Journal of Organometallic Chemistry, 235 (1982) 231—241
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE GEOMETRY OF MIXED ALKENE-ALKYNE COMPLEXES: THE STRUCTURES OF ACETYLACETONATO(ETHYLENE)(HEXAFLUOROBUT-2-YNE)RHODIUM(I) AND ACETYLACETONATO(CYCLOOCTENE)-(HEXAFLUOROBUT-2-YNE)RHODIUM(I)

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(Received March 26th, 1982)

Summary

The crystal and molecular structures of the title complexes are described. Crystals of $Rh(C_5H_7O)(C_4F_6)(C_2H_4)$ are triclinic, a 7.89(2), b 12.64(3), c 8.57(2) Å, α 95.9(2), β 121.1(2), γ 94.8(2)°, $Z = 2$, space group $P\bar{1}$. Full matrix least-squares refinement has returned the residual, R, as 0.053. Crystals of $Rh(C_5H_7O)(C_4F_6)(C_8H_{14})$ are monoclinic, a 14.16(3), b 17.89(3), c 15.71(3) Å, β 97.5(2)°, $Z = 8$, space group $B2_1/c$. Block-diagonal least-squares refinement has returned R as 0.048. Both complexes are monomeric with square planar inner coordinations. The olefin and acetylene groups are approximately perpendicular to the square coordination planes.

The Rh—C and Rh—O distances are (i) ethylene; olefin 2.142(14), 2.171(17) Å, acetylene 2.016(10), 2.042(11) Å, acetylacetone 2.015(6), 2.033(7) Å; (ii) cyclooctene; olefin 2.163(13), 2.196(11) Å, acetylene 2.034, 2.059(10) Å, acetylacetone 2.017(8), 2.038(7) Å. The average 'bend-back' angle of the substituted acetylenes is 30.1° for both complexes, which is low compared with most other hexafluorobut-2-yne complexes.

Introduction

Whereas metal-catalysed cyclotrimerisations of acetylenes have been extensively studied, the cooligomerisation of mixtures of acetylenes and olefins has only recently been investigated [1]. It has been suggested that these reactions proceed through metallacyclopentene or metallacyclopentadiene intermediates [2]. The metallacyclopentene intermediate itself is presumably derived from a mixed acetylene olefin precursor, and hence the specific reaction products will

0022-328X/82/0000—0000/$02.75

be dictated in part by the relative strengths of the metal—acetylene and metal—olefin bonds. Recently, some mono-acetylene mono-olefin complexes of rhodium(I) were synthesised [3] and we now present details of the refined X-ray structures of two of these complexes.

Experimental

Crystals of the two complexes were generously supplied by Dr. R.D.W. Kemmitt of the University of Leicester. Preliminary precession photographs were recorded to establish the space groups and to determine unit cell dimensions. The relevant crystal data are listed in Table 1. The space group of the cyclooctene complex has been retained as $B2_1/c$ rather than the conventional $P2_1/c$ (No. 14) in order to keep the β angle reasonably close to 90°. Intensity data were collected on a Stoe Weissenberg diffractometer using graphite-monochromated Mo-K_α radiation and the ω scan technique [4]. The optimum scan width was computed for each reflection. The scan rate was 1° min^{-1} with stationary background measurements of 20 s at each end of the scan range. No attenuators were required as no reflection exceeded 7000 c s^{-1}, nor were absorption corrections deemed necessary. The data sets were corrected for Lorentz and polarisation effects in the normal manner.

Structure determination and refinement

Rhodium atom positions were deduced from Patterson syntheses and the

TABLE 1

CRYSTAL DATA

Compound	Rh(acac)(C_4F_6)(C_2H_4)	Rh(acac)(C_4F_6)(C_8H_{14})
Formula weight	392.11	474.25
Colour and habit	yellow/orange plates	yellow needles
Forms developed		{100} {010} {001}
Crystal system	triclinic	monoclinic
Systematically absent reflections	no absences	hkl when $h + l = 2n + 1$ $h0l$ when $l = 2n + 1$ $0k0$ when $k = 2n + 1$
Space group	$P\bar{1}$	$B2_1/c$
a	7.89(2) Å	14.16(3) Å
b	12.64(3)	17.89(3)
c	8.57(2)	15.71(3)
α	95.9(2)°	
β	121.1(2)	97.5(2)°
γ	94.8(2)	
V	718.57 Å^3	3945.65 Å^3
Z	2	8
D(obs)		1.577 g cm^{-3} (by flotation in aqueous KI)
D(calc)	1.81 g cm^{-3}	1.60 g cm^{-3}
μ(Mo-K_α)	11.23 cm^{-1}	9.14 cm^{-1}
F(000)	384	1736
Layers collected	$hk0 \rightarrow hk7$	$hk0 \rightarrow hk12$
Max. sin θ/λ	0.5947	0.6246
No. observed reflections	1228 $I > 2\sigma(I)$	1296 $I > 2\sigma(I)$
Crystal size	approx. 0.2 × 0.2 × 0.2	0.31 × 0.15 × 0.15 mm

remaining non-hydrogen atoms from subsequent electron density maps. Atomic scattering factors and dispersion corrections were taken from standard listings [5]. The function minimised in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Residuals quoted are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2\}^{1/2}$.

(a) Rh(acac)(C_4F_6)(C_2H_4). The structure was refined using the SHELX program [6]. The full least-squares matrix was employed, although the atoms were grouped into blocks for the final cycles. Initial isotropic refinement with unit weights returned $R = 0.15$, thereafter the atoms were assigned anisotropic thermal parameters, and a weighting parameter, g, was refined [$w\ \alpha\ 1/\sigma^2(F) + gF^2$]. Hydrogen atoms were located by a combination of a 'difference' electron density map and expected geometries, and they were included in fixed positions in the final cycles. The terminal residuals and weighting parameter were $R = 0.053$, $R_w = 0.054$, and $g = 0.00085$.

(b) Rh(acac)(C_4F_6)(C_8H_{14}). The structure was refined using a local block-diagonal program SFLS. Initial isotropic refinement using unit weights returned $R = 0.12$. On assigning anisotropic thermal parameters to the rhodium and six fluorine atoms the residual fell to 0.068. The weighting scheme was then

TABLE 2

POSITIONAL PARAMETERS FOR Rh(acac)(C_4F_6)(C_2H_4)

Atom	*x/a*	*y/b*	*z/c*
Rh	0.2664(1)	0.2433(1)	0.0915(1)
F(1)	0.3088(18)	0.2325(7)	0.5310(13)
F(2)	0.3113(18)	0.3917(9)	0.5241(15)
F(3)	0.5708(14)	0.3369(11)	0.6781(12)
F(4)	0.8740(12)	0.3896(8)	0.5067(13)
F(5)	0.8207(12)	0.2624(7)	0.3101(15)
F(6)	0.7501(14)	0.4125(9)	0.2421(16)
O(1)	0.0376(11)	0.1777(6)	−0.1650(10)
O(2)	0.3563(9)	0.0982(5)	0.1458(9)
C(1)	0.2379(24)	0.3951(10)	−0.0029(20)
C(2)	0.1127(22)	0.3821(13)	0.0536(23)
C(9)	0.4053(19)	0.3147(9)	0.5196(17)
C(10)	0.4390(20)	0.3028(9)	0.3680(16)
C(11)	0.5439(18)	0.3112(9)	0.3012(17)
C(12)	0.7401(18)	0.3424(10)	0.3361(18)
C(13)	−0.1818(17)	0.0484(11)	−0.4257(15)
C(14)	0.0013(15)	0.0776(9)	−0.0228(15)
C(15)	0.1031(16)	−0.0023(9)	−0.1479(15)
C(16)	0.2705(14)	0.0104(8)	0.0326(14)
C(17)	0.3668(17)	−0.0858(9)	0.0987(15)
H(1A)	0.1671	0.3653	−0.1483
H(1B)	0.3718	0.4359	0.0534
H(2A)	−0.0195	0.3592	−0.0052
H(2B)	0.1721	0.4192	0.1890
H(13A)	−0.2905	0.0910	−0.4392
H(13B)	−0.1491	0.0639	−0.5207
H(13C)	−0.2393	−0.0308	−0.4548
H(15)	0.0541	−0.0764	−0.2234
H(17A)	0.3366	−0.1423	−0.0062
H(17B)	0.5184	−0.0648	0.1817
H(17C)	0.3187	−0.1184	0.1751

changed to one of the form $w = 1/(a + bF + cF^2)$, where the coefficients a, b and c could be adjusted after each cycle. A 'difference' map enabled the positions of all hydrogen atoms to be deduced, and they were included in the least-squares refinement with fixed isotropic temperature factors of 5.0 Å^2. All other atoms were refined anisotropically for six cycles, by which time the parameter shifts had converged. Final values were $R = 0.048$, $R_w = 0.047$, $a = 2.8439$, $b = -0.1852$, $c = 0.0041$.

The refined atomic positions for Rh(acac)(C_4F_6)(C_2H_4) and Rh(acac)(C_4F_6)(C_8H_{14}) are listed in Tables 2 and 5 respectively. Thermal parameters and structure factor tables are available on request from the authors (G.R.C.).

The structure of Rh(acac)(C_4F_6)(C_2H_4)

The complex is monomeric. The molecular geometry and atomic numbering are illustrated in Fig. 1. The coordination geometry about rhodium is best described as square planar, with the olefin and acetylene ligands, (both considered to be monodentate) lying approximately perpendicular to the square plane (Table 8).

Bond distances and angles together with least-squares estimated standard deviations are given in Tables 3 and 4 respectively. All are normal values. The C—F bond lengths have been corrected to allow for the artificial shortening effect of the high thermal anisotropy of the fluorine atoms [7]. The packing of the molecules into the crystal can be seen in the stereopair diagrams of Fig. 2. Of the ten closest intermolecular approaches (<3.5 Å) seven are F···F contacts. None is sufficiently short that it would be expected to influence the coordination geometry.

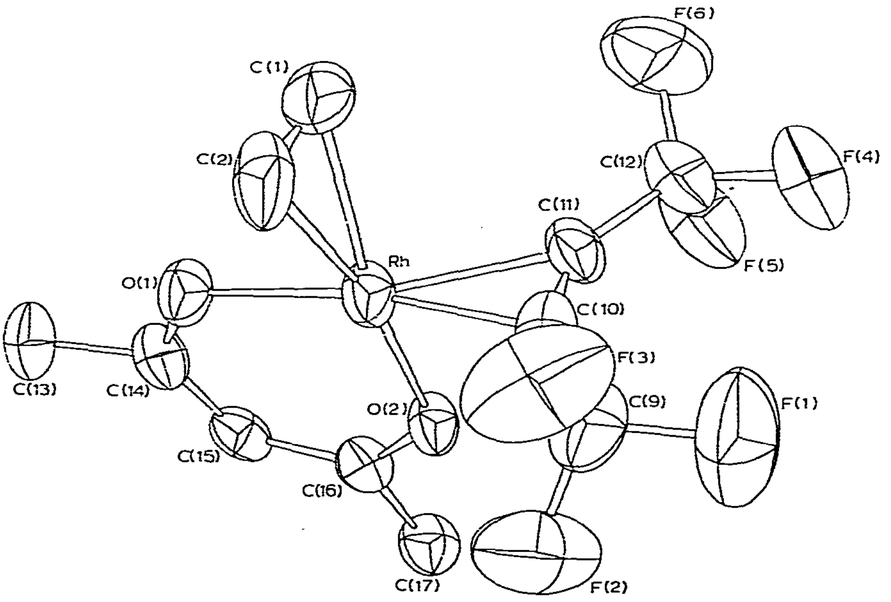

Fig. 1. Molecular geometry and atomic numbering for Rh(acac)(C_4F_6)(C_2H_4). Anisotropic ellipses represent 50% probability boundaries.

TABLE 3

BOND DISTANCES (Å) FOR Rh(acac)(C_4F_6)(C_2H_4)

Rh—O(1)	2.015(6)	F(6)—C(12)	1.282(21)
Rh—O(2)	2.033(7)	O(1)—C(14)	1.279(13)
Rh—C(1)	2.142(14)	O(2)—C(16)	1.267(11)
Rh—C(2)	2.171(17)	C(1)—C(2)	1.31(3)
Rh—C(10)	2.042(11)	C(9)—C(10)	1.45(2)
Rh—C(11)	2.016(10)	C(10)—C(11)	1.23(2)
F(1)—C(9)	1.278(19)	C(11)—C(12)	1.43(2)
F(2)—C(9)	1.281(19)	C(13)—C(14)	1.509(13)
F(3)—C(9)	1.288(12)	C(14)—C(15)	1.370(16)
F(4)—C(12)	1.316(13)	C(15)—C(16)	1.403(12)
F(5)—C(12)	1.298(18)	C(16)—C(17)	1.493(15)

TABLE 4

BOND ANGLES (°) FOR Rh(acac)(C_4F_6)(C_2H_4)

O(1)—Rh—O(2)	92.0(3)	F(2)—C(9)—F(3)	103.1(11)
O(1)—Rh—C(1)	87.0(4)	F(2)—C(9)—C(10)	115.3(12)
O(1)—Rh—C(2)	85.9(4)	F(3)—C(9)—C(10)	112.1(14)
O(1)—Rh—C(10)	164.4(6)	Rh—C(10)—C(9)	135.3(10)
O(1)—Rh—C(11)	160.4(6)	Rh—C(10)—C(11)	71.2(8)
O(2)—Rh—C(1)	160.1(6)	C(9)—C(10)—C(11)	153.5(10)
O(2)—Rh—C(2)	164.3(6)	Rh—C(11)—C(10)	73.5(7)
O(2)—Rh—C(10)	89.0(4)	Rh—C(11)—C(12)	140.1(12)
O(2)—Rh—C(11)	87.0(4)	C(10)—C(11)—C(12)	146.3(12)
C(1)—Rh—C(2)	35.4(8)	F(4)—C(12)—F(5)	103.3(10)
C(1)—Rh—C(10)	97.2(5)	F(4)—C(12)—F(6)	102.1(10)
C(1)—Rh—C(11)	87.3(5)	F(4)—C(12)—C(11)	114.8(15)
C(2)—Rh—C(10)	88.9(6)	F(5)—C(12)—F(6)	107.4(16)
C(2)—Rh—C(11)	100.1(5)	F(5)—C(12)—C(11)	113.8(10)
C(10)—Rh—C(11)	35.3(7)	F(6)—C(12)—C(11)	114.2(11)
Rh—O(1)—C(14)	123.8(6)	O(1)—C(14)—C(13)	113.4(10)
Rh—O(2)—C(16)	124.3(6)	O(1)—C(14)—C(15)	127.5(8)
Rh—C(1)—C(2)	73.5(10)	C(13)—C(14)—C(15)	119.0(10)
Rh—C(2)—C(1)	71.1(10)	C(14)—C(15)—C(16)	126.2(9)
F(1)—C(9)—F(2)	104.1(15)	O(2)—C(16)—C(15)	126.1(10)
F(1)—C(9)—F(3)	104.5(12)	O(2)—C(16)—C(17)	115.3(7)
F(1)—C(9)—C(10)	116.3(11)	C(15)—C(16)—C(17)	118.5(9)

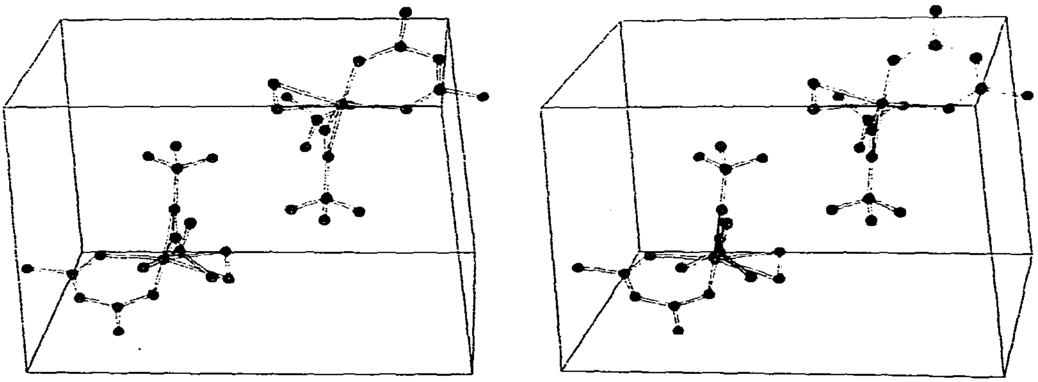

Fig. 2. Stereoscopic diagrams showing the molecular packing for Rh(acac)(C_4F_6)(C_2H_4).

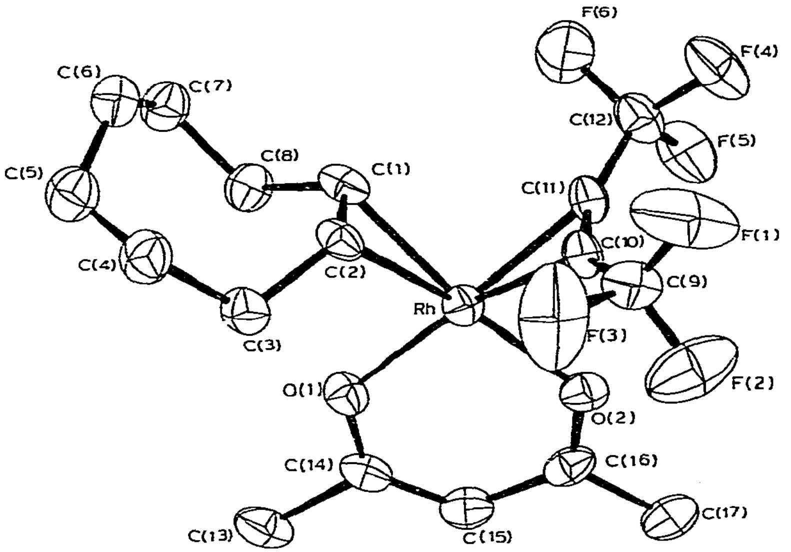

Fig. 3. Molecular geometry and atomic numbering for Rh(acac)(C_4F_6)(C_8H_{14}). Anisotropic ellipses represent 50% probability boundaries.

The structure of Rh(acac)(C_4F_6)(C_8H_{14})

The complex is monomeric. The molecular geometry and atomic numbering are depicted in Fig. 3. Bond distances and angles together with least-squares estimated standard deviations are listed in Tables 6 and 7 respectively. The C—F distances have been corrected for the effects of thermal libration. The coordination geometry about rhodium is again best described as square planar, with the acetylene and olefin lying approximately perpendicular to the square plane. It is somewhat surprising, in view of the bulk of the cyclooctene group,

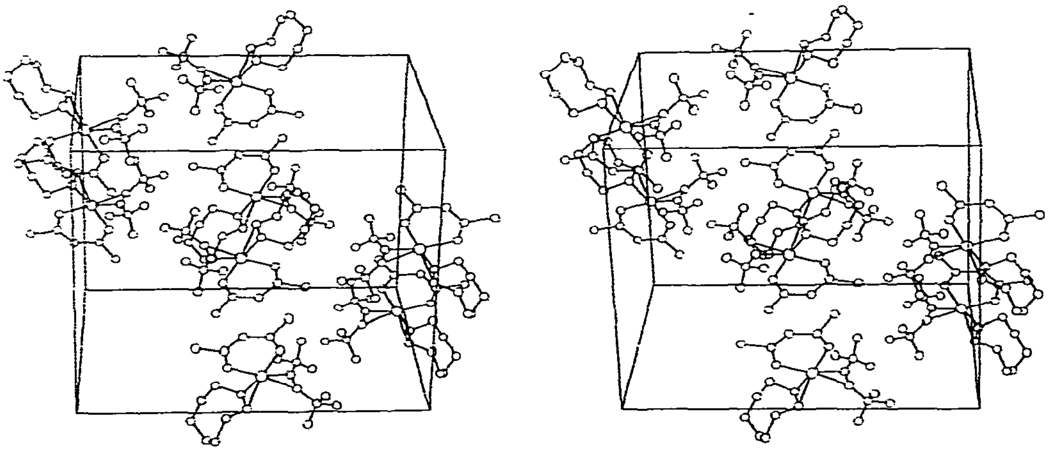

Fig. 4. Stereoscopic diagrams showing the molecular packing for Rh(acac)(C_4F_6)(C_8H_{14}).

TABLE 5

POSITIONAL PARAMETERS FOR Rh(acac)(C_4F_6)(C_8H_{14})

Atom	*x/a*	*y/b*	*z/c*
Rh	0.30566(6)	0.03003(5)	0.04022(6)
F(1)	0.3303(7)	0.2494(5)	−0.0720(7)
F(2)	0.4377(6)	0.2093(5)	0.0253(7)
F(3)	0.4198(8)	0.1607(5)	−0.0974(8)
F(4)	0.0946(8)	0.1919(8)	−0.0459(10)
F(5)	0.1016(6)	0.1570(7)	0.0747(7)
F(6)	0.0643(6)	0.0892(7)	−0.0190(11)
O(1)	0.3458(5)	−0.0703(4)	0.0947(5)
O(2)	0.3324(5)	0.0805(5)	0.1557(5)
C(1)	0.2324(8)	−0.0240(6)	−0.0755(7)
C(2)	0.3261(8)	−0.0117(6)	−0.0853(8)
C(3)	0.3977(8)	−0.0749(7)	−0.0853(8)
C(4)	0.3989(9)	−0.1044(8)	−0.1755(9)
C(5)	0.3030(13)	−0.1263(8)	−0.2243(11)
C(6)	0.2385(13)	−0.1738(9)	−0.1840(10)
C(7)	0.1563(10)	−0.1404(8)	−0.1416(10)
C(8)	0.1889(9)	−0.0985(8)	−0.0599(9)
C(9)	0.3734(9)	0.1883(7)	−0.0392(10)
C(10)	0.3048(7)	0.1358(5)	−0.0114(8)
C(11)	0.2224(8)	0.1194(6)	0.0008(8)
C(12)	0.1236(8)	0.1422(8)	0.0014(9)
C(13)	0.3920(9)	−0.1635(7)	0.1994(9)
C(14)	0.3714(7)	−0.0808(6)	0.1750(7)
C(15)	0.3818(8)	−0.0277(7)	0.2383(7)
C(16)	0.3620(8)	0.0499(7)	0.2261(7)
C(17)	0.3777(9)	0.0996(8)	0.3039(8)
H(1A)	0.1887	0.0113	−0.1043
H(2B)	0.3259	0.0299	−0.1267
H(3A)	0.3781	−0.1157	−0.0473
H(3B)	0.4622	−0.0562	−0.0616
H(4A)	0.4413	−0.1497	−0.1724
H(4B)	0.4264	−0.0649	−0.2104
H(5A)	0.3177	−0.1554	−0.2769
H(5B)	0.2693	−0.0800	−0.2430
H(6A)	0.2770	−0.2018	−0.1372
H(6B)	0.2082	−0.2091	−0.2288
H(7A)	0.1138	−0.1837	−0.1312
H(7B)	0.1208	−0.1064	−0.1854
H(8A)	0.2379	−0.1294	−0.0224
H(8B)	0.1325	−0.0912	−0.0275
H(13A)	0.4108	−0.1681	0.2626
H(13B)	0.3342	−0.1946	0.1815
H(13C)	0.4457	−0.1819	0.1688
H(15)	0.4048	−0.0441	0.2979
H(17A)	0.3829	0.0694	0.3584
H(17B)	0.4373	0.1295	0.3035
H(17C)	0.3222	0.1351	0.3038

that the olefin-rhodium, acetylene-rhodium, and acetylacetone-rhodium planes are more nearly orthogonal than they are for the simple ethylene complex (Table 8).

TABLE 6

BOND DISTANCES (Å) FOR $Rh(acac)(C_4F_6)(C_8H_{14})$

Rh—O(1)	2.038(7)	C(1)—C(8)	1.503(17)
Rh—O(2)	2.017(8)	C(2)—C(3)	1.519(16)
Rh—C(1)	2.196(11)	C(3)—C(4)	1.514(19)
Rh—C(2)	2.163(13)	C(4)—C(5)	1.522(22)
Rh—C(10)	2.059(10)	C(5)—C(6)	1.451(25)
Rh—C(11)	2.034(10)	C(6)—C(7)	1.535(25)
F(1)—C(9)	1.346(15)	C(7)—C(8)	1.507(19)
F(2)—C(9)	1.336(17)	C(9)—C(10)	1.459(17)
F(3)—C(9)	1.340(18)	C(10)—C(11)	1.241(15)
F(4)—C(12)	1.324(16)	C(11)—C(12)	1.458(16)
F(5)—C(12)	1.303(18)	C(13)—C(14)	1.546(16)
F(6)—C(12)	1.366(17)	C(14)—C(15)	1.369(17)
O(1)—C(14)	1.281(13)	C(15)—C(16)	1.424(18)
O(2)—C(16)	1.256(14)	C(16)—C(17)	1.505(17)
C(1)—C(2)	1.373(16)		

TABLE 7

BOND ANGLES (°) FOR $Rh(acac)(C_4F_6)(C_8H_{14})$

O(1)—Rh—O(2)	90.4(3)	C(6)—C(7)—C(8)	113.5(11)
O(1)—Rh—C(1)	92.0(4)	C(1)—C(8)—C(7)	112.9(11)
O(1)—Rh—C(2)	90.9(4)	F(1)—C(9)—F(2)	107.4(11)
O(1)—Rh—C(10)	164.3(4)	F(1)—C(9)—F(3)	107.0(13)
O(1)—Rh—C(11)	159.9(4)	F(1)—C(9)—C(10)	110.9(11)
O(2)—Rh—C(1)	162.6(4)	F(2)—C(9)—F(3)	106.7(12)
O(2)—Rh—C(2)	160.5(4)	F(2)—C(9)—C(10)	111.8(12)
O(2)—Rh—C(10)	86.2(4)	F(3)—C(9)—C(10)	112.7(11)
O(2)—Rh—C(11)	87.5(4)	Rh—C(10)—C(9)	137.7(8)
C(1)—Rh—C(2)	36.7(4)	Rh—C(10)—C(11)	71.3(7)
C(1)—Rh—C(10)	95.8(4)	C(9)—C(10)—C(11)	151.0(11)
C(1)—Rh—C(11)	84.3(4)	Rh—C(11)—C(10)	73.4(6)
C(2)—Rh—C(10)	87.3(4)	Rh—C(11)—C(12)	137.4(9)
C(2)—Rh—C(11)	97.7(5)	C(10)—C(11)—C(12)	148.9(11)
C(10)—Rh—C(11)	35.3(4)	F(4)—C(12)—F(5)	107.7(14)
Rh—O(1)—C(14)	124.8(7)	F(4)—C(12)—F(6)	103.5(14)
Rh—O(2)—C(16)	126.8(8)	F(4)—C(12)—C(11)	117.1(12)
Rh—C(1)—C(2)	70.3(7)	F(5)—C(12)—F(6)	98.8(13)
Rh—C(1)—C(8)	114.5(8)	F(5)—C(12)—C(11)	114.6(11)
C(2)—C(1)—C(8)	125.7(11)	F(6)—C(12)—C(11)	113.0(11)
Rh—C(2)—C(1)	73.0(7)	O(1)—C(14)—C(13)	113.9(10)
Rh—C(2)—C(3)	115.2(8)	O(1)—C(14)—C(15)	127.1(10)
C(1)—C(2)—C(3)	122.3(10)	C(13)—C(14)—C(15)	119.0(10)
C(2)—C(3)—C(4)	110.4(10)	C(14)—C(15)—C(16)	125.4(10)
C(3)—C(4)—C(5)	116.3(11)	O(2)—C(16)—C(15)	125.5(10)
C(4)—C(5)—C(6)	120.2(14)	O(2)—C(16)—C(17)	117.1(11)
C(5)—C(6)—C(7)	121.2(13)	C(15)—C(16)—C(17)	117.5(11)

Discussion

Olefin-rhodium coordinations

The olefin-rhodium coordinations are characterised by Rh—C distances of 2.142(14), 2.171(17) Å and 2.163(13), 2.196(11) Å, and C—C distances of

1.31(3) and 1.37(2) Å respectively for the ethylene and cyclooctene complexes. It might be expected that the Rh—C distances in the cyclooctene complex would be somewhat longer than those in the ethylene complex but the differences are not significant. Unfortunately, the standard deviations are such as to preclude any informative discussion on the relative C—C distances.

Ethylene—rhodium distances recently observed in other simple ethylene complexes are 2.105, 2.105, 2.115 and 2.134(8) Å in $[h^5\text{-}C_5(C_6H_5)_4Cl]Rh(C_2H_4)_2$ [8]; 2.174, 2.190(12) Å in $Rh(C_2H_4)(C_2F_4)$(acac) [9]; 2.117, 2.118(4) Å in $Rh(C_2H_4)_2$(acac) [9]; 2.167(2) Å in $(\pi\text{-}C_5H_5)(C_2H_4)(C_2F_4)Rh$ [10];2.159,2.165 Å in $Rh(Cl)((C_2H_5)_2NH)(C_2H_4)(CO)$ [11], 2.116, 2.118(2) Å in *trans*-Rh(Cl)-(C_2H_4)(triisopropylphosphine)$_2$ [12], and 2.24, 2.25 Å in $Rh(C_2H_4)_3$(acetonitrile)$_2BF_4$ [13]. It can be seen that in the present complexes, the Rh—ethylene distances lie within the above range.

The cyclooctene—rhodium distances are significantly longer than distances observed in other cyclic olefins of 2.108, 2.116, 2.116, 2.135(6) Å in (but-2-enyl-1-methylallyl ether)(acetylacetonato)rhodium [14] and 2.08, 2.10, 2.10, 2.12(2) Å in di-μ-chlorobis(triphenylphosphite)cycloocta-1,5-diene)dirhodium(I) [15].

Acetylacetone-rhodium coordinations

In both complexes the acetylacetone ligands are planar, with very similar geometries. The Rh—O distances of 2.015(6), 2.033(7) Å and 2.017(8), 2.038(7) Å respectively show a shorter/longer pattern which is consistent in the two complexes. The shorter bond lengths are below the range normally found for Rh—O(acac) bonds (2.025—2.087 Å) [14,16—19]. At the top of this range are bonds which are situated *trans* to a carbonyl group which is known to exert a relatively large structural *trans* influence [17]. In the present complexes the bonds are *trans* to olefins and acetylenes, which exert little or no such influence. In addition we note that no difference in the structural *trans* influences between olefin and hexafluorobut-2-yne ligands can be discerned, since the Rh—O bond of 2.015 Å in the ethylene complex lies *trans* to the acetylene, whereas the bond of 2.017 Å in the cyclooctene complex lies *trans* to the cyclooctene.

In the acetylacetone ligand the metallocyclic C—O and C—C bond lengths exhibit the usual intermediate bond order attributed to an enolate-type resonance in the chelate rings [14,16—19]. The C—O bond lengths average 1.271 Å and the C—C bond lengths average 1.392 Å.

Hexafluorobut-2-yne-rhodium coordination

The hexafluorobut-2-yne ligands are symmetrically π-bonded to the metal atoms with Rh—C distances of 2.016(10) and 2.042(11) Å in the ethylene complex and 2.034 and 2.059(10) Å in the cyclooctene complex. The ligands lie approximately perpendicular to the square coordination planes (Table 8).

Coordination of an acetylene to a metal results in a lengthening of the carbon—carbon bond with a concomitant bending back of any substituent groups from colinearity with the multiple bond. The observed C≡C distance in the free ligand is 1.22 Å [20] and in simple alkynes is approximately 1.20 Å [21], and although the lengthening observed in the two complexes (to 1.23(2) and 1.241(15) Å) is not statistically significant, it is nevertheless most likely a

TABLE 8

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES FOR (i) $Rh(acac)(C_4F_6)(C_2H_4)$ AND (ii) $Rh(acac)(C_4F_6)(C_8H_{14})$

(a) Olefin Rh C(1) C(2)

(i) $0.249X - 0.458Y + 0.854Z - 1.866 = 0$
(ii) $0.192X - 0.898Y + 0.396Z - 0.580 = 0$

(b) Acetylene Rh C(10) C(11)

(i) $0.241X - 0.908Y + 0.343Z - 2.343 = 0$
(ii) $0.051X + 0.388Y + 0.920Z + 1.002 = 0$

Displacements (i) C(9) −0.010 C(12) −0.042
(ii) C(9) 0.019 C(12) 0.096

(c) Acetylacetone Rh O(1) O(2) C(14) C(15) C(16)

(i) $0.909X + 0.164Y - 0.383Z - 1.743 = 0$
(ii) $0.975X + 0.162Y - 0.156Z - 4.133 = 0$

Displacements (i) Rh 0.004 O(1) −0.008 O(2) 0.002 C(14) 0.005 C(15) 0.004 C(16) −0.007
C(13) −0.045 C(17) 0.049
(ii) Rh −0.006 O(1) 0.017 O(2) −0.002 C(14) −0.016 C(15) 0.001
C(16) 0.006 C(13) −0.078 C(17) 0.023

Dihedral angles

Plane	Plane	(i)	(ii)
1	2	86.36	88.52
1	3	86.50	88.85
2	3	88.55	88.24

real effect. The extent of the lengthening as the bond order is reduced upon coordination is smaller than those found in many other coordinated acetylenes (see for example Table VIII of reference 22). Unfortunately many of the structure determinations have been carried out on platinum complexes, and the uncertainties in the positions of carbon atoms in close proximity to such a heavy metal are invariably high.

The observed bend-back angles in the present complexes are 26.5 and 33.7° (av. 30.1°) in the ethylene complex, and 29.0 and 31.1° (av. 30.1°) in the cyclooctene complex. Typical bend-back angles in other hexafluorobut-2-yne complexes are 30—40° [22] although values as high as 45.5(8)° have been observed [23] and the low values observed here are consistent with the small lengthening of the carbon—carbon multiple bond. Although the average bend-back angles are identical in the two complexes, there is a greater disparity between the individual values in the ethylene complex. This is most likely a consequence of the individual CF_3 groups adopting their most favourable positions so as to minimise any of the F···F intermolecular contacts described earlier. It is noteworthy that more close contacts involve F atoms on C(12) than on C(9), and that C(12) is more displaced from the Rh, C(10), C(11) plane than is C(9) (Table 8).

Acknowledgement

We thank the University of Auckland for the award of study leave to G.R.C. and Dr. R.D.W. Kemmitt for supplying the crystals.

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