Synthesis, structural characterization, and catalytic behaviour in Heck coupling of palladium(II) complexes containing pyrimidine-functionalized N-heterocyclic carbenes†

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Received 24th January 2008, Accepted 2nd May 2008
First published as an Advance Article on the web 19th June 2008
DOI: 10.1039/b801264d

$[Pd(L1)_2(CH_3CN)](PF_6)_2$ (L1 = 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene, **3**) and $[Pd(L2)_2](PF_6)_2$ (L2 = 1-(2-picolyl)-3-(2-pyrimidyl)imidazolylidene **4**), prepared *via* carbene transfer reactions of $[Ag(L1)_2]PF_6$ (**1**) and $[Ag_2(L2)_2](PF_6)_2$ (**2**) with palladium salts, respectively, have been fully characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The X-ray crystal structures of complexes **1–4** are reported. Complex **3** is an unusual pentacoordinated palladium complex, in which the palladium is coordinated by two imidazolylidene, two pyridine, and one acetonitrile molecule in a square-pyramidal geometry. The apical position is occupied by a pyrimidine nitrogen atom with a relatively long Pd–N distance (2.762(6) Å). Complex **4** is a typical square-planar palladium complex with palladium surrounded by two pairs of *cis*-arranged pyridine and imidazolylidene ligands. The complexes exhibit good catalytic activities in the Heck coupling reaction of aryl bromides and activated aryl chlorides under mild conditions.

Introduction

The palladium-catalyzed Heck coupling reaction of aryl halides and olefins has proven to be a powerful method for the preparation of aryl substituted olefins.[1] Although Heck reactions catalyzed by palladium–phosphine systems have achieved great success over the last decade, in some cases the phosphine ligands are not easily available, air-sensitive and quite expensive.[2] These disadvantages of such catalysts set limits to the wide application in practical synthetic processes. The development of catalyst systems with non-phosphine ligands[3] or ligandless catalysts[4] is of practical interest and thus has been receiving great attention.

Heck coupling reactions often require high temperature (normally 110–180 °C) to proceed, even with activated aryl bromides.[1,2] Only a few catalyst systems can catalyze Heck–Mizoroki reactions at a temperature below 100 °C.[3a,5] The high thermal stability of transition metal complexes of N-heterocyclic carbenes (NHCs) makes these complexes particularly suitable for Heck coupling reactions.[6] The strong σ-donating character of NHCs has proven to be responsible for the stability and enhanced catalytic activity of metal–NHC complexes.[6,7] The air and moisture stability of such complexes provides more convenience in handling especially for industrial application. The first application of Pd–NHC complexes for the Heck reaction of aryl bromides and activated aryl chlorides was reported by Herrmann *et al.* in 1995.[8] Since then, a number of monodentate and bidentate NHC ligands have been shown to have good activity in Pd-catalyzed Heck reactions.[9]

Previous reports demonstrate that variation of the N-substituents of NHCs has a limited effect on the electronic density of the carbenic carbon atom.[10] However, variation of the substituents offers an avenue for tuning the catalytic activity of metal–NHC complexes by altering the steric bulk of the NHCs.[1b,6] Provided that one or two heteroaryls is incorporated at the N-positions, the situation would be changed since such hemilable ligands may exert electronic influence on the metal through coordination. The labile character of the heteroaryl group ensures the ease of creation of an unsaturated coordination site and stabilization of the catalytically active species after reductive elimination in the catalytic cycle. The employment of hemilable bidentate NHC ligands would also be a good choice for the stabilization of the *in situ* generated active species.[11] As an extension of our studies on the chemistry of heteroaryl functionalized NHC ligands,[12] herein we describe the synthesis and structural characterization of palladium complexes of pyrimidine functionalized NHC ligands, $[Pd(L1)_2(CH_3CN)](PF_6)_2$ (L1 = 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene, **3**) and $[Pd(L2)_2](PF_6)_2$ (L2 = 1-(2-picolyl)-3-(2-pyrimidyl)imidazolylidene **4**), which were prepared *via* carbene transfer reactions with $[Ag(L1)_2]PF_6$ (**1**) and $[Ag_2(L2)_2](PF_6)_2$ (**2**), respectively. Both palladium complexes are efficient catalysts for the Heck coupling reaction of aryl bromides and activated aryl chlorides.

Results and discussion

The two imidazolium salts, $[HL1]PF_6$ and $[HL2]PF_6$, could be easily prepared from the reactions of 2-chloropyrimidine and N-*n*-butylimidazole and *N*-picolylimidazole in refluxing toluene, and subsequent treatment of the resultant imidazolium chlorides with NH_4PF_6. They are isolated as colorless solids. As shown in Scheme 1, deprontonation of the imidazolium salts with Ag_2O in acetonitrile at room temperature yielded $[Ag(L1)_2]PF_6$

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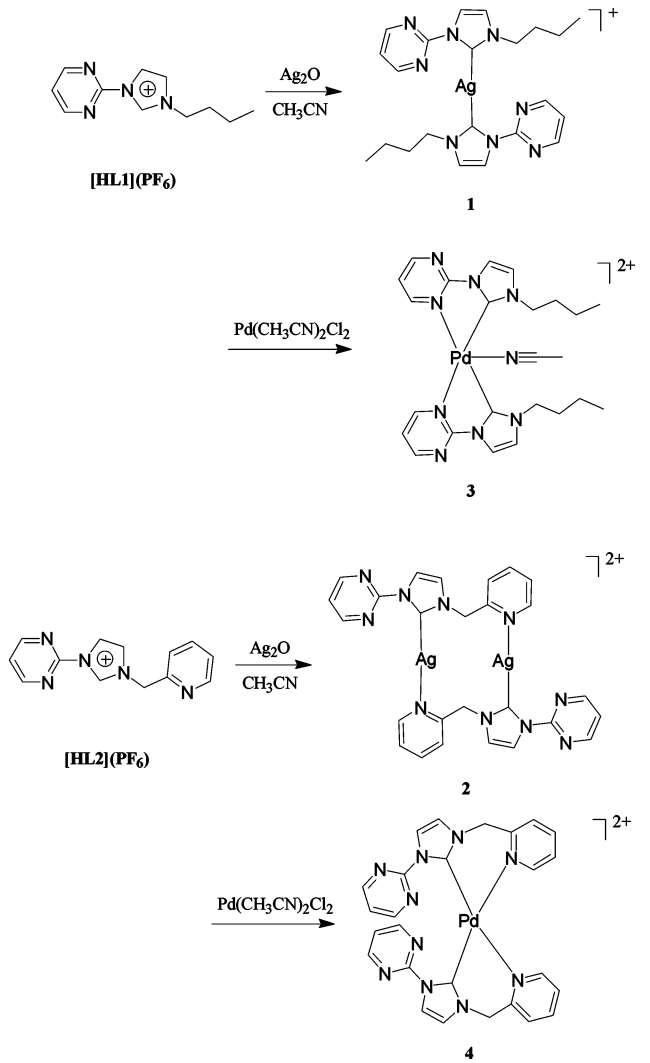
† CCDC reference numbers 675961–675964 for **1–4**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b801264d



Scheme 1

(**1**) and $[Ag_2(L2)_2](PF_6)_2$ (**2**), respectively. Palladium complexes, $[Pd(L1)_2(CH_3CN)](PF_6)_2$ (**3**) and $[Pd(L2)_2](PF_6)_2$ (**4**), were obtained from the carbene transfer reactions of the silver–NHC complexes and $Pd(CH_3CN)_2Cl_2$. These complexes have been characterized by NMR spectroscopy and elemental analyses. The formation of the Ag– and Pd–NHC complexes was confirmed by the absence of the ^{1}H NMR resonance for the acidic NCHN protons at 10.2 ppm, where the resonance signals of $[HL1]PF_6$ and $[HL2]PF_6$ were found. In the ^{13}C NMR spectra of the silver complexes, the resonances ascribed to the carbenic carbon atoms appeared at 182.5 and 180.2 ppm, respectively, which fall in the range of ^{13}C chemical shifts for Ag–C complexes.[13] For the two palladium complexes, the resonance signals assignable to the carbenic carbons were observed at 171.5 and 159.7 ppm for **3** and **4**, respectively. The ^{13}C chemical shifts of known Pd–NHC complexes appear in the range of 182.4–149.5 ppm depending upon the ancillary ligands,[14]

Although the pentacoordinate complex contains two inequivalent 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene ligands in its solid state (see Fig. 3), its ^{1}H and ^{13}C NMR spectra show only one set of resonance signals assigned to the ligand. This result indicates that the complex in solution may lose one molecule of acetonitrile and form a normal square-planar complex similar to **4**.

Complexes **1–4** have been further characterized by X-ray diffraction analysis. As shown in Fig. 1, complex **1** is mononuclear. The central silver is bicoordinated by two imidazolylidenes in a linear fashion. The Ag–C bond distances are normal for $Ag(NHC)_2$ species.[13] The two imidazolylidene rings coordinated to the same silver atom are nearly coplanar as evidenced by the small dihedral angle of 4.12°. The two pyrimidine rings are also approximately coplanar with their attached imidazolylidene rings with the dihedral angles of 9.59 and 4.53°, respectively. Another structural feature of the compound is that the two *n*-butyl groups directed towards the same side of the coordination plane. Usually the two imidazolylidene rings of silver complexes having linear $Ag(NHC)_2$ conformation are bisected.[13] These structural characteristics of the complex allow close approach of two molecules (Fig 1b). The intermolecular Ag · · · Ag and Ag · · · C (imidazolylidene) distances

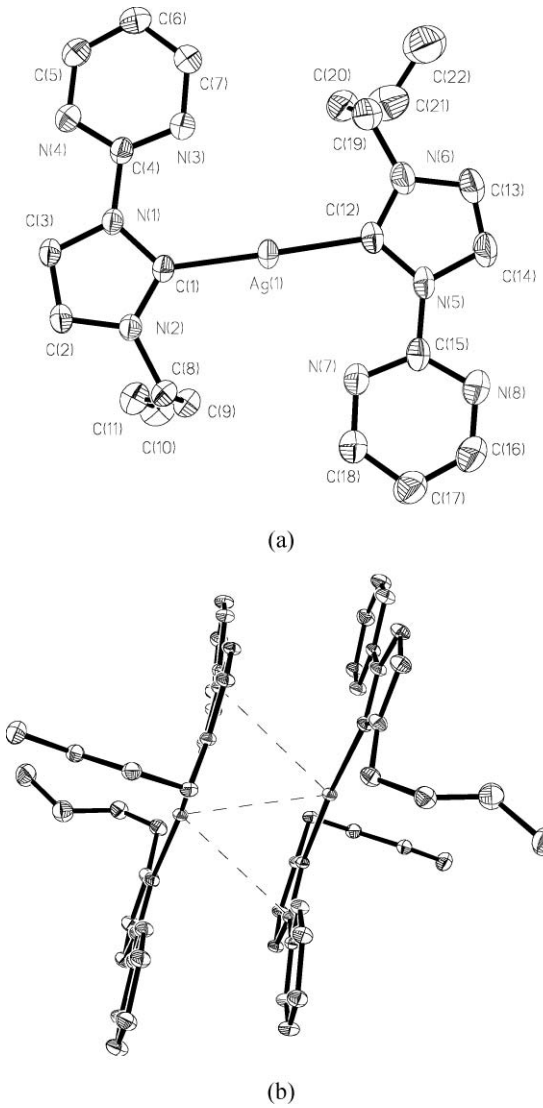


Fig. 1 Perspective view of (a) the molecular structure of $[Ag(L1)_2]^{2+}$. Thermal ellipsoids are drawn at 30% probability level. (b) The weak intermolecular Ag–π and Ag–Ag interaction. Selected bond distances [Å] and angles [°]: Ag(1)–C(1) 2.097(3), Ag(1)–C(12) 2.104(4), C(1)–Ag(1)–C(12) 175.77(13).

are 3.275 Å and 3.509 Å, indicating somewhat weak Ag–π and Ag–Ag interactions. Both intermolecular and intramolecular Ag–Ag contacts are often observed for silver–NHC complexes.[15] The Ag–π interaction is also seen in a pyrazole-functionalized NHC silver complex.[16]

The molecular structure of **2** is shown in Fig. 2. Two silver atoms are bound together by two 1-(2-picolyl)-3-(2-pyrimidyl)imidazolylidene ligands forming a metallacyle. Similar to **1**, the pyrimidine groups are not coordinated, and thus 1-(2-picolyl)-3-(2-pyrimidyl)imidazolylidene acts as a bidentate ligand rather than as the expected tridentate pincer ligand. Each silver ion is bicoordinated by a pyridine and a imidazolylidene group. The Ag–C and Ag–N bond distances are consistent with those of silver complexes having C–Ag–N moieties. The silver atoms are closely contacted with a Ag(1)–Ag(2) distance of 3.131(1) Å, which shows a very weak Ag–Ag interaction. Similar disilver complexes containing bis(NHC) ligands have been reported previously.[17]

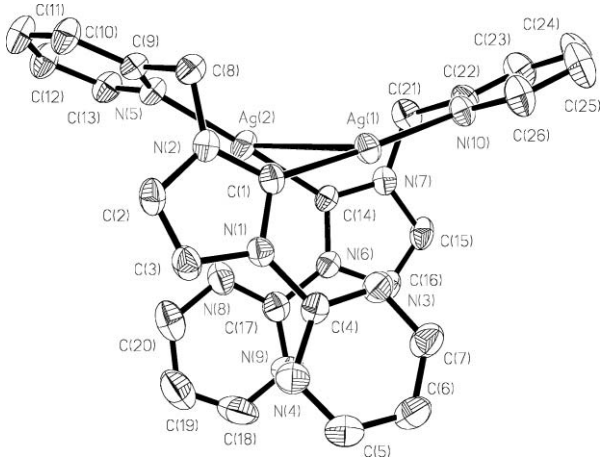


Fig. 2 Perspective view of the molecular structure of $[Ag_2(L2)_2]^{2+}$. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances [Å] and angles [°]: Ag(1)–Ag(2) 3.131(1), Ag(1)–C(1) 2.108(6), Ag(1)–N(10) 2.187(5), Ag(2)–C(14) 2.100(6), Ag(2)–N(5) 2.149(5), C(1)–Ag(1)–N(10) 175.2(2), C(14)–Ag(2)–N(5) 178.0(2).

Complex **3** is an unusual pentacoordinated palladium complex, in which the palladium is surrounded by two imidazolylidene, two pyridine, and one acetonitrile molecule in a square-pyramidal geometry. The structure of **3** is shown in Fig. 3. Both two 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene ligands are coordinated in bidentate fashion. The square plane is formed by atoms C(1) and N(1) of one 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene molecule, the C(12) atom of the second 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene ligand, and the N(8) atom of the acetonitrile molecule; the apical position is occupied by atom N(4) of the second 1-*n*-butyl-3-(2-pyrimidyl)imidazolylidene ligand. The Pd–C and Pd–N(equatorial) bond distances do not show distinct differences from the known typical Pd–NHC complexes.[13] The crystal structure indicates a long range interaction (2.762(6) Å) between the planar palladium and the apical nitrogen atom. The presence of the five-coordinate species is suggested assuming a weak apical Pd–N interaction on the basis of Pd–N bond distances in the range 2.576(4)–2.805(5) Å.[18–20]

The coordination and organometallic compounds of Pd(II) tend to adopt square-planar coordination geometry. Pentacoordinate

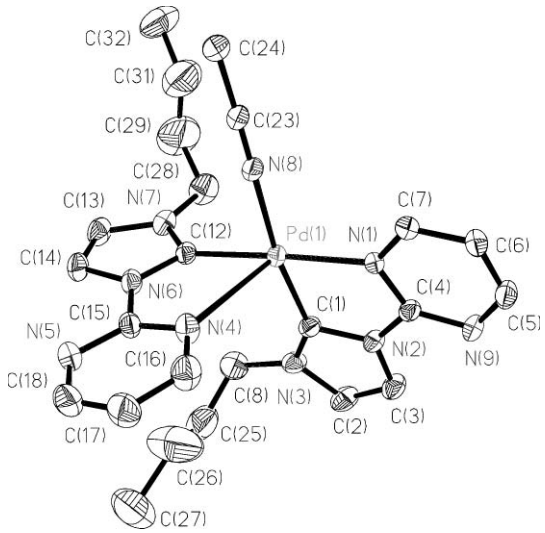


Fig. 3 Perspective view of the molecular structure of $[Pd(L1)_2(CH_3CN)]^{2+}$. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances [Å] and angles [°]: Pd(1)–C(1) 1.987(7), Pd(1)–C(12) 1.987(7), Pd(1)–N(8) 2.051(6), Pd(1)–N(1) 2.074(5), Pd(1)–N(4) 2.762(6), C(1)–Pd(1)–C(12) 98.0(3), C(1)–Pd(1)–N(8) 171.0(3), C(12)–Pd(1)–N(8) 87.1(2), C(1)–Pd(1)–N(1) 80.6(3), C(12)–Pd(1)–N(1) 177.6(2), N(8)–Pd(1)–N(1) 94.6(2), C(1)–Pd(1)–N(4) 100.3(2), C(12)–Pd(1)–N(4) 69.5(2), N(8)–Pd(1)–N(4) 88.5(2), N(1)–Pd(1)-N(4) 108.7(2).

Pd(II) complexes are uncommon. A few such complexes with distorted trigonal bipyramidal or square pyramidal environments supported by phenanthroline[19] or polyphosphine[20] ligands are known. The Pd(II) complexes of N-heterocyclic carbenes are usually tetracoordinated displaying square-planar geometry.[13,21] Complex **3** represents the first example of pentacoordinated palladium(II) complex containing NHC ligands.

Complex **4** is a typical square-planar palladium complex with palladium surrounded by two pyridine and two imidazolylidene ligands. A structural drawing of the cation is provided in Fig. 4.

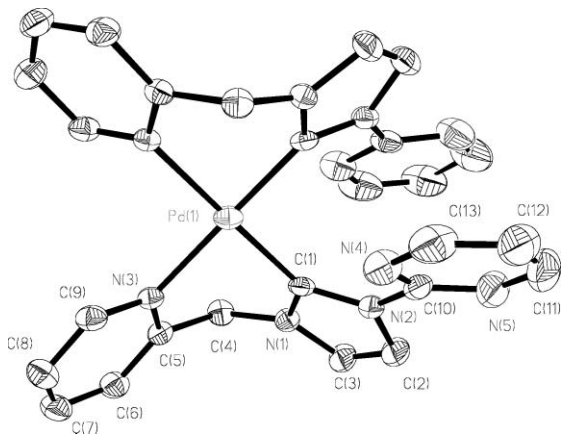
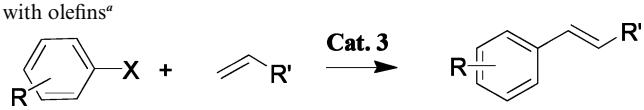


Fig. 4 Perspective view of the molecular structure of $[Pd(L2)_2]^{2+}$. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances [Å] and angles [°]: Pd(1)–C(1) 1.963(6), Pd(1)–N(3) 2.088(5), C(1)#1–Pd(1)–C(1) 92.7(4), C(1)–Pd(1)–N(3)#1 179.2(2), C(1)–Pd(1)–N(3) 86.5(2), N(3)#1–Pd(1)–N(3) 94.3(3). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 3/2$.

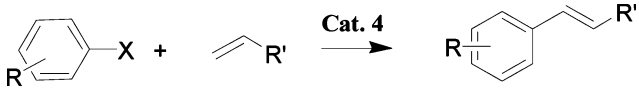
Table 1 Heck coupling of aryl halides with olefins[a]



Entry	Aryl halide	Olefin	Cat. **3** (mol%)	Additive	*T*/°C	Time/h	GC yield (isolated yield) (%)
1	4-Bromoacetophenone	*n*-butyl acrylate	0.01	none	120	1	100 (95)
2	4-Bromoacetophenone	*n*-butyl acrylate	0.01	none	80	6	100
3	4-Bromoacetophenone	styrene	0.01	none	120	1	100 (98)
4	4-Bromoacetophenone	styrene	0.01	none	80	6	100
5	4-Bromobenzaldehyde	*n*-butyl acrylate	0.01	none	120	1	100 (93)
6	4-Bromobenzaldehyde	*n*-butyl acrylate	0.01	none	80	6	100
7	4-Bromobenzaldehyde	styrene	0.01	none	120	1	100 (91)
8	4-Bromobenzaldehyde	styrene	0.01	none	80	6	100
9	Bromobenzene	*n*-butyl acrylate	0.01	none	120	1	64
10	Bromobenzene	*n*-butyl acrylate	0.1	none	120	6	100 (95)
11	Bromobenzene	styrene	0.1	none	120	6	100 (95)
12	4-Bromotoluene	*n*-butyl acrylate	0.1	none	120	6	17.5
13	4-Bromotoluene	*n*-butyl acrylate	1	none	120	20	58
14	4-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	120	20	90
15	4-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	100 (90)
16	4-Bromotoluene	styrene	1	*n*-Bu_4NBr	140	20	96 (90)/4[b]
17	2-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	80 (78)
18	2-Bromotoluene	styrene	1	*n*-Bu_4NBr	140	20	85 (80)
19	4-Bromoanisole	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	100 (97)
20	4-Bromoanisole	styrene	1	*n*-Bu_4NBr	140	20	90 (89)/10[b]
21	4-Chloroacetophenone	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	100
22	4-Chloroacetophenone	styrene	1	*n*-Bu_4NBr	140	20	88/12[b]

[a] Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), catalyst **3**, NaOAc (2.0 mmol), DMAc (3 mL). [b] Yield of *cis*- product.

Table 2 Heck coupling of aryl halides with olefins[a]



Entry	Aryl halide	Olefin	Cat. **4** (mol%)	Additive	*T*/°C	Time/h	Yield[b] (%)
23	4-Bromoacetophenone	*n*-butyl acrylate	0.01	none	120	2	100
24	4-Bromoacetophenone	*n*-butyl acrylate	(0.01)	none	80	20	100
25	4-Bromoacetophenone	styrene	0.01	none	120	2	100
26	4-Bromoacetophenone	styrene	0.01	none	80	20	100
27	4-Bromobenzaldehyde	*n*-butyl acrylate	0.01	none	120	2	100
28	4-Bromobenzaldehyde	*n*-butyl acrylate	0.01	none	80	20	100
29	4-Bromobenzaldehyde	styrene	0.01	none	120	2	100
30	4-Bromobenzaldehyde	styrene	0.01	none	80	20	100
31	Bromobenzene	*n*-butyl acrylate	0.01	none	120	20	36
32	Bromobenzene	*n*-butyl acrylate	1	*n*-Bu_4NBr	120	20	100
33	Bromobenzene	styrene	1	*n*-Bu_4NBr	120	20	100
34	4-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	120	20	90
35	4-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	100
36	4-Bromotoluene	styrene	1	*n*-Bu_4NBr	140	20	92/8[c]
37	2-Bromotoluene	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	69
38	2-Bromotoluene	styrene	1	*n*-Bu_4NBr	140	20	80
39	4-Bromoanisole	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	85
40	4-Bromoanisole	styrene	1	*n*-Bu_4NBr	140	20	75/11[c]
41	4-Chloroacetophenone	*n*-butyl acrylate	1	*n*-Bu_4NBr	140	20	87
42	4-Chloroacetophenone	styrene	1	*n*-Bu_4NBr	140	20	83/6[c]

[a] Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), catalyst **4**, NaOAc (2.0 mmol), DMAc (3 mL). [b] GC yield. [c] Yield of *cis*- product.

Two pyrimidine groups are not coordinated. Both the two pyridine and two imidazolylidene ligands are *cis*-positioned. The Pd–C and Pd–N distances are not unusual, and are similar to those of known palladium complexes.[14] The imidazolylidene ring and its *trans*-positioned pyridine ring are almost coplanar as indicated by the small dihedral angle of 3.35° between the two rings. The C–Pd–C angle (92.7(4)°) is slightly smaller than that of N–Pd–N (94.3(3)°) due to the geometric constraint of the ligand.

Catalytic activities for Heck coupling reaction

The palladium-catalyzed Heck coupling reaction has been widely employed for the preparation of aryl olefins. The Heck coupling

reactions of aryl bromides with *n*-butyl acrylate and styrene were examined by using **3** and **4** as the catalyst precursors. The results were summarized in Tables 1 and 2. Under the conditions often used for other palladium catalysts, *i.e.* using NaOAc as the base and dimethylacetamide (DMAc) as the solvent,[22] both **3** and **4** exhibit excellent catalytic activities for aryl bromides bearing electron-withdrawing substituents.

Generally, the Heck coupling reaction requires reaction temperatures higher than 110 °C.[1] As can be seen from Table 1, our catalysts are so active that allows the olefination reactions of activated bromides bearing acetyl or formyl groups with *n*-butyl acrylate or styrene proceed at 80 °C by using only 0.01 mol% of **3** or **4**. These reactions could be completed within 6 hours with 100% conversion (entries 2, 4, 6, and 8). Raising the reaction temperature to 120 °C, these reactions could achieve 100% conversion even within 1 hour at the same catalyst loadings (entries 1, 3, 5, and 7). The reactions of styrene and *n*-butyl acrylate did not show distinctly different reactivities (entries 1–8). The corresponding coupled products could be isolated in 91–98% yields. In the case of *n*-butyl acrylate, only the *trans* isomer was detected, whereas for the coupling reactions of styrene *cis* olefins were also observed as minor products in not more than 15% yields. For the activated bromide substrates, the palladium–NHC catalysts are even more effective than most of known palladium catalysts such as phospha-palladacycle[23] and Pd–phosphine–imidazolium salt systems.[24]

Complex **3** has also been applied to the cross coupling of electron-neutral and electron-rich bromides. As expected, the reactivities of these two bromides are comparatively lower. For instance, at 0.01 mol% catalyst loading and 120 °C the reaction only gave 64% conversion of phenyl bromide within 1 hour. To reach complete conversion, the coupling reaction requires higher catalyst loading (0.1 mol%) and long reaction time (entries 9–11). When deactivated *p*-tolyl bromide was used as the substrate, only 58% of the bromide could be coupled to the product even using 1 mol% of **3** at 120 °C within 20 hours (entry 13). To ensure the reactions go to completion, a further increase of the reaction temperature to 140 °C and addition of *n*-Bu_4NBr as an additive are needed. It has been known that addition of *n*-Bu_4NBr as a cocatalyst enhances the activity of many catalytic systems,[22d,25] and *n*-Bu_4NBr is able to activate and stabilize the *in situ* generated palladium(0) species, which is believed to be the real catalytically active species. Actually, the reaction yields could be improved by adding 20 mol% of *n*-Bu_4NBr (entries 14–16). As expected, *o*-tolyl bromide displays much lower reactivity than other bromides due to steric hindrance (entries 17 and 18). The catalyst is also efficient for the coupling of deactivated *p*-bromoanisole with *n*-butyl acrylate and styrene at the elevated temperature (140 °C, entries 19–20), and the corresponding coupling products were obtained in good yields.

Attempts had also been made to test the reactivity of aryl chlorides which are cheaper and more easily available starting materials. It is noteworthy that the catalyst works well for activated aryl chloride using 1 mol% palladium at 140 °C (21 and 22) giving quantitative yields. In the case of styrene, a *trans*- : *cis*- ratio of 88 : 12 was observed. Unfortunately, the catalyst is totally ineffective for deactivated aryl chlorides. Actually, only a few catalyst systems show good catalyst activity for the olefination of aryl chlorides.[9a,26,27]

For the coupling reactions of activated aryl bromides, complex **4** showed higher catalytic activities than similar complexes which have both chelating hemilabile ligands.[28] Without any additives, at 80 °C and 0.01 mol% catalyst loading, both styrene and *n*-butyl acrylate could be coupled in 100% conversion within 20 h (entries 24, 26, 28, and 30). Raising the temperature to 120 °C, the reaction time could be shortened to 2 hours to reach 100% conversion. Complex **4** also exhibits high activity towards various aryl bromides with moderate to excellent yields (entries 31–40) with catalyst loading of 1 mol%. The catalyst also works for activated chlorides and afforded the coupled products in good yields (entries 41 and 42). Unfortunately, the catalyst shows no catalytic activity for aryl chlorides bearing electron-donating substituents.

In summary, we have described the synthesis and structural characterization of two palladium complexes containing pyrimidine functionalized N-heterocyclic carbenes. Complex **3** has an unusual square-pyramidal structure, which represents the first example of penta-coordinated Pd–NHC complex. These palladium complexes show high catalytic activity for the Heck olefination of aryl bromides without the need of additional ligands under mild conditions. The methodology is applicable to a variety of electron-deficient aryl bromides and chlorides and electron-rich bromides. Good to excellent yields were obtained.

Experimental section

General procedures

All the chemicals were obtained from commercial suppliers and used without further purification. *N*-Picolylimidazole[29] was prepared according to the known procedure. The C, H, and N elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm and coupling constants (J) are expressed in Hz.

Synthesis

[HL1](PF$_6$). A solution of 2-chloropyrimidine (3.0 g, 26.2 mmol) in toluene (15 mL) was added to *N*-butylimidazole (3.9 g, 31.4 mmol). The mixture was refluxed overnight to yield a brown solid. The solid was filtered and washed with 10 mL of diethyl ether and dried. The solid was dissolved in 10 mL of water and slowly added to an aqueous solution of NH_4PF_6 in a 1 : 1.1 molar ratio. The mixture was stirred for 30 min at room temperature and the resulting precipitate was separated by filtration and dried under vacuum. Yield: 9.12 g, 75%. Anal. Calcd for $C_{11}H_{15}F_6N_4P$: C, 37.94; H, 4.34; N, 16.09. Found: C, 38.07; H, 4.35; N, 16.40%. ^1H NMR (400 MHz, DMSO-d_6): 10.2 (s, NCHN, 1H), 9.04 (d, *m*-$C_4H_3N_2$, $J = 5.2$, 2H), 8.48, 8.03 (both s, NCHCHN, each 1H), 7.75 (t, *p*-$C_4H_3N_2$, $J = 4.8$, 1H), 4.33 (t, $CH_2CH_2CH_2CH_3$, $J = 7.2$, 2H), 1.87 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.31 (m, $CH_2CH_2CH_2CH_3$, 2H), 0.93 (t, $CH_2CH_2CH_2CH_3$, $J = 5.6$, 3H).

[HL2](PF$_6$). The compound was prepared according to the same procedure as for [HL1](PF$_6$) starting from *N*-pyridylmethylimidazole and 2-chloropyrimidine. Yield: 72%.

Anal. Calcd for $C_{13}H_{12}F_6N_5P$: C, 40.74; H, 3.16; N, 18.27. Found: C, 40.95; H, 3.35; N, 18.40%. ^{1}H NMR (400 MHz, DMSO-d_6): 10.3 (s, NCHN, 1H), 9.06 (d, *m*-$C_4H_3N_2$, J = 4.8, 2H), 8.56 (d, *m*-C_5H_4N, J = 4.4, 1H), 8.51, 8.03 (both s, NCHCHN, each 1H), 7.9 (t, *m*-C_5H_4N, J = 7.6, 1H), 7.78 (t, *p*-$C_4H_3N_2$, J = 4.8, 1H), 7.55 (d, *o*-C_5H_4N, J = 7.2, 1H), 7.41 (t, *p*-C_5H_4N, J = 6.0, 1H), 5.73 (s, CH_2, 2H).

[Ag(L1)$_2$](PF$_6$) (1). To a slurry of Ag_2O (24 mg, 0.1 mmol) in 10 mL of CH_3CN was added [HL1](PF$_6$) (69.6 mg, 0.2 mmol). The mixture was protected from light and stirred at ambient temperature until the Ag_2O was dissolved. The solution was filtered through Celite to remove a small amount of precipitate. The clear filtrate was then evaporated to dryness. The residue was washed with diethyl ether and dried. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its CH_3CN solution. Yield: 56 mg, 85%. Anal. Calcd for $C_{22}H_{28}AgF_6N_8P$: C, 40.20; H, 4.29; N, 17.05. Found: C, 40.43; H, 4.35; N, 17.19%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.82 (d, *m*-$C_4H_3N_2$, J = 4.8, 4H), 8.29, 7.82 (both d, NCHCHN, J = 1.6, each 2H), 7.60 (t, *p*-$C_4H_3N_2$, J = 5.2, 2H), 4.30 (t, $CH_2CH_2CH_2CH_3$, J = 7.2, 4H), 1.87 (m, $CH_2CH_2CH_2CH_3$, 4H), 1.29 (m, $CH_2CH_2CH_2CH_3$, 4H), 0.87 (t, $CH_2CH_2CH_2CH_3$, J = 7.2, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 182.5 (Ag–*C*), 159.7, 155.5, 123.7, 121.5, 119.9, 118.4, 52.3, 32.9, 19.4, 13.7, 1.4.

[Ag$_2$(L2)$_2$](PF$_6$)$_2$·CH$_3$CN (2). The compound was prepared according to the same procedure as for **1** starting from [HL2](PF$_6$) and Ag_2O. Yield: 72%. Anal. Calcd for $C_{28}H_{25}Ag_2F_{12}N_{11}P_2$: C, 32.93; H, 2.47; N, 15.09. Found: C, 32.95; H, 2.63; N, 15.24%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.68 (d, *m*-$C_4H_3N_2$, J = 4.4, 4H), 8.61 (d, *m*-C_5H_4N, J = 4.0, 2H), 8.28, 7.80 (both d, NCHCHN, J = 1.6, each 2H), 7.97 (t, *m*-C_5H_4N, J = 7.6, 2H), 7.64 (d, *o*-C_5H_4N, J = 7.6, 2H), 7.53 (t, *p*-$C_4H_3N_2$, J = 4.8, 2H), 7.47 (t, *p*-C_5H_4N, J = 6.0, 2H), 5.70 (s, CH_2, 4H), 2.07 (s, CH_3CN, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): 180.2 (Ag–*C*), 159.5, 154.7, 154.3, 152.1, 140.4, 126.3, 125.4, 124.1, 121.4, 121.2, 118.4, 57.8, 1.4.

[Pd(L1)$_2$(CH$_3$CN)](PF$_6$)$_2$ (3). A sample of Pd(CH$_3$CN)$_2$Cl$_2$ (52 mg, 0.2 mmol) was added to acetonitrile (10 mL) and silver carbene **1** (137 mg, 0.2 mmol) was added. The solution was stirred for 10 h at ambient temperature. The reaction mixture was filtered through Celite and the filtrate was concentrated to 5 mL. Addition of 20 mL diethyl ether gave a pale yellow solid. Yield: 125 mg, 74%. Anal. Calcd for $C_{24}H_{31}F_{12}N_9P_2Pd$: C, 34.24; H, 3.71; N, 14.97. Found: C, 34.43; H, 3.90; N, 15.13%. ^{1}H NMR (400 MHz, DMSO-d_6): 9.09 (d, *m*-$C_4H_3N_2$, J = 4.2, 4H), 8.44, 7.91 (both d, NCHCHN, J = 2.0, each 2H), 7.81 (t, *p*-$C_4H_3N_2$, J = 4.8, 2H), 3.99, 3.59 (both d, $CH_2CH_2CH_2CH_3$, each 2H), 2.07 (s, CH_3CN, 3H), 1.59, 1.39 (both m, $CH_2CH_2CH_2CH_3$, each 2H), 1.11 (m, $CH_2CH_2CH_2CH_3$, 4H), 0.77 (t, $CH_2CH_2CH_2CH_3$, J = 7.2, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 171.5 (Pd–C), 160.0, 155.2, 154.6, 125.3, 121.6, 120.7, 51.4, 32.6, 19.5, 13.8, 1.5.

[Pd(L2)$_2$](PF$_6$)$_2$·CH$_3$CN (4). The compound was prepared according to the same procedure as for **3** starting from silver carbene **2** and Pd(CH$_3$CN)$_2$Cl$_2$. Yield: 68%. Anal. Calcd for $C_{28}H_{25}F_{12}N_{11}P_2Pd$: C, 36.88; H, 2.76; N, 16.90. Found: C, 37.01; H, 2.77; N, 17.34%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.83 (d, *m*-$C_4H_3N_2$, J = 4.8, 2H), 8.50 (d, *m*-C_5H_4N, J = 5.6, 1H), 8.28 (t, *m*-C_5H_4N, J = 7.6, 1H), 8.05 (d, *o*-C_5H_4N, J = 7.6, 1H), 7.69, 7.64 (both d, NCHCHN, J = 1.6, each 1H), 7.67 (t, *p*-C_5H_4N, J = 6.0, 1H), 7.54 (t, *p*-$C_4H_3N_2$, J = 4.8, 1H), 6.21, 5.97 (both d, CH_2, J = 14.8, each 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 159.7 (Pd–C), 159.3, 154.2, 153.6, 153.1, 142.1, 126.6, 126.4, 124.1, 121.4, 121.1, 118.5, 55.7, 1.5.

X-Ray structural determination

Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a MoKα radiation (λ = 0.71073 Å) by using an ω–2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the *SMART* and *SAINT* software.[30] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F_2 using *SHELXTXL* package.[31] Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and U_{iso}(H) = −1.2–1.5U_{eq}(C). Further details of the structural analyses are summarized in Table 3.

Table 3 Summary of X-ray crystallographic data for complexes **1–4**

	1	**2**	**3**	**4**
Formula	$C_{22}H_{28}AgF_6N_8P$	$C_{28}H_{25}Ag_2F_{12}N_{11}P_2$	$C_{24}H_{31}F_{12}N_9P_2Pd$	$C_{30}H_{28}F_{12}N_{12}P_2Pd$
M	657.36	1021.27	841.94	952.98
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$C2/c$
a/Å	11.3286(2)	14.645(2)	9.467(1)	20.944(2)
b/Å	19.3969(4)	18.615(2)	24.486(2)	12.853(1)
c/Å	25.0274(5)	15.032(2)	14.774(2)	14.223(2)
β/deg	101.8260(10)	112.860(2)	101.008(2)	96.152(2)
V/Å^3	5382.78(18)	3776.0(9)	3361.7(6)	3806.7(7)
Z	8	4	4	4
D_{calc}/Mg m^{-3}	1.622	1.796	1.664	1.663
Reflections collected	30316	18562	16800	9235
Reflections unique, R_{int}	4752, 0.0180	6660, 0.0326	5928, 0.0359	3352, 0.0453
Goodness-of-fit on F^2	1.073	1.066	1.085	1.135
R ($I > 2\sigma I$)	0.0375, 0.1070	0.0433, 0.1024	0.0615, 0.1547	0.0615, 0.1809
R (all data)	0.0414, 0.1126	0.0786, 0.1302	0.0895, 0.1787	0.0884, 0.2169

General procedure for the Heck reactions

A Schlenk tube was charged with aryl halide (1.0 mmol), olefin (1.5 mmol), NaOAc (2.0 mmol), an appropriate amount of Pd catalyst with or without 20 mol% of *n*-Bu_4NBr, and DMAc (3 mL). The solution was stirred at an appropriate temperature under nitrogen. After several hours, the mixture was then allowed to cool to room temperature and added to 20 mL of water. The product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using petroleum ether as eluent to give the desired product. The detailed reaction conditions were given in Table 1.

Acknowledgements

We are grateful to the support of the NSF of China (20572096), NSF of Zhejiang Province (R405066) and Qianjiang Project (2007R10006) for financial support.

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