

Di- μ -iodo-bis[dicarbonylrhodium(I)]Sylvain Burger, Bruno Therrien
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Key indicators

Single-crystal X-ray study

T = 153 K

Mean $\sigma(\text{O}-\text{C}) = 0.013 \text{ \AA}$

R factor = 0.053

wR factor = 0.141

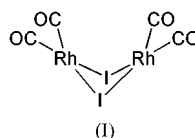
Data-to-parameter ratio = 18.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title dinuclear Rh complex, $[\text{Rh}_2\text{I}_2(\text{CO})_4]$, adopts a V-shape conformation with an intramolecular Rh...Rh distance of 3.385 (1) Å. The molecules are connected in a zigzag fashion, with intermolecular Rh...Rh distances of 3.637 (2) Å.

Comment

$[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ is used in catalysis for the carbonylation of methanol to give acetic acid (Paulik & Roth, 1968; Forster, 1976; Krzywicki & Marczewski, 1979; Thomas *et al.*, 2002). It is one of the most important homogeneously catalysed industrial processes (Weissermel & Arpe, 1997). The catalytic reaction requires the use of iodide promoters (Parshall & Ittel, 1992), which convert methanol, prior to carbonylation, into the actual methyl iodide substrate. For this reason, the iodide analogue $[\text{Rh}_2\text{I}_2(\text{CO})_4]$, (I), has been synthesized, with the hope of improving the catalytic activity for the carbonylation of methanol. The complex had already been observed in the reaction of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ with KI under 1 atmosphere of CO pressure, but not structurally characterized (Fulford *et al.*, 1990). We report here a modified synthesis and the single-crystal X-ray structure analysis of $[\text{Rh}_2\text{I}_2(\text{CO})_4]$, the iodine analogue of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$.



Di- μ -chloro-bis[dicarbonylrhodium(I)] was structurally characterized for the first time by Dahl *et al.* (1961), then more recently by Walz & Scheer (1991). The molecular structure of di- μ -iodo-bis[dicarbonylrhodium(I)] is very similar, but the presence of bridging iodines instead of chlorines gives a less hindered complex. As for $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$, the Rh^I atoms in (I) are both in a square-planar geometry, surrounded by two carbonyl groups and two bridging halogen ligands. The dinuclear complex adopts a V-shape conformation (Fig. 1), with an intramolecular Rh...Rh distance of 3.385 (1) Å. The molecules are linked by metal-metal contacts, the intermolecular Rh...Rh distances being 3.637 (2) Å. These two Rh...Rh distances are longer than those observed for $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$, where the values are 3.138 (1) (intramolecular) and 3.324 (1) Å (intermolecular). The same zigzag arrangement of molecules is observed in the solid state (Fig. 2). The two $\text{RhI}_2(\text{CO})_2$ moieties are planar, with a mean deviation of the fitted atoms of 0.0547 Å for Rh1 and 0.0394 Å for Rh2. The angle between the two planes is 59.1 (1)°.

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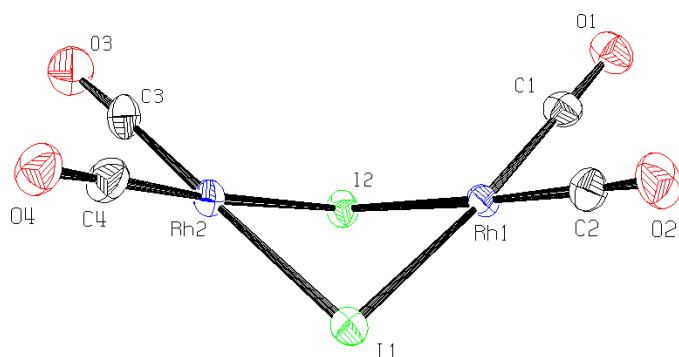


Figure 1
The molecular structure of $[\text{Rh}_2\text{I}_2(\text{CO})_4]_2$. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Di- μ -iodo-bis[dicarbonylrhodium(I)] was prepared according to a previously described method (Powell & Shaw, 1968). Under 5 bar of carbon monoxide, a methanol solution (20 ml) of rhodium triiodide hydrate (500 mg) was refluxed (363 K) until the black solution turned red (48 h). After cooling to room temperature, the solution was evaporated to dryness. The dark red residue was washed with hexane and filtered. ^{13}C NMR (CD_3CN): 203.21 p.p.m. IR (KBr, cm^{-1}): 2078 (s), 2074 (s), 2040 (s), 2028 (s), 1390 (w), 578 (m). Red crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a methanol solution.

Crystal data

$[\text{Rh}_2\text{I}_2(\text{CO})_4]_2$	$D_x = 3.742 \text{ Mg m}^{-3}$
$M_r = 571.66$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6307 reflections
$a = 9.4160 (13) \text{ \AA}$	$\theta = 2.2\text{--}25.9^\circ$
$b = 9.589 (1) \text{ \AA}$	$\mu = 9.31 \text{ mm}^{-1}$
$c = 11.3024 (16) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 96.091 (17)^\circ$	Block, red
$V = 1014.7 (2) \text{ \AA}^3$	$0.7 \times 0.3 \times 0.3 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS diffractometer	1774 reflections with $I > 2\sigma(I)$
φ oscillation scans	$R_{\text{int}} = 0.089$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 26.1^\circ$
$T_{\text{min}} = 0.127$, $T_{\text{max}} = 0.458$	$h = -11 \rightarrow 11$
6101 measured reflections	$k = -11 \rightarrow 11$
1980 independent reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0974P)^2 + 2.9244P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 3.71 \text{ e \AA}^{-3}$
1980 reflections	$\Delta\rho_{\text{min}} = -2.67 \text{ e \AA}^{-3}$
110 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.0052 (6)

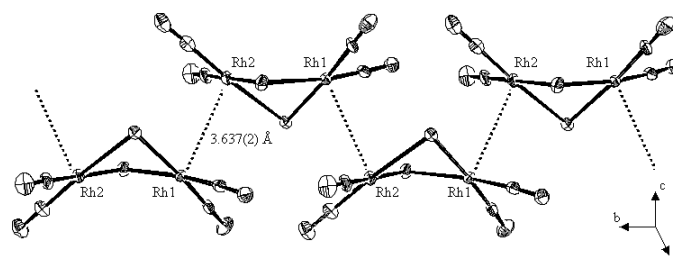


Figure 2
The zigzag arrangement of $[\text{Rh}_2\text{I}_2(\text{CO})_4]$ molecules along the b axis.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Rh1—I2	2.6554 (9)	Rh2—I1	2.6617 (9)
Rh1—I1	2.6661 (9)	Rh2—I2	2.6712 (10)
C2—Rh1—C1	90.2 (4)	I1—Rh2—I2	89.01 (3)
I2—Rh1—I1	89.25 (3)	Rh2—I1—Rh1	78.82 (3)
C4—Rh2—C3	90.1 (4)	Rh1—I2—Rh2	78.84 (3)

All residual electron densities greater than 1 e \AA^{-3} are observed around the I and Rh atoms, at distances ranging from 0.92 to 1.90 \AA .

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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