1,4-Addition of Hexafluorobut-2-yne to Co-ordinated Cyclo-octa-1,5-diene: Crystal and Molecular Structure of (Acetylacetonato)aqua{7—8-η-7,8-bis(trifluoromethyl)bicyclo[4.2.2]dec-7-ene-2,5-diyl}rhodium(III)

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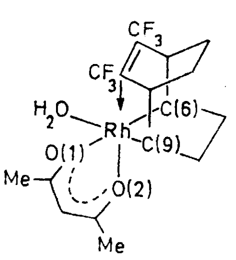
Crystals of the title compound (1) are monoclinic, space group *C*2/*c*, with *a* = 8.84(1), *b* = 19.34(2), *c* = 22.61(2) Å, β = 102.8(5)°, *Z* = 8. The structure was refined by least-squares analysis of counter intensities to *R* 0.092 for 1 591 reflexions. Mean bond lengths are: Rh–C 2.05, Rh–C(olefinic) 2.09, Rh–O(*trans* to C) 2.05, Rh–O(*trans* to olefinic bond) 2.18, and $Rh–OH_2$ 2.32 Å. Possible intermediates to the formation of the adduct are discussed.

WE have recently been interested in the reactions of acetylenes with metal–olefin complexes. In a preliminary report [1] on part of this work two ways in which hexafluorobut-2-yne (C_4F_6) can add to co-ordinated cyclo-octa-1,5-diene (cod) were described. We now report in full the crystal structure of an adduct (1) in which there has been 1,4-addition of C_4F_6 to the co-ordinated cod ligand. (1) Is obtained by treating the reaction product of C_4F_6 and $[Rh(cod)Cl]_2$ with sodium acetylacetonate.



(1)

Showing arbitrary crystallographic numbering

EXPERIMENTAL

Crystal Data.—$C_{17}H_{21}F_6O_3Rh\cdot\frac{1}{2}H_2O$, $M = 499.1$, Monoclinic, $a = 8.84(1)$, $b = 19.34(2)$, $c = 22.61(2)$ Å, $\beta = 102.8(5)°$, $U = 3\,770$ Å^3, $Z = 8$, $D_c = 1.76$ g cm^{-3}, $F(000) = 2\,008$. Space group *C*2/*c* or *Cc* (systematic absences: hkl when $h + k = 2n + 1$ and $h0l$ when $l = 2n + 1$). Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 9.6 cm^{-1}. The structure was successfully refined in *C*2/*c*.

Crystals of (1) were grown from diethyl ether–light petroleum (b.p. 40—60 °C) solutions and are commonly thin plates on {001}. Unit-cell dimensions were obtained from oscillation and Weissenberg photographs by use of Cu-K_α ($\lambda = 1.5419$ Å) radiation. Intensity data were collected from a crystal of dimensions *ca.* 0.058 × 0.012 × 0.003 cm mounted about *a*. The intensities of reflexions with $\sin\theta/\lambda < 0.6$ Å^{-1} were measured for the layers 0—9kl on a Stoe Weissenberg diffractometer by use of monochromatic Mo-K_α radiation and an ω-scan technique. Reflexions with $\sin\theta/\lambda > 0.1$ Å^{-1} and $I > 2\sigma(I)$ were corrected for Lorentz, polarisation, and absorption effects.[2]

Scattering factors for the atoms were taken from ref. 3. The structure was solved by conventional heavy-atom methods and block-diagonal least-squares refinement reduced *R* to 0.092 $[R' = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o| = 0.094]$ for 1 591 reflexions.† The weighting scheme, given by $w = (12.25 - 0.454|F_o| + 0.01|F_o|^2)^{-1}$, was introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. Hydrogen atoms were not located or included in the structure-factor calculations but a correction for the anomalous dispersion [4] due to rhodium was included. Refined temperature factors were anisotropic for rhodium and fluorine atoms and isotropic for carbon and oxygen atoms. The maximum shift in the final cycle was 0.1 σ. A difference-Fourier synthesis calculated at the end of the refinement shows no maxima or minima with an absolute value >0.3 eÅ^{-3}.

Final atomic co-ordinates and thermal parameters are listed in Table 1. The molecular geometry and atom numbering are shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21610 (8 pp., 1 microfiche).‡

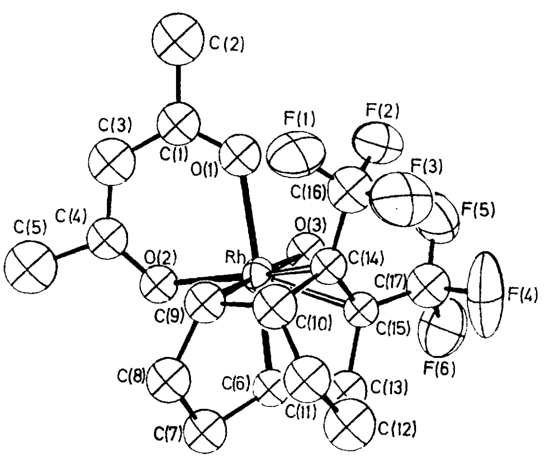


FIGURE 1 Molecular geometry and atom numbering. Thermal ellipsoids are scaled to 50% probability

DISCUSSION

Bond lengths and angles for the title compound are listed in Tables 2 and 3 respectively. The Rh–O(acac)

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† Differences between this paper and the preliminary communication are due to inclusion of a further 203 reflexions, with $2\sigma(I) < I < 3\sigma(I)$, in the refinement.

‡ See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[1] A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J.C.S. Chem. Comm.*, 1974, 797.

[2] J. de Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014; N. W. Alcock, *ibid.*, 1969, **A25**, 518.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 1

Final atomic co-ordinates and thermal parameters, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11} *	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rh	0.093 1(2)	0.083 4(1)	0.144 4(1)	3.18(7)	3.12(7)	3.52(7)	−0.06(8)	1.17(4)	−0.40(7)
F(1)	0.301 6(19)	0.029 1(8)	0.035 5(7)	8.4(9)	7.2(8)	8.3(9)	2.8(7)	3.4(7)	1.6(7)
F(2)	0.455 2(14)	0.071 4(7)	0.110 7(6)	5.4(6)	6.5(8)	6.3(7)	0.8(6)	1.8(5)	1.3(5)
F(3)	0.399 1(22)	0.127 5(10)	0.027 6(9)	9.6(11)	9.9(11)	11.7(12)	4.0(9)	7.9(10)	1.6(9)
F(4)	0.412 8(23)	0.243 5(11)	0.133 0(8)	10.9(12)	12.5(13)	9.1(1))	1.9(10)	0.6(7)	−8.0(11)
F(5)	0.451 2(15)	0.156 4(8)	0.187 3(7)	5.0(7)	8.8(10)	7.7(9)	−0.8(7)	0.0(6)	−0.3(6)
F(6)	0.312 5(19)	0.235 7(8)	0.209 9(7)	8.8(10)	7.4(9)	7.4(9)	−3.4(7)	0.2(7)	−1.7(7)

	x/a	y/b	z/c	B/Å^2
O(1)	0.233 4(16)	−0.009 9(7)	0.151 1(6)	4.7(3)
O(2)	−0.065 7(14)	0.024 5(7)	0.175 2(6)	3.9(2)
O(3)	0.214 4(14)	0.095 5(6)	0.245 7(6)	4.1(3)
O(4)	0.5 †	0.019 5(16)	0.25 †	8.9(7)
C(1)	0.183 7(25)	−0.070 6(11)	0.152 2(10)	5.0(5)
C(2)	0.299 6(34)	−0.128 3(15)	0.151 2(13)	7.3(6)
C(3)	0.029 7(28)	−0.087 6(14)	0.156 8(11)	6.0(5)
C(4)	−0.082 2(25)	−0.039 0(11)	0.167 1(10)	4.6(4)
C(5)	−0.236 8(34)	−0.068 6(15)	0.175 8(13)	7.4(7)
C(6)	−0.044 0(22)	0.168 5(10)	0.141 4(9)	3.7(4)
C(7)	−0.210 2(26)	0.156 4(12)	0.105 2(10)	5.1(5)
C(8)	−0.202 4(27)	0.099 9(12)	0.058 7(10)	5.3(5)
C(9)	−0.039 2(24)	0.070 6(11)	0.058 2(9)	4.6(4)
C(10)	0.056 8(27)	0.119 0(12)	0.025 3(10)	5.3(5)
C(11)	0.001 5(20)	0.190 3(13)	0.001 5(11)	5.8(5)
C(12)	0.011 3(32)	0.246 8(16)	0.052 2(12)	7.2(6)
C(13)	0.063 1(24)	0.219 9(11)	0.118 310)	4.5(4)
C(14)	0.203 1(21)	0.124 5(10)	0.079 4(8)	3.6(4)
C(15)	0.198 9(21)	0.173 7(9)	0.122 8(8)	3.3(3)
C(16)	0.340 5(27)	0.087 3(14)	0.063 8(10)	5.8(5)
C(17)	0.341 7(27)	0.199 3(12)	0.163 0(11)	5.3(5)

* Anisotropic temperature factor in the form: $\exp[-2\pi(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. † Parameters fixed by symmetry.

bond lengths are (acac = acetylacetonato) Rh–O(2), 2.05 *trans* to the olefinic bond [C(14)=C(15)], and Rh–O(1), 2.18 Å *trans* to C(6) reflecting the larger *trans*-influence of a σ-bonded carbon atom. The Rh–O(2) bond length compares well with the mean Rh–O(acac) bond length in the Rh^I complexes [(cod)Rh(acac)] [5] (2.060 Å) and [$(C_2H_4)_2$Rh(acac)] [6] (2.042 Å). The Rh–OH_2 bond is rather long when compared with those in [Rh$(AsMe_3)_2$-{$C(CF_3)$}$_4$Cl]·H_2O [2.24 Å *trans* to $C(CF_3)$ (ref. 7)], Cs_2[$RhCl_5(H_2O)$] [2.10 Å *trans* to Cl (ref. 8)], and [Me_4N][$RhCl_4(H_2O)_2$] [2.03 Å *trans* to OH_2 (ref. 9)].

The Rh–C(6) and Rh–C(9) bonds [2.04(2) and 2.05(2) Å respectively], are equal despite differing *trans*-ligands.

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

Rh–O(1)	2.18(1)	C(9)–C(10)	1.56(3)
Rh–O(2)	2.05(1)	C(10)–C(11)	1.52(4)
Rh–O(3)	2.32(1)	C(11)–C(12)	1.57(4)
		C(12)–C(13)	1.55(4)
Rh–C(6)	2.04(2)	C(13)–C(6)	1.54(3)
Rh–C(9)	2.05(2)		
		C(10)–C(14)	1.58(3)
Rh–C(14)	2.09(2)	C(13)–C(15)	1.48(3)
Rh–C(15)	2.09(2)	C(14)–C(16)	1.52(3)
		C(15)–C(17)	1.47(3)
O(1)–C(1)	1.26(3)		
O(2)–C(4)	1.25(3)	C(14)–C(15)	1.37(3)
C(1)–C(2)	1.52(4)		
C(4)–C(5)	1.53(4)	C(16)–F(1)	1.30(3)
C(1)–C(3)	1.43(3)	C(16)–F(2)	1.33(3)
C(4)–C(3)	1.42(3)	C(16)–F(3)	1.32(3)
C(6)–C(7)	1.53(3)	C(17)–F(4)	1.33(3)
C(7)–C(8)	1.53(3)	C(17)–F(5)	1.30(3)
C(8)–C(9)	1.55(3)	C(17)–F(6)	1.34(3)

The distance from Rh to the midpoint of the olefinic bond [C(14)=C(15)] is 1.97 Å which falls between the equivalent distances of 1.885 to C_2F_4 and 2.074 Å to C_2H_4 in [$(C_2H_4)(C_2F_4)$Rh(acac)].[6] The C(14)=C(15) bond length (1.37 Å) shows the expected lengthening of a double bond on co-ordination to the metal and the olefin geometry is non-planar as illustrated in Figure 2.

The geometry of the acac ligand is normal and the bond lengths and angles in the original cyclo-octadiene fragment are mostly unexceptional. The angles Rh–C(6)–C(13), Rh–C(9)–C(10), C(6)–C(13)–C(15), and C(9)–

TABLE 3

Bond angles (°), with estimated standard deviations in parentheses

O(2)–Rh–O(1)	86.5(5)	C(10)–C(14)–C(16)	110(2)
O(2)–Rh–O(3)	85.5(5)	C(13)–C(15)–C(14)	121(2)
O(2)–Rh–C(6)	90.7(6)	C(10)–C(14)–C(15)	117(2)
O(2)–Rh–C(9)	88.1(7)	C(14)–C(15)–C(17)	121(2)
O(1)–Rh–C(3)	83.3(5)	C(15)–C(14)–C(16)	130(2)
O(1)–Rh–C(9)	99.3(7)		
O(3)–Rh–C(6)	95.3(6)	Rh–C(6)–C(13)	97(1)
C(6)–Rh–C(9)	81.7(8)	Rh–C(9)–C(10)	97(1)
O(1)–Rh–C(6)	177.0(7)	C(6)–C(13)–C(15)	98(2)
O(3)–Rh–C(9)	172.9(7)	C(9)–C(10)–C(14)	96(2)
		Rh–C(6)–C(7)	113(1)
Rh–O(1)–C(1)	125(1)	Rh–C(9)–C(8)	106(1)
Rh–O(2)–C(4)	124(1)		
C(1)–C(3)–C(4)	125(2)	C(13)–C(6)–C(7)	120(2)
O(1)–C(1)–C(2)	117(2)	C(6)–C(7)–C(8)	107(2)
O(1)–C(1)–C(3)	124(2)	C(7)–C(8)–C(9)	117(2)
C(2)–C(1)–C(3)	119(2)	C(8)–C(9)–C(10)	113(2)
O(2)–C(4)–C(5)	115(2)	C(9)–C(10)–C(11)	123(2)
O(2)–C(4)–C(3)	128(2)	C(10)–C(11)–C(12)	114(2)
C(3)–C(4)–C(5)	117(2)	C(11)–C(12)–C(13)	115(2)
		C(12)–C(13)–C(16)	118(2)
C(13)–C(15)–C(17)	114(2)		

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[5] P. A. Tucker, W. Scutcher, and D. R. Russell, *Acta Cryst.*, 1975, **B31**, 592.

[6] J. A. Evans, D. R. Russell, and P. A. Tucker, to be published.

[7] J. T. Mague, *J. Amer. Chem. Soc.*, 1971, **93**, 3550.

[8] C. K. Thomas and J. A. Stanko, *J. Co-ordination Chem.*, 1973, **2**, 231.

[9] C. K. Thomas and J. A. Stanko, *J. Co-ordination Chem.*, 1973, **2**, 211.

C(10)–C(14) are smaller than might be expected presumably in order to bring the olefin close to the metal.

The title compound is isolated from the reaction of sodium acetylacetonate with the adduct obtained by treating [Rh(cod)Cl]$_2$ with C_4F_6. This adduct * is likely to be very similar to the tetrameric complex isolated from the reaction of C_4F_6 with [Rh(norb)Cl]$_2$[10] [(2) norb = norbornadiene]. It is of interest to consider whether the available structural information can give any clue to the mechanism of the 1,4-addition.

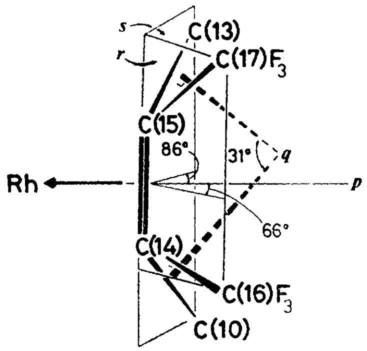
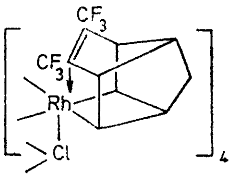
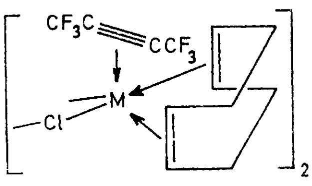


FIGURE 2 Geometry of the co-ordinated olefinic grouping. Line *p* passes through the rhodium atom and the midpoint of the C(14)=C(15) bond. The normals to planes C(13), C(15), C(17), and C(10), C(14), C(16) intersect at point *q*. The complements of the angles between *p* and the normals to planes *r* and *s* are shown; these complementary angles would be 90° in a planar olefin



(2)

The 1,4-addition of a dienophile to unco-ordinated cod is unknown and, in consequence, it is possible that the metal holds the ligand in a favourable conformation for addition to occur. However, both free and co-ordinated cod adopt the twisted boat conformation. In the free molecule the 2 ··· 5-distances are 3.05 Å[11] which are reduced on co-ordination to 2.74 Å.[5] This contraction may assist a concerted addition to co-ordinated cod, but the effect is unlikely to be of major significance as the equivalent distances in free and co-ordinated norbornadiene are nearly equal [2.369 (ref. 12) and 2.383 Å (ref. 13) respectively], and although homo-Diels–Alder addition of C_4F_6 is reported with both free and co-ordinated norbornadiene, reaction occurs far more easily when the diene is co-ordinated.[10]



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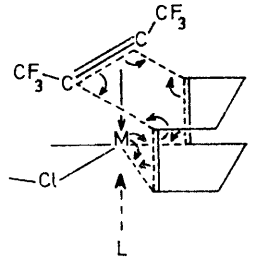

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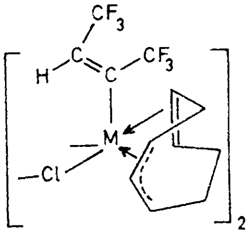

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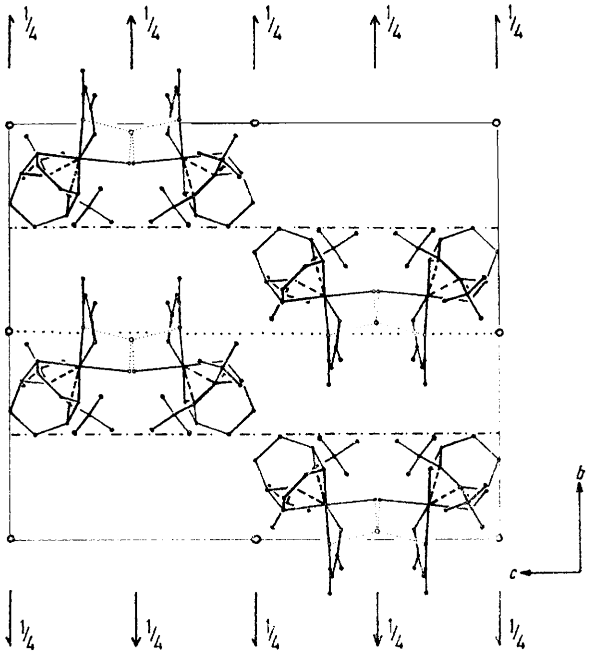

FIGURE 3 Molecular packing projected on [011]

It seems likely that the reaction proceeds *via* an acetylene complex. Support for this supposition is the isolation of the complex (3) from the room-temperature

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* There are at least two crystal modifications: (i) orthorhombic, $a = 33.53$, $b = 25.37$, $c = 14.09$ Å, space group *Pccn*, crystals of which appear to decompose on irradiation; and (ii) monoclinic, $a = 20.04$, $b = 18.33$, $c = 18.03$ Å, $\beta = 76.2°$, space group $P2_1/n$, the limited data set (Cu-K_α, $\theta_{max.}$ 60°) of which has not yielded a solution.

[10] J. A. Evans, R. D. W. Kemmitt, B. Y. Kimura, and D. R. Russell, *J.C.S. Chem. Comm.*, 1972, 509.

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[12] V. Schomaker, unpublished results, but see *J. Amer. Chem. Soc.*, 1960, **82**, 5450.

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reaction of C_4F_6 with $[Ir(cod)Cl]_2$.[14] 1,4-Addition may then occur by a concerted process such as indicated (4),† or in a stepwise fashion. Present evidence suggests the latter, firstly because the facile 1,3-addition of hexafluorobut-2-yne to co-ordinated butadiene has been shown to proceed stepwise,[15] and secondly if $[Ir(cod)Cl_2]$ is allowed to react with C_4F_6 at 90 °C the complex (5) is isolated.[14]

The reaction of C_4F_6 with [Rh(cod)(acac)] [16] or [Ir(cod)(acac)] [1] does not produce a 1,4-addition product, presumably because the initial reaction involves 1,4-addition of C_4F_6 across the metal–acac ring to produce a five-co-ordinated intermediate in which the metal formally achieves eighteen electrons in its valence shell. Formation of a second acetylene complex is thus unlikely and the reaction follows a different course.

The molecular packing is illustrated in Figure 3. Pairs of molecules appear to be held together by weak hydrogen bonds to a water molecule, O(4), on the two-fold axis. The O(1) $\cdots$ O(4) and O(3) $\cdots$ O(4) distances are 2.92 and 2.91 Å respectively, but since the structure determination is not of sufficient accuracy to enable location of the hydrogen atoms the precise nature of the hydrogen bonding remains uncertain.

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[5/1368 *Received*, 11*th July*, 1975]

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† The L in (4) is a neutral ligand, such as a solvent molecule or bridging chlorine, which completes the co-ordination sphere of Rh^{III}.

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[16] D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.