Di-μ-methanolato-bis[(η^4-tetrafluoro-benzobarrelene)rhodium(I)]

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The versatile synthetic precursor methanolate-bridged title rhodium complex, [Rh$_2$(CH$_3$O)$_2$(C$_{12}$H$_6$F$_4$)$_2$] or [Rh(μ-OCH$_3$)-(tfbb)]$_2$ [tfbb = tetrafluorobenzobarrelene or 3,4,5,6-tetra-fluorotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene], 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 O atoms from two bridging methanolate groups and by the olefinic bonds of a tfbb ligand. Comparison of the bite angles of tfbb, norbornadiene (nbd) and cyclooctadiene (cod) olefins in their η^4-coordination to rhodium reveals similarities between the tfbb and nbd ligands, which are much more rigid than cod. The short distance found between the distorted square-planar metal centres [2.8351 (4) Å] has been related to the syn conformation of the folded core 'RhORhO' ring.

Comment

Facile access to rhodium complexes bearing the tetrafluoro-benzobarrelene (tfbb) diolefin 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, [Rh(μ-OMe)(tfbb)]$_2$ (Usón et al., 1985), has allowed entry into a broad spectrum of neutral or cationic polynuclear complexes. Furthermore, replacing tfbb with the well known diolefin cycloocta-1,5-diene (cod) often has remarkable consequences for the structures and nuclearity of the complexes (Mena et al., 2011).

In the present study, [Rh(μ-OMe)(tfbb)]$_2$, (I) (Fig. 1), has been shown to be a dinuclear Rh complex formed by two Rh(tfbb) fragments related by a crystallographic twofold axis symmetrically bridged by a pair of methanolate ligands. Rhodium exhibits a slightly distorted square-planar coordination involving two O atoms and the olefinic bonds of the tfbb ligands to which they are bonded in a η^2-C=C fashion. The Rh—C bond lengths are in the range 2.084 (2)–

2.111 (2) Å (Table 1). The main indication of the slight deviation from an ideal square-planar arrangement is the fact that the Rh^I centre lies 0.0721 (2) Å out of the least-squares plane formed by the two O atoms and the mid-points of the C1=C2 and C4=C5 olefinic bonds (denoted Ct1 and Ct2, respectively); this displacement of the Rh centre is towards the less sterically hindered part of the molecule. Moreover, a dihedral angle of 86.21 (8)° is found between this coordination plane [formed by O1, O1^i, Ct1 and Ct2; symmetry code: (i) x, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$] and the plane defined by olefinic atoms C1, C2, C4 and C5. This value shows that the tfbb ligand approaches the metal atom with a not completely symmetrical coordination of the olefinic C atoms, but generating shorter Rh—C bond lengths for atoms C2 and C4.

(I)
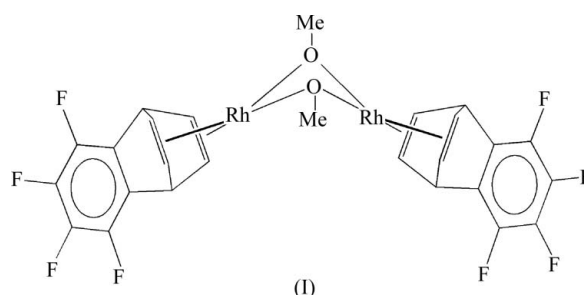
The coordination of the tfbb ligands to the metal centre in (I) is similar to that found in the [Rh(μ_2-NH$_2$)(tfbb)]$_3$ trimer (Mena et al., 2011), as indicated by the mean Rh—Ct distances of 1.978 (3) and 2.001 (3) Å (Ct being the centroid of a C=C bond) found in the methanolate dimer, (I), and in the amido trimer, respectively. The Ct1—Rh1—Ct2 bite angle in (I) [71.4 (1)°] is very close to that found in the trimer [mean value = 70.8 (2)°] and remains well within the narrow range observed in the Cambridge Structural Database (CSD, Version 5.32; 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, norbornadiene (nbd) and cod diolefins with rhodium reveals that the bite angle is similar and varies in a comparable narrow range in Rh–tfbb and Rh–nbd complexes (bite angles between 65.8 and 73.8° are
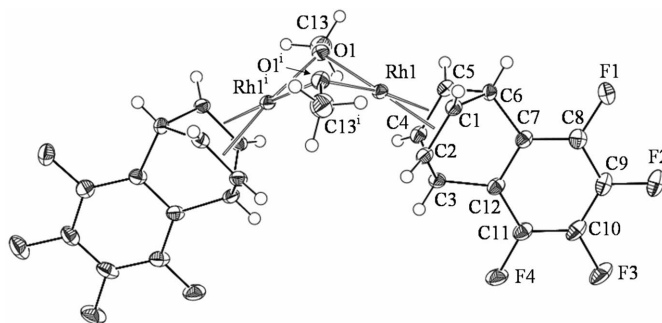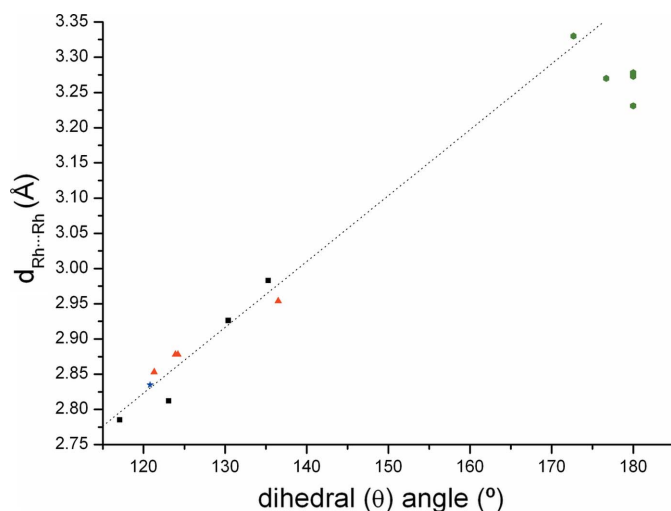

Figure 1
A view of the molecular structure of [Rh(μ-OMe)(tfbb)]$_2$, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) x, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$.]
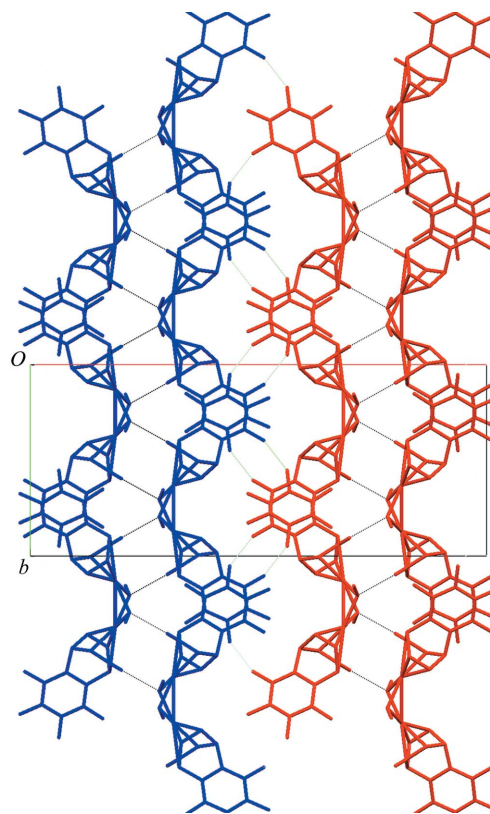
Figure 2
A graph showing the relationship between the Rh···Rh intermetallic distance (d) *versus* central core folding (θ). Planar–*anti*, folded–*syn*–*a* and folded–*syn*–*e* core 'RhORhO' ring compounds are represented by triangles, circles and squares, respectively. Compound (I) is identified by a star. The dashed line shows the linear fit of folded–*syn* compounds.

found in the latter), while for the 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—O^i and O—Rh^i—O^i is 120.79 (5)°. Accordingly, a short intermetallic separation of 2.8351 (4) Å was observed. This value, shorter than that observed in the related [Rh(μ-OMe)(cod)]$_2$ complex (3.231 Å; Tanaka *et al.*, 1983), is towards the lower limit of the range (2.785–3.33 Å) reported for dinuclear rhodium compounds involving two bridging O atoms (CSD; Allen, 2002). In fact, an analysis of 13 dinuclear square-planar rhodium(I) complexes of the type 'Rh$_2$(μ-OZ)$_2$' (Z is any atom) having two substituted oxide bridges and nondisordered dinuclear 'RhORhO' central cores revealed a clear correlation (Fig. 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 $\theta > 172°$ (zone I) and a broader distribution with $117 < \theta < 137°$ (zone II).

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

Figure 3
The hydrogen-bonding network in (I), viewed along the c axis. Dark dotted lines represent hydrogen-bond interactions along a helix (two helices are represented in blue and red in the electronic version of the paper). Short F···F contacts between the helices are depicted as grey (green) dotted lines.

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

The molecular parameters for (I) lie in zone II, where the shortest intermetallic distances for 'Rh$_2$(μ-OZ)$_2$' (between 2.78 and 2.95 Å) can be found. It is noteworthy that this classification cannot easily be related to the bridging group or the rhodium ligands: [Rh(μ-OH)(cod)]$_2$ exhibits a folded ring with a *syn* conformation (Selent & Ramm, 1995), while [Rh(μ-OMe)(cod)]$_2$ and [Rh(μ-OH)(triphenylphosphine)]$_2$ exhibit planar rings with *anti* conformations (Tanaka *et al.*, 1983; Brune *et al.*, 1988). However, for dinuclear complexes exhibiting *syn* conformations, bulky siloxo-derivative bridging groups tend to occupy axial positions, while complexes with ethanolate- and hydroxide-bridging ligands exhibit a *syn*–*e* conformation, very close to the geometry observed in compound (I).

Concerning the crystal packing of (I), the hydrogen-bonding network [H1···O1^{ii} = 2.57 (3) Å, C1···O1^{ii} = 3.424 (3) Å and C1—H1···O^{ii} = 158 (3)°; symmetry code: (ii) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$] displayed in Fig. 3 shows a helical arrangement of molecules.

Furthermore, molecules of neighbouring helices are connected through short contacts between F atoms (CF···FC interactions). F-atom characteristics (high electronegativity, low polarizability and small size) distinguish it from Cl, Br and I, and therefore its ability to form C—H···F, F···F and C—F···π interactions has been argued (Reichenbächer et al., 2005). The shortest intermolecular distance between F atoms in (I) is 2.850 (4) Å for F2···F4($-x$, $y - \frac{1}{2}$, $z - \frac{1}{2}$) and, according to the similar values of the C—F···F angles [150.5 (2) and 151.9 (2)°], this contact corresponds to a type-I halogen–halogen interaction (Sakurai et al., 1963; Desiraju & Parthasarathy, 1989). These values also agree with those reported for other CF···FC type-I interactions with distances between 2.659 and 2.899 Å (Hibbs et al., 2004; Chopra et al., 2006; Hathwar & Guru Row, 2011). These previous experimental and theoretical charge-density analyses 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, albeit weakly, to the packing stability.

Experimental

The synthesis of the title complex is well known and quite accessible (Usón et al., 1985). The complex was obtained by direct reaction of the dimer [Rh(μ-Cl)(cod)]$_2$ with a methanol solution of potassium hydroxide in dichloromethane. Single crystals were obtained by recrystallization from dichloromethane and hexane.

Crystal data

[Rh$_2$(CH$_3$O)$_2$(C$_{12}$H$_6$F$_4$)$_2$]	V = 2244.6 (2) Å^3
M_r = 720.22	Z = 4
Orthorhombic, $Pnna$	Mo $K\alpha$ radiation
a = 25.7648 (17) Å	μ = 1.56 mm^{-1}
b = 10.8166 (7) Å	T = 100 K
c = 8.0542 (5) Å	0.18 × 0.04 × 0.04 mm

Data collection

Bruker APEX DUO system diffractometer	18639 measured reflections
Absorption correction: numerical (absorption corrections based on face indexing, using APEX2; Bruker, 2008) T_{min} = 0.900, T_{max} = 1.000	3241 independent reflections 2700 reflections with $I > 2\sigma(I)$ R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.069	
S = 1.09	
3241 reflections	$\Delta\rho_{max}$ = 0.78 e Å^{-3}
197 parameters	$\Delta\rho_{min}$ = −0.48 e Å^{-3}

All H atoms (except those of the methyl group) were included in the model in observed positions and refined freely. Final C—H distances varied from 0.87 (3) to 0.95 (3) Å. The H atoms of the

Table 1
Selected geometric parameters (Å, °).

Ct1 and Ct2 are the centroids of the C1≡C2 and C≡C5 bonds, respectively.

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, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$.

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_{iso}(H) = 1.5U_{eq}(C).

Data collection: APEX2 (Bruker, 2008); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Bruno et al., 2002); software used to prepare material for publication: publCIF (Westrip, 2010).

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