Crystal Structure of *trans*-(Dicyano)bis(triphenylphosphine)palladium(II) Dichloromethane Solvate

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The title palladium(II) compound, $[\text{Pd}(\text{PPh}_3)_2(\text{CN})_2]$ (**1**, Fig. 1) was obtained from the reaction of $\text{Pd}(\text{PPh}_3)_4$ with Me_3SiCN (1:1 molar ratio) in benzene (at 80°C for 2 h). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a mixture of CH_2Cl_2 and C_6H_6 (ca. 1:4 by volume). Table

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data

Formula: $\text{PdP}_2\text{N}_2\text{C}_{38}\text{H}_{30} + \text{CH}_2\text{Cl}_2$
Formula weight = 767.95
Crystal system: monoclinic $C2/c$ (No. 15)
$a = 12.228(4)\text{\AA}$
$b = 14.235(6)$
$c = 20.473(3)$
$\beta = 93.87(3)^\circ$
$V = 3554(2)\text{\AA}^3$
$D_c = 1.434\text{ g/cm}^3$
$\mu = 7.93\text{ cm}^{-1}$
Crystal size: $0.15 \times 0.15 \times 0.20\text{ mm}$
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)
No. of reflection measured = 4574
No. of unique reflections = 4413
$R_{\text{int}} = 0.02$
$2\theta_{\text{max}} = 55.0$
No. of reflection used = 3012 ($I > 2.0\sigma(I)$)
No. of parameters = 209
$R = 0.033$ (on F) $R_w = 0.038$
Goodness-of-fit: 1.68
$(\Delta/\sigma)_{\text{max}} = 0.02$
$(\Delta\rho)_{\text{max}} = 0.42\text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.60\text{ e\AA}^{-3}$
Measurement: MAC Science Co. Ltd. MXC18K
Structure determination: texsan (1.9)
Treatment of hydrogen atoms: geometric calculation
Refinement: full-matrix least-squares

1 summarizes the crystal and experimental data. During the data collection at room temperature, decay was not observed. All intensity data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by a direct method (sir 92), and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located geometrically and were not refined. The final atomic parameters are given in Table 2.

The Pd complex molecule and the solvate molecule lay on a crystallographic twofold axis. Some selected geometric parameters are given in Table 3. As shown in Fig. 2, the Pd atom was coordinated by two P and two C atoms in square-planar arrangement. The coordination geometry around Pd atom was essentially identical with the geometries found in

Table 2 Positional parameters and B_{eq}

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Pd(1)	0.0000	0.75063(2)	0.2500	2.266(6)
Cl(1)	0.0581(1)	1.0973(1)	0.19188(6)	8.07(4)
P(1)	-0.09438(5)	0.74761(5)	0.14709(3)	2.28(1)
N(1)	0.2305(2)	0.7421(2)	0.1905(1)	4.03(6)
C(1)	-0.2070(2)	0.8309(2)	0.1436(1)	2.54(6)
C(2)	-0.1839(3)	0.9227(2)	0.1637(2)	3.55(7)
C(3)	-0.2651(3)	0.9896(2)	0.1611(2)	4.44(9)
C(4)	-0.3704(3)	0.9652(3)	0.1408(2)	5.2(1)
C(5)	-0.3945(3)	0.8755(3)	0.1215(2)	5.5(1)
C(6)	-0.3128(3)	0.8074(2)	0.1220(2)	3.73(7)
C(7)	-0.0206(2)	0.7742(2)	0.0748(1)	2.58(6)
C(8)	-0.0408(3)	0.8537(2)	0.0373(1)	3.56(7)
C(9)	0.0152(3)	0.8690(3)	-0.0186(2)	4.54(9)
C(10)	0.0912(3)	0.8057(3)	-0.0373(2)	4.56(9)
C(11)	0.1126(3)	0.7272(3)	0.0000(2)	4.75(9)
C(12)	0.0581(3)	0.7116(2)	0.0558(2)	3.87(8)
C(13)	-0.1499(2)	0.6314(2)	0.1293(1)	2.58(6)
C(14)	-0.1889(3)	0.6064(2)	0.0660(2)	3.89(8)
C(15)	-0.2320(3)	0.5176(2)	0.0536(2)	4.62(9)
C(16)	-0.2363(3)	0.4541(2)	0.1036(2)	4.13(8)
C(17)	-0.1956(3)	0.4764(2)	0.1657(2)	4.08(8)
C(18)	-0.1525(3)	0.5654(2)	0.1788(1)	3.25(7)
C(19)	0.1468(2)	0.7477(2)	0.2115(1)	2.86(5)
C(20)	0.0000	1.1680(5)	0.2500	6.8(2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

Table 3 Selected bond length (Å), bond angles (°) and torsion angles (°)

Pd(1) - P(1)	2.3333(6)	Pd(1) - C(19)	2.009(3)
P(1) - C(1)	1.814(3)	P(1) - C(7)	1.825(3)
P(1) - C(13)	1.816(3)	N(1) - C(19)	1.140(4)
P(1) - Pd(1) - P(1)	177.89(4)	P(1) - Pd(1) - C(19)	92.63(8)
P(1) - Pd(1) - C(19)*	87.33(8)	P(1) - C(7) - C(12)	119.0(2)
C(19) - Pd(1) - C(19)*	177.7(2)	Pd(1) - P(1) - C(1)	110.60(9)
Pd(1) - P(1) - C(7)	119.17(9)	Pd(1) - P(1) - C(13)	110.70(9)
C(7) - P(1) - C(13)	103.0(1)	C(1) - P(1) - C(7)	104.3(1)
C(1) - P(1) - C(13)	108.3(1)	Pd(1) - C(19) - N(1)	177.0(3)
Pd(1)-P(1)-C(1)-C(2)	50.8(2)	P(1)-Pd(1)-P(1)*C(13)*	14.7(1)
Pd(1)-P(1)-C(1)-C(6)	-129.3(2)	P(1)-Pd(1)-C(19)-N(1)	-106(4)
Pd(1)-P(1)-C(7)-C(8)	-112.6(2)	P(1)-C(1)-C(2)-C(3)	178.8(3)
Pd(1)-P(1)-C(7)-C(12)	68.4(3)	P(1)-C(7)-C(8)-C(9)	-177.8(3)
Pd(1)-P(1)-C(13)-C(14)	-166.1(2)	P(1)-C(13)-C(14)-C(15)	-179.3(3)
Pd(1)-P(1)-C(13)-C(18)	13.0(3)	C(1)-P(1)-Pd(1)-C(19)	-136.4(1)
P(1)-Pd(1)-P(1)*C(1)*	134.8(1)	C(7)-P(1)-Pd(1)-C(19)	-15.6(1)
P(1)-Pd(1)-P(1)*C(7)*	-104.4(1)	C(13)-P(1)-Pd(1)-C(19)	103.5(1)

* Symmetry operation code: $-x, y, 1/2-z$.Pd(PPh₃)₂X₂ (**2**, X = Cl¹; **3**, X = I²).

The Pd-P distance 2.3333(6) Å was slightly longer than the corresponding distances in **2** [2.345(1) Å] and **3** [2.345(2) Å]. The angles P(1)-Pd(1)-P(1)* and C(19)-Pd(1)-C(19)* were 177.8° and 177.7°, respectively. The corresponding angles were 175.2° and 177.8° in **2**, and 178.8° and 168.8° in **3**. The least square plane through the four atoms (P(1), P(1)* C(19), C(19)*) was coplanar to within 0.002 Å. The Pd atom was displaced by 0.043 Å from the mean plane towards the P atoms. The corresponding value was 0.7 Å in **2**. The deviation from the

Fig. 2 ORTEP drawing of Pd(II) compound (**1**) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.planarity was less than the deviations in **2** and **3**.

One dichloromethane molecule was occluded per one Pd-complex. The shortest distance between solvate molecule and Pd complex was 3.540 Å for Cl(1)-C(17)(0.5 + x, 0.5 - y, z).

References

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