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Positional disorder manifested as compositional in a pseudo-C_2-symmetrical Pd complex

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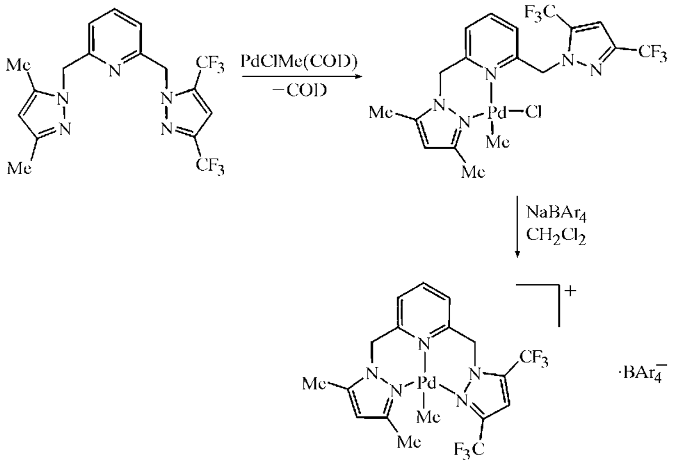
The title compound {2-[3,5-bis(trifluoromethyl)-1*H*-pyrazol-1-ylmethyl]-6-(3,5-dimethyl-1*H*-pyrazol-1-ylmethyl)pyridine}-methylpalladium(II) tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate, $[Pd(C_{18}H_{18}F_6N_5)][B(C_8H_3F_6)_4]$, crystallizes as discrete cations and anions. The cation possesses a pseudo-twofold axis about which positional disorder of the tridentate ligand is exhibited. The four substituents on the two pyrazole rings exhibit CH_3/CF_3 disorder, while all other atoms are ordered. Thus, this disorder can be conveniently described ‘locally’ as compositional, while ‘globally’ for the entire tridentate ligand it is positional. The anion also exhibits typical rotational positional disorder in three of the CF_3 groups. All disordered CF_3 groups were modeled with idealized C_{3v} geometry.

Comment

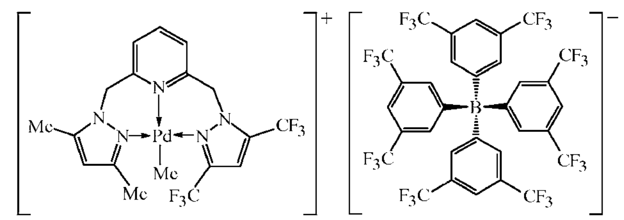
Cationic palladium(II) complexes of symmetrical α-diimine ligands with bulky aryl substituents on the N atoms are known to efficiently catalyze α-olefin oligomerization and polymerization reactions (Brookhart *et al.*, 1995; Ittel *et al.*, 2000; Gibson & Spitzmesser, 2003). These cationic α-diimine palladium complexes are often prepared by direct halide abstraction using silver or alkali metal salts of weakly coordinating ligands. The weakly coordinating ligands do not compete with an incoming monomer for the vacant coordination site of an active catalyst (Mecking, 2000; Mecking *et al.*, 1998; Bianchini *et al.*, 2006). The role of the weakly coordinating ligands is therefore only to stabilize the active catalysts. In our attempts to utilize bis(pyrazol-1-ylmethyl)pyridine–palladium–chloromethyl complexes to catalyze olefin reactions, we found that such complexes yielded inactive cationic species when the Cl atom in the precursor complexes was abstracted (Ojwach *et al.*, 2007). We were able to establish by X-ray crystallography that the cationic species formed after chloride abstraction had both pyrazolyl units strongly bound to palladium. This is in contrast to the chloromethyl precursor complex composition where only one pyrazolyl unit binds to palladium (Ojwach *et al.*, 2007). The strong binding of the pyrazolyl units to palladium in the cationic species was believed to be responsible for the inability of the cationic species to catalyze α-olefin reactions.

During our studies of the factors that render cationic palladium complexes with strongly coordinated bis(pyrazol-1-ylmethyl)pyridine ligands inactive for α-olefin oligomerization and polymerization reactions, we replaced the CH_3 groups on one of the pyrazolyl units in the bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine ligand with CF_3 groups. We aimed to synthesize a hemilabile ligand, which upon complexation with palladium would allow olefin coordination to the metal center (Jeffrey & Rauchfuss, 1979; Shi *et al.*, 2002). We succeeded in preparing the desired palladium precursor complexes and the expected cationic palladium species (see reaction scheme below).



(I)
Ar=3,5-$(CF_3)_2C_6H_3$

Unfortunately, the cationic species showed no catalytic activity in olefin reactions. Spectroscopic data for the cation indicate that the tridentate ligand forms strong Pd—N bonds, whereas the CF_3 substituents do not make the pyrazolyl unit labile. We confirmed the coordination of the ligand by X-ray crystallography and report here the structure of this complex, (I).



(I)

Ionic compound (I) crystallizes as discrete anions and cations. The Pd center in the cationic complex bears a large η^3-ligand and a methyl group (Fig. 1). Both the cation and the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion exhibit rotational positional disorder.

The most interesting aspect of the cationic structure is the disorder. The complex contains a pseudo-twofold axis passing

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along the Pd—C1 vector and exhibits positional rotational disorder about it. A 180° rotation about the axis superimposes the two pyrazole rings to make the CH_3 and CF_3 groups appear disordered, whereas all other non-H atoms remain ordered. Since there is no ambiguity as to the composition of the η^3-ligand, the CH_3/CF_3 disorder is positional; however, it is manifested as compositional and was modeled as such. The CH_3/CF_3 disorder ratio is 86.5 (3):13.5 (3)%. This disorder can be thought of as positional in a 'global' molecular sense and compositional in a 'local' substituent sense. The geometries of the disordered CF_3 groups were modeled with a C_{3v} idealized arrangement based on a density functional theory (DFT) computation for 3-trifluoromethyl-1*H*-pyrazole.

The overall geometry of the Pd cation cannot be higher than C_1, and even with a symmetrical substitution pattern of the pyrazole rings it cannot exceed C_s because of the ligated methyl group. The Pd1 coordination polygon defined by atoms C1, N1, N3 and N5 is irregular and slightly distorted from a number of possible geometries, such as D_{2d} and D_{4h}. The four ligating atoms are coplanar within 0.07 Å. The eccentricity of atom Pd1 is 0.078 (3) Å and it is displaced by 0.0139 (14) Å from the least-squares plane of the ligated atoms. The geometry about the Pd atom is typical and can be summarized as follows: the Pd atom has a distorted square-planar geometry, with angles around the central Pd atom ranging from 85.77 (10) to 93.62 (12)° and an average value of 90 (4)° (Table 1). Atoms Pd1, N1, N3, N5 and C1 are coplanar within 0.06 Å. The average Pd—N_{pz} (pz is pyrazole) distance and N_{pz}—Pd—N_{py} (py is pyridine) angle in (I) are statistically similar to the averages for the nine relevant compounds (Table 2) in the Cambridge Structural Database (CSD; Version 1.10; Allen, 2002); however, the Pd—N_{py} distance in (I) is significantly longer than the average for the similar compounds in the CSD. This difference can be attributed to the *trans* influence of the methyl group. In seven of the nine related compounds, the ligand *trans* to the pyridine ring is a Cl atom, in one it is another pyridine group, and in [2,6-bis(3,5-dimethylpyrazolylmethyl)pyridine]methylpalladium(II) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, compound (II), it is a methyl group. The Pd—N_{py} distance in (I) is similar to the distance of 2.128 (2) Å in (II). The metal complex in (II) differs from the cation in (I) only in that it has all methyl groups substituted on the pyrazole rings (Ojwach *et al.*, 2007).

The dihedral angles between the best fitting least-squares planes defined by the ring pyrazole atoms, ring pyridine atoms and four ligating atoms are given in Table 3. These angles are similar to those for other compounds with the same tridentate pyrazolylmethylpyridine ligands; thus a pseudo-C_2 geometry of the ligand is preferred to a pseudo-C_s geometry.

The bond distances and angles in the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion (Fig. 2) are typical, as confirmed by a *Mogul* structural check (Bruno *et al.*, 2004). The geometry around the B atom is slightly distorted tetrahedral. The average angle around atom B1 is 109.5 (11)°, but the angles range from 107.8 (2) to 110.6 (2)°. The F atoms on three of the CF_3 groups in the anion show rotational positional disorder over three positions each. The F atoms attached to atom C26 are disordered in a 42.0 (4):29.2 (3):28.8 (3)% ratio, those attached to C42 are disordered in a 52.3 (3):33.3 (5):-14.3 (4)% ratio, and those attached to atom C50 are disordered in a 54.0 (3):38.3 (4):7.7 (3)% ratio. All of these disordered F atoms in the anion were refined isotropically, and the CF_3 groups were refined with restraints. The geometries of the disordered CF_3 groups were modeled with a C_{3v} idealized arrangement based on a DFT computation for $PhCF_3$. It is quite common for the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion in crystal structures to contain some disorder. Our data mining of the CSD revealed that in 295 out of 512 instances of this anion in the CSD there was some disorder in the anion.

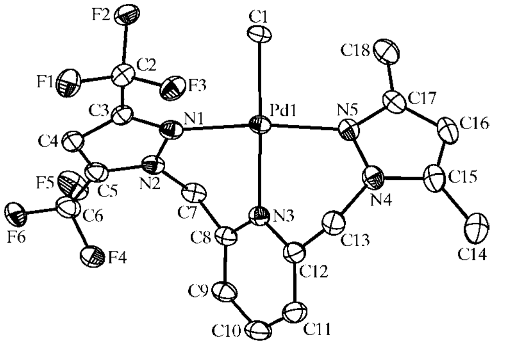

Figure 1
The molecular structure of the cation of (I). Displacement ellipsoids are shown at the 50% probability level. All H atoms and all minor components of disordered atoms have been omitted for clarity.

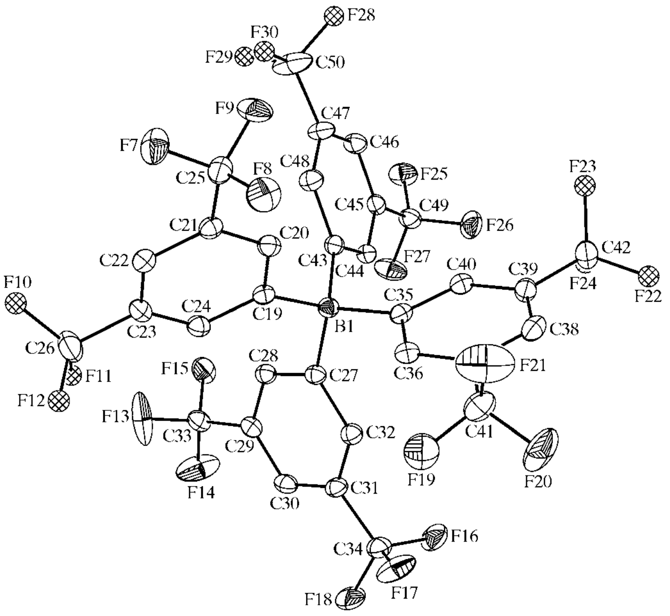

Figure 2
The molecular structure of the anion of (I). Displacement ellipsoids are shown at the 50% probability level. All H atoms and all minor components of disordered atoms have been omitted for clarity. The disordered F atoms in the anion that were refined isotropically are shown with crosshatched circles.

Experimental

To a J-Young NMR tube containing a solution of the palladium precursor complex (4.00 mg, 0.007 mmol) in $CDCl_3$ (0.2 ml) was added a solution of $NaBAr_4$ [Ar is 3,5-$(CF_3)_2C_6H_3$] (6.00 mg, 0.007 mmol) in $CDCl_3$ (0.2 ml) (see reaction scheme in the *Comment*), and the ^1H NMR spectrum was acquired after vigorous shaking. The solution was left to stand at room temperature for several days to afford colorless single crystals of (I) suitable for X-ray analysis. ^1H NMR ($CDCl_3$): δ 1.27 (*s*, 3H, CH_3, Pd—Me), 2.17 (*s*, 3H, CH_3, pz), 2.33 (*s*, 3H, CH_3, pz), 5.16 (*d*, 2H, CH_2, $^2J_{HH}$ = 15.6 Hz), 5.63 (*s*, 1H, pz), 5.98 (*s*, 1H, pz), 6.20 (*d*, 2H, CH_2, $^2J_{HH}$ = 17.4 Hz), 6.71 (*d*, 1H, py, $^3J_{HH}$ = 8.2 Hz), 7.23 (*d*, 2H, py, $^3J_{HH}$ = 8.6 Hz), 7.34 (*t*, 1H, py, $^3J_{HH}$ = 8.3 Hz), 7.48 (*s*, 4H, BAr_4^-), 7.66 (*s*, 8H, BAr_4^-). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ 62.6 (*s*, BAr_4^-), −60.2 (*s*, CF_3, pz), −56.0 (*s*, CF_3, pz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 5.7, 11.5, 15.0, 52.1, 55.8, 109.2, 117.5, 122.6, 124.7, 134.7, 142.0, 48.8, 152.2, 162.6.

Crystal data

$[Pd(C_{18}H_{18}F_6N_5)](C_{32}H_{12}BF_{24})$
M_r = 1388.00
Monoclinic, $P2_1/n$
a = 10.9194 (4) Å
b = 18.0256 (7) Å
c = 27.1635 (11) Å
β = 96.865 (1)°
V = 5308.2 (4) Å^3
Z = 4
Mo- $K\alpha$ radiation
μ = 0.50 mm^{-1}
T = 105 (2) K
0.36 × 0.31 × 0.26 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.841, T_{max} = 0.881
92342 measured reflections
14211 independent reflections
12423 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.154
S = 1.01
14211 reflections
823 parameters
109 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.16 e Å^{-3}
$\Delta\rho_{min}$ = −1.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—N5	2.030 (3)	Pd1—C1	2.061 (3)
Pd1—N1	2.049 (3)	Pd1—N3	2.127 (3)
N5—Pd1—N1	172.77 (10)	N5—Pd1—N3	87.76 (11)
N5—Pd1—C1	93.62 (12)	N1—Pd1—N3	85.77 (10)
N1—Pd1—C1	93.07 (11)	C1—Pd1—N3	175.40 (12)

Table 2
Distances and angles (Å, °) in (I) compared with those for nine similar compounds in the CSD[a].

	(I)	CSD average
$Pd—N_{pz}$	2.039 (13)	2.03 (2)
$Pd—N_{py}$	2.127 (3)	2.04 (4)
$N_{pz}—Pd—N_{py}$	86.8 (14)	86.4 (16)

(*a*) Cambridge Structural Database (Version 1.10; Allen, 2002).

Table 3
Dihedral angles (°) between least-squares planes in the cation.

Least-squares plane	N1/N2/C3–C5	N4/N5/C15–C17	N3/C8–C12
C1/N1/N3/N5	51.14 (11)	39.44 (11)	42.48 (12)
N1/N2/C3–C5	–	87.86 (12)	70.32 (10)
N4/N5/C15–C17	–	–	61.06 (12)

All H atoms were placed in idealized locations and refined as riding with appropriate displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms]. Default effective C—H distances were adopted (secondary Csp^3—H = 0.99 Å, primary Csp^3—H = 0.98 Å and tertiary Csp^2—H = 0.95 Å).

The geometry of all disordered CF_3 groups was modeled on the basis of pbepbe/6–311++G(df,pd) DFT computations to conform to C_{3v} symmetry. This was achieved with the following restraints: the C—F distances were allowed to refine as one free variable FVAR2; the F···F separations were restrained to 1.607 (3) times FVAR2; the C_{ipso}···F separations were restrained to 1.746 (11) times FVAR2. This was achieved with DFIX commands in *SHELXTL* (Sheldrick, 2008). Attempts to conduct the refinement with SAME instructions did not result in computationally stable refinements. All disordered F atoms, except F1, F2 and F3, were refined isotropically.

There are two large peaks (~2 e Å^{-3}) in the final difference map in the vicinity of the disordered group at C50, which may represent additional positions of the F atoms. No attempt to refine this CF_3 group as disordered over four positions was made.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *publCIF* (Westrip, 2008) and *modiCIFer* (Guzei, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3199). Services for accessing these data are described at the back of the journal.

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