Crystal structure of dichloro[1,3-bis(5-methyl-3-phenylpyrazol-1-yl)propan-2-ol]palladium(II), $Pd[(C_{10}H_9N_2)_2C_3H_5OH]Cl_2$

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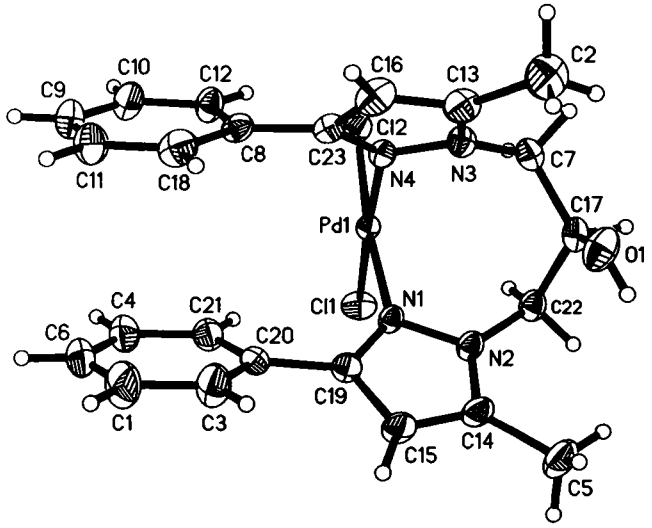
Received July 4, 2005, accepted and available on-line August 26, 2005; CCDC no. 1267/1586



Abstract

$C_{23}H_{24}Cl_2N_4OPd$, monoclinic, $P12_1/c1$ (no. 14), $a = 8.887(2)$ Å, $b = 16.192(3)$ Å, $c = 16.228(3)$ Å, $\beta = 97.08(3)°$, $V = 2317.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.078$, $T = 273$ K.

Source of material

A solution of 0.1 g (0.268 mmol) of the newly synthesized ligand 1,3-bis(5-methyl-3-phenylpyrazol-1-yl)propan-2-ol (Hmppzhp) [6-9] in 10 ml of methanol was treated with 6.4 mg (0.268 mmol) of LiOH and stirred for 30 min, followed by addition of a solution of 95 mg (0.536 mmol) of $PdCl_2$ in 10 ml of methanol and stirred further for 3 h at 50 °C. After removal of the insoluble impurities the light yellow solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 in order to remove the metal salts. The solvent of the resulting extract was completely removed and the residue was then extracted with MeCN. The yellow solution allowed to stand at room temperature, brown crystals suitable for X-ray diffraction analysis were obtained after a few days (decomp. 210-212 °C).

Discussion

From the point of view of ligand design, nitrogen donor ligands, for which in principle a great variety of synthetic strategies are available, may generate catalytically active complexes which are complementary to the known phosphine-based systems [1]. In this paper, the crystal structure of a novel palladium complex coordinated by a bidentate ligand containing two pyrazoline units is presented. The Pd(II) complexation is characterized by two coordinated chlorine atoms and two nitrogen atoms from two pyrazoline rings, while the hydroxyl group does not participate in the ligation. The Cl1, Cl2, N1, N4, and Pd1 atoms are in the same plane. The palladium atom has a marginally distorted square planar environment with bond angles of 90.92(5)° (∠N1–Pd1–Cl1), 91.87(5)° (∠N4–Pd1–Cl2), 86.36(7)° (∠N1–Pd1–N4), and 90.64(3)° (∠Cl1–Pd1–Cl2). The two chlorine atoms coordinate the palladium atom in a *cis* fashion with the bond distances of 2.2773(7) Å (Pd1—Cl1) and 2.2886(8) Å (Pd1—Cl2) which are comparable to those found for related Pd complexes [2-5]. The bond lengths of Pd1—N1 (2.030(2) Å) and Pd1—N4 (2.022(2) Å) are also of the order found for the related structures [2-5].

Table 1. Data collection and handling.

Crystal:	brown block, size 0.3 × 0.4 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	58.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17640, 6223
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4764
$N(param)_{refined}$:	280
Programs:	SHELXS-97 [11], SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.6822	0.8345	0.5607	0.099
H(1B)	4e	0.0715	0.8911	0.1207	0.099
H(2A)	4e	0.1922	0.7113	0.0630	0.112
H(2B)	4e	0.1832	0.6631	0.1460	0.112
H(2C)	4e	0.2712	0.6250	0.0771	0.112
H(3A)	4e	0.4835	0.8643	0.4597	0.081
H(4A)	4e	0.9706	0.9386	0.4234	0.075
H(5A)	4e	0.0548	1.0189	0.1905	0.098
H(5B)	4e	0.0701	1.0618	0.2777	0.098
H(5C)	4e	0.0175	0.9695	0.2685	0.098
H(6A)	4e	0.9239	0.8728	0.5426	0.088
H(7A)	4e	0.3209	0.8080	0.0044	0.052
H(7B)	4e	0.4453	0.8750	0.0278	0.052
H(9A)	4e	1.1327	0.7291	0.3906	0.080
H(10A)	4e	1.1182	0.7817	0.2593	0.070
H(11A)	4e	0.9179	0.6885	0.4439	0.082
H(12A)	4e	0.8849	0.7927	0.1793	0.059
H(15A)	4e	0.2973	0.9654	0.3912	0.058
H(16A)	4e	0.4985	0.6398	0.2300	0.063
H(17A)	4e	0.1887	0.9226	0.0151	0.053
H(18A)	4e	0.6831	0.6968	0.3644	0.068
H(21A)	4e	0.7733	0.9707	0.3221	0.058
H(22A)	4e	0.3826	1.0049	0.0926	0.049
H(22B)	4e	0.2151	1.0241	0.1062	0.049

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4e	0.63651(2)	0.93177(1)	0.16063(1)	0.02753(8)	0.03336(9)	0.0283(1)	0.00024(6)	0.00615(6)	0.00307(7)
C(1)	4e	0.7002(4)	0.8621(2)	0.5127(2)	0.084(2)	0.125(3)	0.040(2)	0.027(2)	0.008(2)	0.029(2)
C(2)	4e	0.2460(3)	0.6754(2)	0.1035(2)	0.055(2)	0.057(2)	0.112(3)	-0.020(1)	0.006(2)	-0.002(2)
C(3)	4e	0.5814(3)	0.8803(2)	0.4524(2)	0.053(2)	0.109(3)	0.042(2)	0.013(2)	0.013(1)	0.021(2)
C(4)	4e	0.8718(3)	0.9244(2)	0.4308(2)	0.049(2)	0.081(2)	0.055(2)	0.004(1)	-0.007(1)	-0.005(2)
C(5)	4e	0.0820(3)	1.0108(2)	0.2490(2)	0.038(1)	0.095(2)	0.066(2)	0.018(1)	0.016(1)	0.009(2)
C(6)	4e	0.8440(4)	0.8846(2)	0.5016(2)	0.067(2)	0.105(3)	0.044(2)	0.027(2)	-0.010(2)	-0.002(2)
C(7)	4e	0.3650(3)	0.8439(2)	0.0488(2)	0.043(1)	0.051(2)	0.036(1)	-0.005(1)	0.000(1)	-0.001(1)
C(8)	4e	0.7600(3)	0.7466(1)	0.2631(2)	0.050(1)	0.036(1)	0.038(1)	0.010(1)	0.010(1)	0.007(1)
C(9)	4e	1.0390(3)	0.7337(2)	0.3584(2)	0.066(2)	0.073(2)	0.055(2)	0.018(2)	-0.012(2)	0.007(2)
C(10)	4e	1.0307(3)	0.7648(2)	0.2806(2)	0.047(1)	0.071(2)	0.057(2)	0.011(1)	0.003(1)	0.013(2)
C(11)	4e	0.9107(4)	0.7091(2)	0.3901(2)	0.094(2)	0.068(2)	0.041(2)	0.017(2)	-0.001(2)	0.020(2)
C(12)	4e	0.8906(3)	0.7713(2)	0.2328(2)	0.048(1)	0.059(2)	0.039(2)	0.009(1)	0.002(1)	0.015(1)
C(13)	4e	0.3883(3)	0.7169(2)	0.1415(2)	0.046(1)	0.039(1)	0.067(2)	-0.006(1)	0.011(1)	-0.001(1)
C(14)	4e	0.2447(2)	0.9830(2)	0.2652(2)	0.036(1)	0.054(2)	0.046(2)	0.007(1)	0.014(1)	0.002(1)
C(15)	4e	0.3297(3)	0.9648(2)	0.3388(2)	0.042(1)	0.067(2)	0.041(2)	0.007(1)	0.019(1)	0.005(1)
C(16)	4e	0.4988(3)	0.6894(2)	0.2011(2)	0.056(1)	0.036(1)	0.068(2)	-0.001(1)	0.017(1)	0.016(1)
C(17)	4e	0.2427(2)	0.9049(2)	0.0685(2)	0.036(1)	0.053(1)	0.042(2)	-0.001(1)	-0.003(1)	0.007(1)
C(18)	4e	0.7698(3)	0.7145(2)	0.3428(2)	0.071(2)	0.053(2)	0.050(2)	0.009(1)	0.016(1)	0.017(1)
C(19)	4e	0.4747(2)	0.9450(1)	0.3203(2)	0.037(1)	0.047(1)	0.034(1)	0.0008(9)	0.011(1)	0.004(1)
C(21)	4e	0.7538(3)	0.9436(2)	0.3701(2)	0.047(1)	0.054(2)	0.044(2)	0.001(1)	0.002(1)	0.001(1)
C(22)	4e	0.2952(3)	0.9833(1)	0.1159(2)	0.039(1)	0.046(1)	0.037(1)	0.0049(9)	0.002(1)	0.009(1)
C(23)	4e	0.6117(2)	0.7493(1)	0.2106(2)	0.042(1)	0.036(1)	0.038(1)	0.0037(9)	0.012(1)	0.006(1)
C(20)	4e	0.6066(3)	0.9224(1)	0.3808(2)	0.043(1)	0.050(1)	0.029(1)	0.007(1)	0.005(1)	-0.001(1)
N(1)	4e	0.4780(2)	0.9508(1)	0.2386(1)	0.0257(8)	0.041(1)	0.034(1)	0.0032(7)	0.0066(7)	0.0048(8)
N(2)	4e	0.3352(2)	0.9743(1)	0.2049(1)	0.0306(8)	0.047(1)	0.035(1)	0.0047(7)	0.0072(8)	0.0069(9)
N(3)	4e	0.4334(2)	0.7920(1)	0.1168(1)	0.0343(9)	0.038(1)	0.044(1)	-0.0044(8)	0.0032(8)	0.0023(9)
N(4)	4e	0.5719(2)	0.8120(1)	0.1589(1)	0.0330(8)	0.0338(9)	0.034(1)	0.0003(7)	0.0045(7)	0.0031(8)
O(1)	4e	0.1388(2)	0.8601(1)	0.1090(1)	0.0398(9)	0.070(1)	0.089(2)	-0.0013(8)	0.0104(9)	0.014(1)
Cl(1)	4e	0.69491(8)	1.06876(4)	0.16294(5)	0.0602(4)	0.0372(3)	0.0609(4)	-0.0083(3)	0.0199(3)	-0.0010(3)
Cl(2)	4e	0.79483(7)	0.90881(4)	0.06195(4)	0.0446(3)	0.0601(4)	0.0379(3)	0.0125(3)	0.0173(3)	0.0098(3)

Acknowledgment. We would like to thank the Shaanxi Normal University for research grants.

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