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(η^4-Norbornadiene)bis(tetrahydrofuran-κO)-rhodium(I) tetrafluoroborate

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Key indicators

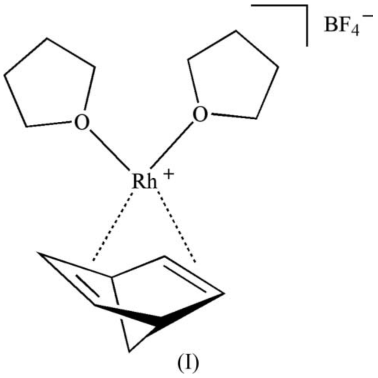
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 20.3

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

The title complex, $[Rh(C_7H_8)(C_4H_8O)_2]BF_4$, contains a rhodium(I) centre coordinated in a square-planar manner by two tetrahydrofuran molecules and the mid-points of the double bonds of an η^4-coordinated norbornadiene ligand.

Comment

Although solvent complexes of rhodium have long been recognized as important species in homogeneous hydrogenation (Schrock & Osborn, 1971; Landis & Halpern, 1987), few examples relevant to hydrogenation processes have been structurally characterized by X-ray crystallography because of their inherent lability (Weller *et al.*, 2000; Werner *et al.*, 2000). The same is true for the corresponding substrate complexes (Schmidt *et al.*, 2005). Here we report the crystal structure of the complex $[(NBD)Rh(THF)_2]BF_4$ (NBD = norbornadiene; Fig. 1), (I), which represents the second isolated and structurally characterized mononuclear bis-THF complex of Rh to date. While the THF solvate published by Weller *et al.* (2000) was reported to suffer from twinning and solvent loss, we were pleased to find that the quality of the crystal examined by us was very good. Rhodium is in a square-planar environment, the deviation from the least-square plane formed by the atoms O1 and O2 and the mid-points of the C9—C10 and C12—C13 bonds being 0.008 (1) Å. The donor double bonds show lengths of 1.419 (4) and 1.410 (4) Å, which are in the middle of the range for analogous complexes [range from 1.153 to 1.551 Å with a mean of 1.383 Å according to a database search (Cambridge Structural Database; Version 5.28, November 2006; Allen, 2002) performed on the 'Rh(NBD)' fragment; number of hits 196].



(I)

The Rh—O bonds were found to be both of similar lengths [2.155 (2) and 2.163 (2) Å], while in the $[(COD)Rh(THF)_2]$ analogue examined by Weller *et al.* (2000) one was found to be significantly shorter [2.135 (6) Å at 100 K], which might be ascribed to the different counter-ions. The THF ligands are coordinated *via* the lone pair of electrons as indicated by the bond angles at the O atoms (Table 1).

Experimental

The synthesis of $[(NBD)_2Rh]BF_4$ followed the procedure of Fryzuk & Bosnich (1977). $[(NBD)RhCl]_2$ (842 mg, 1.827 mmol) and $AgBF_4$ (712 mg, 3.655 mmol) were dissolved in 15 ml of dichloromethane and 0.4 ml of NBD were added. The solution was stirred at room temperature for 1 h. The precipitated AgCl was filtered off and THF (15 ml) was added. The dichloromethane was removed under vacuum, whereupon solid $[(NBD)_2Rh]BF_4$ precipitated, which was filtered off (1.112 g, 2.973 mmol). The mother liquor was concentrated *in vacuo* and stored at room temperature in a Schlenk flask under nitrogen for about two weeks, after which single crystals of the title compound had formed.

Crystal data

$[Rh(C_7H_8)(C_4H_8O)_2]BF_4$
$M_r = 426.06$
Monoclinic, $P2_1/c$
$a = 12.010$ (6) Å
$b = 9.580$ (5) Å
$c = 17.098$ (7) Å
$\beta = 121.20$ (3)°
$V = 1682.7$ (14) Å^3
$Z = 4$
$D_x = 1.682$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.06$ mm^{-1}
$T = 110$ (2) K
Block, yellow
0.70 × 0.52 × 0.48 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.524$, $T_{max} = 0.630$
20904 measured reflections
4213 independent reflections
3563 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 28.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.00$
4213 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.35$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—C9	2.101 (3)	Rh1—O1	2.155 (2)
Rh1—C10	2.108 (3)	Rh1—O2	2.163 (2)
Rh1—C12	2.112 (3)	C9—C10	1.419 (4)
Rh1—C13	2.125 (3)	C12—C13	1.410 (4)
C9—Rh1—C10	39.40 (11)	C13—Rh1—O1	159.89 (9)
C9—Rh1—C12	81.20 (10)	C9—Rh1—O2	157.48 (10)
C10—Rh1—C12	68.04 (10)	C10—Rh1—O2	161.05 (10)
C9—Rh1—C13	67.73 (10)	C12—Rh1—O2	100.69 (9)
C10—Rh1—C13	81.31 (11)	C13—Rh1—O2	99.54 (9)
C12—Rh1—C13	38.87 (11)	C1—O1—Rh1	122.39 (15)
C9—Rh1—O1	99.09 (9)	C4—O1—Rh1	118.98 (16)
C10—Rh1—O1	98.20 (9)	C5—O2—Rh1	123.79 (17)
C12—Rh1—O1	158.09 (9)	C8—O2—Rh1	122.86 (16)

H atoms were placed in calculated positions and refined using a riding model with C—H distances of 0.98–0.99 Å and $U_{iso}(H) = 1.3U_{eq}(C)$. The highest residual electron-density peaks are close to the F atoms of the tetrafluoroborate counter-anion.

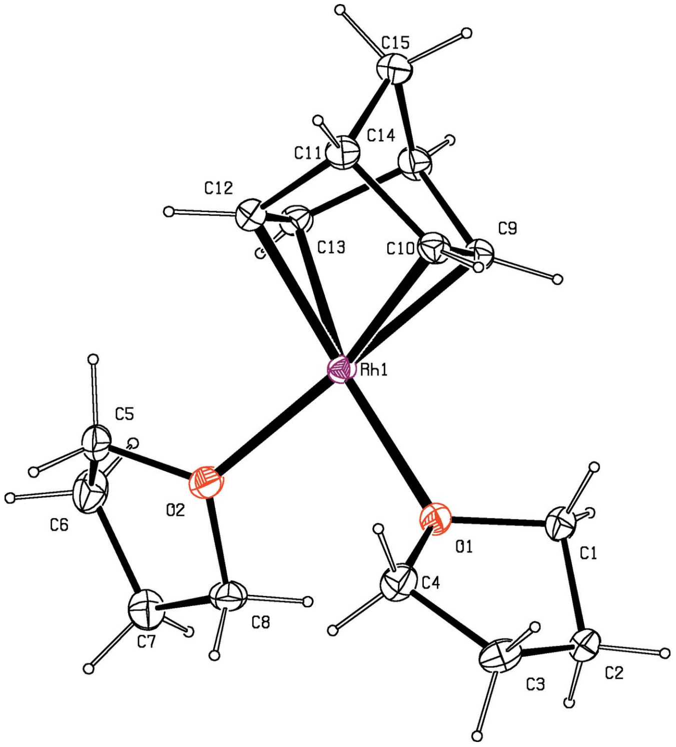


Figure 1
The structure of the cation of (I), with displacement ellipsoids drawn at the 30% level. The BF_4^- anion is not shown for clarity. H atoms are drawn with arbitrary radius.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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m518 Braun *et al.* • $[Rh(C_7H_8)(C_4H_8O)_2]BF_4$ *Acta Cryst.* (2007). E**63**, m517–m518