Heteroatom Chemistry
Volume 16, Number 7, 2005

# Suzuki Reaction of Aryl Chlorides Using Saturated *N*-Heterocarbene Ligands

Ismail Özdemir,[1] Sedat Yaşar,[1] Serpil Demir,[1] and Bekir Çetinkaya[2]

[1]*Inönü University, Department of Chemistry, Faculty of Science and Art, , 44280 Malatya, Turkey*

[2]*Ege University, Department of Chemistry, Faculty of Science, , 35100 Bornova-İzmir, Turkey*

*Received 4 April 2005; revised 26 April 2005*

ABSTRACT: *From readily available starting materials, six 1,3-dialkyl-imidazolinium bromides (***2a–f***) have been prepared and characterized by conventional spectroscopic methods and elemental analyses. The incorporation of saturated N-heterocyclic carbenes into palladium precatalysts gives high catalyst activity in the Suzuki coupling of deactivated aryl chloride substrates in aqueous media. The complexes were generated in the presence of* $Pd(OAc)_2$ *by in situ deprotonation of* **2a–f**. © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:557–561, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20140

## *INTRODUCTION*

The palladium-catalyzed cross-coupling reaction of aryl halides with boronic acids (the Suzuki reaction) is one of the most efficient methods for construction of $C_{aryl}$–$C_{aryl}$ bonds and has found widespread use in organic and polymer syntheses [1]. Although several other cross-coupling reactions are available to produce biaryls, the Suzuki reaction has been the most used over the course of the last few years, since it has several advantages compared with other available methods. One of the advantages of the Suzuki reaction is the innocuous nature of boronic acids, which are generally nontoxic and thermally, air, and moisture stable. In addition to being environmentally safer, the handling and removal of boron-containing by-products is easy when compared with other organometallic reagents, especially in large-scale synthesis. Another key advantage is that the Suzuki reaction can be carried out under mild conditions and tolerates a variety of functional groups in the starting aryl halides and aryl boronic acids. It is now well established that almost any palladium catalyst precursor promotes the coupling of aryl iodides and bromides with organoboron compounds, under mild reaction conditions [2]. Moreover, significant advances have been recently achieved in catalyst design for the coupling of the less reactive and cheaper aryl chlorides [3]. For example, the replacement of the commonly used triarylphosphines ligands with bulky electron-rich phosphines or carbenes, generates very active catalysts for the coupling of aryl chlorides [4].

Recently, a major study on Suzuki reactions has focused on increasing the activity of the catalysts and 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 [5], Fu [6], and Herrmann [7] as well as several other groups. The use of water as a solvent for chemical reactions clearly has both economical and environmental advantages because it is inexpensive,

*Correspondence to:* Ismail Özdemir; e-mail: iozdemir@inonu.edu.tr.

Contract grant sponsor: Technological and Scientific Research Council of Turkey (TÜBİTAK).
Contract grant number: TÜBITAK TBAG-2474 (104T085).
Contract grant sponsor: Inönü University Research Fund.
Contract grant number: BAP 2005/42.

abundant, nontoxic, nonflammable, and readily separable from organic compounds [8]. There have been a number of reports of the palladium-mediated Suzuki reaction being performed using water as solvents [9] which 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 a catalyst [10]. Recently, we have developed improved procedures Heck and Suzuki reactions of aryl chlorides making use of novel ligands 1,3-dialkyl-imidazolinium salts [11], 1-alkylimidazoline, $\alpha$-bis(imine) [12].

Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions. In order to find more efficient palladium catalysts, we have prepared a series of new 1,3-dialkyl-imidazolinium salts, **2**, (Scheme 1), containing a saturated imidazole ring and we now report the use of the in situ generated catalytic system composed of commercially available and stable reagents, the $Pd(OAc)_2$ as palladium source, 1,3-dialkyl-imidazolinium salts (**2a–f**) as a carbene precursor and $Cs_2CO_3$ as a base for cross-coupling of aryl chlorides with phenyl boronic acid in aqueous media.

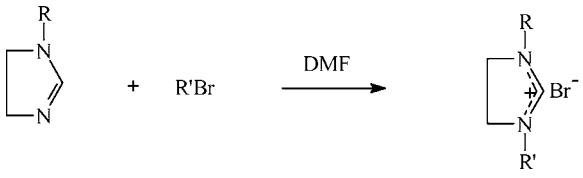
## *RESULTS AND DISCUSSION*

Dialkyl-imidazolinium salts, **2**, are conventional NHC precursors. According to Scheme 1, the salts **2a–f** were obtained in almost quantitative yield by quarternazition of 1-alkyl-imidazoline [13] in DMF with alkyl halides (Scheme 1). The structures of **2a–f** 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 as a typical singlet in the $^1H$-decoupled mode in the 157.5, 158.5, 159.2, 157.6, 158.7, and 158.5 ppm respectively for imidazolinium salts **2a–f**. The $^1H$ NMR spectra of the imidazolinium salts further supported the assigned structures; the resonances for C(2)—H were observed as sharp singlets in the 8.78, 8.94, 8.87, 9.06, 9.13, and 9.18 ppm respectively for **2a–f**. The IR data for imidazolinium salts **2a–f** clearly indicate the presence of the —C=N— group with a $\nu$(C=N) vibration at 1444, 1479, 1483, 1464, 1452, and 1456 $cm^{-1}$ respectively for **2a–f**. The NMR values are similar to those found for other 1,3-dialkylimidazolinium salts [11].

It has been found that the in situ formation of the ligand by deprotonation of the imidazolinium chlorides leads to significantly better results than the use of the preformed carbene [14].

To find optimum conditions, a series of experiments have been performed with 4-chlorotoluene 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 were shown in Table 1.

Under those conditions, *p*-chloroacetophenone, *p*-chlorotoluene, *p*-chlorobenzaldehyde, *p*-chloroanisole, and chlorobenzene react very cleanly with phenylboronic acid in goods yields (Table 1, entries

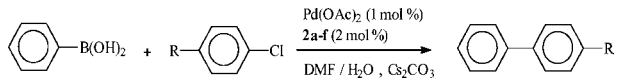



**1** **2**

| | | |
|---|---|---|
| **2a** | R = $CH_2C_6H_2(CH_3)_3$-2,4,6 | R' = $CH_2C_6H_4(o\text{-}C_6H_5)$ |
| **2b** | R = $CH_2CH_2OCH_3$ | R' = $CH_2C_6H_4(o\text{-}C_6H_5)$ |
| **2c** | R = $CH_2CH_2OC_2H_5$ | R' = $CH_2C_6H_4(o\text{-}C_6H_5)$ |
| **2d** | R = $CH_2C_6H_2(CH_3)_3$-2,4,6 | R' = $CH_2CH_2C_6H_5$ |
| **2e** | R = $CH_2CH_2OCH_3$ | R' = $CH_2CH_2C_6H_5$ |
| **2f** | R = $CH_2CH_2OC_2H_5$ | R' = $CH_2CH_2C_6H_5$ |

**SCHEME 1** Synthesis of 1,3-dialkylimidazolinium salts.

**TABLE 1** The Suzuki Coupling Reaction of Aryl Chlorides with Phenylboronic Acid




| *Entry* | *R* | *LHX* | *Yield(%)*[a,b,c,d] |
|---|---|---|---|
| 1 | $COCH_3$ | **2a** | 79 |
| 2 | $COCH_3$ | **2b** | 84 |
| 3 | $COCH_3$ | **2c** | 83 |
| 4 | $COCH_3$ | **2d** | 91 |
| 5 | $COCH_3$ | **2e** | 88 |
| 6 | $COCH_3$ | **2f** | 92 |
| 7 | $CH_3$ | **2a** | 75 |
| 8 | $CH_3$ | **2b** | 73 |
| 9 | $CH_3$ | **2c** | 71 |
| 10 | $CH_3$ | **2d** | 76 |
| 11 | $CH_3$ | **2e** | 80 |
| 12 | $CH_3$ | **2f** | 83 |
| 13 | CHO | **2a** | 89 |
| 14 | CHO | **2b** | 86 |
| 15 | CHO | **2c** | 89 |
| 16 | CHO | **2d** | 91 |
| 17 | CHO | **2e** | 89 |
| 18 | CHO | **2f** | 94 |
| 19 | $OCH_3$ | **2a** | 77 |
| 20 | $OCH_3$ | **2b** | 71 |
| 21 | $OCH_3$ | **2c** | 73 |
| 22 | $OCH_3$ | **2d** | 76 |
| 23 | $OCH_3$ | **2e** | 84 |
| 24 | $OCH_3$ | **2f** | 82 |
| 25 | H | **2a** | 79 |
| 26 | H | **2b** | 83 |
| 27 | H | **2c** | 85 |
| 28 | H | **2d** | 82 |
| 29 | H | **2e** | 86 |
| 30 | H | **2f** | 88 |

[a]Reaction conditions:1.0 mmol of R-$C_6H_4Cl$-*p*, 1.3 mmol of phenylboronic acid, 2 mmol $Cs_2CO_3$, 1 mmol % $Pd(OAc)_2$, 2 mmol % **2**, water (3 mL)-DMF (3 mL).
[b]Purity of compounds is checked by NMR, and yields are based on arylchloride.
[c]All reactions were monitored by GC.
[d]Temperature 50°C, 3 h.

4, 6, 12, 18, 23, and 30). From the results in Table 1, it is evident that the NHC precursors that contain electron-donating ethoxyethyl or methoxyethyl substituent (**2b, 2c, 2e, 2f**) 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 [15].

## *CONCLUSION*

We have developed a highly effective, easy to handle, and environmentally benign process for palladium-mediated Suzuki cross-coupling in aqueous media using saturated 1,3-dialkylimidazolidin-2-ylidene ligands. The procedure is simple and efficient toward various aryl chlorides and does not require induction periods. To further exploit the advantageous properties displayed by the palladium/*N*-heterocyclic carbene systems, catalytic investigations focusing on a number of cross-coupling reactions are ongoing in our laboratory.

## *EXPERIMENTAL*

$^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz ($^1$H), 75.47 MHz ($^{13}$C). Chemical shifts ($\delta$) are given in ppm relative to TMS, coupling constants ($J$) in Hz. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer, wave numbers in $cm^{-1}$. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

*1-(2,4,6-Trimethylbenzyl)-3-(2-phenylbenzyl)-imidazolinium bromide (***2a***):* To a solution of 1-(2,4,6-trimethylbenzyl) imidazoline (2.02 g, 10 mmol) in DMF (5 mL) was added slowly 2-phenylbenzyl bromide (2.49 g, 10.07 mmol) at 25°C and the resulting mixture was stirred at room temperature for 8 h. Diethylether (15 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethylether (3 × 10 mL), dried under vacuum, the crude product was recrystallized from ethanole/diethylether (2:1). mp 241–241.5°C, and the yield was 4.22 g, 94%, $\upsilon_{(CN)} = 1444$ $cm^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 2.26 and 2.27 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.32 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.66 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.51 and 3.61 (m, 4H, $NCH_2CH_2N$), 4.88 (s, 2H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 7.21–7.54 (m, 9H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 8.78 (s, 1H, NC*H*N); $^{13}$C{H}NMR ($\delta$, $CDCl_3$): 20.5 and 21.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 125.5, 128.9, 138.0, and 139.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 46.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 47.9 and 48.3 ($NCH_2CH_2N$), 50.5 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 127.9, 128.7, 129.0, 129.4, 129.9, 130.0, 130.4, 130.8, 139.9, 142.5 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 157.5 (NCHN). Found: C 69.45, H 6.51, N 6.26%. Calcd for $C_{26}H_{29}N_2Br$: C 69.48, H 6.50, N 6.23%.

*1-(Methoxyethyl)-3-(2-phenylbenzyl)imidazolinium bromide (***2b***)* was prepared in the same way as **2a** from 1-(2-methoxyethyl) imidazoline (1.28 g, 10 mmol) and 2-phenylbenzyl bromide (2.49 g, 10.07 mmol) to give white crystals of **2b** in 3.41 g, 91% yield, mp 91.5–92.0°C, $\upsilon_{(CN)} = 1479$ $cm^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 3.34 (s, 3H, $CH_2CH_2OCH_3$), 3.87

(t, *J* 11.2 Hz, 2H, $CH_2CH_2OCH_3$), 3.48 (t, *J* 11.2 Hz, 2H, $CH_2CH_2OCH_3$), 3.56 and 3.64 (t, *J* 3.6 Hz, 4H, $NCH_2CH_2N$), 4.81 (s, 2H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 7.27–7.52 (m, 9H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 8.94 (s, 1H, NCHN]; $^{13}C\{H\}$NMR ($\delta$, $CDCl_3$): 59.1 ($CH_2CH_2OCH_3$), 69.9 ($CH_2CH_2OCH_3$), 48.3 ($CH_2CH_2OCH_3$), 47.7 and 49.8 ($NCH_2CH_2N$), 50.6 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 128.0, 128.7, 128.9, 129.2, 129.5, 129.9, 130.5, 130.8, 140.1, 142.5 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 158.5 (NCHN). Found: C 60.83, H 6.15, N 7.50%. Calcd for $C_{19}H_{23}N_2OBr$: C 60.80, H 6.18, N 7.46%

*1-(Ethoxyethyl)-3-(2-phenylbenzyl)imidazolinium bromide (***2c***)* was prepared in the same way as **2a** from 1-(2-ethoxyethyl) imidazoline (1.42 g, 10 mmol) and 2-phenylbenzyl bromide (2.49 g, 10.07 mmol) to give white crystals of **2c** in 3.38 g, 87% yield, mp = 92–92.5°C, $\upsilon_{(CN)} = 1483$ cm$^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 1.12 (t, J 3.0 Hz, 3H, $CH_2CH_2OCH_2CH_3$), 3.47 (q, J 3.6 Hz, 2H, $CH_2CH_2OCH_2CH_3$), 3.51 and 3.53 (m, 4H, $CH_2CH_2OCH_2CH_3$), 3.50 and 3.89 (t, *J* 4.8 Hz, 4H, $NCH_2CH_2N$), 4.86 (s, 2H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 7.24–7.55 (m, 9H, $CH_2C_6H_4(o\text{-}C_6H_5)$, 8.87 (s, 1H, NCHN]; $^{13}C\{H\}$NMR ($\delta$, $CDCl_3$): 15.1 ($CH_2CH_2OCH_2CH_3$), 66.6 ($CH_2CH_2OCH_2CH_3$), 67.4 ($CH_2CH_2OCH_2CH_3$), 50.2 ($CH_2CH_2OCH_2CH_3$), 48.2 and 49.5 ($NCH_2CH_2N$), 47.6 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 127.8, 128.5, 128.7, 128.9, 129.2, 129.8, 130.2, 130.6, 139.9, 142.2 ($CH_2C_6H_4(o\text{-}C_6H_5)$, 159.2 (NCHN). Found: C 61.73, H 6.50, N 7.21%. Calcd for $C_{20}H_{25}N_2OBr$: C 61.70, H 6.47, N 7.19%.

*1-(2,4,6-Trimethylbenzyl)-3-(2-phenylethyl)imidazolinium bromide (***2d***)* was prepared in the same way as **2a** from 1-(2,4,6-trimethylbenzyl) imidazoline (2.02 g, 10 mmol) and 2-phenylethyl bromide (1.86 g, 10.05 mmol) to give white crystals of **2d** in 3.56 g, 92% yield, mp 205–205.5°C, $\upsilon_{(CN)} = 1464$ cm$^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 2.14 and 2.19 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.77 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.67 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.69 and 3.93 (t, *J* 9.6 and *J* 11.6 Hz, 4H, $NCH_2CH_2N$), 2.97 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 3.88 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 7.19 (m, 5H, $CH_2CH_2C_6H_5$), 9.06 (s, 1H, NCHN); $^{13}C\{H\}$NMR ($\delta$, $CDCl_3$): 20.3 and 21.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 125.4, 128.9, 137.9, and 139.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 49.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 48.2 and 49.1 ($NCH_2CH_2N$), 46.4 ($CH_2CH_2C_6H_5$), 33.8 ($CH_2CH_2C_6H_5$), 127.4, 129.1, 129.9, 136.7 ($CH_2CH_2C_6H_5$), 157.6 (NCHN). Found: C 65.13, H 7.00, N 7.25%. Calcd for $C_{21}H_{27}N_2Br$: C 65.11, H 7.02, N 7.23%.

*1-(Methoxyethyl)-3-(2-phenylethyl)imidazolinium bromide (***2e***)* was prepared in the same way as **2a** from 1-(2-methoxyethyl) imidazoline (1.28 g, 10 mmol) and 2-phenylethyl bromide (1.86 g, 10.05 mmol) to give white crystals of **2e** in 2.66 g, 85% yield, mp 70–70.5°C, $\upsilon_{(CN)} = 1452$ cm$^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 3.24 (s, 3H, $CH_2CH_2OCH_3$), 3.86 and 3.95 (m, 4H, $CH_2CH_2OCH_3$), 3.49 and 3.66 (t, *J* 4.8 Hz, 4H, $NCH_2CH_2N$), 2.97 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 3.81 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 7.21 (m, 5H, $CH_2CH_2C_6H_5$), 9.13 (s, 1H, NCHN); $^{13}C\{H\}$NMR ($\delta$, $CDCl_3$): 59.1 ($CH_2CH_2OCH_3$), 69.5 ($CH_2CH_2OCH_3$), 49.8 ($CH_2CH_2OCH_3$), 48.1 and 49.5 ($NCH_2CH_2N$), 49.1 ($CH_2CH_2C_6H_5$), 34.2 ($CH_2CH_2C_6H_5$), 127.3, 129.0, 129.1, 136.9 ($CH_2CH_2C_6H_5$), 158.7 (NCHN). Found C 53.65, H 6.76, N 8.95%. Calcd for $C_{14}H_{21}N_2OBr$: C 53.68, H 6.75, N 8.94%

*1-(Ethoxyethyl)-3-(2-phenylethyl)imidazolinium bromide (***2f***)* was prepared in the same way as **2a** from 1-(2-ethoxyethyl) imidazoline (1.42 g, 10 mmol) and 2-phenylethyl bromide (1.86 g, 10.05 mmol) to give white crystals of **2f** in 2.62 g, 80% yield, mp 83–84°C, $\upsilon_{(CN)} = 1456$ cm$^{-1}$. $^1$H NMR ($\delta$, $CDCl_3$): 0.99 (t, *J* 7.2 Hz, 3H, $CH_2CH_2OCH_2CH_3$), 3.33 (q, *J* 7.2 Hz, 2H, $CH_2CH_2OCH_2CH_3$), 3.81 and 3.89 (m, 4H, $CH_2CH_2OCH_2CH_3$), 3.44 and 3.57 (t, *J* 4.8 Hz, 4H, $NCH_2CH_2N$), 2.91 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 3.74 (t, *J* 7.2 Hz, 2H, $CH_2CH_2C_6H_5$), 7.11 (m, 5H, $CH_2CH_2C_6H_5$), 9.18 (s, 1H, NCHN); $^{13}C\{H\}$NMR ($\delta$, $CDCl_3$): 15.3 ($CH_2CH_2OCH_2CH_3$), 66.7 ($CH_2CH_2OCH_2CH_3$), 67.5 ($CH_2CH_2OCH_2CH_3$), 49.3 ($CH_2CH_2OCH_2CH_3$), 48.2 and 49.2 ($NCH_2CH_2N$), 49.9 ($CH_2CH_2C_6H_5$), 34.1 ($CH_2CH_2C_6H_5$), 127.2, 128.9, 129.0, 136.8 ($CH_2CH_2C_6H_5$), 158.5 (NCHN). Found C 55.03, H 7.10, N 8.55%. Calcd for $C_{15}H_{23}N_2OBr$: C 55.05, H 7.08, N 8.56%.

## *General Procedure for the Suzuki Coupling Reaction*

$Pd(OAc)_2$ (1.0 mmol %), 1,3-dialkylimidazolinium salts, **2** (2 mmol %), aryl chloride (1.0 mmol), phenylboronic acid (1.3 mmol), $Cs_2CO_3$ (2 mmol) water (3 mL)-DMF (3 mL) were added to a small Schlenk tube, and the mixture was heated at 50°C for 3 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. The purity of the compounds was checked by NMR and yields are based on arylchloride.

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