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Use of bis(benzimidazolium)–palladium system as a convenient catalyst for Heck and Suzuki coupling reactions of aryl bromides and chlorides

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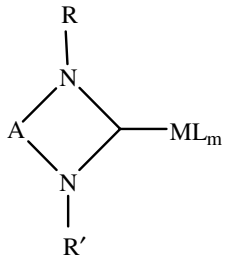
Six new, sterically demanding bis(benzimidazolium) salts (2a–f) as NHC precursors have been synthesized and characterized. These salts, in combination with palladium acetate, provide active catalysts for the cross-coupling of aryl chlorides and bromides under mild conditions in aqueous media. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Heck; Suzuki; carbene; palladium; benzimidazol-2-ylidene

INTRODUCTION

The use of *N*-heterocyclic carbenes (NHCs) as ligands for transition metal complexes was described 37 years ago by Öfele[1] and Wanzlick and Schönhrr.[2] Transition metal complexes incorporating 1,3-diorganyl *N*-heterocyclic carbene (NHC) ligands, such as imidazol-2-ylidene, imidazolidin-2-ylidene, benzimidazol-2-ylidene and 3,4,5,6-tetrahydopyrimidin-2-ylidene have attracted a great deal of interest in recent years.[3–10] They are often synthesized via the reaction of an azol(in)ium salt (LHX) with a basic salt such as $Pd(OAc)_2$ to give $M(NHC)L_m$.



$M(NHC)L_m$

A
CH=CH
C_6H_4-*o*
CH_2CH_2
$(CH_2)_3$

R, R′ = alkyl, aryl

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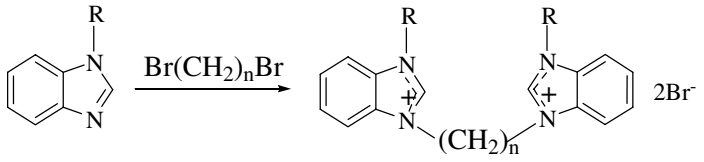
Research in this area was motivated principally by the use of these complexes as catalyst precursors. Many different catalytic applications of NHC complexes have now been described.[11–13] Palladium-catalysed cross-coupling reactions are particularly attractive because of their versatility for forming of C–C bonds.[14–16] The main advantages of the coupling processes are based on the ready availability of starting materials and the broad tolerance of palladium catalysts to various functional groups. These studies revealed the crucial role played by the ancillary ligands in the efficiency of these reactions. Sterically hindered, electron-rich alkyl phosphines[17] and carbene[18] ligands have received increasing interest in recent years. However, the phosphine ligands and the phosphine–palladium complexes are labile to air and moisture at high temperatures, placing significant limits on their synthetic utility. Therefore, from a practical point of view, the development of more stable ligands leading to more reactive catalysts is of importance for palladium-catalysed Heck and Suzuki coupling reactions. Recently, nucleophilic *N*-heterocyclic carbenes (NHCs),[19] with stronger σ-donor properties than bulky tertiary phosphines,[20] have emerged as a new family of ligands. In contrast to metal phosphine complexes, the metal–NHC complexes appear to be extraordinarily stable towards heat, air and moisture due to the high dissociation energies of the metal–carbon bond.[21]

The ancillary ligand (NHC) coordinated to the metal centre has a number of important roles in homogeneous catalysis such as providing a stabilizing effect and governing activity and selectivity by steric and electronic parameters. The number, nature and position of the substituents on the



1 **2**

2a R = $CH_2C_6H_2(CH_3)_3$-2,4,6 n = 1
2b R = $CH_2C_6H_2(CH_3)_3$-2,4,6 n = 2
2c R = $CH_2C_6H_2(CH_3)_3$-2,4,6 n = 3
2d R = $CH_2C_6H_2(CH_3)_3$-2,4,6 n = 4
2e R = $CH_2C_6H_2(OCH_3)_3$-3,4,5 n = 2
2f R = $CH_2C_6H_2(OCH_3)_3$-3,4,5 n = 4

Scheme 1. Synthesis of ligand precursors.

nitrogen atom(s) and/or NHC ring have been found to play a crucial role in driving the catalytic activity. While many modifications to the five-membered ring of the ligand aryl substituent have been described, relatively little attention has been given to the effect of the hetero ring size.[22]

For the present study, we selected the bis(benzimidazolidin-2-ylidene) precursors (**2**). This choice was guided by several considerations. An important characteristic of the carbene ligands in active complexes is their strong electron donating effect. In the course of our search for NHC-based ligands, we have already reported on the use of an *in situ*-formed imidazolidin-2-ylidenepalladium(II) system which shows high activities in various coupling reactions of aryl bromides and chlorides.[23–25] In order to obtain an even more stable and active system we have investigated benzo-annelated derivatives.[26,27]

In order to find more efficient palladium catalysts, we prepared a series of new bis(benzimidazolium) salts, **2a–f** (Scheme 1), containing the benzyl moiety, and we report here *in-situ* Pd-carbene based catalytic systems for the Heck and Suzuki coupling reactions in aqueous media.

EXPERIMENTAL

All reactions for the preparation of 1-alkylbenzimidazole (**1**) and bis(benzimidazolium) salts[27,28] (**2a–f**) were carried out under argon using standard Schkenk-type flasks. Test reactions for the catalytic activity of catalysts in the Suzuki and Heck cross-coupling reactions were carried out in air. All reagents were purchased from Aldrich Chemical Co. The solvents were distilled prior to use: Et_2O over Na, DMF over BaO, and EtOH over Mg.

All ^{1}H and ^{13}C-NMR were performed in DMSO-d_6. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed by Tubıtak (Ankara, Turkey) Microlab.

Synthesis of 3,3′-bis(2,4,6-trimethylbenzyl)-1,1′-methylenedi(benzimidazolium)dibro-mide (2a)

To a solution of 1-(2,4,6-trimethylbenzyl)benzimidazole (2.50 g; 10 mmol) in dimethylformamide (DMF; 10 ml) was added slowly dibromomethane (0.86 g, 5 mmol) at 25 °C and the resulting mixture was stirred at RT for 6 h and heated for 10 h at 80 °C. Diethyl ether (15 ml) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3 × 15 ml), and dried under vacuum. The precipitate was then crystallized from ethanol–diethyl ether (4 : 1); m.p. 276–277 °C, with a yield of 2.83 g, 84%; $\nu_{(CN)} = 1570$ cm^{-1}. Anal. found: C, 62.35; H, 5.65; N, 8.30. Calcd for $C_{35}H_{38}N_4Br_2$: C, 62.32; H, 5.68; N, 8.31%.

^{1}H NMR (δ, DMSO): 9.47 [s, 2H, NC*H*N]; 8.44 and 8.22 [d, 4H, $J = 7.6$ Hz, NC_6H_4N]; 7.79 [quint, 4H, $J = 8.8$ Hz, NC_6H_4N]; 7.13 [s, 2H, $-CH_2-$]; 7.07 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 5.57 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 2.34 and 2.21 [s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6]. ^{13}C {H}NMR (δ, DMSO): 143.3 [NCHN]; 139.4, 131.8, 130.2 and 125.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 139.8, 132.1, 128.3, 127.8, 114.9 and 114.2 [NC_6H_4N]; 46.0 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 55.4 [$-CH_2-$]; 19.9 and 21.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6].

Synthesis of 3,3′-bis(2,4,6-trimethylbenzyl)-1,1′-ethylenedi(benzimidazolium)dibromide (2b)

Compound **2b** was prepared in the same way as **2a**, from 1-(2,4,6-trimethylbenzyl)-benzimidazole (2.50 g; 10 mmol) and 1,2-dibromoethane (0.94 g, 5 mmol) to give white crystals (yield: 3.13 g, 91%); m.p. 287.5–288.0 °C; $\nu_{(CN)} = 1557$ cm^{-1}.

Anal. found: C, 62.78; H, 5.84; N, 8.10. Calcd for $C_{36}H_{40}N_4Br_2$: C, 62.80; H, 5.86; N, 8.14%.

^{1}H NMR (δ, DMSO): 9.16 [s, 2H, NC*H*N]; 8.12 and 7.77 [d, 4H, $J = 8.4$ Hz, NC_6H_4N]; 7.71 and 7.61 [t, 4H, $J = 7.6$ Hz, NC_6H_4N]; 5.06 [s, 4H, $-CH_2CH_2-$]; 6.98 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 5.55 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 2.29 and 2.14 [s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6]. ^{13}C{H} NMR (δ, DMSO): 142.5 [NCHN], 139.1, 131.5, 130.2 and 126.0 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 139.6, 132.0, 131.9, 127.7,

114.6 and 113.7 [NC_6H_4N]; 46.2 $CH_2C_6H_2(CH_3)_3$-2,4,6]; 45.9 [$-CH_2CH_2-$]; 19.9 and 21.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6].

Synthesis of 3,3′-bis(2,4,6-trimethylbenzyl)-1,1′-propylenedi(benzimidazolium)-dibromide (2c)

This compound was prepared in the same way as **2a** from 1-(2,4,6-trimethylbenzyl)-benzimidazole (2.50 g; 10 mmol) and 1,3-dibromopropane (1.00 g, 5 mmol) to give white crystals (yield: 3.05 g, 87%); m.p. 185.0–186.0 °C; $\nu_{(CN)} = 1562\ cm^{-1}$. Anal. found: C, 63.28; H, 6.00; N, 7.95. Calcd for $C_{37}H_{42}N_4Br_2$: C, 63.25; H, 6.03; N, 7.97%.

^{1}H NMR (δ, DMSO): 9.07 [s, 2H, NC*H*N]; 8.13 and 7.71 [m, 8H, NC_6H_4N]; 4.54 [t, $J = 8.0$ Hz, 4H, $-CH_2CH_2CH_2-$]; 2.47 [quint, 2H, $J = 8.0$ Hz, $-CH_2CH_2CH_2-$]; 6.99 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 5.59 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 2.26 and 2.22 [s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6]. ^{13}C{H} NMR (δ, DMSO): 141.9 [NCHN]; 139.1, 131.7, 130.2 and 126.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 139.4, 132.3, 132.1, 127.4, 114.6 and 114.5 [NC_6H_4N]; 45.9 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 44.8 and 56.7 [$-CH_2CH_2CH_2-$]; 20.1 and 21.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6].

Synthesis of 3,3′-bis(2,4,6-trimethylbenzyl)-1,1′-butylenedi(benzimidazolium)dibro-mide (2d)

This compound was prepared in the same way as **2a** from 1-(2,4,6-trimethylbenzyl)-benzimidazole (2.50 g; 10 mmol) and 1,4-dibromobuthane (1.08 g, 5 mmol) to give white crystals (yield: 3.18 g, 89%); m.p. 162.5–163.0 °C; $\nu_{(CN)} = 1561\ cm^{-1}$. Anal. found: C, 63.66; H, 6.20; N, 7.84. Calcd for $C_{38}H_{44}N_4Br_2$: C, 63.69; H, 6.19; N, 7.82%.

^{1}H NMR (δ, DMSO): 9.19 [s, 2H, NC*H*N]; 8.10 and 7.71 [m, 8H, NC_6H_4N]; 4.48 [m, 4H, $-CH_2CH_2CH_2CH_2-$]; 1.82 [m, 4H, $-CH_2CH_2CH_2CH_2-$]; 6.97 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 5.62 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 2.26 and 2.20 [s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6]. ^{13}C{H}NMR (δ, DMSO): 142.9 [NCHN], 139.0, 131.9, 130.2 and 126.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 139.3, 132.3, 132.2, 127.4, 114.7 and 114.5 [NC_6H_4N]; 56.7 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 46.8 and 45.8 [$-CH_2CH_2CH_2CH_2-$]; 20.0 and 20.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6].

Synthesis of 3,3′-bis(3,4,5-trimethoxybenzyl)-1,1′-ethylenedi(benzimidazolium)dibro-mide (2e)

Compound **2e** was prepared in the same way as **2a** from 1-(3,4,5-trimethoxybenzyl)-benzimidazole (2.98 g; 10 mmol) and 1,2-dibromoethane (0.94 g, 5 mmol) to give white crystals (yield: 3.64 g, 93%); m.p. 285.0–286.0 °C, $\nu_{(CN)} = 1595\ cm^{-1}$. Anal. found: C, 55.13; H, 5.10; N, 7.15. Calcd for $C_{36}H_{40}N_4O_6Br_2$: C, 55.11; H, 5.14; N, 7.14%.

^{1}H NMR (δ, DMSO): 10.10 [s, 2H, NC*H*N]; 8.06 and 7.78 [d, 4H, $J = 8.4$ Hz, NC_6H_4N]; 7.56 and 7.38 [t, 4H, $J = 7.6$ Hz, NC_6H_4N]; 5.18 [s, 4H, $-CH_2CH_2-$]; 6.96 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 5.61 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.77 and 3.64 [s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]. ^{13}C{H} NMR (δ, DMSO): 153.9 [NCHN]; 143.7, 138.7, 129.4 and 107.6 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 131.9, 131.4, 127.5, 127.3, 114.7 and 113.6 [NC_6H_4N]; 60.7 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 51.1 [$-CH_2CH_2$-]; 56.9 and 56.7 [$CH_2C_6H_2(OCH_3)_3$-3,4,5].

Synthesis of 3,3′-bis(3,4,5-trimethoxybenzyl)-1,1′-butylenedi (benzimidazolium)-dibromide (2f)

This compound was prepared in the same way as **2a** from 1-(3,4,5-trimethoxybenzyl)-benzimidazole (2.98 g; 10 mmol) and 1,4-dibromobuthane (1.08 g, 5 mmol) to give white crystals (yield: 3.33 g, 82%); m.p. 164.5–165.0 °C; $\nu_{(CN)} = 1593\ cm^{-1}$. Anal. found: C, 56.19; H, 5.45; N, 6.90. Calcd for $C_{38}H_{44}N_4O_6Br_2$: C, 56.17; H, 5.46; N, 6.89%.

^{1}H NMR (δ, DMSO): 10.20 [s, 2H, NC*H*N]; 8.12 and 7.65 [m, 8H, NC_6H_4N]; 4.61 [m, 4H, $-CH_2CH_2CH_2CH_2-$]; 2.06 [m, 4H, $-CH_2CH_2CH_2CH_2-$]; 6.99 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 5.66 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.73 and 3.61 [s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]. ^{13}C{H} NMR (δ, DMSO): 153.8 [NCHN]; 143.0, 138.4, 129.8 and 107.3 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 131.9, 131.6, 127.4, 127.3, 114.7 and 114.5 [NC_6H_4N]; 60.7 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 50.8 [$-CH_2CH_2CH_2CH_2-$]; 46.9 [$-CH_2CH_2CH_2CH_2-$]; 56.8 and 56.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5].

General procedure for the Heck coupling reactions

$Pd(OAc)_2$ (1.5 mmol%), bis(benzimidazolium) bromides, **2** (1.5 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), C_2CO_3 (2 mmol), water (3 ml)-DMF (3 ml) were added to a small Schlenk tube and the mixture was heated at 80 °C for 1 h. At the conclusion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1 : 5), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and yields are based on aryl bromide.

General Procedure for the Suzuki Coupling reaction

$Pd(OAc)_2$ (1.5 mmol %), bis(benzimidazolium) bromides, **2** (1.5 mmol%), aryl chloride (1.0 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (2 mmol), water (3 ml) and DMF (3 ml) were added to a small Schlenk tube and the mixture was heated at 80 °C for 1 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and yields are based on aryl chloride.

RESULTS AND DISCUSSION

In the following sections we discuss the synthesis and characterization of the bis(benzimidazolium) bromides (**2**), their use in the Heck and Suzuki coupling reactions, and the results of these studies.

Synthesis and characterization of the salts, 2

According to Scheme 1, the salts (**2**) were obtained in almost quantitative yield by quarternization of 1-alkylbenzimidazole

(**1**) in DMF with $Br(CH_2)_nBr$ ($n = 1–4$).[28] The salts are air- and moisture-stable both in the solid state and in solution.

The structures of **2a–f** were determined by their characteristic spectroscopic data and elemental analyses. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^1H-decoupled mode at 143.3, 142.5, 141.9, 142.9, 153.9 and 153.8 ppm, respectively, for benzimidazolium bromides **2a–f**. The ^1H NMR spectra of the benzimidazolium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets in the 9.47, 9.16, 9.07, 9.19, 10.10 and 10.20 ppm, respectively, for **2a–f.** The IR data for benzimidazolium salts **2a–f** clearly indicate the presence of the —C═N– group with a ν(C═N) vibration at 1570, 1557, 1562, 1561, 1595 and 1593 cm^{-1} respectively for **2a–f**. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolium salts.[27,28] An important feature of the ligand precursors (**2**) is their easy preparation.

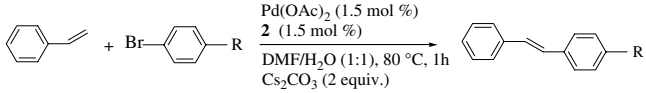
The Heck reaction

Heck reactions, typically catalysed by palladium complexes in solution, are of growing interest in organic and fine-chemical synthesis. The Heck reaction[29,30] has been shown to be very useful for the preparation of disubstituted olefins in particular. The rate of the coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, Heck reactions conducted with a tertiary phosphine[31] or NHC[13,32] complexes often require high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we surveyed Cs_2CO_3, K_2CO_3 and K_3PO_4. Finally, we found that use of 1.5% mol $Pd(OAc)_2$, 1.5 mol% **2**, and 2 equiv. Cs_2CO_3 in DMF–H_2O (1 : 1) at 80 °C led to the best conversion within 1 h. We initially tested the catalytic activity of $Pd(OAc)_2$–**2a** for the coupling of 4-bromoacetophenone with styrene (Table 1, entry 1).

A control experiment indicated that the coupling reaction did not occur in the absence of **2a**. Under the determined reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups react with styrene, affording the coupled products in excellent yields. As expected, electron-deficient bromides were beneficial for the conversions. Enhancements in activity, although less significant, are also observed using 4-bromoacetophenone instead of 4-bromobenzaldehyde (entries 1–5 and 7–12, respectively).

A systematic study on the substituent effect in the bis(benzimidazolium) salts **2** indicated that the 3,3′-di(benzyl)-1,1′-ethylenedi(benzimidazolium) (**2b, 2e**) notably increased the reaction rate and the yield of the product. These results indicated that the catalytic system generated *in situ* from bis(benzimidazolium) salts and $Pd(OAc)_2$ has an activity which is superior or comparable to the imidazolinium–$Pd(OAc)_2$ system.[23–25] However, chloroarenes basically do not react under standard conditions, and yields are less than 4%.

Table 1.



Entry	R	2	Yield (%)
1	$COCH_3$	**a**	92
2	$COCH_3$	**b**	97
3	$COCH_3$	**c**	94
4	$COCH_3$	**d**	94
5	$COCH_3$	**e**	95
6	$COCH_3$	**f**	92
7	CHO	**a**	93
8	CHO	**b**	90
9	CHO	**c**	95
10	CHO	**d**	93
11	CHO	**e**	95
12	CHO	**f**	92
13	H	**a**	87
14	H	**b**	90
15	H	**c**	89
16	H	**d**	85
17	H	**e**	91
18	H	**f**	87
19	OCH_3	**a**	79
20	OCH_3	**b**	87
21	OCH_3	**c**	84
22	OCH_3	**d**	86
23	OCH_3	**e**	89
24	OCH_3	**f**	82
25	CH_3	**a**	83
26	CH_3	**b**	88
27	CH_3	**c**	80
28	CH_3	**d**	85
29	CH_3	**e**	91
30	CH_3	**f**	77

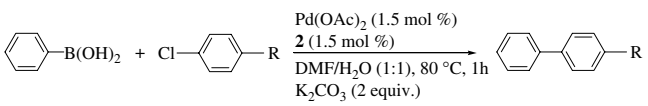
Reaction conditions: 1.0 mmol R-C_6H_4X-*p*, 1.5 mmol styrene, 2 mmol Cs_2CO_3, 1.5 mmol% $Pd(OAc)_2$, 1.5 mmol% **2**, water (3 ml) and DMF (3 ml). Purity of compounds was checked by NMR and yields are based on arylbromide; 80 °C, 1 h.

The Suzuki coupling

Palladium-catalysed coupling via Suzuki reaction has become, over the last 10 years, the method of choice for biaryl and heterobiaryl synthesis.[33] These moieties are widely present in numerous classes of organic compounds, such as natural products, pharmaceuticals, agrochemicals and ligands for asymmetric synthesis and in new materials, such as liquid crystals.[34] The reaction generally results in excellent yields when performed at temperatures of 80–100 °C with aryl iodides and bromides. Recently, the Suzuki reaction of aryl chlorides catalysed by palladium–tertiary phosphine[31] and palladium–NHC[35–38] systems has been studied extensively due to the economically attractive nature of the starting materials.

Here, various bis(benzimidazolium) salts (**2a–f**) were compared as ligand precursors under the same reaction conditions. To survey the reaction parameters for the catalytic Suzuki reaction, we chose to examine Cs_2CO_3, K_2CO_3 and K_3PO_4 as solvent and DMF–H_2O (1 : 1) and dioxane as solvent. We found that the reactions performed in DMF–H_2O (1 : 1) with Cs_2CO_3 or K_2CO_3 as the base at 80 °C appeared to be best. We started our investigation with the coupling of chlorobenzene and phenylboronic acid, in the presence of $Pd(OAc)_2$–**2**. Table 2 summarizes the results obtained in the presence of **2a–f** (Table 2, entries 1–6).

Table 2.



Entry	R	2	Yield (%)
1	H	**a**	88
2	H	**b**	81
3	H	**c**	83
4	H	**d**	81
5	H	**e**	85
6	H	**f**	90
7	CH_3	**a**	75
8	CH_3	**b**	81
9	CH_3	**c**	78
10	CH_3	**d**	73
11	CH_3	**e**	83
12	CH_3	**f**	77
13	OCH_3	**a**	82
14	OCH_3	**b**	79
15	OCH_3	**c**	89
16	OCH_3	**d**	79
17	OCH_3	**e**	88
18	OCH_3	**f**	84
19	$COCH_3$	**a**	91
20	$COCH_3$	**b**	98
21	$COCH_3$	**c**	97
22	$COCH_3$	**d**	96
23	$COCH_3$	**e**	97
24	$COCH_3$	**f**	90
25	CHO	**a**	85
26	CHO	**b**	88
27	CHO	**c**	91
28	CHO	**d**	90
29	CHO	**e**	93
30	CHO	**f**	86

Reactions conditions: 1.0 mmol R-C_6H_4Cl-*p*, 1.2 mmol phenylboronic acid, 2 mmol K_2CO_3, 1.5 mmol% $Pd(OAc)_2$, 1.5 mmol% **2**, water (3 ml) and DMF (3 ml). Purity of compounds was checked by NMR and yields are based on arylchloride. All reactions were monitored by GC; 80 °C, 1 h.

The scope of the coupling with respect to the aryl chloride component was also investigated. Specifically, **2b** and **2e** are effective ligand precursors for the coupling of unactivated, activated and deactivated chlorides (entries 1–25). With chlorobenzene, 4-chloroanisole, 4-chloroacetophenone and 4-chlorobenzaldehyde a similar activity sequence was observed. In summary, we have demonstrated that *in situ* generated benzimidazolidin-2-ylidene complexes of palladium are very effective for Suzuki coupling reactions.

CONCLUSIONS

We are pleased to find that, among the various NHC precursurs, bis(benzimidazolium) salts (**2**) are excellent ligand precursors for the different functionalization of aryl halides, in particular, aryl chlorides for Suzuki reaction. The cross-coupling results obtained using a $Pd(OAc)_2$–**2** mixture do not necessarily indicate a palladium–carbene complex as the active catalyst species. Depending on the type of coupling reaction, excellent yields of the desired products were obtained. In general, **2b** and **2e**-based catalysts appear to be more efficient for the Heck reactions of aryl bromides, but their activity is much lower for the coupling of aryl chlorides. Once again, we observed that the *in situ* formed Pd–NHC catalysts, which consist of mixtures of palladium and ligands, gave better yields in the coupling reactions compared with the isolated carbene palladium(II) complexes. It is believed that there might be special reaction conditions in which a different order of reactivity may be observed. Detailed investigations, focusing on benzimidazolin-2-ylidene substituent effects, functional group tolerance and catalytic activity in this and other coupling reactions, are ongoing.

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