

***trans*-Bis[3,5-bis(trifluoromethyl)-1*H*-pyrazole- κ N²]dichloropalladium(II) monohydrate**Lara C. Spencer,^a Ilia A. Guzei,^{a*} Stephen O. Ojwach^b
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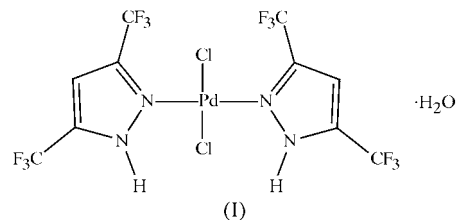
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The palladium(II) center in the title compound, *trans*-[PdCl₂-(C₅H₂F₆N₂)₂].H₂O, possesses a distorted square-planar geometry. The NH groups are positioned on the same side of the PdN₂Cl₂ coordination plane. Four symmetry-independent strong hydrogen bonds of three types (N—H...Cl, N—H...Cl and O—H...Cl) hold the structure together.

Comment

Since the seminal discovery that late transition metal α -diimine complexes oligomerize or polymerize α -olefins (Brookhart *et al.*, 1995) there has been an intensive search for other nitrogen-based late transition metal complexes that can also catalyze olefin oligomerization and polymerization with improved catalyst performance (Mecking, 2000). The key highlights of Brookhart-type catalysts are electrophilicity of the catalyst's metal center, which facilitates olefin coordination, and steric bulk of the ligand backbone, which determines the formation of oligomers or polymers (Ittel *et al.*, 2000; Gibson & Spitzmesser, 2003). Recently, we reported that pyrazole nickel, [NiBr₂(3,5-*R*₂pzH)₂] (Nelana *et al.*, 2004), and pyrazole palladium, [PdCl₂(3,5-*R*₂pzH)₂] (Li *et al.*, 2002) (*R* = H, Me and 'Bu), complexes form active ethylene polymerization catalysts. In an attempt to enhance the electrophilicity of the metal center to achieve greater catalytic activity, we synthesized the title compound, (I), bearing the electron-withdrawing CF₃ substituents. It was presumed that the CF₃ groups would reduce the donor ability of the pyrazole ligand, resulting in an electron-deficient metal center in the catalyst formed, thereby giving greater catalytic activity. However, our preliminary density functional theory (DFT) studies did not confirm this assumption; attempts to activate compound (I) with methylaluminoxane (MAO) to produce an active olefin polymerization catalyst resulted in the decomposition of (I). We report here the synthesis and structure of (I).

The Pd complex (I) (Fig. 1) exhibits a distorted square-planar geometry. The pyrazole ligands are *trans* to each other



and the NH groups are on the same side of the Pd coordination plane. Both pyrazole groups are tilted to the same side relative to the plane but to different degrees, displaying Cl1—Pd—N1—N2 and N4—N3—Pd—Cl1 torsion angles of 112.33 (13) and 98.51 (14)°, respectively; the two planar pyrazole rings have an interplanar angle of 22.09 (11)°. Of 14 relevant complexes found in the Cambridge Structural Database (hereafter CSD; Version 5.27, update of May 2006; Allen, 2002), only four complexes have torsion angles that correspond to the pyrazole rings being tilted to the same side relative to the coordination plane but to different extents, sometimes differing by up to 8°. The related compound [PdCl₂(3,5-*t*Bu₂pzH)₂].CH₂Cl₂ (Li *et al.*, 2002) has angles of 77.2 and 84.9°. In all of these compounds, the substituent on the non-coordinating N atom of the pyrazole rings was a H atom. The remaining ten complexes have the pyrazole rings residing on opposite sides of the metal coordination plane. All of these compounds, such as *trans-anti*-dichlorobis{1-[2-(methoxy)ethoxymethyl]-3,5-dimethylpyrazole- κ N}palladium(II), with torsion angles of 77.6 and -102.4° (Boixassa *et al.*, 2003a), have groups other than hydrogen attached to the non-coordinated pyrazole N atom. The ligand–metal–ligand angles larger than 90° involving Cl1 may be due to steric crowding as two CF₃ groups are directed toward that Cl atom.

Both the Pd—Cl bond lengths in (I) (Table 1) compare well in length to the average Pd—Cl separation of 2.30 (2) Å calculated for 471 complexes reported in the CSD. Within compound (I), the Pd—Cl₂ bond length is statistically signif-

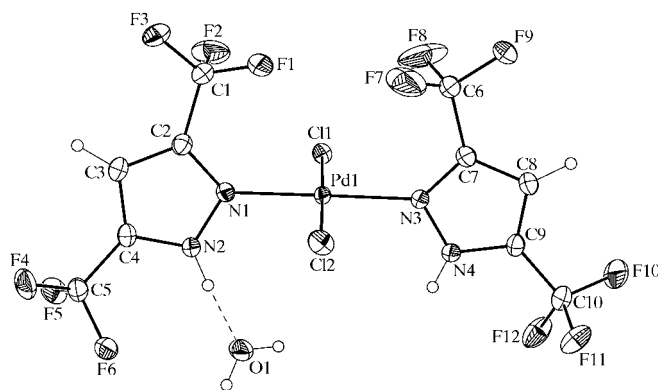


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids. The dashed lined indicates a hydrogen bond.

icantly shorter than the Pd—Cl1 bond length. The fact that atom Cl1 participates in two different types of hydrogen bonding with the solvent water molecule and the pyrazole NH group while atom Cl2 only participates in hydrogen bonding with the solvent water molecule (see below) may explain this distortion from square-planar geometry. The Pd—N bond lengths [average 2.016 (7) Å] in (I) agree well with the average separation of 2.016 (16) Å calculated for 19 Pd—pyrazole complexes in the CSD and fall within the reported range of 2.001–2.071 Å.

An interesting feature of (I) is that one solvent water molecule per Pd complex is also present in the lattice. While no similar compounds have been reported with solvent water in the lattice, compound [PdCl₂(3,5-^tBu₂pzH)₂] (Li *et al.*, 2002) has been reported as a solvate with either one dichloromethane molecule or one-half of a diethyl ether molecule. *trans*-[PtCl₂(3,5-Me₂pzH)₂] (Boixassa *et al.*, 2003b), which is similar to (I) except that the central atom is platinum and the substituents on the pyrazole rings are methyl groups instead of CF₃ groups, does not include a solvent water molecule and forms a dimer *via* hydrogen bonds between the NH groups and the Cl atoms. The larger CF₃ groups in (I) might prevent dimer formation and leave interstitial cavities in the lattice for the water molecules to occupy.

This water molecule participates in three hydrogen-bonding interactions with the NH atoms of a pyrazole ring and the Cl atoms (Fig. 2 and Table 2). The hydrogen-bonding interaction between the water solvent molecule and the NH group in (I) is significantly stronger, as indicated by a relatively short N···O distance of 2.609 (2) Å, than the hydrogen-bonding interactions for five relevant compounds in the CSD [averaging 2.99 (3) Å]. The N—H···O angle (entry 1 in Table 2) falls

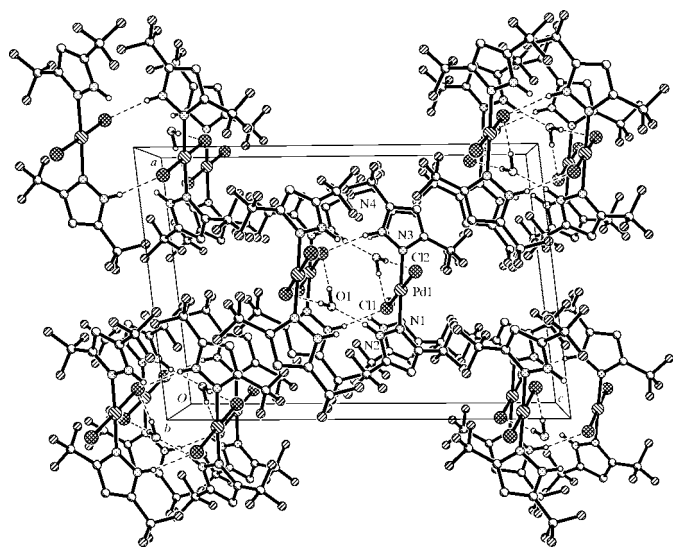


Figure 2
Packing diagram, viewed along the *b* axis, showing the hydrogen-bond interactions. H atoms attached to C atoms have been omitted for clarity. Only several selected atoms are labeled. The details of the hydrogen bonding are in the *Comment* and Table 2.

within the range 150–170° for these five compounds. The O···Cl hydrogen-bonding lengths (entries 2 and 3 in Table 2) are shorter than the average of 3.24 (7) Å found for 16 compounds with similar hydrogen bonds in the CSD and the O—H···Cl bond angles are within the range 152–177° found for these compounds. A fourth intermolecular hydrogen bond, of N—H···Cl type (entry 4 in Table 2), has N···Cl shorter than the range of distances (3.179–3.347 Å) found for 24 complexes with similar hydrogen bonds in the CSD and is significantly stronger than the average of 3.210 (4) Å for the N···Cl distance found in the similar compound [PdCl₂(C₅H₈N₂)₂] (Cheng *et al.*, 1990). Overall, the molecules of (I) participating in hydrogen-bonding interactions are arranged into columns propagating in the *b* direction with no hydrogen-bond links between the columns (Fig. 2).

Experimental

To a solution of 3,5-bis(trifluoromethyl)pyrazole (0.21 g, 1.00 mmol) in CH₂Cl₂ (20 ml) was added a solution of [PdCl₂(NCMe)₂] (0.13 g, 0.50 mmol) in CH₂Cl₂ (20 ml). The orange solution was stirred for 3 h. After the reaction period, hexane (20 ml) was added and the solution kept at 269 K to give orange crystals suitable for single-crystal X-ray analysis (yield 0.18 g, 60%). ¹H NMR (DMSO-*d*₆): δ 7.45 (2H, s, 4H-pz). Analysis calculated for C₁₀H₄Cl₂F₁₂N₄Pd·H₂O: C 19.90, H 1.00, N 9.30%; found: C 19.90, H 1.00, N 9.27%.

Crystal data

[PdCl ₂ (C ₅ H ₂ F ₆ N ₂) ₂]·H ₂ O	Z = 4
<i>M_r</i> = 603.49	<i>D_x</i> = 2.149 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo Kα radiation
<i>a</i> = 12.5046 (5) Å	<i>μ</i> = 1.41 mm ⁻¹
<i>b</i> = 8.1964 (3) Å	<i>T</i> = 100 (2) K
<i>c</i> = 18.3119 (7) Å	Block, orange
<i>β</i> = 96.480 (1)°	0.46 × 0.36 × 0.22 mm
<i>V</i> = 1864.85 (12) Å ³	

Data collection

Bruker SMART CCD 1000 area-detector diffractometer	15027 measured reflections
0.30° <i>ω</i> scans	3807 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	3582 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.564, <i>T</i> _{max} = 0.747	<i>R</i> _{int} = 0.020
	<i>θ</i> _{max} = 26.4°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0295 <i>P</i>) ² + 1.7857 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.020	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.054	(Δ/σ) _{max} = 0.002
<i>S</i> = 1.02	Δρ _{max} = 0.75 e Å ⁻³
3807 reflections	Δρ _{min} = -0.58 e Å ⁻³
277 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Pd1—N1	2.0106 (15)	Pd1—Cl2	2.2748 (5)
Pd1—N3	2.0213 (15)	Pd1—Cl1	2.3004 (5)
N1—Pd1—N3	176.99 (6)	N1—Pd1—Cl1	90.93 (5)
N1—Pd1—Cl2	88.08 (5)	N3—Pd1—Cl1	91.98 (5)
N3—Pd1—Cl2	89.01 (5)	Cl2—Pd1—Cl1	179.005 (18)

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>
N2—H2...O1	0.88	1.75	2.609 (2)	164
O1—H1W...Cl2 ⁱ	0.96 (2)	2.19 (2)	3.1268 (16)	165 (2)
O1—H2W...Cl1 ⁱⁱ	0.96 (2)	2.17 (2)	3.1160 (16)	173 (2)
N4—H4...Cl1 ⁱⁱ	0.88	2.26	3.1168 (16)	164

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

The water molecule was refined with an idealized geometry, with the O—H distances restrained to 0.958 (1) Å, a H...H separation of 1.514 (2) Å and a H—O—H angle of 104.45°. All other H atoms were placed in idealized locations and refined as riding, with C—H and N—H distances of 0.95 and 0.88 Å, respectively. For all H atoms, $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C,N,O})$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; 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*.

The manuscript was prepared with the beta test version 1.0.1 of program *publCIF* (Westrip, 2006) to be released by the

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3015). Services for accessing these data are described at the back of the journal.

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