

Double cyclometallation of bis[3-(3-bromophenyl)-pyrazol-1-yl]methane in the bis[acetylacetonatopalladium(II)] complex

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The cyclometallation of aryl and pyrazolyl rings yields the bis[acetylacetonatopalladium(II)] complex, $[\text{Pd}_2(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{19}\text{H}_{12}\text{Br}_2\text{N}_4)] \cdot 0.5\text{C}_2\text{H}_3\text{N}$, with five- and six-membered chelate rings. The five-membered ring PdNCCC [Pd—C 1.969 (9) and Pd—N 2.013 (8) Å] is planar, whereas the six-membered ring PdNNCNC [Pd—C 1.971 (9) and Pd—N 2.023 (7) Å] has a boat conformation. The Pd—O(acac) distances clearly demonstrate a *trans* influence, the O atoms in *trans* positions to carbon forming longer Pd—O bonds than those in *trans* positions to nitrogen [Pd—O 2.092 (6) Å versus 2.014 (6) Å for the Pd atom in the five-membered ring and 2.044 (7) Å versus 1.999 (6) Å for the Pd atom in the six-membered ring].

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Key indicators

Single-crystal X-ray study

$T = 297$ K

Mean $\sigma(\text{C}-\text{C}) = 0.016$ Å

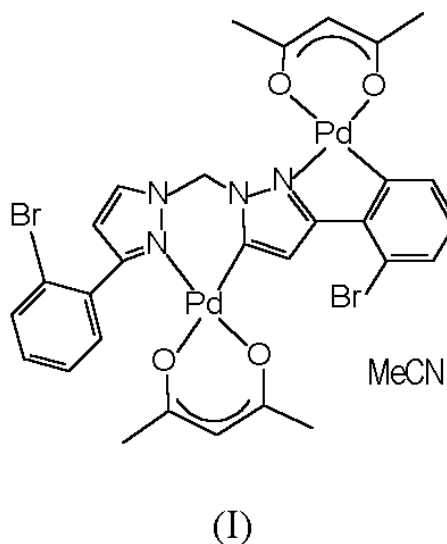
Disorder in solvent or counterion

R factor = 0.055

wR factor = 0.143

Data-to-parameter ratio = 10.5

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



Experimental

The compound was synthesized as described by Alonso *et al.* (1994). Recrystallization first from dichloromethane/hexane and then from acetonitrile afforded colourless crystals suitable for X-ray analysis.

Crystal data

$[\text{Pd}_2(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{19}\text{H}_{12}\text{Br}_2\text{N}_4)] \cdot 0.5\text{C}_2\text{H}_3\text{N}$

$M_r = 887.66$

Monoclinic, $C2/c$

$a = 35.262$ (3) Å

$b = 8.3791$ (5) Å

$c = 24.9461$ (17) Å

$\beta = 120.536$ (6)°

$V = 6348.4$ (8) Å³

$Z = 8$

$D_x = 1.858$ Mg m⁻³

Cu $K\alpha$ radiation

Cell parameters from 55 reflections

$\theta = 5.5$ – 45.0°

$\mu = 12.44$ mm⁻¹

$T = 297$ (2) K

Prismatic, colourless

$0.18 \times 0.15 \times 0.12$ mm

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (XPREP; Bruker, 2000)
 $T_{\min} = 0.377$, $T_{\max} = 0.929$
 5165 measured reflections
 4209 independent reflections
 3848 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 56.8^\circ$
 $h = -38 \rightarrow 1$
 $k = -9 \rightarrow 1$
 $l = -23 \rightarrow 27$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.143$
 $S = 1.12$
 4209 reflections
 399 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 138.5779P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.10 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.000049 (9)

Difference Fourier synthesis revealed three peaks in the vicinity of the twofold axis which had no short contacts with the atoms of the complex. These peaks were attributed to the solvate acetonitrile molecule, which partially occupies the corresponding positions in the crystal. Varying the occupancies of the atoms of the solvate yielded the best discrepancy values for the model with half-occupied solvate atom positions. Therefore, these atoms were included in the subsequent refinement, first in the isotropic and then in the anisotropic approximation, with site-occupation factors fixed at 0.5. The introduction of the solvate atoms brought noticeable improvement in the overall precision of the structure. All H atoms were placed in idealized positions and included in the refinement in the riding-model approximation with U_{iso} equal to $1.2U_{\text{eq}}$ of the carrier atom (U_{iso} equal to $1.5U_{\text{eq}}$ for methyl H atoms). The geometry of the diffractometer installation did not allow us to collect data with 2θ higher than 113.5° , which is a probable reason for the spurious peaks in the vicinity of the heavy atoms (maximum residual density peak of $2.45 \text{ e } \text{\AA}^{-3}$ is located at 0.97 \AA from atom Pd2).

Data collection: XSCANS (Bruker, 2000); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular

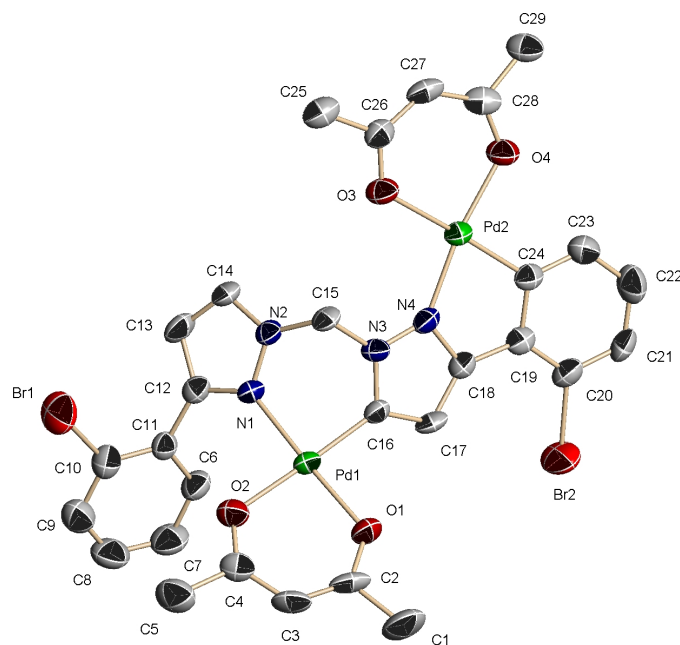


Figure 1
 A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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