

Julia Wiedermann,^a David Benito-Garagorri,^a Karl Kirchner^a and Kurt Mereiter^{b*}^aInstitute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria, and ^bInstitute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Vienna, AustriaCorrespondence e-mail:
kurt.mereiter@tuwien.ac.at

Key indicators

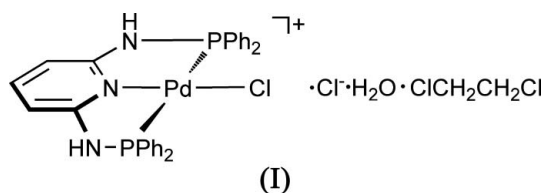
Single-crystal X-ray study
T = 297 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.035
wR factor = 0.090
Data-to-parameter ratio = 21.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**[*N,N'*-Bis(diphenylphosphino)pyridine-2,6-diamine- κ^3P,N^1,P']chloropalladium(II) chloride monohydrate 1,2-dichloroethane solvate**

The title compound, $[\text{PdCl}(\text{C}_{29}\text{H}_{25}\text{N}_3\text{P}_2)]\text{Cl}\cdot\text{H}_2\text{O}\cdot\text{C}_2\text{H}_4\text{Cl}_2$, contains a cationic pincer-type PNP complex with Pd in a square-planar coordination. The complexes form dimers which are π - π stacked *via* their pyridine rings and linked into chains *via* hydrogen bonds *via* four-membered rings of two chloride anions and two water molecules. Pairs of 1,2-dichloroethane molecules are entrapped in pockets of the structure and show weak interactions with palladium.

Received 17 April 2006
Accepted 19 April 2006

Comment

Tridentate pincer-type ligands in which a central phenyl group (PCP-type) or pyridine (PNP-type) contains $-X-PR_2$ substituents in the two *ortho* positions ($X = \text{CH}_2, \text{NH}, \text{O}$; $R = \text{alkyl}, \text{aryl}$ *etc.*) are of considerable interest in transition metal chemistry and catalysis (van der Boom & Milstein, 2003). After an early exploration (Schirmer *et al.*, 1987) we have recently expanded the access to such ligands and their complexes by showing that modularly designed PNP-type ligands can be conveniently synthesized from 2,6-diaminopyridine and various chlorophosphines $R_2\text{P}\text{Cl}$ and have proved that they are useful in transition metal catalysis (Benito-Garagorri *et al.*, 2006). During ongoing work we obtained the title compound, (I) (Fig. 1), which can be formulated as $[\text{PdCl}(\text{PNP-Ph})]\cdot\text{Cl}\cdot\text{H}_2\text{O}\cdot\text{C}_2\text{H}_4\text{Cl}_2$ [PNP-Ph = bis(diphenylphosphino)-2,6-diaminopyridine].



The $[\text{PdCl}(\text{PNP-Ph})]$ group consists of a flat core (Ph excluded) with an r.m.s. aplanarity of 0.032 \AA and a $\text{P1}\cdots\text{P2}$ separation of $4.514 (1) \text{ \AA}$. The palladium coordination is square planar with the typical pincer-complex distortion, causing the $\text{P1}-\text{Pd}-\text{P2}$ angle to deviate notably from 180° (Table 1). In the crystal structure, inversion symmetry results in adjacent complex molecules being stacked above each other with their pyridine rings mutually parallel to form π - π stacked pairs with a ring-ring perpendicular distance of 3.429 \AA and a ring slippage of 0.460 \AA . These π - π stacked pairs and their spatial arrangement are visualized in Figs. 2 and 3. No other π - π stacking contacts are present.

A typical property of diaminopyridine-based PNP complexes is that their NH groups tend to form comparatively strong hydrogen bonds with suitable acceptors, in this case, the

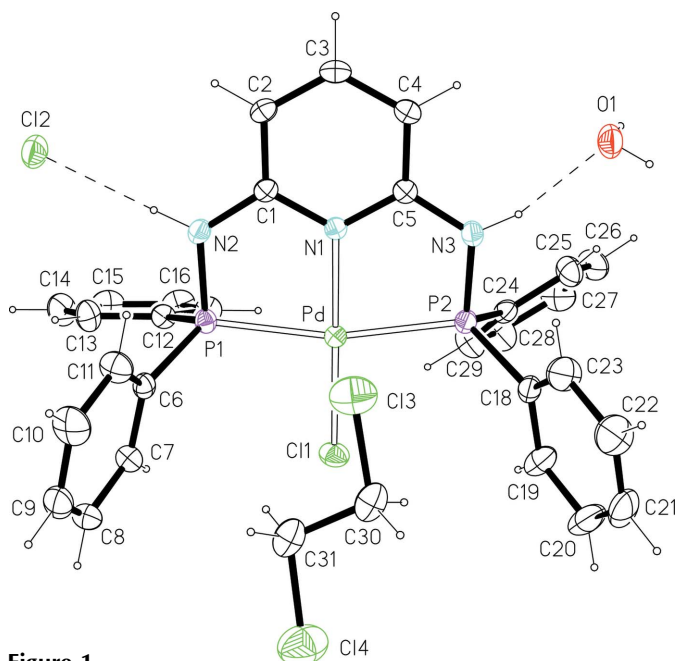


Figure 1
Asymmetric unit of (I), shown with 20% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

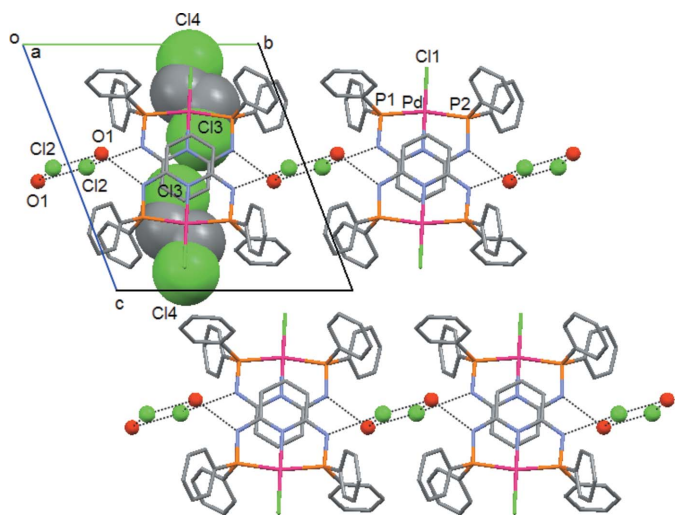


Figure 2
Packing diagram of (I) with capped sticks for [PdCl(PNP-Ph)], small spheres for Cl₂ and H₂O, and large packing spheres for C₂H₄Cl₂ molecules; H atoms have been omitted.

free chloride anion Cl₂ and the water molecule H₂O₁ (Table 2). In the crystal structure, these two units are also mutually hydrogen bonded and form a rhombus-shaped hydrogen-bonded ring, Cl₂(H₂O)₂ (Fig. 2). The resulting threefold coordination figures are an approximate T-shape for Cl₂ and distorted trigonal pyramidal for H₂O₁. The Cl₂(H₂O)₂ rings link π - π stacked pairs of [PdCl(PNP-Ph)] complexes into infinite {[PdCl(PNP-Ph)]₂·Cl₂(H₂O)₂} chains parallel to the *b* direction. Entrapped in elongated pockets between these chains are pairs of 1,2-dichloroethane molecules with a *trans*-configuration and an orientational disorder described in the *Experimental* section. Each dichloroethane molecule has a

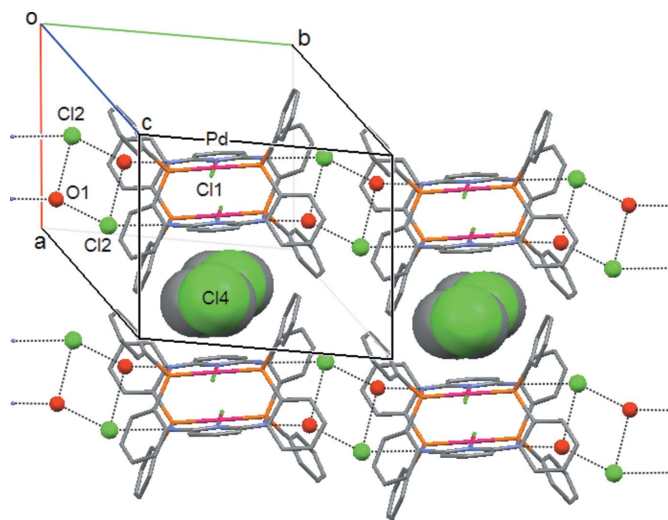


Figure 3
Packing diagram of (I) in a side view of Fig. 2, showing the [PdCl(PNP-Ph)]₂·Cl₂(H₂O)₂ chains, pyridine π -stacking and C₂H₄Cl₂ solvent cavities in cross section.

short [3.418 (2) Å] Cl₃...Cl₃(2 - *x*, 1 - *y*, 1 - *z*) contact to its neighbouring molecule (Fig. 2) and a 3.438 (1) Å Cl₃...Pd separation in the perpendicular direction.

Interestingly, the nickel complex [NiCl(PNP-Ph)]Cl·H₂O of Schirmer *et al.* (1987) [triclinic, space group *P* $\bar{1}$, *a* = 9.126 (4) Å, *b* = 12.377 (4) Å, *c* = 13.519 (6) Å, α = 102.96 (3)°, β = 107.53 (4)°, γ = 94.71 (3)°, *V* = 1400 (1) Å³, *Z* = 2], contains chains which are practically identical to those seen in (I). They extend along *b*, have a pyridine π - π stacking distance of 3.52 Å, but show an interlocked arrangement with a phenyl-phenyl π - π stacking interaction that is missing in (I) because of the presence of the C₂H₄Cl₂-filled pockets at corresponding places.

Experimental

After synthesis (Benito-Garagorri *et al.*, 2006), crystals of (I) were obtained by slow evaporation over several days of a saturated solution in C₂H₄Cl₂ at room temperature and in humid air.

Crystal data

[PdCl(C₂₉H₂₅N₃P₂)]Cl·H₂O·
C₂H₄Cl₂

M_r = 771.73

Triclinic, *P* $\bar{1}$

a = 10.7915 (10) Å

b = 12.2186 (11) Å

c = 13.5664 (12) Å

α = 69.072 (1)°

β = 89.275 (1)°

γ = 84.607 (1)°

V = 1663.0 (3) Å³

Z = 2

D_x = 1.541 Mg m⁻³

Mo *K* α radiation

μ = 1.00 mm⁻¹

T = 297 (2) K

Block, yellow

0.40 × 0.30 × 0.27 mm

Data collection

Bruker SMART CCD

diffractometer

ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

T_{min} = 0.66, *T_{max}* = 0.76

22229 measured reflections

8236 independent reflections

6816 reflections with *I* > 2 σ (*I*)

R_{int} = 0.030

θ_{max} = 28.3°

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.090$
 $S = 1.03$
 8236 reflections
 389 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.3436P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.95 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Pd—N1	2.0135 (19)	Pd—P2	2.2750 (7)
Pd—P1	2.2705 (7)	Pd—Cl1	2.2957 (7)
N1—Pd—P1	83.58 (6)	N1—Pd—Cl1	179.32 (6)
N1—Pd—P2	83.11 (6)	P1—Pd—Cl1	95.98 (3)
P1—Pd—P2	166.39 (2)	P2—Pd—Cl1	97.36 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots Cl2	0.86	2.25	3.101 (2)	169
N3—H3N \cdots O1	0.86	1.95	2.784 (3)	163
O1—H1WA \cdots Cl2 ⁱ	0.80	2.42	3.221 (3)	179
O1—H1WB \cdots Cl2 ⁱⁱ	0.80	2.32	3.117 (2)	171

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

H atoms attached to pyridine and phenyl rings were placed in calculated positions ($C-H = 0.93 \text{ Å}$) and refined as riding. The water molecule was idealized ($O-H = 0.80 \text{ Å}$ and $H-O-H = 108^\circ$) and refined as a rigid group ($N-H = 0.86 \text{ Å}$ and methyl $C-H = 0.97 \text{ Å}$).

The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. The C atoms of the 1,2-dichloroethane molecule are disordered and occurred in two pairs of adjacent positions corresponding to an approximately 180° rotation about the Cl—Cl axis of the molecule. They were refined in x, y, z, U_{ij} and complementary occupancies [final values 0.68 (1) and 0.32 (1)] applying distances and U_{ij} restraints.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*, *SADABS* (Sheldrick, 1996) and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*.

Financial support by the FWF Austrian Science Fund is gratefully acknowledged (project No. P16600-N11). DBG thanks the Basque Government (Eusko Jurlaritz/Gobierno Vasco) for a doctoral fellowship.

References

- Benito-Garagorri, D., Becker, E., Wiedermann, J., Lackner, W., Pollak, M., Mereiter, K., Kisala, J. & Kirchner, K. (2006). *Organometallics*, **25**, 1900–1913.
- Boom, M. E. van der & Milstein, D. (2003). *Chem. Rev.* **103**, 1759–1792.
- Bruker (1999). *SAINTE* (Version 6.01), *SMART* (Version 5.054), *SHELXTL* (Version 5.1) and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Schirmer, W., Flörke, U. & Haupt, H.-J. (1987). *Z. Anorg. Allg. Chem.* **545**, 83–97.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.