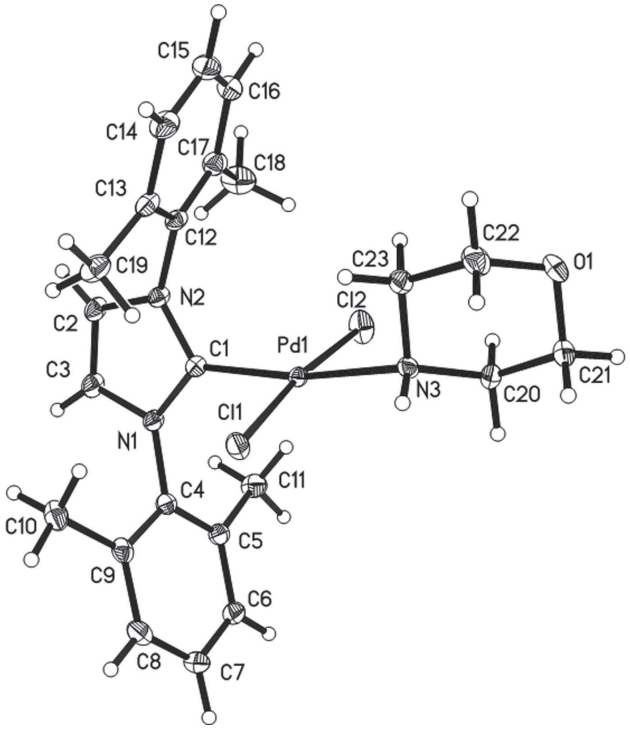
Li Guo-Xing*

The crystal structure of dichlorido-(1,3-bis(2,6-dimethylphenyl)-1H-imidazol-2(3H)-ylidene)-(morpholine-κ^1*N*)palladium(II), $C_{23}H_{29}Cl_2N_3OPd$(II)



https://doi.org/10.1515/ncrs-2018-0140
Received May 6, 2018; accepted June 26, 2018; available online July 13, 2018

Abstract

$C_{23}H_{29}Cl_2N_3OPd$, monoclinic, $P2_1/c$ (no. 14), $a = 9.6053(2)$ Å, $b = 17.4544(4)$ Å, $c = 14.5156(3)$ Å, $\beta = 104.6440(10)°$, $V = 2354.55(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0184$, $wR_{ref}(F^2) = 0.0455$, $T = 173(2)$ K.

CCDC no.: 1851691

Source of material

The title compound can be easily obtained in moderate yield according to the literature method [4, 5]. Crystals suitable for

Table 1: Data collection and handling.

Crystal:	Prismatic, yellow
Size:	0.18 × 0.14 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (λ = 0.71073 Å)
μ:	1.035 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, Φ and ω
Θ_{max}, completeness:	26.0°, >99%
N(hkl)$_{measured}$, N(hkl)$_{unique}$, R_{int}:	40421, 4597, 0.0285
Criterion for I_{obs}, N(hkl)gt:	$I_{obs} > 2\sigma(I_{obs})$, 4336
N(param)$_{refined}$:	280
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Pd1	0.44186(2)	0.59504(2)	0.29572(2)	0.01842(6)
Cl1	0.32834(4)	0.54006(2)	0.40204(3)	0.02876(10)
Cl2	0.56841(5)	0.63652(3)	0.19015(3)	0.03942(12)
O1	0.89028(13)	0.66326(8)	0.51956(10)	0.0367(3)
N1	0.16752(14)	0.56973(8)	0.14050(10)	0.0224(3)
N2	0.20747(15)	0.68840(8)	0.17615(9)	0.0217(3)
N3	0.63118(15)	0.59150(8)	0.40947(10)	0.0217(3)
H3	0.612(2)	0.5607(10)	0.4470(13)	0.029(5)
C1	0.26041(17)	0.61708(9)	0.19956(11)	0.0202(3)
C2	0.08339(19)	0.68556(10)	0.10234(12)	0.0276(4)
H2	0.0270	0.7279	0.0732	0.033
C3	0.05872(19)	0.61143(10)	0.08013(13)	0.0293(4)
H3A	−0.0187	0.5912	0.0321	0.035
C4	0.17304(17)	0.48724(9)	0.14617(11)	0.0227(3)
C5	0.25769(18)	0.44817(10)	0.09693(12)	0.0243(3)
C6	0.26825(19)	0.36889(10)	0.10829(13)	0.0295(4)
H6	0.3263	0.3405	0.0764	0.035
C7	0.1951(2)	0.33122(11)	0.16551(14)	0.0341(4)
H7	0.2058	0.2774	0.1744	0.041
C8	0.1064(2)	0.37145(11)	0.20989(13)	0.0315(4)
H8	0.0542	0.3446	0.2472	0.038
C9	0.09252(18)	0.45072(10)	0.20068(12)	0.0263(4)
C10	−0.0065(2)	0.49396(12)	0.24746(14)	0.0344(4)
H10A	0.0483	0.5331	0.2900	0.052
H10B	−0.0499	0.4583	0.2843	0.052
H10C	−0.0825	0.5186	0.1985	0.052
C11	0.3302(2)	0.48919(11)	0.03107(14)	0.0335(4)
H11A	0.2582	0.5172	−0.0170	0.050
H11B	0.3788	0.4519	−0.0005	0.050

***Corresponding author: Li Guo-Xing,** College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou Zhejiang Province, 325035, People's Republic of China, e-mail: ligxwd@126.com

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H11C	0.4011	0.5253	0.0676	0.050
C12	0.25905(18)	0.75756(9)	0.22851(11)	0.0234(3)
C13	0.21991(19)	0.76937(10)	0.31388(12)	0.0265(4)
C14	0.2689(2)	0.83622(11)	0.36419(14)	0.0360(4)
H14	0.2466	0.8456	0.4233	0.043
C15	0.3494(2)	0.88902(12)	0.32915(15)	0.0401(5)
H15	0.3824	0.9341	0.3646	0.048
C16	0.3822(2)	0.87697(11)	0.24367(15)	0.0363(4)
H16	0.4363	0.9144	0.2201	0.044
C17	0.3374(2)	0.81065(10)	0.19069(13)	0.0298(4)
C18	0.3732(3)	0.79944(13)	0.09689(15)	0.0470(5)
H18A	0.4613	0.7689	0.1062	0.071
H18B	0.3878	0.8494	0.0701	0.071
H18C	0.2938	0.7726	0.0530	0.071
C19	0.1239(2)	0.71428(11)	0.34830(14)	0.0353(4)
H19A	0.0417	0.7009	0.2955	0.053
H19B	0.0892	0.7382	0.3994	0.053
H19C	0.1782	0.6678	0.3725	0.053
C20	0.77465(18)	0.57412(11)	0.39448(13)	0.0287(4)
H20A	0.7915	0.6069	0.3427	0.034
H20B	0.7770	0.5200	0.3744	0.034
C21	0.8937(2)	0.58740(11)	0.48402(15)	0.0341(4)
H21A	0.8834	0.5503	0.5335	0.041
H21B	0.9879	0.5783	0.4700	0.041
C22	0.7553(2)	0.67698(12)	0.54095(14)	0.0364(4)
H22A	0.7543	0.7293	0.5670	0.044
H22B	0.7421	0.6401	0.5899	0.044
C23	0.63340(18)	0.66859(10)	0.45247(12)	0.0266(4)
H23A	0.5408	0.6777	0.4689	0.032
H23B	0.6437	0.7078	0.4053	0.032

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 [3]. The C—H distances in CH_3 were restrained to 0.96 Å with U_{iso} values to be $1.5U_{eq}$(C). Vinylic and aromatic C—H distances were restrained to 0.93 Å with U_{iso} values to be $1.2U_{eq}$(C).

Discussion

N-Heterocyclic carbene-palladium(II) complexes, which usually are air- and thermal-stable, have shown excellent catalytic activity in the cross-coupling reactions [6–8]. Recently it was found that besides the carbene, the anicillary ligands played important roles in the complexes [9–13]. N-Heterocyclic carbene-Pd(II) complexes using morpholine as the anicillary ligand were used in the coupling of aryl sulfomates with arylboronic acids [4].

In the title compound, the Pd center is coordinated by four ligands: one carbene carbon atom, one N atom from morpholine, and two chlorine atoms, giving a slightly distorted square-planar geometry. It is noted here that the H atom on the N atom of morpholine kept untouched in this case. In such structure, the NHC and the N atom are trans to each other [C1—Pd1—N3 = 169.56(9)°, Cl1—Pd1—Cl2 = 173.55(3)°].

Acknowledgements: I acknowledge the financial support from Wenzhou University for the publication fee.

References

1. Bruker AXS Inc.: Bruker AXS SADABS, Version 2.03, SAINT, Version 6.02, Bruker AXS Inc. Madison, WI, USA (2002).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.
4. 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.
5. Wang, Z.-Y.; Chen, G.-Q.; Shao, L.-X.: N-Heterocyclic carbene-palladium(II)-1-methylimidazole complex-catalyzed Suzuki-Miyaura coupling of aryl sulfonates with arylboronic acids. J. Org. Chem. **77** (2012) 6608–6614.
6. Froese, R. D. J.; Lombardi, C.; Pompeo, M.; Rucker, R. P.; Organ, M. G.: Designing Pd-N-heterocycic carbene complexes for high reactivity and selectivity for cross-coupling applications. Acc. Chem. Res. **50** (2017) 2244–2253.
7. Valente, C.; Calimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G.: The Development of bulky palladium NHC complexes for the most-challenging cross-coupling reactions. Angew. Chem. Int. Ed. **51** (2012) 3314–3332.
8. Fortman, G. C.; Nolan, S. P.: N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: a perfect union. Chem. Soc. Rev. **40** (2011) 5151–5169.
9. 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.
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–CN coupling of aryl chlorides. RSC Adv. **6** (2016) 24484–24490.
12. Liu, F.; Zhu, Y.-R.; Song, L.-G.; Lu, J.-M.: Synthesis of N-heterocyclic carbene–$CPdCl_2$–C(iso)quinoline complexes and their application in arylamination at low catalyst loadings. Org. Biomol. Chem. **14** (2016) 2563–2571.
13. Zhang, Z.-M.; Gao, Y.-J.; Lu, J.-M.: Synthesis of N-heterocyclic carbene-Pd(II) complexes and their catalytic activity in the Buchwald-Hartwig amination of aryl chlorides. Tetrahedron **73** (2017) 7308–7314.