Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dichloro[(4*S*,4′*S*)-4,4′-diisopropyl-2,2′-bi-1,3-oxazoline]palladium(II)

Jozef Kožíšek,[a]* Marek Fronc,[a] Ingrid Svoboda,[b] Peter Kapitán[c] and Tibor Gracza[c]

[a]Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, [b]Strukturforschung, FB11 Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany, and [c]Department of Organic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, Bratislava 81237, Slovak Republic

Correspondence e-mail: kozisek@cvt.stuba.sk

Key indicators

Single-crystal X-ray study
T = 301 K
Mean σ(C–C) = 0.008 Å
R factor = 0.025
wR factor = 0.060
Data-to-parameter ratio = 18.7

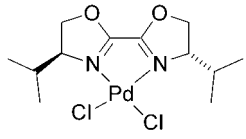
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 29 October 2004
Accepted 11 November 2004
Online 20 November 2004

The title compound, $[PdCl_2(C_{12}H_{20}N_2O_2)]$, consists of discrete complex molecules. The palladium center is in a square-planar geometry coordinated by two chloro anions and two N-donor atoms, with mean Pd—Cl and Pd—N bond distances of 2.278 (1) and 2.029 (2) Å, respectively.

Comment

The title compound, (I), is a chiral catalyst for kinetic resolution of racemic unsaturated polyols in palladium(II)-catalysed cyclizations.



(I)

The structural investigation of (I) (Fig. 1) has been undertaken in order to better understand the catalytic properties in the series of similar compounds.

The Pd—Cl [2.276 (1) and 2.279 (1) Å] and Pd—N [2.022 (3) and 2.036 (3) Å] interatomic distances, as well as the N—C [1.278 (5) Å], C—C [1.465 (6) Å] and C—N [1.276 (5) Å] bond distances within the unsaturated five-membered metallocycle are in good agreement with those found in the Cambridge Structural Database (CSD, Version 1.6, 2003 release; Allen, 2002) for compounds with refcodes ABUYAX (Comerlato *et al.*, 2001) and SUXBAO (Dupont *et al.*, 2001), where the Pd—Cl and Pd—N bond distances fall in the ranges 2.280–2.308 and 2.003–2.025 Å, respectively. In analogous compounds containing saturated five-membered rings, the corresponding distances are in the range 2.294–2.351

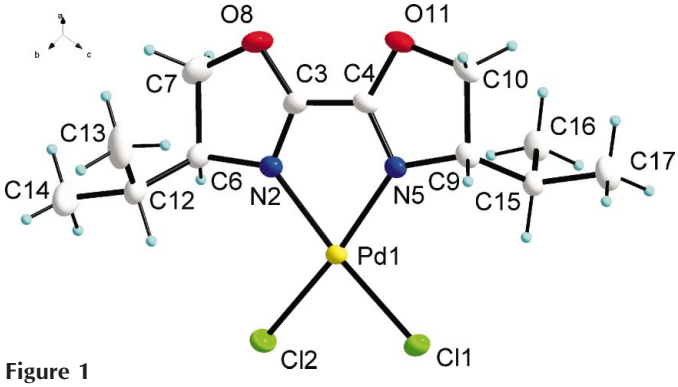


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

and 2.017–2.087 Å for compounds with refcodes SOYQOM (Kuhn *et al.*, 1998), IQUFAB (Boyle *et al.*, 2004), EDTAPD01 (Luo *et al.*, 1999) and LUHRIP (Slyudkin *et al.*, 2002). The main difference in the geometry of saturated and unsaturated metallocycles is in the N—Pd—N angle, which in (I) and the two above-mentioned unsaturated compounds [79.6 (1), 79.3 and 79.4°, respectively] is significantly smaller than those found in the saturated ones (81.4–85.8°). The only weak hydrogen bonds are intramolecular (Fig. 2 and Table 1) and contribute to the stabilization of the conformer.

Experimental

The title compound was prepared from $Pd(MeCN)_2Cl_2$ by a modified procedure (Uozomi *et al.*, 1999) for the synthesis of [(*S*)-2,2′-bis(4,4-dimethyloxazolin-2-yl)-1,1′-binaphthyl]palladium(II) trifluoromethylacetate. A solution of (*S*,*S*)-2,2′-bisoxazolyl (Ghosh *et al.*, 1998; Müller *et al.*, 1991; Bolm *et al.*, 1991; 56 mg, 0.249 mmol, 1.05 equivalents) in dichloromethane (2 ml) was added to $Pd(MeCN)_2Cl_2$ (61 mg, 0.237 mmol) in dichloromethane (2 ml). The mixture was stirred for 15 min, resulting in a clear solution. The title compound was slowly crystallized by precipitation with Et_2O to give brown needles [m.p. 525–527 K, $[\alpha]_D^{25}$ = +137 (*c*, 0.162, MeOH)].

Crystal data

$[PdCl_2(C_{12}H_{20}N_2O_2)]$
M_r = 401.60
Monoclinic, $P2_1$
a = 6.3388 (13) Å
b = 12.790 (3) Å
c = 10.196 (2) Å
β = 103.74 (3)°
V = 803.0 (3) Å^3
Z = 2
D_x = 1.661 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3272 reflections
θ = 3.2–26.3°
μ = 1.49 mm^{-1}
T = 301 (2) K
Prism, brown
0.54 × 0.20 × 0.18 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: analytical face-indexed (*CrysAlis RED*; Oxford Diffraction, 2003)
T_{min} = 0.501, T_{max} = 0.776
5523 measured reflections
3239 independent reflections
3120 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.4°
$h = -4 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.060
S = 1.08
3239 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.6348P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0084 (12)
Absolute structure: Flack (1983), 1967 Friedel pairs
Flack parameter = −0.05 (3)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13A···N2	0.96	2.73	3.047 (9)	100
C16—H16A···N5	0.96	2.63	2.960 (6)	101

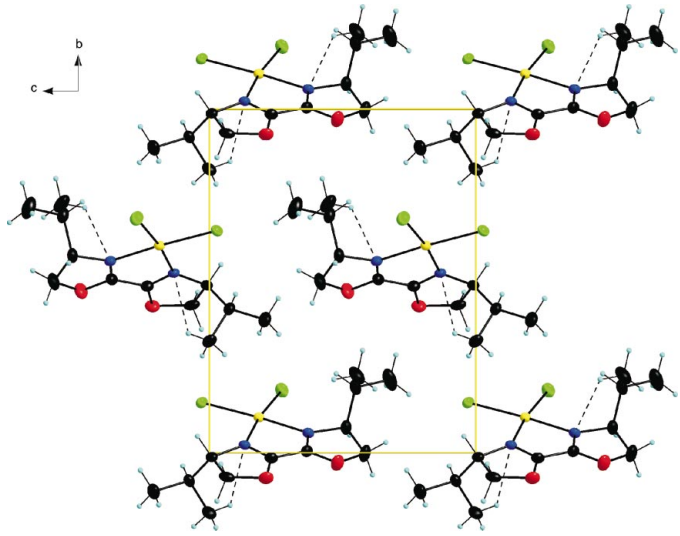


Figure 2
Packing diagram, viewed down the *a* axis. Intermolecular C—H···N hydrogen bonds are shown as dashed lines.

H atoms were positioned geometrically and treated as riding atoms (C—H = 0.96–0.98 Å), with U_{iso}(H) values set at 1.2U_{eq} of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

The authors thank the Grant Agency of the Slovak Republic (grant Nos. 1/9255/02 and 1/7314/20, and APVT-27-030202).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bolm, C., Weickhardt, K., Zehnder, M. & Ranff, T. (1991). *Chem. Ber.* **124**, 1173–1180.
Boyle, R. C., Mague, J. T. & Fink, M. J. (2004). *Acta Cryst.* E**60**, m40–m41.
Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Comerlato, N. M., Crossetti, G. L., Howie, R. A., Tibultino, P. C. D. & Wardell, J. L. (2001). *Acta Cryst.* E**57**, m295–m297.
Dupont, J., Ebeling, G., Delgado, M. R., Consorti, C. S., Burrow, R., Farrar, D. H. & Lough, A. (2001). *Inorg. Chem. Commun.* **4**, 471–474.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Ghosh, A. R., Packiaravan, M. & Cappiello, J. (1998). *Tetrahedron Asymmetry*, **9**, 1–45.
Kuhn, N., Grathwohl, M., Steimann, M. & Henkel, G. (1998). *Z. Naturforsch. Teil B*, **53**, 997–1003.
Luo, X.-M., Chen. X.-H., Shanmuga Sundara Raj, S., Fun, H.-K. & Zhu, L.-G. (1999). *Acta Cryst.* C**55**, 1220–1222.
Müller, D., Umbricht, G., Weber, B. & Phaltz, A. (1991). *Helv. Chim. Acta*, **74**, 232–240.
Oxford Diffraction (2001). *CrysAlis CCD*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Oxford Diffraction (2003). *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Slyudkin, O. P., Khlestkin, V. K., Tikhonov, A. Y., Naumov, D. Y., Izarova, N. V. & Turchinovich, A. A. (2002). *Russ. J. Inorg. Chem.* **47**, 60–67.
Uozomi, Y., Kyota, H., Kato, K., Ogasawara, M. & Hayashi, T. (1999). *J. Org. Chem.* **64**, 1620–1625.