Z. Kristallogr. NCS 220 (2005) 465-466

Crystal structure of (2,6-diisopropyl-phenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl-methylene]-aminopalladium(II) dichloromethane trisolvate, $Pd(C_{26}H_{30}N_2)Cl_2 \cdot 3CH_2Cl_2$

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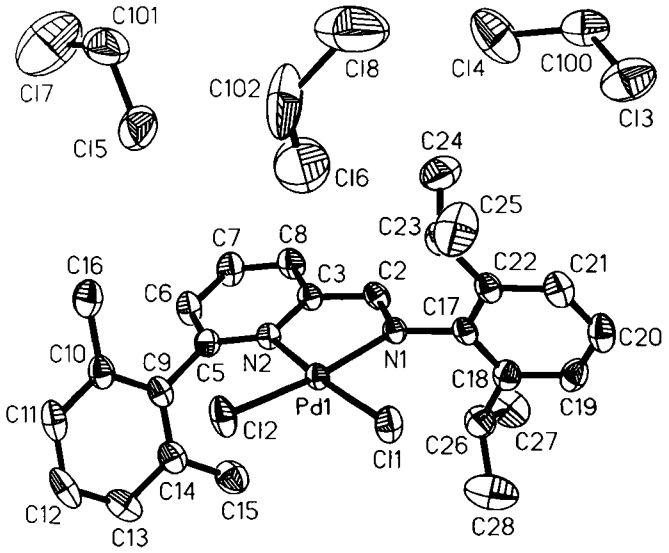
Received July 11, 2005, accepted and available on-line September 13, 2005; CCDC no. 1267/1594



Abstract

$C_{29}H_{36}Cl_8N_2Pd$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 16.5460(8)$ Å, $b = 17.995(1)$ Å, $c = 11.817(1)$ Å, $V = 3518.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.037$, $wR_{ref}(F^2) = 0.099$, $T = 193$ K.

Source of material

A stirred solution of 0.229 g (0.81 mmol) of (2,6-diisopropyl-phenyl)-[6-(2,6-dimethyl-phenyl)-pyridine-2-yl-methylene]-amine and 0.223 g (0.79 mmol) of $[PdCl_2COD]$ in 30 mL of THF was heated at 70 °C for 18 h. The solvent was removed under vacuum and the residue washed with hexane, then dissolved in 50 mL of dichloromethane and filtered over quartz. The resulting orange solution was concentrated and yellow-orange needle-shaped crystals were grown at –25 °C (yield 76 %, m.p. 255 °C).

Discussion

Neutral metal complexes of iminopyridine ligands, for instance the title complex, have been introduced recently since they were used as catalysts for bis-alkoxycarbonylation of styrene [1], selective oligomerization of ethylene [2-3] and for atom transfer radical polymerization [4].

The palladium centres are coordinated by a chelating iminopyridine ligand [5] and by two chloro ligands. The palladium atom lies in the coordination N_2Cl_2 plane (only 0.097 Å deviations above). The sum of the binding angles is 360°. The chelating angle $N_{pyridine}$–Pd–N_{imino} is 80.57° and reflects the small size of the ligand. The bulky phenyl substituents in the 6-position of the pyridine and at the imino N atom are twisted with regard to the pyridine ring with the dihedral angles of 71.8° and 93.2°, respectively. Both phenyl rings form a dihedral angle of 60.2°. The shortening of C6—N2 bond (1.27 Å) indicates the imino function and the Pd—N_{imino} bond is slightly shorter than the Pd—$N_{pyridine}$ bond. Three uncoordinated dichloromethane molecules per complex molecule were found. The absolute structure was confirmed by a value of Flack parameter $x = 0.00(4)$.

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Table 1. Data collection and handling.

Crystal:	yellow-orange prism, size 0.5 × 0.5 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	11.57 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	51.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15504, 6465
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6266
$N(param)_{refined}$:	361
Programs:	SIR97 [6], SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4a	0.7048	0.2611	0.8999	0.036
H(6)	4a	0.6026	0.1056	1.2899	0.046
H(7)	4a	0.7323	0.1076	1.2159	0.051
H(8)	4a	0.7576	0.1784	1.0526	0.045
H(11)	4a	0.3181	0.0633	1.2895	0.051
H(12)	4a	0.2735	0.1717	1.3762	0.062
H(13)	4a	0.3514	0.2789	1.3689	0.056
H(15A)	4a	0.4661	0.3447	1.3127	0.074
H(15B)	4a	0.5023	0.3200	1.1929	0.074
H(15C)	4a	0.5469	0.2960	1.3073	0.074
H(16A)	4a	0.5029	0.0411	1.1352	0.077
H(16B)	4a	0.4104	0.0192	1.1143	0.077
H(16C)	4a	0.4550	–0.0065	1.2279	0.077
H(19)	4a	0.6499	0.5043	0.7237	0.048
H(20)	4a	0.6338	0.4571	0.5420	0.050
H(21)	4a	0.5964	0.3339	0.5167	0.046
H(23)	4a	0.5417	0.2079	0.7377	0.048
H(24A)	4a	0.6266	0.1270	0.6391	0.104
H(24B)	4a	0.6766	0.1835	0.7168	0.104
H(24C)	4a	0.6715	0.1967	0.5831	0.104
H(25A)	4a	0.4587	0.2461	0.5853	0.113
H(25B)	4a	0.4893	0.1626	0.5669	0.113
H(25C)	4a	0.5304	0.2293	0.4982	0.113
H(26)	4a	0.6195	0.4023	0.9825	0.054
H(27A)	4a	0.7182	0.4933	1.0244	0.092
H(27B)	4a	0.7280	0.5109	0.8923	0.092

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(27C)	4a	0.7543	0.4316	0.9411	0.092
H(28A)	4a	0.5712	0.5237	1.0197	0.118
H(28B)	4a	0.5125	0.4814	0.9334	0.118
H(28C)	4a	0.5746	0.5426	0.8874	0.118
H(10A)	4a	0.8113	0.2828	0.2089	0.076

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(10B)	4a	0.8345	0.3477	0.2958	0.076
H(10C)	4a	0.5434	–0.0555	0.8149	0.103
H(10D)	4a	0.6311	–0.0200	0.7965	0.103
H(10E)	4a	0.5788	–0.0517	0.3912	0.141
H(10F)	4a	0.6413	–0.1062	0.4521	0.141

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}
N(1)	4a	0.5914(2)	0.2877(2)	0.8874(3)	0.021(2)	0.029(2)	0.027(2)	–0.004(2)	0.001(2)	0.002(2)
C(2)	4a	0.6523(2)	0.2551(3)	0.9313(3)	0.021(2)	0.042(3)	0.027(2)	–0.002(2)	0.001(2)	0.001(2)
C(3)	4a	0.6397(3)	0.2088(3)	1.0296(4)	0.020(2)	0.033(2)	0.030(2)	–0.003(2)	–0.001(2)	0.002(2)
N(2)	4a	0.5627(2)	0.2051(2)	1.0688(3)	0.022(2)	0.029(2)	0.025(2)	–0.001(2)	–0.003(1)	0.004(1)
C(5)	4a	0.5496(3)	0.1680(3)	1.1670(4)	0.031(2)	0.032(2)	0.026(2)	–0.002(2)	–0.003(2)	0.003(2)
C(6)	4a	0.6130(3)	0.1320(3)	1.2218(5)	0.026(3)	0.050(3)	0.037(3)	–0.003(2)	–0.003(2)	0.016(2)
C(7)	4a	0.6899(3)	0.1338(3)	1.1793(5)	0.029(3)	0.051(3)	0.047(3)	0.003(2)	–0.005(2)	0.019(3)
C(8)	4a	0.7045(3)	0.1743(3)	1.0824(5)	0.020(2)	0.049(3)	0.043(3)	0.000(2)	0.000(2)	0.008(2)
C(9)	4a	0.4700(3)	0.1695(3)	1.2230(4)	0.024(3)	0.046(3)	0.020(2)	–0.001(2)	–0.005(2)	0.007(2)
C(10)	4a	0.4237(3)	0.1049(3)	1.2296(4)	0.032(3)	0.043(3)	0.032(3)	–0.002(2)	–0.002(2)	0.011(2)
C(11)	4a	0.3505(3)	0.1069(4)	1.2861(5)	0.031(3)	0.061(4)	0.036(3)	–0.010(3)	–0.003(2)	0.019(3)
C(12)	4a	0.3239(4)	0.1712(4)	1.3376(5)	0.033(3)	0.085(5)	0.037(3)	–0.009(3)	0.012(3)	0.005(3)
C(13)	4a	0.3702(3)	0.2349(4)	1.3330(4)	0.038(3)	0.065(4)	0.038(3)	0.006(3)	0.005(2)	–0.004(3)
C(14)	4a	0.4450(3)	0.2357(3)	1.2757(4)	0.032(2)	0.049(3)	0.031(2)	–0.003(3)	–0.001(2)	0.003(2)
C(15)	4a	0.4943(4)	0.3050(3)	1.2718(5)	0.051(4)	0.054(3)	0.043(3)	–0.007(3)	0.004(3)	–0.009(2)
C(16)	4a	0.4504(4)	0.0333(3)	1.1716(6)	0.048(3)	0.046(3)	0.061(4)	–0.015(3)	0.005(3)	0.004(3)
C(17)	4a	0.6034(3)	0.3352(3)	0.7897(4)	0.016(2)	0.037(3)	0.028(2)	–0.001(2)	0.002(2)	0.003(2)
C(18)	4a	0.6232(3)	0.4094(3)	0.8075(4)	0.024(2)	0.038(3)	0.042(3)	–0.004(2)	0.001(2)	0.005(2)
C(19)	4a	0.6350(3)	0.4538(3)	0.7137(5)	0.034(3)	0.033(3)	0.054(3)	–0.005(2)	0.000(3)	0.010(2)
C(20)	4a	0.6254(3)	0.4259(4)	0.6058(5)	0.027(3)	0.056(4)	0.042(3)	–0.004(2)	–0.003(2)	0.020(3)
C(21)	4a	0.6035(3)	0.3526(3)	0.5912(5)	0.031(3)	0.053(3)	0.031(3)	–0.005(2)	–0.005(2)	0.005(2)
C(22)	4a	0.5916(3)	0.3053(3)	0.6827(4)	0.022(2)	0.040(3)	0.029(2)	–0.001(2)	0.001(2)	0.004(2)
C(23)	4a	0.5680(4)	0.2250(3)	0.6660(4)	0.047(3)	0.042(3)	0.031(2)	–0.008(2)	0.001(2)	–0.001(2)
C(24)	4a	0.6420(5)	0.1791(4)	0.6499(7)	0.076(5)	0.043(4)	0.089(5)	–0.001(4)	0.017(4)	–0.008(4)
C(25)	4a	0.5060(5)	0.2148(4)	0.5705(6)	0.101(6)	0.067(4)	0.059(4)	–0.030(4)	–0.030(4)	–0.002(3)
C(26)	4a	0.6303(4)	0.4428(3)	0.9265(5)	0.050(3)	0.039(3)	0.047(3)	–0.012(3)	0.005(3)	–0.007(2)
C(27)	4a	0.7153(4)	0.4723(4)	0.9480(6)	0.051(4)	0.080(5)	0.054(4)	–0.012(3)	–0.012(3)	–0.013(4)
C(28)	4a	0.5665(5)	0.5030(5)	0.9432(7)	0.057(4)	0.096(6)	0.083(5)	0.009(4)	–0.006(4)	–0.037(5)
Cl(1)	4a	0.41422(7)	0.33011(8)	0.8335(1)	0.0244(6)	0.0500(8)	0.0432(7)	0.0025(5)	–0.0023(5)	0.0212(6)
Cl(2)	4a	0.36443(7)	0.21215(9)	1.0189(1)	0.0188(5)	0.0672(9)	0.0419(7)	–0.0047(5)	–0.0019(5)	0.0249(6)
Pd(1)	4a	0.48466(2)	0.25895(2)	0.95794(3)	0.0178(1)	0.0288(2)	0.0245(1)	–0.0008(1)	–0.0008(1)	0.0046(1)
Cl(4)	4a	0.7584(2)	0.2596(2)	0.3826(2)	0.114(2)	0.158(3)	0.0475(9)	0.002(2)	0.004(1)	0.004(1)
Cl(5)	4a	0.5452(2)	0.0648(1)	0.8718(2)	0.141(2)	0.053(1)	0.074(1)	–0.029(1)	0.021(1)	–0.0103(9)
Cl(3)	4a	0.7101(1)	0.3700(1)	0.2163(2)	0.064(1)	0.068(1)	0.122(2)	0.006(1)	–0.005(1)	–0.011(1)
Cl(6)	4a	0.6653(2)	0.0054(2)	0.4855(3)	0.146(3)	0.113(2)	0.111(2)	–0.021(2)	0.006(2)	–0.012(2)
C(100)	4a	0.7901(4)	0.3149(4)	0.2701(7)	0.042(4)	0.066(5)	0.081(5)	0.001(3)	–0.003(3)	–0.018(4)
Cl(8)	4a	0.6918(2)	–0.0697(2)	0.2762(4)	0.133(3)	0.126(3)	0.206(4)	–0.033(2)	0.061(3)	–0.083(3)
Cl(7)	4a	0.6177(3)	–0.0641(2)	0.9726(4)	0.160(3)	0.114(2)	0.217(4)	0.013(2)	–0.063(3)	0.012(3)
C(101)	4a	0.5852(6)	–0.0235(5)	0.8500(8)	0.093(6)	0.076(6)	0.089(6)	–0.016(5)	0.028(5)	–0.031(5)
C(102)	4a	0.6367(8)	–0.0592(7)	0.4089(8)	0.15(1)	0.119(9)	0.080(6)	–0.066(8)	–0.036(7)	0.056(6)

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support.

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