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Tricarbonyl(η^5-cyclopentadienyl)-(trifluorohydroxyborato)tungsten

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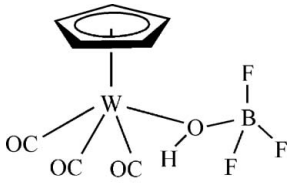
The title compound, $[W(C_5H_5)(HOBF_3)(CO)_3]$, has a four-legged piano-stool geometry which is typically found for $C_5H_5W(CO)_3X$ complexes. The $HOBF_3^-$ anion is the hydrolysis product of BF_4^- and is coordinated *via* oxygen.

Comment

$[C_5H_5W(CO)_3]BF_4$ was first described by Beck *et al.* (1978) and used as a reactive intermediate (Werner *et al.*, 1987). All attempts to crystallize $[(C_5H_5)W(CO)_3]BF_4$ for X-ray diffraction failed and the compound was described as extremely sensitive towards hydrolysis (Appel *et al.*, 1987; Beck *et al.*, 1989). We were able to obtain crystals of the first reaction product in the hydrolytic process for $[(C_5H_5)W(CO)_3]BF_4$ that has been described before for the hydrolysis of $[(C_5H_5)W(CO)_3]BF_4$ to $(CO)_5ReFBF_3$ (Raab *et al.*, 1981).



(I)

The crystal structure analysis showed that the $HOBF_3$ ligand is coordinated through the O atom (Fig. 1). The W—O distance of 2.155 (3) Å is significantly shorter than the W—O distance for coordinated water in $(CO)_3(P^iPr_3)_2WOH_2$ of 2.320 (5) Å (Kubas *et al.*, 1992) and even shorter than the W—O distance for coordinated water in $H_2(\eta^1\text{-}O_2CBu^t)_2(PMe_3)_3WOH_2$ of 2.224 (2) Å (Zhu *et al.*, 2005). It is in the same range as the coordinated $HOBF_3^-$ anion in $(CO)_5ReO(H)BF_3$ with an Re—O distance of 2.167 Å (Beck *et al.*, 1986). The $HOBF_3$ ligands of the title compound interact *via* an O—H···F hydrogen bond hydrogen bond which links the molecules into extended zigzag chains that run parallel to the [010] direction (Table 2 and Fig. 2).

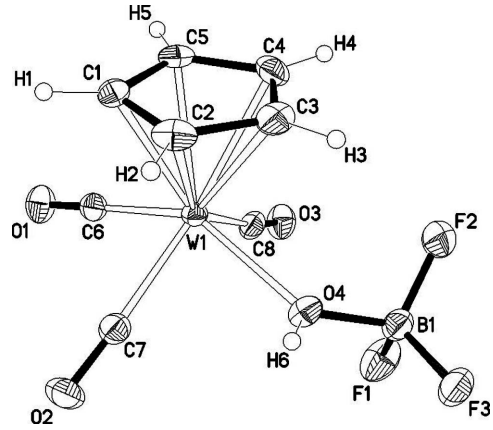


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

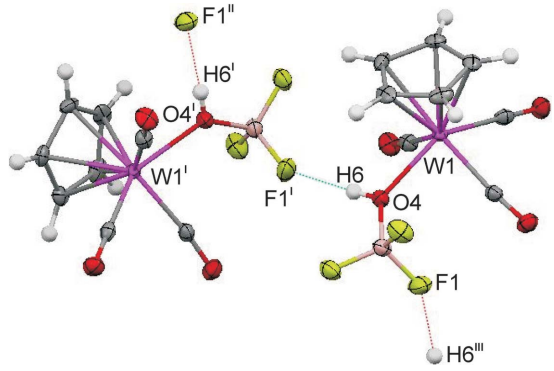


Figure 2
View of the interactions of anions *via* hydrogen bonding. [Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y+1, z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.]

In an initial structure model, a weakly coordinating BF_4^- anion was assumed rather than the hydrolysis product $HOBF_3^-$. After convergence of the refinement at apparently convincing agreement factors, however, both the B—F distance and the displacement parameters (see *Refinement* section) indicated that the atom bridging W and B could be better refined as oxygen. When the bridging atom was modelled as an F atom, its distance from boron [1.485 (5) Å] was significantly longer than B—F distances found in the Cambridge Structural Database (Version 5.31; CSD; Allen, 2002) for tetrafluoroborate anions bound to metal centres *via* F [1.398 (23) Å] as observed for example in $[CuL_2O(H)BF_3]BF_4$ (where L is 6-methyl-2,2′-bipyridine) containing both types of ligands discussed (Onggo *et al.*, 1991). In the correct model, the B1—O4 distance [1.474 (5) Å] is nearly the same as the B—O distance in $(CO)_5ReO(H)BF_3$ (1.476 Å) (Beck *et al.*, 1986). IR spectra of the bulk material show a broad ν(OH) band, indicating that the crystallizing product is only $C_5H_5W(CO)_3O(H)BF_3$.

For the cyclopentadienyl ligand, a slip distortion (distance of the W atom projection on the ring plane from the ring centre of gravity) of 0.106 Å is observed, with shorter metal–carbon bonds to C1 and C5, and longer W—C2, W—C3 and W—C4 distances (Table 1). The cyclopentadienyl (Cp) ligand

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is tilted due to the strong *trans* effect of the CO ligands, as described previously for $[Et_4N][C_5H_5Mo(CO)_2(\eta^2\text{-}O_2CO)]$ (Curtis & Han, 1985) and $[C_5H_5TaCl_2(CO)_2(THF)]$ (THF is tetrahydrofuran) (Kwon & Curtis, 1990). This effect has also been explained theoretically (Chinn *et al.*, 1983).

Experimental

The synthesis was carried out by the reaction of $Cp(CO)_3WCH_3$ with $HBF_4{\cdot}OEt_2$ (1:2 molar ratio) in CH_2Cl_2 for 30 min at 253 K. A deep-red solution was formed immediately. The solvent was reduced at room temperature and red–orange crystals suitable for X-ray diffraction formed in 20% yield [m.p. 407 K (decomposition)]. IR [ATR (attenuated total reflection) technique using a diamond crystal, cm^{-1}]: CO ligands: 2083 (*s*), 2017 (*s*), 1969 (*s*); $HOBF_3^-$ anion: 3401 (*br*), 1083 (*m*).

Crystal data

$[W(C_5H_5)(HOBF_3)(CO)_3]$
M_r = 417.79
Monoclinic, $P2_1/n$
a = 10.7679 (17) Å
b = 8.5489 (14) Å
c = 11.4313 (18) Å
β = 95.297 (2)°
V = 1047.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 11.07 mm^{-1}
T = 100 K
0.14 × 0.12 × 0.06 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.345, T_{max} = 0.437
12253 measured reflections
2507 independent reflections
2289 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.043
S = 1.03
2507 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

In an initial structure model, a weakly coordinated BF_4^- anion was assumed rather than the hydrolysis product $HOBF_3^-$. After convergence of the refinement at apparently convincing agreement factors, however, both the B1—F distance and displacement parameters show that atom X bridging W and B could be better refined as oxygen. In the initial tetrafluoroborate model, the B—X distance of 1.485 (5) Å was significantly longer than the B—F distances found in the CSD for tetrafluoroborate anions bonded to metals by F [metal-F—BF_3 = 1.398 (23) Å], and much longer than the terminal B—F distances [1.370 (31) Å]. When X was refined as fluorine, a displacement parameter significantly larger than expected was obtained [U_{iso}(W1) = 0.01394 (6) Å^2, $U_{iso}(X)$ = 0.0374 (7) Å^2 and U_{iso}(B1) = 0.0226 (10) Å^2], and two rigid-bond alerts were obtained in connection with these displacement parameters (Spek, 2009): PLAT230_ALERT_2_C Hirshfeld Test Diff for F—B1 6.63 su and PLAT232_ALERT_2_C Hirshfeld Test Diff (M—X) W1—F 9.52 su. According to the rigid-bond postulate, the components of the anisotropic displacement parameters along chemical bonds are assumed to be equal in magnitude. Large differences supposedly indicate contamination of these parameters with other effects. Atomic sites assigned the wrong scattering type (*e.g.* Ag *versus* Br) should generate 'problem signals' with this test (Hirshfeld, 1976).

Table 1
Selected geometric parameters (Å, °).

W1—O4	2.155 (3)	W1—C3	2.363 (4)
W1—C5	2.271 (4)	O4—B1	1.474 (5)
W1—C1	2.274 (3)	F1—B1	1.397 (5)
W1—C2	2.323 (4)	F2—B1	1.380 (5)
W1—C4	2.347 (4)	F3—B1	1.376 (5)
B1—O4—W1	131.2 (2)	B1—O4—H6	120 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H6···F1^{i}	0.77 (5)	1.94 (5)	2.708 (4)	177 (6)

Symmetry code: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

After correctly assigning the atomic scattering factor for O to X, the following results were obtained: (*a*) the displacement parameter for X became unexceptional [$U_{iso}(X)$ = 0.0217 (6) Å^2]; (*b*) a local electron-density maximum, peak No. 5, represented the missing hydroxy H atom; free refinement of this atom resulted in reasonable geometry and an intermolecular hydrogen bond; (*c*) agreement factors R and $wR2$ improved (0.0201 *versus* 0.0208 and 0.043 *versus* 0.046, respectively); (*d*) the distance pattern became normal for $HOBF_3$ coordinated to metal (in the CSD, the average B—O distance is 1.472 Å); and (*e*) the above-mentioned rigid-bond alerts disappeared.

The Cp H atoms were refined in calculated positions, riding on C atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The OH hydrogen was located in a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3068). Services for accessing these data are described at the back of the journal.

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