

*d*<sup>0</sup> metals (Hubert-Pfalzgraf, 1987). Such a geometry has already been observed in the hexanuclear complex synthesized through the same reaction [Zr—O—C = 179.5 (6)°] (Schmid, Mosset & Galy, 1991).

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## Quasi-One-Dimensional Structure of *cis*-Dichlorobis(2,6-dimethylphenyl isocyanide)-palladium(II), [Pd{2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC}<sub>2</sub>Cl<sub>2</sub>]

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**Abstract.** C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Pd, *M<sub>r</sub>* = 439.66, triclinic, *P* $\bar{1}$ , *a* = 8.2168 (9), *b* = 10.4799 (7), *c* = 10.8272 (12) Å,  $\alpha$  = 85.966 (7),  $\beta$  = 80.018 (10),  $\gamma$  = 86.929 (7)°, *V* = 915.14 (16) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.596 Mg m<sup>-3</sup>,  $\mu$  = 1.29 mm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.70930 Å, *F*(000) = 439.95, *T* = 293 K. The structure was refined to *R* = 0.034, *wR* = 0.030 for 2100 observed reflections. The Pd atom has a square-planar coordination with the two Cl atoms and the two isocyanide groups in *cis* configurations. The dihedral angles between the xylenyl isocyanide planes and the Pd coordination plane are 20.9 (1) and 46.6 (1)°. The compound forms a quasi linear chain with Pd···Pd separations of 4.186 (2) and 4.061 (2) Å, and a Pd···Pd···Pd angle of 170.17 (2)°.

**Introduction.** [Pd{2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC}<sub>2</sub>Cl<sub>2</sub>] (1) can be obtained from direct reaction between xylenyl isocyanide and palladium(II) dichloride in aqueous solutions or from photochemical decomposition of hexakis(xylenyl isocyanide)dipalladium(I) hexafluorophosphate, dichlorotetrakis(xylenyl isocyanide)-dipalladium(I) hexafluorophosphate or dichlorotetrakis(xylenyl isocyanide)dipalladium(I) in chloroform solutions (Yamamoto & Yamazaki, 1985). (1) is of some interest in catalysis; the related *cis*-dichlorobis(phenyl isocyanide)palladium(II) compound (2) is found to be an efficient catalyst in hydroformylation reactions (Mondal, Banerjee &

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Sen, 1980). The presence of methyl groups at the *ortho* positions in (1) should induce important intramolecular steric hindrance and should influence molecular structure, crystal packing and reactivity. In the course of our work, we have noticed that (1) crystallizes from acetonitrile or chloroform/ether solutions forming long needles from which suitable single crystals were available for X-ray diffraction analysis. After solving the X-ray single-crystal diffraction data, we find that contrary to most analogous non-planar compounds (*cis*-PdCl<sub>2</sub>L<sub>2</sub>; L = bulky ligand), a quasi-one dimensional (1D) structure is found despite the distorted structure of (1). We are currently investigating the design of new 1D compounds using mono- and diisocyanide ligands with Pd<sup>II</sup>, Ag<sup>I</sup> and Au<sup>I</sup> metals. This work describes the crystal and molecular structures of (1).

**Experimental.** Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Mo *K*α radiation; lattice parameters determined from 24 reflections (40 ≤ 2θ ≤ 45°); 2θ/ω technique; three standard reflections monitored every 60 min without significant deviation. Crystal: 0.20 × 0.20 × 0.20 mm; −8 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 10, −11 ≤ *l* ≤ 11; 2364 unique measured reflections; *R*<sub>int</sub> = 0.016, 2100 observed with *I*<sub>net</sub> ≥ 2.5σ*I*<sub>net</sub>, 2θ<sub>max</sub> = 44.7°; *R* = 0.034, *wR* = 0.030, *S* = 3.00; (Δ/σ)<sub>max</sub> = 0.004; max. and min. density peaks = 0.790 and −0.480 e Å<sup>-3</sup>. The *NRCVAX* system (Gabe, Lee & Le Page, 1985) was used for all calculations. The structure was solved by the application of direct methods and refined by full-matrix least squares on *F* using weights [*w* = 1/σ<sup>2</sup>(*F*)] based

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Table 1. Final coordinates and  $B_{eq}$  values ( $\text{\AA}^2$ ) for non-H atoms with e.s.d.'s in parentheses
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}$
Pd	0.24274 (8)	0.01158 (5)	0.01133 (5)	3.61 (3)
Cl(1)	0.1542 (3)	0.2049 (2)	-0.0722 (2)	5.3 (1)
Cl(2)	0.3475 (3)	-0.0632 (2)	-0.1828 (2)	5.9 (1)
N(1)	0.1273 (6)	0.1203 (5)	0.2683 (5)	3.8 (3)
N(2)	0.3423 (7)	-0.2484 (5)	0.1295 (5)	3.9 (3)
C(1)	0.1652 (9)	0.0766 (6)	0.1730 (6)	4.0 (4)
C(2)	0.0842 (8)	0.1739 (6)	0.3853 (6)	3.5 (3)
C(3)	0.1539 (8)	0.1171 (6)	0.4848 (6)	3.6 (3)
C(4)	0.1075 (9)	0.1716 (8)	0.5996 (6)	4.8 (4)
C(5)	0.0077 (1)	0.2793 (8)	0.6106 (7)	5.6 (5)
C(6)	-0.0589 (9)	0.3345 (7)	0.5097 (8)	5.1 (4)
C(7)	-0.0200 (8)	0.2833 (7)	0.3915 (6)	4.0 (3)
C(8)	-0.0905 (9)	0.3401 (7)	0.2811 (7)	6.1 (4)
C(9)	0.2695 (9)	0.0038 (7)	0.4708 (6)	5.0 (4)
C(10)	0.3108 (9)	-0.1488 (7)	0.0846 (6)	4.0 (4)
C(11)	0.3727 (8)	-0.3752 (6)	0.1756 (6)	3.4 (3)
C(12)	0.3180 (8)	-0.4730 (6)	0.1141 (6)	3.6 (3)
C(13)	0.3502 (9)	-0.5972 (7)	0.1607 (7)	4.7 (4)
C(14)	0.4296 (9)	-0.6199 (7)	0.2606 (7)	4.9 (4)
C(15)	0.4785 (8)	-0.5207 (7)	0.3201 (6)	4.5 (4)
C(16)	0.4521 (8)	-0.3964 (6)	0.2770 (6)	3.4 (3)
C(17)	0.5068 (9)	-0.2881 (7)	0.3412 (7)	5.5 (4)
C(18)	0.2282 (9)	-0.4463 (6)	0.0059 (7)	5.3 (4)

Table 2. Bond lengths ( $\text{\AA}$ ) and valence angles ( $^\circ$ ) with e.s.d.'s in parentheses

Pd—Cl(1)	2.294 (2)	C(4)—C(5)	1.36 (1)
Pd—Cl(2)	2.303 (2)	C(5)—C(6)	1.38 (1)
Pd—C(1)	1.915 (6)	C(6)—C(7)	1.40 (1)
Pd—C(10)	1.906 (7)	C(7)—C(8)	1.49 (1)
N(1)—C(1)	1.145 (8)	C(11)—C(12)	1.395 (9)
N(1)—C(2)	1.403 (8)	C(11)—C(16)	1.370 (9)
N(2)—C(10)	1.157 (9)	C(12)—C(13)	1.39 (1)
N(2)—C(11)	1.411 (8)	C(12)—C(18)	1.49 (1)
C(2)—C(3)	1.388 (9)	C(13)—C(14)	1.36 (1)
C(2)—C(7)	1.392 (9)	C(14)—C(15)	1.37 (1)
C(3)—C(4)	1.389 (9)	C(15)—C(16)	1.37 (1)
C(3)—C(9)	1.48 (1)	C(16)—C(17)	1.50 (1)
Cl(1)—Pd—Cl(2)	93.36 (6)	C(5)—C(6)—C(7)	120.8 (6)
Cl(1)—Pd—C(1)	86.7 (2)	C(2)—C(7)—C(6)	115.6 (6)
Cl(1)—Pd—C(10)	178.3 (2)	C(2)—C(7)—C(8)	122.4 (6)
Cl(2)—Pd—C(1)	177.4 (2)	C(6)—C(7)—C(8)	121.9 (6)
Cl(2)—Pd—C(10)	88.0 (2)	Pd—C(10)—N(2)	175.8 (6)
C(1)—Pd—C(10)	91.9 (3)	N(2)—C(11)—C(12)	117.0 (5)
C(1)—N(1)—C(2)	178.9 (6)	N(2)—C(11)—C(16)	119.4 (6)
C(10)—N(2)—C(11)	174.3 (6)	C(12)—C(11)—C(16)	123.6 (6)
Pd—C(1)—N(1)	175.7 (6)	C(11)—C(12)—C(13)	115.9 (6)
N(1)—C(2)—C(3)	117.7 (7)	C(11)—C(12)—C(18)	122.2 (6)
N(1)—C(2)—C(7)	117.3 (6)	C(13)—C(12)—C(18)	121.9 (6)
C(3)—C(2)—C(7)	124.9 (6)	C(12)—C(13)—C(14)	121.3 (6)
C(2)—C(3)—C(4)	116.3 (6)	C(13)—C(14)—C(15)	120.9 (6)
C(2)—C(3)—C(9)	122.3 (5)	C(14)—C(15)—C(16)	120.3 (6)
C(4)—C(3)—C(9)	121.4 (6)	C(11)—C(16)—C(15)	118.0 (6)
C(3)—C(4)—C(5)	121.1 (7)	C(11)—C(16)—C(17)	121.7 (6)
C(4)—C(5)—C(6)	121.2 (6)	C(15)—C(16)—C(17)	120.4 (6)

on counting statistics. Linear absorption correction was applied with max. and min. transmission factors of 0.7489 and 0.7502, respectively. Anisotropic thermal parameters were refined for all non-H atoms. All H atoms were geometrically placed and assigned isotropic temperature factors corresponding to their attached atoms but were not refined. No abnormally short contacts were noted. Atomic scattering factors

stored in the *NRCVAX* program are those from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B, pp. 99–101).

**Discussion.** Table 1\* gives the final atomic parameters with their  $B_{eq}$  values and Fig. 1 shows the molecular structure of (1) with the atom-numbering scheme. The molecular geometry is shown in Table 2. The central Pd atom has a *cis* square-planar coordination with two Cl atoms and two xylene isocyanide groups in agreement with the IR and far-IR spectroscopic results;  $\nu(\text{N}\equiv\text{C}) = 2190$  and  $2216 \text{ cm}^{-1}$ ;  $\nu(\text{Pd}-\text{Cl}) = 314$  and  $334 \text{ cm}^{-1}$ . The average Pd—Cl [2.302 (2)] and Pd—C [1.925 (7) Å] bond lengths are normal; Pd—Cl = 2.301 (2) and Pd—C = 1.933 (7) Å in *cis*-PdCl<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub> (Kitano & Hori, 1981). Nonetheless, a distortion ( $\sim 3^\circ$ ) from the theoretical  $90^\circ$  value of the Cl(1)—Pd—Cl(2) angle is observed.

Intramolecular steric hindrance interactions are evident; the C(9)⋯C(17) separation is only 3.76 (1) Å

\* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53636 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

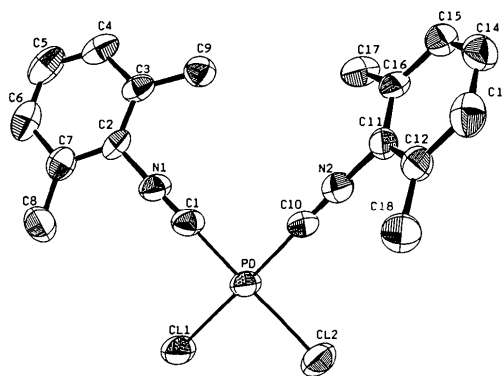


Fig. 1. Structure of (1) with the numbering scheme. The ellipsoid encloses the region in which the center of the atom is found with 50% probability.

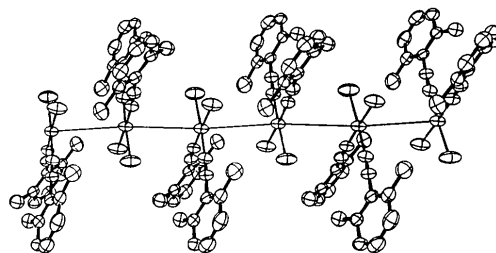


Fig. 2. View of the 1D structure of (1) along the *a* axis. (Only five molecules are shown. The Pd⋯Pd⋯Pd chain is infinite.)

with a short H(9a)⋯H(17b) distance of ~2.7 Å. As a result, the dihedral angles between the xylenyl groups and Pd coordination plane are 20.9 (1) and 46.6 (1)°. The dihedral angle between the two xylenyl ligands is 43.8 (2)°. There are other examples in which relatively close intramolecular contacts between methyl groups of two adjacent xylenyl ligands are observed. For instance, methyl–methyl separations of 3.89 and 3.532 Å, and dihedral angles of 35.85, and 9.52 and 16.04° have been reported for *trans*-FeCl<sub>2</sub>·[2,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>NC]<sub>4</sub> (Drew, Dodd, Williamson & Willy, 1986) and Re<sub>2</sub>(CO)<sub>6</sub>[2,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>NC]<sub>4</sub> (Harris, Boeyens & Coville, 1985), respectively.

Other minor effects are also noticed; the Pd—C(1)—N(1) and Pd—C(10)—N(2) angles are bent outward from each other by 4.3 (7) and 4.2 (7)°, respectively, and the C(10) and C(1) atoms lie at -0.119 (8) and +0.174 (8) Å from the Pd coordination plane.

The crystal packing attracts significant interest (Fig. 2). Obvious quasi-one-dimensional (1D) packing is observed; (1) crystallizes in a 1D fashion via an alternating pattern *ABABAB* . . . (Fig. 2) where the *AB* unit possesses the *C<sub>i</sub>* local point group. The two Pd⋯Pd intermolecular separations are 4.186 (2) and 4.061 (2) Å and the Pd⋯Pd⋯Pd angle is 170.17 (2)°. The Pd⋯Pd distances are larger than the van der Waals radii (3.20 Å; Cotton, Wilkinson & Gauss, 1987) and *M*⋯*M* distances found for other related 1D Pd and Pt complexes, which typically range from 2.8–3.5 Å (Miller, 1982). Occasionally, greater values for Pt⋯Pt distances are found: 3.60 Å for Sr[Pt(CN)<sub>4</sub>]<sub>2</sub>·5H<sub>2</sub>O (Krogmann & Stephan, 1968); ~3.71 Å for Na<sub>2</sub>[Pt(CN)<sub>4</sub>]<sub>2</sub>·3H<sub>2</sub>O (Johnson, Koch & Williams, 1977); 3.554 and 3.855 Å for [Cu(en)<sub>2</sub>][Pt(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] (en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) (Krogmann, 1968). (1) appears to be the first example of

an organometallic Pd compound which exhibits a 1D structure in the solid state. However, the long Pd⋯Pd excludes the possibility of any strong Pd⋯Pd interactions. Indeed, the solid state and solution UV–visible spectra of (1) are almost identical in the aromatic region (220–300 nm), and exhibit only a small shift of the low-energy band going from 310 (shoulder) to ~320 nm in the solid state. We come to the conclusion that only crystal packing forces are responsible for the 1D structure of (1).

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## Structure of 1% Copper(II)-Doped Dichlorobis(1,2-dimethylimidazole)zinc(II)

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**Abstract.** [Zn<sub>0.99</sub>Cu<sub>0.01</sub>Cl<sub>2</sub>(C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 328.43, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.587 (1), *b* = 7.1324 (7), *c* = 16.356 (2) Å, β = 112.87 (1)°, *V* = 1460.4 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.50 (1), *D<sub>x</sub>* = 1.492 g cm<sup>-3</sup>, μ(Mo Kα, λ = 0.71073 Å) = 20.8 cm<sup>-1</sup>, *F*(000) = 672.0, *T* =

297 (1) K, *R* = 0.028 for 1782 unique observed reflections. The structure contains discrete dichlorobis(1,2-dimethylimidazole)zinc(II) molecules. Pseudotetrahedral N<sub>2</sub>Cl<sub>2</sub> coordination about zinc is effected by coordination to two imidazole and two