 24 h at 110°C, the tube was opened and volatile material was removed. Slow evaporation of the solution gave bright yellow crystals of (2), (0.43g, 78%), which was identified by its i.r. and ^{19}F n.m.r. spectrum.¹

Reaction of $[Rh_2(dpm.C_4F_6)_2(C_4F_6)(CO)_2]$ with hexafluorobut-2-yne at 110°C.

An excess of hexafluorobut-2-yne (2.0 cm^3) was condensed (-196°C) onto a solution of $[Rh_2(dpm.C_4F_6)_2(C_4F_6)(CO)_2]$, (1.0g, 0.88 mmol), in diethyl ether contained in a Carius tube (150 cm^3). After shaking at 110°C for 24 h the tube was opened and volatile material was removed. Slow evaporation of the solution gave bright yellow crystals of (2), (0.71g, 85%), which was identified by its i.r. and ^{19}F n.m.r. spectrum.¹

Crystal Data - $C_{36}H_{38}F_{18}O_6Rh_2$ (1), $M = 1114.5$, triclinic, $a = 15.34 \pm 0.02$,

$b = 18.50 \pm 0.03$, $c = 16.01 \pm 0.03 \text{ \AA}$, $\alpha = 83.9 \pm 0.3$, $\beta = 99.2 \pm 0.3$,

$\gamma = 89.5 \pm 0.5^\circ$, $V = 4460 \text{ \AA}^3$, $D_m = 1.65 \text{ g.cm}^{-3}$ (by flotation), $Z = 4$,

$D_c = 1.66 \text{ g.cm}^{-3}$, $F(000) = 2216$. Mo K_α radiation, $\lambda = 0.7107 \text{ \AA}$, $\mu(Mo-K_\alpha) = 8.5 \text{ cm}^{-1}$. Space group $P\bar{1}$ (C_i^1 , No.2).

Crystals grown from diethyl ether/light petroleum solutions (b.p. < 40°C) were orange-yellow plates on {001}. X-ray intensities were measured at 24-27°C on a Stoe Weissenberg diffractometer using $Mo-K_\alpha$ radiation and an ω -scan technique. Unit cell dimensions were measured from precession

photographs using Mo-K α radiation. Because of crystal decompositions, two crystals were used for data collection, the first to collect layers h 0 l through h 7 l and the second to collect layers h 0 l and h 8 l through h 18 l . The data from the first crystal were scaled to that from the second crystal by use of the h 0 l reflections.

Of the measured data 4661 unique reflections were regarded as having significant intensity ($I > 2\sigma(I)$). These intensities were corrected for Lorentz and polarisation effects but not for absorption. The least-squares refinement was carried out at the University of Manchester Regional Computing Centre using the 'X-Ray System' program package. Atomic scattering factors were taken from Ref. 11, including full correction for anomalous scattering by rhodium.¹²

Structure Determination - The positions of the non-hydrogen atoms of the two molecules in the asymmetric unit were deduced using standard heavy atom methods.

Hydrogen atoms were not located or included in the structure factor calculations. Blocked-matrix least-squares refinement of positional and isotropic thermal parameters for all non-hydrogen atoms reduced R to 0.150. A difference Fourier synthesis calculated at this stage of the refinement indicated that four of the twelve trifluoromethyl groups were disordered and for each of these four groups six fluorine atoms were subsequently refined, each with half occupancy. A weighting scheme with $\omega = (49.73 - 0.0671|F_o| + 0.010|F_o|^2)^{-1}$ was introduced in order that $\omega\Delta^2$ be approximately independent of $|F_o|$. The function minimised was $\Sigma\omega\Delta^2$. In subsequent cycles of refinement, anisotropic temperature factors

After further cycles refinement converged with an R of 0.098 ($R_w = \Sigma \frac{\omega}{|F_o| - |F_c|} = 0.122$) for 4515 reflections.[†] In the final cycles of refinement 146 reflections with small intensity and poor agreement between

[†] A list of observed and calculated structure factors is available on request.

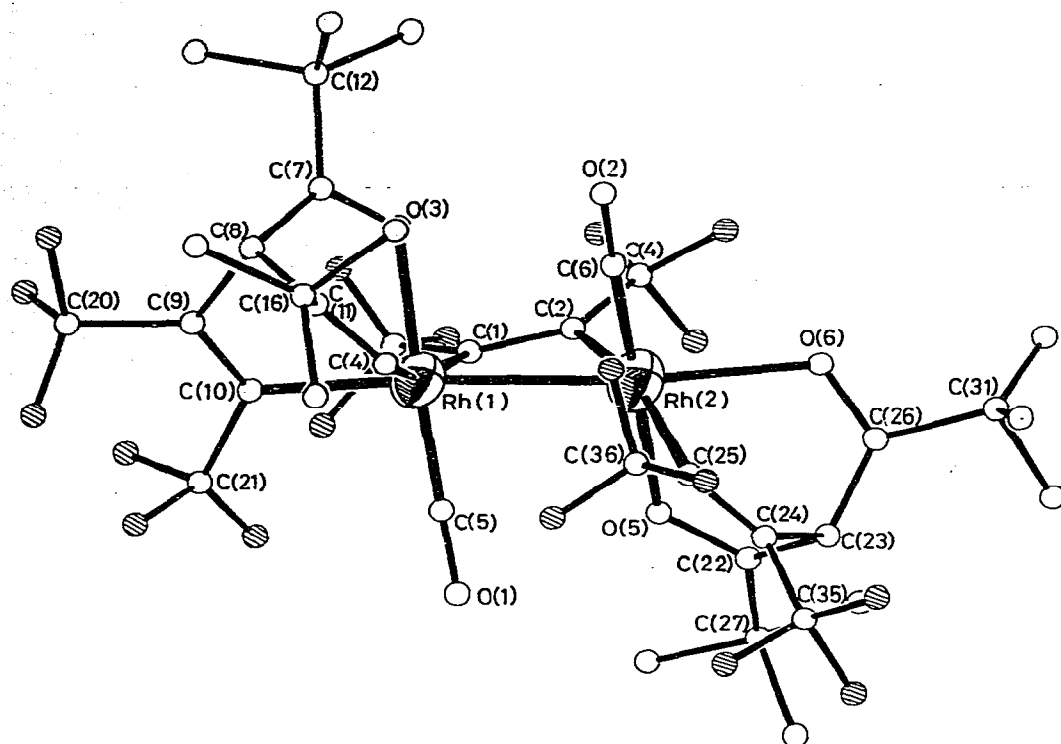


Fig.1. Molecular geometry and atom numbering for molecule (I), molecule (II) is essentially identical. The F atoms of two CF_3 groups are disordered (attached to C(11) and C(20), only one orientation is shown. Terminal methyl carbon and fluorine atoms are not labelled as they have different orientations in each molecule. Fluorine atoms are shaded.

F_{O} and F_{C} were excluded from the data set. Parameters of equivalent atoms from molecules (I) and (II) were refined in the same block because of an approximate relationship between them ($x_1, y_1, z_1 = 0.58-x, \frac{1}{2}-y, 1-z$). In the penultimate cycle layer scale factors were refined to check the data scaling but only small variations in scale factor were observed. The maximum shift in the final cycle was 0.3σ . A difference Fourier synthesis calculated at the end of the refinement showed no maxima or minima with an absolute value greater than $0.8 \text{ e}\text{\AA}^{-3}$.

Table 1 Final atomic coordinates and thermal parameters with estimated standard deviations (in parentheses).

	Molecule (I)				Molecule (II)			
	x/a	y/b	z/c	U	x/a	y/b	z/c	U
Rh(1)	-0.0528(1)	0.2156(1)	0.7623(1)	•	0.5256(1)	0.2459(1)	0.2407(1)	•
Rh(2)	0.1076(1)	0.1506(1)	0.7656(2)	•	0.6792(1)	0.3486(1)	0.2208(2)	•
O(1)	0.036(2)	0.320(1)	0.656(1)	0.097(6)	0.648(2)	0.183(1)	0.351(2)	0.116(8)
O(2)	0.006(1)	0.022(1)	0.819(1)	0.095(6)	0.564(1)	0.460(1)	0.185(1)	0.087(6)
O(3)	-0.105(1)	0.142(1)	0.846(1)	0.075(5)	0.444(1)	0.359(1)	0.154(1)	0.061(4)
O(4)	-0.122(1)	0.152(1)	0.667(1)	0.073(5)	0.482(1)	0.351(1)	0.333(1)	0.069(5)
O(5)	0.185(1)	0.245(1)	0.770(1)	0.069(5)	0.760(1)	0.254(1)	0.242(1)	0.078(5)
O(6)	0.246(1)	0.102(1)	0.835(1)	0.090(6)	0.804(2)	0.395(1)	0.172(1)	0.096(6)
C(1)	0.023(2)	0.241(1)	0.877(2)	0.057(7)	0.561(2)	0.256(1)	0.139(2)	0.074(8)
C(2)	0.083(2)	0.188(1)	0.695(2)	0.070(7)	0.623(2)	0.302(1)	0.113(2)	0.070(7)
C(3)	-0.022(2)	0.296(2)	0.924(2)	0.106(11)	0.512(2)	0.202(2)	0.078(2)	0.106(11)
C(4)	0.136(3)	0.179(2)	0.866(3)	0.135(14)	0.652(3)	0.316(2)	0.033(3)	0.136(15)
C(5)	0.002(2)	0.281(2)	0.695(2)	0.082(9)	0.600(2)	0.223(2)	0.308(2)	0.066(5)
C(6)	0.046(2)	0.076(2)	0.804(2)	0.078(8)	0.607(2)	0.428(1)	0.199(2)	0.072(8)
C(7)	-0.181(2)	0.123(2)	0.833(2)	0.079(8)	0.367(2)	0.376(1)	0.169(2)	0.061(7)
C(8)	-0.240(2)	0.148(1)	0.755(2)	0.064(7)	0.340(1)	0.351(1)	0.248(1)	0.045(6)
C(9)	-0.248(2)	0.234(1)	0.740(2)	0.059(7)	0.336(2)	0.266(1)	0.256(2)	0.056(6)
C(10)	-0.176(2)	0.274(1)	0.741(2)	0.072(8)	0.412(2)	0.227(1)	0.255(2)	0.063(7)
C(11)	-0.194(2)	0.127(1)	0.671(2)	0.067(7)	0.404(2)	0.372(1)	0.321(2)	0.067(7)
C(12)	-0.217(2)	0.073(1)	0.802(2)	0.068(7)	0.314(2)	0.425(1)	0.095(2)	0.065(7)
C(13)	-0.148(2)	0.056(2)	0.977(2)	0.108(11)	0.369(3)	0.446(2)	0.022(3)	0.112(12)
C(14)	-0.293(3)	0.125(3)	0.931(3)	0.151(16)	0.223(3)	0.363(3)	0.066(3)	0.157(17)
C(15)	-0.260(3)	0.097(2)	0.870(3)	0.143(15)	0.293(3)	0.497(2)	0.129(3)	0.122(13)
C(16)	-0.243(3)	0.084(2)	0.605(2)	0.102(11)	0.391(2)	0.420(2)	0.390(2)	0.088(9)
C(17)	-0.209(3)	0.096(2)	0.523(3)	0.118(12)	0.431(3)	0.394(2)	0.479(3)	0.117(12)
C(18)	-0.208(3)	-0.002(2)	0.644(3)	0.136(15)	0.415(2)	0.497(2)	0.367(2)	0.096(10)
C(19)	-0.342(4)	0.085(3)	0.602(3)	0.166(18)	0.262(3)	0.423(2)	0.384(3)	0.139(15)
C(20)	-0.349(3)	0.260(2)	0.717(3)	0.122(13)	0.246(2)	0.235(2)	0.273(2)	0.106(10)
C(21)	-0.182(2)	0.350(2)	0.726(2)	0.084(9)	0.420(2)	0.148(2)	0.285(2)	0.104(11)
C(22)	0.258(2)	0.248(1)	0.749(2)	0.060(6)	0.843(2)	0.253(1)	0.257(2)	0.052(7)
C(23)	0.284(2)	0.179(1)	0.715(2)	0.069(7)	0.681(2)	0.325(2)	0.292(2)	0.095(10)
C(24)	0.215(2)	0.152(1)	0.648(2)	0.077(8)	0.829(2)	0.349(1)	0.363(2)	0.074(8)
C(25)	0.137(2)	0.128(1)	0.666(2)	0.065(7)	0.747(2)	0.368(1)	0.346(2)	0.075(8)
C(26)	0.307(2)	0.113(1)	0.791(2)	0.074(8)	0.874(2)	0.382(2)	0.223(2)	0.088(9)
C(27)	0.305(2)	0.310(2)	0.756(2)	0.091(9)	0.690(2)	0.188(2)	0.259(2)	0.088(9)
C(28)	0.330(5)	0.335(5)	0.673(5)	0.271(35)	0.955(3)	0.169(2)	0.341(3)	0.144(16)
C(29)	0.268(3)	0.366(2)	0.603(3)	0.140(15)	0.828(4)	0.123(3)	0.252(4)	0.170(19)
C(30)	0.394(5)	0.296(4)	0.822(4)	0.219(27)	0.952(4)	0.203(3)	0.181(4)	0.168(19)
C(31)	0.384(2)	0.068(2)	0.800(2)	0.103(10)	0.944(2)	0.433(2)	0.198(2)	0.089(9)
C(32)	0.443(4)	0.082(3)	0.726(4)	0.185(21)	0.958(6)	0.474(5)	0.259(6)	0.286(39)
C(33)	0.422(4)	0.050(4)	0.692(4)	0.195(22)	0.951(5)	0.460(4)	0.118(5)	0.280(28)
C(34)	0.349(6)	-0.011(5)	0.784(6)	0.276(38)	1.026(4)	0.366(3)	0.216(4)	0.226(23)
C(35)	0.246(3)	0.156(2)	0.558(3)	0.120(13)	0.888(3)	0.345(2)	0.445(3)	0.107(11)
C(36)	0.070(2)	0.096(2)	0.605(2)	0.091(9)	0.697(2)	0.399(2)	0.407(2)	0.932(10)
F(1) ⁺	-0.048(3)	0.265(2)	0.988(3)	0.135(15)	0.553(3)	0.185(2)	0.016(3)	0.099(11)
F(2) ⁺	0.030(3)	0.344(2)	0.945(3)	0.113(12)	0.430(3)	0.193(3)	0.088(3)	0.124(15)
F(3) ⁺	-0.027(3)	0.363(2)	0.879(3)	0.112(12)	0.497(3)	0.140(3)	0.132(3)	0.142(16)
F(11) ⁺	0.040(3)	0.299(2)	1.000(3)	0.115(13)	0.439(3)	0.228(2)	0.047(3)	0.111(13)
F(21) ⁺	-0.063(6)	0.320(5)	0.901(6)	0.263(36)	0.479(5)	0.242(4)	-0.012(5)	0.214(27)
F(31) ⁺	-0.098(2)	0.288(1)	0.934(2)	0.066(8)	0.554(2)	0.152(2)	0.062(2)	0.079(9)
F(4)	0.183(2)	0.118(2)	0.987(2)	0.189(11)	0.690(2)	0.379(2)	0.018(2)	0.199(12)
F(5)	0.107(3)	0.166(2)	1.044(3)	0.252(17)	0.611(3)	0.236(2)	-0.036(3)	0.250(17)

F(6)	0.211(2)	0.216(2)	0.982(2)	0.215(13)	0.725(2)	0.278(2)	0.031(2)	0.209(12)
F(7) [†]	-0.388(2)	0.214(2)	0.772(3)	0.078(10)	0.191(2)	0.270(2)	0.222(2)	0.077(10)
F(8) [†]	-0.354(2)	0.321(2)	0.760(2)	0.079(9)	0.237(3)	0.171(2)	0.265(3)	0.095(11)
F(9) [†]	-0.375(3)	0.261(3)	0.641(3)	0.151(15)	0.226(3)	0.262(2)	0.338(3)	0.110(11)
F(71) [†]	-0.400(3)	0.216(2)	0.717(3)	0.103(13)	0.191(3)	0.294(2)	0.256(3)	0.112(14)
F(81) [†]	-0.372(5)	0.270(5)	0.780(5)	0.198(25)	0.209(4)	0.205(3)	0.208(4)	0.147(17)
F(91) [†]	-0.358(3)	0.312(3)	0.680(4)	0.149(17)	0.263(3)	0.181(3)	0.334(4)	0.137(16)
F(10)	-0.230(2)	0.378(1)	0.655(2)	0.150(6)	0.368(2)	0.129(2)	0.347(2)	0.189(11)
F(11)	-0.110(2)	0.387(1)	0.723(2)	0.134(7)	0.488(2)	0.114(1)	0.278(2)	0.142(8)
F(12)	-0.210(2)	0.387(1)	0.789(2)	0.138(8)	0.360(2)	0.112(1)	0.230(2)	0.154(9)
F(13)	0.281(2)	0.097(1)	0.544(2)	0.149(8)	0.924(2)	0.405(2)	0.468(2)	0.176(10)
F(14)	0.184(2)	0.173(2)	0.499(2)	0.175(10)	0.847(2)	0.321(1)	0.518(2)	0.164(9)
F(15)	0.308(2)	0.204(2)	0.554(2)	0.179(10)	0.959(2)	0.302(2)	0.455(2)	0.155(12)
F(16)	0.105(1)	0.058(1)	0.548(1)	0.127(7)	0.747(2)	0.441(1)	0.457(2)	0.131(7)
F(17)	0.019(1)	0.049(1)	0.638(1)	0.095(5)	0.637(1)	0.446(1)	0.357(1)	0.102(5)
F(18)	0.019(1)	0.147(1)	0.555(1)	0.112(6)	0.681(2)	0.351(1)	0.451(2)	0.132(7)

[†] Atoms so marked have occupancy 0.5

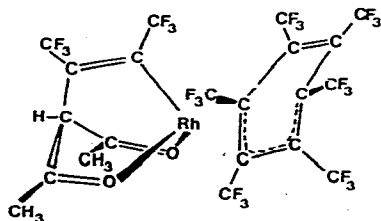
* Temperature factors for the Rh atoms are in the form $\exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + 2U_{12}hkab + 2U_{13}hlac + 2U_{23}kblc)]$ where the quantities U_{ij} are

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh1 (Molecule I)	0.049(1)	0.057(1)	0.068(2)	-0.003(1)	0.019(1)	-0.019(1)
Rh2 (Molecule I)	0.050(1)	0.061(1)	0.064(2)	-0.002(1)	0.018(1)	-0.013(1)
Rh1 (Molecule II)	0.044(1)	0.056(1)	0.064(2)	-0.000(1)	0.011(1)	-0.010(1)
Rh2 (Molecule II)	0.048(1)	0.053(1)	0.060(2)	-0.003(1)	0.017(1)	-0.017(1)

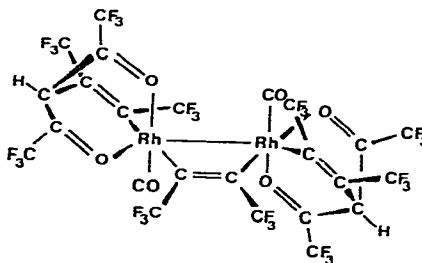
Final atomic coordinates and thermal parameters with estimated standard deviations are listed in Table 1. The molecular geometry and atom numbering are shown in Fig.1.

Results and Discussion

Hexafluorobut-2-yne reacts with $[\text{Rh}(\text{dpm})(\text{CO})_2]_2$ in diethyl ether solution to give a good yield of a bright yellow crystalline adduct (1) which is stable under



(1)



(2)

normal atmospheric conditions, is soluble in most common organic solvents and can be conveniently recrystallised from dichloromethane-methanol. The complex has been fully characterised by a combination of X-ray crystallographic, n.m.r., and i.r. spectroscopic investigations. The i.r. spectrum of (1) contains two strong absorptions at 2089 and 2003 cm^{-1} which can be assigned to the stretching frequencies of two terminal carbonyl groups. In addition, two strong bands at 1679 and 1668 cm^{-1} , $\nu(\text{C}=\text{O})$, and two weak bands at 1507 and 1580 cm^{-1} , $\nu(\text{C}=\text{C})$, characterise the presence of the two bicyclic systems formed by the 1,4-addition of hexafluorobut-2-yne to the rhodium dipivaloylmethanato ring. These bands are of similar intensity and occur in virtually identical positions to absorptions found in the i.r. spectra of (2) and $[\text{Rh}(\text{dpm}.\text{C}_4\text{F}_6)(\text{C}_6(\text{CF}_3)_4\text{H}_4)]$, which both contain the same bicyclic unit.¹ By elimination, therefore, a strong band at 1639 cm^{-1} may be attributed to the C=C stretching frequency of the bridging alkyne, and agrees favourably with a similar absorption found in the i.r. spectrum of $[\text{Rh}_2\text{Cp}_2(\text{C}_4\text{F}_6)(\text{CO})_2]$.⁴ The structure of this cyclopentadienyl complex has been determined by a single crystal X-ray study.⁸ This complex, which has been prepared by the reaction of hexafluorobut-2-yne with $[\text{RhCp}(\text{CO})_2]$, has an analogous structure to (1), both complexes containing a bridging alkyne co-ordinated parallel to a rhodium-rhodium bond. The dimetallacyclobutene ring system has also been shown to exist in $[\text{Pt}_3(\text{CF}_3\text{C}_2\text{CF}_3)_4(\text{COD})_2]$,¹³ $[\text{Pt}_2(\text{PhC}_2\text{Ph})(\text{COD})_2]$,¹⁴ $[\text{Ir}_4(\text{CO})_8\{(\text{MeOCO})_2\text{C}_2\}_4]$ ¹⁵ and $[\text{Fe}_2(\text{CO})_8(\text{tetrafluorobenzene})]$.¹⁶ This mode of bonding of an alkyne to two metal atoms is in contrast to the situation found in such complexes as $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R})]$ in which the alkyne lies perpendicular to the metal-metal bond.

The reaction of hexafluorobut-2-yne with $[\text{Rh}(\text{dpm})(\text{CO})_2]$ at 110°C produces the previously characterised complex (2).¹ Reaction of hexafluorobut-2-yne with $[\text{RhCp}(\text{CO})_2]$ gives the hexa-kis(trifluoromethyl) benzene complex $[\text{RhCp}(\text{C}_6(\text{CF}_3)_6)]$.¹⁷ However, this reaction, as well as the reactions of other disubstituted alkynes with $[\text{MCp}(\text{CO})_2]$, (M = Co, Rh, Ir) also produces many other products including cyclopentadienone complexes and trinuclear

species.⁴⁻¹⁰ Complexes analogous to these have not been observed from $[\text{Rh}(\text{dpm})(\text{CO})_2]$. The reaction of hexafluorobut-2-yne with (1) at 110°C also produces the complex (2).

The molecular geometry and atom numbering for (1) are shown in Fig. 1. The two independent molecules are essentially identical varying only in the orientation of terminal groupings attached to C(31) and C(27). Final atomic coordinates and thermal parameters are listed in Table 1. Bond lengths and some bond angles are listed in Tables 2 and 3 respectively.

Table 2. Bond lengths (Å) with estimated standard deviations (in parentheses).

The equivalent values for molecule (II) follow those for molecule (I).[†]

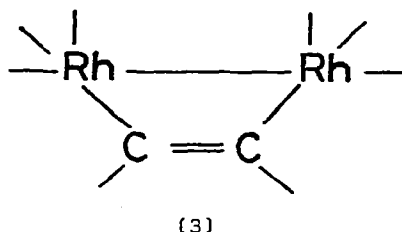
Rh(1)-Rh(2)	2.685(3)	2.684(3)	C(7)-O(3)	1.21(4)	1.28(3)
			C(11)-O(4)	1.21(4)	1.24(3)
Rh(1)-C(1)	2.11(3)	2.05(3)	C(22)-O(5)	1.23(4)	1.26(3)
Rh(2)-C(2)	2.12(3)	2.07(3)	C(26)-O(6)	1.27(4)	1.24(4)
Rh(1)-C(5)	1.83(3)	1.77(3)			
Rh(2)-C(6)	1.71(3)	1.81(3)	C(8)-C(7)	1.45(4)	1.42(4)
Rh(1)-C(10)	2.13(3)	2.09(3)	C(23)-C(22)	1.51(4)	1.58(4)
Rh(2)-C(25)	2.12(3)	2.17(3)	C(8)-C(11)	1.69(4)	1.50(4)
			C(23)-C(26)	1.62(4)	1.42(5)
Rh(1)-O(3)	2.09(2)	2.08(2)			
Rh(2)-O(5)	2.14(2)	2.10(2)	C(8)-C(9)	1.58(3)	1.51(3)
Rh(1)-O(4)	2.18(2)	2.19(2)	C(23)-C(24)	1.51(4)	1.60(5)
Rh(2)-O(6)	2.28(2)	2.32(2)			
			C(7)-C(12)	1.53(4)	1.54(3)
C(1)-C(2)	1.20(4)	1.32(4)	C(11)-C(16)	1.50(5)	1.57(5)
			C(22)-C(27)	1.38(4)	1.40(4)
C(9)-C(10)	1.32(4)	1.39(4)	C(26)-C(31)	1.45(5)	1.52(5)
C(24)-C(25)	1.34(4)	1.28(4)			
			C(5)-O(1)	1.10(4)	1.13(4)
C(1)-C(3)	1.54(5)	1.50(5)	C(6)-O(2)	1.20(4)	1.14(3)
C(2)-C(4)	1.31(5)	1.44(6)			
C(9)-C(20)	1.59(5)	1.57(5)			
C(10)-C(21)	1.41(4)	1.48(4)			
C(24)-C(35)	1.60(6)	1.45(5)			
C(25)-C(36)	1.48(4)	1.50(5)			

[†] C-C(Me) and C-F bond lengths have mean values of 1.52 Å and 1.30 Å respectively.

Table 3. Selected bond angles ($^{\circ}$) with estimated standard deviations (in parentheses). The equivalent value for molecule (II) follows that of molecule (I).

Rh(1)-C(1)-C(2)	108(2)	104(2)	Rh(1)-Rh(2)-O(5)	98.9(4)	98.1(4)
Rh(2)-C(2)-C(1)	111(2)	111(2)	Rh(1)-Rh(2)-O(6)	167.5(4)	166.7(4)
Rh(1)-C(1)-C(3)	115(3)	123(3)	Rh(1)-Rh(2)-C(25)	108.9(5)	107.8(5)
Rh(2)-C(2)-C(4)	117(3)	122(3)	Rh(1)-Rh(2)-C(6)	80.9(4)	80.6(4)
C(3)-C(1)-C(2)	136(3)	131(3)	O(5)-Rh(2)-O(6)	79.6(8)	80.4(8)
C(4)-C(2)-C(1)	132(3)	126(3)	O(5)-Rh(2)-C(25)	85.9(9)	83.5(9)
			O(5)-Rh(2)-C(6)	176.7(9)	177.5(8)
Rh(2)-Rh(1)-O(3)	95.8(4)	97.0(4)	O(6)-Rh(2)-C(25)	83.5(9)	85.3(9)
Rh(2)-Rh(1)-O(4)	99.6(4)	100.6(4)	O(6)-Rh(2)-C(6)	100.0(9)	100.4(9)
Rh(2)-Rh(1)-C(10)	176.0(5)	174.2(5)	C(6)-Rh(2)-C(25)	97.3(11)	98.8(12)
Rh(2)-Rh(1)-C(5)	80.8(5)	80.2(4)			
O(3)-Rh(1)-O(4)	84.1(8)	82.7(8)	C(2)-Rh(2)-Rh(1)	67.7(5)	68.1(5)
O(3)-Rh(1)-C(10)	87.8(9)	86.9(9)	C(2)-Rh(2)-O(5)	82.4(9)	82.9(9)
O(3)-Rh(1)-C(5)	174.5(9)	175.5(19)	C(2)-Rh(2)-O(6)	99.8(9)	98.7(9)
O(4)-Rh(1)-C(10)	82.4(9)	84.0(9)	C(2)-Rh(2)-C(25)	167.0(12)	165.0(12)
O(4)-Rh(1)-C(5)	100.6(8)	101.2(9)	C(2)-Rh(2)-C(6)	94.6(11)	94.6(12)
C(5)-Rh(1)-C(10)	95.5(11)	95.6(12)			
			Rh(1)-O(3)-C(7)	121(1)	120(1)
C(1)-Rh(1)-Rh(2)	69.6(5)	72.2(6)	Rh(1)-O(4)-C(11)	123(1)	118(1)
C(1)-Rh(1)-O(3)	80.7(9)	81.5(9)	Rh(2)-O(5)-C(22)	127(2)	125(2)
C(1)-Rh(1)-O(4)	160.2(9)	161.6(9)	Rh(2)-O(6)-C(26)	120(1)	114(2)
C(1)-Rh(1)-C(10)	109.5(13)	104.3(13)			
C(1)-Rh(1)-C(5)	94.2(11)	94.3(12)	Rh(1)-C(10)-C(21)	116(3)	116(3)
			Rh(1)-C(10)-C(9)	122(3)	122(3)
Rh(1)-C(5)-O(1)	179(3)	180(4)	Rh(2)-C(25)-C(36)	120(3)	120(3)
Rh(2)-C(6)-O(2)	177(3)	177(3)	Rh(2)-C(25)-C(24)	115(3)	116(3)
			C(9)-C(10)-C(21)	121(3)	120(3)
			C(24)-C(25)-C(36)	124(3)	124(3)
O(3)-C(7)-C(12)	118(2)	112(2)	C(8)-C(9)-C(10)	121(2)	120(2)
O(3)-C(7)-C(8)	123(3)	121(2)	C(8)-C(9)-C(20)	110(2)	116(2)
C(8)-C(7)-C(12)	119(3)	127(2)	C(10)-C(9)-C(20)	129(2)	124(2)
O(4)-C(11)-C(16)	123(3)	113(2)	C(23)-C(24)-C(35)	112(3)	110(3)
O(4)-C(11)-C(8)	115(2)	121(3)	C(23)-C(24)-C(25)	121(3)	121(3)
C(8)-C(11)-C(16)	122(3)	125(2)	C(25)-C(24)-C(35)	127(3)	129(3)
O(5)-C(22)-C(23)	112(2)	113(2)			
O(5)-C(22)-C(27)	119(3)	119(2)	C(7)-C(8)-C(9)	112(2)	109(2)
C(23)-C(22)-C(27)	128(3)	125(2)	C(7)-C(8)-C(11)	108(2)	110(2)
O(6)-C(26)-C(23)	114(2)	122(3)	C(9)-C(8)-C(11)	102(2)	108(2)
O(6)-C(26)-C(31)	123(3)	109(3)	C(22)-C(23)-C(24)	115(2)	111(3)
C(23)-C(26)-C(31)	123(3)	126(3)	C(22)-C(23)-C(26)	111(2)	109(3)
			C(24)-C(23)-C(26)	107(2)	109(3)

The mean Rh-Rh bond length (2.684Å) falls in the middle of the range exhibited by the dinuclear complexes $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$ (2.386Å),¹⁸ $[\text{Rh}_2(\text{OAc})_2(\text{dmg})_2(\text{PPh}_3)_2]$ (2.618Å)¹⁹ and $[\text{Rh}_2(\text{dmg})_4(\text{PPh}_3)_2]$ (2.936Å),²⁰ and is less than twice the estimated octahedral covalent radius for Rh^{III} (2.78Å).²¹ In $[\text{Rh}_2\text{Cp}_2(\text{C}_4\text{F}_6)(\text{CO})_2]$ the Rh-Rh bond length is 2.680Å. The mean C(1)-C(2) bond length of 1.26(4)Å is suggestive of (though rather short for) a double bond and the Rh-C(1) and Rh-C(2) bond lengths are similar to the sum of covalent radii (2.14Å) for Rh and C(sp²). The central part of the molecule may therefore be formulated as the dirhodacyclobutene ring, (3).



There are three chemically distinct types of Rh^{III}-O bond with mean lengths of 2.30Å (trans to Rh), 2.19Å (trans to the carbon of the bridging acetylene) and 2.10Å (trans to carbonyl) which may be compared with the mean Rh^I-O bond length in (2) (2.16Å).¹ Therefore the trans-influence decreases as the trans ligand goes from a metal atom to vinylic ligand to a carbonyl ligand.

Bond lengths and angles in the bicyclic system formed by 1,4 addition of C₄F₆ to the β-diketonatorhodium ring are unexceptional being similar to those in complexes of Rh,¹ Ir²² and Pd²³ containing a similar grouping. The geometry exhibited by the carbonyl ligands is normal.

The positioning of different atoms trans to the Rh-Rh bond in the two halves of the molecule is, at first sight curious. Molecular models suggest that alternative structures with two C(CF₃) atoms or two O(dpm) atoms trans to the Rh-Rh bond are unfavourable because these result in improbably short Me...Me and CF₃...CF₃ contacts respectively. Equally a C(CF₃) atom trans

to carbonyl is disallowed for steric reasons. These observations imply that a change of atom trans to the Rh-Rh bond at Rh(1) would force a corresponding change at Rh(2).

In contrast to all other dimetallacyclobutene rings, the dirhodacyclobutene ring is not planar, the deviations of atoms from the ring plane are given in Table 4. The carbon-carbon bond is inclined by an average of 15° to the rhodium-rhodium bond. The ligands cis to the Rh-Rh bond exhibit a staggered orientation and this is responsible for, but limited by the dimetallacyclobutene ring. Thus the mean angle between mean planes (ii) and (iii) in Table 4 is 27.3° . The staggering is probably necessary to avoid

Table 4. Deviations of atoms from Least Squares Planes. Starred atoms define the planes, perpendicular distances from the planes are in Å.

Plane	Molecule (I)			Molecule (II)		
	(i)	(ii)	(iii)	(i)	(ii)	(iii)
Distance of						
Rh(1)	0*	0*	0.00*	0*	0*	0.01*
Rh(2)	0*	0.10*	0*	0*	0.10*	0*
C(1)	0.16*	-0.30*		0.17*		
C(2)	-0.16*		0.23*	-0.17*		0.26*
C(3)	0.37			0.40		
C(4)	-0.53			-0.58		
O(4)	-0.81	-0.28*		-0.82	-0.28*	
C(25)	0.63		0.23*	0.72		0.25*
C(10)	0.14	0.06*		0.18	0.08*	
O(6)	-0.07		0.01*	-0.08		0.03*
C(5)	1.76	1.82		1.70	1.77	
C(6)	-1.64		-1.69	-1.72		-1.78
O(3)	-1.99	-2.08		-1.98	-2.07	
O(5)	2.02		2.10	2.00		2.07

strong interaction of the fluorine atoms, attached to C(36), with atom O(4). There are no exceptionally short intramolecular non-bonded contacts.

The molecular packing is illustrated in Fig.2. Four intermolecular contacts are shorter than the sum of Van der Waals radii, the shortest involving C(20) of molecule I and F(1) of molecule II (2.83Å).

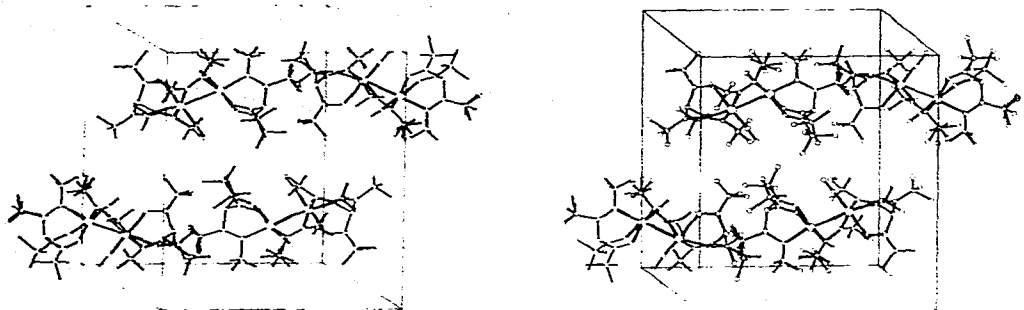


Fig.2. Stereoscopic ORTEP drawing of the unit cell contents.

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