

Two polymorphs of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$

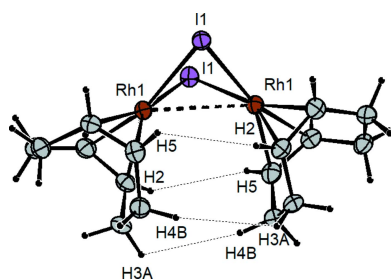
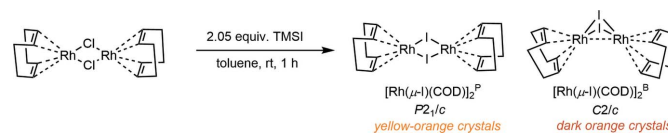
David R. Ullery, Curtis E. Moore and Christine M. Thomas*

100 W. 18th Ave., Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA. *Correspondence e-mail: thomas.3877@osu.edu

The solid-state structure of di- μ -iodido-bis[[1,2,5,6- η]-cycloocta-1,4-diene]rhodium(I), $[\text{Rh}_2\text{I}_2(\text{C}_8\text{H}_{12})_2]$ or $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$, was determined from two crystals with different morphologies, which were found to correspond to two polymorphs containing Rh dimers with significantly different molecular structures. Both polymorphs are monoclinic and the $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ molecules in each case possess C_{2v} symmetry. However, the core geometry of the butterfly-shaped Rh_2I_2 core differs substantially. In the $C2/c$ polymorph, the core geometry of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ is bent, with a hinge angle of $96.13(8)^\circ$ and a $\text{Rh}\cdots\text{Rh}$ distance of $2.9612(11)\text{ \AA}$. The $P2_1/c$ polymorph features a more planar $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ core geometry, with a hinge angle of $145.69(9)^\circ$ and a $\text{Rh}\cdots\text{Rh}$ distance of $3.7646(5)\text{ \AA}$.

1. Chemical context

Compounds of the type $[\text{M}(\mu\text{-X})(\text{COD})]_2$ ($M = \text{Ir}, \text{Rh}, X = \text{Cl}, \text{Br}, \text{I}$) are ubiquitous synthons for Rh and Ir catalysts. As a representative example, $[\text{Rh}(\text{COD})(\text{DPEphos})]\text{BF}_4$ catalyzes the hydroamination of vinylarenes with anti-Markovnikov selectivity, and is prepared *via* the reaction of $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ with two equivalents of AgBF_4 and two equivalents of DPEphos (Utsunomiya *et al.*, 2003). Within the series $[\text{M}(\mu\text{-X})(\text{COD})]_2$ ($M = \text{Ir}, \text{Rh}; X = \text{Cl}, \text{Br}, \text{I}$), all compounds have been structurally characterized with the notable exception of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ (De Ridder & Imhoff, 1994; Pettinari *et al.*, 2002; Cotton *et al.*, 1986; Yamagata *et al.*, 2007*a,b*). Thus, crystallographic characterization of the title compound was pursued to complete the series.



2. Structural commentary

Crystallization of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ in toluene at 236 K produced two types of crystals with different colors and morphologies, namely dark-orange and yellow-orange blocks. A representative crystal of each type was subjected to single crystal X-ray diffraction, revealing two different polymorphs of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ containing dimers with significantly different structural features. X-ray diffraction of the dark-orange crystals revealed that $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ crystallized in the monoclinic $C2/c$ space group in this polymorph. The molecular structure of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ exhibited a C_{2v} -symmetric geometry featuring a bent Rh_2I_2 diamond core (Fig. 1). The hinge angle, defined as the angle between the

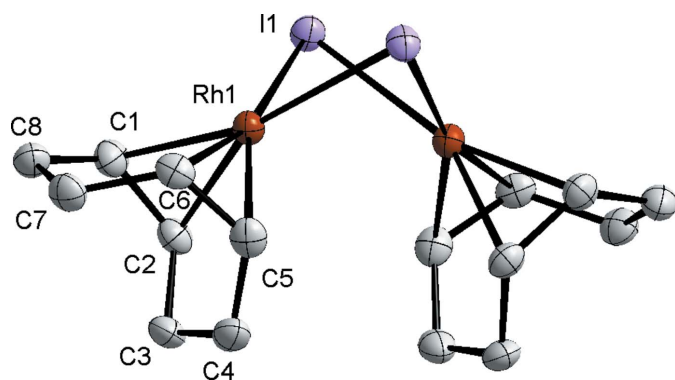


Figure 1
Bent structure of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ within the monoclinic $C2/c$ polymorph. Independent atoms are labelled, while the other half of the molecule is symmetry-generated through a twofold rotation axis. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are removed for clarity.

intersecting planes that contain the iodide ligands and each rhodium, is $96.13(8)^\circ$ and the $\text{Rh}\cdots\text{Rh}$ distance is $2.9612(11)\text{ \AA}$. $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ exhibits a geometry significantly different from that of $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-Br})(\text{COD})]_2$, which both exhibit more planar Rh_2X_2 cores with hinge angles of $169.08(6)$ and $148.74(7)^\circ$ and $\text{Rh}\cdots\text{Rh}$ distances of $3.5169(6)$ and $3.5648(14)\text{ \AA}$, respectively (De Ridder & Imhoff, 1994; Pettinari *et al.*, 2002). However, the hinge angle of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ is similar to that of $[\text{Ir}(\mu\text{-I})(\text{COD})]_2$ [$95.26(1)^\circ$; Yamagata *et al.*, 2007b].

X-ray diffraction of the yellow–orange crystals revealed a different polymorph of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$, this time crystallizing in the monoclinic $P2_1/c$ space group. The geometry of the dirhodium dimer in the $P2_1/c$ polymorph $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ differs significantly from the $C2/c$ polymorph $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$. The Rh_2I_2 core geometry of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ is more planar, with a hinge angle of $145.69(9)^\circ$ and a $\text{Rh}\cdots\text{Rh}$ distance of $3.7646(5)\text{ \AA}$ (Fig. 2). The molecular structure of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ is therefore similar to $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-Br})(\text{COD})]_2$ (De Ridder & Imhoff, 1994; Pettinari *et al.*, 2002).

A previous theoretical study found relatively small energetic differences ($< 10\text{ kcal mol}^{-1}$) between planar and bent $[\text{Rh}(\mu\text{-X})(\text{L})]_2$ geometries (Aullón *et al.*, 1998). By analyzing

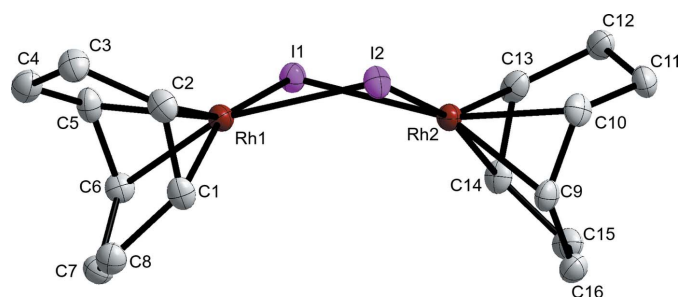


Figure 2
Planar structure of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ within the monoclinic $P2_1/c$ polymorph. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are removed for clarity.

the donor–acceptor interactions between d_z^2 and p_z orbitals of the two metal atoms, it was determined that the stability of bent morphologies increases as the electronegativity of the bridging ligand decreases. The degree of bending was predicted to increase in the order $\text{Cl} < \text{Br} < \text{I}$, consistent with the observation of a bent structure for $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ but not $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-Br})(\text{COD})]_2$ (Aullón *et al.*, 1998). Moreover, Aullón and coworkers predicted the bent form to be more stable for Ir than for Rh, in line with the exclusive observation of a bent geometry for $[\text{Ir}(\mu\text{-I})(\text{COD})]_2$, but the possibility of both planar and bent forms for $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$.

There is no meaningful difference between the two independent $\text{Rh}\text{—I}$ distances in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ [$2.7072(7)$ and $2.6975(7)\text{ \AA}$]. The four $\text{Rh}\text{—I}$ distances in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ are slightly less symmetric: the bonds between I2 and the two Rh centers [$2.6833(4)$ and $2.6738(4)\text{ \AA}$] are slightly shorter than those associated with I1 [$2.6998(4)$ and $2.7061(4)\text{ \AA}$]. Similarly, the $\text{Rh}\text{—C}$ distances in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ are more symmetric, ranging from $2.115(6)$ to $2.122(6)\text{ \AA}$, while the $\text{Rh}\text{—C}$ distances in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ range from $2.117(4)$ to $2.131(4)\text{ \AA}$. The average $\text{Rh}\text{—C}$ distance in the bent and planar structures are similar to the average $\text{Rh}\text{—C}$ distances reported for the $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-Br})(\text{COD})]_2$ analogues (De Ridder & Imhoff, 1994; Pettinari *et al.*, 2002), with all four compounds having an average $\text{Rh}\text{—C}$ distance of 2.12 \AA . As expected based on the inherent differences in covalent radii, the average $\text{Rh}\text{—I}$ distances in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ and $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ (2.70 and 2.69 \AA , respectively) are considerably longer than the average $\text{Rh}\text{—Br}$ and $\text{Rh}\text{—Cl}$ distances in $[\text{Rh}(\mu\text{-Br})(\text{COD})]_2$ and $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ (2.54 and 2.38 \AA , respectively).

3. Supramolecular features

The structural differences between the dimers in the two polymorphs of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ are attributed to differences

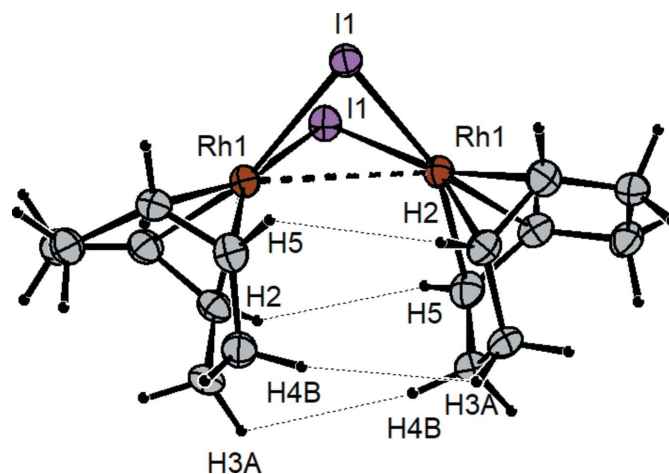


Figure 3
Diagram of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ showing weak intramolecular $\text{C}\text{—H}\cdots\text{H}\text{—C}$ dispersion interactions between the two COD molecules on the two Rh centers.

Table 1
Experimental details.

	$[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$	$[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$
Crystal data		
Chemical formula	$[\text{Rh}_2\text{I}_2(\text{C}_8\text{H}_{12})_2]$	$[\text{Rh}_2\text{I}_2(\text{C}_8\text{H}_{12})_2]$
M_r	675.97	675.97
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	12.3414 (16), 11.8176 (17), 11.9374 (15)	10.4505 (5), 19.390 (1), 8.6271 (4)
β (°)	96.690 (3)	101.523 (2)
V (Å ³)	1729.2 (4)	1712.92 (14)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	5.47	5.52
Crystal size (mm)	0.10 × 0.06 × 0.03	0.15 × 0.14 × 0.09
Data collection		
Diffractometer	Nonius Kappa APEXII	Nonius Kappa APEXII
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
T_{min} , T_{max}	0.062, 0.093	0.057, 0.093
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15175, 1775, 1320	38760, 3519, 2922
R_{int}	0.080	0.051
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.079, 1.03	0.025, 0.055, 1.07
No. of reflections	1775	3519
No. of parameters	103	205
No. of restraints	4	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.36, -0.79	1.26, -0.67

Computer programs: APEX3 and SAINT (Bruker, 2017), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

in crystal packing and weak interatomic forces. The bent and planar geometries are likely similar in energy. Stabilization of the bent geometry in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{B}}$ arises from intramolecular dispersion forces between the C–H bonds of the cyclooctadiene ligands on the two Rh centers within each molecule. Indeed there are four close C–H...H–C contacts ($\text{H}2 \cdots \text{H}5 = 2.64 \text{ \AA}$; $\text{H}3\text{A} \cdots \text{H}4\text{B} = 2.66 \text{ \AA}$) between the alkene and methylene hydrogen atoms made possible by the bent geometry (Fig. 3). In the case of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$, no such intramolecular C–H...H–C interactions are present. The shortest intermolecular interactions in $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ are two $\text{Rh} \cdots \text{H} - \text{C}$ contacts in the apical positions of Rh2

($\text{Rh}2 \cdots \text{H}16\text{A}(1 - x, 1 - y, -z) = 2.67 \text{ \AA}$; $\text{Rh}2 \cdots \text{H}3\text{A}(2 - x, 1 - y, 1 - z) = 2.93 \text{ \AA}$) that could, at best, be labeled as weak intermolecular agostic interactions (Fig. 4). Consistent with the intermolecular interactions in the planar structure, the $P2_1/c$ has a higher density (2.621 g cm^{-3}) than the bent $C2/c$ polymorph (2.597 g cm^{-3}), indicative of tighter crystal packing.

4. Synthesis and crystallization

$[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ was prepared according to the procedure described by J. A. Hlina *et al.* (2017). Under a nitrogen

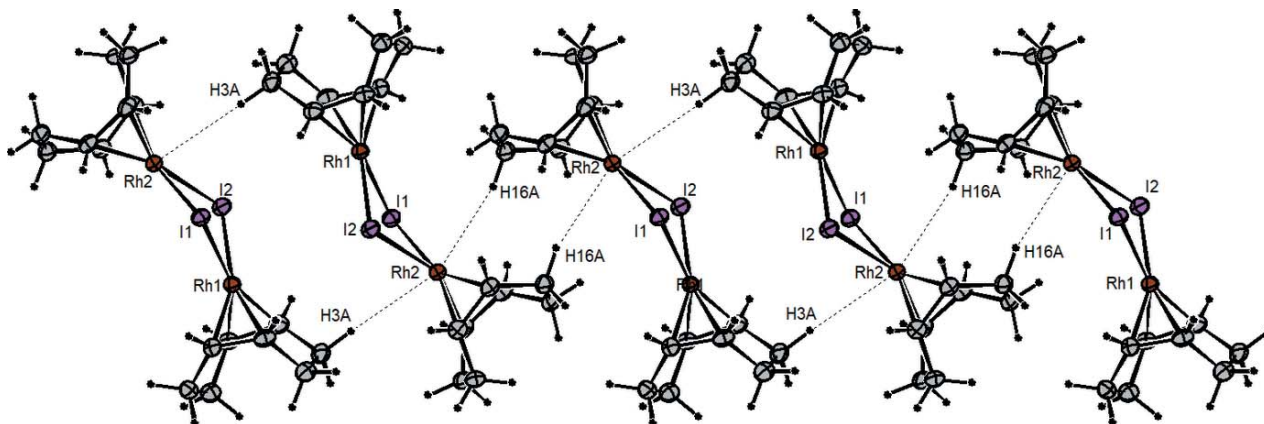


Figure 4
Diagram of $[\text{Rh}(\mu\text{-I})(\text{COD})]_2^{\text{P}}$ showing weak intermolecular C–H...Rh interactions between adjacent molecules.

atmosphere, $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ (312.0 mg, 0.6323 mmol) was added to toluene (5 mL) and trimethylsilyl iodide (184.6 μL , 1.297 mmol). The reaction mixture turned dark red and rust-colored crystals precipitated from the solution. The solid was isolated, washed with hexanes and dried *in vacuo* to yield the final product $[\text{Rh}(\mu\text{-I})(\text{COD})]_2$ as a red–brown crystalline solid (358.5 mg, 84%). X-ray quality crystals were grown from a concentrated solution of toluene at 236 K, resulting in crystals with two different morphologies. ^1H NMR (C_6D_6): 1.15–1.28 (*m*, 8H, $-\text{CHH}-$), 1.90–2.05 (*m*, 8H, $-\text{CHH}-$), 4.62–4.70 (*m*, 8H, $=\text{CH}$). A single species was observed by ^1H NMR spectroscopy and the ^1H NMR spectrum did not contain any broad features indicative of dynamic behavior or inter-conversion between the two isomers in solution.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Crystals were mounted on MiTeGen Micromounts with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100 (2) K using φ and ω scans. Solution by direct methods (*SHELXT*) produced a complete phasing model for refinement. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (*SHELXL2018*). All carbon-bonded methylene hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in *SHELXL2018*. All carbon-bonded methine hydrogen atoms were located in the difference map. Their C–H distances were restrained to a target value of 1.00 (2) Å. For all H atoms, displacement parameter $U_{\text{iso}}(\text{H})$ values were set to 1.2 times $U_{\text{eq}}(\text{C})$.

Acknowledgements

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References

- Aullón, G., Ujaque, G., Lledós, A., Alvarez, S. & Alemany, P. (1998). *Inorg. Chem.* **37**, 804–813.
- Bruker (2017). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cotton, F. A., Lahuerta, P., Sanau, M. & Schwotzer, W. (1986). *Inorg. Chim. Acta*, **120**, 153–157.
- De Ridder, D. J. A. & Imhoff, P. (1994). *Acta Cryst.* **C50**, 1569–1572.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Hlina, J. A., Wells, J. A. L., Pankhurst, J. R., Love, J. B. & Arnold, P. L. (2017). *Dalton Trans.* **46**, 5540–5545.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Pettinari, C. F., Marchetti, F., Cingolani, A., Bianchini, G., Drozdov, A., Vertlib, V. & Troyanov, S. (2002). *J. Organomet. Chem.* **651**, 5–14.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Utsunomiya, M., Kuwano, R., Kawatsura, M. & Hartwig, J. F. (2003). *J. Am. Chem. Soc.* **125**, 5608–5609.
- Yamagata, T., Nagata, M., Mashima, K. & Tani, K. (2007a). *Acta Cryst.* **E63**, m1498.
- Yamagata, T., Nagata, M., Mashima, K. & Tani, K. (2007b). *Acta Cryst.* **E63**, m2402.

supporting information

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Computing details

For both structures, data collection: *APEX3* (Bruker, 2017); cell refinement: *SAINTE* (Bruker, 2017); data reduction: *SAINTE* (Bruker, 2017); program(s) used to solve structure: *ShelXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Di- μ -iodido-bis{[(1,2,5,6- η)-cycloocta-1,4-diene]rhodium(I)} (B)

Crystal data

$[\text{Rh}_2\text{I}_2(\text{C}_8\text{H}_{12})_2]$
 $M_r = 675.97$
 Monoclinic, *C2/c*
 $a = 12.3414$ (16) Å
 $b = 11.8176$ (17) Å
 $c = 11.9374$ (15) Å
 $\beta = 96.690$ (3)°
 $V = 1729.2$ (4) Å³
 $Z = 4$

$F(000) = 1264$
 $D_x = 2.597$ Mg m⁻³
 Mo *K* α radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2574 reflections
 $\theta = 2.8\text{--}23.3^\circ$
 $\mu = 5.47$ mm⁻¹
 $T = 100$ K
 Block, dark orange
 0.10 × 0.06 × 0.03 mm

Data collection

Nonius Kappa APEXII
 diffractometer
 Radiation source: sealed tube, fine-focus
 Graphite monochromator
 Detector resolution: 7.9 pixels mm⁻¹
 ω and φ scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\text{min}} = 0.062$, $T_{\text{max}} = 0.093$

15175 measured reflections
 1775 independent reflections
 1320 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.080$
 $\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.4^\circ$
 $h = -15 \rightarrow 15$
 $k = -14 \rightarrow 14$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.079$
 $S = 1.03$
 1775 reflections
 103 parameters
 4 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.79$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.52770 (3)	0.20354 (3)	0.40381 (4)	0.02475 (15)
Rh1	0.38142 (4)	0.31608 (4)	0.25934 (4)	0.02137 (15)
C1	0.2885 (6)	0.3639 (6)	0.3898 (6)	0.0274 (16)
H1	0.309 (5)	0.316 (5)	0.458 (3)	0.033*
C2	0.3652 (5)	0.4497 (6)	0.3749 (5)	0.0255 (15)
H2	0.433 (3)	0.456 (5)	0.429 (4)	0.031*
C3	0.3323 (6)	0.5616 (5)	0.3199 (6)	0.0294 (16)
H3A	0.380935	0.621981	0.354264	0.035*
H3B	0.256778	0.580087	0.333793	0.035*
C4	0.3390 (6)	0.5579 (5)	0.1903 (6)	0.0312 (17)
H4A	0.282371	0.608659	0.152182	0.037*
H4B	0.410972	0.587248	0.175166	0.037*
C5	0.3237 (5)	0.4422 (6)	0.1410 (6)	0.0273 (16)
H5	0.357 (5)	0.418 (5)	0.074 (3)	0.033*
C6	0.2378 (5)	0.3707 (5)	0.1589 (5)	0.0229 (15)
H6	0.219 (5)	0.306 (3)	0.107 (4)	0.028*
C7	0.1447 (5)	0.4044 (6)	0.2257 (5)	0.0295 (16)
H7A	0.076675	0.366941	0.192462	0.035*
H7B	0.133403	0.487216	0.219759	0.035*
C8	0.1680 (5)	0.3714 (6)	0.3502 (6)	0.0286 (16)
H8A	0.134470	0.428113	0.396580	0.034*
H8B	0.133657	0.297304	0.361920	0.034*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0234 (3)	0.0275 (2)	0.0232 (3)	0.00135 (18)	0.00190 (18)	0.00455 (18)
Rh1	0.0203 (3)	0.0237 (3)	0.0200 (3)	0.0009 (2)	0.0018 (2)	0.0007 (2)
C1	0.031 (4)	0.029 (4)	0.024 (4)	0.000 (3)	0.007 (3)	-0.004 (3)
C2	0.028 (4)	0.027 (4)	0.022 (4)	0.004 (3)	0.003 (3)	-0.004 (3)
C3	0.030 (4)	0.020 (4)	0.038 (4)	0.005 (3)	0.006 (3)	-0.002 (3)
C4	0.028 (4)	0.024 (4)	0.042 (5)	0.003 (3)	0.006 (3)	0.008 (3)
C5	0.025 (4)	0.034 (4)	0.022 (4)	0.004 (3)	-0.001 (3)	0.004 (3)
C6	0.025 (4)	0.025 (4)	0.017 (4)	0.002 (3)	-0.006 (3)	-0.003 (3)
C7	0.024 (4)	0.029 (4)	0.034 (4)	0.005 (3)	-0.001 (3)	0.002 (3)
C8	0.029 (4)	0.026 (4)	0.031 (4)	0.002 (3)	0.006 (3)	0.005 (3)

Geometric parameters (Å, °)

I1—Rh1	2.6975 (7)	C1—C8	1.509 (9)
I1—Rh1 ⁱ	2.7072 (7)	C2—C3	1.510 (9)
Rh1—Rh1 ⁱ	2.9612 (11)	C3—C4	1.560 (9)
Rh1—C1	2.115 (6)	C4—C5	1.492 (9)
Rh1—C2	2.122 (6)	C5—C6	1.392 (9)
Rh1—C5	2.119 (7)	C6—C7	1.526 (9)
Rh1—C6	2.121 (6)	C7—C8	1.532 (9)
C1—C2	1.413 (9)		
Rh1—I1—Rh1 ⁱ	66.45 (2)	C6—Rh1—I1	164.61 (18)
I1—Rh1—I1 ⁱ	85.13 (2)	C6—Rh1—Rh1 ⁱ	136.51 (18)
I1 ⁱ —Rh1—Rh1 ⁱ	56.621 (18)	C6—Rh1—C2	90.3 (2)
I1—Rh1—Rh1 ⁱ	56.933 (19)	C2—C1—Rh1	70.8 (4)
C1—Rh1—I1 ⁱ	165.07 (19)	C2—C1—C8	124.6 (6)
C1—Rh1—I1	92.3 (2)	C8—C1—Rh1	112.6 (4)
C1—Rh1—Rh1 ⁱ	132.91 (19)	C1—C2—Rh1	70.3 (4)
C1—Rh1—C2	39.0 (2)	C1—C2—C3	122.2 (6)
C1—Rh1—C5	97.7 (3)	C3—C2—Rh1	114.2 (5)
C1—Rh1—C6	81.1 (3)	C2—C3—C4	111.4 (5)
C2—Rh1—I1 ⁱ	155.75 (18)	C5—C4—C3	113.4 (5)
C2—Rh1—I1	93.32 (18)	C4—C5—Rh1	111.4 (5)
C2—Rh1—Rh1 ⁱ	102.57 (18)	C6—C5—Rh1	70.9 (4)
C5—Rh1—I1	157.07 (18)	C6—C5—C4	124.1 (6)
C5—Rh1—I1 ⁱ	90.08 (18)	C5—C6—Rh1	70.8 (4)
C5—Rh1—Rh1 ⁱ	102.03 (18)	C5—C6—C7	123.7 (6)
C5—Rh1—C2	82.0 (3)	C7—C6—Rh1	114.5 (4)
C5—Rh1—C6	38.3 (2)	C6—C7—C8	111.9 (5)
C6—Rh1—I1 ⁱ	97.57 (17)	C1—C8—C7	112.7 (5)

Symmetry code: (i) $-x+1, y, -z+1/2$.Di- μ -iodido-bis{[(1,2,5,6- η)-cycloocta-1,4-diene]rhodium(I)} (P)

Crystal data

[Rh₂I₂(C₈H₁₂)₂]
M_r = 675.97
 Monoclinic, *P*2₁/*c*
a = 10.4505 (5) Å
b = 19.390 (1) Å
c = 8.6271 (4) Å
 β = 101.523 (2)°
V = 1712.92 (14) Å³
Z = 4

F(000) = 1264
D_x = 2.621 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 9797 reflections
 θ = 2.6–26.4°
 μ = 5.52 mm⁻¹
T = 100 K
 Block, yellow-orange
 0.14 × 0.14 × 0.09 mm

Data collection

Nonius Kappa APEXII
 diffractometer
 Radiation source: sealed tube, fine-focus
 Graphite monochromator

Detector resolution: 7.9 pixels mm⁻¹
 ω and ϕ scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.057$, $T_{\max} = 0.093$
 38760 measured reflections
 3519 independent reflections
 2922 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -24 \rightarrow 24$
 $l = -9 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.055$
 $S = 1.07$
 3519 reflections
 205 parameters
 8 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.73024 (3)	0.56233 (2)	0.46409 (3)	0.02018 (8)
I2	0.89372 (2)	0.46580 (2)	0.19408 (3)	0.02188 (8)
Rh1	0.80485 (3)	0.42940 (2)	0.45350 (4)	0.01765 (9)
Rh2	0.72305 (3)	0.57016 (2)	0.14928 (4)	0.01730 (9)
C1	0.7956 (4)	0.3230 (2)	0.3955 (5)	0.0205 (9)
H1	0.778 (4)	0.318 (2)	0.280 (2)	0.025*
C2	0.9215 (4)	0.3392 (2)	0.4781 (5)	0.0229 (9)
H2	0.990 (3)	0.346 (2)	0.416 (4)	0.027*
C3	0.9741 (4)	0.3226 (2)	0.6498 (5)	0.0253 (10)
H3A	1.059815	0.345583	0.683485	0.030*
H3B	0.988454	0.272270	0.660875	0.030*
C4	0.8836 (4)	0.3453 (2)	0.7597 (5)	0.0261 (10)
H4A	0.827646	0.306003	0.776878	0.031*
H4B	0.937029	0.358549	0.863519	0.031*
C5	0.7978 (4)	0.4056 (2)	0.6927 (5)	0.0241 (10)
H5	0.814 (4)	0.4466 (15)	0.756 (5)	0.029*
C6	0.6732 (4)	0.3985 (2)	0.5982 (5)	0.0198 (9)
H6	0.607 (3)	0.4340 (16)	0.602 (5)	0.024*
C7	0.6093 (4)	0.3303 (2)	0.5424 (5)	0.0234 (9)
H7A	0.529071	0.339182	0.462128	0.028*
H7B	0.583454	0.306526	0.632950	0.028*
C8	0.6995 (4)	0.2832 (2)	0.4711 (5)	0.0240 (9)
H8A	0.748312	0.253106	0.555256	0.029*
H8B	0.645911	0.253237	0.390385	0.029*

C9	0.6610 (4)	0.5469 (2)	-0.0943 (5)	0.0206 (9)
H9	0.679 (4)	0.4967 (11)	-0.103 (5)	0.025*
C10	0.7642 (4)	0.5945 (2)	-0.0773 (5)	0.0208 (9)
H10	0.847 (3)	0.5720 (19)	-0.087 (5)	0.025*
C11	0.7443 (4)	0.6700 (2)	-0.1207 (5)	0.0247 (10)
H11A	0.665144	0.675101	-0.204767	0.030*
H11B	0.819921	0.686915	-0.162912	0.030*
C12	0.7293 (4)	0.7139 (2)	0.0242 (5)	0.0237 (9)
H12A	0.816605	0.729810	0.079190	0.028*
H12B	0.676206	0.755212	-0.012730	0.028*
C13	0.6659 (4)	0.6751 (2)	0.1393 (5)	0.0228 (9)
H13	0.685 (4)	0.693 (2)	0.250 (3)	0.027*
C14	0.5529 (4)	0.6343 (2)	0.0998 (5)	0.0210 (9)
H14	0.501 (3)	0.626 (2)	0.181 (4)	0.025*
C15	0.4755 (4)	0.6267 (2)	-0.0676 (5)	0.0240 (9)
H15A	0.485798	0.669082	-0.128031	0.029*
H15B	0.381741	0.621703	-0.064695	0.029*
C16	0.5200 (4)	0.5641 (2)	-0.1526 (5)	0.0233 (9)
H16A	0.466146	0.523646	-0.136871	0.028*
H16B	0.504985	0.573709	-0.267501	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02462 (15)	0.01759 (15)	0.01827 (15)	0.00106 (11)	0.00414 (11)	0.00015 (11)
I2	0.02106 (15)	0.02275 (16)	0.02346 (15)	0.00440 (11)	0.00840 (11)	0.00442 (12)
Rh1	0.01825 (17)	0.01641 (17)	0.01870 (17)	0.00044 (13)	0.00467 (13)	0.00062 (13)
Rh2	0.01825 (17)	0.01664 (17)	0.01712 (17)	0.00074 (13)	0.00379 (13)	0.00049 (13)
C1	0.028 (2)	0.014 (2)	0.021 (2)	0.0024 (17)	0.0100 (18)	-0.0021 (18)
C2	0.024 (2)	0.018 (2)	0.029 (2)	0.0044 (18)	0.0087 (18)	0.0019 (19)
C3	0.021 (2)	0.026 (2)	0.029 (2)	0.0061 (18)	0.0056 (18)	0.004 (2)
C4	0.032 (3)	0.022 (2)	0.023 (2)	0.0001 (19)	0.0030 (19)	-0.0015 (19)
C5	0.033 (3)	0.021 (2)	0.019 (2)	0.001 (2)	0.0093 (19)	0.0014 (19)
C6	0.019 (2)	0.019 (2)	0.022 (2)	0.0040 (17)	0.0069 (17)	-0.0012 (18)
C7	0.021 (2)	0.024 (2)	0.026 (2)	-0.0016 (18)	0.0056 (18)	0.0011 (19)
C8	0.028 (2)	0.020 (2)	0.024 (2)	0.0007 (18)	0.0052 (18)	-0.0011 (18)
C9	0.026 (2)	0.023 (2)	0.013 (2)	0.0013 (18)	0.0045 (17)	-0.0008 (18)
C10	0.023 (2)	0.025 (2)	0.018 (2)	0.0030 (18)	0.0099 (17)	-0.0014 (18)
C11	0.027 (2)	0.025 (2)	0.023 (2)	-0.0018 (19)	0.0065 (18)	0.0073 (19)
C12	0.029 (2)	0.018 (2)	0.022 (2)	-0.0015 (18)	0.0003 (18)	0.0016 (18)
C13	0.029 (2)	0.017 (2)	0.021 (2)	0.0051 (18)	-0.0001 (18)	-0.0013 (18)
C14	0.024 (2)	0.017 (2)	0.022 (2)	0.0081 (18)	0.0060 (18)	0.0019 (18)
C15	0.024 (2)	0.020 (2)	0.028 (2)	0.0031 (18)	0.0020 (19)	0.0023 (19)
C16	0.026 (2)	0.023 (2)	0.019 (2)	-0.0014 (18)	0.0011 (18)	-0.0002 (18)

Geometric parameters (Å, °)

I1—Rh1	2.6998 (4)	C2—C3	1.509 (6)
I1—Rh2	2.7061 (4)	C3—C4	1.531 (6)
I2—Rh1	2.6833 (4)	C4—C5	1.516 (6)
I2—Rh2	2.6738 (4)	C5—C6	1.398 (6)
Rh1—C1	2.120 (4)	C6—C7	1.516 (6)
Rh1—C2	2.117 (4)	C7—C8	1.526 (5)
Rh1—C5	2.131 (4)	C9—C10	1.404 (6)
Rh1—C6	2.120 (4)	C9—C16	1.496 (6)
Rh2—C9	2.120 (4)	C10—C11	1.514 (6)
Rh2—C10	2.137 (4)	C11—C12	1.547 (6)
Rh2—C13	2.117 (4)	C12—C13	1.501 (6)
Rh2—C14	2.142 (4)	C13—C14	1.405 (6)
C1—C2	1.400 (6)	C14—C15	1.514 (6)
C1—C8	1.514 (6)	C15—C16	1.538 (6)
Rh1—I1—Rh2	88.274 (12)	C2—C1—Rh1	70.6 (2)
Rh2—I2—Rh1	89.290 (12)	C2—C1—C8	122.2 (4)
I2—Rh1—I1	85.839 (12)	C8—C1—Rh1	113.4 (3)
C1—Rh1—I1	159.56 (12)	C1—C2—Rh1	70.8 (2)
C1—Rh1—I2	93.80 (11)	C1—C2—C3	124.9 (4)
C1—Rh1—C5	90.54 (16)	C3—C2—Rh1	111.4 (3)
C2—Rh1—I1	161.67 (12)	C2—C3—C4	113.4 (3)
C2—Rh1—I2	90.72 (11)	C5—C4—C3	112.2 (3)
C2—Rh1—C1	38.60 (16)	C4—C5—Rh1	113.8 (3)
C2—Rh1—C5	81.67 (16)	C6—C5—Rh1	70.4 (2)
C2—Rh1—C6	97.81 (16)	C6—C5—C4	123.8 (4)
C5—Rh1—I1	96.17 (12)	C5—C6—Rh1	71.2 (2)
C5—Rh1—I2	161.76 (12)	C5—C6—C7	124.8 (4)
C6—Rh1—I1	91.38 (11)	C7—C6—Rh1	110.9 (3)
C6—Rh1—I2	159.83 (11)	C6—C7—C8	112.4 (3)
C6—Rh1—C1	81.93 (16)	C1—C8—C7	112.6 (3)
C6—Rh1—C5	38.41 (16)	C10—C9—Rh2	71.4 (2)
I2—Rh2—I1	85.902 (12)	C10—C9—C16	125.0 (4)
C9—Rh2—I1	157.60 (12)	C16—C9—Rh2	111.8 (3)
C9—Rh2—I2	92.63 (12)	C9—C10—Rh2	70.1 (2)
C9—Rh2—C10	38.52 (16)	C9—C10—C11	123.0 (4)
C9—Rh2—C14	81.27 (16)	C11—C10—Rh2	113.4 (3)
C10—Rh2—I1	163.81 (12)	C10—C11—C12	111.3 (3)
C10—Rh2—I2	92.82 (11)	C13—C12—C11	112.8 (3)
C10—Rh2—C14	89.99 (16)	C12—C13—Rh2	110.5 (3)
C13—Rh2—I1	92.62 (12)	C14—C13—Rh2	71.7 (2)
C13—Rh2—I2	155.19 (12)	C14—C13—C12	125.6 (4)
C13—Rh2—C9	97.80 (16)	C13—C14—Rh2	69.8 (2)
C13—Rh2—C10	81.78 (16)	C13—C14—C15	123.3 (4)
C13—Rh2—C14	38.53 (16)	C15—C14—Rh2	113.5 (3)
C14—Rh2—I1	95.06 (11)	C14—C15—C16	112.1 (3)

C14—Rh2—I2

166.28 (11)

C9—C16—C15

112.7 (3)
