

(3,8,9,14-Tetraethyl-2,4,13,15-tetramethyltripyrinato)(trifluoroacetato)-palladium(II)

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Received 1 December 2006

Accepted 21 December 2006

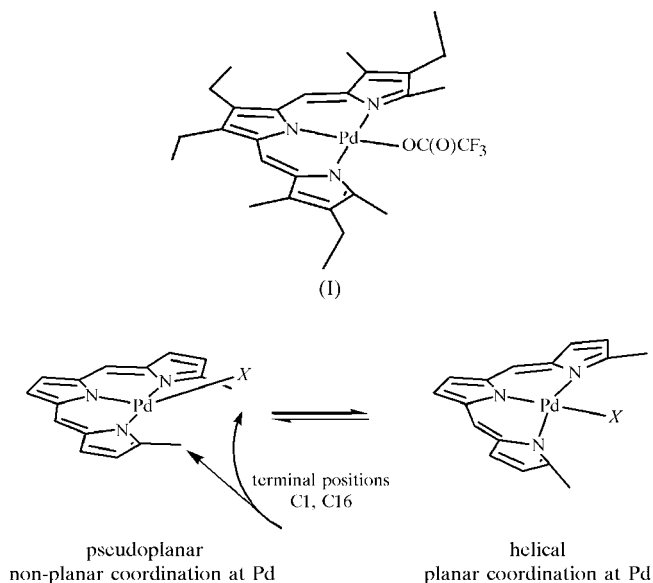
Online 23 January 2007

In the crystal structure, the title compound {systematic name: [2,5-bis(4-ethyl-3,5-dimethyl-2*H*-pyrrol-2-ylidenemethyl)-1*H*-pyrrolato](trifluoroacetato)palladium(II)}, [Pd(C₂F₃O₂)(C₂₇H₃₄N₃)], forms chiral molecules with a helical distortion of the tripyrrinate ligand backbone and an essentially planar PdN₃O core, with Pd–N distances ranging from 1.977 (3) to 2.045 (3) Å and a Pd–O distance of 2.051 (2) Å. This distortion of the organic ligand is considered as the conformational answer to the steric interaction of the terminal methyl groups of the tripyrrinate ligand with the donor O atom of the trifluoroacetate group.

Comment

The structure of the title complex, (I), was determined as part of a continuing study (Bröring *et al.*, 2001, 2002, 2003) of neutral palladium(II) complexes of tripyrrinate ligands, (trpy)PdX. Neutral palladium(II) complexes of such α,ω -dimethyltripyrinate ligands are typically characterized by the steric repulsion that is present between the formally negatively charged coligand (in particular the donor atom of that coligand) and the C1 and C16 methyl groups situated at the termini of the open-chain tripyrrole (methyl termini). The steric overcrowding at the open site of the linear tripyrrole, which can be quantified by an analysis of the van der Waals radii of the involved methyl groups and ligand donor atom (Bröring *et al.*, 2007), leads to strained, non-planar structures for (2,15-dimethyl-3,4,7,8,13,14-hexaethyltripyrinato)(trifluoroacetato)palladium(II) and the azido, chlorido, bromido and iodido complexes of the same (trpy)Pd fragment (Bröring *et al.*, 2001, 2002, 2003), and in the case of (2,15-dimethyl-3,4,13,14-tetraethyltripyrinato)(trifluoroacetato)palladium(II) even a fluxional behaviour has been observed, *i.e.* a dynamic interconversion process between two different non-planar conformations in solution (see scheme). These two limiting conformations have so far been the only ones observed for (trpy)PdX species, and they have been named pseudoplanar

and helical in accordance with the respective tripyrrole conformations. In the pseudoplanar conformation (*C_s* symmetry of the tripyrrin ligand), the Pd^{II} centre is bound in an intermediate situation between distorted square-planar and distorted tetrahedral, while for the helical form (*C₂* symmetry of the tripyrrin ligand), a planar coordination of the palladium(II) ion results. The pseudoplanar scenario is present in the majority of compounds, while the helical form has been observed in only two cases so far, both of which employ the trifluoroacetate ligand.



(Trpy)PdOAc^F, (I) (Fig. 1), crystallizes in the monoclinic system (space group *P*2₁/*c*, with *Z* = 4). The CF₃ group of the trifluoroacetate ligand shows disorder and is refined in two orientations with occupancies of 60.0 (4) and 40.0 (4)%. The Pd^{II} atom is bound in an almost square-planar fashion, with a deviation of the Pd atom from the mean PdN₃O plane of 0.0177 (3) Å, and N2–Pd1–O1 and N1–Pd1–N3 bond angles of 178.79 (11) and 177.08 (11)°, respectively. Two long and one short Pd–N bond (Table 1), the latter being that to the central N2 donor, are present in the coordination unit. The alternating C–C bond lengths of the tripyrrolic ligand perimeter C2–C15 indicate an unequal charge distribution, and it can be proposed that the negative charge of the deprotonated trpy ligand is located mainly at the central C₄N unit. This interpretation would also be in agreement with the above-mentioned finding of a short Pd1–N2 bond and with the differences in the C–N bond lengths of N1 and N3 that indicate the presence of imino-like substructures at these positions. In order to create a sufficiently large binding pocket for atom O1 of the trifluoroacetate ligand within a square-planar coordination geometry, the positions of the terminal methyl groups (C1H₃ and C16H₃) of (I) are characterized by displacements of 1.127 (4) and –1.364 (5) Å from the mean PdN₃O plane. These displacements are achieved by a pronounced helical twist and non-planar structure of the trpy ligand, similar to the ruffled conformation shown by a number

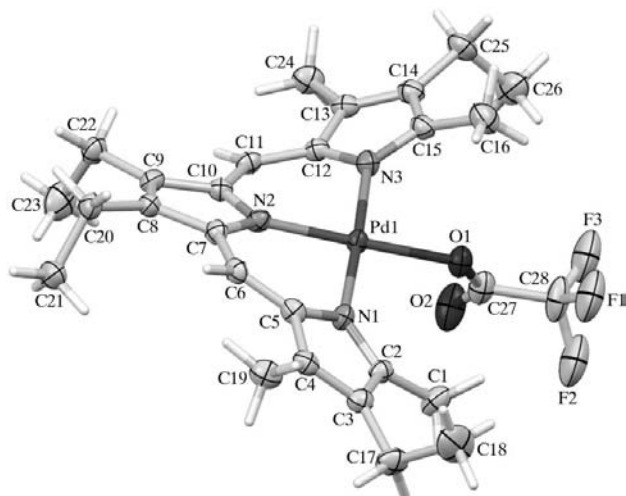


Figure 1

A perspective drawing of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Only the preferred orientation of the disordered CF₃ group is shown.

of metalloporphyrins (Senge, 2000), which can be quantified by the dihedral angles between the mean planes of adjacent C₄N units of 35.4 (2) and 28.0 (2)°. The overall twist as measured by the dihedral angle between the mean planes of the opposite C₄N rings is as large as 57.8 (2)°. These values are within the ranges of 25.7 (2)–38.3 (2)° and 54.8 (2)–63.8 (2)°, respectively, found earlier for related compounds (Bröring *et al.*, 2001, 2002).

The pronounced non-planarity of (I) in the crystal seems to be in contrast to the apparent planarity and C_{2v} symmetry observed by ambient-temperature ¹H NMR spectroscopy. More explicitly, the H atoms of the methylene groups from the ethyl groups of the trpy ligands do not split diastereotopically but give a simple quartet signal, and the F atoms produce a singlet in the ¹⁹F NMR spectrum. These data indicate a racemization process in addition to the rotation of the trifluoroacetate group around the Pd–O1 and C27–C28 bonds in solution, all of which are fast on the NMR time scale. Obviously, the non-planar structure is caused by the steric influence of the terminal methyl groups of the tripyrrin system on the anionic coligand. Only through a severe twist of the tripyrrin system can the binding atom O1 of the trifluoroacetate group find enough space to coordinate to the central Pd^{II} metal as part of a distorted square-planar geometry. The bound O atom of the trifluoroacetate ligand is thereby located almost ideally amid the terminal methyl groups, with C1···C16, C1···O1 and C16···O1 distances of 5.861 (6), 2.933 (5) and 2.935 (5) Å, respectively. These C_{methyl}···O values undercut the sum of the van der Waals values (Bondi, 1964) by as much as 17.2%, thus indicating significant intramolecular strain being stored in the compound. Owing to the helicity of the trpy ligand, the complex is chiral in the solid state and both enantiomers are found in the unit cell in a 1:1 ratio.

Experimental

3,4-Diethyl-2,5-diformylpyrrole (175 mg, 1.4 mmol) and 3-ethyl-2,4-dimethylpyrrole (354 mg, 2.8 mmol) were dissolved in trifluoroacetic acid (10 ml) and heated under reflux for 10 h. After cooling to room temperature, all volatiles were removed *in vacuo*, and the resulting dark residue was treated with a slurry of palladium(II) acetate (317 mg, 1.4 mmol) and sodium acetate (347 mg, 4.23 mmol) in dichloromethane (50 ml). After stirring at room temperature for 16 h, the mixture was again taken to dryness, then redissolved in dichloromethane and filtered. From the filtrate, the title compound was isolated by chromatography on silica with dichloromethane (dark green fraction) and subsequent recrystallization from dichloromethane/hexane. The process yields a green air-stable powder (50% yield). Combustion analysis: found C 54.94, H 5.67, N 6.62%; C₂₈H₃₄F₃N₃O₂Pd requires: C 55.31, H 5.64, N 6.91%. ¹H NMR (400 MHz, CD₂Cl₂): δ 6.75 (s, 2H), 2.53 (q, *J* = 7.6 Hz, 4H), 2.31 (q, *J* = 7.6 Hz, 4H), 2.30 (s, 6H), 2.15 (s, 6H), 1.12 (t, *J* = 7.6 Hz, 6H), 1.01 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 173.6, 142.1, 140.6, 138.3, 137.8, 136.8, 119.6, 18.2, 17.8, 17.2, 13.9, 9.8. ¹⁹F NMR (376 MHz, CD₂Cl₂): δ –74.2. UV/Vis (CH₂Cl₂): λ_{max} (ε l mol^{–1} cm^{–1}) = 270 (17000), 355 (42000), 446 (13000), 650 (32000), 679 nm (43000). Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of (I) in dichloromethane/hexane.

Crystal data

[Pd(C ₂ F ₃ O ₂)(C ₂₇ H ₃₄ N ₃)]	<i>Z</i> = 4
<i>M_r</i> = 608.17	<i>D_x</i> = 1.482 Mg m ^{–3}
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.9511 (6) Å	<i>μ</i> = 0.73 mm ^{–1}
<i>b</i> = 24.128 (2) Å	<i>T</i> = 193 (2) K
<i>c</i> = 12.6581 (9) Å	Block, violet
<i>β</i> = 94.806 (8)°	0.34 × 0.20 × 0.13 mm
<i>V</i> = 2724.2 (4) Å ³	

Data collection

Stoe IPDS-I diffractometer	21198 measured reflections
<i>φ</i> scans	5284 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	4084 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.886, <i>T</i> _{max} = 0.906	<i>R</i> _{int} = 0.034
	<i>θ</i> _{max} = 26.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.039	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0584 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.103	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.19	(Δ/ <i>σ</i>) _{max} = 0.006
5284 reflections	Δ <i>ρ</i> _{max} = 1.18 e Å ^{–3}
343 parameters	Δ <i>ρ</i> _{min} = –0.84 e Å ^{–3}

Table 1

Selected geometric parameters (Å, °).

N1–Pd1	2.045 (3)	N3–Pd1	2.033 (3)
N2–Pd1	1.977 (3)	Pd1–O1	2.051 (2)
N2–Pd1–N3	88.62 (11)	N2–Pd1–O1	178.79 (11)
N2–Pd1–N1	89.04 (11)	N3–Pd1–O1	90.19 (11)
N3–Pd1–N1	177.10 (11)	N1–Pd1–O1	92.14 (10)

The rotations of the idealized methyl H atoms around C1–C2, C4–C19, C13–C24, C15–C16, C17–C18, C20–C21, C22–C23 and C25–C26 were varied. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.93–0.97 Å. The disordered CF₃ group was refined with constrained equivalent anisotropic displacement

parameters for both atom types (C and F). Additionally, the similarity restraint SAME (*SHELXL97*; Sheldrick, 1997) was applied to the two parts of the disordered group.

Data collection: *WinXpose* in *X-AREA* (Stoe & Cie, 2003); cell refinement: *WinCell* in *X-AREA*; data reduction: *WinIntegrate* in *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4.1; Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3060). Services for accessing these data are described at the back of the journal.

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