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Crystal structure of chlorido-(5-acetyl-2-(5-methylpyridin-2-yl)benzen-1-ido- κ^2 C,N)-pyridine- κ N-palladium(II), $C_{19}H_{17}ClN_2OPd$

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.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.20 × 0.18 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.21 mm ^{−1}
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	26.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7717, 3608, 0.048
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2869
$N(\text{param})_{\text{refined}}$:	219
Programs:	SHELX [1]

Source of material

The title compound was obtained from the bridge-splitting reaction of the corresponding palladacyclic dimer of 1-(4-(5-methylpyridin-2-yl)phenyl) ethanone and pyridine according to literature [2]. Crystallization from dichloromethane/petroleum ether at room temperature to give the title compound.

Experimental details

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

Comment

Palladacycles/palladium(II) complexes have been widely applied in organic reactions as highly efficient catalysts [3–5]. Moreover, palladacycles are also emerging as the most versatile candidates for luminescent devices [3, 6–8]. In these studies, ancillary ligands can effectively improve the solubility and properties of palladacycles due to the poor solubility of the corresponding palladacyclic dimers [9, 10].

The title crystal structure shows that the title complex adopts a *trans* configuration of the coordinated pyridine to

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Abstract

$C_{19}H_{17}ClN_2OPd$, monoclinic, $P2_1/c$ (no. 14), $a = 9.0720(8)$ Å, $b = 10.9390(10)$ Å, $c = 17.9604(7)$ Å, $\beta = 97.054(6)^\circ$, $V = 1768.9(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0389$, $wR_{\text{ref}}(F^2) = 0.0816$, $T = 293(2)$ K.

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.7037(4)	0.4311(3)	0.53883(17)	0.0309(8)
C2	0.7977(4)	0.5320(3)	0.54623(18)	0.0335(8)
H2	0.8433	0.5531	0.5937	0.040*
C3	0.8256(4)	0.6023(3)	0.48502(19)	0.0333(8)
C4	0.7549(4)	0.5731(3)	0.41428(19)	0.0407(9)
H4	0.7699	0.6213	0.3732	0.049*
C5	0.6621(4)	0.4725(4)	0.40480(19)	0.0395(9)
H5	0.6164	0.4523	0.3572	0.047*
C6	0.6368(4)	0.4013(3)	0.46626(18)	0.0318(8)
C7	0.5385(4)	0.2955(3)	0.46148(19)	0.0339(8)
C8	0.4657(5)	0.2440(4)	0.3963(2)	0.0458(10)
H8	0.4793	0.2759	0.3496	0.055*
C9	0.3730(5)	0.1449(4)	0.4016(2)	0.0534(11)
H9	0.3263	0.1089	0.3581	0.064*
C10	0.3486(4)	0.0983(3)	0.4707(2)	0.0417(9)
C11	0.4279(4)	0.1518(3)	0.5330(2)	0.0384(9)
H11	0.4160	0.1209	0.5802	0.046*
C12	0.9299(4)	0.7085(3)	0.4931(2)	0.0395(9)
C13	1.0110(5)	0.7378(4)	0.5690(2)	0.0528(11)
H13A	1.0733	0.6702	0.5863	0.079*
H13B	0.9404	0.7527	0.6037	0.079*
H13C	1.0710	0.8094	0.5655	0.079*
C14	0.2430(5)	−0.0050(4)	0.4797(3)	0.0587(12)
H14A	0.2724	−0.0460	0.5265	0.088*
H14B	0.2451	−0.0619	0.4391	0.088*
H14C	0.1443	0.0267	0.4793	0.088*
C15	0.9360(5)	0.4005(4)	0.7026(2)	0.0455(10)
H15	0.9769	0.3461	0.6711	0.055*
C16	1.0297(5)	0.4710(4)	0.7507(2)	0.0565(12)
H16	1.1321	0.4646	0.7514	0.068*
C17	0.9711(5)	0.5501(4)	0.7974(2)	0.0599(12)
H17	1.0328	0.5989	0.8302	0.072*
C18	0.8196(6)	0.5571(4)	0.7956(2)	0.0635(13)
H18	0.7773	0.6105	0.8272	0.076*
C19	0.7319(5)	0.4844(4)	0.7465(2)	0.0499(11)
H19	0.6293	0.4888	0.7458	0.060*
Cl1	0.59105(15)	0.16988(11)	0.70898(5)	0.0644(3)
N1	0.5207(3)	0.2457(3)	0.52885(15)	0.0333(7)
N2	0.7880(3)	0.4070(3)	0.69933(14)	0.0347(7)
O1	0.9505(3)	0.7704(3)	0.43929(15)	0.0575(8)
Pd1	0.65116(3)	0.31886(2)	0.61815(2)	0.03228(10)

the palladacyclic ligand nitrogen. The Pd atom is in a slightly distorted square planar environment bonded to the chlorido ligand, the nitrogen atom of the pyridine and the nitrogen atom and the C atom of the 1-(4-(5-methylpyridin-2-yl)phenyl) ethanone. The bicyclic system formed by the palladacycle and the pyridyl ring of the palladacyclic ligand is approximately coplanar (dihedral angle of 4.7°). The coordinated pyridine plane is almost perpendicular to the square plane formed by the Pd(II) center (dihedral angles of 107.3°). The Pd–C, Pd–N bond lengths of the title complex are similar to those of the related palladacycles [7, 8, 10, 11]. Although

many structures of palladacycles have been determined, few reports discuss the intermolecular interactions in these complexes [12, 13]. In the crystal chlorine atom forms C–H···Cl hydrogen bonds with the adjacent C–H group of the palladacyclic ligand (Cl···H = 2.896 Å) [13–15], which construct a 1D chain structure. In addition, the oxygen atom of acetyl group also forms C–H···O hydrogen bonds with the two adjacent C–H group of the coordinated pyridines (O···H = 2.512 and 2.608 Å) [16, 17], which give rise to a 2D architecture.

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References

- Sheldrick, G. M.: A short history of SHELXTL. *Acta Crystallogr. A* **64** (2008) 112–122.
- Xiao, Z. Q.; Xu, C.; Li, H. M.; Han, X.; Wang, Z. Q.; Fu, W. J.; Hao, X. Q.; Song, M. P.: Two fluorescent cyclopalladated arylpyrazine complexes: synthesis, crystal structures and application in the double Suzuki coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid. *Transition Met. Chem.* **40** (2015) 501–508.
- Dupont, J.; Consorti, C. S.; Spencer, J.: The potential of palladacycles: more than just precatalysts. *Chem. Rev.* **105** (2005) 2527–2571.
- Wu, Y. J.; Huo, S. Q.; Gong, J. F.; Cui, X. L.; Ding, L.; Ding, K. L.; Du, C. X.; Liu, Y. H.; Song, M. P.: Studies on the cyclometallation of ferrocenylimines. *J. Organomet. Chem.* **637–639** (2001) 27–46.
- Xu, C.; Li, H. M.; Yuan, X. E.; Xiao, Z. Q.; Wang, Z. Q.; Fu, W. J.; Ji, B. M.; Hao, X. Q.; Song, M. P.: *N*-Heterocyclic carbene (NHC)-modulated Pd/Cu cocatalyzed three-component synthesis of 2,6-diarylquinolines. *Org. Biomol. Chem.* **12** (2014) 3114–3122.
- Sicilia, V.; Fornies, J.; Fuertes, S.; Martin, A.: New dicyano cyclometalated compounds containing Pd(II)–Ti(II) bonds as building blocks in 2D extended structures: synthesis, structure, and luminescence studies. *Inorg. Chem.* **51** (2012) 10581–10589.
- Xu, C.; Wang, Z. Q.; Yuan, X. E.; Han, X.; Xiao, Z. Q.; Fu, W. J.; Ji, B. M.; Hao, X. Q.; Song, M. P.: Solid state fluorescent palladacycles with *N*-heterocyclic carbene-based ancillary ligands at room temperature. *J. Organomet. Chem.* **777** (2015) 1–5.
- Xu, C.; Li, H. M.; Xiao, Z. Q.; Wang, Z. Q.; Tang, S. F.; Ji, B. M.; Hao, X. Q.; Song, M. P.: Cyclometalated Pd(II) and Ir(III) 2-(4-bromophenyl)pyridine complexes with *N*-heterocyclic carbenes (NHCs) and acetylacetonate (acac): synthesis, structures, luminescent properties and application in one-pot oxidation/Suzuki coupling of aryl chlorides containing hydroxymethyl. *Dalton Trans.* **43** (2014) 10235–10247.
- Mancilha, F. S.; Barloy, L.; Rodembusch, F. S.; Dupont, J.; Pfeffer, M.: Cyclopalladated complexes of 4-aryl-2,1,3-benzothiadiazoles: new emitters in solution at room temperature. *Dalton Trans.* **40** (2011) 10535–10544.
- Han, X.; Li, H. M.; Xu, C.; Xiao, Z. Q.; Wang, Z. Q.; Fu, W. J.; Hao, X. Q.; Song, M. P.: Water-soluble palladacycles containing

- hydroxymethyl groups: synthesis, crystal structures and use as catalysts for amination and Suzuki coupling of reactions. *Transition Met. Chem.* **41** (2016) 403–411.
11. Li, H. M.; Xu, C.; Hao, X. Q.; Li, Z.; Wang, Z. Q.; Fu, W. J.; Song, M. P.: Cationic cyclopalladated ferrocenylpyrimidine complex as an efficient catalyst for the synthesis of substituted biaryl methanol by the Suzuki reaction in water. *Inorg. Chim. Acta* **404** (2013) 236–240.
 12. Antelo, J. M.; Adrio, L.; Pereira, M. T.; Ortigueira, J. M.; Fernandez, J. J.; Vila, J. M.: Synthesis and structural characterization of palladium and platinum bimetallic compounds derived from bidentate P,S-palladacycle metaloligands. *Cryst. Growth Des.* **10** (2010) 700–708.
 13. Xu, C.; Wang, Z. Q.; Zhang, Y. P.; Dong, X. M.; Hao, X. Q.; Fu, W. J.; Ji, B. M.; Song, M. P.: Synthesis and structural characterization of palladacycles with polydentate ligands by a stepwise coupling route-palladacycles containing halides as efficient catalysts and substrates. *Eur. J. Inorg. Chem.* **31** (2011) 4878–4888.
 14. Brammer, L.; Bruton, E. A.; Sherwood, P.: Understanding the behavior of halogens as hydrogen bond acceptors. *Cryst. Growth Des.* **1** (2001) 277–290.
 15. Albert, J.; DAndrea, L.; Granell, J.; Tavera, R.; Font-Bardia, M.; Solans, X.: Synthesis and reactivity towards carbon monoxide of an optically active endo five-membered ortho-cyclopalladated imine: X-ray molecular structure of *trans*-(ν -Cl)₂[Pd(k²-C,N-(R)-C₆H₄-CHN-CHMe-Ph)]₂. *J. Organomet. Chem.* **692** (2007) 3070–3080.
 16. Steiner, T.: The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.* **41** (2002) 48–76.
 17. Nangia, A.: Database research in crystal engineering. *CrystEngComm* **4** (2002) 93–101.