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Synthesis, structural characterization and catalytic activity of two *N*-heterocyclic carbene–phosphine palladium(II) complexes

Chen Xu [a,*], Xin-Qi Hao [b], Zhen Li [b], Xin-Ming Dong [b], Lu-Meng Duan [b], Zhi-Qiang Wang [a], Bao-Ming Ji [a], Mao-Ping Song [b,*]

[a] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan 471022, China*
[b] *Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, China*

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ABSTRACT

Two new *N*-heterocyclic carbene (NHC)-phosphine palladium(II) complexes Pd(IMeo)PPh_3I_2 **1** and Pd(IMeo) $P(C_6H_4$-*p*-$Me)_3I_2$ **2** (IMeo = 1,3-di-4-methoxyphenyl- imidazolin-2-ylidene) have been easily prepared from the reaction of the corresponding iodide-bridged NHC dimer with phosphine ligands in high yields. Complexes **1** and **2** were characterized by elemental analysis, IR, ^1H NMR, ESI-MS and single-crystal X-ray analysis. Complex **1** adopts a *trans* geometry in the solid state, while **2** is *cis*. The common features of the structures of these complexes are intermolecular C–H···I and C–H···O hydrogen bonds. These complexes were found to be efficient catalysts for the Suzuki reaction of aryl bromides.

In recent years, *N*-heterocyclic carbenes (NHCs) and their transition-metal complexes have been the focus of intense research in organometallic chemistry and homogeneous catalysis [1–3]. Most significantly, NHCs palladium(II) complexes derived from imidazolium precursors have been successfully developed as highly active precatalysts for the coupling reactions [4–5]. In these cases, NHCs not only exhibit strong σ-donor ability which could enhance the oxidative addition of aryl halides, but also promote the reductive elimination of the coupling products because of their steric hindrance [6–7]. Nevertheless, bis(phosphine) complexes of palladium(II) are even better known and are more widely used as precatalysts for various coupling reactions [8–9]. Despite the success of both types of ligands, there are few reports involving mixed NHC-phosphine palladium(II) complexes [10–14]. Usually, they are prepared by reaction of the corresponding halogen-bridged NHC dimers with phosphine ligands, and most of them adopted *trans*-configuration of the coordinated phosphines to the C atoms of NHCs in the solid state, only a few *cis* NHC-phosphine palladium(II) complexes have been reported [15–17]. Here, we synthesized two new *trans*/*cis* *N*-heterocyclic carbene–phosphine palladium(II) complexes **1** and **2** (Scheme 1). The crystal structures and catalytic activity in the Suzuki reaction of these complexes are also investigated.

NHC precursor 1,3-di-4-methoxyphenylimidazolium chloride was prepared according to the literature method starting from 4-methoxybenzenamine [18]. The preparation of **1** and **2** is as follows: a total of the above imidazolium salt (0.5 mmol), $Pd(OAc)_2$ (0.5 mmol), K(O*t*-Bu) (1.0 mmol) and NaI (2.0 mmol) were dissolved in 20 mL dry THF under nitrogen. Then the mixture was stirred for 24 h at room temperature. The formed brown solids (yield: 85%) were collected by filtration, which can be assigned to be a corresponding iodide-bridged NHC palladium(II) dimers $[Pd(IMeo)I_2]_2$ [10,15]. Because of its poor solubility in common organic solvents, without further purification, it was directly subjected to bridge-splitting reaction with monophosphine ligands (1.0 mmol) PPh_3 or $P(C_6H_4$-*p*-$Me)_3$ in dry CH_2Cl_2 at room temperature for 1 h. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The second band was collected and afforded complex **1** [19] or **2** [20] after the evaporation of the solvent.

The two complexes are air and moisture stable both in the solid state and in solution. They are very soluble in chloroform, dichloromethane and acetone, but insoluble in petroleum ether and n-hexane. These complexes were fully characterized by elemental analysis, IR, ^1H NMR and ESI-MS. The ^1H NMR spectra of complexes **1** and **2** were consistent with the proposed structures and showed only one set of signals in a symmetrical surrounding indicating the exclusive formation of the isomer. For example, the signals of methyl for complexes **1** and **2** are single at δ 3.92 and similar peaks at δ 3.93, 2.33, respectively. As expected, the positive mode ESI mass spectra show a base peak at *m*/*z* = 775 and 818 corresponding to the $[M\text{-}I]^+$ cations. In order to further investigate the structures of these complexes, their detailed structures have been determined by X-ray single-crystal diffraction.

The crystals were obtained by recrystallization from Me_2CO–petroleum ether solution at room temperature. The molecules are shown in Figs. 1–2. As can be seen, the molecule of **1** adopts a *trans*

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* Corresponding authors. Tel.: +86 371 67763207; fax: +86 371 67766667.
E-mail addresses: xubohan@163.com (C. Xu), maopingsong@zzu.edu.cn (M.-P. Song).

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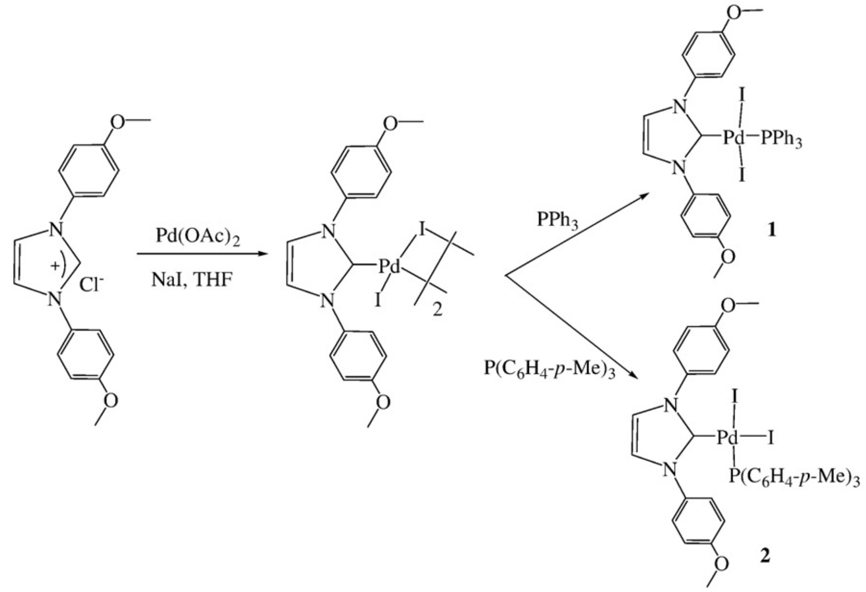


Scheme 1. Synthesis of **1**–**2**.

configuration of the coordinated phosphine to the C atom of NHC. Surprisingly, the single crystal X-ray analysis of **2** reveals a *cis*-configuration in the solid state. In each complex, the Pd atom is in a slightly distorted square-planar environment bonded to the phosphorus atom, the iodine atoms, the C atom of NHC. The deviations of the Pd atom from the plane are 0.0242 and 0.0306 Å for complexes **1**–**2**, respectively. The Pd–C$_{carb}$ [2.006(6) Å] and Pd–P [2.2782(15) Å] bond lengths of *cis* complex **2** are similar to those of related *cis* complexes [15–17], while they are shorter than those of *trans* complex **1** [2.034(3) Å and 2.3396(9) Å] and related *trans* complexes [10–14]. Another difference between **1** and **2** is dihedral angles (42.4°, 44.9° and 35.8°, 66.4°, respectively for **1** and **2**) between imidazole ring plane and those of phenyl rings attached to the N atoms.

The imidazole ring plane of NHC is almost perpendicular to the square plane formed by the Pd(II) center (dihedral angles of 77.8° and 79.2° for complexes **1**–**2**, respectively). In this type of arrangement the *N*-substituents of NHC reduce the steric interaction with phosphine ligand. In addition, we also investigated the intermolecular interactions in crystal structures of **1** and **2.** The common features of these complexes are intermolecular C–H···I and C–H···O hydrogen bonds [21–23]. In complex **1**, there are two types of intermolecular

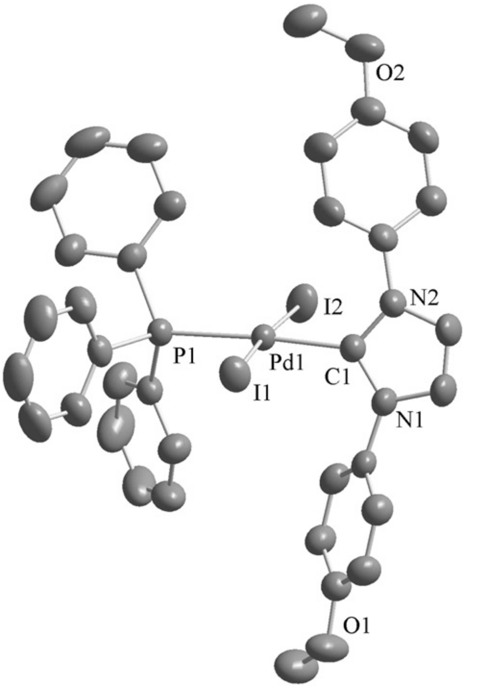


Fig. 1. Molecular structure of complex **1**. Displacement parameters are drawn at the 50% level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.034(3), Pd(1)–P(1) 2.3396(9), Pd(1)–I(1) 2.5852(5), Pd(1)–I(2) 2.6267(5), and C(1)–Pd(1)–I(1) 85.39(9), I(1)–Pd(1)–P(1) 93.59(2), P(1)–Pd(1)–I(2) 91.14(2), I(2)–Pd(1)–C(1) 89.81(9).

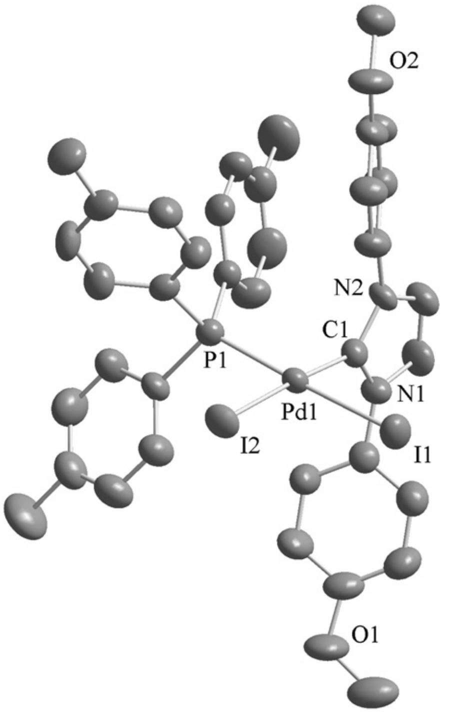


Fig. 2. Molecular structure of complex **2**. Displacement parameters are drawn at the 50% level. H atoms and Me$_2$CO are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.006(6), Pd(1)–P(1) 2.2782(15), Pd(1)–I(1) 2.6444(6), Pd(1)–I(2) 2.6402(6), and C(1)–Pd(1)–P(1) 93.64(16), P(1)–Pd(1)–I(2) 89.56(4), I(2)–Pd(1)–I(1) 90.654(19), I(1)–Pd(1)–C(1) 86.18(16).

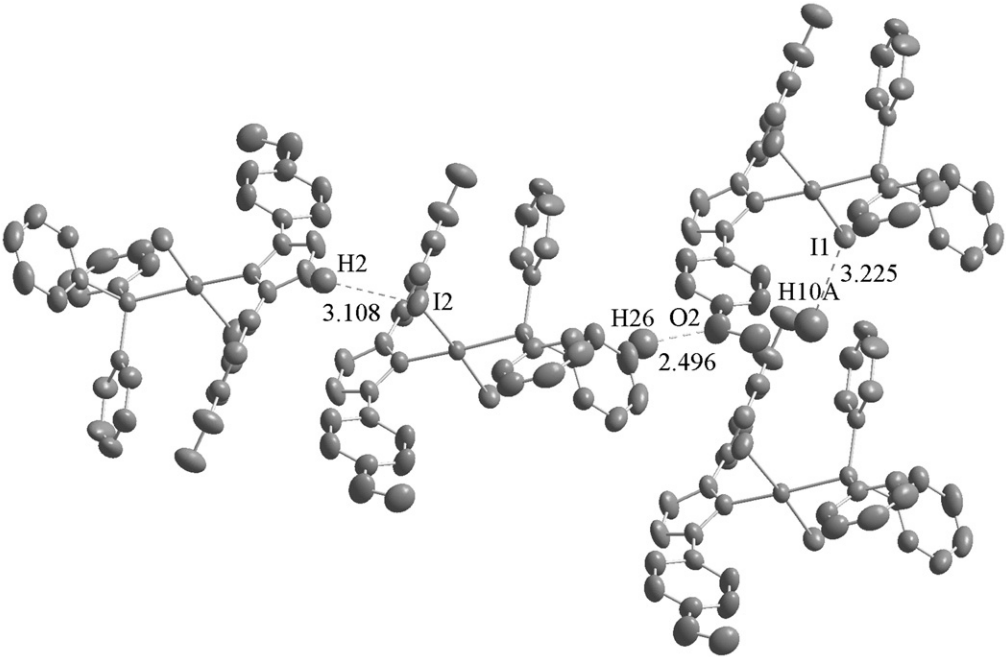


Fig. 3. The C–H···I and C–H···O hydrogen bonds of complex **1** (non-hydrogen bonding H atoms are omitted for clarity).

C–H···I (I2···H2 = 3.108 Å, 140.0° and I1···H10A = 3.225 Å, 107.0°) hydrogen bonds, and intermolecular C–H···O (O2···H26 = 3.108 Å, 142.8°) hydrogen bonds (Fig. 3). Like **1**, **2** also has intermolecular C–H···O (O1···H17B = 2.677 Å, 134.6°) hydrogen bonds, one iodine atom is involved in C–H···I hydrogen bonds to three different hydrogen atoms of three neighboring molecules (I2···H22 = 3.291 Å, 170.5°; I2···H31C = 3.201 Å, 158.9° and I2···H3 = 3.161 Å, 144.7°), while the other iodine atom does not participate in hydrogen bonding (Fig. 4).

Furthermore, we have examined the activity of complexes **1** and **2** for the Suzuki reaction. In the present study, our initial exploration of the reaction focused on the coupling of bromobenzene with phenyl boronic acid (Table 1, entries 1–2) [24]. Based on our previous experiments in palladium-catalyzed Suzuki coupling reactions [25–26], the reaction was performed under nitrogen atmosphere in dioxane in the presence of Cs_2CO_3 as base at 100 °C for 12 h. Complexes **1** and **2** exhibited high activity and produced the coupled products in 97% and 99% yields with a catalyst loading of 0.5 mol%. Similar to the result of bromobenzene, excellent yields (95% and 98%) were obtained in the case of electron-rich 4-bromotoluene (entries 3–4). Under these reaction conditions, complex **2** was slightly more active than complex **1**. The possible reason for the result was that $P(C_6H_4\text{-}p\text{-}Me)_3$ promoted oxidative addition of aryl halides to the Pd intermediate by making palladium more electron rich and increased the reaction rate consequently.

Then the activity of the $Pd(OAc)_2$/carbene precursor ImeoHCl catalytic system in the above reaction was investigated (Table 1, entry 5). Complexes **1**–**2** were more active than the $Pd(OAc)_2$/ImeoHCl and the $Pd/P(C_6H_4\text{-}p\text{-}Me)_3$ complexes [27]. Reaction of *ortho*-substituent 2-bromotoluene also gave high yield by using 0.5 mol% of **2** (96%, entry 6). For electron-deficient aryl bromides

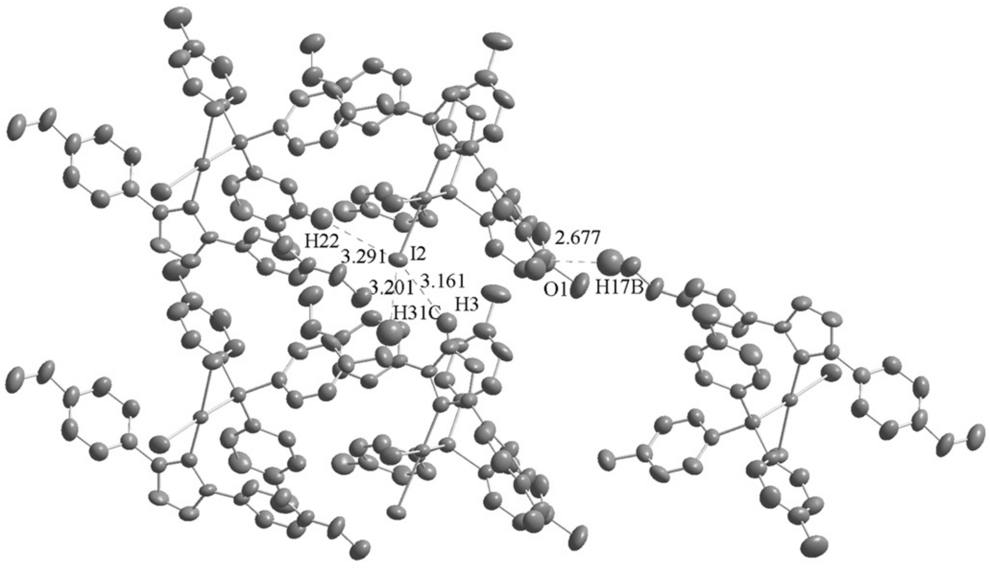
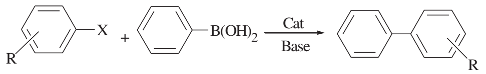


Fig. 4. The C–H···I and C–H···O hydrogen bonds of complex **2** (non-hydrogen bonding H atoms and Me_2CO are omitted for clarity).

Table 1
Suzuki coupling of aryl halides with phenyl boronic acid catalyzed by complexes **1** and **2**[a].



Entry	X	R	Catalyst (mol% Pd)	Yield[b] (%)
1	Br	H	**1** (0.5)	97
2	Br	H	**2** (0.5)	99
3	Br	*p*-CH_3	**1** (0.5)	95
4	Br	*p*-CH_3	**2** (0.5)	98
5	Br	*p*-CH_3	$Pd(OAc)_2$/ImeoHCl (1/2)	87
6	Br	*o*-CH_3	**2** (0.5)	96
7	Br	*p*-COMe	**2** (0.1)	98
8	Br	*p*-NO_2	**2** (0.1)	99
9	Br	*p*-NO_2	**2** (0.05)	99
10	Cl	H	**2** (0.5)	13
11	Cl	H	**2** (2.0)	32
12	Cl	*p*-NO_2	**2** (1.0)	86

[a] Reaction conditions: aryl halides (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), Cs_2CO_3 (0.75 mmol), dioxane (5 mL), 100 °C, 12 h.
[b] Isolated yields.

such as 4-bromoacetophenone and 4-bromonitrobenzene, they could be coupled very efficiently with a catalytic loading as low as 0.1 mol% (entries 7–8). The catalytic loadings could be lowered to 0.05 mol% without loss of activity (entry 9). We next investigated Suzuki coupling of chlorobenzene under the same reaction conditions. However, complex **2** was almost inactive under the above reaction conditions (entry 10). Increasing catalyst loading to 2 mol% only gave 32% yield (entry 11). For activated chlorides such as 4-chloronitrobenzene, the yield of the coupled product could reach 86% by using 1 mol% of **2** (entry 12).

In conclusion, two new *trans*/*cis* *N*-heterocyclic carbene–phosphine palladium(II) complexes have been prepared from the reaction of the corresponding NHC dimers with phosphine ligands. Single-crystal X-ray analysis confirms that there are intermolecular C–H···I and C–H···O hydrogen bonds in the crystals of **1**–**2**. These complexes are efficient catalysts for the Suzuki reaction of aryl bromides.

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Appendix A. Supplementary material

CCDC 841990–841991 contain the supplementary crystallographic data for **1**–**2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.12.009.

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[19] Characterization data for **1**: m.p. = 255–257 °C. Found (calcd) % for $C_{35}H_{31}I_2N_2O_2PPd$: C, 46.82 (46.56); H, 3.18 (3.46); N 3.35 (3.10). IR (KBr, cm^{-1}): 2925, 1611, 1509, 1432, 1314, 1284, 1247, 1167, 1092, 1023, 831, 746, 728, 692, 679. ESI-MS $(M-I)^+$ *m/z*: 775; ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.91 (d, 4H, Ar–H), 7.42 (m, 6H, Ar–H), 7.26–7.34 (m, 11H, Ar–H), 7.05 (d, 4H, Ar–H), 3.92 (s, 6H, $-OCH_3$).
[20] Characterization data for **2**: m.p. 202–203 °C. Found (calcd) % for $C_{38}H_{37}I_2N_2O_2$-PPd: C, 48.63 (48.30); H, 3.67 (3.95); N 3.21 (2.96). IR (KBr, cm^{-1}): 2922, 1609, 1511, 1442, 1246, 1118, 1174, 1095, 1023, 835, 807, 728, 709, 682. ESI-MS $(M-I)^+$ *m/z*: 818; ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.93 (d, 4H, Ar–H), 7.26–7.31 (m, 8H, Ar–H), 7.06 (m, 10H, Ar–H), 3.93 (s, 6H, $-OCH_3$), 2.33 (s, 9H, $-CH_3$).
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