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rac-[2-(1-Aminoethyl)phenyl-κ^2C^1,N](hexafluoroacetylacetonato-κ^2O,O')palladium(II)

Beatrice Calmuschi and Ulli Englert*

Institute of Inorganic Chemistry, RWTH Aachen University, Prof.-Pirlet-Straße 1, 52074 Aachen, Germany

Correspondence e-mail:
ullrich.englert@ac.rwth-aachen.de

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From a quasi-racemic mixture of structurally related palladium complexes of opposite chirality, no quasi-racemic crystals were obtained. Rather, ligand exchange resulted in conventional racemic crystals. The crystal and molecular structures of the title complex, $[Pd(C_8H_{11}N)(C_5F_6O_2)]$, are reported.

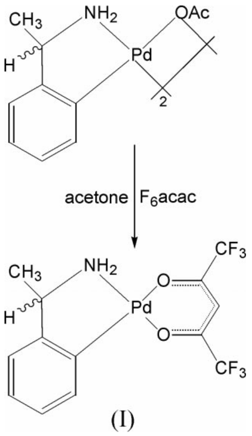
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.057
wR factor = 0.138
Data-to-parameter ratio = 15.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

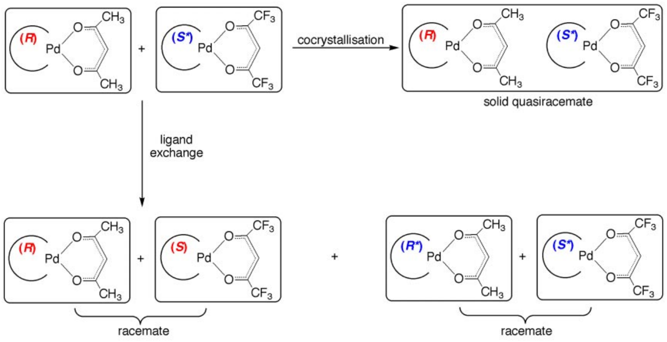
Comment

Preferred mirror-image recognition in the solid state (Wallach, 1895; Brock *et al.*, 1991; Eliel *et al.*, 2001) is not limited to single-component crystals: closely related compounds of opposite chirality may form so-called quasi-racemates (Fredga, 1960). We have exploited this preference for heterochiral crystals for the synthesis of ordered binary solids (Englert *et al.*, 2002; Kalf *et al.*, 2002; Reemers & Englert, 2002). Quasi-racemic crystals of electronically different constituents can be promising candidates for crystal engineering of well ordered solids in noncentrosymmetric space groups. Our present research (Calmuschi, Alesi & Englert, 2004) aims to produce cocrystallization of square-planar palladium complexes. Tetracoordinated Pd^{II} represents a metal centre at the borderline between inertness and lability. Our interest in neutral inert palladium complexes appropriate for cocrystallization experiments induced us to prepare the enantiomerically pure complexes *rac*-[$\kappa C,\kappa N$-2-{(1′-amino)ethyl}phenyl]hexafluoroacetylacetonatopalladium(II), (I), and (*S*)-[$\kappa C,\kappa N$-2-{(1′-amino)ethyl}phenyl]hexafluoroacetylacetonatopalladium(II) (Calmuschi & Englert, 2005*a*) and (*S*)-[$\kappa C,\kappa N$-2-{(1′-amino)ethyl}phenyl]acetylacetonatopalladium(II) (Calmuschi & Englert, 2005*b*).



(I)

Orthometallation results in a thermodynamically stable and kinetically inert chelate ring. A second bidentate mononegative ligand may then complete the coordination of a square-planar complex. For this purpose, we have used acetylacetone and its derivative, hexafluoroacetylacetone. Inertness plays a key role in our experiments: ligand-exchange on the timescale of cocrystallization will result in partial or total racemization and, probably, formation of racemic crystals, as shown in the scheme below. One of these racemization products, the title complex, (I), has been characterized by single-crystal X-ray diffraction.



Heterochiral *rac*-(I) crystallizes in the centrosymmetric space group $C2/c$. Selected bond distances and angles are listed in Table 1. With regard to intermolecular interactions, no classical hydrogen bonds were found.

Packing coefficients indicate that this heterochiral crystal, with 70.4% space-filling, is packed more efficiently than the homochiral ones, namely the hexafluoroacetylacetonate and acetylacetonate (Calmuschi & Englert, 2005*a*,*b*), with values of 69.1 and 68.3%, respectively.

Experimental

The dinuclear intermediates in the scheme were prepared according to the procedure of Fuchita *et al.* (1997) and/or Vicente *et al.* (1997). Structural characterization of the products of the cyclopalladation reaction pathway for unsubstituted and para-substituted primary amines has already been published (Calmuschi & Englert, 2002; Calmuschi, Alesi & Englert, 2004; Calmuschi, Jonas & Englert, 2004). The monomeric title complex was prepared according to the procedure published in a previous paper (Calmuschi & Englert, 2005*a*).

Crystal data

$[Pd(C_8H_{11}N)(C_5F_6O_2)]$
$M_r = 433.63$
Monoclinic, $C2/c$
$a = 23.283\ (12)$ Å
$b = 8.824\ (6)$ Å
$c = 15.562\ (10)$ Å
$\beta = 112.5743\ (13)^\circ$
$V = 2952\ (3)$ Å^3
$Z = 8$

$D_x = 1.951$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.5$–27.0°
$\mu = 1.33$ mm^{-1}
$T = 293\ (2)$ K
Rod, yellow
0.65 × 0.12 × 0.10 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.478$, $T_{\max} = 0.878$
3450 measured reflections
3220 independent reflections

2123 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 27.0^\circ$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 11$
$l = -19 \rightarrow 18$
3 standard reflections every 120 min

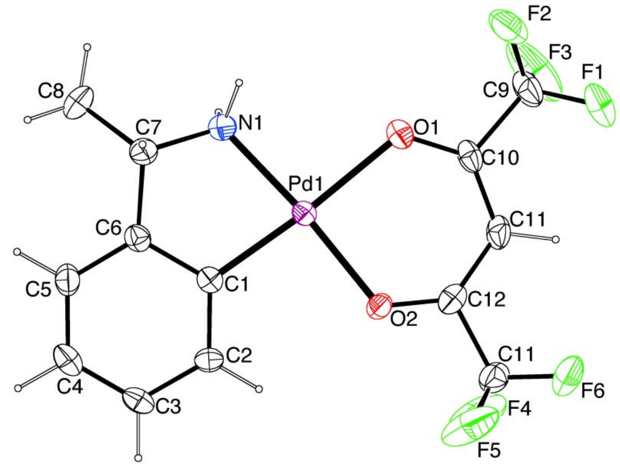


Figure 1
A plot of the molecule of (I) in the crystal structure. Displacement ellipsoids are drawn at 30% probability and H atoms are shown with arbitrary radius.

intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.138$
$S = 0.99$
3220 reflections
209 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.18$ e Å^{-3}
$\Delta\rho_{\min} = -1.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—C1	1.959 (6)	Pd1—O1	2.110 (5)
Pd1—N1	2.024 (6)	O1—C10	1.246 (9)
Pd1—O2	2.030 (5)	O2—C12	1.248 (8)
C1—Pd1—N1	81.7 (3)	C1—Pd1—O1	174.7 (2)
C1—Pd1—O2	93.6 (2)	N1—Pd1—O1	93.8 (2)
N1—Pd1—O2	173.3 (2)	O2—Pd1—O1	90.74 (19)

H atoms were placed in calculated positions and refined using a riding model, with C—H distances of 0.98 Å and N—H distances of 0.95 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$. Methyl groups were allowed to rotate as rigid groups. The maximium and minimum residual electron-density peaks are close (1.09 and 1.03 Å, respectively) from atom Pd1.

Data collection: *CAD-4 Operations Manual* (Enraf-Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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