

Di- μ -methoxy-bis(tetrafluorobenzobarrelene)dirhodium(I)

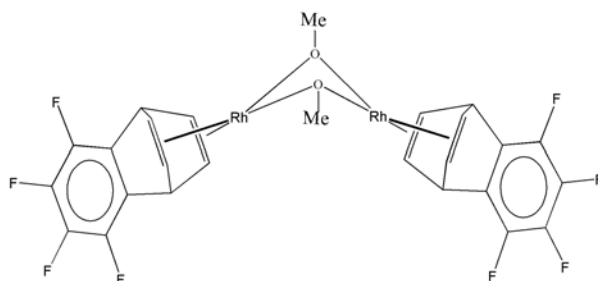
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Abstract

The versatile synthetic precursor methoxy-bridged Rhodium complex [$\{\text{Rh}(\mu\text{-OCH}_3)(\text{tfbb})\}_2$] (tfbb= tetrafluorobenzobarrelene, $\text{C}_{12}\text{H}_6\text{F}_4$) has been structurally characterized. The asymmetric unit contains half a molecule that can be expanded *via* a twofold axis. The title compound has been shown to be a dinuclear rhodium complex where each metal centre is coordinated by two oxygen atoms from two bridging methoxy groups and by the olefinic bonds of a tfbb ligand. Comparison of the bite angles of tfbb, norbornadiene (nbd) or cyclooctadiene (cod) olefins in their η^4 -coordination to the rhodium reveals similarities between tfbb and nbd ligands, which are much more rigid than cod. The short distance found between the distorted square-planar metal centers, 2.8350 (4) Å, has been related to the *syn* configuration of the folded core "RhORhO" ring.



1. Comment

Facile access to rhodium complexes bearing the tetrafluorobenzobarrelene diolefin ($\text{C}_{12}\text{H}_6\text{F}_4$, tfbb) has promoted the development of a rich rhodium organometallic chemistry within the last few years (Esteruelas & Oro, 1999). In particular, the basicity of the title complex [$\{\text{Rh}(\mu\text{-OMe})(\text{tfbb})\}_2$] (Usón, 1985) has allowed entry into a broad spectrum of neutral or cationic polynuclear complexes. Furthermore, replacing tfbb the well-known diolefin 1,5-cyclooctadiene (cod) with tfbb often has remarkable consequences for their structures and nuclearity of the complexes (Mena *et al.*, 2011).

The title compound (**1**) has been shown to be a dinuclear Rh complex formed by two crystallographically related $\text{Rh}(\text{tfbb})$ fragments symmetrically bridged by a pair of μ -methoxy ligands. Rhodium exhibits a slightly distorted square-planar coordination involving two O atoms and the olefinic bonds of tfbb ligands to which they are bounded in a η^2 C=C fashion. The Rh—C bond distances are in the range 2.084 (2)–2.111 (2) Å. The main indication of the slight deviation from the ideal square-planar arrangement is the fact that the rhodium lies 0.0721 (2) Å out of the least-squares plane formed by the two O atoms and the midpoints of C1=C2 and C4=C5 olefinic bonds (Ct1 and Ct2, respectively), in the opposite direction of the other rhodium atom. Moreover, a dihedral angle of 86.21 (8)° is found between this coordination plane (formed by O1, O1ⁱ, Ct1 and Ct2) and the plane defined by the olefinic C1, C2, C4 and C5 atoms. This value indicates that tfbb ligand is not perpendicularly coordinated to the metal coordination plane, but hardly twisted towards the inner part of the molecule.

The coordination of the tfbb ligands to the metal centre in **1** is similar to those found in the trimer [$\{\text{Rh}(\mu_2\text{-NH}_2)(\text{tfbb})\}_3$] (Mena *et al.*, 2011), as indicated by the mean Rh—Ct distances of 1.978 (3) and 2.001 (3) Å (Ct being the centroid of a C=C bond), found in the methoxo dimer (**1**) and in the amido trimer, respectively. The Ct1—Rh1—Ct2 bite angle in the dimer [71.4 (1)°] is very close to those found in the trimer [mean value 70.8 (2)°] and remains well within the narrow range observed in the Cambridge Structural Database, version 5.32 (CSD; Allen, 2002) for Rh-tfbb complexes (66.9–73.0°), showing the relative rigidity of this diolefin. Interestingly, an analysis of the coordination of tfbb, nbd (nbd = norbornadiene, C₇H₈) and cod diolefins with rhodium metal atom reveals that the bite angle is similar and it varies in a comparable narrow range in Rh-tfbb and Rh-nbd complexes (bite angles between 65.8 and 73.8° are found in the later), while for the cyclooctadiene (cod) ligand it is larger and much more flexible, as indicated by the higher observed values and by a wider distribution of bite angles, ranging from 75.5 to 91.9°.

The four membered "RhORhO" ring shows a folded conformation: the dihedral angle (θ) between the coordination planes defined by O—Rh—Oⁱ and O—Rhⁱ—Oⁱ was found to be 120.79 (5)°. Accordingly, a short intermetallic separation of 2.8350 (4) Å was observed. This value, shorter than that observed in the related [$\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2$] complex (3.231 Å (Tanaka, 1983)), is in the lower limit of the range (2.785 to 3.33 Å) reported for dinuclear rhodium compounds bridged by two oxygen atoms (CSD; Allen, 2002). In fact, an analysis of 13 dinuclear square-planar rhodium (I) complexes of type "Rh₂(μ-OZ)₂" having two substituted-oxo bridges and non-disordered dinuclear "RhORhO" central cores revealed a clear correlation (Figure 2) between the intermetallic distance (d) and the four-membered ring folding (θ). Notably, the obtained total distribution is clearly bimodal, with a narrow distribution at $\theta > 172^\circ$ (zone I) and a broader one with $117 < \theta < 137^\circ$ (zone II).

The first group of structures comprises μ-hydroxo [$\{\text{Rh}(\mu\text{-OH})(L)\}_2$] (L = substituted-phosphines; Okazaki, 2009; Brune, 1988; Gevert, 1996), and alkoxo bridged [$\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2$] (Tanaka, 1983) and [$\{\text{Rh}(\mu\text{-diphenylphenoxy})(\text{CO})\}_2$] (Chebi, 1990) complexes. Two molecular structures were found where crystallographically independent atoms formed nearly planar rings with *anti* configuration; while in three structures the "RhORhO" ring lies across an inversion center. In this case, the symmetry constrains the four atoms to be coplanar ($\theta = 180^\circ$) and the complexes also exhibit an *anti* configuration. Intermetallic distances, longer than 3.23 Å, well over the reported attracting interaction distances, are observed within this group.

The second group (zone II) corresponds to geometries formed by crystallographically independent atoms or by atoms related by a twofold rotation axis in [$\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2$] Selent, 1995) or dibenzocyclooctatetraene (Singh, 2008), in [$\{\text{Rh}(\mu\text{-OEt})(\text{cod})\}_2$] (Ramm, 1996) or [$\{\text{Rh}(\mu\text{-OSiZ})(L)\}_2$] with Z = methyl or phenyl groups and L = cod, norbornadiene or carbonyl ligands (Marciniec, 1996; Krzyzanowski, 1996; Vizi-Orosz, 1994). A linear correlation exists between d and θ (Figure 2) for all these complexes with *syn* configurations in the folded rings.

The molecular parameters for **1** lie in zone II, where the shortest intermetallic distances for "Rh₂(μ-OZ)₂" (between 2.78 and 2.95 Å) can be found. It is noteworthy that this classification can not be easily related to the bridging group or the rhodium ligands: [$\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2$] exhibit a folded-ring with *syn* configuration (Selent, 1995) while [$\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2$] and [$\{\text{Rh}(\mu\text{-OH})(\text{triphenylphosphine})\}_2$] complexes exhibiting planar rings with *anti* configurations (Tanaka, 1983; Brune, 1988). However, for dinuclear complexes exhibiting *syn* conformations, bulky siloxo-derivatives bridging groups tend to occupy axial positions, while complexes with ethoxo- and hydroxo- bridging ligands exhibit a *syn-e* conformation, very close to the geometry observed in compound **1**.

Concerning the crystal packing of **1**, the hydrogen bonding network (C1—H1[⋯]Oⁱⁱ 158 (3)°, C1[⋯]O1ⁱⁱ 3.424 (3) Å, H1[⋯]O1ⁱⁱ 2.57 (3) Å; symmetry code: ii) $-x + 1/2, y - 1/2, -z + 1/2$) displayed in Figure 3, shows an arrangement of molecules in an helix.

Furthermore, molecules of neighbouring helices are connected through short contacts among fluorine atoms (CF \cdots FC interactions). Fluorine atom characteristics (high electronegativity, low polarizability and small size) distinguish it from Cl, Br and I, and therefore, its ability to form C—H \cdots F, F \cdots F and C—F \cdots π interactions has been argued (Reichenbacher, 2005). Intermolecular distance between F atoms in **1** is 2.850 (4) Å, and according to the similar values of the C—F \cdots F angles [150.5 (2) and 151.9 (2)°], this contact correspond to a type I halogen \cdots halogen interaction (Sakurai, 1963; Desiraju, 1989). These values also agree with those reported in other CF \cdots FC type I interactions with distances between 2.659 and 2.899 Å (Hibbs, 2004; Chopra, 2006; Hatwar, 2011). These previous experimental and theoretical charge density analysis show that according to their topological characteristics (charge density, laplacian and energy densities), these interactions correspond to weak closed-shell interactions. Therefore, they may contribute, although weakly, to the packing stability.

2. Synthesis and crystallization

The synthesis of the title complex [$\{\text{Rh}(\mu\text{-OCH}_3)(\text{tfbb})\}_2$] is well known and quite accessible, as reported by Usón *et al.* (1985).

3. Refinement

All hydrogen atoms (but those of the methyl group) were included in the model in observed positions and freely refined. Final C—H distances vary from 0.87 (3) to 0.95 (3) Å. Hydrogen atoms of the methyl group have been included in idealized positions and constrained to ride on their parent atoms, with a C—H distance of 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Table 1

Experimental details

Crystal data	
Chemical formula	C ₂₆ H ₁₈ F ₈ O ₂ Rh ₂
M_r	720.22
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	100
a, b, c (Å)	25.7648 (17), 10.8166 (7), 8.0542 (5)
V (Å ³)	2244.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.56
Crystal size (mm)	0.18 \times 0.04 \times 0.04
Data collection	
Diffractometer	Bruker <i>APEX</i> DUO system diffractometer
Absorption correction	Numerical Absorption corrections based on face indexing, including in <i>APEX2</i> package (Bruker AXS, 2008).
$T_{\text{min}}, T_{\text{max}}$	0.900, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18639, 3241, 2700
R_{int}	0.032

$(\sin \theta/\lambda)_{\max}$ (\AA^{-1}) 0.713

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S 0.029, 0.069, 1.09

No. of reflections 3241

No. of parameters 197

H-atom treatment H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{\AA}^{-3}$) 0.78, -0.48

Computer programs: *APEX2* v. 2008.4 (Bruker AXS, 2008), *APEX2* v. 2008.4, *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *ORTEP* (Farrugia, 1997), *publCIF* (Westrip, 2010).

Table 2

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

Rh1-Ct1	1.977 (2)	Rh1-C2	2.084 (2)
Rh1-Ct2	1.980 (2)	Rh1-C4	2.096 (2)
Rh1-O1	2.0687 (17)	Rh1-C5	2.105 (3)
Rh1-O1 ⁱ	2.0700 (18)	Rh1-Rh1 ⁱ	2.8351 (4)
Rh1-C1	2.111 (2)	O1-C13	1.398 (4)
O1-Rh1-O1 ⁱ	76.03 (9)	O1 ⁱ -Rh1-Ct2	172.35 (9)
O1-Rh1-Ct1	178.16 (9)	Ct1-Rh1-Ct2	71.4 (1)
O1-Rh1-Ct2	107.10 (9)	Rh1-O1-C13	123.83 (17)
O1 ⁱ -Rh1-Ct1	105.28 (9)		

Symmetry code:(i) x,-y+1/2,-z+1/2. Ct1 and Ct2 are the centroids of the C1=C2 and C4=C5 bonds, respectively.

Acknowledgements

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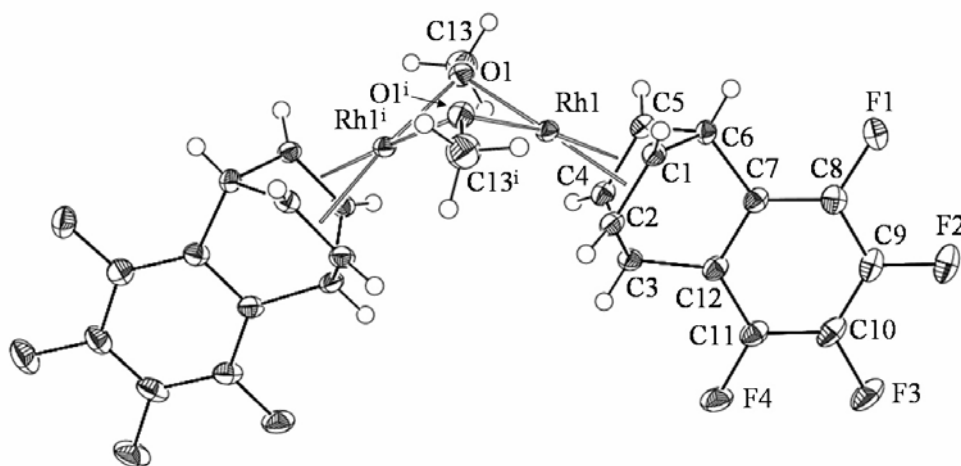


Figure 1

A view of the molecular structure of $[\{\text{Rh}(\mu\text{-OMe})(\text{tfbb})\}_2]$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $x, 1/2 - y, 1/2 - z$.

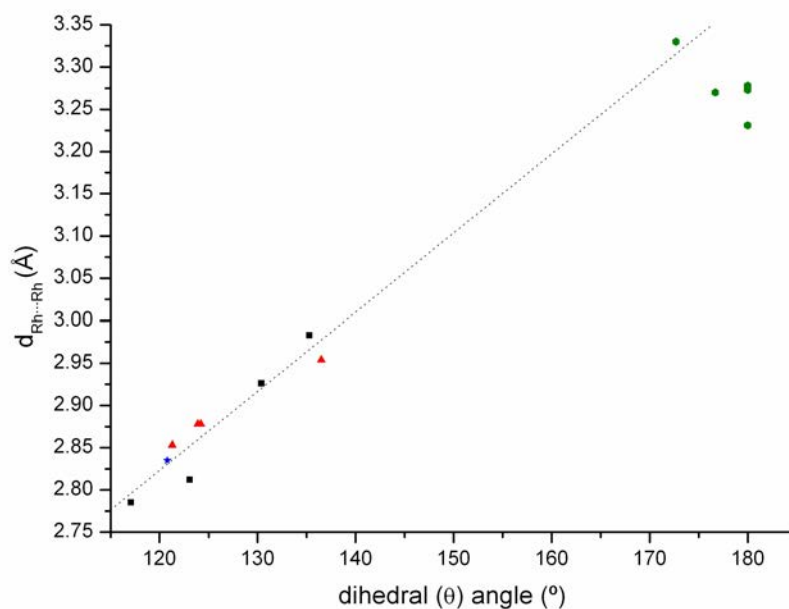


Figure 2

Rh \cdots Rh intermetallic distance (d) vs central core folding (θ). Planar-*anti*, folded-*syn-a* and folded-*syn-e* core "RhORhO" ring compounds are represented by green triangles, red circles and black squares, respectively. Compound **1** is identified by a blue star. The dashed line shows the linear fit of folded-*syn* compounds. Colours only appear in the online version of the journal.

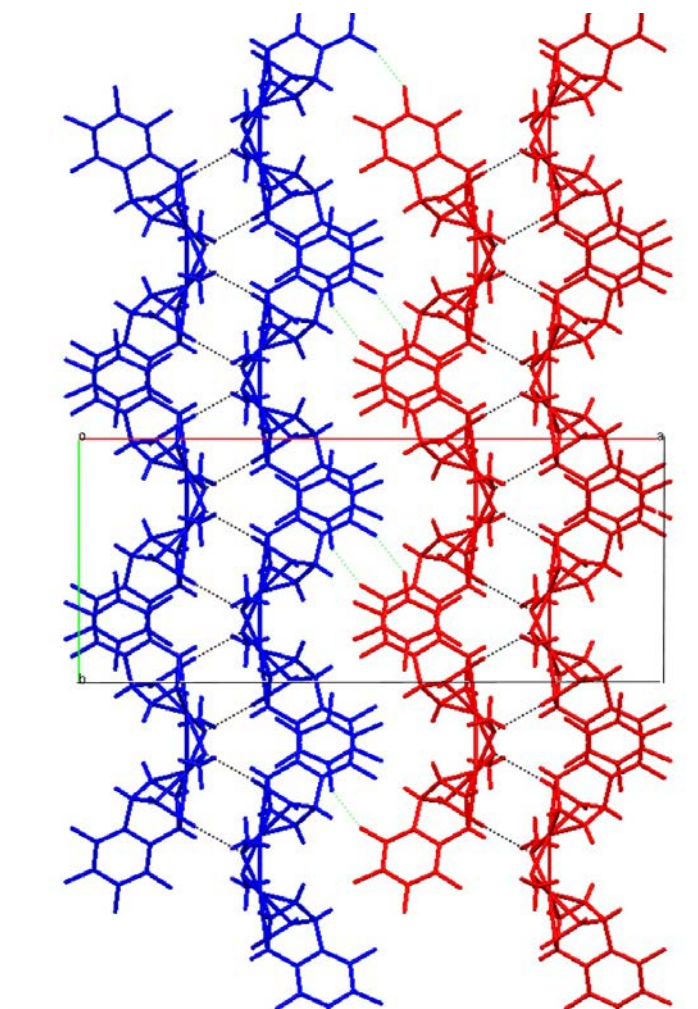


Figure 3

Hydrogen-bonding network viewed along the *c* axis. Black dotted lines represent hydrogen-bond interactions along an helix (two helices are represented in blue and red colours). Short F...F contacts between both helices are depicted in green dotted lines. Colours only appear in the online version of the journal.

supporting information

Di- μ -methoxy-bis(tetrafluorobenzobarrelene)dirhodium(I)

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Computing details

Data collection: *APEX2* v. 2008.4 (Bruker AXS, 2008); cell refinement: *APEX2* v. 2008.4; data reduction: *APEX2* v. 2008.4; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I)*Crystal data*C₂₆H₁₈F₈O₂Rh₂ $M_r = 720.22$ Orthorhombic, *Pnma*

Hall symbol: -P 2a 2bc

 $a = 25.7648$ (17) Å $b = 10.8166$ (7) Å $c = 8.0542$ (5) Å $V = 2244.6$ (2) Å³ $Z = 4$ $F(000) = 1408$ $D_x = 2.131$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1665 reflections

 $\theta = 1.6$ – 30.5° $\mu = 1.56$ mm⁻¹ $T = 100$ K

Prism, yellow

 $0.18 \times 0.04 \times 0.04$ mm*Data collection*

Bruker APEX DUO system

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω rotations with narrow frames scans

Absorption correction: numerical

Absorption corrections based on face indexing,

including in *APEX2* package (Bruker AXS, 2008). $T_{\min} = 0.900$, $T_{\max} = 1.000$

18639 measured reflections

3241 independent reflections

2700 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$ $\theta_{\text{max}} = 30.5^\circ$, $\theta_{\text{min}} = 1.6^\circ$ $h = -36 \rightarrow 25$ $k = -15 \rightarrow 15$ $l = -11 \rightarrow 11$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$ $wR(F^2) = 0.069$ $S = 1.09$

3241 reflections

197 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 2.9733P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.78$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Rh1	0.186170 (7)	0.128786 (16)	0.18310 (2)	0.01614 (7)
C1	0.17620 (9)	-0.0619 (2)	0.2294 (3)	0.0172 (5)
C2	0.13232 (9)	0.0046 (2)	0.2804 (3)	0.0180 (5)
C3	0.09150 (9)	0.0183 (2)	0.1437 (3)	0.0192 (5)
C4	0.12506 (9)	0.0905 (2)	0.0193 (3)	0.0188 (5)
C5	0.16925 (9)	0.0258 (2)	-0.0319 (3)	0.0189 (5)
C6	0.17376 (9)	-0.1031 (2)	0.0466 (3)	0.0173 (5)
C7	0.12316 (9)	-0.1718 (2)	0.0178 (3)	0.0189 (5)
C8	0.11702 (10)	-0.2853 (2)	-0.0563 (3)	0.0215 (5)
C9	0.06843 (11)	-0.3375 (2)	-0.0750 (3)	0.0246 (5)
C10	0.02536 (10)	-0.2756 (3)	-0.0170 (4)	0.0260 (6)
C11	0.03088 (10)	-0.1618 (2)	0.0580 (4)	0.0228 (5)
C12	0.07936 (9)	-0.1079 (2)	0.0737 (3)	0.0192 (5)
F1	0.15846 (6)	-0.34857 (14)	-0.1154 (2)	0.0264 (3)
F2	0.06287 (7)	-0.44752 (16)	-0.1494 (2)	0.0351 (4)
F3	-0.02232 (6)	-0.32576 (17)	-0.0346 (2)	0.0369 (4)
F4	-0.01184 (6)	-0.10354 (15)	0.1168 (2)	0.0297 (4)
O1	0.21743 (6)	0.29470 (16)	0.1036 (2)	0.0203 (4)
C13	0.20877 (12)	0.3451 (3)	-0.0538 (4)	0.0342 (7)
H13A	0.2345	0.3124	-0.1319	0.051*
H13B	0.2119	0.4353	-0.0482	0.051*
H13C	0.1739	0.3228	-0.0917	0.051*
H1	0.1994 (12)	-0.095 (3)	0.301 (4)	0.017 (7)*
H3	0.0644 (12)	0.060 (3)	0.178 (3)	0.019 (7)*
H5	0.1874 (11)	0.048 (3)	-0.123 (4)	0.021 (8)*
H4	0.1122 (10)	0.162 (2)	-0.035 (3)	0.009 (6)*
H6	0.2011 (12)	-0.142 (3)	0.012 (4)	0.018 (7)*
H2	0.1230 (11)	0.020 (3)	0.390 (4)	0.023 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh1	0.01252 (9)	0.01531 (10)	0.02061 (10)	-0.00020 (7)	-0.00073 (7)	0.00046 (7)
C1	0.0144 (10)	0.0153 (10)	0.0220 (12)	0.0005 (8)	-0.0024 (9)	0.0021 (9)
C2	0.0155 (10)	0.0166 (11)	0.0219 (12)	-0.0023 (9)	-0.0006 (10)	0.0022 (9)
C3	0.0124 (10)	0.0178 (11)	0.0274 (13)	0.0019 (9)	-0.0009 (9)	0.0005 (10)
C4	0.0166 (11)	0.0172 (11)	0.0225 (12)	-0.0006 (9)	-0.0049 (9)	0.0025 (9)
C5	0.0173 (11)	0.0191 (11)	0.0203 (12)	-0.0033 (9)	-0.0015 (9)	0.0006 (10)

supporting information

C6	0.0169 (10)	0.0128 (10)	0.0222 (12)	0.0003 (8)	-0.0007 (9)	-0.0002 (9)
C7	0.0179 (11)	0.0173 (11)	0.0215 (12)	-0.0013 (9)	-0.0029 (9)	0.0038 (9)
C8	0.0252 (12)	0.0195 (11)	0.0200 (12)	0.0011 (10)	-0.0029 (10)	0.0033 (10)
C9	0.0317 (14)	0.0180 (11)	0.0242 (13)	-0.0053 (10)	-0.0078 (11)	0.0013 (10)
C10	0.0235 (12)	0.0268 (13)	0.0278 (14)	-0.0101 (11)	-0.0084 (11)	0.0049 (11)
C11	0.0175 (11)	0.0228 (12)	0.0279 (13)	-0.0023 (10)	-0.0038 (10)	0.0063 (11)
C12	0.0160 (10)	0.0183 (11)	0.0235 (12)	-0.0014 (9)	-0.0035 (9)	0.0043 (10)
F1	0.0326 (9)	0.0186 (7)	0.0280 (8)	0.0035 (6)	0.0002 (7)	-0.0027 (6)
F2	0.0444 (10)	0.0237 (8)	0.0372 (10)	-0.0100 (8)	-0.0081 (8)	-0.0055 (7)
F3	0.0256 (8)	0.0356 (9)	0.0495 (11)	-0.0155 (7)	-0.0089 (8)	0.0024 (9)
F4	0.0143 (7)	0.0322 (9)	0.0428 (10)	-0.0020 (6)	-0.0012 (7)	0.0033 (8)
O1	0.0184 (8)	0.0195 (8)	0.0230 (9)	-0.0012 (7)	0.0032 (7)	0.0010 (7)
C13	0.0341 (16)	0.0325 (15)	0.0362 (17)	-0.0007 (12)	0.0008 (13)	0.0010 (13)

Geometric parameters (Å, °) for (I)

Rh1—Ct1	1.977 (2)	C5—C6	1.535 (3)
Rh1—Ct2	1.980 (2)	C5—H5	0.90 (3)
Rh1—O1	2.0687 (17)	C6—C7	1.519 (3)
Rh1—O1 ⁱ	2.0700 (18)	C6—H6	0.87 (3)
Rh1—C1	2.111 (2)	C7—C8	1.374 (3)
Rh1—C2	2.084 (2)	C7—C12	1.398 (3)
Rh1—C4	2.096 (2)	C8—F1	1.354 (3)
Rh1—C5	2.105 (3)	C8—C9	1.381 (4)
Rh1—Rh1 ⁱ	2.8351 (4)	C9—F2	1.340 (3)
C1—C2	1.401 (3)	C9—C10	1.378 (4)
C1—C6	1.540 (4)	C10—F3	1.350 (3)
C1—H1	0.90 (3)	C10—C11	1.379 (4)
C2—C3	1.529 (4)	C11—F4	1.354 (3)
C2—H2	0.93 (3)	C11—C12	1.384 (3)
C3—C12	1.510 (3)	O1—C13	1.398 (4)
C3—C4	1.537 (4)	C13—H13A	0.9800
C3—H3	0.88 (3)	C13—H13B	0.9800
C4—C5	1.399 (3)	C13—H13C	0.9800
C4—H4	0.95 (3)		
O1—Rh1—O1 ⁱ	76.03 (9)	C5—C4—Rh1	70.90 (14)
O1—Rh1—Ct1	178.16 (9)	C3—C4—Rh1	96.47 (16)
O1—Rh1—Ct2	107.10 (9)	C5—C4—H4	123.9 (16)
O1 ⁱ —Rh1—Ct1	105.28 (9)	C3—C4—H4	121.1 (16)
O1 ⁱ —Rh1—Ct2	172.35 (9)	Rh1—C4—H4	113.1 (16)
Ct1—Rh1—Ct2	71.4 (1)	C4—C5—C6	113.2 (2)
O1—Rh1—C2	159.19 (8)	C4—C5—Rh1	70.20 (15)
O1 ⁱ —Rh1—C2	101.82 (9)	C6—C5—Rh1	97.25 (16)
O1—Rh1—C4	105.61 (8)	C4—C5—H5	122 (2)
O1 ⁱ —Rh1—C4	153.36 (9)	C6—C5—H5	122 (2)
C2—Rh1—C4	66.98 (10)	Rh1—C5—H5	115 (2)
O1—Rh1—C5	106.57 (9)	C7—C6—C5	108.48 (19)
O1 ⁱ —Rh1—C5	167.17 (8)	C7—C6—C1	108.8 (2)
C2—Rh1—C5	80.23 (10)	C5—C6—C1	97.70 (19)
C4—Rh1—C5	38.90 (10)	C7—C6—H6	114.3 (19)

O1—Rh1—C1	161.69 (8)	C5—C6—H6	112 (2)
O1 ⁱ —Rh1—C1	106.94 (9)	C1—C6—H6	115 (2)
C2—Rh1—C1	39.02 (9)	C8—C7—C12	119.2 (2)
C4—Rh1—C1	80.02 (10)	C8—C7—C6	127.1 (2)
C5—Rh1—C1	66.62 (10)	C12—C7—C6	113.7 (2)
O1—Rh1—Rh1 ⁱ	46.78 (5)	F1—C8—C7	120.9 (2)
O1 ⁱ —Rh1—Rh1 ⁱ	46.74 (5)	F1—C8—C9	118.0 (2)
C2—Rh1—Rh1 ⁱ	116.96 (7)	C7—C8—C9	121.1 (2)
C4—Rh1—Rh1 ⁱ	114.97 (7)	F2—C9—C10	119.8 (2)
C5—Rh1—Rh1 ⁱ	143.35 (7)	F2—C9—C8	120.6 (3)
C1—Rh1—Rh1 ⁱ	146.75 (7)	C10—C9—C8	119.6 (2)
C2—C1—C6	113.3 (2)	F3—C10—C9	120.1 (2)
C2—C1—Rh1	69.43 (14)	F3—C10—C11	119.9 (3)
C6—C1—Rh1	96.83 (15)	C9—C10—C11	119.9 (2)
C2—C1—H1	123.6 (19)	F4—C11—C10	119.0 (2)
C6—C1—H1	121.3 (19)	F4—C11—C12	120.4 (2)
Rh1—C1—H1	115 (2)	C10—C11—C12	120.6 (3)
C1—C2—C3	113.2 (2)	C11—C12—C7	119.4 (2)
C1—C2—Rh1	71.55 (14)	C11—C12—C3	127.0 (2)
C3—C2—Rh1	97.19 (16)	C7—C12—C3	113.6 (2)
C1—C2—H2	125.5 (19)	Rh1—O1—C13	123.83 (17)
C3—C2—H2	119.2 (18)	C13—O1—Rh1	123.83 (17)
Rh1—C2—H2	114.1 (19)	C13—O1—Rh1 ⁱ	122.34 (17)
C12—C3—C2	108.9 (2)	Rh1—O1—Rh1 ⁱ	86.47 (7)
C12—C3—C4	109.4 (2)	O1—C13—H13A	109.5
C2—C3—C4	97.55 (19)	O1—C13—H13B	109.5
C12—C3—H3	115 (2)	H13A—C13—H13B	109.5
C2—C3—H3	111.7 (19)	O1—C13—H13C	109.5
C4—C3—H3	113 (2)	H13A—C13—H13C	109.5
C5—C4—C3	113.3 (2)	H13B—C13—H13C	109.5
O1—Rh1—C1—C2	-175.3 (2)	C4—Rh1—C5—C6	-112.1 (2)
O1 ⁱ —Rh1—C1—C2	87.95 (15)	C1—Rh1—C5—C6	-8.53 (14)
C4—Rh1—C1—C2	-65.58 (16)	Rh1 ⁱ —Rh1—C5—C6	-169.49 (9)
C5—Rh1—C1—C2	-103.87 (17)	C4—C5—C6—C7	52.2 (3)
Rh1 ⁱ —Rh1—C1—C2	55.3 (2)	Rh1—C5—C6—C7	123.74 (18)
O1—Rh1—C1—C6	-63.0 (3)	C4—C5—C6—C1	-60.7 (2)
O1 ⁱ —Rh1—C1—C6	-159.67 (13)	Rh1—C5—C6—C1	10.87 (17)
C2—Rh1—C1—C6	112.4 (2)	C2—C1—C6—C7	-52.9 (3)
C4—Rh1—C1—C6	46.80 (15)	Rh1—C1—C6—C7	-123.40 (16)
C5—Rh1—C1—C6	8.50 (13)	C2—C1—C6—C5	59.7 (2)
Rh1 ⁱ —Rh1—C1—C6	167.69 (9)	Rh1—C1—C6—C5	-10.82 (17)
C6—C1—C2—C3	1.4 (3)	C5—C6—C7—C8	124.9 (3)
Rh1—C1—C2—C3	90.03 (19)	C1—C6—C7—C8	-129.9 (3)
C6—C1—C2—Rh1	-88.66 (18)	C5—C6—C7—C12	-54.5 (3)
O1—Rh1—C2—C1	175.9 (2)	C1—C6—C7—C12	50.8 (3)
O1 ⁱ —Rh1—C2—C1	-102.39 (15)	C12—C7—C8—F1	178.5 (2)
C4—Rh1—C2—C1	103.01 (17)	C6—C7—C8—F1	-0.8 (4)
C5—Rh1—C2—C1	64.72 (16)	C12—C7—C8—C9	-0.6 (4)
Rh1 ⁱ —Rh1—C2—C1	-149.62 (13)	C6—C7—C8—C9	-179.9 (2)
O1—Rh1—C2—C3	63.8 (3)	F1—C8—C9—F2	0.1 (4)

O1 ⁱ —Rh1—C2—C3	145.51 (14)	C7—C8—C9—F2	179.1 (2)
C4—Rh1—C2—C3	-9.09 (15)	F1—C8—C9—C10	-179.8 (2)
C5—Rh1—C2—C3	-47.38 (16)	C7—C8—C9—C10	-0.7 (4)
C1—Rh1—C2—C3	-112.1 (2)	F2—C9—C10—F3	0.2 (4)
Rh1 ⁱ —Rh1—C2—C3	98.28 (15)	C8—C9—C10—F3	-180.0 (2)
C1—C2—C3—C12	52.1 (3)	F2—C9—C10—C11	-179.3 (2)
Rh1—C2—C3—C12	125.10 (18)	C8—C9—C10—C11	0.6 (4)
C1—C2—C3—C4	-61.4 (2)	F3—C10—C11—F4	1.7 (4)
Rh1—C2—C3—C4	11.54 (18)	C9—C10—C11—F4	-178.8 (2)
C12—C3—C4—C5	-52.6 (3)	F3—C10—C11—C12	-178.6 (2)
C2—C3—C4—C5	60.5 (3)	C9—C10—C11—C12	0.9 (4)
C12—C3—C4—Rh1	-124.60 (17)	F4—C11—C12—C7	177.5 (2)
C2—C3—C4—Rh1	-11.46 (18)	C10—C11—C12—C7	-2.1 (4)
O1—Rh1—C4—C5	97.18 (15)	F4—C11—C12—C3	-3.9 (4)
O1 ⁱ —Rh1—C4—C5	-172.93 (16)	C10—C11—C12—C3	176.4 (3)
C2—Rh1—C4—C5	-103.46 (16)	C8—C7—C12—C11	2.0 (4)
C1—Rh1—C4—C5	-64.94 (15)	C6—C7—C12—C11	-178.6 (2)
Rh1 ⁱ —Rh1—C4—C5	146.33 (13)	C8—C7—C12—C3	-176.8 (2)
O1—Rh1—C4—C3	-150.32 (14)	C6—C7—C12—C3	2.6 (3)
O1 ⁱ —Rh1—C4—C3	-60.4 (2)	C2—C3—C12—C11	126.6 (3)
C2—Rh1—C4—C3	9.03 (14)	C4—C3—C12—C11	-127.8 (3)
C5—Rh1—C4—C3	112.5 (2)	C2—C3—C12—C7	-54.7 (3)
C1—Rh1—C4—C3	47.56 (15)	C4—C3—C12—C7	50.8 (3)
Rh1 ⁱ —Rh1—C4—C3	-101.18 (14)	O1 ⁱ —Rh1—O1—C13	-169.8 (2)
C3—C4—C5—C6	0.6 (3)	C2—Rh1—O1—C13	-83.3 (3)
Rh1—C4—C5—C6	89.50 (19)	C4—Rh1—O1—C13	-17.3 (2)
C3—C4—C5—Rh1	-88.88 (19)	C5—Rh1—O1—C13	23.2 (2)
O1—Rh1—C5—C4	-94.50 (15)	C1—Rh1—O1—C13	88.4 (3)
O1 ⁱ —Rh1—C5—C4	165.6 (3)	Rh1 ⁱ —Rh1—O1—C13	-127.1 (2)
C2—Rh1—C5—C4	65.27 (15)	O1 ⁱ —Rh1—O1—Rh1 ⁱ	-42.68 (8)
C1—Rh1—C5—C4	103.60 (16)	C2—Rh1—O1—Rh1 ⁱ	43.8 (3)
Rh1 ⁱ —Rh1—C5—C4	-57.35 (19)	C4—Rh1—O1—Rh1 ⁱ	109.81 (9)
O1—Rh1—C5—C6	153.36 (13)	C5—Rh1—O1—Rh1 ⁱ	150.35 (8)

supporting information

O1 ⁱ —Rh1—C5—C6	53.5 (4)	C1—Rh1—O1—Rh1 ⁱ	-144.4 (3)
C2—Rh1—C5—C6	-46.87 (15)		

Symmetry code: (i) $x, -y+1/2, -z+1/2$.

Selected geometric parameters (Å, °)

Rh1-Ct1	1.977 (2)	Rh1-C2	2.084 (2)
Rh1-Ct2	1.980 (2)	Rh1-C4	2.096 (2)
Rh1-O1	2.0687 (17)	Rh1-C5	2.105 (3)
Rh1-O1 ⁱ	2.0700 (18)	Rh1-Rh1 ⁱ	2.8351 (4)
Rh1-C1	2.111 (2)	O1-C13	1.398 (4)
O1-Rh1-O1 ⁱ	76.03 (9)	O1 ⁱ -Rh1-Ct2	172.35 (9)
O1-Rh1-Ct1	178.16 (9)	Ct1-Rh1-Ct2	71.4 (1)
O1-Rh1-Ct2	107.10 (9)	Rh1-O1-C13	123.83 (17)
O1 ⁱ -Rh1-Ct1	105.28 (9)		

Symmetry code:(i) $x, -y+1/2, -z+1/2$. Ct1 and Ct2 are the centroids of the C1=C2 and C4=C5 bonds, respectively.