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Aqua(η^4-1,5-cyclooctadiene)[1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole]rhodium(I) tetrafluoroborate

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Key indicators

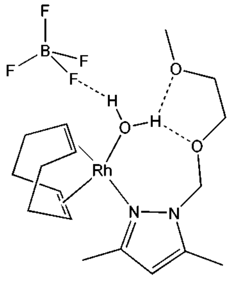
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.043
wR factor = 0.117
Data-to-parameter ratio = 15.7

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

The title complex, $[Rh(C_8H_{12})(C_9H_{16}N_2O_2)(H_2O)](BF_4)$ or $[RhL(COD)(H_2O)](BF_4)$, is a monomer in the solid state. The Rh^I centre is in a square-planar arrangement. The four coordination sites are occupied by the N atom of the pyrazole ligand, the O atom from a water molecule and the centroids of the two cyclooctadiene olefin bonds. The structure is stabilized by hydrogen bonds between the coordinated water molecule and the two O atoms of the ether groups of the pyrazole ligand and one of the F atoms of the BF_4 unit.

Comment

The organic compound 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (L) is a potential polydentate ligand that can coordinate to a metal centre by the unsubstituted N atom and by the O atoms of the ether groups. The reactivity of this ligand toward $[RhCl(COD)]_2$ has been investigated with the aim of proving its chelating ability. This led to the formation of the title compound, $[RhL(COD)(H_2O)](BF_4)$, (I).



(I)

The rhodium complex has a square-planar geometry (Fig. 1 and Table 1), the metal centre being linked to the four olefin C atoms of the 1,5-cyclooctadiene ligand, to the non-substituted N atom of the pyrazole ring, and to the O atom of a coordinated water molecule. The Rh atom lies 0.0052 (3) Å out of the coordination plane. It thus appears that L acts as a monodentate ligand, since the O atoms of the ether groups do not participate in the ligation to the metal centre. Intramolecular hydrogen bonds are observed between atoms O10 and O13 of the pendant ether arm and the coordinated water molecule [O10$\cdots$H1a = 2.64 (3) Å and O13$\cdots$H1a = 1.89 (2) Å]. As a result of these intramolecular interactions, a stable seven-membered ring including Rh1 is formed. In addition, a hydrogen bond between one of the F atoms of the BF_4 unit and the water molecule is also observed [F4$\cdots$H1b = 1.91 (2) Å]. The Rh1—N2 bond length in (I) [2.103 (3) Å] is equal, within experimental error, to the Rh—N bond length

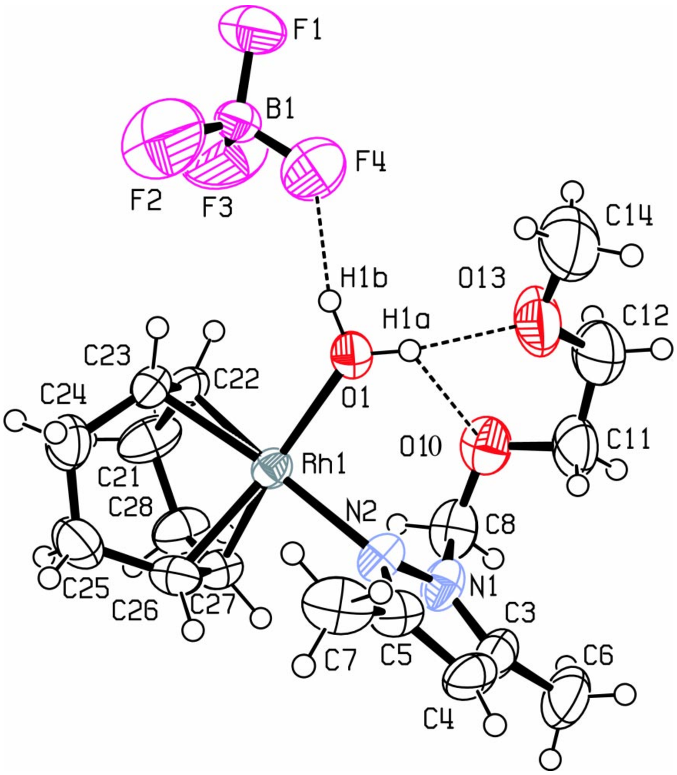


Figure 1
The structure of the title compound, showing the numbering scheme, with displacement ellipsoids drawn at the 30% probability level.

[2.109 (9) Å] found in the parent compound [Rh(COD)Cl(dmpz)] (dmpz = 3,5-dimethylpyrazole) (Decker *et al.*, 1983). This Rh—N distance is also comparable to other reported values for Rh complexes containing 1,5-cyclooctadiene and pyrazole chelate ligands [2.097 (7)–2.216 (8) Å; Oro *et al.*, 1984; Schnyder *et al.*, 1997; Mathieu *et al.*, 2001; Boixassa *et al.*, 2003]. The Rh1—O1 bond length in (I) [2.127 (3) Å] compares well with the corresponding Rh—O$_{\rm water}$ distances in several Rh$^{\rm I}$–aqua complexes found in the literature, including [Rh(PPh$_3$)$_2$(CO)(H$_2$O)]$^+$·ClO$_4^-$·CH$_2$Cl$_2$ [2.127 (4) Å; Cross *et al.*, 1993]. Finally, as observed in the crystal structure of the parent complex [RhCl(COD)(dmpz)] (Decker *et al.*, 1983), the mean plane of the heterocycle is almost perpendicular to the Rh coordination mean plane [89.83 (13)°].

Experimental

The ligand 1-(2-methoxyethoxymethyl)-3,5-dimethylpyrazole (*L*) was synthesized by dropwise addition of methoxyethoxymethyl chloride (2.47 g, 19 mmol) to a solution of 3,5-dimethylpyrazole (1.68 g, 17 mmol) in dichloromethane (15 ml) at 273 K, in the presence of triethylamine (2.71 g, 27 mmol). The mixture was stirred for 30 min at room temperature. The ammonium salt and the amine were extracted with water (2 × 15 ml). The organic phase was dried over anhydrous sodium sulfate. The dichloromethane was removed under reduced pressure, yielding *L* as a pale yellow oil (yield: 3.03 g, 95%). The title compound, (I), was prepared as follows: AgBF$_4$ (0.065 g, 0.34 mmol) was added to a solution of [RhCl(COD)]$_2$ (0.082 g, 0.17 mmol) in tetrahydrofuran (20 ml). After stirring for 30 min, the white precipitate of AgCl was filtered off. To the filtered yellow solution, *L* (0.061 g, 0.34 mmol) was added. The solution was stirred overnight at room temperature. The solvent was then removed under reduced pressure, yielding a yellow oil. The oil was dissolved in a dichloromethane/diethyl ether mixture and small yellow crystals of the complex [Rh*L*(COD)(H$_2$O)](BF$_4$) were obtained upon standing at room temperature. ^{1}H NMR (250 MHz, CDCl$_3$, p.p.m.): δ 6.05 (*s*, 2H, NCH$_2$O), 5.93 [*s*, 1H, CH (pyrazole)], 4.07 (*br*, 2H, H$_2$O), 3.75 [*br*, 4H, CH (COD)], 3.70 (*m*, 2H, OCH$_2$), 3.49 (*m*, 2H, OCH$_2$), 3.25 (*s*, 3H, OCH$_3$), 2.76 (*s*, 3H, CCH$_3$), 2.51 [*b*, 4H, CH$_2$ (COD)], 2.32 (*s*, 3H, CCH$_3$), 1.80 [*m*, 4H, CH$_2$ (COD)]. ^{13}C NMR (62.9 MHz, CDCl$_3$, p.p.m.): δ 151.9 (CCH$_3$), 144.9 (CCH$_3$), 108.4 [CH (pyrazole)], 78.1 [CH (COD)], 77.4 (NCH$_2$O), 71.5 (OCH$_2$), 68.3 (OCH$_2$), 59.1 (OCH$_3$), 30.5 [CH$_2$ (COD)], 14.8 (CH$_3$), 11.6 (CH$_3$). Analysis calculated for C$_{17}$H$_{30}$BF$_4$N$_2$O$_3$Rh (M_r = 500.15) (%): C 40.82, H 6.05, N 5.60; found: C 40.39, H 6.16, N 5.35.

Crystal data

[Rh(C$_8$H$_{12}$)(C$_9$H$_{16}$N$_2$O$_2$)(H$_2$O)](BF$_4$)
M_r = 500.15
Monoclinic, $P2_1/c$
a = 10.0023 (10) Å
b = 23.2203 (17) Å
c = 9.2977 (10) Å
β = 102.368 (12)°
V = 2109.3 (4) Å^3
Z = 4
D_x = 1.575 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.1–26.1°
μ = 0.86 mm^{-1}
T = 293 (2) K
Block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: refined from ΔF (Parkin *et al.*, 1995)
$T_{\rm min}$ = 0.776, $T_{\rm max}$ = 0.837
16245 measured reflections
4070 independent reflections
3630 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\rm max}$ = 26.1°
$h = -12 \rightarrow 12$
$k = -28 \rightarrow 27$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 0.99
4070 reflections
260 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 4.0982P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.90 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—O1	2.123 (3)	Rh1—C23	2.127 (3)
Rh1—N2	2.103 (3)	Rh1—C26	2.104 (4)
Rh1—C22	2.126 (4)	Rh1—C27	2.101 (4)
O1—Rh1—N2	88.99 (12)	C23—Rh1—C27	96.61 (15)
O1—Rh1—C22	94.45 (14)	C26—Rh1—C27	38.77 (16)
O1—Rh1—C23	90.33 (13)	Rh1—N2—N1	123.1 (2)
O1—Rh1—C26	158.08 (15)	Rh1—N2—C5	130.1 (3)
O1—Rh1—C27	163.13 (14)	Rh1—C22—C21	112.4 (3)
N2—Rh1—C22	159.22 (13)	Rh1—C22—C23	71.1 (2)
N2—Rh1—C23	162.80 (13)	Rh1—C23—C22	71.0 (2)
N2—Rh1—C26	92.26 (15)	Rh1—C23—C24	110.9 (3)
N2—Rh1—C27	88.83 (14)	Rh1—C26—C25	112.6 (3)
C22—Rh1—C23	37.89 (15)	Rh1—C26—C27	70.5 (2)
C22—Rh1—C26	92.09 (16)	Rh1—C27—C26	70.7 (2)
C22—Rh1—C27	81.95 (15)	Rh1—C27—C28	111.7 (3)
C23—Rh1—C26	82.09 (16)		

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$a\cdots$O10	0.852 (18)	2.64 (3)	3.166 (4)	121 (3)
O1—H1$a\cdots$O13	0.852 (18)	1.89 (2)	2.729 (5)	167 (4)
O1—H1$b\cdots$F4	0.845 (18)	1.91 (2)	2.731 (5)	164 (4)

H atoms attached to C atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH_2) and 0.97 Å (CH_3), and an isotropic displacement parameter equal to 1.2 times U_{eq} of the parent atom. The H atoms of the water molecule were located at the final stage of the refinement using the program *HYDROGEN* (Nardelli, 1999); their isotropic displacement parameters were set to 1.2 times U_{eq} of the O atom and they were held fixed during the final refinement.

Data collection: *IPDS* (Stoe & Cie, 2000); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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