Crystal and Molecular Structure of *acb*[1,2-Bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-*O′,O,C*^{1}]-*fde*{1,4—5,β-η-[bis(trifluoromethyl)ethylene]oct-4-enyl}iridium(III): an Addition Product of Hexafluorobut-2-yne with Co-ordinated Cyclo-octa-1,5-diene

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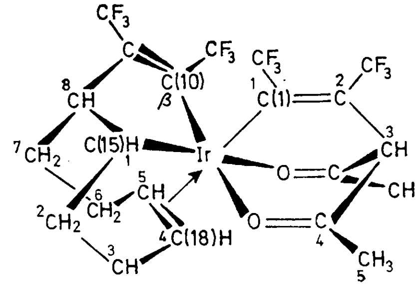
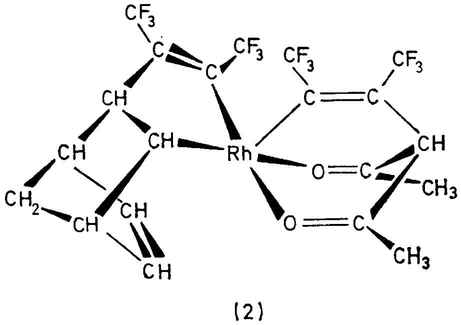
The structure of the title compound has been determined from *X*-ray diffractometer data by the heavy-atom method. Crystals are triclinic, space group $P\bar{1}$, with $a = 13.415 \pm 0.015$, $b = 11.448 \pm 0.012$, $c = 8.435 \pm 0.009$ Å, $\alpha = 70.2 \pm 0.4$, $\beta = 113.6 \pm 0.5$, $\gamma = 103.5 \pm 0.5°$. Block-diagonal least-squares refinement of the atomic-parameters converged at R 0.048 for 4 642 reflections. The compound is shown to have been formed by 1,4-addition of hexafluorobut-2-yne to an acetylacetonatoiridium ring, with a second acetylene molecule inserted between the metal and an olefinic carbon atom. Bond lengths are: Ir–O 2.183, 2.240; Ir–C 2.061, 2.006, 2.075; and Ir–C (olefin) 2.269, 2.347 Å. The molecular geometry is compared with that in related molecules.

RECENTLY we reported two ways in which an acetylene may add to a metal diene complex and,[1] on the basis of an *X*-ray structure determination, formulated the addition product obtained [2] on treating (acetylacetonato)(cyclo-octa-1,5-diene)iridium(I) with hexafluorobut-2-yne as (1). The product of the corresponding reaction with (acetylacetonato)(norbornadiene)rhodium(I) has been assigned a similar structure, (2), on the basis of i.r., ^{1}H n.m.r., and ^{19}F n.m.r. spectra; [3] however in (2) there is no evidence for co-ordination of the second olefinic bond of the diene to the metal. We now describe the detailed crystal and molecular structure of (1).



(1)



(2)

Showing the systematic numbering system

EXPERIMENTAL

Crystal Data.†—$C_{21}H_{19}F_{12}IrO_2$, $M = 723.6$, Triclinic, $a = 13.415 \pm 0.015$, $b = 11.448 \pm 0.012$, $c = 8.435 \pm 0.009$ Å, $\alpha = 70.2 \pm 0.4$, $\beta = 113.6 \pm 0.5$, $\gamma = 103.5 \pm 0.5°$, $U = 1109.8$ Å^3, $Z = 2$, $D_c = 2.15$ g cm^{-3}, $F(000) = 692$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 66.2 cm^{-1}.

Crystals of (1) were grown from diethyl ether. Unit-cell dimensions were obtained from precession photographs by use of Mo-K_α radiation. The intensities of reflections with $\sin\theta/\lambda < 0.75$ Å^{-1} were measured on a Stoe Weissenberg diffractometer by use of monochromatic Mo-K_α radiation and a ω-scan technique. Data were collected in ten layers $hk0$—9 from a crystal of dimensions *ca*. $0.028 \times 0.021 \times 0.016$ cm. The intensities of the 4 642 reflections with $\sin\theta/\lambda > 0.1$ Å^{-1} and $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects. No corrections were made for absorption in view of the approximately equidimensional cross-section of the crystal.

Structure Determination.—Scattering factors for the atoms

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† The cell dimensions have been redetermined, with greater accuracy, since the appearance of ref. 2.

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

[2] A. C. Jarvis and R. D. W. Kemmitt, unpublished results.

[3] D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt, and B. Y. Kimura, *J.C.S. Dalton*, 1972, 2549; D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1970, 331.

were taken from ref. 4. The structure was solved by conventional heavy-atom methods. The positional and anisotropic thermal parameters of the non-hydrogen atoms were refined by use of a block-diagonal least-squares procedure, each block containing the parameters of one atom. During the least-squares refinement corrections to the structure factors for anomalous dispersion of the iridium atom were made.[5] Hydrogen atoms were not included in the structure-factor calculations. In the final cycles a weighting scheme, with the weight given by $w = (2.47 - 0.144\,|F_o| + 0.0046\,|F_o|^2)^{-1}$, was introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. The final R was 0.048 and R' 0.050 $[R' = \Sigma w(|F_o| - |F_c|)\,|\,\Sigma w\,|F_o|]$ for 4 642 reflections. The maximum shift in the final cycle was 0.02σ.* A difference-Fourier synthesis calculated at the end of the refinement shows no maxima > 0.8 eÅ^{-3}.

DISCUSSION

The molecular geometry and atom numbering are shown in Figure 1. Final atom co-ordinates are listed in Table 1, and bond lengths and angles are in Tables 2 and 3. The C–F bond lengths have been corrected for libration effects as previously described.[6]

TABLE 1

Final atomic co-ordinates, with standard deviations (in parentheses) calculated from the least-squares treatment

	x/a	*y/b*	*z/c*
Ir	0.24097(3)	0.28086(3)	0.19194(4)
F(1)	0.1145(9)	0.6783(11)	−0.3002(16)
F(2)	0.2754(9)	0.7386(7)	−0.2022(12)
F(3)	0.2264(15)	0.6268(9)	−0.3693(13)
F(4)	0.0961(8)	0.4172(9)	−0.3642(9)
F(5)	0.1542(9)	0.2456(6)	−0.2141(9)
F(6)	0.2593(9)	0.4011(11)	−0.3009(14)
F(7)	0.4831(9)	0.1854(9)	0.0759(20)
F(8)	0.5070(7)	0.2348(11)	0.3040(14)
F(9)	0.4446(7)	0.3609(7)	0.0492(14)
F(10)	0.2495(9)	−0.1219(8)	0.0545(17)
F(11)	0.4141(9)	−0.0538(8)	0.1790(16)
F(12)	0.3321(12)	0.0322(11)	−0.0957(15)
O(1)	0.1382(6)	0.3925(6)	0.2143(9)
O(2)	0.3743(5)	0.4270(5)	0.2884(9)
C(1)	0.2122(6)	0.4047(7)	−0.0606(10)
C(2)	0.2201(7)	0.5262(7)	−0.0779(11)
C(3)	0.2451(8)	0.5699(7)	0.0897(12)
C(4)	0.3560(8)	0.5365(8)	0.2268(12)
C(5)	0.4414(11)	0.6396(10)	0.2869(18)
C(6)	0.1585(8)	0.5076(8)	0.1739(12)
C(7)	0.0963(11)	0.5861(11)	0.1996(17)
C(8)	0.2065(10)	0.6398(8)	−0.2396(14)
C(9)	0.1813(10)	0.3656(9)	−0.2314(13)
C(10)	0.3256(8)	0.1850(8)	0.1385(12)
C(11)	0.2762(9)	0.0724(8)	0.1116(12)
C(12)	0.4387(10)	0.2397(10)	0.1374(19)
C(13)	0.3190(13)	−0.0149(10)	0.0612(19)
C(14)	0.1755(10)	0.0225(8)	0.1654(13)
C(15)	0.1198(8)	0.1360(7)	0.1308(12)
C(16)	0.0453(10)	0.1112(11)	0.2427(17)
C(17)	0.1108(11)	0.1184(12)	0.4403(16)
C(18)	0.2252(10)	0.1897(9)	0.4664(12)
C(19)	0.3117(8)	0.1411(8)	0.4766(11)
C(20)	0.3164(11)	0.0068(8)	0.4852(14)
C(21)	0.2134(11)	−0.0571(8)	0.3621(15)

The molecule is an octahedral complex of Ir$^{\text{III}}$ with atoms O(1), O(2), C(10), C(15), and C(1), and the mid-point of the C(18)–C(19) bond as vertices. The mean planes through the atoms defining each of the three square planes of the octahedron are given in Table 4.

The bonds from iridium to C(10) and C(15), both *trans* to oxygen, have significantly different lengths, the variation being larger than expected on the basis of hybridisation differences alone. Indeed the Ir–C(10) bond is shorter than the sum of covalent radii[7] for the atoms (2.08 Å). It is also shorter than in other iridium

TABLE 2

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

Ir–O(1)	2.183(7)	C(18)–C(19)	1.36(2)
Ir–O(2)	2.240(6)	C(14)–C(15)	1.53(1)
Ir–C(1)	2.061(7)	C(15)–C(16)	1.55(2)
Ir–C(10)	2.006(9)	C(16)–C(17)	1.56(2)
Ir–C(15)	2.075(8)	C(20)–C(21)	1.56(2)
Ir–C(18)	2.269(9)	Mean	1.55(1)
Ir–C(19)	2.347(8)		
		O(1)–C(6)	1.24(1)
C(8)–F(1)	1.35(1)	O(2)–C(4)	1.23(1)
C(8)–F(2)	1.35(1)	C(4)–C(5)	1.51(1)
C(8)–F(3)	1.37(1)	C(6)–C(7)	1.48(1)
C(9)–F(4)	1.36(1)		
C(9)–F(5)	1.33(1)	C(3)–C(4)	1.51(1)
C(9)–F(6)	1.38(1)	C(3)–C(6)	1.51(1)
C(12)–F(7)	1.33(1)	C(3)–C(2)	1.54(1)
C(12)–F(8)	1.37(1)	C(11)–C(14)	1.52(2)
C(12)–F(9)	1.35(1)	C(2)–C(8)	1.52(1)
C(13)–F(10)	1.37(1)	C(1)–C(9)	1.52(1)
C(13)–F(11)	1.33(1)	C(10)–C(12)	1.50(2)
C(13)–F(12)	1.34(1)	C(11)–C(13)	1.50(1)
Mean	1.351(5)	Mean	1.51(1)
C(10)–C(11)	1.35(1)	C(17)–C(18)	1.53(2)
C(1)–C(2)	1.33(2)	C(19)–C(20)	1.53(1)

TABLE 3

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

O(2)–Ir–C(10)	99.8(3)	Ir–C(2)–C(4)	118.5(6)
O(1)–Ir–O(2)	82.9(2)	C(21)–C(14)–C(15)	114.7(9)
O(1)–Ir–C(15)	96.5(3)	C(14)–C(15)–C(16)	113.9(8)
C(10)–Ir–C(15)	81.5(4)	C(15)–C(16)–C(17)	113.0(9)
C(1)–Ir–C(1)	83.2(3)	C(16)–C(17)–C(18)	113.5(9)
C(1)–Ir–O(2)	85.8(3)	C(19)–C(20)–C(21)	116.7(9)
C(1)–Ir–C(10)	90.5(3)	C(20)–C(21)–C(14)	112.8(8)
C(1)–Ir–C(15)	100.1(3)	C(17)–C(18)–C(19)	123.6(9)
C(18)–Ir–C(19)	34.3(4)	C(18)–C(19)–C(20)	127.4(9)
Ir–C(1)–C(2)	118.9(6)	Ir–C(15)–C(14)	108.2(6)
Ir–C(10)–C(11)	116.3(8)	Ir–C(15)–C(16)	108.9(6)
Ir–C(1)–C(9)	123.8(5)		
Ir–C(10)–C(12)	118.7(7)	C(11)–C(14)–C(21)	107.7(9)
C(2)–C(1)–C(9)	117.3(7)	C(11)–C(14)–C(15)	106.9(7)
C(11)–C(10)–C(12)	125.0(9)	C(2)–C(4)–C(5)	121.4(9)
C(1)–C(2)–C(8)	132.2(8)	C(1)–C(6)–O(7)	120.9(10)
C(10)–C(11)–C(13)	127.0(11)	C(2)–C(4)–C(3)	119.8(7)
C(1)–C(2)–C(3)	119.3(7)	C(1)–C(6)–C(3)	119.8(8)
C(10)–C(11)–C(14)	115.2(8)	C(5)–C(4)–C(3)	118.8(8)
C(8)–C(2)–C(3)	108.5(7)	C(7)–C(6)–C(3)	119.2(8)
C(13)–C(11)–C(14)	117.1(8)	C(4)–C(3)–C(2)	110.5(8)
Ir–C(1)–C(6)	119.2(6)	C(6)–C(3)–C(2)	109.8(7)

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* Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21329 (24 pp., 1 microfiche).

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

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

[6] D. R. Russell and P. A. Tucker, *J.C.S. Dalton*, 1975, preceding paper.

[7] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960.

complexes (2.05—2.16 Å) except for [Ir$(PPh_3)_2$(CO)Cl-$(C_7H_6N_2)$] (2.01 Å).[8] The short Ir–C(10) bond may result from a contraction of the metal orbitals due to the relatively electropositive nature of the carbon atom.

TABLE 4

Equations of planes and, in square brackets, the distances (Å) of atoms from the planes. The equation of the plane is in the form $lx + my + nz = p$, with co-ordinates and distances (Å) referred to orthogonal axes a, b,* and c'

Plane	Atoms defining plane	l	m	n	p
(*a*)	Ir, O(1), O(2), C(10), C(15)	0.0531	0.5383	−0.8411	−0.253
	[Ir 0.00, O(1) 0.11, O(2) −0.11, C(10) 0.12, C(15) −0.12, C(1) 2.04, C(18) −2.13, C(19) −2.28]				
(*b*)	Ir, O(2), C(1), M†, C(15)	0.8714	−0.4354	−0.2261	−0.288
	[Ir 0.02, O(1) −2.12, O(2) 0.03, C(10) 2.02, C(15) 0.03, C(1) −0.05, M† −0.05, C(18) −0.72, C(19) 0.61]				
(*c*)	Ir, O(1), C(1), C(10), M†	0.5977	0.6046	0.5265	4.146
	[Ir 0.00, O(1) −0.05, O(2) 2.22, C(10) −0.05, C(15) −2.04, C(1) 0.06, M† 0.04, C(18) −0.15, C(19) 0.25]				
(*d*)	Ir, C(10)—(14)	0.1749	−0.4160	0.8924	1.256
	[Ir −0.09, C(10) −0.02, C(11) −0.06, C(12) 0.12, C(13) −0.09, C(14) 0.15, C(15) −0.44, C(1) −2.02]				
(*e*)	C(18)—(20)	0.0476	0.2455	−0.9682	−3.510
(*f*)	C(17)—(19)	0.0953	0.3553	−0.9299	−3.082
(*g*)	Ir, C(10)—(12)	0.0993	−0.4454	0.8898	0.926
	[Ir 0.00, C(10) −0.01, C(11) 0.00, C(12) 0.00]				
(*h*)	C(10), C(11), C(13), C(14)	0.2711	−0.4039	0.8737	1.536
	[C(10) 0.02, C(11) −0.05, C(13) 0.02, C(14) 0.02]				

Dihedral angles (°) between planes

(*a*)–(*b*)	89.9	(*e*)–(*f*)	7.2
(*a*)–(*c*)	94.9	(*g*)–(*h*)	10.2
(*b*)–(*c*)	82.0		

† M is the midpoint of the C(18)–C(19) vector.

However the Ir–C(1) bond, also with a trifluoromethyl substituent, is longer than Ir–C(10), which would suggest that a co-ordinated olefin has a larger *trans*-influence than oxygen of a co-ordinated ketone group.

The Ir–O(1) and Ir–O(2) bonds, *trans* to C(10) and C(15) respectively, are different in length, with the former being the shorter. Both Ir–O bonds are longer than the Ir–OH_2 bond (2.06 Å) in the $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ anion [9] and than the sum of covalent radii [7] for the atoms (2.06 Å), which suggests that these bonds are weak.

The distance (2.205 Å) of the iridium atom from the centre of the olefinic C(18)–C(19) bond is long compared with that in most other olefin complexes of the metal {*e.g.* 2.008—2.117 Å in [IrL_2Me(cyclo-octadiene)][10] where L_2 = $(PPhMe_2)_2$ or $PPh_2 \cdot [CH_2]_2 \cdot PPh_2$}, except for [(cyclo-octadiene)$_2$Ir$(SnCl_3)$] in which the values range from 2.15 to 2.23 Å.[11] However this is the first reported structure of an iridium(III) olefin complex.

The geometry of the bicyclic system formed by 1,4-addition of hexafluorobut-2-yne to the acetylacetonato-iridium ring is similar to that previously reported for such systems.[3,6] As expected the carbon–oxygen bonds are shorter than observed in the original delocalised β-diketonate ligand and angles of the type C(1)–C(2)–C(8) are large due to steric repulsion between adjacent trifluoromethyl groups. The C(10)–C(11)–C(12) angle in the present complex is large for a similar reason. The molecular geometry of (1) is such that fluorine atoms attached to C(1) are close to those attached to C(12). In solution, if there is free rotation about the C–C(F_3) bonds, these fluorine atoms could approach as close as 2.4 Å, which may explain an additional doublet coupling of the quartet resonances of the α-trifluoromethyl groups observed in the ^{19}F n.m.r. spectrum. However in the crystal structure the shortest contact [F(6) ··· F(9) 2.98 Å] is unexceptional when compared with the sum of van der Waals radii [7] of the atoms (2.7 Å).

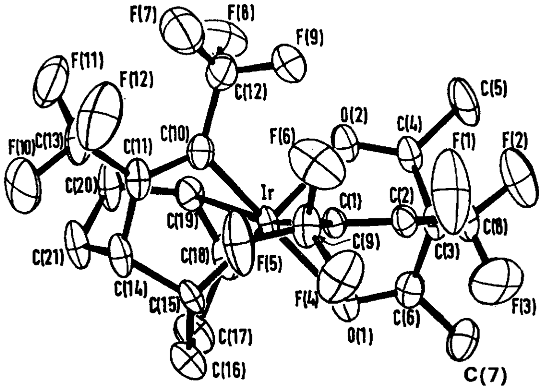

FIGURE 1 Molecular geometry and atom numbering system used in the analysis; thermal ellipsoids are scaled to 50% probability

The iridacyclopentene ring shows some evidence of strain. The co-ordination about atom C(11) is significantly non-planar (Table 4) and there is an angle of 10° between the co-ordination planes of atoms C(10) and C(11). Atom C(15) is on the same side of the mean Ir–C(10)–C(11)–C(14) plane as atom C(1); the alternative conformation, with C(15) on the opposite side of the mean plane, would not allow co-ordination of the C(18)–C(19) bond to the metal.

Co-ordination of the C(18)–C(19) double bond to iridium also imposes constraints on the eight-membered ring of the original cyclo-octadiene ligand. This ring cannot achieve a twisted boat conformation (Figure 2) as it does in free [12] or co-ordinated cyclo-octadiene [13]

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[8] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645.

[9] M. Clechanowicz, W. P. Griffith, D. Pawson, A. C. Skapski, and M. J. Cleare, *Chem. Comm.*, 1971, 876.

[10] M. R. Churchill and S. A. Bezman, *J. Organometallic Chem.*, 1971, **31**, C43.

[11] P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 455.

[12] L. Hedberg and K. Hedberg, Abstracts, National Meeting Amer. Crystallographic Assoc., July 1964.

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

because atom C(18) would approach the iridium atom more closely than C(19). Instead there is a conformational change such that the C(14)–C(15) and C(18)–C(19) bonds are no longer parallel (see Figure 2) and there is a twist about the C(18)–C(19) bond of 7.2°. Even so, the Ir–C(18) distance is significantly shorter than Ir–C(19). Since the C(18)–C(19) bond is approximately parallel (the angle is 6°) to the Ir–O(1)–O(2)–C(10)–C(15) mean plane, the difference is mainly due to a lateral displacement of the centre of this bond from the ideal position for octahedral co-ordination.

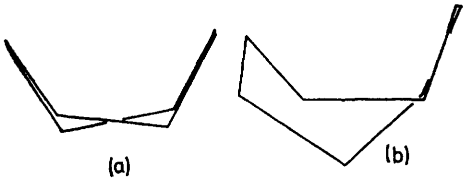

FIGURE 2 Conformations of (a) cyclo-octadiene in the free molecule or when co-ordinated to a metal, and (b) the cyclo-octene ring in complex (1)

Barlex *et al.*[3] concluded from spectral data that in compound (2), the norbornadiene rhodium analogue of compound (1), the remaining olefinic bond of the norbornadiene fragment is not co-ordinated to the metal. A molecular model of (2) based on the structure of (1) supports this conclusion as the smaller, more rigid, norbornadiene system does not allow the olefinic bond to approach the metal closely enough to interact.

The molecular packing is illustrated in Figure 3. There are no intermolecular contacts shorter than the sum of van der Waals radii[7] for the atoms. The more important contacts between molecules, from the point of view of the molecular packing, are between carbon and fluorine atoms with distances in the range 3.37—3.58 Å.

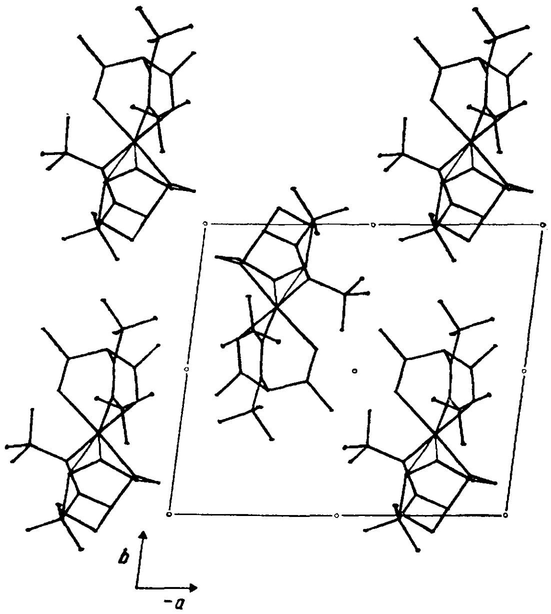

FIGURE 3 Molecular packing projected along [001]

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