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Dichloro[*N*,*N*′-bis(2,6-diisopropylphenyl)-1,2-ethanediimine-*N*,*N*′]palladium

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.075
Data-to-parameter ratio = 21.8

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

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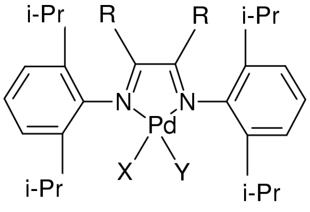
The structure of the title complex, $[PdCl_2(C_{26}H_{36}N_2)]$, represented as LPdCl$_2$, where L denotes the substituted 1,2-ethanediimine ligand, is described and compared with those of the analogous LPdClMe and L'PdMe$_2$ complexes (L' is the closely related substituted 2,3-butanediimine ligand) previously reported by Tempel, Johnson, Huff, White & Brookhart [*J. Am. Chem. Soc.* (2000), **122**, 6686–6700].

Comment

α-Diimines, RN═CR'—CR'═NR, have been widely used as ligands in transition metal complexes (van Koten & Vrieze, 1982; Vonzelewsky *et al.*, 1994; Paw *et al.*, 1998; Kaes *et al.*, 2000; Farrell & Vlcek, 2000; van Slageren *et al.*, 2000; Hicks *et al.*, 2001). Several of the α-diimine complexes have found application as catalysts. For example, cationic palladium and nickel(II) complexes of bulky aryl-substituted α-diimines, ArN═CR—CR═NAr′, have been shown to be excellent polymerization catalysts for ethylene and α-alkenes (Gottfried & Brookhart, 2001; Ittel *et al.*, 2000; Tempel *et al.*, 2000; Liimatta *et al.*, 2001; Mecking, 2001; Albietz *et al.*, 2000).



(I) R = H; X = Y = Cl
(II) R = H; X = Cl; Y = Me
(III) R = Me; X = Y = Me

Selected geometric parameters of the title complex, (I), are shown in Table 1, along with data for two previously reported related compounds, chloro[*N*,*N*′-bis(2,6-diisopropylphenyl)-1,2-ethanediimine-*N*,*N*′]methylpalladium, (II), and [*N*,*N*′-bis(2,6-diisopropylphenyl)-2,3-butanediimine-*N*,*N*′]dimethylpalladium, (III) (Tempel *et al.*, 2000).

Compound (I) (Fig. 1) has a square planar geometry, with a distortion mainly arising from the small, 79.29 (6)°, bite angle, N1–Pd–N2, of the chelating diimine ligand. Distortions from square planar geometry in (I) are also indicated by the torsion angles, Cl2–Pd–N1—C1 = 32.4 (5) and Cl1–Pd–N2—C2 = 14.1 (4)°. The diimine bite angle in (I), although much less than the ideal value of 90°, is noticeably larger than those in (II) [76.2 (4)°] and (III) [74.81 (15)°], other neutral Pd^{II}–diimine complexes, as well as those in the Pd^0 complexes, [η^2-(E)-but-2-enedinitrile](N,N'-diphenyl-1,7,7-trimethylbi-

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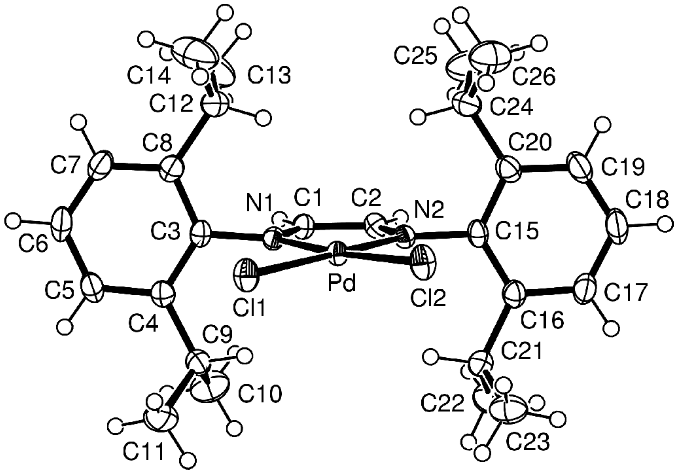

Figure 1
The molecule of (I) showing the atom labels (*ORTEP*-3; Farrugia, 1997). Non-H atoms are shown as 50% displacement ellipsoids and H atoms as open circles.

cyclo[2.2.1]heptane-2,3-diimine-*N,N′*)palladium(0) [77.31 (9)°] (Ellis & Spek, 2001) and {bis[(2,6-diisopropylphenyl)imino]-acenaphthene}(maleic anhydride)palladium(0) [77.78 (19)°] (van Asselt *et al.*, 1994). The diimine bite angle in the cationic complex, [(2,6-bis-diisopropyl-*N*-(2- pyridinylmethylene)-phenylamine)methyl(acetonitrile)palladium] {B[3,5-$(CF_3)_2$-$C_6H_3]_4$} [78.8 (2)°] (Meneghetti *et al.*, 1999) is, however, similar to that in (I). The angles between the plane of the –Pd–N1—C1—C2—N2– ring in (I) and the aryl ring planes are 80.66 (5)° [C3–C8] and 82.73 (6)° [C15–C21]. Thus, as in other similar complexes, the bulky isopropyl substituents effectively block approaches to the Pd atom from axial directions. A small degree of electron delocalization in the diimine ligand in (I) is indicated by the bond lengths, N1—C1 = 1.280 (2), C1—C2 = 1.460 (3) and C2—N2 = 1.282 (2) Å. More delocalization in the N═C—C═N fragments of the ligands is apparent in (II) and (III). The bond lengths in (I) are only slightly different from those in the free ligand, [*N,N′*-bis(2,6-diisopropylphenyl)-1,2-ethanediimine], for which N—C = 1.265 (4) and C—C = 1.467 (4) Å (CSD refcode DARVEX; Laine *et al.*, 1999).

Experimental

The *N,N′*-bis(2,6-diisopropylphenyl)-1,2-ethanediimine ligand (*L*) was prepared by a modification of a published procedure (tom Dieck & Dietrich, 1984). Methanoic acid (88%, 0.5 ml, 11.5 mmol) and an aqueous solution of glyoxal (40%, 4.6 ml, 39.0 mmol) were successively added to a vigorously stirred suspension of 2,6-diisopropylaniline (14.9 ml, 79 mmol) and freshly dehydrated sodium sulfate (25 g) in CH_2Cl_2 (100 ml). After 5 min, a further amount of sodium sulfate (25 g) was added, and the reaction mixture was stirred at room temperature for 1 d. The mixture was filtered and the solid extracted with CH_2Cl_2 (3 × 15 ml). The combined organic material was evaporated *in vacuo*, and the residue recrystallized from ethanol at 293 K; yield 10.3 g, 70%, m.p. 376 K. Dichloro(*N,N′*-bis(2,6-diisopropylphenyl)-1,2-ethanediimine-*N,N′*)palladium, (I) was prepared by a modification of a published procedure (van der Poel *et al.*, 1980). To a stirred solution of $PdCl_2(PhCN)_2$ (0.41 g, 1.07 mmol) (Anderson & Lin, 1990) in CH_2Cl_2 (50 ml) was added *L* (0.46 g, 1.22 mmol) at room temperature. After 2 h, the reaction mixture was concentrated *in vacuo* to 5 ml and hexane (15 ml) added to complete the precipitation of the the title compound. This was washed with hexane (3 × 10 ml) and dried *in vacuo*, yield 0.54 g, 98%, m.p. 551 K (decomposition). Suitable crystals were obtained from acetone solution. Analysis, found: C 56.06, H 6.85, N 5.19%; calculated for $C_{26}H_{36}Cl_2N_2Pd$: C 56.64, H 6.56, N, 5.06%. ^1H NMR (200 MHz, CD_2Cl_2): δ: 1.23(*d*, 12H, *J* = 6.8 Hz, Me), 1.45(*d*, 12H, *J* = 6.8 Hz, Me), 3.25(sept, 4H, *J* = 6.8 Hz, Me_2CH), 7.27–7.48 (*m*, 6H, aryl), 8.15 (*s*, 2H, CH═N).

Table 1
Selected geometric parameters (Å,°) for (I), (II) and (III).

	(I)	(II)	(III)
Pd—*X*	2.2834 (5)	2.300 (4)	2.033 (5)
Pd—*Y*	2.2799 (5)	2.020 (11)	2.023 (6)
Pd—N1	2.0142 (15)	2.033 (9)	2.133 (4)
Pd—N2	2.0248 (14)	2.208 (9)	2.145 (4)
N1—C1	1.280 (2)	1.315 (16)	1.317 (6)
C1—C2	1.460 (3)	1.434 (17)	1.366 (8)
C2—N2	1.282 (2)	1.262 (18)	1.297 (6)
X—Pd—N1	93.66 (4)	99.9 (3)	100.17 (19)
X—Pd—N2	172.75 (4)	174.9 (3)	174.3 (2)
Y—Pd—N1	173.44 (4)	170.4 (5)	174.97 (19)
Y—Pd—N2	95.17 (4)	94.3 (4)	99.6 (2)
N1—Pd—N2	79.29 (6)	76.2 (4)	74.81 (15)
X—Pd—*Y*	91.963 (17)	89.7 (4)	85.5 (2)
Pd—N1—C1	114.91 (12)	117.6 (8)	114.2 (3)
N1—C1—C2	115.54 (16)	115.3 (12)	118.2 (4)
C1—C2—N2	116.18 (16)	119.5 (11)	118.1 (4)
C2—N2—Pd	114.08 (12)	111.3 (8)	114.7 (3)

Notes: atom labels are primarily those of (I) with *X* = Cl1 and *Y* = Cl2, *X* = Cl and *Y* = Me for (II) and *X* = *Y* = Me for (III). Data for (II) and (III) are from Tempel *et al.* (2000).

Crystal data

$[PdCl_2(C_{26}H_{36}N_2)]$
$M_r = 553.87$
Monoclinic, $P2_1/a$
$a = 13.7198$ (1) Å
$b = 15.3812$ (2) Å
$c = 13.8702$ (2) Å
$\beta = 110.3873$ (5)°
$V = 2743.64$ (6) $Å^3$
$Z = 4$

$D_x = 1.341$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26074 reflections
$\theta = 2.9$–27.5°
$\mu = 0.89$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius Kappa CCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.673$, $T_{max} = 0.767$
42 903 measured reflections

6279 independent reflections
5446 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -19 \rightarrow 19$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.075$
$S = 1.08$
6279 reflections
288 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.8819P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.78$ e $Å^{-3}$
$\Delta\rho_{min} = -0.90$ e $Å^{-3}$

In the final stages of the refinement one reflection, −2 0 1, showing particularly poor agreement was suppressed. The H atoms were introduced in calculated positions with C—H and $U_{\rm iso}$ 0.95 Å and 1.2 times $U_{\rm eq}$ of the non-H to which they are attached (1.00 Å for tertiary C—H and for methyl H 0.98 Å and 1.5 times $U_{\rm eq}$).

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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