

***trans*-Bis(benzylamine)dichloro-
palladium(II) bis(dimethyl sulfoxide)
solvate**Andreas Decken,^{a*} Gisia L. Pisegna,^b Christopher M. Vogels^b and Stephen A. Westcott^b^aDepartment of Chemistry, University of New Brunswick, PO Box 45222, Fredericton, New Brunswick, Canada E3B 6E2, and ^bDepartment of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada E4L 1G8
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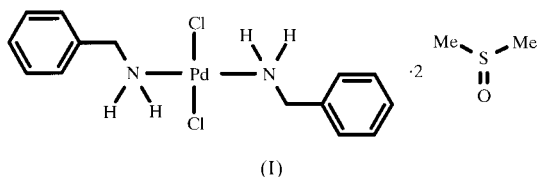
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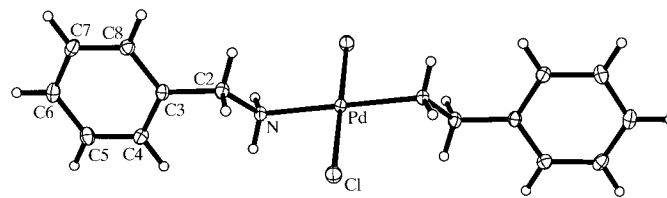
The title compound, $[\text{PdCl}_2(\text{C}_7\text{H}_9\text{N})_2] \cdot 2\text{C}_2\text{H}_6\text{OS}$, crystallizes with two molecules of dimethyl sulfoxide (DMSO) in monoclinic space group $P2_1/n$. The Pd complex is centrosymmetric and thus the phenyl rings of the benzylamine ligands are *exo* with respect to one another. The crystal packing reveals $\text{NH} \cdots \text{O}$ and $\text{CH} \cdots \text{Cl}$ hydrogen bonds between the organometallic molecule and the DMSO molecules, resulting in infinite chains. The distances of the *ortho*-H atoms on the phenyl ring to the metal center are in the range 4.71–5.34 Å, precluding any significant intramolecular $\text{Pd} \cdots \text{H}$ interactions.

Comment

The chemistry of cyclopalladated compounds is a rich and diverse area of organometallic chemistry that has applications in organic synthesis and homogeneous catalysis (Ryabov, 1990, for leading references; Selvakumar & Vancheesan, 1996; Pfeffer, 1992). Although early work (Cope & Friedrich, 1968; Cockburn *et al.*, 1973) suggested that only tertiary amines undergo such cyclometallation reactions, recent studies have described the synthesis of various orthopalladated primary benzylamine derivatives (Vicente *et al.*, 1997). The intricate mechanism of this reaction, however, is still not well understood. In the presence of excess amine, the 16-electron PdCl_2L_2 ($L = \text{amine}$) adducts, usually a mixture of *cis* and *trans* isomers, can be considered as starting materials in cyclopalladations (Ryabov, 1990). The reaction is believed to



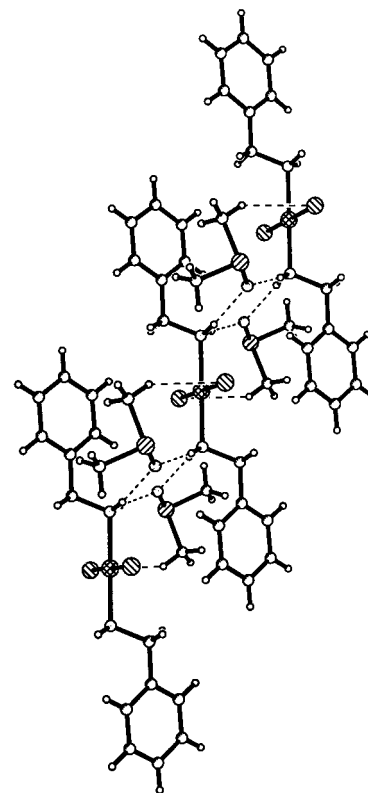
proceed *via* initial dissociation of one amine to give a coordinatively unsaturated 14-electron intermediate which can then undergo intramolecular C–H bond activation to give the

**Figure 1**

The structure of (I) showing the atomic labeling scheme and 30% probability displacement ellipsoids.

desired organometallic dimer. Bis(amine) complexes of palladium have also received much attention as plausible intermediates in amination reactions (Widenhoefer & Buchwald, 1996; Seligson & Trogler, 1991). We have undertaken an X-ray diffraction study of $[\text{PdCl}_2(\text{NH}_2\text{CH}_2\text{Ph})_2]$, (I), to examine any possible inter- or intramolecular interactions which may facilitate cyclopalladations.

The molecular structure of (I) is shown in Fig. 1 and selected interatomic distances and angles are compared in Table 1. The metal atom lies in the center of a slightly distorted square-planar arrangement of *trans* Cl and N ligands, with an N–Pd–Cl angle of $89.86(5)^\circ$. Pd–N [2.046(2) Å] and Pd–Cl [2.3072(7) Å] bond lengths lie well within the range of distances reported previously (Vicente *et al.*, 1997; Navarro-Ranninger *et al.*, 1993; Seligson & Trogler, 1991; Iball *et al.*, 1975). Intermolecular Pd \cdots Pd distances of 7.242(2) Å are significantly longer than those for *cis*-dichloro(ethylenediamine)palladium(II) at 3.369 Å (Iball *et al.*, 1975). The distance of the *ortho*-H atoms on the phenyl ring to the metal center are in the range 4.713–5.339 Å, precluding any signifi-

**Figure 2**

The packing diagram of (I).

cant intramolecular Pd···H interactions. The molecules are packed in such a way that each DMSO solvent molecule bridges two palladium complex molecules through long-range intermolecular H···Cl (2.789 Å) and H···O bonds (2.035 and 2.092 Å), resulting in the formation of the infinite chains shown in Fig. 2. We are presently investigating the chemistry of other palladium–amine complexes in the hope of providing further mechanistic evidence for cyclopalladations and related reactions.

Experimental

trans-PdCl₂(NH₂CH₂Ph)₂ was prepared by modification of a known procedure (Cope & Friedrich, 1968). Benzylamine (0.25 g, 2.3 mmol) was added to a stirred solution of Na₂PdCl₄ (0.32 g, 1.1 mmol) in methanol. After stirring for 1 h, the orange precipitate was filtered and washed with cold hexane (2 × 5 ml) and then with cold water (2 × 5 ml). Orange–yellow crystals of the product (36% yield) were obtained by dissolving the solid in DMSO and cooling to 273 K. NMR spectra were recorded on a Jeol 270 spectrometer. ¹H NMR (CDCl₃, 270 MHz, p.p.m.): δ 3.26 (*br s*, 2H), 3.95 (*br m*, 2H), 7.35 (*ov m*, 5H). ¹³C{¹H} (DMSO-*d*₆, 67.8 MHz, p.p.m.) NMR: δ 47.7 (CH₂), 127.6, 128.3, 128.6, 138.5.

Crystal data

[PdCl ₂ (C ₇ H ₉ N) ₂] ₂ ·2C ₂ H ₆ OS	<i>D</i> _x = 1.556 Mg m ⁻³
<i>M</i> _r = 547.86	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 12980 reflections
<i>a</i> = 7.242 (2) Å	<i>θ</i> = 3.00–30.64°
<i>b</i> = 16.187 (5) Å	<i>μ</i> = 1.216 mm ⁻¹
<i>c</i> = 10.596 (3) Å	<i>T</i> = 173 (1) K
<i>β</i> = 109.700 (10)°	Plate, yellow
<i>V</i> = 1169.4 (6) Å ³	0.38 × 0.23 × 0.12 mm
<i>Z</i> = 2	

Data collection

Rigaku AFC-8/Mercury CCD diffractometer	3088 independent reflections
<i>ω</i> scans	2703 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: analytical (<i>CrystalClear</i> 1.2; Rigaku MSC/SSI, 1999)	<i>R</i> _{int} = 0.018
<i>T</i> _{min} = 0.500, <i>T</i> _{max} = 0.864	<i>θ</i> _{max} = 30.64°
12890 measured reflections	<i>h</i> = 0 → 9
	<i>k</i> = -22 → 22
	<i>l</i> = -14 → 14

Table 1

Selected geometric parameters (Å, °).

Pd–N	2.046 (2)	Pd–Cl ⁱ	2.3072 (7)
Pd–N ⁱ	2.046 (2)	N–C2	1.481 (2)
Pd–Cl	2.3072 (7)	C2–C3	1.510 (3)
N–Pd–N ⁱ	180	Cl–Pd–Cl ⁱ	180
N–Pd–Cl	89.86 (5)	N–C2–C3	115.0 (2)
N ⁱ –Pd–Cl	90.14 (5)		

Symmetry code: (i) $-x, -y, 1 - z$.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0150P)^2 + 1.2000P]$
<i>R</i> (<i>F</i>) = 0.026	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> (<i>F</i> ²) = 0.060	(<i>Δ</i> / <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.085	<i>Δρ</i> _{max} = 0.80 e Å ⁻³
3088 reflections	<i>Δρ</i> _{min} = -0.73 e Å ⁻³
130 parameters	Extinction correction: <i>SHELXL</i> 93 (Sheldrick, 1993)
H atoms constrained	Extinction coefficient: 0.0117 (18)

The data are complete to *θ* = 26.4° and 85.3% complete to *θ* = 30.64°. H atoms were included in calculated positions with N–H = 0.90 Å and C–H = 0.96 Å, and were treated as riding. Three separate common *U*_{iso} values were refined for the N–H and CH₂, the aromatic C–H and the methyl H atoms.

Data collection: *CrystalClear*1.2 (Rigaku MSC/SSI, 1999); cell refinement: *CrystalClear*1.2; data reduction: *CrystalClear*1.2; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1279). Services for accessing these data are described at the back of the journal.

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