Heteroatom Chemistry
Volume 15, Number 6, 2004

Palladium-Catalyzed Suzuki Reaction Using 1,3-Dialkylbenzimidazol-2-ylidene Ligands in Aqueous Media

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Received 27 April 2004

ABSTRACT: *From readily available starting compounds, six functionalized 1,3-dialkylbenzimidazolium salts (***2a–c** *and* **4a–c***) have been prepared and characterized by conventional spectroscopic methods and elemental analyses. A highly effective, easy to handle, and environmentally benign process for palladium-mediated Suzuki cross-coupling was developed. The in situ prepared three-component systems* $Pd(OAc)_2$*/1,3-dialkylbenzimidazolium chlorides and* Cs_2CO_3 *catalyze quantitatively the Suzuki cross-coupling of deactivated aryl chlorides.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:419–423, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20034

INTRODUCTION

Transition-metal-catalyzed cross-coupling is a versatile and highly useful transformation, which yields a variety of organic compounds. In particular, the Suzuki cross-coupling reaction, which is the palladium-catalyzed cross-coupling reaction of organic halides with organoboron compounds, represents one of the most important methods of forming sp^2–sp^2 carbon–carbon bonds in synthetic chemistry, as well as in industrial applications [1]. In the past few years, many attempts have been made to develop effective palladium complexes, which can act as highly active catalysts for this reaction [2]. These studies revealed the crucial role played by the ancillary ligands in increasing the efficiency of these reactions. Sterically hindered, electron-rich alkyl phosphines [3] and carbene [4] ligands have received increasing interest in recent years. However, the development of the new ligands or the application of existing ligands in this reaction, particularly the one involving aryl chlorides as substrates, is still of considerable importance. Since the discovery of stable imidazoline-2-ylidenes [5], much interest has been generated in the chemistry of both free heteroatom carbenes and metal complexes of these ligands. Most recently, the synthesis and application of 1,3-dialkylimidazolium salts have been reviewed [6]. The late transition metal *N*-heterocyclic carbene complexes have been employed as catalysts for the formation of furans [7], cyclopropanation [8], olefin metathesis [9] and cycloisomerization [10], and Heck and Suzuki coupling reactions [11].

Recently, a major study on Suzuki reactions has focused on increasing the activity of the catalysts and

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Contract grant sponsor: Technological and Scientific Research Council of Turkey (TÜBİTAK).
Contract grant number: TÜBİTAK COST D17.
Contract grant sponsor: Inönü University Research Fund.
Contract grant number: BAP 2003/66.

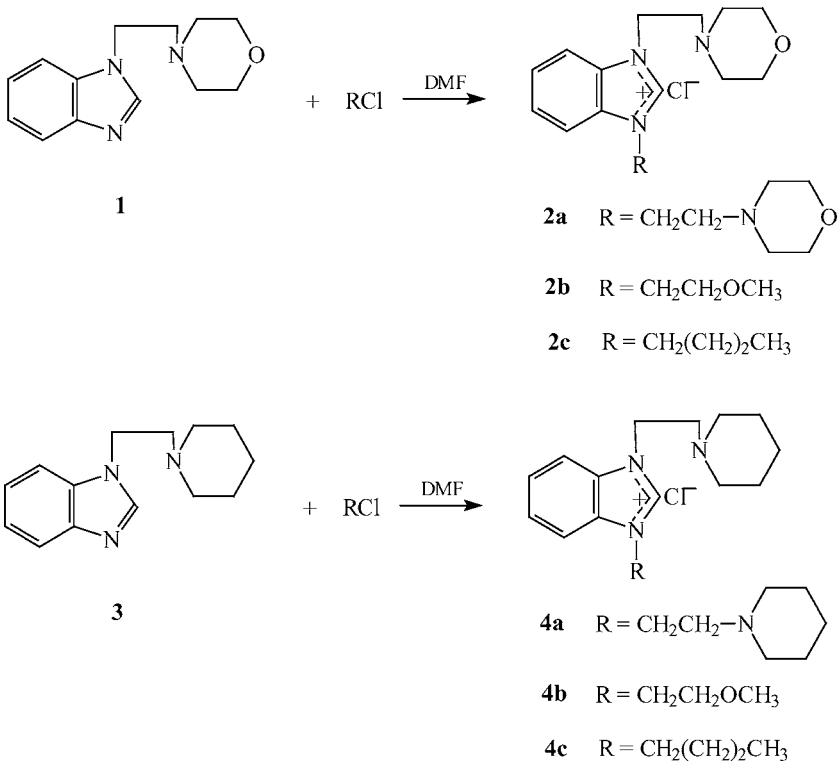
decreasing the catalyst loading. This has included the use of additives, the modification of the catalyst, and changing the solvents. A major advance achieved by increasing the catalytic activity is the extension of the Suzuki reaction to unactivated aryl chlorides, as noted by the research groups of Buchwald [3], Fu [12], and Herrmann [13], as well as several other groups. Clearly, the use of water as a solvent for chemical reactions has both economical and environmental advantages because it is inexpensive, abundant, nontoxic, nonflammable, and readily separable from organic compounds [14]. There have been a number of reports of the palladium-mediated Suzuki reaction being performed using water as a solvent [15] that relates to the coupling of the aryl boronic acids with aryl iodides or activated bromide and aryl chlorides but involves the use of an oxime-carbapalladacycle as the catalyst [16]. Recently, we have developed improved procedures for Heck and Suzuki reactions of aryl chlorides by making use of novel ligands 1,3-bis(dialkyl)imidazolium salts, 1-alkylimidazoline, and α-bis(imine) [17].

In order to find more efficient palladium catalysts we have prepared a series of new 1,3-dialkylbenzimidazolium chlorides (**2a–c** and **4a–c**, Scheme 1),containing a benzimidazole ring and we report here in situ Palladium–carbene based catalytic system for the Suzuki coupling reaction in aqueous media.

RESULTS AND DISCUSSION

Dialkylbenzimidazolium salts (**2a–c** and **4a–c**) are conventional NHC precursors. According to Scheme 1, the salts **2a–c** and **4a–c** were obtained in almost a quantitative yield by quarternazition of 1-alkylbenzimidazoles **1** and **3** in DMF with functionalized alkyl halides [18,19]. The salts are air- and moisture-stable both in the solid state and in solution. The structures of **2a–c** and **4a–c** were determined by their characteristic spectroscopic data and elemental analyses (experimental section). ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared in the ^{1}H-decoupled mode as a singlet at $\delta = 144.6 \pm 0.8$ ppm. In the ^{1}H NMR spectra for C(2)—H a sharp singlet at $\delta = 10.77 \pm 0.76$ ppm was observed. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolium salts [19]. The IR data clearly indicate the presence of the —C=N- group with a ν(C=N) vibration at $1563 \pm 3 cm^{-1}$.

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions. A wide range

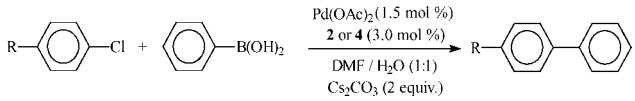


SCHEME 1

of bases and solvents, as well as catalysts, have been employed with varying degrees of success according to the substrates.

To find optimum conditions a series of experiments has been performed with 4-chloroanisole and phenylboronic acid as model compounds. As a base, Cs_2CO_3 was the best choice in water/ DMF systems. In addition, the reactions were performed in air and without degassing the water prior to use. After having established the optimized coupling reaction conditions, the scope of the reaction and efficiencies of the salts were evaluated by investigating the coupling of $C_6H_5B(OH)_2$ with various *p*-substituted aryl chlorides. The results are shown in Table 1. Under those conditions, *p*-chloroanisole, *p*-chlorobenzaldehyde, *p*-chlorotoluene, *p*-chloroacetophenone, and chlorobenzene react very cleanly with phenylboronic acid in good yields (Table 1, entries 2, 5, 8, 14, 22, and 29).

TABLE 1 The Suzuki Coupling of Aryl Chloride with Phenylboronic acid



Entry	*R*	*Salt*	*Yield*[a,b,c,d] *(%)*
1	OCH_3	**2a**	81
2	OCH_3	**2b**	92
3	OCH_3	**2c**	84
4	OCH_3	**4a**	83
5	OCH_3	**4b**	97
6	OCH_3	**4c**	86
7	CHO	**2a**	81
8	CHO	**2b**	97
9	CHO	**2c**	88
10	CHO	**4a**	89
11	CHO	**4b**	95
12	CHO	**4c**	82
13	CH_3	**2a**	81
14	CH_3	**2b**	90
15	CH_3	**2c**	79
16	CH_3	**4a**	79
17	CH_3	**4b**	89
18	CH_3	**4c**	85
19	$COCH_3$	**2a**	90
20	$COCH_3$	**2b**	96
21	$COCH_3$	**2c**	84
22	$COCH_3$	**4a**	92
23	$COCH_3$	**4b**	95
24	$COCH_3$	**4c**	91
25	H	**2a**	79
26	H	**2b**	88
27	H	**2c**	76
28	H	**4a**	80
29	H	**4b**	90
30	H	**4c**	79

[a]Reactions conditions: 1.0 mmol of R-C_6H_4Cl-*p*, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1.50 mol % $Pd(OAc)_2$, 3.0 mol % **2** or **4**, water (3 mL)–DMF (3 mL).
[b]Purity of compounds is checked by NMR and yields are based on arylchloride.
[c]All reactions are monitored by TLC.
[d]80°C, 6 h.

Table 1 summarizes our results from the screening of six benzimidazolium salts for Suzuki cross-coupling reaction. Several trends are readily apparent. First, the use of saturated NHC ligand precursors **2a–c** and **4a–c** allowed lower reaction temperatures (80°C), shorter reaction times, and lower base loadings in aqueous media. The procedure is simple and does not require induction periods. Second, the scope of this reaction is broad and includes aryl chlorides that are activated or deactivated. Third, all complexes led to good conversions at low catalyst concentration (1.5 mol %). It is evident that the NHC precursors that contain the electron-donating methoxyethyl substituent (**2c**, **4c**) are the most effective of the salts examined. The coordinating ability of the alkoxy group may be an important contributor to the increase in reactivity, as has been demonstrated by previous examples [20].

CONCLUSION

From readily available starting compounds, six 1,3-dialkylbenzimidazolium salts (**2a–c** and **4a–c**) have been prepared and characterized. A convenient and highly user-friendly method for Suzuki cross-coupling reaction is presented which employs a catalyst formed in situ from $Pd(OAc)_2$, the readily accessible and fully air stable benzimidazolium salt. The new ligand family allows highly efficient coupling reactions of electron-rich as well as electron-poor aryl chlorides with phenylboronic acid under mild conditions. This oncept for making catalysts in situ opens the way for the discovery of many new catalysts via the interaction of commercially available metal complexes and suitable electron-releasing ligands. To further exploit the advantageous properties displayed by the palladium/benzimidazolin-2-ylidene systems, catalytic investigations focusing on a number of cross-coupling reactions are ongoing.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H) and 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, and coupling constants (J) in Hz. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer; the wave numbers are given in cm^{-1}. Melting points were measured

in open capillary tubes with an Electrothermal-9200 melting point apparatus and were uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

*1,3-Di(2-morpholineethyl)benzimidazolium chloride (**2a**)*

To a solution of 1-(2-morpholineethyl)benzimidazole (1.10 g, 4.76 mmol) in DMF (1 mL), 4-(2-chloroethyl)morpholine (0.72 g, 4.81 mmol) was added; the resulting solution was stirred for 1 h at room temperature and heated for 12 h at 80°C. Et_2O (10 mL) was added to the reaction mixture. A white solid was precipitated in this period. The precipitate was then crystallized from EtOH/Et_2O (1:2). Yield: 3.60 g, 90%, mp 184–186°C. IR, ν: 1562 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 3.22 (m, 8H, NCH_2CH_2O), 3.90 (m, 8H, NCH_2CH_2O), 3.80 (m, 4H, NCH_2CH_2N), 5.05 (t, $J = 5.6$ Hz, 4H, NCH_2CH_2N), 7.67–8.24 (m, 4H, Ar-*H*), 10.65 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 41.5 (N*C*H_2CH_2N), 51.9 (N*C*H_2CH_2O), 54.1 (NCH_2*C*H_2N), 63.7 (NCH_2*C*H_2O), 114.6, 127.3, 131.8 (Ar-*C*), 145.3 (2-*C*H). Found: C, 60.04; H, 7.89; N, 15.21%. Calcd for $C_{19}H_{29}N_4O_2Cl$: C, 59.91; H, 7.67; N, 14.70%.

*1-(2-Methoxyethyl)-3-(2-morpholineethyl)-benzimidazolium chloride (**2b**)*

This compound was prepared from 1-(2-morpholineethyl)benzimidazole (1.47 g, 6.36 mmol) and 2-methoxyethyl chloride (0.61 g, 6.40 mmol) in DMF (1 mL). Yield: 1.50 g, 72%, mp 127–128°C. IR, ν: 1564 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 2.67 (m, 4H, NCH_2CH_2O), 3.04 (m, 2H, NCH_2CH_2N), 3.35 (s, 3H, OCH_3), 3.69 (t, $J = 4.4$ Hz, 4H, NCH_2CH_2O), 3.96 (t, $J = 4.4$ Hz, 2H, CH_2CH_2OCH_3), 4.81 (t, $J = 4.8$ Hz, 2H, CH_2CH_2OCH_3), 4.81 (t, $J = 4.8$, 2H, NCH_2CH_2N), 7.61–7.81 (m, 4H, Ar-*H*), 11.33 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 44.2 (N*C*H_2CH_2N), 47.9 (*C*H_2CH_2OCH_3), 53.5 (N*C*H_2CH_2O), 56.2 (NCH_2*C*H_2N), 59.4 (O*C*H_3), 66.8 (NCH_2*C*H_2O), 70.6 (CH_2*C*H_2OCH_3), 112.9, 114.2, 127.1, 127.2, 131.4, 132.2 (Ar-*C*), 144.5 (2-*C*H). Found: C, 59.03; H, 7.89; N, 13.32%. Calcd for $C_{16}H_{24}N_3O_2Cl$: C, 58.97; H, 7.42; N, 12.89%.

*1-Butyl-3-(2-morpholineethyl)benzimidazolium chloride (**2c**)*

This compound was prepared from 1-(2-morpholineethyl)benzimidazoline (1.63 g, 7.06 mmol) and 1-butyl chloride (0.66 g; 7.11 mmol) in DMF (1 mL). Yield: 1.96 g, 86%, mp 137–138°C. IR, ν: 1560 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 0.94 (t, $J = 7.2$ Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.40 (hex., $J = 8$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.98 (p, $J = 8$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 2.66 (m, 4H, NCH_2CH_2O), 3.01 (m, 2H, NCH_2CH_2N), 3.63 (m, 4H, NCH_2CH_2O), 4.52 (t, $J = 7.2$ Hz, 2H, CH_2CH_2CH_2CH_3), 4.85 (m, 2H, NCH_2CH_2N), 7.60–7.80 (m, 4H, Ar-*H*), 11.52 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 13.7, 20.0, 47.6, 51.4 (*C*H_2*C*H_2*C*H_2*C*H_3), 44.0 (N*C*H_2CH_2N), 53.5 (N*C*H_2CH_2O), 56.2 (NCH_2*C*H_2N), 66.7 (NCH_2*C*H_2O), 113.2, 113.4, 127.2, 127.4, 131.4, 131.6 (Ar-*C*), 144.4 (2-*C*H). Found: C, 62.67; H, 8.45; N, 12.54%. Calcd for $C_{17}H_{26}N_3OCl$: C, 63.04; H, 8.09; N, 12.97%.

*1-3-Di(2-piperidineethyl)benzimidazolium chloride (**4a**)*

This compound was prepared from 1-(2-piperidineethyl)benzimidazole (1.30 g, 5.67 mmol) and 1-(2-chloroethyl)piperidine (0.85 g, 5.73 mmol) in DMF (1 mL). Yield: 1.61 g, 75%, mp 237–238°C. IR, ν: 1562 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 1.43 (m, 4H, $CH_2CH_2CH_2CH_2CH_2$), 1.76 (m, 8H, $CH_2CH_2CH_2CH_2CH_2$), 3.71 (m, 4H, NCH_2CH_2N), 3.61 (m, 8H, CH_2CH_2CH_2CH_2CH_2), 5.04 (m, 4H, NCH_2CH_2N), 7.68–8.22 (m, 4H, Ar-*H*), 11.28 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 22.3, 23.1, 42.1 (*C*H_2(*C*H_2)$_3$*C*H_2), 53.4, 54.5 (N*C*H_2*C*H_2N), 114.9, 127.6, 132.1 (Ar-*C*), 145.4 (2-*C*H). Found: C, 67.41; H, 9.23; N, 14.10%. Calcd for $C_{21}H_{33}N_4Cl$: C, 66.91; H, 8.82; N, 14.86%.

*1-(2-Methoxyethyl)-3-(2-piperidineethyl)-benzimidazolium chloride (**4b**)*

This compound was prepared from 1-(2-piperidineethyl)benzimidazole (1.98 g, 8.65 mmol) and 2-chloroethyl chloride (0.82 g, 11.31 mmol) in DMF (1 mL). Yield: 2.23 g, 80%, mp 146–147°C. IR, ν: 1560 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 1.37 (m, 6H, $CH_2CH_2CH_2CH_2CH_2$), 2.45 (m, 4H, CH_2CH_2CH_2CH_2CH_2), 3.26 (s, 3H, OCH_3), 3.28 (m, 2H, NCH_2CH_2N), 3.81 (t, $J = 4.8$ Hz, 2H, CH_2CH_2OCH_3), 4.74 (t, $J = 5$ Hz, 2H, CH_2CH_2OCH_3), 4.74 (t, $J = 5$ Hz, 2H, NCH_2CH_2N), 7.64–8.15 (m, 4H, Ar-*H*), 10.01 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 47.1 (N*C*H_2CH_2N), 47.4, 54.1 (*C*H_2(*C*H_2)$_3$*C*H_2), 56.0 (NCH_2*C*H_2N), 58.9 (CH_2*C*H_2OCH_3), 69.9 (O*C*H_3), 114.5, 114.7, 127.1, 127.2, 131.7, 131.8 (Ar-*C*), 143.9 (2-*C*H). Found: C, 63.74; H, 8.52; N, 13.21%. Calcd for $C_{17}H_{26}N_3OCl$: C, 63.04; H, 8.09; N, 12.97%.

*1-Butyl-3-(2-piperidineethyl)benzimidazolium chloride (**4c**)*

This compound was prepared from 1-(2-piperidineethyl)benzimidazole (1.56 g, 6.81 mmol) and

1-buthyl chloride (0.64 g, 6.87 mmol) in DMF (1 mL). Yield: 1,84 g, 84%, mp 156–157°C. IR, ν: 1565 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ: 0.90 (t, $J = 7.2$ Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.32 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.38 (m, 6H, $CH_2(CH_2)_3CH_2$), 1.89 (p, $J = 7.2$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 2.38 (m, 4H, $CH_2(CH_2)_3CH_2$), 2.74 (m, 2H, NCH_2CH_2N), 4.55 (t, J =7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$), 4.64 (m, 2H, NCH_2CH_2N), 7.64–8.13 (m, 4H, Ar-*H*), 10.07 (s, 1H, 2-C*H*). ^{13}C NMR ($CDCl_3$) δ: 14.4, 20.1, 31.7, 54.8 ($CH_2(CH_2)_2CH_3$), 24.6, 26.6, 45.4 ($CH_2(CH_2)_3CH_2$), 47.4, 56.2 (NCH_2CH_2N), 114.8, 114.9, 127.5, 132.0, 132.2 (Ar-*C*), 143.9 (2-*C*H). Found: C, 67.56; H, 8.12; N, 13.21%. Calcd for $C_{18}H_{28}N_3Cl$: C, 67.16; H, 8.76; N, 13.05%.

General Procedure for the Suzuki-Type Coupling Reactions

$Pd(OAc)_2$ (1.5 mmol %), 1,3-dialkylbenzimidazolium salt, **2a–c** and **4a–c** (3 mmol %), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), and water (3 mL)–DMF (3 mL) were added in a small Schlenk tube under argon and the mixture was heated at 80°C for 6 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, filtered through a pad of silicagel with copious washings, concentrated, and purified by flash chromatography on silicagel. Purity of compounds was checked by NMR and the yields are based on arylchloride.

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