

***cis*-Bis[(3-aminopropyl)dimethylphosphine- $\kappa^2N,P$ ]palladium(II) dichloride methanol solvate**Takayoshi Suzuki,<sup>a\*</sup> Atsushi Hasegawa,<sup>b</sup> Hiroshi Yamaguchi,<sup>b</sup> Kazuo Kashiwabara<sup>b</sup> and Hideo D. Takagi<sup>b</sup><sup>a</sup>Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan, and <sup>b</sup>Graduate School of Science and Research Center for Materials Science, Nagoya University, Furocho, Chikusa, Nagoya 464-8602, Japan  
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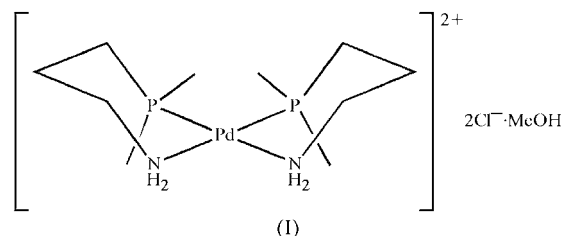
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In the title compound, *cis*-[Pd(C<sub>5</sub>H<sub>14</sub>NP)<sub>2</sub>]Cl<sub>2</sub>·CH<sub>4</sub>O, the coordination geometry around the Pd<sup>II</sup> center is distorted square planar, with a *cis*-P<sub>2</sub>N<sub>2</sub> configuration of the two chelating (3-aminopropyl)dimethylphosphine (pdmp) ligands. The six-membered pdmp chelate rings adopt chair conformations, and pairing of the chairs designates the complex cation as a (C<sub>s</sub>)-chair<sub>2</sub> conformer. The distances between the Pd<sup>II</sup> center and the Cl<sup>-</sup> anions are greater than 4.5 Å, indicating no obvious interaction.

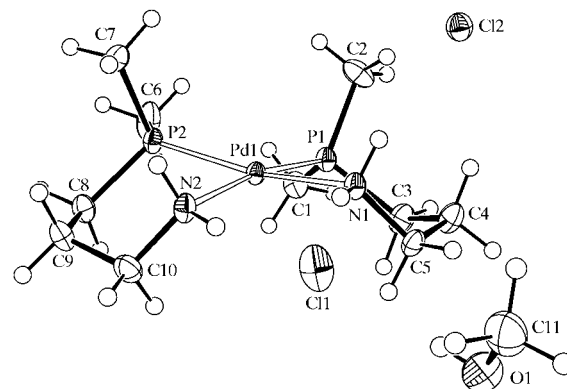
**Comment**

In transition metal complexes with chelating ligands, the chelate ring size, *i.e.* the number of backbone C atoms between two ligating atoms, often exerts severe effects on the thermal stabilities, molecular structures and chemical reactivities of the complexes (Stoppioni *et al.*, 1982; Poverenov *et al.*, 2005). Aminoalkylphosphines are bidentate ligands that can form chelate rings of a variety of sizes, and their metal complexes have recently attracted much interest as effective homogeneous catalysts (Müller *et al.*, 2002; Andrieu *et al.*, 2006). We have previously prepared a number of transition metal complexes bearing (2-aminoethyl)dimethylphosphine (edmp, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>), which is one of the most fundamental and less sterically demanding of the aminoalkylphosphines, forming a five-membered chelate ring (Kashiwabara *et al.*, 1997; Suzuki *et al.*, 1994, 1996; Kita *et al.*, 1994; Kinoshita *et al.*, 1980, 1981). In contrast, to our knowledge, there have so far been no reports on the metal complexes of (3-aminopropyl)dimethylphosphine (pdmp, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>), which gives the corresponding six-membered amine–phosphine chelate ring. In the present study, we have prepared the first example of a pdmp complex of palladium(II), *viz.* *cis*-[Pd(pdmp)<sub>2</sub>]Cl<sub>2</sub>·MeOH, (I), and

compared the crystal structure with those of the analogous edmp and related complexes.



The analysis revealed that the Pd<sup>II</sup> complex cation in (I) possesses two chelating pdmp ligands in a *cis*-P<sub>2</sub>N<sub>2</sub> configuration (Fig. 1). The chelate bite angles are 86.40 (5) and 88.54 (6)° (Table 1), which are larger than those of edmp in *cis*-[Pd(edmp)<sub>2</sub>]Cl(BF<sub>4</sub>), (II) [83.9 (3) and 84.5 (3)°; Suzuki *et al.*, 1996]. This fact infers that the steric interaction between mutually *cis*-positioned –PMe<sub>2</sub> groups is somewhat larger in (I) than in (II). In general, in four-coordinate square-planar complexes, the *trans*-P<sub>2</sub>N<sub>2</sub> isomer is advantageous with regard to the intramolecular steric congestion arising from the bulky substituents on P atoms, but the strong *trans* influence of the phosphine ligands tends to stabilize the *cis*-P<sub>2</sub>N<sub>2</sub> configuration. The preferential formation of the *cis* isomer in complex (I) indicates that the *trans* influence of the –PMe<sub>2</sub> group is still the primary effect for determining the complex geometry, even in the sterically more demanding pdmp six-membered chelate ring system. The coordination geometry around the Pd<sup>II</sup> center is significantly distorted from square planar. The dihedral angle between the Pd/P1/N1 and Pd/P2/N2 planes is 14.5 (1)°. This tetrahedral distortion of the Pd<sup>II</sup> coordination geometry is much larger than that observed in the related 8-dimethylphosphinoquinoline (Me<sub>2</sub>Pqn) complex *cis*-[Pd(Me<sub>2</sub>Pqn)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (the corresponding dihedral angle is 10.3°), where a severe steric repulsion was expected between *ortho* H atoms of mutually *cis*-positioned quinolyl donor groups (Suzuki *et al.*, 1995). It is noteworthy that the edmp complex (II) adopts an almost planar PdP<sub>2</sub>N<sub>2</sub> coordination (Suzuki *et al.*, 1996). In (I), each six-membered pdmp chelate ring adopts a chair conformation, and pairing of these chairs designates the complex cation as a (C<sub>s</sub>)-chair<sub>2</sub> conformer. This

**Figure 1**

An ORTEP-3 (Farrugia, 1997) view of the components of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

is in contrast to a similar (3-aminopropyl)diphenylphosphine complex, *cis*-[Pt(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]Cl<sub>2</sub>, which was characterized as a (C<sub>2</sub>)-chair<sub>2</sub> conformer (Habtemariam *et al.*, 2001). In the (C<sub>s</sub>)-chair<sub>2</sub> conformer, greater steric congestion is expected between the substituents on the mutually *cis*-positioned P-donor atoms than in the (C<sub>2</sub>)-chair<sub>2</sub> conformer. In fact, the C1···C6 distance is 3.257 (3) Å and the closest H···H contact between the two methyl groups is 2.29 Å for H1C···H6A, which is nearly the sum of the van der Waals radii of two H atoms (2.44 Å).

The Pd—P and Pd—N bond lengths in (I) (Table 1) are comparable to those in (II) [Pd—P = 2.243 (3) and 2.248 (3) Å, and Pd—N = 2.123 (10) and 2.153 (10) Å]. One of the most intriguing differences in the crystal structures of (I) and (II) is the location of the Cl<sup>−</sup> anion(s). In (II), the anion is located above the Pd<sup>II</sup> coordination plane, with a Pd···Cl distance of 3.166 (3) Å, indicating a weak interaction between these atoms. In the crystal structure of *cis*-[Pd(Ph<sub>2</sub>Pqn)<sub>2</sub>]Cl<sub>2</sub> (Ph<sub>2</sub>Pqn is 8-diphenylphosphinoquinoline), the two Cl<sup>−</sup> anions are located above and below the Pd<sup>II</sup> coordination plane, with Pd···Cl distances of 3.262 (3) and 3.386 (3) Å (Suzuki, 2004). In contrast to these compounds, complex (I) does not exhibit any interaction between the Pd<sup>II</sup> center and the Cl<sup>−</sup> anions (> 4.5 Å), although one side of the Pd<sup>II</sup> coordination plane is sterically open for such an interaction. Instead, hydrogen-bonding interactions between the coordinated amino groups of the pdmp ligands and the Cl<sup>−</sup> counter-anions are effective in (I) (Table 2). It is expected that these hydrogen bonds stabilize the less preferable (C<sub>s</sub>)-chair<sub>2</sub> conformer. The methanol molecule is hydrogen bonded to atom Cl1 and not coordinated to the Pd atom, the Pd1···O1 distance being 3.800 (2) Å.

## Experimental

Compound (I) was prepared by the reaction of [PdCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>] (283 mg, 0.74 mmol) and pdmp (0.25 ml, 2.1 mmol) in acetonitrile (50 ml). The crude product obtained by evaporation of the solvent was purified by Sephadex LH-20 column chromatography using methanol as eluant. Evaporation of the solvent from the eluate left a white powder of [Pd(pdmp)<sub>2</sub>]Cl<sub>2</sub>·MeOH·H<sub>2</sub>O (yield 223 mg, 55%). Analysis calculated for C<sub>10</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>·CH<sub>4</sub>O·H<sub>2</sub>O: C 28.4, H 7.36, N 6.02%; found: C 28.6, H 7.33, N 6.01%. When the compound was recrystallized from dimethyl sulfoxide by vapor diffusion of diethyl ether, colorless needle-shaped crystals of the monohydrate were obtained. Analysis calculated for C<sub>10</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>·H<sub>2</sub>O: C 27.7, H 6.97, N 6.46%; found: C 27.9, H 6.80, N 6.49%. Crystals of the methanol solvate, (I), suitable for X-ray analysis were deposited by vapor diffusion of diethyl ether into a methanol solution.

### Crystal data

[Pd(C <sub>5</sub> H <sub>14</sub> NP) <sub>2</sub> ]Cl <sub>2</sub> ·CH <sub>4</sub> O	Z = 4
M <sub>r</sub> = 447.65	D <sub>x</sub> = 1.549 Mg m <sup>−3</sup>
Monoclinic, P2 <sub>1</sub> /c	Mo Kα radiation
a = 9.904 (6) Å	μ = 1.41 mm <sup>−1</sup>
b = 9.654 (6) Å	T = 193 (2) K
c = 20.130 (13) Å	Prism, colorless
β = 94.228 (11)°	0.20 × 0.10 × 0.10 mm
V = 1920 (2) Å <sup>3</sup>	

### Data collection

Rigaku Mercury diffractometer	14453 measured reflections
ω scans	4289 independent reflections
Absorption correction: multi-scan (Jacobson, 1998)	4026 reflections with I > 2σ(I)
T <sub>min</sub> = 0.766, T <sub>max</sub> = 0.872	R <sub>int</sub> = 0.024
	θ <sub>max</sub> = 27.5°

### Refinement

Refinement on F <sup>2</sup>	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.0206P) <sup>2</sup> + 1.828P]
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )] = 0.029	where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
wR(F <sup>2</sup> ) = 0.056	(Δ/σ) <sub>max</sub> = 0.004
S = 1.11	Δρ <sub>max</sub> = 0.57 e Å <sup>−3</sup>
4289 reflections	Δρ <sub>min</sub> = −0.49 e Å <sup>−3</sup>
177 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

Pd1—N1	2.137 (2)	Pd1—P1	2.2528 (13)
Pd1—N2	2.151 (2)	Pd1—P2	2.2577 (14)
N1—Pd1—N2	89.53 (7)	N1—Pd1—P2	167.98 (5)
N1—Pd1—P1	88.54 (6)	N2—Pd1—P2	86.40 (5)
N2—Pd1—P1	170.58 (5)	P1—Pd1—P2	97.26 (3)

**Table 2**

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2	0.92	2.41	3.325 (3)	171
N1—H1B···Cl1 <sup>i</sup>	0.92	2.31	3.195 (3)	162
N2—H2A···Cl1 <sup>i</sup>	0.92	2.44	3.356 (3)	174
N2—H2B···Cl2 <sup>ii</sup>	0.92	2.53	3.339 (3)	147
O1—H01···Cl1	0.79 (4)	2.36 (4)	3.138 (3)	171 (3)

Symmetry codes: (i) −x, −y, −z + 2; (ii) −x, y − ½, −z + ½.

H atoms bonded to C and N atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H distances of 0.98 and 0.99 Å, N—H distances of 0.92 Å, and U<sub>iso</sub>(H) values of 1.2U<sub>eq</sub>(C,N). The hydroxy H atom of the methanol molecule was located in a difference map and refined isotropically.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSO, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3009). Services for accessing these data are described at the back of the journal.

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