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Crystal structure of dichlorido(1,3-bis(2,6-dimethyl-phenyl)-1*H*-3 λ^4 -imidazol-2-yl)(isoquinoliny)palladium(IV), C₂₈H₂₇Cl₂N₃Pd

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Abstract

C₂₈H₂₇Cl₂N₃Pd, monoclinic (no. 15), *C*2/*c*, *a* = 24.7394(17) Å, *b* = 15.9451(11) Å, *c* = 27.4301(19) Å, β = 107.8650°, *V* = 10293.7(12) Å³, *Z* = 16, *R*_{gt}(*F*) = 0.0249, *wR*_{ref}(*F*²) = 0.1168, *T* = 100(2) K.

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One of two crystallographic independent complexes of the title crystal structure is shown in the figure (Hydrogen atoms are omitted for clarity). Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Wavelength:	Size 0.38 × 0.30 × 0.21 mm
μ :	Mo $K\alpha$ radiation (0.71073 Å)
Diffractometer, scan mode:	9.5 cm ⁻¹
2 θ _{max} , completeness:	Bruker SMART, φ and ω
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	51°, >99%
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	40064, 9545, 0.023
<i>N</i> (<i>param</i>) _{refined} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 8840
Programs:	621
	SHELX [2], PLATON [3], Bruker programs [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Pd1	0.459110(7)	0.760520(11)	0.077465(7)	0.01685(9)
Pd2	0.328109(7)	0.763580(11)	0.680928(7)	0.01838(9)
Cl1	0.38753(3)	0.78847(4)	0.00321(2)	0.03124(15)
Cl2	0.52997(3)	0.73020(5)	0.15176(3)	0.03362(17)
C13	0.29095(2)	0.64026(4)	0.64163(2)	0.02759(15)
C14	0.36369(2)	0.88587(4)	0.72354(2)	0.02639(14)
N1	0.38175(8)	0.80543(12)	0.13905(8)	0.0205(4)
N2	0.43160(8)	0.91079(12)	0.13062(8)	0.0220(4)
N3	0.50141(8)	0.68814(12)	0.03626(7)	0.0200(4)
N4	0.23438(8)	0.80530(13)	0.72509(8)	0.0226(4)
N5	0.20706(8)	0.81950(13)	0.64325(8)	0.0241(4)
N6	0.41070(9)	0.72993(12)	0.67796(9)	0.0242(5)
C1	0.42139(9)	0.82941(14)	0.11727(8)	0.0185(4)
C2	0.36769(11)	0.87117(16)	0.16599(10)	0.0272(5)
H2	0.3414	0.8698	0.1841	0.033*
C3	0.39889(10)	0.93643(16)	0.16103(10)	0.0272(5)
H3	0.3989	0.9894	0.1752	0.033*
C4	0.35214(10)	0.72536(15)	0.13024(10)	0.0207(5)
C5	0.30132(10)	0.72146(15)	0.09022(10)	0.0219(5)
C6	0.27456(10)	0.64325(15)	0.08060(10)	0.0267(5)
H6	0.2411	0.6378	0.0536	0.032*
C7	0.29653(10)	0.57444(16)	0.11000(10)	0.0290(6)
H7	0.2788	0.5226	0.1022	0.035*
C8	0.34527(10)	0.58254(15)	0.15140(11)	0.0288(6)
H8	0.3588	0.5363	0.1722	0.035*
C9	0.37439(10)	0.65816(15)	0.16262(10)	0.0242(5)
C10	0.27525(11)	0.79831(16)	0.06047(10)	0.0284(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H10A	0.2383	0.7848	0.0378	0.043*
H10B	0.2990	0.8178	0.0409	0.043*
H10C	0.2719	0.8415	0.0838	0.043*
C11	0.42575(11)	0.66875(18)	0.20889(11)	0.0346(6)
H11A	0.4591	0.6731	0.1982	0.052*
H11B	0.4292	0.6211	0.2310	0.052*
H11C	0.4217	0.7187	0.2269	0.052*
C12	0.46810(10)	0.96579(14)	0.11335(9)	0.0241(5)
C13	0.44496(11)	1.00687(16)	0.06628(10)	0.0291(5)
C14	0.48116(13)	1.05694(17)	0.04886(11)	0.0371(6)
H14	0.4675	1.0838	0.0174	0.044*
C15	0.53688(13)	1.0671(2)	0.07758(13)	0.0447(7)
H15	0.5607	1.0996	0.0648	0.054*
C16	0.55805(12)	1.03052(19)	0.12466(13)	0.0449(7)
H16	0.5955	1.0406	0.1441	0.054*
C17	0.52407(11)	0.97784(17)	0.14412(10)	0.0328(6)
C18	0.38311(12)	0.99943(18)	0.03574(12)	0.0398(7)
H18A	0.3606	1.0308	0.0523	0.060*
H18B	0.3720	0.9415	0.0336	0.060*
H18C	0.3773	1.0212	0.0019	0.060*
C19	0.54712(13)	0.9394(2)	0.19663(12)	0.0484(8)
H19A	0.5362	0.9732	0.2210	0.073*
H19B	0.5878	0.9368	0.2061	0.073*
H19C	0.5321	0.8839	0.1963	0.073*
C20	0.50519(10)	0.71469(15)	−0.01028(10)	0.0235(5)
H20	0.4880	0.7652	−0.0235	0.028*
C21	0.53265(10)	0.67089(16)	−0.03785(9)	0.0253(5)
H21	0.5346	0.6921	−0.0688	0.030*
C22	0.55837(9)	0.59299(15)	−0.01965(9)	0.0223(5)
C23	0.58718(10)	0.54188(16)	−0.04546(10)	0.0289(5)
H23	0.5907	0.5594	−0.0767	0.035*
C24	0.60997(11)	0.46692(16)	−0.02512(11)	0.0307(6)
H24	0.6280	0.4333	−0.0431	0.037*
C25	0.60650(10)	0.43994(16)	0.02248(10)	0.0295(5)
H25	0.6225	0.3889	0.0359	0.035*
C26	0.57983(10)	0.48784(15)	0.04919(10)	0.0261(5)
H26	0.5780	0.4698	0.0809	0.031*
C27	0.55491(9)	0.56495(14)	0.02868(9)	0.0211(5)
C28	0.52563(9)	0.61564(14)	0.05427(9)	0.0211(5)
H28	0.5231	0.5972	0.0857	0.025*
C29	0.25216(9)	0.79640(14)	0.68308(9)	0.0204(5)
C30	0.17859(10)	0.83349(19)	0.71118(11)	0.0346(6)
H30	0.1572	0.8443	0.7331	0.041*
C31	0.16147(10)	0.84212(19)	0.65991(10)	0.0335(6)
H31	0.1259	0.8598	0.6395	0.040*
C32	0.26512(10)	0.78183(16)	0.77674(10)	0.0221(5)
C33	0.28907(10)	0.84458(15)	0.81256(10)	0.0238(5)
C34	0.31916(10)	0.81904(17)	0.86167(10)	0.0288(5)
H34	0.3364	0.8590	0.8862	0.035*
C35	0.32392(13)	0.73535(17)	0.87480(12)	0.0334(6)
H35	0.3459	0.7194	0.9075	0.040*
C36	0.29650(12)	0.67525(17)	0.84006(11)	0.0333(6)
H36	0.2980	0.6194	0.8501	0.040*
C37	0.26647(11)	0.69737(15)	0.78971(10)	0.0270(5)
C38	0.28045(11)	0.93603(15)	0.79949(11)	0.0310(6)
H38A	0.3009	0.9690	0.8286	0.046*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H38B	0.2407	0.9492	0.7904	0.046*
H38C	0.2942	0.9484	0.7711	0.046*
C39	0.23604(14)	0.63211(18)	0.75201(12)	0.0435(7)
H39A	0.1981	0.6508	0.7348	0.065*
H39B	0.2347	0.5806	0.7697	0.065*
H39C	0.2559	0.6231	0.7274	0.065*
C40	0.20230(9)	0.81445(16)	0.58928(9)	0.0253(5)
C41	0.17134(12)	0.74774(17)	0.56115(12)	0.0312(6)
C42	0.16627(13)	0.7445(2)	0.50941(12)	0.0400(7)
H42	0.1462	0.7007	0.4895	0.048*
C43	0.19056(13)	0.8055(2)	0.48698(11)	0.0434(8)
H43	0.1874	0.8016	0.4524	0.052*
C44	0.21932(12)	0.8720(2)	0.51535(11)	0.0404(7)
H44	0.2348	0.9131	0.4995	0.049*
C45	0.22555(10)	0.87858(17)	0.56745(10)	0.0302(6)
C46	0.14431(12)	0.68169(19)	0.58547(12)	0.0416(7)
H46A	0.1705	0.6653	0.6178	0.062*
H46B	0.1347	0.6338	0.5633	0.062*
H46C	0.1105	0.7040	0.5908	0.062*
C47	0.25472(13)	0.95241(19)	0.59853(13)	0.0435(7)
H47A	0.2317	0.9737	0.6183	0.065*
H47B	0.2601	0.9955	0.5760	0.065*
H47C	0.2909	0.9352	0.6211	0.065*
C48	0.45050(11)	0.79070(17)	0.67788(11)	0.0316(6)
H48	0.4391	0.8465	0.6745	0.038*
C49	0.50545(13)	0.77251(18)	0.68259(13)	0.0353(7)
H49	0.5311	0.8155	0.6832	0.042*
C50	0.52355(10)	0.68830(17)	0.68655(9)	0.0265(5)
C51	0.58043(11)	0.66335(19)	0.69259(11)	0.0347(6)
H51	0.6084	0.7036	0.6951	0.042*
C52	0.59394(11)	0.5795(2)	0.69470(11)	0.0370(6)
H52	0.6312	0.5635	0.6989	0.044*
C53	0.55207(11)	0.51690(19)	0.69065(10)	0.0341(6)
H53	0.5618	0.4604	0.6919	0.041*
C54	0.49747(11)	0.53995(17)	0.68497(10)	0.0298(5)
H54	0.4699	0.4989	0.6818	0.036*
C55	0.48224(10)	0.62540(15)	0.68380(9)	0.0234(5)
C56	0.42653(10)	0.65107(15)	0.68004(9)	0.0235(5)
H56	0.3996	0.6099	0.6790	0.028*

Source of material

According to our very recent reported method, the title product can be obtained in moderate yield [1]. Crystals suitable for X-ray diffraction were grown in a mixture of ethyl acetate and petroleum ether.

Experimental details

All hydrogen atoms attached to C atoms were introduced using the HFIX command in the SHELXL program [2]. The C—H distances in CH₃ were restrained to 0.96 Å with *U*_{iso} values to be 1.5*U*_{eq}(C). Vinylic and aromatic C—H distances were restrained to 0.93 Å with *U*_{iso} values to be 1.2*U*_{eq}(C) [3, 4].

Discussion

During the past years, N-heterocyclic carbene-palladium(II) complexes bearing different N-containing ancillary ligands have been proven efficient catalysts in C—C and C—N coupling reactions [1, 5–12]. There are two crystallographic complex in the asymmetric unit. The structural parameters of both complexes are very similar. The Pd—C_{carbene} and Pd—N bond lengths of the title product are 1.974(2) and 2.1048(19) Å, respectively. In addition, both of them are longer than that of its *i*-propyl analogue, that of which are 1.960(3) and 2.093(3) Å, respectively [1]. Therefore, it maybe draw the conclusion that stronger σ effect exsits in the latter complex, and may be the result of its higher catalytic activity [13].

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References

1. Liu, F.; Zhu, Y.-R.; Song, L.-G.; Lu, J.-M.: Synthesis of N-heterocyclic carbene-PdCl₂-(iso)quinoline complexes and their application in arylation at low catalyst loadings. *Org. Biomol. Chem.* **14** (2016) 2563–2571.
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr. D* **65** (2009) 148–155.
4. Bruker AXS Inc.: Bruker AXS SADABS, Version 2.03, SAINT, Version 6.02, Bruker AXS Inc. Madison, Winsconsin, USA, 2002.
5. Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Sayah, M.; Valente, C.: Pd-catalyzed aryl amination mediated by well defined, N-heterocyclic carbene (NHC)-Pd precatalysts, PEPPSI. *Chem. Eur. J.* **14** (2008) 2443–2452.
6. Chen, M.-T.; Vivic, D. A.; Turner, M. L.; Navarro, O.: (N-Heterocyclic carbene)PdCl₂(TEA) complexes: studies on the effect of the 'throw-away' ligand in catalytic activity. *Organometallics* **30** (2011) 5052–5056.
7. Chen, M.-T.; Vivic, D. A.; Chain, W. J.; Turner, M. L.; Navarro, O.: Inhibited catalyst activation in (N-heterocyclic carbene)PdCl₂(diethylamine) complexes by intramolecular hydrogen bonding. *Organometallics* **30** (2011) 6770–6773.
8. Zhu, L.; Gao, T.-T.; Shao, L.-X.: Well-defined NHC-Pd(II)-Im (NHC = N-heterocyclic carbene; Im = 1-methylimidazole) complexes catalyzed amination of aryl chlorides. *Tetrahedron* **67** (2011) 5150–5155.
9. Wang, Z.-Y.; Ma, Q.-N.; Li, R.-H.; Shao, L.-X.: Palladium-catalyzed Suzuki-Miyaura coupling of aryl sulfamates with arylboronic acids. *Org. Biomol. Chem.* **11** (2013) 7899–7906.
10. Huang, P.; Wang, Y.-X.; Yu, H.-F.; Lu, J.-M.: N-Heterocyclic carbene-palladium(II)-4,5-dihydrooxazole complexes: synthesis and catalytic activity toward amination of aryl chlorides. *Organometallics* **33** (2014) 1587–1593.
11. Zhao, X.-Y.; Zhou, Q.; Lu, J.-M.: Synthesis and characterization of N-heterocyclic carbene-palladium(II) chlorides-1-methylindazole and -1-methylpyrazole complexes and their catalytic activity toward C—N coupling of aryl chlorides. *RSC Adv.* **6** (2016) 24484–24490.
12. Wu, X.; Tamm, M.: Transition metal complexes supported by highly basic imidazolin-2-iminato and imidazolin-2-imine N-donor ligands. *Coord. Chem. Rev.* **260** (2014) 116–138.
13. Lv, H.; Zhu, L.; Tang, Y.-Q.; Lu, J.-M.: Structure-cactivity relationship of N-heterocyclic carbene-CPd(II)-Cimidazole complexes in Suzuki-Miyaura coupling between 4-methoxyphenyl chloride and phenylboronic acid. *Appl. Organometal. Chem.* **28** (2014) 27–31.