Chen Xu* and Xin-Hua Lou

Crystal structure of chlorido-(4-chloro-6-(*p*-tolyl)pyrimidine- κ^2C,N)-(triphenylphosphane- κP) palladium(II), $C_{29}H_{23}Cl_2N_2PPd$

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.33 × 0.25 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.99 mm ⁻¹
Diffractometer, scan mode:	CCD, φ and ω
θ_{max} , completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12971, 4900, 0.024
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4178
$N(param)_{refined}$:	317
Programs:	Bruker [1], SHELX [2]

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Abstract

$C_{29}H_{23}Cl_2N_2PPd$, monoclinic, $P2_1/c$ (no. 14), $a = 9.4028(16)$ Å, $b = 30.928(5)$ Å, $c = 9.3071(16)$ Å, $\beta = 103.222(2)^\circ$, $V = 2634.8(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0423$, $wR_{ref}(F^2) = 0.1047$, $T = 296(2)$ K.

CCDC no.: 1941813

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 compound was obtained from the bridge-splitting reaction of the corresponding palladacyclic dimer of 4-chloro-6-*p*-tolylpyrimidine and PPh_3 according to literature [3] and

recrystallized from dichloromethane/petroleum ether solution at room temperature.

Experimental details

Hydrogen atoms were added using the riding models implemented in the SHELX system.

Comment

Cyclopalladated complexes are one of the most developed and studied classes of precatalysts because of their structural versatility and easy synthetic accessibility [3–8]. Among them, a wide variety of phosphines adducts of palladacycles have been successfully used in the coupling reactions [9–13]. In general, these adducts combine the stability induced by the presence of a palladacycle with the high activity commonly associated with phosphine ligands, and are more active than the corresponding dimeric palladacycles. As a continuation of our interest in the synthesis and application of palladacycles containing halides [3, 14], we report the crystal structure of the title complex.

The single-crystal X-ray analyses shows that the Pd atom is in a slightly distorted square-planar environment, being coordinated by a P atom, the chlorine atom, and the C atom and the nitrogen atom of the pyrimidine ligand. The deviations of the Pd atom from the plane is 0.056 Å. The pyrimidyl and phenyl ring are approximately coplanar, making a dihedral angle of 1.8°, which is less than that of the related free arylpyrimidine ligand [15]. The Pd–P and Pd–N bond lengths of the title complex are similar to those of

*Corresponding author: Chen Xu, College of Food and Pharmacy, Luoyang Normal University, Luoyang 471022, China; and School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China, e-mail: xubohan@163.com. <https://orcid.org/0000-0003-4128-2035>

Xin-Hua Lou: College of Food and Pharmacy, Luoyang Normal University, Luoyang 471022, China

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

Atom	x	y	z	U _{iso} */U _{eq}
Pd1	0.70081(3)	0.155348(9)	0.78562(3)	0.04096(12)
Cl1	0.4003(2)	0.34148(6)	0.5807(3)	0.1416(9)
Cl2	0.55600(12)	0.12064(4)	0.57329(11)	0.0567(3)
P1	0.81789(11)	0.09272(3)	0.86925(10)	0.0378(2)
N1	0.5958(4)	0.21451(11)	0.7198(4)	0.0502(8)
N2	0.4239(5)	0.25952(15)	0.5625(5)	0.0775(13)
C1	0.6553(5)	0.24902(14)	0.8031(5)	0.0549(11)
C2	0.5974(6)	0.28981(15)	0.7643(7)	0.0742(15)
H2	0.6347	0.3142	0.8184	0.089*
C3	0.4839(6)	0.29268(18)	0.6438(7)	0.0771(16)
C4	0.4834(5)	0.22157(17)	0.6056(6)	0.0679(13)
H4	0.4430	0.1975	0.5512	0.082*
C5	0.7769(5)	0.23830(13)	0.9250(5)	0.0508(10)
C6	0.8523(6)	0.26962(15)	1.0219(6)	0.0700(14)
H6	0.8238	0.2984	1.0091	0.084*
C7	0.9666(6)	0.25862(17)	1.1348(6)	0.0748(15)
H7	1.0140	0.2799	1.1987	0.090*
C8	1.0126(5)	0.21647(16)	1.1553(5)	0.0596(12)
C9	0.9406(5)	0.18524(14)	1.0571(5)	0.0521(10)
H9	0.9742	0.1569	1.0685	0.063*
C10	0.8214(4)	0.19453(12)	0.9432(4)	0.0441(9)
C11	1.1362(6)	0.2036(2)	1.2836(6)	0.0871(18)
H11A	1.2042	0.2271	1.3076	0.131*
H11B	1.1852	0.1787	1.2568	0.131*
H11C	1.0973	0.1968	1.3677	0.131*
C12	0.9910(4)	0.08706(13)	0.8125(4)	0.0419(9)
C13	1.0578(6)	0.12305(16)	0.7721(5)	0.0648(13)
H13	1.0157	0.1501	0.7756	0.078*
C14	1.1870(7)	0.1194(2)	0.7263(7)	0.0880(18)
H14	1.2315	0.1441	0.7003	0.106*
C15	1.2499(6)	0.0801(2)	0.7187(6)	0.0767(16)
H15	1.3370	0.0780	0.6879	0.092*
C16	1.1850(6)	0.04388(18)	0.7565(5)	0.0681(13)
H16	1.2268	0.0169	0.7498	0.082*
C17	1.0563(5)	0.04720(14)	0.8051(5)	0.0559(11)
H17	1.0135	0.0224	0.8329	0.067*
C18	0.7247(4)	0.04154(13)	0.8084(4)	0.0423(9)
C19	0.7111(5)	0.02755(14)	0.6636(5)	0.0550(11)
H19	0.7448	0.0449	0.5966	0.066*
C20	0.6475(5)	−0.01220(15)	0.6189(5)	0.0648(13)
H20	0.6397	−0.0214	0.5223	0.078*
C21	0.5961(5)	−0.03806(16)	0.7146(6)	0.0682(14)
H21	0.5544	−0.0647	0.6839	0.082*
C22	0.6067(6)	−0.02433(16)	0.8553(6)	0.0710(14)
H22	0.5712	−0.0416	0.9209	0.085*
C23	0.6703(5)	0.01538(14)	0.9022(5)	0.0560(11)
H23	0.6760	0.0243	0.9987	0.067*
C24	0.8589(4)	0.08700(12)	1.0698(4)	0.0397(8)
C25	0.7514(5)	0.09895(13)	1.1422(5)	0.0497(10)
H25	0.6611	0.1085	1.0883	0.060*
C26	0.7784(6)	0.09669(15)	1.2954(5)	0.0605(12)
H26	0.7058	0.1044	1.3435	0.073*
C27	0.9102(6)	0.08330(18)	1.3744(5)	0.0717(14)
H27	0.9275	0.0819	1.4767	0.086*
C28	1.0180(6)	0.07181(18)	1.3050(5)	0.0729(15)
H28	1.1087	0.0632	1.3607	0.087*
C29	0.9936(5)	0.07287(14)	1.1532(5)	0.0526(10)
H29	1.0665	0.0642	1.1066	0.063*

the related palladacycles [3, 14, 16, 17]. In the crystal there exist weak C—H···Cl hydrogen bonds [18–20], the coordinated chlorine atom forms hydrogen bonds with the adjacent C—H group of the PPh₃ ligand (Cl···H = 2.849, 2.861 and 2.943 Å). In addition, the chlorine atom in the pyrimidine ring also forms C—H···Cl hydrogen bonds with the adjacent C—H group of *p*-tolylpyrimidyl moiety and PPh₃ ligand (Cl···H = 2.887 and 2.945 Å), which are attributed to construct the 3D architecture.

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