Xiao-Yun Zhao and Lian-Hui Chen*

The crystal structure of tetrachlorido-bis{1,3-bis(2,6-diisopropylphenyl)-1*H*-3 λ^4 -imidazol-2-yl}-(μ_2 -pyrimidine- $\kappa^2 N:N'$)dipalladium(IV) – dichloromethane (1/2), C₆₀H₈₀Cl₈N₆Pd₂

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.12 × 0.08 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.91 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	30.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	33348, 20057, 0.050
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 11824
$N(\text{param})_{\text{refined}}$:	701
Programs:	Olex2 [1], SHELX [2, 3], Spek [4], Bruker [5]

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Abstract

C₆₀H₈₀Cl₈N₆Pd₂, triclinic, $P\bar{1}$ (no. 2), $a = 10.8703(10)$ Å, $b = 17.0284(15)$ Å, $c = 18.9595(17)$ Å, $\alpha = 83.1960(10)^\circ$, $\beta = 88.909(2)^\circ$, $\gamma = 71.523(2)^\circ$, $V = 3304.5(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0488$, $wR_{\text{ref}}(F^2) = 0.1213$, $T = 130$ K.

CCDC no.: 1940960

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

The title product was obtained by the previous methods reported by Lu and Shao's groups [6–13]. Under N₂ atmosphere, a mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.275 mmol), PdCl₂ (0.25 mmol), K₂CO₃ (0.375 mmol), THF (2.0 mL) and pyrimidine (0.5 mmol) was stirred at 80 °C for 12 h. The solvent was then removed

under reduced pressure, and the residue was purified by careful flash chromatography on silica gel to give the title product in good yield as a yellow solid. Crystals of the title compound were obtained by recrystallization from dichloromethane and ethyl acetate.

Experimental details

All hydrogen atoms attached to C atoms were introduced using the HFIX command in the Olex 21.2 program [1–3]. The C–H distances in CH₃ were restrained to 0.98 Å with U_{iso} values to be 1.5 $U_{\text{eq}}(\text{C})$. Vinylic and aromatic C–H distances were restrained to 0.95 Å with U_{iso} values to be 1.2 $U_{\text{eq}}(\text{C})$. The C–H distances in CH in the isopropyl groups were restrained to 1.00 Å with U_{iso} values to be 1.2 $U_{\text{eq}}(\text{C})$ [4, 5].

Comment

During the past years, the groups of Lu and Shao have developed some *N*-heterocyclic carbene (NHC)-palladium(II) complexes having different *N*-containing ancillary ligands. In addition, they were found to be excellent catalysts in the cross-coupling of aryl chlorides, implying that subtle changing of the ancillary ligands, various efficient catalysts can be achieved [6–13]. In 2012, Wang's group reported the synthesis of a linear dinuclear NHC-Pd(II) complex using bidentate pyrazine as the ancillary ligand [14]. This result thus prompted to further synthesis similar NHC-Pd(II) complex using other bidentate ligand. Herein, we report the crystal structure of the title compound using pyrimidine as the ancillary ligand.

*Corresponding author: Lian-Hui Chen, College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou Zhejiang Province 325035, P.R. China, e-mail: lhchen@wzu.edu.cn, Shaolix@163.com. <https://orcid.org/0000-0002-6440-9986>

Xiao-Yun Zhao: College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou Zhejiang Province 325035, P.R. China

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Pd1	0.32675(3)	0.80614(2)	0.78631(2)	0.01931(7)
Pd2	0.46962(3)	0.45234(2)	0.73397(2)	0.01896(7)
Cl1	0.30881(9)	0.79747(5)	0.90750(4)	0.0278(2)
Cl2	0.35011(9)	0.81176(6)	0.66556(5)	0.0299(2)
Cl3	0.25522(9)	0.52398(6)	0.75020(5)	0.0296(2)
Cl4	0.68336(9)	0.38385(5)	0.71236(5)	0.02754(19)
N1	0.4663(3)	0.68818(17)	0.79806(15)	0.0208(6)
N2	0.5260(3)	0.54846(17)	0.77164(14)	0.0198(6)
N3	0.0635(3)	0.93120(17)	0.78850(15)	0.0209(6)
N4	0.2070(3)	0.99135(17)	0.76020(15)	0.0201(6)
N5	0.3872(3)	0.30146(17)	0.75799(14)	0.0205(6)
N6	0.4342(3)	0.32303(18)	0.64774(15)	0.0232(6)
C1	0.1920(3)	0.9155(2)	0.77674(17)	0.0203(7)
C2	0.4243(3)	0.3554(2)	0.71040(17)	0.0190(7)
C3	0.4484(4)	0.6277(2)	0.76470(18)	0.0212(7)
H3	0.375019	0.642006	0.733674	0.025*
C4	0.6312(3)	0.5291(2)	0.81383(18)	0.0230(7)
H4	0.690021	0.473875	0.818406	0.028*
C5	0.6560(4)	0.5876(2)	0.8508(2)	0.0272(8)
H5	0.730602	0.573310	0.880868	0.033*
C6	0.5698(3)	0.6671(2)	0.84285(19)	0.0252(8)
H6	0.583196	0.707861	0.869251	0.030*
C7	−0.0010(4)	1.0165(2)	0.77892(19)	0.0266(8)
H7	−0.091404	1.043114	0.783632	0.032*
C8	0.0880(4)	1.0537(2)	0.76188(19)	0.0271(8)
H8	0.073053	1.112050	0.752580	0.033*
C9	0.0006(3)	0.8674(2)	0.8043(2)	0.0254(8)
C10	−0.0207(4)	0.8269(3)	0.7473(2)	0.0339(9)
C11	−0.0806(5)	0.7657(3)	0.7634(3)	0.0554(14)
H11	−0.094790	0.735777	0.726791	0.067*
C12	−0.1191(6)	0.7481(4)	0.8306(3)	0.0672(16)
H12	−0.160733	0.706681	0.839936	0.081*
C13	−0.0984(5)	0.7900(3)	0.8861(3)	0.0520(13)
H13	−0.125875	0.776835	0.932560	0.062*
C14	−0.0378(4)	0.8510(2)	0.8736(2)	0.0294(8)
C15	−0.0186(4)	0.8976(2)	0.9337(2)	0.0304(9)
H15	0.053796	0.920689	0.921006	0.036*
C16	0.0166(4)	0.8420(3)	1.0047(2)	0.0407(11)
H16A	−0.057164	0.823771	1.020839	0.061*
H16B	0.037874	0.873568	1.040012	0.061*
H16C	0.091758	0.793201	0.998609	0.061*
C17	−0.1420(4)	0.9709(3)	0.9422(2)	0.0434(11)
H17A	−0.159182	1.009944	0.898475	0.065*
H17B	−0.129902	0.999647	0.982054	0.065*
H17C	−0.215633	0.949894	0.951426	0.065*
C18	0.0162(4)	0.8487(3)	0.6717(2)	0.0388(10)
H18	0.093433	0.868254	0.673870	0.047*
C19	0.0531(5)	0.7739(3)	0.6290(3)	0.0576(14)
H19A	0.116456	0.726306	0.656326	0.086*
H19B	0.091085	0.788333	0.583948	0.086*
H19C	−0.024594	0.759195	0.619292	0.086*
C20	−0.0957(5)	0.9214(3)	0.6342(2)	0.0568(14)
H20A	−0.174338	0.905048	0.633863	0.085*
H20B	−0.071806	0.934915	0.585200	0.085*
H20C	−0.111867	0.970428	0.659674	0.085*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C21	0.3300(3)	1.0043(2)	0.74054(19)	0.0235(8)
C22	0.4183(4)	0.9997(2)	0.7951(2)	0.0268(8)
C23	0.5369(4)	1.0083(3)	0.7747(2)	0.0367(10)
H23	0.599721	1.004723	0.810103	0.044*
C24	0.5655(4)	1.0218(3)	0.7042(2)	0.0415(11)
H24	0.648278	1.026055	0.691501	0.050*
C25	0.4747(4)	1.0292(2)	0.6520(2)	0.0363(10)
H25	0.494803	1.040731	0.603627	0.044*
C26	0.3534(4)	1.0202(2)	0.66863(19)	0.0268(8)
C27	0.2554(4)	1.0288(2)	0.6106(2)	0.0338(9)
H27	0.195709	0.997172	0.628860	0.041*
C28	0.1732(5)	1.1216(3)	0.5922(2)	0.0461(12)
H28A	0.129783	1.143228	0.634899	0.069*
H28B	0.108014	1.126246	0.555582	0.069*
H28C	0.229904	1.153978	0.574439	0.069*
C29	0.3165(5)	0.9941(3)	0.5434(2)	0.0447(12)
H29A	0.359929	1.031577	0.518755	0.067*
H29B	0.248939	0.989448	0.512213	0.067*
H29C	0.380152	0.938844	0.555943	0.067*
C30	0.3837(4)	0.9927(2)	0.8726(2)	0.0337(9)
H30	0.310508	0.968848	0.877441	0.040*
C31	0.3358(5)	1.0801(3)	0.8961(2)	0.0465(12)
H31A	0.404197	1.106251	0.888976	0.070*
H31B	0.313955	1.076110	0.946504	0.070*
H31C	0.258643	1.113953	0.867857	0.070*
C32	0.4959(5)	0.9357(3)	0.9208(3)	0.0558(14)
H32A	0.534359	0.883107	0.900611	0.084*
H32B	0.463154	0.924220	0.968169	0.084*
H32C	0.561819	0.963136	0.924520	0.084*
C33	0.3782(4)	0.2348(2)	0.7254(2)	0.0282(8)
H33	0.355882	0.188197	0.747415	0.034*
C34	0.4068(4)	0.2484(2)	0.6571(2)	0.0291(8)
H34	0.408071	0.213383	0.621444	0.035*
C35	0.3506(3)	0.3110(2)	0.83094(18)	0.0214(7)
C36	0.4490(4)	0.2922(2)	0.88326(18)	0.0243(8)
C37	0.4103(4)	0.2944(2)	0.9533(2)	0.0325(9)
H37	0.474201	0.281820	0.990049	0.039*
C38	0.2811(4)	0.3146(3)	0.9708(2)	0.0381(10)
H38	0.257179	0.314850	1.019297	0.046*
C39	0.1862(4)	0.3345(2)	0.9180(2)	0.0344(9)
H39	0.097584	0.348574	0.930825	0.041*
C40	0.2182(4)	0.3342(2)	0.84649(19)	0.0254(8)
C41	0.1120(4)	0.3572(2)	0.7897(2)	0.0301(8)
H41	0.151232	0.368450	0.742951	0.036*
C42	0.0010(4)	0.4361(3)	0.8020(3)	0.0437(11)
H42A	−0.045264	0.424741	0.844924	0.066*
H42B	−0.059188	0.452722	0.761077	0.066*
H42C	0.036399	0.481194	0.807950	0.066*
C43	0.0572(5)	0.2846(3)	0.7848(3)	0.0474(12)
H43A	0.126420	0.236153	0.771446	0.071*
H43B	−0.012841	0.301744	0.748947	0.071*
H43C	0.023370	0.269933	0.831071	0.071*
C44	0.5919(4)	0.2685(2)	0.86557(19)	0.0273(8)
H44	0.598157	0.283376	0.813292	0.033*
C45	0.6605(4)	0.3178(2)	0.9035(2)	0.0343(9)
H45A	0.612251	0.377474	0.894527	0.051*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H45B	0.748677	0.307682	0.885622	0.051*
H45C	0.664502	0.299927	0.954723	0.051*
C46	0.6594(4)	0.1745(2)	0.8825(2)	0.0420(11)
H46A	0.650755	0.157528	0.933050	0.063*
H46B	0.751558	0.161282	0.871120	0.063*
H46C	0.619121	0.144462	0.854002	0.063*
C47	0.4543(4)	0.3619(2)	0.57822(18)	0.0242(8)
C48	0.3477(4)	0.4261(2)	0.54612(19)	0.0309(9)
C49	0.3665(5)	0.4588(3)	0.4766(2)	0.0400(11)
H49	0.298491	0.503327	0.452720	0.048*
C50	0.4813(5)	0.4275(3)	0.4425(2)	0.0431(11)
H50	0.491649	0.450980	0.395635	0.052*
C51	0.5815(4)	0.3625(3)	0.4754(2)	0.0368(10)
H51	0.658991	0.340536	0.450265	0.044*
C52	0.5711(4)	0.3284(2)	0.54488(19)	0.0297(8)
C53	0.6825(4)	0.2560(2)	0.5797(2)	0.0346(9)
H53	0.663949	0.247913	0.631450	0.041*
C54	0.8132(4)	0.2718(3)	0.5730(2)	0.0442(11)
H54A	0.835913	0.277058	0.522808	0.066*
H54B	0.880106	0.225016	0.599096	0.066*
H54C	0.807428	0.323368	0.592890	0.066*
C55	0.6904(5)	0.1755(3)	0.5488(2)	0.0491(12)
H55A	0.609736	0.162308	0.558150	0.074*
H55B	0.763648	0.129735	0.570951	0.074*
H55C	0.702819	0.182986	0.497369	0.074*
C56	0.2174(4)	0.4539(3)	0.5811(2)	0.0356(10)
H56	0.233430	0.439914	0.633548	0.043*
C57	0.1476(5)	0.5486(3)	0.5668(3)	0.0516(13)
H57A	0.204779	0.578659	0.580983	0.077*
H57B	0.068002	0.563238	0.594342	0.077*
H57C	0.125761	0.564086	0.516084	0.077*
C58	0.1322(5)	0.4051(3)	0.5598(3)	0.0557(13)
H58A	0.117021	0.415708	0.508205	0.084*
H58B	0.049078	0.422589	0.583856	0.084*
H58C	0.175425	0.345388	0.573376	0.084*
Cl5	0.09977(16)	0.56877(10)	0.97597(10)	0.0889(6)
Cl6	0.37155(14)	0.54195(9)	0.94423(7)	0.0637(4)
C59	0.2112(5)	0.5988(3)	0.9193(2)	0.0522(13)
H59A	0.194887	0.590249	0.870026	0.063*
H59B	0.197951	0.658917	0.920213	0.063*
Cl7	0.3030(2)	0.21462(14)	0.43612(11)	0.1153(8)
Cl8	0.22549(17)	0.36718(10)	0.33731(8)	0.0739(4)
C60	0.3448(6)	0.2885(4)	0.3872(5)	0.116(3)
H60A	0.412098	0.261285	0.354161	0.139*
H60B	0.385976	0.315192	0.419234	0.139*

In the crystal structure, two nearly square-planar Pd(II) centers were found bridged by the bidentate pyrimidine ligand. Both palladium centers are coordinated by four ligands such as NHC, pyrimidine, and two chloro ligands in a slightly distorted square-planar geometry. Both palladium centers have the similar bond lengths and bond angles. For example, the bond lengths around the palladium centers are: Pd(1)—Cl(1) = 2.2934(9); Pd(1)—Cl(2) = 2.2927(9);

Pd(1)—N(1) = 2.088(3); Pd(1)—C(1) = 1.961(3); Pd(2)—Cl(3) = 2.2965(9); Pd(2)—Cl(4) = 2.2991(9); Pd(2)—N(2) = 2.120(3); Pd(2)—C(2) = 1.966(3). The bond angles around the palladium centers are: Cl(1)—Pd(1)—Cl(2) = 178.38(4); N(1)—Pd(1)—Cl(1) = 89.04(8); N(1)—Pd(1)—Cl(2) = 89.40(8); C(1)—Pd(1)—Cl(1) = 90.08(10); C(1)—Pd(1)—Cl(2) = 91.49(10); Cl(3)—Pd(2)—Cl(4) = 177.29(4); N(2)—Pd(2)—Cl(3) = 90.57(8); N(2)—Pd(2)—Cl(4) = 89.43(8); C(2)—Pd(2)—Cl(3) = 91.04(10); C(2)—Pd(2)—Cl(4) = 89.29(10); C(2)—Pd(2)—N(2) = 173.02(12)°. In addition, the bond lengths and bond angles are all comparable to those found in the pyrazine derived analogue [14, 15].

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