

***α*-Chloro-*b*-chloromethyl-*dc*-(3-4- $\eta$ -2,2,*N,N*-tetramethyl-3-butenylamine-*N*)-  
palladium(II), C<sub>9</sub>H<sub>19</sub>Cl<sub>2</sub>NPd**

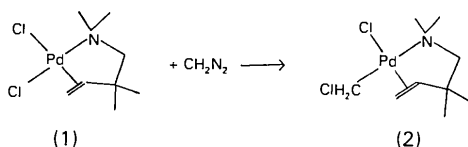
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(Received 25 April 1984; accepted 12 July 1984)

**Abstract.**  $M_r = 318.6$ , monoclinic,  $P2_1/n$ ,  $a = 6.574$  (2),  $b = 12.171$  (4),  $c = 16.158$  (3) Å,  $\beta = 101.42$  (2)°,  $V = 1267.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.67$  g cm<sup>-3</sup>,  $F(000) = 640$ ,  $\mu(\text{Mo } K\alpha) = 18.3$  cm<sup>-1</sup>,  $\lambda = 0.70926$  Å,  $T = 294$  K,  $R = 0.052$  for 2471 observed data. The Pd atom has a slightly distorted square-planar coordination [Pd–Cl 2.334 (2), Pd–N 2.198 (6), Pd–C(olefin) 2.175 (7) and 2.143 (8), Pd–CH<sub>2</sub>Cl 2.039 (8) Å] with the CH<sub>2</sub>Cl moiety *trans* to the N atom. The five-membered ring has an envelope conformation, with the quaternary C atom 0.61 (1) Å above the plane of the other four atoms.

**Introduction.** The reaction (McCrimble, Ferguson, Ruhl & Sneddon, 1984) of dichloro(3-4- $\eta$ -2,2,*N,N*-tetramethyl-3-butenylamine-*N*)palladium(II) (1) with diazomethane in ether–ethanol leads *inter alia* to the carbene insertion product (2) (the title compound). The structure and stereochemistry of this product could not be readily determined by spectroscopic methods; our X-ray analysis establishes the structure and shows that the CH<sub>2</sub>Cl moiety is *trans* to the N atom.



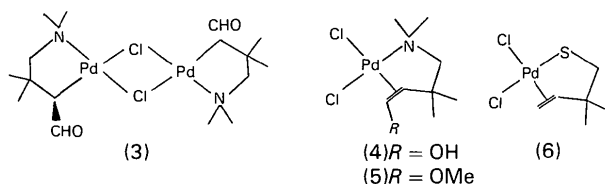
**Experimental.** Colourless crystals. CAD-4 diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation. 25 reflections ( $10 < \theta < 15^\circ$ ) for measuring lattice constants for data collection, crystal  $0.15 \times 0.20 \times 0.30$  mm.  $2 < \theta < 27^\circ$  ( $h$  0 to 8,  $k$  0 to 15,  $l$  -20 to 20),  $\omega$ - $2\theta$  scans,  $\omega$ -scan width ( $0.60 + 0.35 \tan\theta$ )°. Intensities of three reflections monitored every 3 h of exposure time showed no significant variation. Lp corrections. 2768 unique reflections, 2471 (89.3%) with  $I > 3\sigma(I)$ , where  $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$ ,  $S$  = scan count and  $B$  = time-averaged background count. Absorption correction not considered necessary. Heavy-atom method using the *NRC* crystal structure package (Gabe, Larson, Wang & Lee, 1981). Refinement by block-diagonal least-squares calculations on  $F$ . H atoms from difference syntheses

included at their idealized positions (C–H 0.95 Å) but not refined. Final  $R = 0.052$ ,  $R_w = 0.075$  for 2471 observed data,  $R = 0.055$  for all data,  $w = 1/\sigma^2(F)$ . Final difference map showed peaks ( $0.8 - 0.4 e \text{ \AA}^{-3}$ ) near the heavy atoms but the remainder of the map was essentially featureless. Max. coordinate  $\Delta/\sigma = 0.10$  for  $x$  of C(4), max. thermal-parameter  $\Delta/\sigma = 0.11$  for  $U_{22}$  of C(4), mean  $\Delta/\sigma = 0.02$ . Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Other computer programs included *XANADU* (Roberts & Sheldrick, 1975) and *ORTEPII* (Johnson, 1976).

**Discussion.** Final fractional coordinates with mean isotropic temperature factors are in Table 1.\* Table 2 contains molecular dimensions.

The crystal structure of (2) (Fig. 1) contains discrete monomeric molecules (Fig. 2) separated by normal van der Waals distances. Our analysis establishes that the –CH<sub>2</sub>Cl moiety and the N atom are *trans*. The Pd coordination is slightly distorted square-planar; displacements of atoms from the Pd,N,Cl(1),C(9) plane are Pd –0.032 (1), N 0.015 (7), Cl(1) 0.000 (2), C(9) 0.016 (11), C(3) 0.324 (9), C(4) –0.979 (9) Å. The *cis* angles at Pd are in the range  $82.3$  to  $95.8$  (3)°. The chelate ring Pd,N,C(1),C(2),C(3) has a C(2) envelope conformation, with C(2) 0.61 (1) Å from the Pd,N,C(1),C(3) plane; similar conformations with the quaternary carbon C(2) as the flap atom have been found in (3) (Alyea, Dias, Ferguson, McAlees, McCrimble & Roberts, 1977), (4) (McCrimble, Ferguson, McAlees & Ruhl, 1981), (5) (McCrimble, Ferguson, Khan, McAlees & Ruhl, 1981) and (6) (McCrimble, Alyea, Ferguson, Dias, McAlees & Parvez, 1980). The orientation of the –CH<sub>2</sub>Cl moiety is defined by, e.g., the Cl(2)–C(9)–Pd–C(4) torsion angle of  $90.0$  (9)° which places the Cl(2) atom on the same side of the coordination plane as the C(2) atom.

\* Lists of structure factors, anisotropic thermal parameters and the calculated H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39632 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



The Pd–olefin interaction in (2) is asymmetric [Pd–C(3) 2.175 (7), Pd–C(4) 2.143 (8) Å] with the midpoint of the olefin bond 0.327 (9) Å from the Pd,N,Cl(1),C(9) plane. Comparable displacements of the olefin bond midpoints from the Pd coordination plane are found in (4) [molecule 1, 0.61 (1); molecule (2), 0.60 (1) Å] and in (5) [molecule 1, 0.365 (3); molecule 2, 0.580 (3) Å], but the Pd–C(olefin) distances are much more asymmetric [2.101–2.268 (11) Å in the vinyl alcohol (4) and 2.135–2.266 (4) Å in the vinyl ether (5)]. The plane containing the Pd and olefinic C atoms C(3) and C(4) makes an angle of 78.8 (9)° with the Pd, Cl(1),N,C(9) plane, in

agreement with the corresponding angles in (4) (mean 75.5°) and (5) (mean 78.9°).

A markedly longer Pd–N distance [2.198 (6) Å] is found in (2) (with N *trans* to –CH<sub>2</sub>Cl) than is found in (4) [mean 2.071 (9) Å] or (5) [mean 2.085 (2) Å], where N is *trans* to Cl, reflecting differences in *trans* effect between terminal –Cl and –CH<sub>2</sub>Cl. The Pd–C(9)(*sp*<sup>3</sup>) distance in (2) (*trans* to N) [2.039 (8) Å] is, however, comparable to the Pd–C(*sp*<sup>3</sup>) distance in (3) [2.047 (9) Å] where the C atom is *trans* to a bridging Cl. The Pd–Cl(1) bond length [2.334 (2) Å] lies within the range of Pd–Cl distances found for Cl *trans* to olefin in (4) and (5) [2.321–2.357 (3) Å]. The remaining bond lengths [C(*sp*<sup>3</sup>)–N 1.470–1.509 (10), C(*sp*<sup>3</sup>)–C(*sp*<sup>3</sup>) 1.496–1.540 (13), C(*sp*<sup>3</sup>)–C(*sp*<sup>2</sup>) 1.540 (11), C(*sp*<sup>2</sup>)=C(*sp*<sup>2</sup>) 1.347 (12), C(*sp*<sup>3</sup>)–Cl 1.743 (10) Å] are in accord with accepted values.

We thank NSERC Canada for Grants in Aid of Research.

Table 1. Final fractional coordinates for (2) with estimated standard deviations in parentheses, and mean  $B_{\text{iso}}(\text{Å}^2) = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$

|       | <i>x</i>     | <i>y</i>    | <i>z</i>    | $B_{\text{iso}}$ |
|-------|--------------|-------------|-------------|------------------|
| Pd    | 0.11488 (9)  | 0.15313 (4) | 0.07649 (3) | 2.76 (3)         |
| Cl(1) | 0.4047 (3)   | 0.0492 (2)  | 0.1371 (1)  | 4.6 (1)          |
| Cl(2) | 0.2460 (5)   | 0.2415 (3)  | –0.0879 (2) | 7.8 (2)          |
| N     | 0.0442 (10)  | 0.1958 (5)  | 0.1999 (3)  | 3.4 (3)          |
| C(1)  | –0.1298 (13) | 0.2738 (6)  | 0.1863 (5)  | 4.0 (4)          |
| C(2)  | –0.1339 (15) | 0.3496 (6)  | 0.1097 (5)  | 4.2 (5)          |
| C(3)  | –0.1206 (12) | 0.2768 (6)  | 0.0330 (5)  | 3.5 (4)          |
| C(4)  | –0.2042 (13) | 0.1759 (7)  | 0.0178 (5)  | 3.9 (4)          |
| C(5)  | –0.3468 (18) | 0.4035 (9)  | 0.0899 (6)  | 6.5 (7)          |
| C(6)  | 0.0330 (18)  | 0.4350 (7)  | 0.1219 (6)  | 5.6 (7)          |
| C(7)  | 0.2261 (15)  | 0.2411 (7)  | 0.2599 (5)  | 4.9 (5)          |
| C(8)  | –0.0202 (15) | 0.0939 (7)  | 0.2414 (5)  | 5.1 (5)          |
| C(9)  | 0.1819 (16)  | 0.1221 (7)  | –0.0393 (5) | 5.0 (6)          |

Table 2. Interatomic distances (Å) and angles (°)

|               |            |                |            |
|---------------|------------|----------------|------------|
| Pd–Cl(1)      | 2.334 (2)  | C(1)–C(2)      | 1.540 (11) |
| Pd–N          | 2.198 (6)  | C(2)–C(3)      | 1.540 (11) |
| Pd–C(3)       | 2.175 (7)  | C(2)–C(5)      | 1.522 (13) |
| Pd–C(4)       | 2.143 (8)  | C(2)–C(6)      | 1.496 (14) |
| Pd–C(9)       | 2.039 (8)  | C(3)–C(4)      | 1.347 (12) |
| N–C(1)        | 1.470 (10) | C(9)–Cl(2)     | 1.743 (10) |
| N–C(7)        | 1.488 (11) |                |            |
| N–C(8)        | 1.509 (10) |                |            |
| Cl(1)–Pd–N    | 92.8 (2)   | C(1)–N–C(7)    | 111.0 (6)  |
| Cl(1)–Pd–C(3) | 168.7 (2)  | C(1)–N–C(8)    | 108.6 (6)  |
| Cl(1)–Pd–C(4) | 154.5 (2)  | C(7)–N–C(8)    | 106.0 (6)  |
| Cl(1)–Pd–C(9) | 88.7 (3)   | N–C(1)–C(2)    | 113.3 (6)  |
| N–Pd–C(3)     | 82.3 (3)   | C(1)–C(2)–C(3) | 108.0 (6)  |
| N–Pd–C(4)     | 90.4 (3)   | C(1)–C(2)–C(5) | 107.2 (8)  |
| N–Pd–C(9)     | 177.0 (3)  | C(1)–C(2)–C(6) | 114.4 (7)  |
| C(3)–Pd–C(4)  | 36.4 (3)   | C(3)–C(2)–C(5) | 106.0 (7)  |
| C(3)–Pd–C(9)  | 95.8 (3)   | C(3)–C(2)–C(6) | 110.5 (8)  |
| C(4)–Pd–C(9)  | 89.4 (4)   | C(5)–C(2)–C(6) | 110.4 (8)  |
| Pd–N–C(1)     | 108.4 (4)  | C(2)–C(3)–C(4) | 125.8 (7)  |
| Pd–N–C(7)     | 113.1 (5)  | Pd–C(3)–C(2)   | 106.7 (5)  |
| Pd–N–C(8)     | 109.7 (5)  | Pd–C(3)–C(4)   | 70.5 (5)   |
|               |            | Pd–C(4)–C(3)   | 73.1 (5)   |
|               |            | Pd–C(9)–Cl(2)  | 112.0 (4)  |

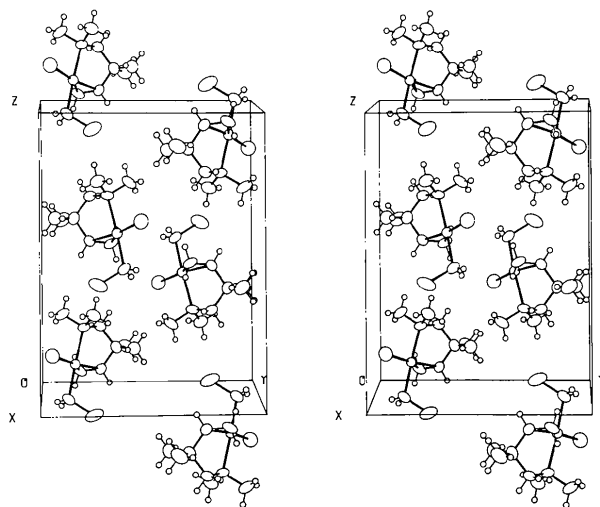


Fig. 1. Stereoview of the crystal structure of (2).

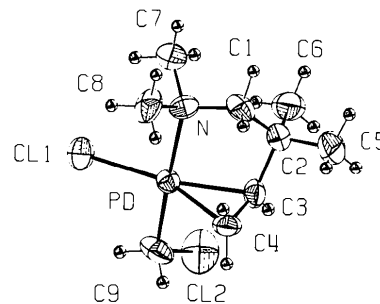


Fig. 2. View of a molecule of (2) with the crystallographic numbering scheme.

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*Acta Cryst.* (1984). **C40**, 2022–2024

**Aqua- $\mu$ -chloro-trichloro- $\mu$ -[3,6-di(2-pyridyl)pyridazine]-dicopper(II),  
[Cu<sub>2</sub>Cl<sub>4</sub>(H<sub>2</sub>O)(C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>)]**

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(Received 2 May 1984; accepted 23 July 1984)

**Abstract.**  $M_r = 521.15$ , monoclinic,  $P2_1/c$ ,  $a = 9.809$  (1),  $b = 9.212$  (1),  $c = 19.316$  (2) Å,  $\beta = 100.4$  (1)°,  $V = 1716.7$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$ (by flotation) = 2.02,  $D_x = 2.016$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 30.57$  cm<sup>-1</sup>,  $F(000) = 1032$ ,  $T = 293$  K, final conventional  $R = 0.048$  for 1227 unique observed reflections. The complex is the same as that previously reported [De Munno, Denti & Dapporto (1983). *Inorg. Chim. Acta*, **74**, 199–203], but in a different environment. It consists of a binuclear unit containing a bridging tetradentate organic ligand, two Cu atoms, two terminal Cl atoms and a Cl bridge. Both Cu atoms are five-coordinated, the apical sites being occupied by a Cl atom and a water molecule.

**Introduction.** Several  $\mu$ -OH binuclear Cu<sup>II</sup> complexes with the tetradentate ligand 3,6-di(2-pyridyl)pyridazine have been synthesized and their structures determined (Ghedini, De Munno, Denti, Manotti Lanfredi & Tiripicchio, 1982; Dapporto, De Munno, Bruno & Romeo, 1983; Dapporto, De Munno, Sega & Mealli, 1984). The crystal structure of a monohydrated  $\mu$ -Cl binuclear Cu<sup>II</sup> complex with the same ligand has also been recently determined (De Munno, Denti & Dapporto, 1983). These binuclear complexes are interesting since their Cu...Cu separations are similar to those reported in oxyhemocyanins: 3.55 and 3.67 Å from EXAFS studies (Co, Hodgson, Eccles & Lontie, 1981; Brown, Powers, Kincaid, Larrabee & Spiro, 1980). In

this paper we report the structure of the anhydrous  $\mu$ -Cl Cu<sup>II</sup> complex with the ligand 3,6-di(2-pyridyl)pyridazine.

**Experimental.** The complex is obtained according to the procedure previously reported (Dapporto, De Munno, Sega & Mealli, 1984). Green parallelepiped crystal 0.04 × 0.10 × 0.10 mm, Siemens Stoe diffractometer, scan range  $2\theta = 3$ –50°, graphite-monochromatized Mo  $K\alpha$  radiation,  $\omega$ - $\theta$  scan technique. 25 reflections for measuring lattice parameters,  $7 < \theta < 15^\circ$ . No systematic loss of intensity of three standard reflections (3 $\bar{3}6$ , 1,  $\bar{1}0$ , 10, 2 $\bar{1}9$ ). 1472 measured reflections with  $\theta < 25^\circ$ , 1227 unique with  $I \geq 3\sigma(I)$ .  $R_{\text{int}}$  (from merging equivalent reflections) 0.036.  $0 \leq h \leq 11$ ,  $0 \leq k \leq 11$ ,  $-23 \leq l \leq 23$ . Absorption ignored. Lp correction. Scattering factors for non-hydrogen atoms (*International Tables for X-ray Crystallography*, 1974, p. 99), and for H atoms (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974, p. 149). Structure solved by Patterson and Fourier techniques (Sheldrick, 1976) and refined by a full-matrix least-squares procedure;  $\sum w(|F_o| - |F_c|)^2$  minimized; anisotropic thermal parameters for Cu, Cl, N, O, and C(5), C(6), C(9), C(10) atoms; isotropic for the other C atoms; H of the linked water molecule (from  $\Delta F$  synthesis) and the other H atoms (calculated) assigned isotropic  $U$  of 0.04 Å<sup>2</sup> and not refined; final