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The crystal structure of dichlorido(1,3-bis(2,6-diisopropyl-phenyl)-1*H*-3 λ^4 -imidazol-2-yl)(3-phenyl-pyridine- κN)palladium(IV), C₃₈H₄₅N₃Cl₂Pd

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.30 × 0.25 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.65 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX II, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	31228, 7483, 0.038
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6525
$N(\text{param})_{\text{refined}}$:	405
Programs:	Bruker [1], SHELX [2], Olex2 [3]

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Abstract

C₃₈H₄₅N₃Cl₂Pd, monoclinic, $P2_1/c$ (no. 14), $a = 12.8249(8)$ Å, $b = 16.0552(9)$ Å, $c = 20.5611(10)$ Å, $\beta = 115.396(3)^\circ$, $V = 3824.5(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0287$, $wR_{\text{ref}}(F^2) = 0.0879$, $T = 173(2)$ K.

CCDC no.: 1902125

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

According to Shao and co-workers' previously reported method, the title product was obtained in good yield [4]. Crystals suitable for X-ray diffraction were grown in a mixture of ethyl acetate and petroleum ether.

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Experimental details

All hydrogen atoms attached to C atoms were introduced using the HFIX command in the SHELXL-2016/6 program [2, 3, 5]. The C–H distances in CH₃ were restrained to 0.98 Å with U_{iso} values to be $1.5U_{\text{eq}}(\text{C})$. Vinylic and aromatic C–H distances were restrained to 0.95 Å with U_{iso} values to be $1.2U_{\text{eq}}(\text{C})$. The C–H distances in CH in the isopropyl groups were restrained to 1.00 Å with U_{iso} values to be $1.2U_{\text{eq}}(\text{C})$ [1, 6].

Comment

Since the preliminary report on the monodentate *N*-heterocyclic carbene-palladium complexes using pyridines as the throw-away ligands was found [7, 8], various such analogues using pyridines as the ancillary ligands have been reported to date [9–13]. According to Lu and some others' work, subtle change on the ancillary ligands will also have significant effect on the catalytic activities of such complexes [14–22]. Herein, we report the crystal structure of the title compound using 3-phenyl-pyridine as the ancillary ligand.

In the crystal structure, the same coordinate mode of the Pd center was obtained compared to those previously reported analogues. The structural parameters around the Pd center are also very similar with those reported ones [23]. For instance, the Pd center also showed slightly distorted square-planar geometry with four ligands. The bond lengths around the Pd centers are: Pd(1)–C(1) = 1.971(2) Å; Pd(1)–N(3) = 2.0985(19) Å; Pd(1)–Cl(1) = 2.3011(6) Å; Pd(1)–Cl(2) = 2.3047(6) Å. The bond angles around the Pd center are: C(1)–Pd(1)–N(3) = 176.02(8)°;

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Pd1	0.39119(2)	0.34061(2)	0.59835(2)	0.01654(7)
Cl1	0.39152(5)	0.26321(3)	0.50424(3)	0.02117(13)
Cl2	0.40178(6)	0.41986(4)	0.69445(3)	0.03110(15)
N1	0.31500(16)	0.19104(12)	0.65283(10)	0.0188(4)
N2	0.49940(16)	0.18828(12)	0.68819(10)	0.0173(4)
N3	0.36909(16)	0.44886(12)	0.53663(11)	0.0201(4)
C1	0.40344(19)	0.23533(14)	0.65041(11)	0.0172(4)
C2	0.3558(2)	0.11707(14)	0.69078(12)	0.0216(5)
H2	0.310731	0.075592	0.699752	0.026*
C3	0.4698(2)	0.11529(14)	0.71217(12)	0.0209(5)
H3	0.521048	0.072149	0.738808	0.025*
C4	0.1947(2)	0.21511(15)	0.62300(13)	0.0232(5)
C5	0.1545(2)	0.25613(16)	0.66792(14)	0.0278(5)
C6	0.0366(3)	0.2748(2)	0.63795(17)	0.0442(8)
H6	0.006001	0.303640	0.666224	0.053*
C7	−0.0360(3)	0.2525(3)	0.56859(18)	0.0574(10)
H7	−0.115808	0.265709	0.549631	0.069*
C8	0.0070(3)	0.2109(2)	0.52633(16)	0.0506(9)
H8	−0.044295	0.195749	0.478566	0.061*
C9	0.1228(2)	0.19079(19)	0.55185(14)	0.0319(6)
C10	0.1688(2)	0.14152(18)	0.50651(14)	0.0337(6)
H10	0.253916	0.151447	0.526965	0.040*
C11	0.1165(3)	0.1704(2)	0.42766(16)	0.0452(8)
H11A	0.036521	0.150996	0.403151	0.068*
H11B	0.161529	0.147363	0.403601	0.068*
H11C	0.118132	0.231406	0.425954	0.068*
C12	0.1505(3)	0.0482(2)	0.51054(19)	0.0527(9)
H12A	0.184787	0.030492	0.561025	0.079*
H12B	0.187422	0.018126	0.484512	0.079*
H12C	0.067660	0.036003	0.488658	0.079*
C13	0.2323(2)	0.27557(16)	0.74613(14)	0.0287(6)
H13	0.313824	0.276109	0.752016	0.034*
C14	0.2071(3)	0.36034(18)	0.77012(18)	0.0451(8)
H14A	0.132460	0.358365	0.772498	0.068*
H14B	0.204810	0.403049	0.735474	0.068*
H14C	0.267952	0.373949	0.817755	0.068*
C15	0.2219(3)	0.20750(17)	0.79504(14)	0.0325(6)
H15A	0.143020	0.206604	0.791059	0.049*
H15B	0.276172	0.218917	0.845021	0.049*
H15C	0.240017	0.153344	0.780383	0.049*
C16	0.61764(19)	0.21177(14)	0.70633(12)	0.0189(5)
C17	0.6763(2)	0.25878(15)	0.76902(13)	0.0232(5)
C18	0.7925(2)	0.27553(16)	0.78841(14)	0.0297(6)
H18	0.835743	0.305958	0.831230	0.036*
C19	0.8459(2)	0.24860(17)	0.74637(16)	0.0348(6)
H19	0.924635	0.262067	0.759930	0.042*
C20	0.7865(2)	0.20263(16)	0.68527(15)	0.0300(6)
H20	0.825175	0.184816	0.657340	0.036*
C21	0.6699(2)	0.18117(15)	0.66288(13)	0.0226(5)
C22	0.6085(2)	0.12357(15)	0.59941(14)	0.0266(5)
H22	0.523448	0.129994	0.583280	0.032*
C23	0.6360(3)	0.14438(19)	0.53585(16)	0.0388(7)
H23A	0.622865	0.203878	0.524701	0.058*
H23B	0.585840	0.111707	0.493755	0.058*
H23C	0.716875	0.130873	0.548364	0.058*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C24	0.6411(2)	0.03294(16)	0.62337(16)	0.0353(6)
H24A	0.725039	0.026339	0.642721	0.053*
H24B	0.603454	−0.004224	0.582003	0.053*
H24C	0.615708	0.018855	0.660684	0.053*
C25	0.6178(2)	0.28740(17)	0.81550(14)	0.0316(6)
H25	0.532804	0.290157	0.784435	0.038*
C26	0.6578(2)	0.37383(18)	0.84868(15)	0.0354(6)
H26A	0.737945	0.370612	0.885115	0.053*
H26B	0.608466	0.392975	0.871223	0.053*
H26C	0.652456	0.413120	0.810906	0.053*
C27	0.6384(4)	0.2243(2)	0.87517(17)	0.0563(10)
H27A	0.610173	0.169542	0.853883	0.085*
H27B	0.596983	0.241935	0.903339	0.085*
H27C	0.721173	0.220967	0.906676	0.085*
C28	0.43413(19)	0.51750(14)	0.56236(13)	0.0207(5)
H28	0.487610	0.519367	0.611662	0.025*
C29	0.4251(2)	0.58555(15)	0.51875(13)	0.0227(5)
H29	0.473259	0.632755	0.537828	0.027*
C30	0.3456(2)	0.58439(14)	0.44738(13)	0.0231(5)
H30	0.339118	0.630481	0.416911	0.028*
C31	0.2749(2)	0.51484(14)	0.42059(13)	0.0212(5)
C32	0.29128(19)	0.44853(14)	0.46747(12)	0.0200(5)
H32	0.244793	0.400292	0.449540	0.024*
C33	0.1863(2)	0.50770(15)	0.34503(13)	0.0240(5)
C34	0.2096(2)	0.53182(15)	0.28702(14)	0.0271(5)
H34	0.281593	0.556597	0.295669	0.032*
C35	0.1272(2)	0.51943(17)	0.21699(14)	0.0341(6)
H35	0.143498	0.535501	0.177859	0.041*
C36	0.0218(2)	0.48409(17)	0.20346(15)	0.0380(7)
H36	−0.033402	0.475003	0.155286	0.046*
C37	−0.0032(2)	0.46186(17)	0.26034(16)	0.0366(6)
H37	−0.076374	0.438827	0.251262	0.044*
C38	0.0789(2)	0.47333(15)	0.33053(14)	0.0290(6)
H38	0.061599	0.457495	0.369339	0.035*

C(1)–Pd(1)–Cl(1) = 88.00(6)°; N(3)–Pd(1)–Cl(1) = 89.26(5)°;
 C(1)–Pd(1)–Cl(2) = 92.64(6)°; N(3)–Pd(1)–Cl(2) = 90.26(5)°;
 Cl(1)–Pd(1)–Cl(2) = 176.73(2)°. In addition, it is worthy of noting here that initial studies on the catalytic activity of the title compound toward the amination reactions between primary and secondary amines with aryl chlorides were examined. It was found that the title compound was a very efficient catalyst for such transformation even at very low catalyst loadings (0.01–0.005 mol%).

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