N-Heterocyclic Carbene–Acetylamide Palladium Complexes and Their Catalytic Activities in Heck–Mizoroki Reactions

Tao Zhang,[a] Sijia Liu,[a] Min Shi,*[a,b] Meixin Zhao[a]

[a] Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. of China
Fax +86(21)64166128; E-mail: mshi@mail.sioc.ac.cn

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. of China

Received 7 March 2008

Abstract: A novel N-heterocyclic carbene-acetylamide ligand derived from binaphthyl-2,2′-diamine (BINAM) and its dinuclear NHC–Pd(II) complex as well as its corresponding complex bearing weakly coordinating acetate counterions, have been successfully synthesized in good yields. The dinuclear NHC–Pd(II) complex has been characterized by X-ray diffraction. Moreover, we found that these complexes are quite effective in Heck–Mizoroki reactions and give the corresponding products in good to excellent yields.

Key words: N-heterocyclic carbene-acetylamide, dinuclear NHC–Pd(II) complex, binaphthyl-2,2′-diamine, Heck–Mizoroki reaction

N-Heterocyclic carbenes (NHCs)[1] represent a growing class of ligand. Due to their stability to air and moisture and their strong σ-donor and poor π-acceptor properties, they can replace phosphine ligands in transition-metal catalysis to provide more effective metal complexes.[2] Significantly, NHC–Pd complexes have emerged as effective catalysts for a variety of coupling reactions,[3] such as the coupling of aryl halides with amines and amides (Buchwald–Hartwig amination),[4a–4c] alkenes (Heck–Mizoroki reaction),[4d] alkynes (Sonogashira reaction),[4e] organomagnesium (Kumada reaction),[4f] organosilicon (Stille reaction),[4g] organoboron (Suzuki reaction),[4h,i] and organostannane reagents.[4j] Furthermore, recent studies have revealed that NHC–Pd(II) complexes bearing weakly coordinating counterions such as acetates, are highly efficient catalysts for C–H activation,[5a] aerobic oxidation of alcohols,[5b,c] hydroarylation of alkynes,[5d] Suzuki coupling[5e–g] and Michael addition reactions.[6] Previously, we reported the synthesis of a novel bis(NHC) ligand based on binaphthyl-2,2′-diamine (BINAM) and its *cis*-chelated bis(NHC)–palladium complex.[7] In addition, we also synthesized a NHC-acetylamide ligand **A** from *trans*-cyclohexane-1,2-diamine and its NHC–palladium complex[8] (Figure 1a). Interestingly, the NHC-acetylamide ligand only coordinates to the metal center through NHC to form a dimeric mono-coordinated NHC–Pd(II) complex. More recently, we also reported two NHC-sulfonamide ligands **B** and **C**, derived from BINAM and their tridentate NHC–Pd(II) complexes as well as the corresponding complexes bearing weakly coordinating acetate counterions in Suzuki coupling reactions[9] (Figure 1b). In this paper, we wish to report the synthesis and characterization of a novel NHC-acetylamide ligand **D**, derived from BINAM and its dinuclear palladium(II) complex, and the corresponding dinuclear NHC–Pd(II) complex bearing weakly coordinating acetate counterions. We also report on their catalytic abilities in the Heck–Mizoroki reaction (Figure 1).

The synthesis of benzimidazolium salt **5** is shown in Scheme 1. Using compound **1**[9] as the starting material to react with acetic anhydride in the presence of acetic acid produced the corresponding product **2** in 89% yield at room temperature (20 °C) in dichloromethane. Reduction

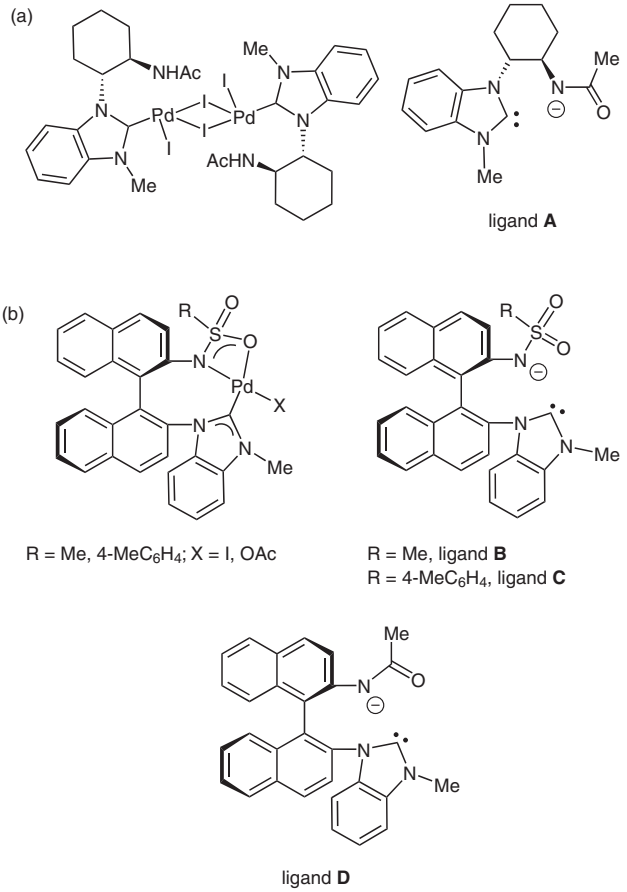
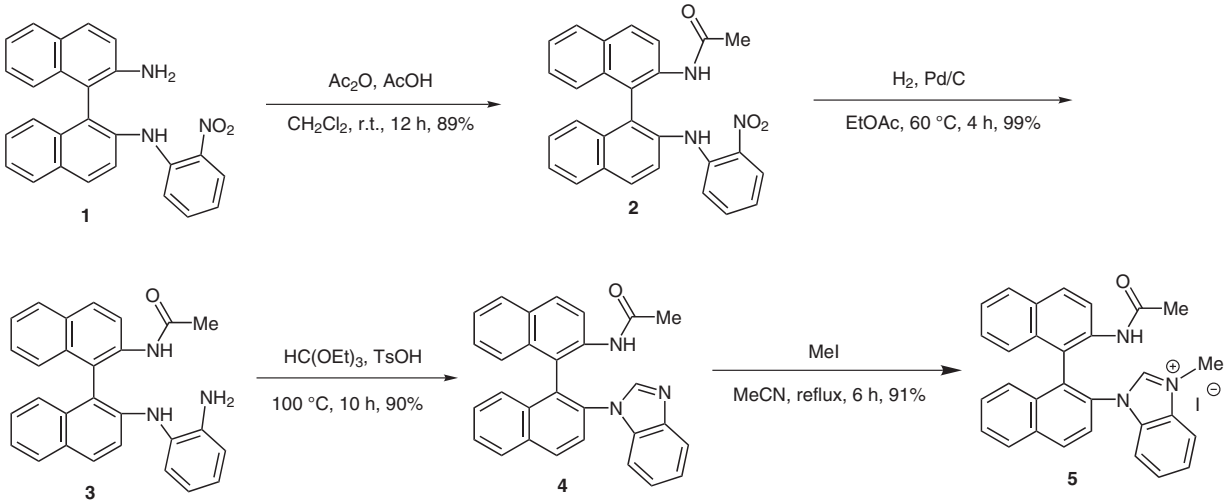


Figure 1 Structure of NHC–Pd(II) complexes and NHC-acetylamide ligand derived from BINAM

SYNTHESIS 2008, No. 17, pp 2819–2824
Advanced online publication: 24.07.2008
DOI: 10.1055/s-2008-1067199; Art ID: C02908SS



Scheme 1 Synthesis of benzimidazolium salt **5**

of **2** by means of Pd/C–H_2 gave compound **3** in 99% yield within four hours. Subsequent cyclization with triethyl orthoformate catalyzed by *p*-toluenesulfonic acid at 100 °C, afforded product **4** in 90% yield after ten hours. The alkylation of the benzimidazole ring of **4** by methyl iodide under reflux for six hours then gave the corresponding benzimidazolium salt **5** in 91% yield.

During the initial examination, we found that when benzimidazolium salt **5** was treated with $Pd(OAc)_2$ at 90 °C in dimethylsulfoxide for two hours in the presence of sodium iodide,[8] guanidine **6** was produced in 36% isolated yield rather than the corresponding NHC–palladium complex (Scheme 2). The structure of guanidine **6** was determined by X-ray diffraction (Figure 2).[10] Attempts to prepare the corresponding NHC–Pd(II) complex by treating benzimidazolium salt **5** with palladium(II) acetate in tetrahydrofuran under reflux[7] were also unsuccessful and **6** was only isolated in very low yield (<10%) in these transformations.

Although the exact mechanism for the formation of guanidine **6** is not known, we assumed that during the formation of the corresponding NHC–palladium(II) complex upon heating, acetic acid was released, which may react with the NHC–palladium(II) complex to form compound **6**. After several examinations, it was found that in the presence of cesium carbonate, the corresponding dinuclear NHC–Pd(II) complex **7** was smoothly produced in 77% yield by treatment of benzimidazolium salt **5** with palladium(II) acetate at room temperature in tetrahydrofuran for 20 hours. Upon treatment of dinuclear NHC–Pd(II) complex **7** with silver acetate in acetonitrile–dichloromethane (1:2) at room temperature for three hours, the corresponding dinuclear NHC–Pd(II) complex **8** bearing weakly coordinating acetate counterions was obtained in 82% yield (Scheme 3). These NHC–Pd(II) complexes were air- and moisture-stable in the solid state and even in the solution state. Their structures were determined by microanalysis, IR and NMR spectroscopic data as well as ESI-MS spectroscopy.

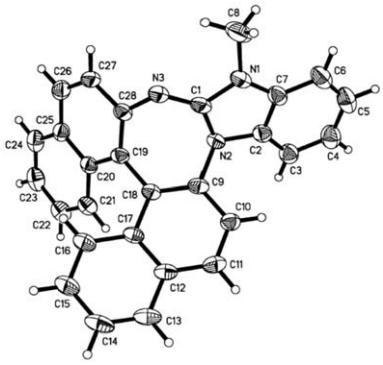
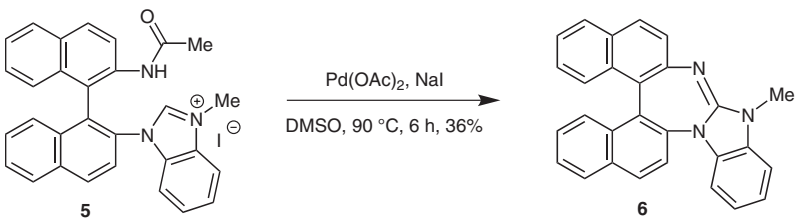
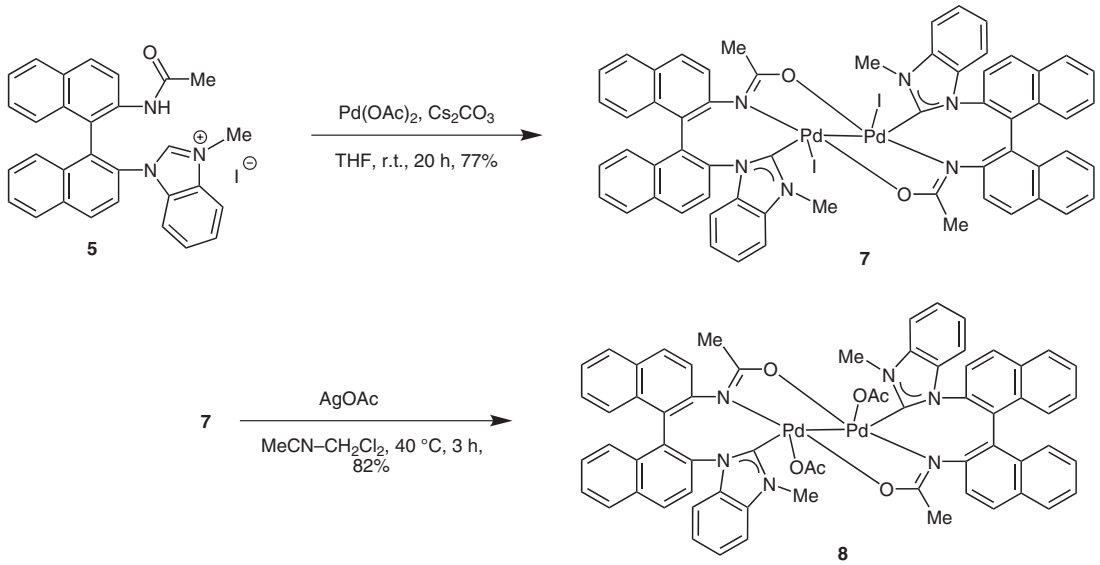


Figure 2 X-ray crystal structure of compound **6**

The crystal structure of **7** was also unambiguously determined by X-ray diffraction.[11] Single crystals of this dinuclear palladium complex suitable for X-ray crystal structure analysis were grown from a petroleum ether–dichloromethane (2:3) mixture. Figure 3 depicts the X-ray crystal structure of dinuclear NHC–Pd(II) complex **7**, which reveals a distorted square-planar geometry around



Scheme 2 Synthesis of compound **6**



Scheme 3 Synthesis of Pd–NHC complexes **7** and **8**

the two metal centers. One of the NHC-acetylamide anion ligands chelates with one palladium center through the NHC and a nitrogen atom in the acetylamide; this palladium was also coordinated by the oxygen atom of a second acetylamide anion ligand and an iodide anion, stabilizing a 16-electron configuration around the metal center. Compared to the Pd–Pd distance [3.126(3) Å] in the NHC–Pd(II) complex **7** as well as to the rather underestimated sum of van der Waals radii (3.26 Å), we believe that metallophilic interaction may exist in the NHC–Pd(II) complex because the Pd–Pd distance seen here is closer to the upper van der Waals limit.[12] The bond lengths of Pd(1)–C(1) and Pd(2)–C(31) are 1.879(17) and 1.91(2) Å, respectively. The C(29)–O(1) bond length [1.19(2) Å] is longer than that of typical C=O double bond lengths, suggesting partial π-conjugation between O(1), C(29) and N(3) [N(3)–C(29) bond length: 1.39(3) Å]. Partial π-conjugation also exists between O(2), C(59) and N(6).

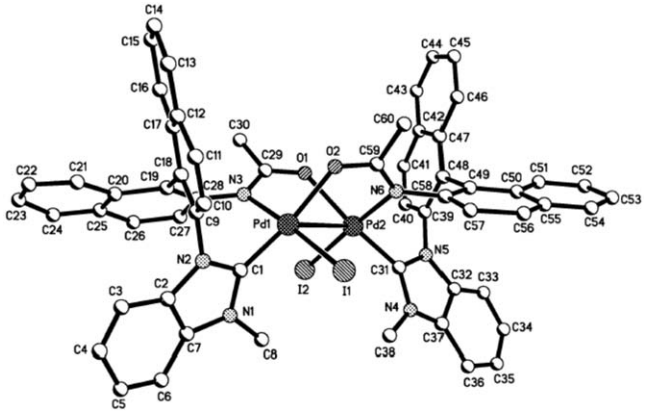
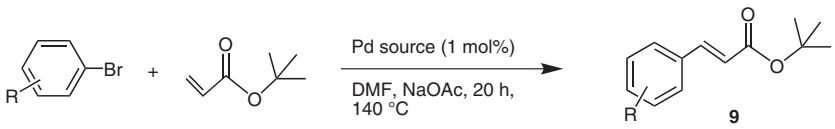


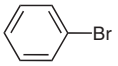
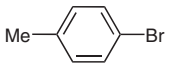
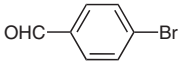
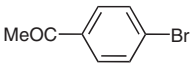
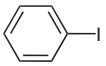
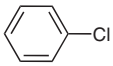
Figure 3 ORTEP drawing of NHC–Pd(II) complex **7** with thermal ellipsoids shown at the 30% probability level; selected bond distances (Å) and angles (°): Pd1–Pd2, 3.126(3); Pd1–C1, 1.879(17); Pd1–N3, 2.062(16); Pd1–O2, 2.095(14); Pd1–I1, 2.588(3); O1–C29, 1.19(2); N3–C29, 1.39(3); N3–C28, 1.39(2); Pd2–C31, 1.91(2); Pd2–N6, 2.029(15); Pd2–O1, 2.131(13); Pd2–I2, 2.588(3); O2–C59, 1.24(2); N6–C59, 1.35(3); N6–C58, 1.41(2); O2–Pd1–N3, 94.4(6); C1–Pd1–N3, 88.8(7); C1–Pd1–I1, 87.7(6); I1–Pd1–O2, 89.4(4); O2–Pd1–C1, 165.4(7); I1–Pd1–N3, 176.2(4); O1–Pd2–N6, 93.5(6); C31–Pd2–N6, 96.54(12); C31–Pd2–I2, 85.7(6); I2–Pd2–O1, 89.2(4); O1–Pd2–C31, 163.5(7); I2–Pd2–N6, 176.7(4)

The application of NHC–Pd(II) complexes **7** and **8** (1.0 mol%) as catalysts for the Heck–Mizoroki coupling reaction was examined. Sodium acetate was used as a base and *N*,*N*-dimethylformamide (DMF) was used as solvent in the reaction of arylbromides with *tert*-butyl acrylate at 140 °C under an argon atmosphere. The results of these experiments are summarized in Table 1. As can be seen, the corresponding coupling products **9** were obtained in 80–99% yields within 20 hours, indicating that these NHC–Pd(II) complexes are quite effective catalysts in the Heck–Mizoroki coupling reaction (Table 1, entries 1–8). NHC–Pd(II) complex **8**, bearing a weakly coordinating acetate counterion, was slightly more effective and gave the coupled products **9a–d** in higher yields than those of NHC–Pd(II) complex **7** under the standard conditions. Furthermore, using NHC–Pd(II) complex **8** as the catalyst in the reaction of iodobenzene with *tert*-butyl acrylate, **9a** was obtained in 99% yield after 20 hours under identical conditions (Table 1, entry 9). However, **9a** was formed in very low yield after 20 hours under identical conditions using NHC–Pd(II) complex **8** as the catalyst in the reaction of chlorobenzene with *tert*-butyl acrylate (Table 1, entry 10), suggesting that these NHC–Pd(II) complexes are not very effective in the Heck–Mizoroki coupling reaction using arylchlorides as the substrates.

In conclusion, we have developed a novel NHC-acetylamide ligand from BINAM and have successfully synthesized its dinuclear palladium complexes **7** and **8**. These complexes have been isolated and characterized by IR, NMR and ESI-MS spectroscopy. Moreover, complex **7** has been characterized by X-ray crystal structure analysis. These interesting NHC-acetylamide complexes have proven to be quite effective catalysts in the Heck–Mizoro-

Table 1 Heck–Mizoroki Reaction Catalyzed by NHC–Pd(II) Complexes **7** and **8**[a]



Entry	Aryl halide	Pd source	Product	Yield (%)[b]
1		**7**	**9a**	80
2		**8**	**9a**	82
3		**7**	**9b**	85
4		**8**	**9b**	86
5		**7**	**9c**	86
6		**8**	**9c**	99
7		**7**	**9d**	99
8		**8**	**9d**	99
9		**8**	**9a**	99
10		**8**	**9a**	<5

[a] Reaction conditions: aryl halide (1 mmol), *tert*-butyl acrylate (1.5 mmol), NaOAc (1.1 mmol), NHC–Pd(II) complex (0.01 mmol), DMF (2 mL).
[b] Isolated yield.

ki coupling reaction of arylbromides and aryliodide with *tert*-butyl acrylate to give the corresponding coupled products in good to high yields. Efforts are underway to elucidate the use of complexes **7** and **8** to catalyze other C–C bond-forming transformations.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX-300 spectrometer as solutions in $CDCl_3$ with TMS as an internal standard. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. Mass spectra and HRMS were recorded with an HP-5989 instrument, a Finnigan MA$^+$ mass spectrometer and a Micromass GCT mass spectrometer. CHN microanalyses were obtained with a Carlo–Erba 1106 analyzer. Organic solvents were dried by standard methods when necessary. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

Compound 1

Under an argon atmosphere, a mixture of 1,1′-binaphthalenyl-2,2′-diamine (568 mg, 2.0 mmol), 2-bromonitrobenzene (404 mg, 2.0 mmol), $Pd_2(dba)_3$ (48 mg, 0.05 mmol), bis(2-diphenylphosphinophenyl)ether (80 mg, 0.15 mmol) and Cs_2CO_3 (2.080 g, 6.4 mmol) was stirred in anhydrous toluene (16 mL) at 80 °C for 48 h. After the reaction mixture was cooled to r.t., the reaction was quenched by the addition of H_2O (40 mL) and the organic compound was extracted with EtOAc (2 × 80 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane–EtOAc, 30:1) to give **1**.

Yield: 680 mg (84%); red solid; mp 179–181 °C (dec.).

IR (CH_2Cl_2): 3300, 3262, 3058, 1611, 1499, 1254, 738 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 2 H, NH_2), 6.67–6.74 (m, 1 H, ArH), 6.96–6.99 (m, 1 H, ArH), 7.12–7.47 (m, 8 H, ArH), 7.76–7.82 (m, 3 H, ArH), 7.92–8.03 (m, 3 H, ArH), 9.27 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 112.1, 116.2, 117.8, 118.1, 121.8, 122.4, 123.3, 125.4, 125.5, 125.7, 126.4, 126.8, 127.1, 128.1, 128.2, 128.2, 129.1, 129.9, 131.4, 133.5, 133.6, 133.9, 135.2, 135.9, 141.5, 142.2.

MS (EI): *m*/*z* = 405 [M$^+$], 388, 370, 341, 267.

Anal. Calcd for $C_{26}H_{19}N_3O_2$: C, 77.02; H, 4.72; N, 10.36. Found: C, 76.99; H, 4.72; N, 10.45.

Compound 2

A mixture of **1** (81 mg, 0.20 mmol), Ac_2O (15 μL, 0.22 mmol) and AcOH (0.12 mL, 2.1 mmol) in CH_2Cl_2 (4.0 mL) was stirred at r.t. for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 4:1) to give the product **2**.

Yield: 79.6 mg (89%); red solid; mp 196.2–198.4 °C (dec.).

IR (CH_2Cl_2): 3470, 3351, 3058, 2248, 1919, 1695, 1614, 1520, 1426, 1282, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, CH_3), 6.60–6.66 (m, 1 H, ArH), 7.07–7.26 (m, 5 H, ArH), 7.28–7.42 (m, 4 H, ArH), 7.70 (d, *J* = 9.0 Hz, 1 H, ArH), 7.83–7.86 (m, 3 H, ArH), 7.94 (t, *J* = 9.0 Hz, 2 H, ArH), 8.47 (d, *J* = 8.4 Hz, 1 H, NH), 8.97 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 115.5, 118.1, 120.53. 120.54, 121.11, 121.12, 121.6, 123.7, 124.5, 124.9, 125.5, 126.4, 126.8, 127.3, 128.1, 129.3, 129.8, 130.8, 131.0, 132.1, 133.1, 133.6, 134.5, 135.2, 135.9, 140.9, 168.3.

MS (ESI): *m*/*z* = 470 [M$^+$ + Na], 447 [M$^+$].

Anal. Calcd for $C_{28}H_{21}N_3O_3$: C, 75.15; H, 4.73; N, 9.39. Found: C, 74.82; H, 4.91; N, 9.35.

Compound 3

A mixture of **2** (447 mg, 1.0 mmol) and 10% Pd/C (60 mg) in EtOAc (60 mL) was stirred under an H_2 atmosphere (1.0 atm) at

60 °C for 4 h. After cooling to r.t., Pd/C was removed by filtration, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane–EtOAc, 2:1 → 1:1) to give **3**.

Yield: 416 mg (99%); white solid; mp 199–201 °C (dec.).

IR (CH_2Cl_2): 3458, 3390, 3054, 2245, 1908, 1676, 1618, 1507, 1500, 1275, 909, 818, 745 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, CH_3), 3.59 (s, 2 H, NH), 4.89 (s, 1 H, NH), 6.55–6.64 (m, 2 H, ArH), 6.86–6.96 (m, 3 H, ArH), 7.13–7.27 (m, 6 H, Ar), 7.34–7.43 (m, 1 H, ArH), 7.78 (d, *J* = 6.3 Hz, 1 H, ArH), 7.81 (d, *J* = 8.4 Hz, 1 H, Ar), 7.89 (d, *J* = 8.4 Hz, 1 H, Ar), 7.99 (d, *J* = 9.0 Hz, 1 H, Ar), 8.51 (d, *J* = 9.0 Hz, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.3, 111.9, 115.8, 116.1, 118.6, 121.14, 121.15, 121.5, 122.8, 123.5, 125.1, 125.3, 126.1, 126.4, 126.96, 127.01, 127.2, 128.2, 128.3, 129.4, 130.0, 131.4, 132.5, 133.4, 135.1, 142.4, 142.7, 168.9.

MS (EI): *m*/*z* = 417 [M^+], 375, 358, 267, 207.

Anal. Calcd for $C_{28}H_{23}N_3O$: C, 80.55; H, 5.55; N, 10.06. Found: C, 80.18; H, 5.54; N, 9.97.

Compound 4

Compound **3** (208 mg, 0.50 mmol) and triethyl orthoformate [$HC(OEt)_3$] (5.0 mL) containing a catalytic amount of TsOH were heated at 100 °C for 24 h. After the excess triethyl orthoformate was removed under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane–EtOAc, 2:3) to give **4**.

Yield: 192 mg (90%); white solid; mp 223–224 °C.

IR (KBr): 3422, 3274, 3054, 2926, 1690, 1597, 1491, 1284, 1236, 820, 743 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, CH_3), 6.06 (s, 1 H, NCHN), 7.10 (d, *J* = 8.1 Hz, 1 H, ArH), 7.24–7.44 (m, 8 H, ArH), 7.62–7.70 (m, 2 H, ArH), 7.80–7.90 (m, 3 H, Ar), 8.10 (d, *J* = 8.4 Hz, 1 H, ArH), 8.27–8.30 (m, 2 H, ArH + NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2, 109.2, 120.2, 120.6, 121.2, 122.8, 123.6, 124.2, 124.9, 125.2, 126.6, 127.1, 127.5, 128.1, 128.4, 128.5, 129.0, 129.7, 130.8, 133.17, 133.19, 134.0, 134.6, 142.4, 142.9, 168.0.

MS (EI): *m*/*z* = 427 [M^+], 384, 369.

Anal. Calcd for $C_{29}H_{21}N_3O$: C, 81.48; H, 4.95; N, 9.83. Found: C, 81.09; H, 5.05; N, 9.76.

Benzimidazolium Salt 5

Compound **4** (86 mg, 0.20 mmol) and MeI (0.24 mL, 4 mmol) in MeCN (4.0 mL) were stirred under reflux for 5 h. After cooling to r.t., volatiles were removed under reduced pressure and the solid compound **5** obtained was used in the next reaction without further purification.

Mp 230–233 °C.

IR (CH_2Cl_2): 3152, 2958, 1676, 1597, 1564, 1499, 1427, 1367, 1270, 1013, 733 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CH_3), 3.91 (s, 3 H, CH_3), 6.96 (s, 2 H, ArH), 7.21 (t, *J* = 7.2 Hz, 1 H, ArH), 7.45–7.72 (m, 8 H, ArH), 7.85–8.00 (m, 3 H, ArH), 8.04 (d, *J* = 8.1 Hz, 1 H, ArH), 8.30 (d, *J* = 8.4 Hz, 1 H, ArH), 8.51 (br, 1 H, NH), 10.16 (br, 1 H, NCHN).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 34.0, 112.91, 112.95, 122.97, 123.03, 124.2, 125.7, 126.4, 126.8, 127.26, 127.31, 127.4, 127.9, 128.3, 128.4, 129.3, 129.6, 130.4, 130.9, 131.0, 131.1, 131.30, 131.33, 132.0, 133.8, 135.47, 135.50, 141.9, 170.3.

MS (EI): *m*/*z* = 442 [M^+ – I], 427, 369, 267.

Anal. Calcd for $C_{30}H_{24}IN_3O$: C, 63.28; H, 4.25; N, 7.38. Found: C, 63.18; H, 4.38; N, 7.20.

Compound 6

Compound **5** (114 mg, 0.20 mmol), NaI (30 mg, 0.20 mmol) and $Pd(OAc)_2$ (44 mg, 0.20 mmol) were stirred at 90 °C in DMSO (5 mL) for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane–EtOAc, 4:1) to give compound **6**. The single crystals for X-ray diffraction were obtained by recrystallization from CH_2Cl_2–petroleum ether.

Yield: 29 mg (36%); yellow solid; mp 248.4–249.5 °C (CH_2Cl_2–petroleum ether).

IR (CH_2Cl_2): 3044, 2919, 1638, 1607, 1578, 1564, 1492, 1428, 1366, 1212, 1093, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.47 (s, 3 H, CH_3), 6.97 (d, *J* = 7.5 Hz, 1 H, ArH), 7.06–7.26 (m, 6 H, ArH), 7.32–7.46 (m, 4 H, ArH), 7.62 (d, *J* = 9 Hz, 1 H, ArH), 7.77–7.84 (m, 4 H, ArH).

MS (EI): *m*/*z* = 397 [M^+].

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{28}H_{19}N_3$: 397.1579; found: 397.1579.

NHC–Pd(II) Complex 7

Compound **5** (114 mg, 0.20 mmol), Cs_2CO_3 (62 mg, 0.20 mmol) and $Pd(OAc)_2$ (44 mg, 0.20 mmol) were stirred at r.t. in THF (10 mL) for 20 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane–EtOAc, 4:1) to give the Pd(II)–NHC complex **7**. The single crystals for X-ray diffraction were obtained by recrystallization from CH_2Cl_2–petroleum ether.

Yield: 104 mg (77%); yellow solid; mp >250 °C (CH_2Cl_2–petroleum ether).

IR (KBr): 3067, 2963, 1701, 1526, 1401, 1134, 742 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 1.58 (s, 6 H, CH_3), 4.01 (s, 6 H, CH_3), 6.83 (d, *J* = 8.1 Hz, 2 H, ArH), 6.91–7.77 (m, 24 H, ArH), 7.99 (d, *J* = 8.4 Hz, 2 H, ArH), 8.32 (d, *J* = 8.4 Hz, 2 H, ArH), 8.51 (d, *J* = 8.7 Hz, 2 H, ArH).

MS (ESI): *m*/*z* = 1221.0 [M^+ – I].

Anal. Calcd for $C_{60}H_{44}I_2N_6O_2Pd_2 \cdot H_2O$: C, 52.77; H, 3.39; N, 6.15. Found: C, 52.19; H, 3.77; N, 5.89.

NHC–Pd(II) Complex 8

Complex **7** (135 mg, 0.10 mmol) was dissolved in MeCN–CH_2Cl_2 (3:1, 10 mL), then AgOAc (35 mg, 0.21 mmol) was added and the mixture was stirred at r.t. for 3 h. The resulting suspension was filtered through Celite to remove AgI, then the solvent was removed under reduced pressure to give the Pd(II)–NHC complex **8**.

Yield: 100 mg (82%); white solid; mp >250 °C.

IR (KBr): 3252, 2848, 2230, 1685, 1457, 1264, 693–818 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6 H, CH_3), 1.85 (s, 6 H, CH_3), 4.08 (s, 6 H, CH_3), 6.89–7.36 (m, 20 H, ArH), 7.59–7.64 (m, 4 H, ArH), 7.69 (d, *J* = 8.7 Hz, 2 H, ArH), 7.92 (d, *J* = 8.1 Hz, 2 H, ArH), 8.12 (d, *J* = 8.4 Hz, 2 H, ArH), 8.30 (d, *J* = 8.7 Hz, 2 H, ArH).

MS (ESI): *m*/*z* = 1153.1 [M^+ + Na + K – 2 × OAc].

Anal. Calcd for $C_{64}H_{50}N_6O_6Pd_2$: C, 63.43; H, 4.16; N, 6.93. Found: C, 64.02; H, 4.16; N, 6.62.

Heck–Mizoroki Reaction; General Procedure

Under an argon atmosphere, *tert*-butyl acrylate (1.5 mmol), aryl halide (1.0 mmol), NaOAc (1.1 mmol) and DMF (2.0 mL) were added successively into a flash-dried Schlenk tube. The reaction mixture was stirred at 140 °C and monitored by TLC (the reaction was usu-

ally complete within 20 h). The reaction was quenched with H_2O (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solution was concentrated under reduced pressure. Pure products were obtained by flash column chromatography (EtOAc–petroleum ether, 1:5).

9a[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 9 H), 6.36 (d, *J* = 16.2 Hz, 1 H), 7.32–7.36 (m, 3 H), 7.46–7.52 (m, 2 H), 7.59 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1, 80.3, 120.1, 127.9, 128.7, 129.9, 134.6, 143.4, 166.2.

9b[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 9 H), 2.35 (s, 3 H), 6.31 (d, *J* = 16.2 Hz, 1 H), 7.58–7.63 (m, 4 H), 7.56 (d, *J* = 16.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 28.1, 80.2, 119.1, 127.9, 129.5, 131.9, 140.1, 143.4, 166.4.

9c[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 9 H), 6.48 (d, *J* = 16 Hz, 1 H), 7.58–7.67 (m, 3 H), 7.89 (d, *J* = 8.1 Hz, 2 H), 10.02 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.0, 80.9, 123.3, 128.3, 130.0, 136.8, 140.3, 141.7, 165.5, 191.4.

9d[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 9 H), 2.62 (s, 3 H), 6.46 (d, *J* = 16.2 Hz, 1 H), 7.58–7.63 (m, 3 H), 7.96 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2, 28.1, 80.9, 122.7, 128.0, 128.8, 137.7, 139.0, 141.9, 165.7, 197.3.

Acknowledgment

We thank the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005), the National Natural Science Foundation of China (20472096, 20672127, 20772030 and 20732008), and the Cheung Kong Scholar Program for financial support.

References

(1) (a) Gstottmayr, C. W. K.; Bohm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1363. (b) Arensten, K.; Caddick, S.; Cloke, F. G. N.; Herring, A. P.; Hitchcock, P. B. *Tetrahedron Lett.* **2004**, *45*, 3511. (c) Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 1253. (d) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451. (e) Dorta, R.; Stevens, E. D.; Scott, N. M.; Chiara, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

(2) (a) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (b) Bourissou, D.; Guerret, O.; GabbaÏ, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617-618*, 616. (d) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617-618*, 70. (e) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499. (f) Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698. (g) Lee, H. M.; Zeng, J. Y.; Hu, C. H.; Lee, M. T. *Inorg. Chem.* **2004**, *43*, 6822.

(3) (a) Herrmann, W. A.; Elison, M.; Fisher, J.; Koecher, C.; Artus, G. R. J. *Angew. Chem. Int. Ed.* **1995**, *34*, 2371. (b) Albert, K.; Gisdakis, P.; Rosch, N. *Organometallics* **1998**, *17*, 1608. (c) Zhang, C.; Trudell, M. L. *Tetrahedron Lett.* **2000**, *41*, 595. (d) Perry, M. C.; Cui, X.-H.; Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13*, 1969. (e) Lee, H.-M.; Lu, C.-Y.; Chen, C.-Y.; Chen, W.-L.; Lin, H.-C.; Chiu, P.-L.; Cheng, P.-Y. *Tetrahedron* **2004**, *60*, 5807. (f) Marshall, C.; Ward, M.-F.; Harrison, W. T. A. *Tetrahedron Lett.* **2004**, *45*, 5703. (g) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125. (h) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768.

(4) (a) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307. (b) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423. (c) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402. (d) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511. (e) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002**, *4*, 1411. (f) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889. (g) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053. (h) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804. (i) Zhang, C.; Trudell, M. L. *Tetrahedron Lett.* **2000**, *41*, 595. (j) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119.

(5) (a) Huynh, H. V.; Le Van, D.; Hahn, F. E.; Hor, T. S. A. *J. Organomet. Chem.* **2004**, *689*, 1766. (b) Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem. Int. Ed.* **2003**, *42*, 3810. (c) Mueller, J. A.; Goller, C. P.; Sigman, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9724. (d) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752. (e) Singh, R.; Viciu, M. S.; Kramareva, N.; Navarro, O.; Nolan, S. P. *Org. Lett.* **2005**, *7*, 1829. (f) Voges, M. H.; Romming, C.; Tilset, M. *Organometallics* **1999**, *18*, 529. (g) Herrmann, W. A.; Kocher, C. *Angew. Chem. Int. Ed.* **1997**, *36*, 2163.

(6) (a) Zhang, T.; Shi, M.; Zhao, M.-X. *Tetrahedron* **2008**, *64*, 2412. (b) Zhang, T.; Shi, M. *Chem. Eur. J.* **2008**, *14*, 3759.

(7) (a) Duan, W.-L.; Shi, M.; Rong, G.-B. *Chem. Commun.* **2003**, 2916. (b) Xu, Q.; Duan, W. L.; Lei, Z. Y.; Zhu, Z. B.; Shi, M. *Tetrahedron* **2005**, *61*, 11225. (c) Chen, T.; Jiang, J.-J.; Xu, Q.; Shi, M. *Org. Lett.* **2007**, *9*, 865; and references cited therein.

(8) (a) Shi, M.; Qian, H.-X. *Appl. Organomet. Chem.* **2005**, *19*, 1083. (b) Shi, M.; Qian, H.-X. *Tetrahedron* **2005**, *61*, 4949.

(9) Zhang, T.; Wang, W.-F.; Gu, X.-X.; Shi, M. *Organometallics* **2008**, *27*, 753; and references cited therein.

(10) The X-ray crystal data for compound **6** have been deposited in the CCDC with number 281153. Empirical formula: $C_{28}H_{19}N_3$; Formula weight: 397.46; Crystal color, habit: colorless, prismatic; Crystal dimensions: 0.480 × 0.378 × 0.216 mm; Crystal system: monoclinic; Lattice type: primitive; Lattice parameters: *a* = 8.7871(8) Å, *b* = 25.373(3) Å, *c* = 9.3514(9) Å, *β* = 101.837(2)°; *V* = 2040.6(3) Å^3; Space group: $P2_1/c$; Z = 4; D_{calc} = 1.294 g/cm^3; F_{000} = 832; Diffractometer: Rigaku AFC7R; Residuals: *R*1, *wR*2: 0.0548, 0.1023.

(11) The X-ray crystal data of NHC–Pd(II) complex **7** have been deposited in the CCDC with number 601088. Empirical formula: $C_{60}H_{48}I_2N_6O_2Pd_2$; Formula weight: 1383.64; Crystal color, habit: colorless, prismatic; Crystal dimensions: 0.138 × 0.115 × 0.040 mm; Crystal system: monoclinic; Lattice type: primitive; Lattice parameters: *a* = 14.496(12) Å, *b* = 20.803(16) Å, *c* = 23.523(19) Å, *β* = 101.179(15)°; *V* = 6959(10) Å^3; Space group: $P2_1/c$; Z = 4; D_{calc} = 1.321 g/cm^3; F_{000} = 2720; Diffractometer: Rigaku AFC7R; Residuals: *R*1, *wR*2: 0.1167, 0.2771.

(12) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 443. (b) Pyykko, P. *Chem. Rev.* **1997**, *97*, 597.

(13) Masllorens, J.; Moreno-Manas, M.; Pla-Quintana, A.; Roglans, A. *Org. Lett.* **2003**, *5*, 1559.