Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A distorted square-planar Pd^{II} complex with a shortened Pd—Cl bond induced by the bulky terpyridyl ligand 6,6″-dimesityl-2,2′:6′,2″-terpyridine

Akira Onoda, Keiko Kawakita, Taka-aki Okamura, Hitoshi Yamamoto and Norikazu Ueyama*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence e-mail: ueyama@chem.sci.osaka-u.ac.jp

Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.144
Data-to-parameter ratio = 17.6

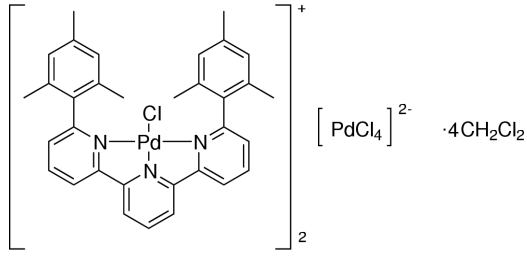
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 10 February 2003
Accepted 15 April 2003
Online 30 April 2003

The title complex, chloro(6,6″-dimesityl-2,2′:6′,2″-terpyridine)palladium(II) tetrachloropalladium(II) dichloromethane tetrasolvate, $[Pd^{II}Cl(dmtpy)]_2[Pd^{II}Cl_4]\cdot 4CH_2Cl_2$ (dmtpy is 6,6″-dimesityl-2,2′:6′,2″-terpyridine, $C_{33}H_{31}N_3$), was synthesized and the crystal structure of the dichloromethane tetrasolvate has been determined. The complex has a distorted square-planar coordination formed by three N atoms and a chloride ion, the distortion caused by the extremely bulky substituted terpyridyl ligand.

Comment

Design of N-chelating ligands with various bulky substituents is an essential approach in developing N-chelating metal catalysts for polymerization. For example, Brookhart and co-workers have reported highly efficient Pd and Ni catalysts with α-diimino ligands for the polymerization of ethylene and α-olefins (Johnson *et al.*, 1995). It has also been reported that control of the bulkiness in pyridine bisimino ligands (3N coordination) contributes to polymerization by their Fe and Co complexes as catalysts (Small *et al.*, 1998; Britovsek *et al.*, 1998). We have synthesized a monochloropalladium complex with a bulky terpyridine ligand, namely 6,6″-dimesityl-2,2′:6′,2″-terpyridine, and determined the effect of the steric hindrance of this ligand, perturbing the metal coordination geometry.



(I)

Fig. 1(*a*) shows the structure of the asymmetric unit of (I). The asymmetric unit consists of one $[Pd^{II}(dmtpy)]^+$ cation, one-half $[Pd^{II}Cl_4]^{2-}$ and two dichloromethane molecules. Fig. 1(*b*) shows the cation part of the structure. The Pd complex, (I), has a distorted square-planar coordination formed by three N atoms and a chloride ion; the distortion is due to the extremely bulky terpyridyl ligand. The Pd1—N21 bond distance [1.953 (4) Å] to the central pyridine ring is shorter than those to the pyridine rings on either side [2.0913 (4) and 2.089 (4) Å]. The N21—Pd1—Cl1 atom lies 0.156 Å from the N11—N12—N31 plane. It has been reported that similar 3N coordination with terpyridine and a chloride gives an almost planar coordination geometry, with similar Pd—N bond distances and an almost linear N—Pd—Cl angle of 193.6°

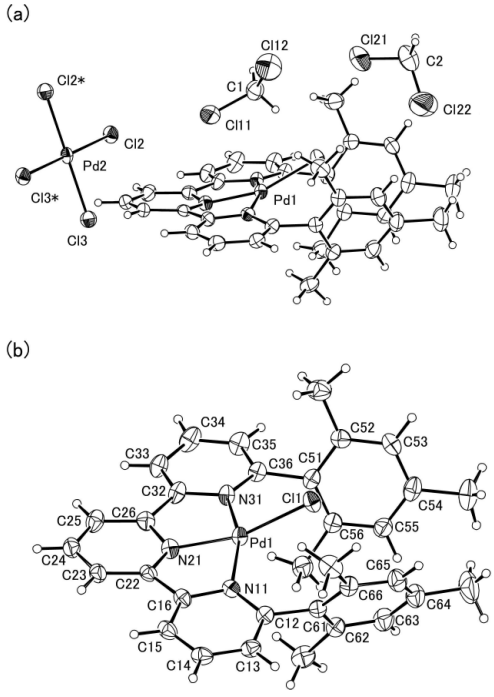


Figure 1
(*a*) The structure of the asymmetric unit of (I), with 25% probability displacement ellipsoids. Atoms C2, Cl121 and Cl122 of one dichloromethane molecule are disordered, and only one set is shown for clarity. (*b*) The cation of (I), showing the labeling of non-H atoms and 25% probability displacement ellipsoids.

(Intille *et al.*, 1973). The bulkiness of the dimesityl groups in the 6,6″-positions of the terpyridine ligand distorts the square-planar coordination towards a tetrahedral geometry, resulting in shortening of the Pd—Cl bond length from 2.331 (1) to 2.286 (1) Å. Our ligand design of bulky derivatives of terpyridine ligands successfully induces a distortion in the Pd coordination geometry.

Experimental

A solution of $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol), mesitylboronic acid (935 mg, 5.7 mmol), 6,6″-dibromo-2,2′:6′,2″-terpyridine (740 mg, 1.9 mmol) and $Na_3PO_4.12H_2O$ (3 g, 7.9 mmol) in a mixture of DME (18 ml) and H_2O (3 ml) was refluxed for 20 h under an argon atmosphere. The solution was cooled to room temperature, and the solvent evaporated under reduced pressure. The residue was extracted with benzene, washed with brine and dried over $MgSO_4$. Solvents were removed under reduced pressure to give a white precipitate, which was collected by filtration and washed with hexane. The precipitate was dried *in vacuo* and recrystallized from toluene to give microcrystals. Yield 510 mg, 57%. (m.p. 553 K). Spectroscopic analysis: ^{1}H NMR ($CDCl_3$ at 298 K): 2.11 (*s*, 12H), 2.35 (*s*, 6H), 6.98 (*s*, 4H), 7.26 (*d*, 2H), 7.83 (*t*, 1H), 7.92 (*t*, 2H), 8.50 (*d*, 2H), 8.59 (*dd*, 2H); analysis calculated for $C_{33}H_{31}N_3$: C 84.40, H 6.65, N 8.95%; found: C 84.04, H 6.55, N 8.92%. A solution of dmtpy (15.0 mg, 0.032 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of *trans*-$Pd(MeCN)_2Cl_2$ (8.3 mg, 0.032 mmol) in CH_2Cl_2(1.0 ml) and stirred at room temperature for 20 h to give a yellow precipitate. The yellow powder was washed with pentane and dried *in vacuo*. The product was recrystallized from dichloromethane/hexane to give crystals suitable for X-ray analysis.

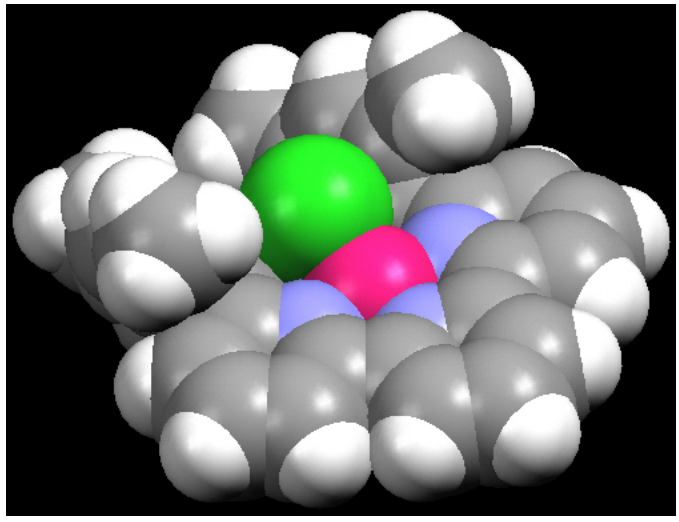


Figure 2
Space-filling drawing of the cation of (I). Key: red (Pd), green (Cl) and purple (N).

Spectroscopic analysis: ^{1}H NMR ($CDCl_3$ at 298 K) 2.18 (*s*, 12H), 2.23 (*s*, 6H), 6.78 (*s*, 4H), 7.39 (2H, *d*), 8.31 (2H, *t*), 8.95 (2H, *d*), 9.00 (1H, *t*), 9.21 (2H, *d*); analysis calculated for $C_{69}H_{68}N_6Pd_3Cl_{12}$: C 48.01. H 3.97, N 4.87%; found: C 47.62, H 3.88, N 4.86%.

Crystal data

$[PdCl(C_{33}H_{31}N_3)]_2[PdCl_4]\cdot4CH_2Cl_2$	$Z = 1$
$M_r = 1810.82$	$D_x = 1.574$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 10.6555$ (7) Å	Cell parameters from 12443 reflections
$b = 21.3398$ (5) Å	$\theta = 2.3$–$27.4°$
$c = 8.5995$ (1) Å	$\mu = 1.23$ mm^{-1}
$\alpha = 91.2124$ (4)°	$T = 200$ K
$\beta = 100.468$ (7)°	Platelet, orange
$\gamma = 83.566$ (7)°	0.15 × 0.15 × 0.05 mm
$V = 1910.75$ (14) Å^3	

Data collection

Rigaku R-AXIS-RAPID Imaging Plate diffractometer	8029 independent reflections
ω scans	4933 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.037$
$T_{min} = 0.777$, $T_{max} = 0.940$	$\theta_{max} = 27.5°$
9543 measured reflections	$h = -13 \rightarrow 13$
	$k = -27 \rightarrow 27$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.144$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
8029 reflections	$\Delta\rho_{min} = -1.36$ e Å^{-3}
455 parameters	

Table 1
Selected geometric parameters (Å, °).

Pd1—N21	1.953 (4)	Pd1—N11	2.091 (4)
Pd1—N31	2.089 (4)	Pd1—Cl1	2.2859 (13)
N21—Pd1—N31	81.28 (18)	N21—Pd1—Cl1	161.42 (14)
N21—Pd1—N11	80.39 (18)	N31—Pd1—Cl1	98.89 (12)
N31—Pd1—N11	160.31 (17)	N11—Pd1—Cl1	100.78 (12)

The H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distances of 0.93 Å and methyl C—H distances of 0.96 Å. Rotating group refinement was used for the methyl groups. One dichloromethane molecule is disordered, with distinct positions with partial occupancies for Cl atoms. The occupancies for the disordered group (Cl21/Cl22 and Cl31/Cl32) are 0.6315:0.3685. These disordered atoms were refined with isotropic displacement parameters.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *TEXSAN* and *MERCURY*.

Support of this work by JSPS Fellowships [for AO, grant 2306(1999–2002)] and a Grant-in-Aid for Scientific Research on Priority Area (A) (No. 10146231) from the Ministry of Education, Science, Sports and Culture, Japan, is gratefully acknowledged.

References

Britovsek, G. J. P., Gibson, V. C., Kimberley, B. S., Maddox, P. J., McTavish, S. J., Solan, G. A., White, A. J. P. & Williams, D. J. (1998). *Chem. Commun.* pp. 849–850.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Higashi. T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Intille, G. M., Pfluger, C. E. & Junior, W. A. B. (1973). *Cryst. Struct. Commun.* **2**, 217–220.

Johnson, L. K., Killiam, C. M., Brookhart, J. (1995). *J. Am. Chem. Soc.* **117**, 6414–6415.

Molecular Structure Corpration (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corpration (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Small, B. L. M., Brookhart, J. & Bennett, A. M. (1998). *J. Am. Chem. Soc.* **120**, 4049–4050.