

***trans*-Dichloro(orthochloroaniline) (triphenylphosphine)palladium(II) dichloromethane solvate**

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Abstract

In the title compound, [PdCl₂(C₆H₅NCl)(C₁₈H₁₅P)]·CH₂Cl₂, the four coordinated Pd(II) complex shows nearly square planar geometry. The coordinated Pd–N, Pd–P and two Pd–Cl bond distances are 2.170 (3), 2.2322 (9), 2.2910 (9) and 2.3104 (9) Å, respectively, along with the angles lying in the range 86.85 (3) – 93.58 (4)°

Comment

Palladium (II) complexes are of current interest due to their antitumor (Faraglia *et al.*, 2001) and catalytic activity (Ali *et al.*, 1996) similar to Pt(II) complexes (Loehrer and Einhorn, 1984). For that reason, a variety of palladium(II) complexes containing nitrogen and sulfur donor ligands such as Pd(2,3-diaminotoluene)Cl₂, Pd(4,5-diaminoxylene)Cl₂ (Perez-Cabre *et al.*, 2004), and Pd(2-benzoylpyridine thiosemicarbazone) have previously been extensively investigated (Rebolledo *et al.*, 2004). In addition, various palladium complexes coordinated to diaminocyclohexane containing ligands proved catalytically active in Heck type reactions (Bravo *et al.*, 2002). Pd(II)-phosphine complexes *cis*-Pd(H₂O)₂(PPh₃)(*p*-CH₃C₆H₄SO₃)·2H₂O, and *cis*-Pd(H₂O)₂(PPh₃)(CH₃SO₃)₂·2CH₂Cl₂ are efficient catalysts for carbonylation of olefins (Cavinato *et al.*, 2004). Here, in continuation of our previous work (Parvez *et al.*, 2004) we report a new convenient synthesis and the crystal structure of a palladium(II) complex containing phosphine and aniline ligands. Palladium(II) complexes are unique due to a strong preference of Pd(II) for square planar coordination in which the ligand framework is proven to be highly stable (PoraiKoshits, 1987). In the title compound, the planar environment of Pd(II) is slightly distorted square. The sum of the bond angles around the Pd1 (Table 1) is 360.00 (5)°. Orthochloroaniline and triphenylphosphine are *trans* to each other with the bond angles of N1–Pd1–P1 and Cl2–Pd1–Cl1 being 174.79 (9)° and 179.16 (4)°, respectively. The metal-ligand bond distances Pd–N, Pd–P and Pd–Cl (Table 1) are in good agreement with those found in Pd(PPh₃)(indoline–N)Cl₂ (Chen *et al.* 1997).

Experimental

Palladium(II) chloride (0.5g, 2.82mmol from E-Merck) was dissolved completely in 20ml distilled water by adding 2–3 drops of dil. HCl. A solution of triphenylphosphine (0.74g, 2.82mmol) in acetone was added dropwise alongwith constant stirring. The reaction mixture was stirred overnight at room temperature. The resulting yellow precipitates of (PdCl₂(PPh₃)(H₂O)) were filtered, washed with diethyl ether and dried under vacuum.(0.23 ml, 2.20mmol) 2-chloroaniline was added dropwise into suspension of (PdCl₂(PPh₃)(H₂O)) (0.97g, 2.20mmol) in 20 ml of CH₂Cl₂ and refluxed for 1 hr resulting in a clear solution. Dark orange crystals were obtained after slow evaporation of the solvent at room temperature.

Crystal data

C ₂₄ H ₂₁ Cl ₃ NPPd.CH ₂ Cl ₂	Mo K α radiation
$M_r = 652.06$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 621 reflections
$P\bar{1}$	$\theta = 2.21\text{--}29.99^\circ$
$a = 10.0120 (2) \text{ \AA}$	$\mu = 1.293 \text{ mm}^{-1}$
$b = 10.3890 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 14.2220 (4) \text{ \AA}$	Prism
$\alpha = 104.6190 (10)^\circ$	Orange
$\beta = 89.9230 (10)^\circ$	$0.32 \times 0.29 \times 0.24 \text{ mm}$
$\gamma = 112.7541 (12)^\circ$	
$V = 1312.30 (5) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.650 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Nonius KappaCCD diffractometer	4057 reflections with $>2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.0350$
Absorption correction: multi-scan HKL2000 (Otwinowski & Minor 1997)	$\theta_{\text{max}} = 29.99^\circ$
$T_{\text{min}} = 0.6800$, $T_{\text{max}} = 0.7400$	$h = -13 \rightarrow 12$
10268 measured reflections	$k = -12 \rightarrow 14$
6247 independent reflections	$l = -19 \rightarrow 18$
	0. standard reflections every 0. reflections intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.0000P]$
$R[F^2 > 2\sigma(F^2)] = 0.0441$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.1164$	$(\Delta/\sigma)_{\text{max}} = 0.000$
$S = 1.014$	$\Delta\rho_{\text{max}} = 0.670 \text{ e \AA}^{-3}$
6247 reflections	$\Delta\rho_{\text{min}} = -0.900 \text{ e \AA}^{-3}$
298 parameters	Extinction correction: none
H-atom parameters constrained	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pd1—N1	2.170 (3)	Pd1—Cl1	2.3104 (9)
Pd1—P1	2.2322 (9)	Cl3—C6	1.724 (4)
Pd1—Cl2	2.2910 (9)	N1—C1	1.427 (5)
N1—Pd1—P1	174.79 (9)	N1—Pd1—Cl1	88.06 (9)
N1—Pd1—Cl2	91.52 (9)	P1—Pd1—Cl1	86.85 (3)
P1—Pd1—Cl2	93.58 (4)	Cl2—Pd1—Cl1	179.16 (4)

All H atoms were initially located in a difference Fourier map and were refined as riding, with N—H = 0.90 \AA , C—H = 0.93–0.97 \AA , and $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}$ (parent atom)..

Data collection: KappaCCD. Cell refinement: HKL Scale pack (Otwinowski & Minor 1997). Data reduction: HKL Scale pack (Otwinowski & Minor 1997). Program(s) used to solve structure: DIRDIFF. Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: maXus, Zortep. Software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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Fig. 1. View of the molecule showing the atom-labeling scheme for atoms discussed in the text. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

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C₂₄H₂₁Cl₃NPPd.CH₂Cl₂

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Supplementary data

The data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages of the journal at

<http://journals.iucr.org/c/journalhomepage.html>

Table S1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pd1	0.03793 (3)	0.02779 (3)	0.21760 (2)	0.03847 (11)
C11	-0.09129 (12)	0.10275 (11)	0.12449 (7)	0.0528 (3)
C12	0.16849 (11)	-0.04633 (11)	0.30827 (7)	0.0501 (2)
C13	-0.32775 (15)	-0.28149 (15)	0.06572 (13)	0.0957 (5)
C14	0.58409 (18)	-0.15758 (18)	0.85652 (15)	0.1068 (6)
C15	0.62230 (16)	0.14137 (16)	0.93286 (11)	0.0915 (4)
P1	0.06090 (10)	0.22256 (10)	0.33833 (7)	0.0364 (2)
N1	0.0009 (4)	-0.1579 (3)	0.0933 (2)	0.0456 (7)
H1A	-0.0486	-0.1489	0.0443	0.055
H1B	0.0885	-0.1509	0.0740	0.055
C1	-0.0742 (4)	-0.3014 (4)	0.1026 (3)	0.0441 (9)
C2	0.0064 (5)	-0.3755 (4)	0.1256 (3)	0.0509 (10)
H2	0.1076	-0.3317	0.1330	0.061
C3	-0.0624 (5)	-0.5117 (5)	0.1371 (3)	0.0599 (11)
H3	-0.0076	-0.5607	0.1508	0.072
C4	-0.2119 (5)	-0.5769 (5)	0.1287 (3)	0.0632 (12)
H4	-0.2577	-0.6689	0.1379	0.076
C5	-0.2931 (5)	-0.5065 (5)	0.1067 (3)	0.0627 (12)
H5	-0.3943	-0.5511	0.1000	0.075
C6	-0.2242 (5)	-0.3685 (4)	0.0945 (3)	0.0535 (10)
C7	-0.1230 (4)	0.2015 (4)	0.3637 (3)	0.0399 (8)
C8	-0.1815 (4)	0.3011 (4)	0.3579 (3)	0.0486 (10)
H8	-0.1251	0.3866	0.3426	0.058
C9	-0.3253 (5)	0.2707 (5)	0.3753 (3)	0.0616 (12)
H9	-0.3654	0.3367	0.3716	0.074
C10	-0.4096 (5)	0.1447 (5)	0.3979 (3)	0.0638 (13)
H10	-0.5056	0.1266	0.4100	0.077
C11	-0.3529 (4)	0.0461 (5)	0.4027 (3)	0.0590 (11)
H11	-0.4105	-0.0399	0.4170	0.071
C12	-0.2092 (4)	0.0746 (4)	0.3861 (3)	0.0504 (10)
H12	-0.1702	0.0079	0.3901	0.061
C13	0.1558 (4)	0.3921 (4)	0.3069 (3)	0.0385 (8)
C14	0.2254 (4)	0.3953 (4)	0.2234 (3)	0.0491 (10)
H14	0.2180	0.3089	0.1798	0.059
C15	0.3060 (5)	0.5256 (5)	0.2038 (3)	0.0598 (11)
H15	0.3536	0.5271	0.1477	0.072
C16	0.3152 (5)	0.6522 (5)	0.2676 (4)	0.0640 (13)
H16	0.3690	0.7399	0.2542	0.077
C17	0.2476 (5)	0.6519 (4)	0.3497 (3)	0.0581 (11)
H17	0.2535	0.7390	0.3918	0.070
C18	0.1699 (4)	0.5230 (4)	0.3712 (3)	0.0507 (10)
H18	0.1265	0.5235	0.4291	0.061
C19	0.1611 (4)	0.2597 (4)	0.4559 (3)	0.0373 (8)
C20	0.3100 (4)	0.3037 (4)	0.4610 (3)	0.0479 (9)
H20	0.3559	0.3074	0.4042	0.058
C21	0.3921 (4)	0.3423 (5)	0.5493 (3)	0.0565 (11)
H21	0.4928	0.3724	0.5518	0.068
C22	0.3261 (5)	0.3362 (5)	0.6323 (3)	0.0592 (11)
H22	0.3817	0.3620	0.6916	0.071
C23	0.1771 (5)	0.2922 (5)	0.6294 (3)	0.0588 (11)
H23	0.1322	0.2882	0.6865	0.071
C24	0.0946 (4)	0.2539 (4)	0.5408 (3)	0.0493 (10)
H24	-0.0060	0.2241	0.5386	0.059
C25	0.5296 (6)	-0.0231 (5)	0.8473 (4)	0.0818 (15)
H25A	0.4263	-0.0546	0.8545	0.098
H25B	0.5431	-0.0092	0.7825	0.098