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Crystal and Molecular Structure of Di-μ-iodo-diiodobis(η^5-ethyltetramethylcyclopentadienyl)dirhodium(III)

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The crystal structure of di-μ-iodo-diiodobis(η^5-ethyltetramethylcyclopentadienyl)dirhodium(III) has been determined from single-crystal X-ray diffraction data collected on a two-circle diffractometer. The analysis was carried out on 1221 reflections and refined by full-matrix least-squares calculations to a final R of 0.051. The crystals are monoclinic, space group $P2_1/c$ with a = *9.237(5),* b = *9.331(5),* c = *16.654(7) Å, β = 102.78(5)° and Z = 2. The complex consists of centrosymmetric iodine-bridged dimers containing a planar Rh(μ-I)$_2$Rh bridge in which Rh···Rh = 4.033(2) Å, Rh–bridge = 2.711, 2.727(2) Å Rh–I_{bridge}–Rh = 95.8(1)°, and I_{bridge}–Rh–I_{bridge} = 84.2(1)°. The Rh–$I_{terminal}$ distance is 2.695(2) Å and the five-membered carbocyclic ring is located at a distance of 1.794(1) Å from the rhodium atom.*

Introduction

The structures of the compounds $[M(\eta^5\text{-}C_5Me_5)X]_2(\mu\text{-}X)_2$ (M = Rh; X = Cl, Br *not* I; M = Ir; X = Cl, Br, I) have all been determined by Churchill and co-workers [1–3]**. This systematic study provides a valuable insight into changes in the geometry of the molecules brought about by a progressive change in the nature of the halide ligands. An additional incentive to trying to understand such effects is that all these halide complexes are active homogeneous hydrogenation catalysts and their catalytic activity is markedly dependent upon the nature of the halide ligand [4].

By serindipity we have prepared and determined the structure of an analogue of the missing member of the above series. We now report the crystal structure of $[Rh(\eta^5\text{-}C_5Me_4Et)I]_2(\mu\text{-}I)_2$ which extends the above investigation into changes brought about by the halide ligands.

The crystal used in the X-ray study was isolated in the course of an investigation into reactions of $[Rh(\eta\text{-}C_5Me_4Et)(\eta\text{-}C_6H_6)](PF_6)_2$ with nucleophiles [5]. Treatment of this rhodium-benzene complex with an ethereal solution of methyl-lithium gave a low yield of the compound $[Rh(\eta\text{-}C_5Me_4Et)I_2]_2$ which, because of the unexpected nature of the product, was not identified by spectroscopic methods and was therefore characterized by X-ray crystallography. The methyl-lithium reagent had been prepared by reaction of lithium with methyl iodide and it has been reported that one of the difficulties with this preparation is to avoid the presence of iodide in the product [6]. It seems probable that the isolated product results from the reaction of $[Rh(C_5Me_4Et)(C_6H_6)](PF_6)_2$ with iodide especially since we have observed that anions such as cyanide, borohydride and methoxide also displace the benzene ring [5]. The more conventional synthesis, outlined below, the metathesis reaction of NaI with $[Rh(C_5Me_4Et)Cl_2]_2$, gave the product $[Rh(C_5Me_4Et)I_2]_2$ in 83% yield.

Experimental

Synthesis of Di-μ-iodobis(η^5-ethyltetramethylcyclopentadienyl)di-iododirhodium(III)

A suspension of $[Rh(C_5Me_4Et)Cl_2]_2$, [7], (0.40 g, 0.62 mmol) and NaI (1 g, 6.67 mmol) in acetone (30 cm^3) was stirred for 30 min and then filtered to remove excess NaI. The filtrate was reduced to dryness *in vacuo* and washed first with cold water (5 cm^3) to remove any remaining sodium iodide and then with ether (10 cm^3). Recrystallisation of the residue from chloroform ether gave dark red crystals of $[Rh(C_5Me_4Et)I_2]_2$ (0.526 g, 83% yield) [Found: C, 26.9; H, 3.3; I, 49.6. $C_{22}H_{34}I_4Rh_2$ requires C, 26.1; H, 3.4; I, 50.2%. ^{1}H n.m.r. ($CDCl_3$): δ 1.00 (3H; t, J = 8 Hz), 1.98 (6H, s), 1.99 (6H, s)

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**Note added in proof. The structure of $[Rh(\eta^5\text{-}C_5Me_5)I]_2(\mu\text{-}I)_2\cdot 2C_6H_5Me$ has recently been reported; M. R. Churchill and S. A. Julis, *Inorg. Chem., 18,* 2918 (1979).

TABLE I. Final Atomic Parameters. Estimated Standard Deviations are given in Parentheses.

(a) Fractional Co-ordinates (×10⁴)

	x	y	z
Rh	6727(1)	508(1)	928(1)
I1	3754(1)	135(1)	707(1)
I2	7168(2)	−2262(1)	1375(1)
C1	8613(15)	1869(17)	957(10)
C2	8802(18)	1159(17)	1704(10)
C3	7638(19)	1548(18)	2086(9)
C4	6735(17)	2554(18)	1564(10)
C5	7301(17)	2754(17)	832(11)
C11	9664(19)	1919(21)	377(13)
C12	10790(21)	3170(22)	626(14)
C21	10112(20)	231(24)	2061(13)
C31	7434(24)	1153(23)	2916(10)
C41	5434(21)	3366(23)	1734(13)
C51	6736(20)	3747(19)	120(12)
H211	9880(50)	−426(50)	2414(49)
H212	10716(50)	484(50)	2374(49)
H213	10620(50)	−387(50)	1708(49)
H311	8057(50)	47(50)	3069(48)
H312	6482(50)	1149(50)	3054(48)
H313	8122(50)	1250(50)	3219(49)
H411	4927(50)	3560(50)	1236(48)
H412	4760(50)	2972(50)	1879(49)
H413	5665(50)	4189(50)	1925(49)
H511	5546(50)	3820(50)	60(48)
H512	6783(50)	4663(50)	284(49)
H513	7160(50)	3398(50)	−403(49)
H111	10259	917	410
H112	9035	2087	−244
H121	11537	3203	211
H122	11418	3002	1248
H123	10194	4172	594

(b) Anisotropic Thermal Parameters (×10⁴) of the Form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	390(8)	371(8)	378(8)	−4(6)	77(6)	−24(6)
I1	421(7)	669(9)	435(9)	−36(6)	149(5)	−117(6)
I2	789(10)	420(8)	782(10)	26(7)	−40(7)	62(7)
C1	207(42)	484(46)	550(45)	−78(42)	83(41)	−163(44)
C2	530(46)	449(46)	400(45)	−75(44)	−222(44)	−48(44)
C3	746(47)	502(46)	338(44)	−288(46)	41(44)	−150(44)
C4	467(45)	606(47)	531(45)	−233(44)	162(43)	−327(44)
C5	441(45)	402(45)	625(46)	−88(44)	149(43)	−105(44)
C11	562(45)	747(48)	1161(48)	−65(46)	559(44)	−90(47)
C12	791(47)	742(48)	1265(49)	−201(47)	533(46)	−144(48)
C21	500(46)	987(49)	1010(49)	20(47)	−322(47)	183(48)
C31	1390(49)	1001(49)	268(45)	−197(49)	237(46)	−136(46)
C41	792(47)	956(49)	1156(48)	137(47)	661(45)	−317(47)
C51	821(47)	403(47)	985(48)	185(46)	338(46)	146(46)

and 2.43 (2H, q). $^{13}C\{^1H\}$ ($CDCl_3$, J $^{103}Rh-^{13}C$ in parentheses): C_5*Me*$_4$Et, δ 11.0, 11.2; C_5Me_4*Et*, 13.3, 19.4; *C*$_5$Me$_4$Et, 95.6(9), 96.7(9), 99.9(8)].

Crystal Data

$Rh_2C_{22}H_{34}I_4$, M_r = 1011.95. Monoclinic, $P2_1/c$, a = 9.237(5), b = 9.331(5), c = 16.654(7) Å, β =

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code

none	x, y, z
(′)	$1.0 - x, -y, -z$

Bond lengths

Rh–I1	2.711(2)	C3–C31	1.481(23)
Rh–I1′	2.727(2)	C3–C4	1.419(23)
Rh–I2	2.695(2)	C4–C41	1.500(23)
Rh–C1	2.148(14)	C4–C5	1.441(22)
Rh–C2	2.149(14)	C5–C51	1.504(24)
Rh–C3	2.157(15)	C21–H211	0.91(7)
Rh–C4	2.182(15)	C21–H212	0.72(6)
Rh–C5	2.177(16)	C21–H213	1.01(7)
C1–C11	1.513(22)	C31–H311	1.18(5)
C1–C2	1.387(21)	C31–H312	0.96(6)
C1–C5	1.443(21)	C31–H313	0.73(6)
C11–C12	1.557(25)	C41–H411	0.88(7)
C2–C21	1.500(23)	C41–H412	0.80(6)
C2–C3	1.413(23)	C41–H413	0.84(5)
		C51–H511	1.08(5)
Rh•••Rh′	4.033(2)	C51–H512	0.90(5)
		C51–H513	1.08(8)

Bond Angles (°)

I1–Rh–I1′	84.2(1)	C3–C2–C21	126.7(17)
I1–Rh–I2	90.1(1)	C2–C3–C4	107.2(14)
I1′–Rh–I2′	92.6(1)	C2–C3–C31	128.5(17)
Rh–I1–Rh′	95.8(1)	C4–C3–C31	123.9(17)
C2–C1–C5	109.7(14)	C3–C4–C5	109.3(14)
C2–C1–C11	128.0(15)	C3–C4–C41	127.2(17)
C5–C1–C11	121.9(15)	C5–C4–C41	123.4(17)
C1–C11–C12	109.8(15)	C1–C5–C4	104.7(15)
C1–C2–C3	108.9(14)	C1–C5–C51	126.8(15)
C1–C2–C21	124.2(17)	C4–C5–C51	128.3(15)

102.78(5)°, $U = 1399.8$ Å^3, D_m (by flotation) = 2.38, $D_c = 2.40$ g cm^{-3}. $Z = 2$ (dimers), Mo-K$_\alpha$, $\lambda = 0.7107$ Å, μ(Mo-K$_\alpha$) = 51.14 cm^{-1}, $F(000) = 936$.

Intensity Measurements

A crystal of dimensions 0.10 × 0.15 × 0.30 mm was mounted with the *c*-axis coincident with the rotation (ω) axis of a Stöe Stadi 2 two-circle diffractometer. Using monochromated Mo-K$_\alpha$ radiation and the background–ω scan–background technique, 1818 unique reflections were measured, of which 1221 had $I > 2\sigma(I)$ and were considered to be observed. [The net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where c = scan time, t = time for background measurements at each end of the scan]. Corrections for Lorentz and polarisation effects were made.

Structure Determination and Refinement

The unique rhodium and iodine atoms (I1, I2) were determined from the three-dimensional Patterson function and the remaining atoms were located from successive difference electron-density maps. The ethyl hydrogen atoms (H111, H112; H121 - H123) were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å); the positions of the remaining methyl hydrogens were refined. Common isotropic temperature factors were applied to H111, H112 and to methyl hydrogens and refined to final values of $U = 0.129(5)$ and 0.167(5) Å^2 respectively. Scattering factors were calculated [8] using an analytical approximation and the weighting scheme adopted was $w = 1.3953/[\sigma^2(F_o) + 0.0008\ (F_o)^2]$. Full matrix refinement with anisotropic temperature factors for all non-hydrogen atoms gave the final $R = 0.051$ and $R'_w = 0.048$. The final difference Fourier map showed no peaks greater than 1.00 e Å^{-3}. Final atomic parameters are listed In Table I, bond distances and angles in Table II. A list of observed and calculated structure factors is available from the Editor.

Calculations

All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer at the SRC Computing Centre, Daresbury, U.K., using the SHELX computing package [9].

Results and Discussion

The complex consists of centrosymmetric halogen-bridged dimers in which the Rh–I$_{\text{bridge}}$ distances are 2.711 and 2.727(2) Å, (Fig. 1). Although the latter values differ significantly, the differences are in sharp contrast to the asymmetric bridging distances found in the ion, $[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$, (Rh–I$_{\text{bridge}}$, 2.679, 3.001(2) Å; [10]). The large difference found in the anion could be ascribed to the *trans* influence of the acetyl group, as has been suggested for the asymmetric Rh–Cl$_{\text{bridge}}$ distances found in $[RhCl_2(C_8H_{15}O_2)(CH_3C_5H_4N)_2]_2$, [11]. As expected, the Rh–I$_{\text{terminal}}$ bond length in the present complex is shorter than either of the bridging distances. The Rh–I2 value of 2.695(2) Å may be compared to the Rh–I$_{\text{terminal}}$ bonds in $[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$, (2.652, 2.699(2) Å), and lies within the range found for most Rh$^{\text{III}}$–I bonds [12–16]. The Rh–I2 distance is, however, considerably shorter than that in $Rh^{III}I(CH_3)(C_{13}H_{22}N_4O_2BF_2)$ (2.813 Å, [17]), where the iodine atom is *trans* to an alkyl group. Selected intramolecular parameters of the three complexes $[\{Rh(C_5Me_4R)X\}_2X_2]$ [R = Me, X = Cl (I) or X = Br (II); R = Et, X = I (III)] are compared in Table III and while variation in many of the bond distances and angles can be correlated with

TABLE III. Comparison of Selected Intramolecular Parameters of $[Rh(\eta^5\text{-}C_5Me_4Et)I]_2(\mu\text{-}I)_2$, (III), and $[Rh(\eta^5\text{-}C_5Me_5)X]_2(\mu\text{-}X)_2$, (X = Cl, (I); Br, (II); [1, 2]).

	(I) $[RhCl]_2(\mu\text{-}Cl)_2$	(II)[a] $[RhBr]_2(\mu\text{-}Br)_2$		(III) $[RhI]_2(\mu\text{-}I)_2$
		Molecule 1	*Molecule 2*	
Rh···Rh	3.7191(6)	3.854(1)	3.841(1)	4.033(2)
$Rh\text{–}X_{terminal}$	2.3967(11)	2.523(1)	2.532(1)	2.695(2)
$Rh\text{–}X_{bridge}$	2.4522(10)	2.577(1)	2.566(1)	2.711(2)
	2.4649(11)	2.587(1)	2.575(1)	2.727(2)
Rh–C(ring)[b]	2.128	2.147	2.144	2.163
Rh···C(Me)[b]	3.252	3.280	3.279	3.301
Rh–Cp[c]	1.7558(3)	1.769(1)	1.769(1)	1.794(1)
$X_{bridge}\text{–}Rh\text{–}X'_{bridge}$	81.71(3)	83.46(3)	83.30(3)	84.2(1)
$X_{bridge}\text{–}Rh\text{–}X_{terminal}$	92.30(4)	90.75(3)	90.26(3)	90.1(1)
	90.73(4)	91.30(3)	92.32(3)	92.6(1)
$Rh\text{–}X_{bridge}\text{–}Rh'$	98.29(3)	96.54(3)	96.70(3)	95.8(1)

[a] Two independent dimer molecules in the asymmetric unit. [b] Average value. [c] Perpendicular distance from the rhodium atom to the five-membered carbocyclic ring.

TABLE IV. Equations of Least-Squares Planes Referred to the Orthogonal Axis System *a*, *b*, c^* with Distances (A) of Relevant Atoms from the Planes in Square Brackets.

Plane A: C1–C5

$-0.4703\,X -0.7574\,Y -0.4530\,Z +5.5965 = 0.0000$ [Cl, –0.004(16); C2, –0.004(16); C3, 0.011(17); C4, –0.014(17); C5, 0.011(16); C11, –0.170(20); C12, –1.683(21). C21, –0.118(21); C31, –0.088(21); C41, –0.118(21); C51, –0.045(18); Rh, 1.794(1)]

Plane B: Rh, I1, I1′, Rh′

$-0.0964\,X +0.9696\,Y -0.2248\,Z +0.4450 = 0.0000$ [Rh, 0.000; I1, 0.000; I1′, 0.000; Rh′, 0.000; I2, –2.693(1)]

Plane C: C1, C11, C12

$-0.5040\,X +0.6184\,Y -0.6030\,Z +3.6907 = 0.0000$ [C1, 0.000; C11, 0.000; C12, 0.000; C2, –1.091(16); C3, –0.628(16); C4, 0.788(16); C5, 1.221(17); Rh, 0.116(1)].

Angles Between Planes (°)

A/B	126.0
A/C	87.6
B/C	38.4

differences in the covalent radii of the halogen atoms, there are a number of further differences worthy of note. Thus the difference in length between the $Rh\text{–}X_{terminal}$ bond and the average $Rh\text{–}X_{bridge}$ distance is dependent upon the size of the halogen and decreases with increasing size of X. A similar trend is found in the related iridium complexes $[Ir(\eta^5\text{-}C_5Me_5)X]_2(\mu\text{-}X)_2$, (X = Cl, Br, I), and has been attributed [3] to the greater polarisability and decreased electronegativity of the larger covalently linked halide ligands.

The arrangement of the iodine atoms about rhodium is such that the coordination geometry about the metal is best described as a 'three-legged piano stool' in which the I–Rh–I angles lie close to 90° (84.2, 90.1, 92.6(1)°; average 89.0°). As found in (I) and (II), it is the angle about rhodium involving both bridging halogens which shows the greatest distortion from 90°. The progression in the value for this $X_{bridge}\text{–}Rh\text{–}X_{bridge}$ angle [X = Cl, 81.71(3); X = Br, 83.46, 83.30(3); X = I, 84.2(1)] appears to reflect the relative size of the halogen atoms.

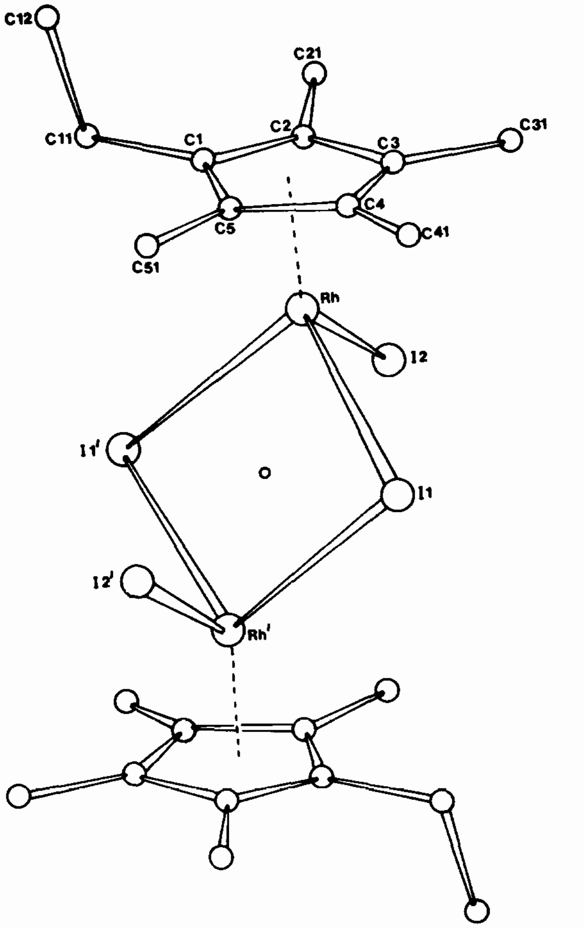

Fig. 1. Molecular structure and atom numbering scheme for $[Rh(\eta^5\text{-}C_5Me_4Et)I]_2(\mu\text{-}I)_2$. Hydrogen atoms have been omitted for clarity.

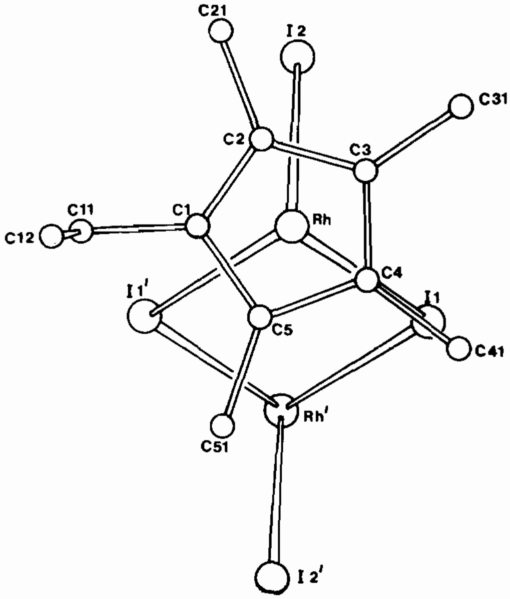

Fig. 2. Projection of portion of $[Rh(\eta^5\text{-}C_5Me_4Et)I]_2(\mu\text{-}I)_2$ onto the cyclopentadienyl ring.

Since the $Rh(\mu\text{-}X)_2Rh$ bridging system is required by crystallographic symmetry to be planar for all three complexes, the accompanying $Rh\text{–}X_{bridge}\text{–}Rh$ angles increase successively from 95.8(1)° [X = I], to 96.54, 96.70(3)° [X = Br] and 98.29(3)° [X = Cl]. The five-membered carbocyclic ring is effectively planar (maximum deviation –0.014 Å, C4) with the substituent carbons displaced significantly out of the best least-square plane and away from the rhodium atom (Table IV). The orientation of the ethyl group is such as to minimise intramolecular interactions, with the resultant dihedral angle between the C1, C11, C12 plane and the C1–C5 mean plane being 87.6°. The rhodium atom lies at a distance of 1.794(1) Å out of the C1–C5 mean plane and it is interesting to note that this is significantly larger than that found for (I), 1.756 Å, and (II), 1.769 Å. The rhodium–carbon linkages range from 2.148(14) to 2.182(15) Å and the average value of 2.163 Å is again greater than that found for the chloride and bromide complexes. The relative values for the three complexes (I–III) of both the Rh–C(ring) and the perpendicular Rh–ring distances indicate that the strength of bonding from the carbocyclic ring to rhodium increases from (III) to (I). Thus the highly electronegative chloride appears to be the most effective of the three halide ligands at removing charge from the metal, thereby facilitating a stronger peralkylcyclopentadienyl–Rh interaction.

The geometry within the carboxylic ring is as expected with the average C–C distance of 1.421 Å lying close to the accepted C–C (π-cyclopentadienyl) distance of approximately 1.43 Å [18] and the average of the internal C–C–C angles (108.0°) being equal to that expected for a planar pentagonal figure. Projection of the $Rh(\mu\text{-}I)_2Rh'$ bridging unit onto one of the carbocyclic rings is shown in Fig. 2; the dihedral angle between the cyclopentadienyl plane and the Rh_2I_2 bridge is 126.0°.

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