

Dichlorobis[2-(3,5-dimethylpyrazolyl-1-carbonyl)-furan]palladium(II) bis[aquatris(pentafluorophenyl)-boron] dihydrate dichloromethane disolvate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.030
wR factor = 0.085
Data-to-parameter ratio = 14.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Reaction of the Pd complex $[(3,5\text{-Me}_2\text{pz-CO-furan})_2\text{PdCl}_2]$ (where pzH is pyrazole) and the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of adventitious water resulted in the formation of the title compound, $[\text{PdCl}_2(\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2)_2] \cdot 2\text{C}_{18}\text{HBF}_{15}\text{O}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_2\text{Cl}_2$, in 60% yield. The Pd complex occupies a crystallographic inversion center and exhibits a square-planar geometry. The two proposed dichloromethane molecules in the formula are highly disordered.

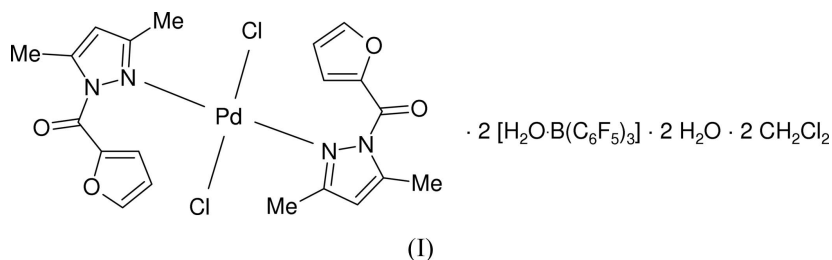
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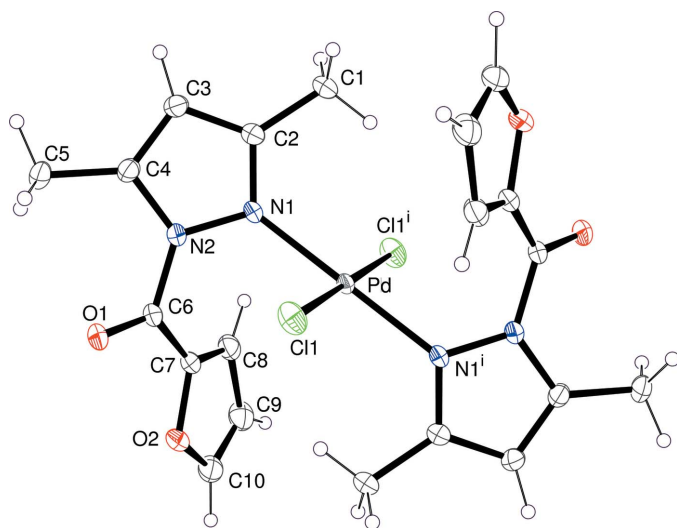
Comment

Late transition metal olefin oligomerization and polymerization catalysts have recently attracted significant attention, since Brookhart *et al.* (1995) discovered that the electrophilicity of metal centers plays a significant role in their catalytic activity and that cationic α -diimine Ni^{II} and Pd^{II} catalysts facilitate olefin coordination prior to their insertion and subsequent chain growth. Results reported by Bazan and co-workers (Komon *et al.*, 2000*a,b*, 2003; Lee *et al.*, 2001) demonstrated the impact of carbonyl coordination to borane in either $\text{B}(\text{C}_6\text{F}_5)_3$ or BF_3 on the catalytic activity of the Shell higher olefin process type catalysts, such as $[(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{-C}(\text{O})\text{O}-\kappa\text{P},\text{O}]\text{Ni}(\nu\text{-CH}_2\text{CMeCH}_2)$ (Keim, 1990).



As part of our investigation of pyrazolyl (pz)–palladium(II) complexes as olefin oligomerization and polymerization catalysts (Guzei *et al.*, 2003, Ojwach *et al.*, 2005), we attempted to improve the ethylene polymerization activity of the dichlorobis[2-(3,5-dimethylpyrazolyl-1-carbonyl)furan]palladium(II) complex by forming a borane adduct of this complex with $\text{B}(\text{C}_6\text{F}_5)_3$, in which the carbonyl O atom binds to the B atom of $\text{B}(\text{C}_6\text{F}_5)_3$.

Unexpectedly, the title compound, (I) was isolated, a result that emphasizes the need for absolutely dry synthesis conditions. The Pd complex in (I) (Fig. 1) occupies a crystallographic inversion center and exhibits a square-planar geometry. The most interesting geometrical feature is the displacement of the Pd atom from the plane of the pyrazole ring by 0.697 (3) Å. Thus, the lone pair of electrons of atom N1 of the pz ligand donates electrons to the Pd atom at

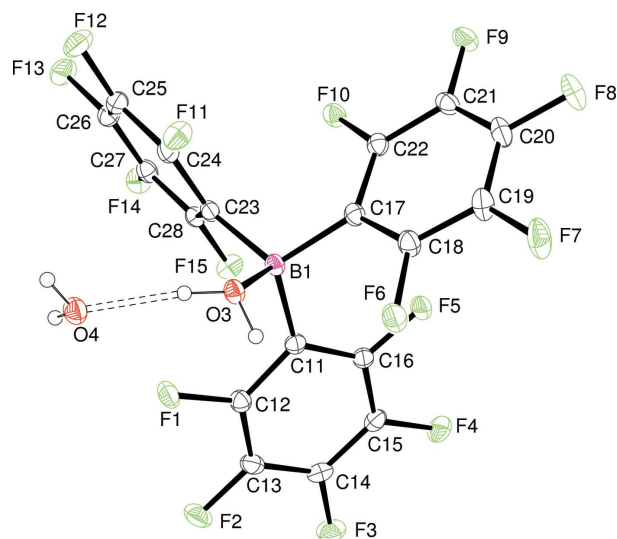
**Figure 1**

The molecular structure of the main molecule of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). (Symmetry code as in Table 1.)

approximately a 20° angle rather than linearly. The Pd–Cl bond in (I) [2.3014 (5) Å; Table 1] is somewhat shorter than the average of 2.33 (4) Å calculated for 2151 Pd–Cl distances in 1306 complexes reported to the Cambridge Structural Database (CSD; Version 5.26, updated May 2005; Allen, 2002). The Pd–Cl distances in these 1252 complexes span the range 2.222–2.516 Å; therefore, the Pd–Cl separation in (I) is within the expected range. The Pd–N bond length in (I) [2.0225 (15) Å] agrees well with the average bond length of 2.03 (4) Å calculated for 214 Pd–N_{pz} bond lengths in 88 complexes reported to the CSD, and falls in the middle of the range for this type of bond (1.928–2.189 Å). The B atom of the tris(pentafluorophenyl)borane–water adduct exhibits a tetrahedral geometry. The B–C bond lengths are normal and the B–OH₂ length of 1.576 (2) Å agrees well with the average of the eight such compounds reported in the CSD [1.57 (3) Å]. Usually, the B–OH and B–OR lengths are shorter and the presence of a water molecule rather than a hydroxy group is chemically reasonable. There are hydrogen-bonding interactions between the borane–water adduct and the uncoordinated water molecules (Fig. 2 and Table 2).

Experimental

To a solution of Pd(3,5-Me₂Pz-CO-furan)₂Cl₂ (0.12 g, 0.22 mmol) in cold toluene (20 ml, 273 K) was added B(C₆F₅)₃ (0.12 g, 0.22 mmol). The mixture was stirred for 2 h to give an orange precipitate. After the reaction period, the mixture was filtered and the residue recrystallized from CH₂Cl₂–hexane at 269 K to give single crystals of (I) suitable for single-crystal X-ray analysis. Yield 0.21 g, 60%. ¹H NMR (CDCl₃): δ 2.24 (s, 6H, CH₃, pz), 2.54 (s, 6H, CH₃, pz), 6.09 (s, 1H, pz), 6.79 (dd, 2H, furan, ³J_{HH} = 3.8 Hz, ⁴J_{HH} = 1.8 Hz), 7.60 (dd, 2H, furan, ³J_{HH} = 3.8 Hz, ⁴J_{HH} = 1.6 Hz), 7.88 (dd, 1H, furan, ³J_{HH} = 3.8 Hz, ⁴J_{HH} = 1.6 Hz); IR (Nujol): ν(C=O) 1694. Analysis calculated for C₅₆H₂₄B₂Cl₂F₃₀N₄O₆Pd·2H₂O·CH₂Cl₂: C 38.20, H 1.77, N 3.07; found: C 39.75, H 1.52, N 4.00%.

**Figure 2**

Detail of (I), showing the interactions involving the B(C₆F₅)₃ and H₂O molecules, and one hydrogen-bonding interaction as a dashed line (30% probability displacement ellipsoids, arbitrary spheres for the H atoms).

Crystal data

[PdCl₂(C₁₀H₁₀N₂O₂)₂]
·2C₁₈HBF₁₅O₂·2H₂O·2CH₂Cl₂
M_r = 1823.60
Triclinic, *P* $\bar{1}$
a = 10.4595 (4) Å
b = 12.5105 (5) Å
c = 13.6969 (6) Å
 α = 81.169 (1) $^\circ$
 β = 77.571 (1) $^\circ$
 γ = 83.037 (1) $^\circ$
V = 1722.30 (12) Å³

Z = 1
D_x = 1.758 Mg m⁻³
Mo *K*α radiation
Cell parameters from 9311 reflections
 θ = 2.0–26.4 $^\circ$
 μ = 0.64 mm⁻¹
T = 173 (2) K
Block, red
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1000 CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
*T*_{min} = 0.78, *T*_{max} = 0.88
14381 measured reflections

6976 independent reflections
6381 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.016
 θ _{max} = 26.4 $^\circ$
h = −13 → 13
k = −15 → 15
l = −17 → 17

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.030
wR (*F*²) = 0.085
S = 1.07
6976 reflections
482 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.5736P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.55 e Å⁻³
Δρ_{min} = −0.46 e Å⁻³

Table 1

Selected geometric parameters (Å, $^\circ$).

Pd–N1	2.0225 (15)	Pd–Cl1	2.3014 (5)
N1–Pd–Cl1 ⁱ	92.04 (5)	N1–Pd–Cl1	87.96 (5)

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H4...O4	0.82 (2)	1.78 (2)	2.5968 (18)	172 (3)
O3—H3...O4 ⁱⁱ	0.84	1.87	2.682 (2)	161
O4—H5...O1 ⁱⁱⁱ	0.82 (2)	1.96 (2)	2.773 (2)	174 (3)

Symmetry codes: (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x - 1, y + 1, z$.

Disordered solvent molecules are present in (I). A significant amount of time was invested in identifying and refining the disordered molecule. Bond length restraints were applied to model the molecules but the resulting isotropic displacement coefficients suggested that the molecule was mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of PLATON (Spek, 2003) was used to correct the diffraction data for disordered scattering effects and to identify the solvent molecule. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 289 Å³, or 17% of the unit-cell volume. The program calculated 105 electrons in the unit cell for the diffuse species. This approximately corresponds to two molecules of toluene in the unit cell (100 electrons) or two molecules of dichloromethane (84 electrons). Note that, while the former possible solvent is closer in the electron count, the latter better corresponds to the results of the elemental analysis and is assumed to be the case here. All H atoms bound to C atoms were placed in idealized locations and refined as riding, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic C atoms, and C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups. One of the H atoms on O3 was treated as riding, with O—H = 0.84 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$; for other H atoms attached to atoms O4 and

O3, O—H distances were restrained to 0.82 Å and U_{iso} values were independently refined.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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