

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73

CRYSTAL STRUCTURES OF TWO *N*-HETEROCYCLIC CARBENE-PALLADACYCLESH. M. Li¹, X. Q. Liu¹, Z. Q. Wang², W. J. Fu², C. Xu²¹College of Life Science, Luoyang Normal University, Luoyang, Henan, P. R. China²College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan, P. R. China

E-mail: xubohan@163.com

Received December, 14, 2014

Revised — February, 21, 2015

The crystal structures of two *N*-heterocyclic carbene (NHC)-palladacycles are determined by single crystal X-ray diffraction. The intermolecular C—H···Cl hydrogen bonds and $\pi\cdots\pi$ interactions are found in the crystals.

DOI: 10.15372/JSC20150530

Keywords: *N*-heterocyclic carbene, palladacycle, C—H···Cl hydrogen bond, $\pi\cdots\pi$ interaction.

N-heterocyclic carbenes (NHCs) have become a paradigmatically new generation of strong σ -donor ligands and are successfully used in the palladium-catalyzed coupling reactions [1, 2]. Among them, a combination of a palladacycle framework with highly donating and sterically demanding NHCs has been reported [3–8]. These adducts were far more active than the corresponding dimeric palladacycle. In addition, NHCs have attracted increasing interest as ancillary ligands that opened new avenues for the design of emitting materials due to their excellent color purity and high stability [9–11]. Recently, we have investigated fluorescent NHC-cyclopalladated 2-(4-ethylphenyl)pyrazine and 2-(4-methoxyphenyl)pyrazine complexes [12]. As a part of our continuous research work, herein, the structures of two NHC [*N,N'*-bis((1,3-di-4-methyl-phenyl)-imidazol)-2-ylidene]-palladacycles are determined by single crystal X-ray diffraction.

Experimental. NHC-palladacycles **1** and **2** were prepared by the literature method [12]. Single crystals suitable for X-ray diffraction were obtained by recrystallization from a CH₂Cl₂-petroleum ether solution at room temperature. Single crystal X-ray diffraction data of complex **1** and **2** were collected on a Xcalibur, Eos, Gemini diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.071073$ nm). Data collection and reduction were performed using the Olex2 software [13]. The structures were solved by direct methods and refined by the least-squares methods using the SHELXL-97 program [14]. All non-hydrogen atoms were refined anisotropically. In the final step of the crystal structure refinement, hydrogen atoms of idealized —CH₂ and —CH₃ groups were added and treated with the riding atom mode; their isotropic displacement factor was chosen as 1.2 and 1.5 times the preceding carbon atom, respectively. The ethyl group in **1** was disordered over positions with the major component having a site occupancy of 0.595(11). Crystal data and experimental details of the structure determinations, selected bond distances and angles, and hydrogen bonding parameters are listed in Tables 1 and 2, respectively. The X-ray diffraction data were deposited with the Cambridge Crystallographic Data Center (CCDC no. 1039124 for **1** and 1013221 for **2**) and are available from the authors at www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystallographic data and structure refinement for **1** and **2**

Parametr	1	2
Empirical formula	C ₂₉ H ₂₇ ClN ₄ Pd	C ₂₈ H ₂₅ ClN ₄ OPd
Formula weight	573.40	575.37
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.1608(4), 11.5312(6), 12.2594(6)	10.0414(6), 11.4653(5), 12.3285(5)
α , β , γ , deg.	67.056(5), 86.629(4), 81.631(4)	67.312(4), 86.019(4), 82.122(4)
<i>V</i> , Å ³	1308.67(11)	1296.95(11)
<i>Z</i>	2	2
<i>D</i> _{calcd} , g/cm ³	1.455	1.473
<i>F</i> (000)	584.0	584.0
Index ranges	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 14
Reflections collected / unique	10857 / 5354	1074 / 5305
GOOF on <i>F</i> ²	1.045	1.046
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0353, 0.0741	0.0311, 0.0637
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0460, 0.0795	0.0389, 0.0671

Table 2

Selected bond lengths (Å) and angles (deg.) for **1** and **2**

	1	2
Pd1—C11	2.4043(8)	Pd1—C11 2.4043(7)
Pd1—N3	2.070(2)	Pd1—N3 2.075(2)
Pd1—C1	1.973(3)	Pd1—C1 1.970(2)
Pd1—C23	1.992(3)	Pd1—C23 1.995(2)
C25—C28 [C28A]	1.449(10) [1.527(16)]	O1—C25 1.374(3)
C28—C29 [C29A]	1.466(11) [1.464(16)]	O1—C28 1.417(4)
N3—Pd1—C11	93.58(7)	N3—Pd1—C11 93.83(6)
C1—Pd1—C11	94.94(8)	C1—Pd1—C11 95.06(7)
C1—Pd1—C23	89.79(12)	C1—Pd1—C23 89.46(10)
C23—Pd1—C11	81.71(11)	C23—Pd1—C11 81.75(9)
C1—Pd1—N3	171.39(10)	C1—Pd1—N3 170.89(8)
C23—Pd1—C11	175.21(9)	C23—Pd1—C11 174.84(7)

Results and discussion. Although many structures of palladacycles have been determined, few reports consider intermolecular interactions in these complexes [15–18]. Thus, we investigated the crystal structures of palladacycles **1** and **2**, focusing on the studies of supramolecular interactions. The single crystal X-ray analysis indicates that these palladacycles are *trans* complexes in the solid state. The molecules are shown in Figs. 1 and 2. The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the C atom of NHC, the chlorine atom, the nitrogen atom, and the C atom of the pyrazine ligand. The bicyclic system formed by the palladacycle and the pyrazyl ring is approximately coplanar (dihedral angles of 1.8° and 2.8° for **1** and **2**). The Pd—C_{carb} and Pd—N bond lengths are found to be in the range of 1.970(2)–1.973(2) Å and 2.070(2)–2.075(2) Å, respectively, which are comparable to those of the related NHC-palladacycles [17]. The imidazole ring plane of NHC is almost perpendicular to the square plane formed by the Pd(II) center (dihedral angles

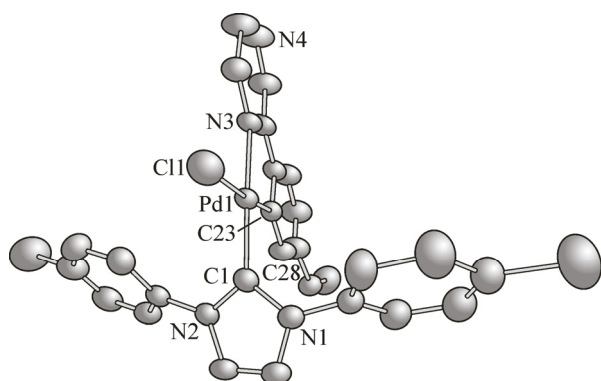


Fig. 1. Molecular structure of **1** drawn with 30 % probability displacement ellipsoids (all hydrogen atoms are omitted for clarity)

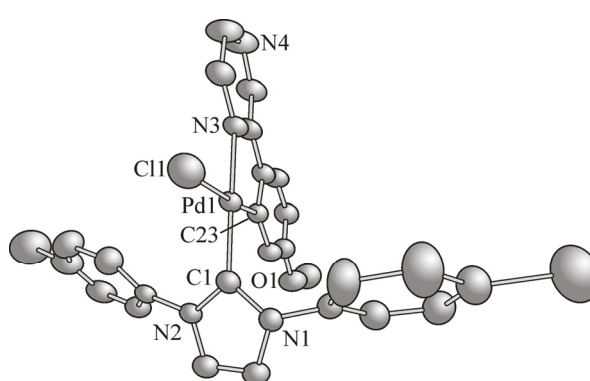


Fig. 2. Molecular structure of **2** drawn with 30 % probability displacement ellipsoids (all hydrogen atoms are omitted for clarity)

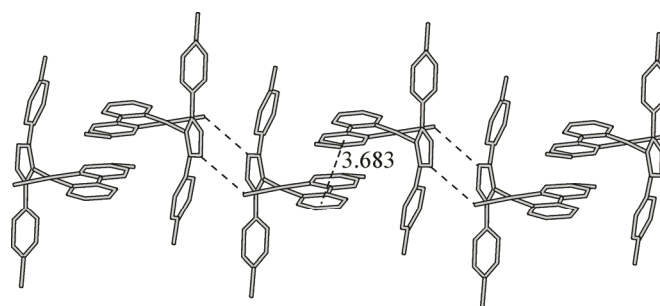


Fig. 3. The 1D supramolecular structure of **1**

of 87.6° and 88.9° for **1** and **2**). In this type of arrangement the N-substituents of NHC reduce the steric interaction with the palladacyclic ligand.

For **1** and **2**, the NHC ligand can serve as an H donor (Fig. 3). Complex **1** exists as a dimer in the crystal due to intermolecular hydrogen bonds between the chlorine atom and the adjacent C—H group of NHC ($\text{Cl}\cdots\text{H} = 2.960 \text{ \AA}$) [19, 20]. The interplanar distance between the two imidazole rings is 5.553 \AA and the Pd—Pd distance is 7.410 \AA . The crystal structure packing of **1** consists of inversion-related pairs of molecules through $\pi\cdots\pi$ interactions [21, 22]. The pairs are arranged in a head-to-tail manner and involve the close interaction of pyrazine and benzene moieties (3.863 \AA). Owing to the $\text{CH}\cdots\text{Cl}$ hydrogen bonds and $\pi\cdots\pi$ interactions, the crystal structure of **1** is extended into a 1D architecture. Basically, the crystal structure of **2** is quite similar to that of **1** owing to the existence of similar hydrogen bonds and intermolecular $\pi\cdots\pi$ interactions in the crystal. The hydrogen bond length ($\text{Cl}\cdots\text{H}$) and the interplanar distance in **2** are 2.959 \AA and 3.721 \AA , respectively. The interplanar distance between the two imidazole rings and the Pd—Pd distance in **2** are 5.539 \AA and 7.401 \AA , respectively.

This work was supported by the Aid Project for the Leading Young Teachers in Henan Provincial Institutions of Higher Education of China (2013GGJS-151), Innovation Scientists and Technicians Troop Construction Projects of Henan Province, and the Science Foundation of Henan Education Department (Nos. 14A150049 and 13A150804).

REFERENCES

1. Kantchev E.A.B., O'Brien C.J., Organ M.G. // *Angew. Chem. Int. Ed.* – 2007. – **46**. – P. 2768.
2. Fortman G.C., Nolan S.P. // *Chem. Soc. Rev.* – 2011. – **40**. – P. 5151.
3. Navarro O., Kelly R.A. III, Nolan S.P. // *J. Am. Chem. Soc.* – 2003. – **125**. – P. 16194.

4. Frey G.D., Schütz J., Herdtweck E., Herrmann W.A. // *Organometallics*. – 2005. – **24**. – P. 4416.
5. Li J.Y., Cui M.J., Yu A.J., Wu Y.J. // *J. Organomet. Chem.* – 2007. – **692**. – P. 3732.
6. Marion N., Navarro O., Mei J.G., Atevens E.D., Scott N.M., Nolan S.P. // *J. Am. Chem. Soc.* – 2006. – **128**. – P. 4101.
7. Kantchev E.A.B., Ying J.Y. // *Organometallics*. – 2009. – **28**. – P. 289.
8. Xu C., Li H.M., Liu H., Zhang Z.Q., Wang Z.Q., Fu W.J., Zhang Y.Q. // *Inorg. Chem. Acta*. – 2012. – **386**. – P. 22.
9. Mercs L., Albrecht M. // *Chem. Soc. Rev.* – 2010. – **39**. – P. 1903.
10. Wiegmann B.P., Jones G., Wagenblast G., Lennartz C., Münster I., Metz S., Kowalsky W., Johannes H.H. // *Organometallics*. – 2012. – **31**. – P. 5223.
11. Visbal R., Gimeno M.C. // *Chem. Soc. Rev.* – 2014. – **43**. – P. 3551.
12. 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. // *J. Organomet. Chem.* – 2015. – **777**. – P. 1.
13. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. // *J. Appl. Crystallogr.* – 2009. – **42**. – P. 339.
14. Sheldrick G.M. // *Acta Cryst. A*. – 2008. – **64**. – P. 112.
15. Xu C., Wang Z.Q., Fu W.J., Lou X.H., Li Y.F., Cen F.F., Ma H.J., Ji B.M. // *Organometallics*. – 2009. – **28**. – P. 1909.
16. Antelo J.M., Adrio L., Pereira M.T., Ortigueira J.M., Fernández J.J., Vila J.M. // *Cryst. Growth Des.* – 2010. – **10**. – P. 700.
17. Xu C., Li H.M., Xiao Z.Q., Wang Z.Q., Tang S.F., Ji B.M., Hao X.Q., Song M.P. // *Dalton Trans.* – 2014. – P. 10235.
18. Chicote M.T., Rubio C., Bautista D., Vicente J. // *Dalton Trans.* – 2014. – P. 15170.
19. Aakeröy C.B., Evans T.A., Seddon K.R., Pálinkó I. // *New J. Chem.* – 1999. – P. 145.
20. Brammer L., Bruton E.A., Sherwood P. // *Cryst. Growth Des.* – 2001. – **1**. – P. 277.
21. Janiak C. // *Dalton Trans.* – 2000. – P. 3885.
22. Malathy Sony S.M., Ponnuswamy M.N. // *Cryst. Growth Des.* – 2006. – **6**. – P. 736.