metal-organic papers

trans-Bis(*tert*-butylamine)dichloropalladium(II)

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Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.008 Å
R factor = 0.038
wR factor = 0.098
Data-to-parameter ratio = 22.8

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

The asymmetric unit of the title complex, *trans*-[PdCl$_2$(NH$_2^t$Bu)$_2$], consists of two independent square-planar molecules, linked together in a hydrogen-bonding network, with the resultant alignment of the *tert*-butyl groups defining a two-dimensional layered structure approximately parallel to (001).

Comment

We have noted that the chemistry of *tert*-butylamine derivatives of palladium frequently differs from other primary amine complexes due to the steric bulk of the *tert*-butyl group. The availability of crystals of the title complex, (I), allowed comparison with other bis(primary amine)dichloro complexes of palladium to determine the structural consequences of steric bulk.

$$\begin{array}{c} NH_2Bu^t \\ | \\ Cl-Pd-Cl \\ | \\ NH_2Bu^t \end{array}$$
(I)
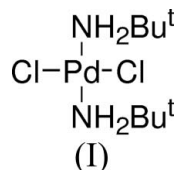
Complex (I) exists as two independent square-planar molecules in the asymmetric unit. The orientation of the *tert*-butylamine groups is such that both molecules are pseudo-centrosymmetric. Analysis of the 14 previously reported bis(primary amine)dichloropalladium(II) structures (Fletcher *et al.*, 1996) gives averages of 2.300 (8) Å and 2.047 (9) Å for the Pd—Cl and the Pd—N bonds, respectively, with a mean deviation of the N—Pd—Cl angles of *ca* 1.4° from the ideal 90°. The Pd—Cl and Pd—N bond lengths in (I) range from 2.3015 (11) to 2.3072 (12) and 2.046 (4) to 2.058 (4) Å, respectively; this indicates that, in this complex, the bulky *tert*-butyl group has no obvious structural consequence, although the average N—Pd—Cl angle in complex (I) does show a significantly smaller deviation from the 90° required by ideal square-planar geometry [0.46° (molecule 1), 0.37° (molecule 2). The molecules are linked together in a hydrogen-bonding network, resulting in the formation of a two-dimensional layered structure, externally defined by the *tert*-butyl groups and approximately parallel to (001).

Experimental

Complex (I) crystallized from a dichloromethane/hexane solution of *trans*-[Pd(η^1-C$_5$H$_5$)(NH$_2^t$Bu)$_2$Cl] and [Pd(η^5-C$_5$H$_5$)(NH$_2^t$Bu)Cl] and was spectroscopically identical to the material synthesized according to the literature method (Nakayama *et al.*, 1984).

Crystal data

$[PdCl_2(C_4H_{11}N)_2]$
$M_r = 323.58$
Triclinic, $P\bar{1}$
$a = 6.2357\ (10)$ Å
$b = 10.6500\ (11)$ Å
$c = 20.472\ (2)$ Å
$\alpha = 94.641\ (8)°$
$\beta = 90.978\ (13)°$
$\gamma = 93.824\ (11)°$
$V = 1351.7\ (3)$ Å^3

$Z = 4$
$D_x = 1.590$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34
 reflections
$\theta = 5.1–12.5°$
$\mu = 1.73$ mm^{-1}
$T = 223\ (2)$ K
Block, orange
$0.6 \times 0.3 \times 0.3$ mm

Data collection

Siemens P4 diffractometer
Profile fitting of $\omega/2\theta$ scans
Absorption correction: ψ scan
 (XSCANS; Siemens, 1996).
 $T_{min} = 0.537$, $T_{max} = 0.594$
7873 measured reflections
6177 independent reflections
5913 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = -8 \rightarrow 1$
$k = -13 \rightarrow 13$
$l = -26 \rightarrow 26$
3 standard reflections
 every 97 reflections
 intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 1.23$
6177 reflections
271 parameters
H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0118P)^2 + 6.285P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -1.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—N12	2.046 (4)	Pd2—N21	2.057 (4)
Pd1—N11	2.050 (4)	Pd2—N22	2.058 (4)
Pd1—Cl11	2.3015 (11)	Pd2—Cl22	2.3051 (12)
Pd1—Cl12	2.3030 (11)	Pd2—Cl21	2.3072 (12)
N12—Pd1—N11	179.27 (16)	N21—Pd2—N22	179.06 (16)
N12—Pd1—Cl11	90.17 (12)	N21—Pd2—Cl22	89.93 (12)
N11—Pd1—Cl11	89.35 (12)	N22—Pd2—Cl22	90.71 (12)
N12—Pd1—Cl12	89.74 (12)	N21—Pd2—Cl21	90.04 (12)
N11—Pd1—Cl12	90.74 (12)	N22—Pd2—Cl21	89.32 (12)
Cl11—Pd1—Cl12	179.34 (5)	Cl22—Pd2—Cl21	179.26 (6)

Table 2
Hydrogen-bond geometry (Å, °).

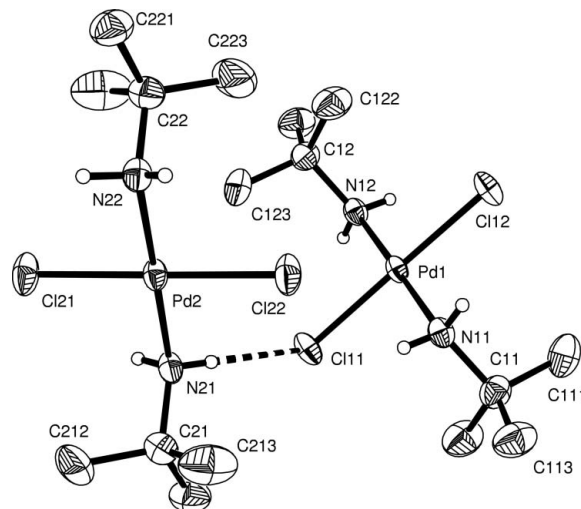| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H112$\cdots$Cl11^i	0.81 (6)	2.62 (6)	3.408 (4)	163 (5)
N12—H121$\cdots$Cl21^{ii}	0.82 (6)	2.75 (6)	3.416 (4)	140 (5)
N12—H122$\cdots$Cl12^{iii}	0.84 (6)	2.60 (6)	3.423 (4)	165 (5)
N21—H211$\cdots$Cl11	0.79 (6)	2.59 (6)	3.327 (4)	157 (5)
N21—H212$\cdots$Cl22^{iii}	0.84 (6)	2.76 (6)	3.502 (4)	148 (5)
N22—H221$\cdots$Cl21^i	0.80 (6)	2.71 (6)	3.481 (4)	164 (5)
N22—H222$\cdots$Cl12^{iv}	0.92 (6)	2.52 (6)	3.347 (4)	149 (4)

Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y - 1, z$; (iii) $x - 1, y, z$; (iv) $x, y + 1, z$.

Figure 1
A view of the two independent molecules in (I). Displacement ellipsoids are drawn at the 50% probability level. *tert*-Butyl H atoms have been omitted. The dashed line indicates a hydrogen bond.

Methyl-H atoms were placed in calculated positions and subsequently constrained to an ideal geometry, with C—H distances of 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, with each group allowed to rotate freely about its C—C bond. The positions of the amine H atoms were identified from a difference Fourier map and allowed to refine freely with fixed isotropic displacement parameters; N—H = 0.79 (6)– 0.92 (6) Å. The highest peak is located 1.21 Å from atom Cl21 and the deepest hole 1.47 Å from atom Cl12.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Siemens, 1995); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

References

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