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THE CRYSTAL AND MOLECULAR STRUCTURE OF μ-μ'-DICHLOROBIS(HEXAFLUOROBUT-2-ENYL)-BIS(CYCLOOCTA-1,5-DIENYL)DIIRIDIUM(III).

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Summary

The title compound is isolated from reaction of hexafluorobut-2-yne with μ-μ'-Dichlorobis(cycloocta-1,5-diene)diiridium(I) at 90°C. Crystals of the complex, solvated with deuterobenzene, are monoclinic, space group $P2_1/n$ with $a = 10.97 \pm 0.02$, $b = 17.96 \pm 0.03$, $c = 11.63 \pm 0.02$ Å, $\beta = 127.4 \pm 0.60°$. The acetylene has abstracted a hydrogen atom forming a σ-bonded *cis*-vinylic group and the original cyclooctadiene, having lost a proton, is coordinated as the cycloocta-1,5-dienyl ligand. Mean bond lengths are Ir-Cl 2.467, Ir-C (allylic) 2.17, I-C (olefinic) 2.36 and Ir-C (vinylic) 2.09 Å.

Introduction

WE recently reported [1] the isolation of complexes I and II from reaction of hexafluorobut-2-yne (C_4F_6) with μ-μ'-Dichlorobis(cycloocta-1,5-diene)diiridium(I) at 90° and 20° respectively. In this paper we report in detail the crystal structure of I.

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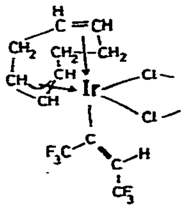
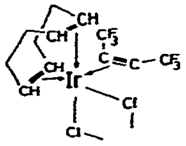
The reactions of C_4F_6 with μ-μ'-Dichlorobis(cycloocta-1,5-diene) dirhodium(I) and (cycloocta-1,5-diene)acetylacetonatoiridium(I) produce complexes in which the acetylene has, respectively, added 1,4 to the cyclooctadiene ligand, and, formed an iridiacyclopentene ring[2]. Complexes similar to II are almost certainly intermediates in the formation of these addition products and it is probable that complexes similar to I are also intermediates. However, because of the higher temperature required to form I, it is likely to be further along any postulated reaction sequence. The formation of I from II would be an important step in such a sequence since the change is from formally five coordinate Ir^I to formally six coordinate Ir^{III} and involves no more than a net proton transfer.



(I)



(II)

Experimental

A few clear pale yellow crystals were isolated from the solution in hexadeuterobenzene used to record the ¹H n.m.r. spectrum. They were parallelipipeds with the forms {100}, {01$\bar{1}$} and {011} developed. The crystals slowly become opaque on standing in air and were therefore sealed in thin-walled glass capillaries. Unit cell dimensions are from oscillation photographs recorded with CuK_α radiation and from 2θ values [MoK_α radiation] optimised on a Weissenberg diffractometer.

Crystal Data - $C_{24}H_{24}Cl_2F_{12}Ir_2.2C_6D_6$ (I), M = 1163.8, monoclinic with a = 10.97 ± 0.02, b = 17.96 ± 0.03, c = 11.63 ± 0.02Å, β = 127.4 ± 0.6°, absences $\underline{h}\ 0\ \underline{l}$ when $\underline{h} + \underline{l} = 2\underline{n} + 1$ and $0\ \underline{k}\ 0$ when $\underline{k} = 2\underline{n} + 1$. λ (Cu-$\underline{K}_\alpha$) = 1.5419, λ (Mo-$\underline{K}_\alpha$) = 0.7107Å. μ (Mo$\underline{K}_\alpha$) = 79.5 cm^{-1}.

Intensities were measured in ten layers ($0\ \underline{k}\ \underline{l}$ through $9\ \underline{k}\ \underline{l}$) on a Stoe Weissenberg diffractometer using monochromatic Mo$\underline{K}_\alpha$ radiation and a ω-scan technique. The 1755 significant [$\underline{I} > 2\sigma(I)$] intensities with $0.1 < \sin\theta/\lambda < 0.6$Å^{-1} measured from a crystal of approximate dimensions 0.032 x 0.014 x 0.014cm were corrected for Lorentz polarisation and absorption effects [3].

Scattering factors were taken from ref. 4, corrections for the anomalous scattering by iridium were from ref. 5. The structure was solved by conventional 'heavy atom' methods. The positional and thermal parameters of the non-hydrogen atoms were refined by a block-diagonal least-squares procedure each block containing the parameters of one atom. Anisotropic thermal parameters were refined for Ir, Cl and F atoms. Hydrogen atoms were not located and not included in the structure factor calculations. Slight crystal decomposition was evident and layer scale factors were refined before anisotropic thermal parameters were introduced. In the final cycles a weighting scheme, with the weight given by $\underline{\omega} = (5.53 - 0.207|\underline{F}_o| + 0.0084|\underline{F}_o|^2)^{-1}$, was introduced in order that $\underline{\omega}\Delta^2$ be approximately independent of $|\underline{F}_o|$. The final $\underline{R}$ was 0.071 and $\underline{R}'$ 0.076 ($\underline{R}' = \Sigma\underline{\omega}(|\underline{F}_o| - |\underline{F}_c|) / \Sigma\underline{\omega}|\underline{F}_o|$) for 1755 reflections. The maximum shift in the final cycle was $0.1\sigma^{\dagger}$. A final difference Fourier synthesis showed no maxima or minima with an absolute height > 0.8eÅ^{-3}. The final atomic coordinates and thermal parameters are listed in Table 1. All anisotropic thermal parameters had real principal components.

Discussion

The molecular geometry and atom numbering of I are shown in Fig. 1.

(Continued on p. 308)

TABLE 1

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

	x/a	y/b	z/c	B_{11}^{+}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ir	-0.0387(1)	-0.0092(1)	0.1388(1)	2.49(4)	2.42(4)	1.80(4)	0.00(3)	1.37(3)	0.07(4)
Cl	0.1094(8)	-0.0687(3)	0.0696(7)	7.9(4)	6.7(3)	6.8(3)	0.9(2)	5.0(3)	1.6(2)
F(1)	-0.387(2)	0.015(1)	-0.070(2)	9.1(10)	10.4(11)	13.6(15)	-1.3(10)	0.4(10)	3.7(9)
F(2)	-0.459(3)	-0.091(2)	-0.067(3)	8.8(11)	17.4(17)	21.6(22)	4.9(15)	10.6(14)	-1.1(11)
F(3)	-0.443(3)	-0.046(3)	-0.222(2)	10.3(16)	54.6(57)	5.7(10)	4.7(21)	1.5(10)	3.6(25)
F(4)	-0.397(5)	-0.203(2)	-0.224(4)	29.7(44)	17.2(23)	13.6(22)	-1.6(18)	-4.4(25)	-5.8(24)
F(5)	-0.361(5)	-0.245(2)	-0.048(5)	32.9(46)	21.5(27)	35.5(45)	-13.3(29)	28.3(41)	-16.1(31)
F(6)	-0.231(4)	-0.271(2)	-0.105(5)	18.4(23)	17.5(20)	49.4(51)	-22.2(30)	22.2(32)	-9.9(18)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
C(1)	-0.111(3)	-0.032(1)	0.269(3)	7.3(5)	C(10)	-0.192(4)	-0.150(2)	-0.005(3)	8.7(7)
C(2)	-0.110(4)	0.049(2)	0.253(3)	9.0(7)	C(11)	-0.218(3)	-0.082(1)	-0.003(3)	6.7(5)
C(3)	0.018(4)	0.101(2)	0.350(4)	10.0(8)	C(12)	-0.376(3)	-0.055(1)	-0.082(3)	8.5(7)
C(4)	0.091(4)	0.098(2)	0.274(3)	8.7(7)	C(13)	-0.408(8)	-0.160(4)	0.239(7)	19.9(21)
C(5)	0.203(4)	0.048(1)	0.311(3)	8.4(6)	C(14)	-0.304(10)	-0.216(4)	0.264(8)	23.4(26)
C(6)	0.283(3)	-0.013(2)	0.429(3)	8.0(6)	C(15)	-0.210(7)	-0.269(3)	0.434(6)	16.7(16)
C(7)	0.174(4)	-0.051(2)	0.462(3)	9.3(7)	C(16)	-0.274(6)	-0.262(2)	0.502(5)	14.0(12)
C(8)	0.023(3)	-0.071(1)	0.329(2)	6.7(5)	C(17)	-0.399(6)	-0.212(3)	0.469(5)	15.4(14)
C(9)	-0.298(4)	-0.212(2)	-0.103(4)	10.4(8)	C(18)	-0.440(6)	-0.161(3)	0.330(5)	15.2(14)

+ Temperature factors in the form

$$\exp\left[-\tfrac{1}{4}\left(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + Bc^{*2}B_{33} + 2hk\,a^*b^*B_{12} + 2kl\,b^*c^*B_{23} + 2hl\,a^*c^*B_{13}\right)\right]$$

TABLE 2 BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES).

Mean C-C (benzene) and C-F bond lengths are 1.51(9) and 1.26(6) Å respectively. The mean C-C-C (benzene) angle is 120 (10): M(1) is the midpoint of the C(4)-C(5) bond and M(2) is the centre of gravity of atoms C(1), C(2) and C(8).

Ir-Cl	2.454(6)	Ir-Cl-Ir'	101.5(9)
Ir-Cl'	2.480(6)		
		Cl-Ir-C(11)	88(1)
Ir-C(1)	2.13(3)	Cl'-Ir-C(11)	90(1)
Ir-C(2)	2.19(3)	M(2)-Ir-C(11)	94
Ir-C(8)	2.18(3)	M(1)-Ir-Cl	95
		M(1)-Ir-Cl'	90
Ir-C(4)	2.35(3)	M(1)-Ir-M(2)	84
Ir-C(5)	2.37(3)	Cl-Ir-Cl'	78.5(6)
		Cl-Ir-M(2)	139
Ir-C(11)	2.09(2)	Cl'-Ir-M(2)	143
C(1)-C(2)	1.47(4)	Ir-C(11)-C(10)	121(2)
C(1)-C(8)	1.38(4)	Ir-C(11)-C(12)	119(2)
C(2)-C(3)	1.47(4)	C(12)-C(11)-C(10)	120(2)
C(3)-C(4)	1.52(4)	C(11)-C(10)-C(9)	130(3)
C(4)-C(5)	1.37(4)		
C(5)-C(6)	1.55(4)	C(1)-C(2)-C(3)	127(3)
C(6)-C(7)	1.61(4)	C(2)-C(3)-C(4)	98(3)
C(7)-C(8)	1.47(4)	C(3)-C(4)-C(5)	121(3)
		C(4)-C(5)-C(6)	132(3)
C(11)-C(12)	1.47(4)	C(5)-C(6)-C(7)	114(2)
C(10)-C(9)	1.51(4)	C(6)-C(7)-C(8)	112(2)
C(11)-C(10)	1.26(4)	C(7)-C(8)-C(9)	126(2)
		C(8)-C(1)-C(2)	119(2)

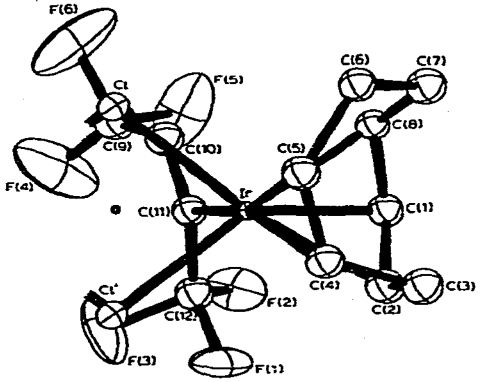


FIGURE 1 Molecular geometry and atom numbering for $[Ir(C_8H_{11})\{C(CF_3)C(CF_3)H\}Cl]_2$. Thermal ellipsoids are scaled to 10% probability.

Bond lengths and angles are listed in Table 2. The complex is a centrosymmetric dimer, each half containing a pseudo-octahedrally co-ordinated Ir^{III} atom if the allyl function is regarded as an anionic four-electron donor occupying two sites of the (distorted) octahedron.

The Ir-C(vinylic) and C=C(vinylic) bond lengths in I [2.09 and 1.26Å resp.] are similar to those reported for the vinylic grouping in the complexes, $Ir\{C(CN) = C(CN)H\}\{C_2(CN)_4\}(PPh_3)_2CO$ (2.09 and 1.29Å) [6] and $Ir(CH = CHB_{10}C_4H_{13})(C{\equiv}CB_{10}C_4H_{13})Cl(PPh_3)_2CO$ (2.08 and 1.29Å) [7]. The vinylic grouping is planar within experimental error. The distance from Ir to the centre of the co-ordinated olefinic bond C(4) = C(5), 2.26Å, is greater than normally found in olefin complexes of Ir^I, but corresponds to values found in Ir^{III} complexes where the olefin in *trans* to a σ-bonded carbon atom [8,9].

The plane of the allyl carbon atoms is inclined 116.4° to the $IrCl_2$ plane. A relationship between this angle, and the difference between the distance of the metal atom to the central allylic carbon

$Cl]_2$, in which all Pd-C distances are equal, the angle is 111.5° [10] whereas, for example, in Pd(π-allyl)($SnCl_3$)(PPh_3), where the metal-central carbon distance is shorter, the angle is 114.5° [11]. The difference between Ir-C(1), 2.13Å, and the mean of Ir-C(2) and Ir-C(8) distances, 2.19Å, although of low significance is in accord with this relationship.

The presence of a co-ordinated double bond in the cyclo-octadienyl ring appears to impose a rotation on the co-ordinated allyl function with respect to the Ir_2Cl_2 plane and about the Ir-Ir vector, relative to the observed orientation in unconstrained π-allyl complexes. This effect can be observed in Fig. 2, where it may also be seen that the Ir-Ir vector intersects the allyl group plane at a point nearer to the central carbon atom than does the Pd-Pd vector in $[Pd(\pi\text{-allyl})Cl]_2$. The absence of any twisting about the C(4)-C(5) bond, and the unexceptional ring angles and ring bond torsion angles [Tables 2 and 3] are indicative of a lack of strain in the cyclo-octadienyl ligand. The mean of the C(3) - C(2) - C(1) - C(8) and C(2) - C(1) - C(8) - C(7) torsion angles [40°] compares with the corresponding angle of 43° in 1,1,3,3-tetramethylallylchloropalladium(II) dimer [12].

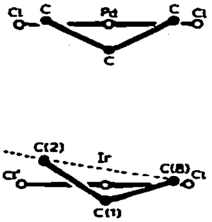


FIGURE 2 Orientation of the π-allylic function:

a) in $[(\pi\text{-allyl})PdCl]_2$

b) in complex I.

The observed difference between the two Ir-Cl bond lengths, together with the different orientations of the two outer allyl carbon atoms [C(2)

TABLE 3 TORSION ANGLES (°) FOR THE RING BONDS IN THE CYCLOOCTADIENYL LIGAND.

C(8)-C(1)-C(2)-C(3)	33	C(4)-C(5)-C(6)-C(7)	33
C(1)-C(2)-C(3)-C(4)	89	C(5)-C(6)-C(7)-C(8)	46
C(2)-C(3)-C(4)-C(5)	91	C(6)-C(7)-C(8)-C(1)	102
C(3)-C(4)-C(5)-C(6)	1	C(7)-C(8)-C(1)-C(2)	47

TABLE 4 MEAN PLANES DEFINED BY ATOMS AND DEVIATIONS (Å) OF SPECIFIED ATOMS FROM THOSE PLANES.

i) C(13), C(14), C(15), C(16), C(17), C(18):
C(13) 0.03, C(14) -0.09, C(15) 0.06
C(16) -0.00, C(17) -0.07, C(18) 0.06

ii) Ir, C(9), C(10), C(11), C(12):
Ir 0.01, C(9) 0.03, C(10) -0.06
C(11) 0.05, C(12) -0.02

iii) Ir, Ir', Cl, Cl':
C(1) -0.35, C(2) 0.50, C(8) 0.09
C(4) 2.18, C(5) 2.32, C(11) -2.09

iv) C(1), C(2), C(8):
C(3) -0.65, C(7) -0.88

v) C(3), C(4), C(5), C(6):
C(3) 0.00, C(4) -0.00, C(5) 0.00
C(6) -0.00

Dihedral angle between planes iii) and iv) is 63.6°

group is unsymmetrically co-ordinated, with C(8) having the greater σ-component. Unfortunately, the two bond lengths C(1) - C(2) and C(1) - C(8), though of low accuracy, do not correlate with this conclusion.

The extreme anisotropic thermal parameters obtained for the fluorine atoms (Table 1 and Fig. 1), frequently observed in compounds containing CF_3 groups, suggest large librational motion or disorder about their respective C-C bonds.

The geometry of the hexadeuterobenzene molecule is poorly determined. The large temperature factors of its carbon atoms suggest considerable libration but it is also possible that the crystal 'decomposition' (*vide supra*) is due to loss of this solvent of crystallisation with a resulting lack of definition. The molecular packing is illustrated in Fig. 3. There are no exceptionally short intermolecular contacts.

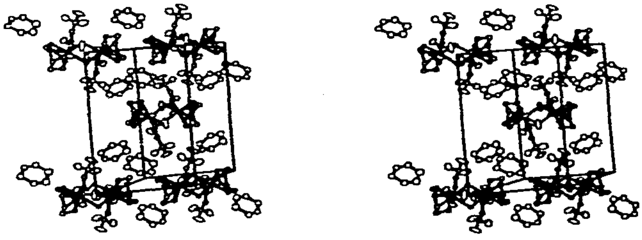


FIGURE 3 ORTEP stereo drawing of the unit cell contents viewed approximately along [100].

Acknowledgements

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