Dichlorobis(di-*tert*-butylcarbodiimide)palladium(II)

By R. A. Anderson and F. W. B. Einstein*

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

Abstract. $PdCl_2(Bu^tN:C:NBu^t)_2$, monoclinic, $P2_1/c$, $a = 9.366$ (6), $b = 10.507$ (7), $c = 12.65$ (1) Å, $\beta = 97.15$ (5)°, $V = 1235.4$ Å^3, $Z = 2$, $D_c = 1.31$, $D_m = 1.27$ g cm^{-3}. Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, μ(Mo $K\alpha$) = 9.35 cm^{-1}, $t = 20$ (1)°C; for 664 observed reflections the final R is 0.078. The Pd atom is on a crystallographic center of symmetry and has a square-planar environment. Each ligand is coordinated to Pd through a N atom; the Pd–N and Pd–Cl distances are 2.06 (2) and 2.289 (6) Å respectively. Two weak Pd···H interactions (~2.5 Å) complete the Pd environment.

Introduction. Brown crystals of the title compound, generally in the shape of triangular plates, were kindly provided by Dr J. D. Cotton of the University of Queensland. Weissenberg photographs of the $h0l$ and $h1l$ layers were taken as well as a precession photograph of the $hk0$ zone. These showed systematic absences for $h0l$ of $l = 2n + 1$ and for $0k0$ of $k = 2n + 1$. The presence of the monoclinic space group $P2_1/c$ was thus indicated.

To obtain accurate cell dimensions six strong

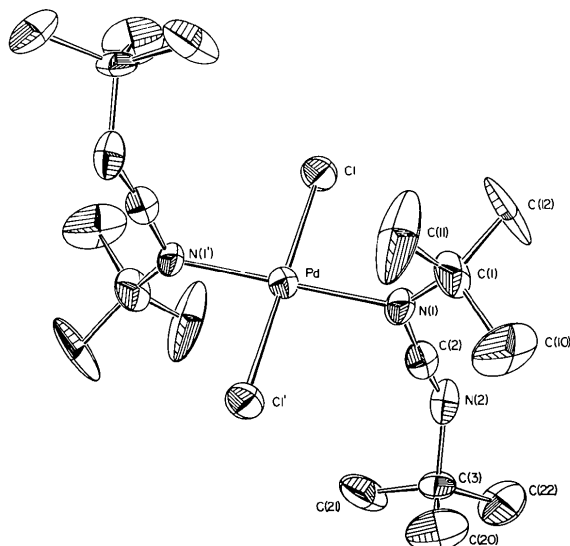* Author to whom correspondence should be addressed.

Fig. 1. The molecular structure of $PdCl_2(Bu^tN:C:NBu^t)_2$.

reflections of $2\theta > 30°$ were centered on the Mo $K\alpha_1$ peak ($\lambda = 0.70926$ Å) and their 2θ values refined by least-squares procedures. A cube-shaped crystal whose edge was 0.03 cm was used for intensity-data collection ($2\theta \leq 35.0°$). These data consisted of 784 measurements of which 664 reflections were considered 'observed', *i.e.* $I > 2.35\sigma(I)$, where $\sigma(I) = |(T) + (t_S/t_B)^2(B_1 + B_2) + (KI)^2|^{1/2}$, $T =$ total count, $t_S =$ scan time, $t_B =$ total background count time, B_1 and B_2 are the background counts, K is a constant equal to 0.03, and I is the net count. A θ–2θ scan of base width 1.5° was used with symmetric background counts of 20 s at each of the scan limits. The take-off angle was 3.5°.

The data were corrected for Lorentz and polarization effects. Routine Patterson and Fourier synthesis methods were used for the structure solution. After several cycles of full-matrix least-squares refinement interspersed with electron-density difference maps, all non-hydrogen atoms were located. Electron-density difference maps based on low-angle data (sin $\theta/\lambda < 0.4$) did not reveal the positions of many of the H atoms, but did indicate the need for anisotropic temperature factors. All reflections were given unit weights initially, but as the refinement proceeded these were replaced by weights derived from counter statistics (*i.e.* $1/\sigma_{F^2}$) giving a final R value of 0.078 ($R_w = 0.100$) where $R = \Sigma||F_o| - |F_c||/\Sigma |F_o|$.

Scattering factors used were those reported by Cromer & Waber (1965). The anomalous dispersion due to Pd was included in the structure-factor cal-

Table 1. *Fractional atomic coordinates with e.s.d.'s* ($\times 10^3$; $\times 10^4$ *for* Cl)

	x	y	z
Pd	0	0	0
Cl	−1930 (6)	623 (6)	820 (5)
N(1)	38 (2)	186 (2)	−39 (2)
N(2)	241 (3)	271 (2)	87 (2)
C(1)	−34 (3)	260 (2)	−131 (2)
C(2)	146 (4)	227 (2)	23 (2)
C(3)	400 (3)	258 (2)	95 (2)
C(10)	84 (3)	331 (3)	−183 (2)
C(11)	−110 (4)	171 (3)	−207 (3)
C(12)	−139 (4)	352 (3)	−92 (3)
C(20)	443 (3)	244 (3)	−22 (2)
C(21)	436 (3)	137 (3)	161 (2)
C(22)	456 (3)	377 (3)	156 (2)

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

Pd—Cl	2·289 (6)	Cl—Pd--N(1)	90·3 (5)
Pd—N(1)	2·06 (2)	Pd—N(1)—C(1)	127 (2)
N(1)—C(1)	1·49 (3)	Pd—N(1)—C(2)	109 (2)
N(1)—C(2)	1·27 (3)	C(2)—N(2)—C(3)	130 (2)
N(2)—C(2)	1·22 (3)	N(1)—C(1)—C(10)	108 (2)
N(2)—C(3)	1·50 (3)	N(1)—C(1)—C(11)	109 (2)
C(1)—C(10)	1·55 (3)	N(1)—C(1)—C(12)	109 (2)
C(1)—C(11)	1·46 (3)	C(10)—C(1)—C(11)	110 (3)
C(1)—C(12)	1·51 (3)	C(10)—C(1)—C(12)	111 (2)
C(3)—C(20)	1·58 (3)	C(11)—C(1)—C(12)	110 (3)
C(3)—C(21)	1·53 (3)	N(2)—C(3)—C(20)	109 (2)
C(3)—C(22)	1·53 (3)	N(2)—C(3)-C(21)	105 (2)
		N(2)—C(3)—C(22)	104 (2)
		C(20)—C(3)—C(21)	112 (2)
		C(20)—C(3)—C(22)	116 (2)
		C(21)—C(3)—C(22)	112 (2)

culation using values listed in *International Tables for X-ray Crystallography* (1962). Computer programs used were those described by Einstein & Jones (1972).

Fig. 1 illustrates the molecule and shows the labeling of the atoms. Table 1 gives the atomic coordinates and Table 2 lists the important interatomic distances and angles.*

Discussion. This study was undertaken to investigate the method of bonding of ligands with hetero multiple bonds to a transition metal. For carbodiimides $RN:C:NR'$ (R,R' = alkyl and aryl) coordination to the metal atom may occur through the nitrogen lone pair or through the π system. In two cases involving Pd^{II} complexes (Khare, Little, Veal & Doedens, 1975; Gasparrini, Misiti & Cernia, 1976) coordination through the N lone pair of similar hetero multiple-bond systems was found. In the reaction between di-*tert*-butylcarbodiimide and *trans*-(PhCN)$_2$PdCl$_2$ in CH$_2$Cl$_2$ (Bycroft & Cotton, 1973) the title compound was obtained. Physical techniques (Bycroft & Cotton, 1973) indicated that the metal is also coordinated to the N atom in a *trans* square-planar arrangement as had

been found in the two earlier examples. This crystal structure analysis confirms these proposals. The Pd atom is on a crystallographic center of symmetry and is linked to two Cl and two N atoms in a square-planar environment. The N(1)—C(2) and C(2)—N(2) bond lengths have been found to be 1·27 (3) and 1·22 (3) Å respectively. These distances indicate multiple-bond character as C—N single and triple bonds have been reported as 1·47 and 1·16 Å respectively (*e.g.* Huheey, 1972).

For the tertiary carbons C(1) and C(3), the bond angles and distances to surrounding atoms are within normal limits. However, Pd and C(11) are close to one another (3·24 Å). This could allow an interaction between Pd and H atoms on C(11), and it has been calculated that the closest a H atom on C(11) could come is 2·5 Å from a Pd atom, completing an irregular octahedral environment. These types of interactions have been proposed in other cases (*e.g.* Cotton & Wilkinson, 1972).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32991 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.