APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 1083–1089
Materials, Nanoscience and Catalysis AOC
Published online 9 September 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.966

A stable dimeric mono-coordinated NHC–Pd(II) complex: synthesis, characterization, and reactivity in Suzuki–Miyaura cross-coupling reaction

Min Shi* and Heng-Xin Qian

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

Received 29 March 2005; Revised 11 June 2005; Accepted 20 June 2005

A stable dimeric mono-coordinated NHC–Pd(II) complex with bridging iodine atoms was synthesized and characterized by single-crystal X-ray diffraction. It has been successfully applied to the Suzuki–Miyaura cross-coupling reaction under aerobic conditions. Good to excellent yields were obtained in most cases with the addition of H_2O.

KEYWORDS: *trans*-cyclohexane-1,2-diamine; Suzuki–Miyaura cross-coupling reaction; dimeric mono-coordinated NHC–Pd(II) complex; crystal structure; benzimidazolium iodide

INTRODUCTION

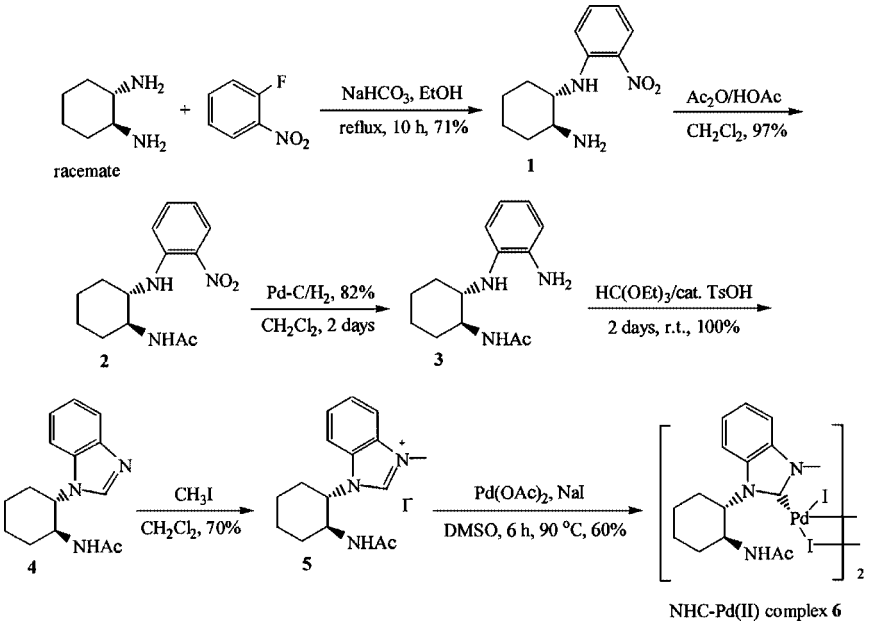
In 1968, Öfele[1] and Wanzlick and Schönherr[2] concurrently described preparation of the first metal complexes of *N*-heterocyclic carbenes (NHCs). However, these reports received little attention until Arduengo and co-workers synthesized stable free carbenes.[3,4] Herrmann's group further expanded this field by preparing numerous NHCs and their metal complexes and applying these complexes in homogeneous catalysis; see Herrmann[5] and Bourissou *et al*.[6] for reviews. Recently, numerous papers concerning this topic have appeared, and complexes of NHCs have been applied as catalysts in a broad range of reactions. Significantly, a number of Pd–NHC complexes have emerged as effective catalysts for a variety of coupling reactions.[7–25]

The palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with arylboronic acids is a powerful method for accessing structurally diversified biaryls; see Suzuki[26] and recent reviews.[27–31] Cross-coupling between aryl bromides,[32–35] chlorides,[36–38] fluorides,[39] tosylates,[40–42] and boronic acids is possible by using palladium complexes with sterically hindered and electron-rich phosphine ligands[43,44] or NHC ligands, such as those developed by Buchwald and co-workers,[37,45–48] Littke and Fu,[36,49] Herrmann and co-workers[50,51] and Nolan and co-workers.[52,53] A number of dimeric mono-coordinated NHC–Pd(II) complexes with bridging halogen atoms have been synthesized by several groups;[9,15,22–25,54–58] for a recent review see Weskamp *et al*.[59] Some of them have achieved great success in catalytic reactions and had their crystal structures analyzed by X-ray diffraction.[22–25] We report herein the synthesis of a new stable dimeric mono-coordinated NHC–Pd(II) complex with bridging iodine atoms, its characterization by X-ray crystal structure analysis and its application in the Suzuki–Miyaura cross-coupling reaction.

RESULTS AND DISCUSSION

The synthesis of the dinuclear NHC–Pd(II) complex **6** is shown in Scheme 1. Using *trans*-cyclohexane-1,2-diamine (1.0 equivalent) as starting material to react with 2-fluoronitrobenzene (1.0 equivalent) in anhydrous ethanol, *N*-(2-nitrophenyl)cyclohexane-1,2-diamine (**1**) (racemate) was obtained in 71% yield under reflux in the presence of $NaHCO_3$. Acylation of **1** with acetic anhydride and acetic acid in CH_2Cl_2 produced *N*-[2-(2-nitrophenylamino)cyclohexyl]acetamide (**2**) in 97% yield. The reduction of **2** with Pd/C in dichloromethane under hydrogen atmosphere (1.0 atm) at room temperature for 2 days afforded

*Correspondence to: Min Shi, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China.
E-mail: mshi@pub.sioc.ac.cn
Contract/grant sponsor: State Key Project of Basic Research; Contract/grant number: G2000048007.
Contract/grant sponsor: Shanghai Municipal Committee of Science and Technology.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant numbers: 203900502; 20025206; 20272069.



Scheme 1. Synthesis of the benzimidazolium salt and NHC–Pd(II) complex **6**.

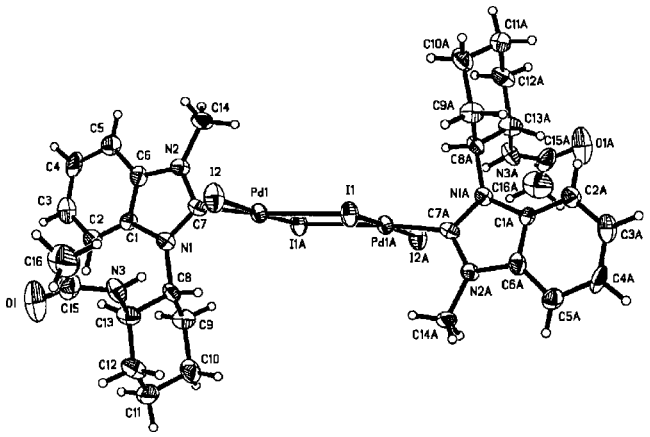


Figure 1. The ORTEP draw of NHC–Pd(II) complex **6**.

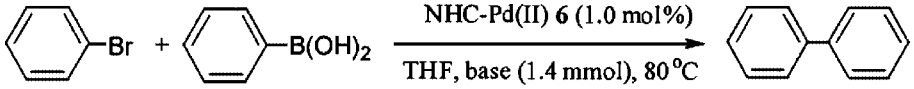
3 in 82% yield. The treatment of **3** at room temperature for 2 days by triethyl orthoformate containing a catalytic amount of tosylate (TsOH) gave compound **4** in quantitative yield (100%). The corresponding benzimidazolium iodide (**5**) was obtained by stirring compound **4** with CH_3I in CH_2Cl_2 at room temperature. Reaction of the NHC precursor **5** with $Pd(OAc)_2$ in the presence of sodium iodide in dimethylsulfoxide (DMSO) at 90 °C for 6 h afforded the desired NHC–Pd(II) complex **6** in 60% yield. Its crystal structure was determined by X-ray diffraction (Fig. 1). This is a dinuclear complex having bridged iodine atoms.

Structural features

The single crystals of this complex suitable for X-ray crystal structure analysis were grown from dichloromethane/ethyl acetate (1/1) solution. The ORTEP diagram is given in Fig. 1. This NHC–Pd(II) complex exists as a dimer with two bridging iodine atoms in the solid state with slightly distorted square plannar geometry about palladium and a crystallographic C_2 axis of symmetry that makes the two units equivalent. The interplanar angle between the diaminocarbene ring and the chelated plane is 89.0°. The Pd–C distance of complex **6** is 1.955(12) Å, which is slightly contracted relative to those in the Herrmann's diiodide complexes;[60,61] see Albert *et al.*[62] for a theoretical study of this system. The length of the Pd–I bond trans to the carbene is 2.673(1) Å, which is longer than that of the two cis bonds (2.605(1) and 2.597(1) Å), demonstrating the trans influence of the strongly σ-donating effect from the NHC ligand.[6] The central plane of Pd–I–Pd–I deviates slightly from a rectangle. The bite angle of Pd–I–Pd is slightly more than 90° (92.96(4)°) and the bite angle of I–Pd–I is slightly less than 90° (87.04(4)°), which resulted from the different steric effects of the terminal iodine atom and the NHC ligand. The Pd–Pd distance in this complex is over 3.5 Å, suggesting that there is no direct metal–metal interaction.

The application of NHC–Pd(II) complex **6** as a catalyst for the Suzuki–Miyaura cross-coupling reaction was examined where both base and solvent effects were carefully examined in the reaction of phenylboronic acid with bromobenzene under ambient atmosphere (we have previously reported the synthesis of a stable axially chiral NHC–Rh(III) complex bearing the same benzimidazolin-2-ylidene moiety and its application in the enantioselective hydrosilylation of methyl ketones[63,64]). The results are summarized in Tables 1 and 2. The use of K_2CO_3 and Cs_2CO_3 as the base in tetrahydrofuran (THF) at 90 °C gave the coupled product biphenyl **7a** in

Table 1. Screening for bases in the NHC–Pd(II) complex **6**-catalyzed Suzuki-type cross-coupling reaction of bromobenzene (1.0 mmol) with phenylboronic acid (1.3 mmol) in THF (2.0 ml)

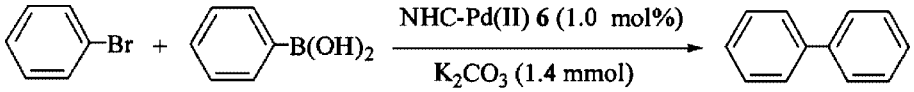


7a

Entry	Base	Time[a] (h)	**7a** yield[b] (%)
1	K_2CO_3	20	52
2	Cs_2CO_3	6	40
3	KOAc	22	13
4	$KF \cdot 2H_2O$	22	8
5	$K_3PO_4 \cdot 3H_2O$	22	6
6	$KOC(CH_3)_3$	22	30

[a] The reaction time for consuming all of the starting materials.
[b] Isolated yields.

Table 2. Screening for solvents in the NHC–Pd(II) complex **6**-catalyzed Suzuki-type cross-coupling reaction of bromobenzene (1.0 mmol) with phenylboronic acid (1.3 mmol) in solvents (2.0 ml)



7a

Entry	Solvent	Time (h)	**7a** yield[a] (%)
1	DMSO	4.5	16
2	CH_3CN	8	12
3	CH_2ClCH_2Cl	12	60
4	DMF	6	71
5	Dioxane	6	5
6	DMA	10	78

[a] Isolated yields.

52% and 40% yields after 20 h and 6 h respectively (Table 1, entries 1 and 2). On the other hand, at 80 °C in *N*,*N*-dimethylacetamide (DMA) with K_2CO_3 as the base, **7a** was obtained in 78% yield after 10 h (Table 2, entry 6). Thus, DMA was the solvent of choice and K_2CO_3 was the preferred base for this reaction. We also examined some additive effects on this reaction and found that, with the addition of water, this coupling reaction could be greatly accelerated in DMA at 90 °C to give **7a** in good yield within 2 h (see Refs 65–67 for the effects of the addition of water to accelerate the Suzuki cross-coupling reaction). The effect of the amount of H_2O on this reaction was examined carefully. The results are summarized in Table 3. The addition of 2.0 molar equivalents of H_2O gave the best result (Table 3, entry 3).

Using these optimized reaction conditions, the Suzuki–Miyaura reaction of a variety of arylhalides, including arylbromides and phenyliodide, with phenylboronic acid were examined. The results are summarized in Table 4. As can be seen, arylbromides and phenyliodide afforded coupling products **7** in 80–97% yield under ambient atmosphere within a short reaction time (Table 4, entries 1–6). For 4-bromoanisole, which has a strong electron-donating group on the benzene ring, the corresponding coupled product **7b** was obtained in 91% yield after 5 h (Table 4, entry 1).

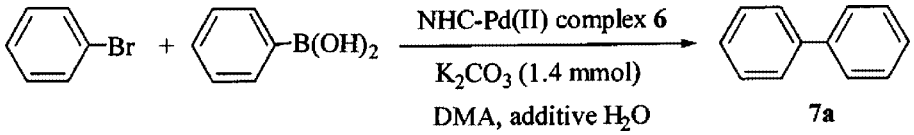
In conclusion, we have obtained the stable dimeric mono-coordinated NHC–Pd(II) complex **6**; this has two bridging iodine atoms and is an effective catalyst for the Suzuki–Miyaura cross-coupling reaction with the addition of H_2O (2.0 molar equivalents). Efforts are under way to use the NHC–Pd(II) complex **6** to catalyze other C–C bond-forming transformations.

EXPERIMENTAL

General remarks

All reactions were conducted in an oven (135 °C) using flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Toluene was distilled from sodium metal; dichloromethane was distilled from calcium hydride; diethyl ether, THF and toluene were distilled from sodium

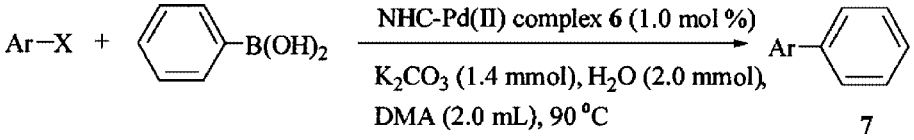
Table 3. The additive effect in the NHC–Pd(II) complex **6**-catalyzed Suzuki-type cross-coupling reaction of bromobenzene (1.0 mmol) with phenylboronic acid (1.3 mmol) in THF (2.0 ml)

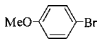
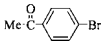


Entry	H_2O additive (mmol)	Time (h)	Temperature (°C)	**7a** yield[a] (%)
1	0	2	90	55
2	1	2	90	68
3	2	2	90	80
4	3	2	90	74
5	4	2	90	74
6	5	2	r.t.	26

[a] Isolated yields.

Table 4. The NHC–Pd(II) complex **6**-catalyzed Suzuki cross-coupling reaction of arylaldehydes (1.0 mmol) with phenylboronic acid (1.3 mmol) in DMA (2.0 ml) and H_2O (2.0 mmol)



Entry	Ar–X	Time (h)	**7** yield[a] (%)
1		5	**7b**, 91
2		1.5	**7c**, 92
3		1.5	**7d**, 93
4		4	**7e**, 97
5		1.5	**7f**, 90
6		2	**7a**, 92
7		2	**7a**, 80

[a] Isolated yields.

metal–benzophenone ketyl. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively using tetramethylsilane (TMS) as standard. Mass spectra were recorded by the electron impact (EI) method. All of the solid compounds reported in this paper gave satisfactory carbon, hydrogen and nitrogen microanalyses (3 and 4 were characterized by high-resolution mass spectrometry (HRMS)). Commercially obtained reagents were used without further purification. All reactions were monitored by thin-layer chromatography with silica-gel-coated plates.

Synthesis of *N*-(2-nitrophenyl)cyclohexane-1, 2-diamine (1)

trans-Cyclohexane-1,2-diamine (228 mg, 2.0 mmol), 2-fluoronitrobenzene (282 mg, 2.0 mmol), and $NaHCO_3$ (185 mg, 2.2 mmol) were stirred in anhydrous ethanol under reflux for 10 h. Then, the reaction mixture was poured into 15 ml of iced water when hot and the mixture stirred for 20 min. The organic compound was extracted with CH_2Cl_2 (2 × 20 ml) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: $CH_2Cl_2/CH_3OH = 20/1$) to give **1** as a red solid (334 mg; yield: 71%). M.p. 78–79 °C. IR (CH_2Cl_2, cm^{-1}): ν 3352, 2932, 2857, 1616, 1573, 1510, 1421, 1270, 1244, 1153, 741. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.24–1.39 (4H, m, CH_2), 1.77–1.79 (2H, m, CH_2), 1.99–2.12 (2H, m, CH_2), 2.77–2.80 (1H, m, CH), 3.28–3.33 (1H, m, CH), 6.59–6.64 (1H, dd, $J_1 = J_2 = 8.4$ Hz, ArH), 8.08 (1H, d, $J = 8.1$ Hz, NH), 8.16 (1H, d, $J = 8.4$ Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.5, 24.9, 31.9, 34.7, 55.4, 59.0, 114.3 (2C), 115.2, 127.0, 136.1, 145.6. MS (EI) m/e 235 (M^+), 189 (5.21), 145 (48.58), 131 (88.32), 56 (100.00). Anal. Found: C, 61.28; H, 7.01; N, 18.06. Calc. for $C_{12}H_{17}N_3O_2$ requires: C, 61.26; H, 7.28; N, 17.86%.

Synthesis of *N*-[2-(2-nitrophenylamino) cyclohexyl]acetamide (2)

N-(2-Nitrophenyl)cyclohexane-1,2-diamine (480 mg, 2.0 mmol) was dissolved in 15 ml of CH_2Cl_2 and 10 ml of acetic acid. Then, Ac_2O (0.3 ml, 3.2 mmol) was added into the reaction mixture. After the mixture was stirred at room temperature for 4 h, aqueous NaOH (4.0 M) was added to neutralize the excess amount of acid. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×20 ml). The organic layers were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: hexane/$CH_2Cl_2 = 1/1$) to give **2** as a yellow solid (540 mg; yield: 97%). M.p. 155–156 °C. IR (CH_2Cl_2, cm^{-1}): ν 3338, 3302, 2940, 2854, 1619, 1573, 1550, 1266, 737. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.41–1.53 (4H, m, CH_2), 1.69–1.77 (2H, m, CH_2), 1.93 (3H, s, CH_3), 2.06–2.16 (2H, m, CH_2), 3.55–3.57 (1H, m, CH), 3.97–4.03 (1H, m, CH), 5.52 (1H, s, *N*H), 6.62 (1H, t, $J = 7.5$ Hz, ArH), 7.05 (1H, d, $J = 8.4$ Hz, ArH), 7.43 (1H, t, $J = 7.5$ Hz, ArH), 8.15 (1H, d, $J = 8.4$ Hz, ArH), 8.28 (1H, d, $J = 7.8$ Hz, NH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 23.2, 23.4, 23.8, 30.6, 30.9, 51.3, 54.9, 114.1, 115.1, 127.0, 131.9, 136.0, 144.9, 170.2. MS (EI) *m/e* 277 (M^+), 183 (19.05), 131 (42.34), 56 (125.12), 43 (100.00). Anal. Found: C, 60.52; H, 6.66; N, 14.90. Calc. for $C_{14}H_{19}N_3O_3$ requires: C, 60.63; H, 6.91; N, 15.15%.

Synthesis of *N*-[2-(2-aminophenylamino) cyclohexyl]acetamide (3)

Under 1 atm of hydrogen atmosphere, a mixture of **2** (750 mg, 2.7 mmol) and 10 wt% Pd/C (150 mg, 0.14 mmol) were stirred in anhydrous CH_2Cl_2 at room temperature for 2 days. The mixture was filtered to remove Pd/C catalyst. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: CH_2Cl_2/EtOAc = 1/1) to give **3** as a white solid (550 mg; yield: 82%). M.p. 98–99 °C. IR (CH_2Cl_2, cm^{-1}): ν 3252 (br), 3059, 2937, 2852, 1656, 1552, 742. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.05–1.29 (4H, m, CH_2), 1.66–1.72 (2H, m, CH_2), 1.81 (3H, s, CH_3), 1.93 (1H, d, $J = 14.2$ Hz, CH_2), 2.23 (1H, d, $J = 14.2$ Hz, CH_2), 2.91–2.99 (1H, m, CH), 3.31 (2H, br, NH_2), 3.77–3.81 (1H, m, CH), 5.57 (1H, d, $J = 8.4$ Hz, NH), 6.46–6.54 (2H, m, ArH), 6.58–6.61 (1H, m, ArH), 6.66–6.71 (1H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 23.4, 24.4, 25.0, 32.3, 32.6, 53.0, 58.3, 110.5, 116.4, 117.3, 120.1, 133.7, 136.6, 171.3. MS (EI) *m/e* 247 (M^+), 145 (87.72), 119 (100.00), 43 (51.01). HRMS (MALDI/DHB): calc. for $C_{14}H_{21}N_3ONa^+$ 270.1577; found: 270.1575.

Synthesis of *N*-(2-benzoimidazol-1-yl-cyclohexyl)acetamide (4)

A mixture of **3** (500 mg, 2.0 mmol), TsOH (30 mg), and $HC(OEt)_3$ (2.0 ml) were stirred at room temperature for 2 days. The volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: EtOAc/CH_2Cl_2/CH_3OH/Et_3N = 8/2/1/0.2) to give **4** as a gray solid (510 mg; yield: 100%). M.p. 198–199 °C. IR (CH_2Cl_2, cm^{-1}): ν 3260, 3068, 2937, 1656, 1553, 1221, 742. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.48–1.58 (2H, m, CH_2), 1.56 (3H, s, CH_3), 1.86–1.95 (3H, m, CH_2), 2.19–2.44 (3H, m, CH_2), 4.16–4.23 (1H, m, CH), 4.32–4.36 (1H, m, CH), 6.22–6.25 (1H, d, $J = 8.4$ Hz, NH), 7.25–7.28 (2H, m, ArH), 7.39–7.42 (1H, m, ArH), 7.44–7.76 (1H, m, ArH), 7.89 (1H, s, =CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 22.9, 24.8, 25.1, 33.0, 33.1, 52.0, 58.8, 109.9, 120.2, 122.1, 122.7, 133.6, 141.3, 143.4, 169.8; MS (EI) *m/e* 257 (M^+), 198 (100.00), 145 (33.01), 119 (30.80), 84 (59.21). HRMS (MALDI/DHB): calc. for $C_{15}H_{20}N_3O^+$ 258.1601; found: 258.1600.

Synthesis of benzimidazolium iodide (5; NHC precursor)

A mixture of **4** (560 mg, 2.2 mmol) and CH_3I (1.0 ml, 11.0 mmol) was stirred in anhydrous CH_2Cl_2 at room temperature for 2 days. A white precipitate was formed. The solid was obtained as a white powder by filtration and washing with diethyl ether (600 mg; yield: 70%). M.p. 238–240 °C. IR (CH_2Cl_2, cm^{-1}): ν 3208, 2939, 2858, 1655, 1567, 1312, 748. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.64–1.68 (2H, m, CH_2), 1.85 (3H, s, CH_3), 1.95–1.96 (2H, m, CH_2), 2.11–2.32 (4H, m, CH_2), 4.22 (3H, s, CH_3), 4.30–4.36 (1H, m, CH), 5.30–5.31 (1H, m, CH), 7.66–7.73 (3H, m, ArH), 8.13–8.14 (1H, m, ArH), 10.32 (1H, s, =CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 22.5, 24.4, 24.5, 31.3, 32.0, 34.0, 52.9, 61.5, 112.2, 115.0, 126.9 (2C), 131.3, 131.4, 140.9, 170.3. MS (MALDI) *m/e* 272 ($M^+ - I$). Anal. Found: C, 48.10; H, 5.66; N, 10.81. Calc. for $C_{16}H_{22}IN_3O$ requires: C, 48.13; H, 5.55; N, 10.52%.

Synthesis of NHC–Pd(II) complex 6

Compound **5** (530 mg, 1.33 mmol) was dissolved in 4 ml of DMSO and stirred at 65 °C; then, $Pd(OAc)_2$ (280 mg, 1.25 mmol) and sodium iodide (188 mg, 1.25 mmol) were added. The oil bath was elevated to 90 °C over a period of 1 h. The mixture was heated for another 5 h. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: EtOAc/$CH_2Cl_2 = 1/1$) to give **6** as an orange solid (510 mg; yield: 60%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of EtOAc/$CH_2Cl_2 = 1/1$. M.p. >300 °C. IR (CH_2Cl_2, cm^{-1}): ν 2940, 2857, 1675, 1448, 1367, 753. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.26–1.29 (2H, m, CH_2), 1.61–1.67 (2H, m, CH_2), 1.68 (3H, s, CH_3), 1.94–2.04 (2H, m, CH_2), 2.40–2.42 (2H, m, CH_2), 4.27 (3H, s, CH_3), 4.91 (1H, br, CH), 5.69 (1H, br, CH), 7.30–7.43 (3H, m, ArH), 7.72–7.73 (1H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 23.2, 24.6, 25.2, 29.5, 33.8, 35.6, 50.2, 64.5, 110.3, 112.6, 112.7, 123.5, 123.6, 132.3, 135.9, 169.7. MS (ESI) *m/e* 504 ($1/2M^+ - I$). Anal. Found: C, 27.98; H, 3.27; N, 5.49. Calc. for $C_{35}H_{48}Cl_6I_4N_6O_2Pd_2$ requires: C, 27.69; H, 3.19; N, 5.54%.

General procedure for the Suzuki–Miyaura cross-coupling reaction of aryl halides with boronic acids

A typical procedure is given below for the reaction expressed in entry 3 of Table 3. The NHC–Pd(II) complex **6** (7.0 mg, 0.05 mmol), potassium carbonate (200 mg, 1.4 mmol), benzenebromide (110 μl, 1.0 mmol), phenylboronic acid (160 mg, 1.3 mmol), DMA (2.0 ml) and H_2O (36 μl, 2.0 mmol) were introduced to a Schlenk tube under ambient inert atmosphere. The mixture was stirred at 100 °C for 2 h. The reaction mixture was diluted with H_2O (10 ml) and Et_2O (10 ml), followed by extraction twice with Et_2O (10 ml). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to give crude product. The pure product was isolated by column chromatography on silica gel (eluent: hexane) to give biphenyl (147 mg; yield: 95%) as a solid and was analyzed by ^1H NMR and IR spectroscopy.

Crystal data for 6

Empirical formula: $C_{17.5}H_{24}N_3OCl_3I_2Pd$; formula weight: 758.95; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a = 27.296(3)$ Å, $b = 9.4001(12)$ Å, $c = 19.675(3)$Å, $\alpha = 90°$, $\beta = 103.457(3)°$, $\gamma = 90°$, $V = 4909.6(11)$ Å^3; space group: $C2/c$; $Z = 8$; $D_{calc} = 2.054$ g cm^{-3}; $F_{000} = 2888$; diffractometer: Rigaku AFC7R; residuals: R, Rw: 0.0554, 0.0804.

Supporting information available

The spectroscopic data of coupling products **7** are available in Supporting Information or from the authors. The X-ray crystal data of NHC–Pd(II) complex **6** (CCDC no. 246794) have been deposited at the Cambridge Crytallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (no. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China (203900502, 20025206 and 20272069) for financial support.

REFERENCES

1. Öfele K. *J. Organometal. Chem.* 1968; **12**: 37.
2. Wanzlick HW, Schönherr HJ. *Angew. Chem. Int. Ed. Engl.* 1968; **7**: 141.
3. Arduengo III AJ, Harlow RL, Kline M. *J. Am. Chem. Soc.* 1991; **113**: 361.
4. Arduengo III AJ, Krafczyk R, Schmutzler R. *Tetrahedron* 1999; **55**: 14 523.
5. Herrmann WA. *Angew. Chem. Int. Ed.* 2002; **40**: 1290.
6. Bourissou D, Guerret O, Gaggaï FP, Bertrand G. *Chem. Rev.* 2000; **100**: 39.
7. Huang J, Nolan SP. *J. Am. Chem. Soc.* 1999; **121**: 9889.
8. Furstner A, Leitner A. *Synlett* 2001; 290.
9. Herrmann WA, Böhm VPW, Gstöttmayr CWK, Grosche MC, Reisinger C, Weskamp T. *J. Organometal. Chem.* 2001; **617–618**: 616.
10. Grasa GA, Hillier AC, Nolan SP. *Org. Lett.* 2001; **3**: 1077.
11. Viciu MS, Grasa GA, Nolan SP. *Organometallics* 2001; **20**: 3607.
12. Grasa GA, Viciu MS, Huang J, Zhang CM, Trudell ML, Nolan SP. *Organometallics* 2002; **21**: 2866.
13. Hillier AC, Grasa GA, Viciu MS, Lee HM, Yang CL, Nolan SP. *J. Organometal. Chem.* 2002; **653**: 69.
14. Viciu MS, Germaneau RF, Navarro-Fernandez O, Stevens ED, Nolan SP. *Organometallics* 2002; **21**: 5470.
15. Pytkowicz J, Roland S, Mangeney P, Meyer G, Jutand A. *J. Organometal. Chem.* 2003; **678**: 166.
16. Eckhardt M, Fu GC. *J. Am. Chem. Soc.* 2003; **125**: 13 642.
17. Zhou JR, Fu GC. *J. Am. Chem. Soc.* 2004; **126**: 1340.
18. Bonnet LG, Douthwaite RE. *Organometallics* 2003; **22**: 4187.
19. Viciu MS, Stevens ED, Petersen JL, Nolan SP. *Organometallics* 2004; **23**: 3752.
20. Marshall C, Ward MF, Harrison WTA. *Tetrahedron Lett.* 2004; **45**: 5703.
21. Wang AE, Zhong J, Xie JH, Zhou QL. *Adv. Synth. Catal.* 2004; **346**: 595.
22. Altenhoff G, Goddard R, Lehmann CW, Glorius F. *J. Am. Chem. Soc.* 2004; **126**: 15 195.
23. Altenhoff G, Goddard R, Lehmann CW, Glorius F. *Angew. Chem. Int. Ed.* 2003; **43**: 3690.
24. Glorius F, Altenhoff G, Goddard R, Lehmann CW. *Chem. Commun.* 2002; 2704.
25. Viciu MS, Kissling RM, Stevens ED, Nolan SP. *Org. Lett.* 2002; **4**: 2229.
26. Suzuki A. In *Metal-Catalyzed Cross-Coupling Reactions*, Diederich F, Stang PJ (eds). Wiley–VCH: Weinheim, 1998; 49.
27. Miyaura N, Suzuki A. *Chem. Rev.* 1995; **95**: 2457.
28. Stanforth SP. *Tetrahedron* 1998; **54**: 263.
29. Suzuki A. *J. Organometal. Chem.* 1999; **576**: 147.
30. Littke AF, Fu GC. *Angew. Chem. Int. Ed.* 2002; **41**: 4176.
31. Kotha S, Lahiri K, Kashinath D. *Tetrahedron* 2002; **58**: 9633.
32. Dai W, Li Y, Zhang Y, Lai KW, Wu J. *Tetrahedron Lett.* 2004; **45**: 1999.
33. Tang ZY, Lu Y, Hu QS. *Org. Lett.* 2003; **5**: 297.
34. Pramick MR, Rosemeier SM, Beranek MT, Nickse SB, Stone JJ, Stockland RA, Baldwin SM, Kastner ME. *Organometallics* 2003; **22**: 523.
35. Hierso JC, Fihri A, Amardeil R, Meunier P, Doucet H, Santelli M, Donnadieu B. *Organometallics* 2003; **22**: 4490.
36. Littke AF, Fu GC. *Angew. Chem. Int. Ed. Engl.* **37**: 3387.
37. Old DW, Wolfe JP, Buchwald SL. *J. Am. Chem. Soc.* 1998; **120**: 9722.
38. Bedford RB, Cazin CSJ, Hazelwood SL. *Angew. Chem. Int. Ed.* 2002; **41**: 4120.
39. Widdowson DA, Wilhelm R. *Chem. Commun.* 2003; 578.
40. Nguyen HN, Huang X, Buchwald SL. *J. Am. Chem. Soc.* 2003; **125**: 11 818.
41. Netherton MR, Fu GC. *Angew. Chem. Int. Ed.* 2002; **41**: 3910.
42. Kirchhoff JH, Netherton MR, Hills ID, Fu GC. *J. Am. Chem. Soc.* 2002; **124**: 13 662.
43. Parshall GW, Ittel S. *Homogeneous Catalysis*. Wiley: New York, 1992.
44. Pignolet LH (ed.). *Homogeneous Catalysis with Metal Phosphine Complexes*. Plenum: New York, 1983.
45. Stambuli JP, Kuwvano R, Hartwig JF. *Angew. Chem. Int. Ed.* 2002; **41**: 4746.
46. Yin J, Rainka MP, Zhang XX, Buchwald SL. *J. Am. Chem. Soc.* 2002; **124**: 1162.
47. Wolfe JP, Buchwald SL. *Angew. Chem. Int. Ed.* 1999; **38**: 2413.

48. Wolfe JP, Singer RA, Yang BH, Buchwald SL. *J. Am. Chem. Soc.* 1999; **121**: 9550.
49. Littke AF, Fu GC. *Angew. Chem. Int. Ed.* 2002; **41**: 4176.
50. Herrmann WA. *Angew. Chem. Int. Ed.* 2002; **41**: 1290.
51. Herrmann WA, Reisiner CP, Spieger M. *J. Organometal. Chem.* 1998; **557**: 93.
52. Hillier AC, Grasa GA, Viciu MS, Lee HM, Yang C, Nolan SP. *J. Organometal. Chem.* 2002; **653**: 69.
53. Zhang C, Huang J, Trudell ML, Nolan SP. *J. Org. Chem.* 1999; **64**: 3804.
54. Enders D, Gielen H, Raabe G, Runsink J, Teles JH. *Chem. Ber.* 1996; **129**: 1483.
55. Weskamp T, Böhm VPW, Herrmann WA. *J. Organometal. Chem.* 1999; **585**: 348.
56. Herrmann WA, Gooßen LJ, Spiegler M. *J. Organometal. Chem.* 1997; **547**: 357.
57. Xu L, Chen W, Bickley JF, Steiner A, Xiao J. *J. Organometal. Chem.* 2000; **598**: 409.
58. Jensen DR, Sigman MS. *Org. Lett.* 2003; **5**: 63.
59. Weskamp T, Böhm VPW, Herrmann WA. *J. Organometal. Chem.* 2000; **600**: 12.
60. Herrmann WA, Elison M, Fischer J, Köcher C, Artus GRJ. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 2371.
61. Herrmann WA, Reisinger CP, Spiegler M. *J. Organometal. Chem.* 1998; **557**: 93.
62. Albert K, Gisdakis P, Rösch N. *Organometallics* 1998; **17**: 1608.
63. Duan WL, Shi M, Rong GB. *Chem. Commun.* 2003; 2916.
64. Shi M, Duan WL. *Appl. Organometal. Chem.* 2005; **19**: 40.
65. Kirchhoff JH, Dai CY, Fu GC. *Angew. Chem. Int. Ed.* 2002; **41**: 1495.
66. Matos K, Soderquist JA. *J. Org. Chem.* 1998; **63**: 461.
67. Köster R, Seidel G, Wrackmeyer B. *Chem. Ber.* 1992; **125**: 617.

