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Palladium-catalysed Suzuki reaction of aryl chlorides in aqueous media using 1,3-dialkylimidazolidin-2-ylidene ligands

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A highly effective, easy to handle and environmentally benign process for palladium-mediated Suzuki cross-coupling is developed. The *in situ* prepared three-component system $Pd(OAc)_2$–1,3-bis(alkyl)imidazolinium chlorides (2a–f) and Cs_2CO_3 catalyses quantitatively the Suzuki cross-coupling of deactivated aryl chlorides. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: palladium; imidazolidin-2-ylidene; aryl halides; phenylboronic acid; Suzuki coupling

INTRODUCTION

The palladium-catalysed cross-coupling of aryl halides with arylboronic acids to form biaryls has emerged as an extremely powerful tool in organic synthesis.[1–3] Ever since the first report in 1981 by Suzuki and co-workers on their preparation of biaryls,[2] a variety of improvements in catalyst precursors have been described. These studies revealed the crucial role played by the ancillary ligands in the efficiency of these reactions. Sterically hindered, electron-rich alky phosphines[5–7] and carbene[8–10] ligands have received increasing interest in recent years. However, the development of new ligands or applications of existing ligands in this reaction, particularly those involving aryl chlorides as substrates, is still of considerable importance. Since the discovery of stable imidazoline-2-ylidenes,[11] 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 was reviewed.[12,13] The late transition metal *N*-heterocyclic carbene (NHC) complexes have been employed as catalysts for the formation of furans,[14] cyclopropanation,[15–17] olefin metathesis[18–22] and cycloisomerization,[23,24] Heck and Suzuki coupling reactions.[25]

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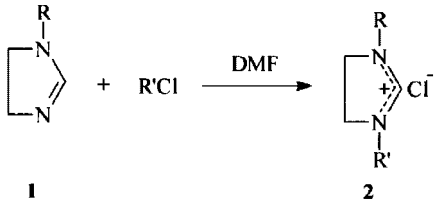
Recently, a major study on Suzuki reactions focused on increasing the activity of the catalysts and decreasing the catalyst loading; this included the use of additives, the modification of the catalyst, and changing the solvents.[26] A major advance achieved by increasing the catalytic activity is the extension of the Suzuki reaction to unactivated aryl chlorides, as noted by the research groups of Buchwald,[5,6] Fu[27], Herrmann,[28] and Doucet.[29] The use of water as a solvent for chemical reactions clearly has both economical and environmental advantages, because it is inexpensive, abundant, nontoxic, nonflammable, and readily separable from organic compounds.[30] There have been a number of reports of palladium-mediated Suzuki reactions being performed using water as solvent[31–33] that relate to the coupling of the aryl boronic acids with aryl iodides or activated bromide and aryl chlorides, but which involve the use of an oxime-carbapalladacycle as the catalyst.[34] Recently, we have developed improved procedures for the Heck and Suzuki reactions of aryl chlorides making use of the novel ligands 1,3-bis(dialkyl)imidazolium salts, 1-alkylimidazoline, and α-bis(imine).[35–38]

In order to find more efficient palladium catalysts, we have prepared a series of new 1,3-bis(alkyl)imidazolinium chloride (**2**; Scheme 1), containing a saturated imidazole ring and we report here an *in-situ* palladium-carbene-based catalytic system for the Suzuki coupling reaction in aqueous media.

EXPERIMENTAL

All reactions were performed using Schlenk-type flasks under argon and standard high-vacuum-line techniques. ^{1}H NMR



1 2

2a R = $CH_2C_6H_2(CH_3)_3$-2,4,6 ; R' = $CH_2C_6H_2(OCH_3)_3$-3,4,5
2b R = $CH_2C_6H_2(CH_3)_3$-2,4,6 ; R' = $C(C_6H_5)_3$
2c R = $CH_2C_6H_2(CH_3)_3$-2,4,6 ; R' = $CH_2C_6H_5$
2d R = *n*-C_4H_9 ; R' = $CH_2C_6H_2(CH_3)_3$-2,4,6
2e R = $CH_2CH_2OCH_3$; R' = $CH_2C_6H_2(OCH_3)_3$-3,4,5
2f R = $CH_2C_6H_5$; R' = $CH_2C_6H_2(OCH_3)_3$-3,4,5

Scheme 1.

and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H) or 75.47 MHz (^{13}C). Chemical shifts δ (ppm) are relative to tetramethylsilane and coupling constants J are in hertz. IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} with a Mattson 1000 spectrophotometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting-point apparatus and are uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

Preparation of 1-(2,4,6-trimethylbenzyl)-3-(3,4,5-trimethoxybenzyl)imidazolinium chloride (2a)

To a solution of 1-(2,4,6-trimethylbenzyl)imidazoline[39] (2.02 g, 10 mmol) in dimethylformamide (DMF; 5 ml) was added slowly 3,4,5-trimethoxybenzyl chloride (2.18 g, 10.06 mmol) at 25 °C and the resulting mixture was stirred at room temperature for 8 h. Diethyl ether (15 ml) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 10 ml), dried under vacuum, and the crude product was recrystallized from ethanol/diethyl ether (2 : 1). M.p. 234.0–234.5 °C; yield: 4.05 g, 97%; $\nu_{(CN)} = 1666\ cm^{-1}$.

Anal. Found: C, 65.93; H, 7.48; N, 6.65. Calc. for $C_{23}H_{31}ClN_2O_3$: C, 65.94; H, 7.46; N, 6.68%.

^1H NMR (δ, $CDCl_3$): 2.25 and 2.16 [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]; 4.79 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 3.73 and 3.61 [t, 4H, $J = 5.2$ Hz, NCH_2CH_2N]; 4.71 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.67 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.79 and 3.72 [s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 9.81 [s, 1H, NCHN]. $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 20.8 and 20.1 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 138.1, 137.7, 128.5 and 125.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 47.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 47.1 and 46.1 [NCH_2CH_2N]; 52.2 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 153.6, 138.9, 129.8 and 106.0 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 60.7 and 56.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 158.5 [NCHN].

Preparation of 1-(2,4,6-trimethylbenzyl)-3-(triphenylmethyl)imidazolinium chloride (2b)

Compound **2b** was prepared in a similar way to **2a**, from 1-(2,4,6-trimethylbenzyl)imidazoline (2.02 g, 10 mmol) and triphenylmethyl chloride (2.80 g, 10.05 mmol), to give white crystals (yield: 4.71 g, 98%); m.p. 147.0–147.5 °C; $\nu_{(CN)} = 1627\ cm^{-1}$.

Anal. Found: C, 79.90; H, 6.89; N, 5.84. Calc. for $C_{32}H_{33}ClN_2$: C, 79.89; H, 6.91; N, 5.82%.

^1H NMR (δ, $CDCl_3$): 2.13 and 2.09 [s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 6.69 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 4.89 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 3.90 and 3.63 [t, 4H, $J = 8.3$ Hz, NCH_2CH_2N]; 7.20 [m, 15H, $C(C_6H_5)_3$]; 8.29 [s, 1H, NCHN]. $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 20.9 and 19.8 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 138.9, 137.9, 128.4 and 125.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 48.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 48.0 and 47.6 [NCH_2CH_2N]; 57.5 [$C(C_6H_5)_3$]; 139.6, 129.6, 129.1 and 128.9 [$C(C_6H_5)_3$]; 158.7 [NCHN].

Preparation of 1-benzyl-3-(2,4,6-trimethylbenzyl)imidazolinium chloride (2c)

Compound **2c** was prepared in a similar way to **2a**, from 1-benzylimidazoline (1.60 g, 10 mmol) and (2,4,6-trimethylbenzyl) chloride (1.70 g, 10.08 mmol) to give white crystals (yield: 3.19 g, 97%); m.p. 235.5–236.0 °C; $\nu_{(CN)} = 1662\ cm^{-1}$.

Anal. Found: C, 73.01; H, 7.64; N, 8.55. Calc. for $C_{20}H_{25}ClN_2$: C, 73.04; H, 7.66; N, 8.52%.

^1H NMR (δ, $CDCl_3$): 2.21 and 2.11 [s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 6.73 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 4.76 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2(C_6H_5)$]; 3.65 and 3.56 [t, 4H, $J = 7.7$ Hz, NCH_2CH_2N]; 7.24 [m, 5H, $CH_2(C_6H_5)$]; 10.37 [s, 1H, NCHN]. $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 21.3 and 20.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 139.4, 133.1, 130.1 and 125.6 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 46.5 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 47.8 and 47.7 [NCH_2CH_2N]; 52.4 [$CH_2(C_6H_5)$]; 138.2, 129.5, 129.3 and 129.1 [$CH_2(C_6H_5)$]; 158.9 [NCHN].

Preparation of 1-*n*-butyl-3-(2,4,6-trimethylbenzyl)imidazolinium chloride (2d)

Compound **2d** was prepared in a similar way to **2a**, from 1-*n*-butylimidazoline (1.26 g, 10 mmol) and 2,4,6-trimethylbenzyl chloride (1.70 g, 10.08 mmol), to give white crystals (yield: 2.70 g, 92%); m.p. 182.5–183.0 °C; $\nu_{(CN)} = 1660\ cm^{-1}$.

Anal. Found: C, 69.21; H, 9.25; N, 9.49. Calc. for $C_{17}H_{27}ClN_2$: C, 69.25; H, 9.23; N, 9.50%.

^1H NMR (δ, $CDCl_3$): 2.26 and 2.17 [s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 6.78 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 4.80 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6]; 3.94 and 3.73 [t, 4H, $J = 9.8$ Hz, NCH_2CH_2N]; 3.53 [t, 2H, $J = 6.0$ Hz, $CH_2CH_2CH_2CH_3$]; 1.57 [quint, 2H, $J = 6.0$ Hz, $CH_2CH_2CH_2CH_3$]; 1.26 [hext, 2H, $J = 7.0$ Hz, $CH_2CH_2CH_2CH_3$]; 0.85 [t, 3H, $J = 7.1$ Hz, $CH_2CH_2CH_2CH_3$]; 9.48 [s, 1H, NCHN]. $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 20.8 and 20.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 138.9, 137.8, 129.8 and 125.3 [$CH_2C_6H_2(CH_3)_3$-2,4,6]; 48.5 [$CH_2C_6H_2$

$(CH_3)_3$-2,4,6]; 48.1 and 46.1 [NCH_2CH_2N]; 47.7 [$CH_2CH_2CH_2CH_3$]; 29.2 [$CH_2CH_2CH_2CH_3$]; 19.5 [$CH_2CH_2CH_2CH_3$]; 13.5 [$CH_2CH_2CH_2CH_3$]; 157.3 [NCHN].

Preparation of 1-methoxyethyl-3-(3,4,5-trimethoxybenzyl)imidazolinium chloride (2e)

Compound **2e** was prepared in a similar way to **2a**, from 1-methoxyethylimidazoline[39] (1.28 g, 10 mmol) and 3,4,5-trimethoxybenzyl chloride (2.18 g, 10.06 mmol) to give white crystals (yield: 3.20 g, 93%); m.p. 129.0–130.0 °C; $\nu_{(CN)} = 1668\ cm^{-1}$.

Anal. Found: C, 55.75; H, 7.28; N, 8.14. Calc. for $C_{16}H_{25}ClN_2O_4$: C, 55.73; H, 7.30; N, 8.12%.

^{1}H NMR (δ, $CDCl_3$): 3.76 [t, 2H, $J = 5.2$ Hz, $CH_2CH_2OCH_3$]; 3.59 [t, 2H, $J = 5.2$ Hz, $CH_2CH_2OCH_3$]; 3.30 [s, 3H, $CH_2CH_2OCH_3$]; 3.92 and 3.82 [t, 4H, $J = 7.6$ Hz, NCH_2CH_2N]; 4.71 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.66 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.83 and 3.78 [s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 10.04 [s, 1H, NCHN]. ^{13}C{H} NMR (δ, $CDCl_3$): 49.9 [$CH_2CH_2OCH_3$]; 62.1 [$CH_2CH_2OCH_3$]; 70.1 [$CH_2CH_2OCH_3$]; 48.5 and 48.1 [NCH_2CH_2N]; 52.8 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 154.1, 138.7, 128.7 and 106.6 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 59.8 and 56.9 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 159.6 [NCHN].

Preparation of 1-benzyl-3-(3,4,5-trimethoxybenzyl)imidazolinium chloride (2f)

Compound **2f** was prepared in a similar way to **2a**, from 1-benzylimidazoline (1.60 g, 10 mmol) and 3,4,5-trimethoxybenzyl chloride (2.18 g, 10.06 mmol), to give white crystals (yield 3.57 g, 95%); m.p. 217.0–217.5 °C; $\nu_{(CN)} = 1668\ cm^{-1}$.

Anal. Found: C, 63.76; H, 6.65; N, 7.45. Calc. for $C_{20}H_{25}ClN_2O_3$: C, 63.74; H, 6.68; N, 7.43%.

^{1}H NMR (δ, $CDCl_3$): 4.76 [s, 2H, $CH_2(C_6H_5)$]; 7.29 [m, 5H, $CH_2(C_6H_5)$]; 4.77 and 4.70 [s, 4H, NCH_2CH_2N]; 4.70 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.65 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.80 and 3.73 [s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 10.58 [s, 1H, NCHN]. ^{13}C{H}NMR (δ, $CDCl_3$): 52.7 [$CH_2(C_6H_5)$]; 132.9, 129.5, 129.3 and 129.1 [$CH_2(C_6H_5)$]; 48.0 and 47.9 [NCH_2CH_2N]; 52.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 154.1, 138.7, 128.5 and 106.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 61.0 and 56.9 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 159.2 [NCHN].

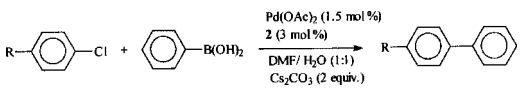
General procedure for the Suzuki-type coupling reactions

$Pd(OAc)_2$ (1.5 mmol%), 1,3-dialkylimidazolinium salts **2a**–**f** (3 mmol%), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), 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 silica gel with copious washings, concentrated and purified by flash chromatography on silica gel. Purity of compounds was checked by NMR and yields are based on aryl chloride.

RESULTS AND DISCUSSION

1,3-Bis(alkyl)imidazolinium chloride (**2**) is a conventional NHC precursors. According to Scheme 1, the salts (**2a**–**f**) were obtained in almost quantitative yield by quarternization of 1-(alkyl)imidazoline[40] in DMF with alkyl halides (Scheme 1). It has been found that the *in situ* formation of the ligand by deprotonation of the imidazolinium chlorides leads to significantly better results than use of the preformed carbene complex.[41,42]

Table 1. The Suzuki coupling reaction of aryl chlorides with phenylboronic acid



Entry	R	Salt	Yield[a] (%)
1	$COCH_3$	**2a**	83
2	$COCH_3$	**2b**	86
3	$COCH_3$	**2c**	92
4	$COCH_3$	**2d**	78
5	$COCH_3$	**2e**	85
6	$COCH_3$	**2f**	95
7	CHO	**2a**	84
8	CHO	**2b**	91
9	CHO	**2c**	88
10	CHO	**2d**	85
11	CHO	**2e**	84
12	CHO	**2f**	93
13	CH_3	**2a**	79
14	CH_3	**2b**	86
15	CH_3	**2c**	90
16	CH_3	**2d**	88
17	CH_3	**2e**	82
18	CH_3	**2f**	88
19	H	**2a**	87
20	H	**2b**	79
21	H	**2c**	80
22	H	**2d**	88
23	H	**2e**	92
24	H	**2f**	94
25	OCH_3	**2a**	82
26	OCH_3	**2b**	89
27	OCH_3	**2c**	84
28	OCH_3	**2d**	86
29	OCH_3	**2e**	93
30	OCH_3	**2f**	91

[a] Reaction conditions: 1.0 mmol of R–C_6H_4Cl-*p*, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1.50 mmol% $Pd(OAc)_2$, 3.0 mmol% **2**, water (3 ml)–DMF (3 ml). Purity of compounds is checked by NMR and yields are based on aryl chloride. All reactions were monitored by thin-layer chromatography. Temperature 80 °C, 6 h.

To find the optimum conditions, a series of experiments was 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 *para*-substituted aryl chlorides. The results were shown in Table 1.

Under these conditions, *p*-chloroacetophenone, *p*-chlorobenzaldehyde, *p*-chlorotoluene, chlorobenzene and *p*-chloroanisole react very cleanly with phenylboronic acid in goods yields (Table 1, entries 6, 12, 15, 23 and 29). The higher performance of the bis(imidazolinium) salts **2** is thought to be due to their better electron-donating ability and greater steric hindrance.

In 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 towards various aryl halides and does not require induction periods. Further study is under way to optimize the reactivity of these 1,3-dialkylimidazolidin-2-ylidene and bis-(NHC) precursors for C–C and C–N coupling with $Pd(OAc)_2$, and work is also under way to compare transition-metal complexes of ruthenium, palladium, rhodium and iridium to explore their catalytic activity.

Acknowledgements

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