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The *in situ* prepared three component system Pd(OAc)₂, 1,3-dialkylbenzimidazolium halides (**1a-e**) and *t*-BuOK catalyses quantitatively the Suzuki cross-coupling of deactivated aryl chloride substrates. 1,3-Dialkylbenzimidazolium salts (**1a-e**) were characterized by conventional spectroscopic methods and elemental analyses.

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Introduction.

A survey of the recent literature leaves no doubt that the palladium-catalyzed cross coupling reaction of aryl halides or -triflates with organoboron compounds, generally referred to as the Suzuki reaction, has evolved into a powerful and popular method for C(sp²)-C(sp²) bond formation. A serious limitation, however, denotes the fact that aryl chlorides, which are the most attractive class of substrates due to their low cost and ready availability, exhibit poor reactivity. Only if the C-Cl bonds are strongly activated by electron withdrawing groups on the arene or by electron deficient heteroaromatic rings, are they amenable to cross coupling under standard conditions [1].

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, modification of the catalyst, and changing of 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 Bedford [2], Indolese [3], Johannsen [4], Nishida [5], Plenio [6] and Beller [7].

Common methodologies used are the palladium mediated coupling of the organic halides with organoboron reagents where monodentate phosphine are usually employed as ancillary ligands [8]. However, the major drawback of these is that the phosphine ligands are comparatively difficult to make or rather expensive. Furthermore, tertiary phosphines require air-free handling to prevent their oxidation and are susceptible to P-C bond cleavage at elevated temperatures [9]. On the other hand, palladium complexes of *N*-heterocyclic carbene ligands (NHC's) [10], in particular, have proved to be excellent catalysts for coupling reactions. High catalyst and phosphine loading are usually required to produce high yields for unactivated aryl halides using this methodology. Significant improvements of catalyst performance have recently brought benefits to fine chemistry *via* simple substitution of a phosphine ligand by a nucleophilic hetero-

cyclic diaminocarbene, such as an imidazolylidene ligand. Illustrative examples are found in various catalytic reactions with palladium catalysts in cross-coupling or Heck reaction [11] and ruthenium catalysts for the formation of furans [12], cyclopropanation [13] or metathesis [14].

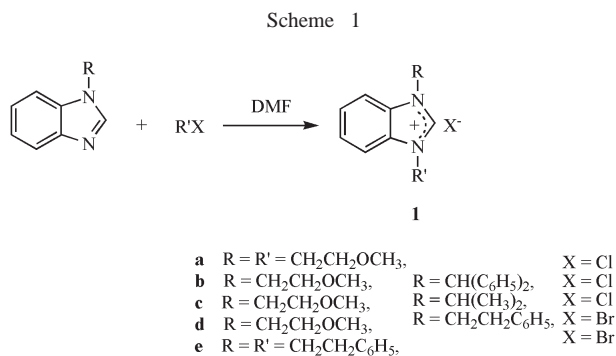
Recently, we developed improved procedures for the Heck and Suzuki reactions of aryl chlorides making use of the novel ligands 1,3-dialkylimidazolium salts, 1-alkylimidazoline and α -bis(imine) [15].

Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of 1,3-dialkylbenzimidazolidin-2-ylidene ligands in coupling reactions is a neglected area. In order to find more efficient palladium catalysts we have prepared a series of 1,3-disubstituted benzimidazolium salts, (**1a-e**) (Scheme 1). We now report the use of *in situ* generated catalytic system composed of commercially available and stable reagents, where Pd(OAc)₂ is the palladium source, 1,3-dialkylbenzimidazolium chloride (**1a-e**) is the carbene precursor and *t*-BuOK is the base for cross coupling of aryl chlorides with phenyl boronic acid.

Results and Discussion.

Dialkylbenzimidazolium salts, (**1a-e**) are conventional NHC precursors. According to Scheme 1, the salts (**1a-e**) were obtained in almost quantitative yields by quarternazition of 1-alkylbenzimidazoles in DMF with alkyl halides [16,17]. The salts are air- and moisture stable both in the solid state and in solution. The structures of **1a-e** were determined by their characteristic spectroscopic data and elemental analyses (experimental section). ¹³C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ¹H-decoupled mode at 143.6, 135.8, 1142.8, 143.6 and 143.0 ppm respectively for imidazolium salts **1a-e**. 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 11.01, 10.59, 10.11, 9.34 and 9.89 ppm respectively for **1a-e**. The IR data for

benzimidazolium salts **1a-e** clearly indicate the presence of the $-C=N-$ group with a $\nu(C=N)$ vibration at 1564, 1550, 1562, 1564 and 1565 cm^{-1} respectively for **1a-e**. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolium salts [17].



Synthesis of 1,3-dialkylbenzimidazolium salts.

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions: A wide range of bases and solvents, as well as catalysts, have been employed with varying degrees of success according to the substrates [1]. To find optimum conditions a series of experiments have been performed with 4-chloroanisole and phenylboronic acid as model compounds. As a base, *t*-BuOK was the best choice

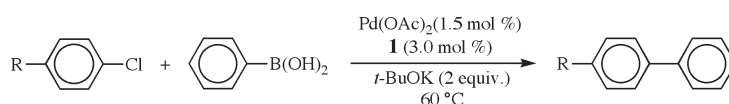
and as a solvent dioxane was found to be better than other solvents. After having established the optimised coupling reaction conditions, the scope of the reaction and efficiencies of the salts were evaluated by investigating the coupling of C₆H₅B(OH)₂ with various *p*-substituted aryl chlorides. The results are summarized 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, entry 2, 4, 9, 14, 18, 19 and 22). From the results in Table 1, it is evident that the NHC precursors that contain electron donating methoxyethyl substituent (**1b**, **1c**, **1d**) 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 [13]. In the Suzuki reaction with 1.5 mmol % Pd(OAc)₂/ 3 mmol % 1,3-dialkylbenzimidazolium salt were achieved in 2 h, at 60 °C; these catalytic activities are comparable to screening results recently described by Bedford [2], Indolese [3] and Johannsen [4].

Previous researchers have reported induction periods for Suzuki reactions promoted by Pd(OAc)₂/imidazolium salts. It was proposed that during these induction periods Pd(II)/NHC complexes were formed and were then slowly reduced to catalytically active Pd(0)/NHC complexes [18]. It is important to note that these induction periods could be avoided with the present catalyst system.

Table 1

The Suzuki coupling of aryl chloride with phenylboronic acid.



Entry	R	LHX	Yield [a,b,c,d] (%)	Entry	R	LHX	Yield [a,b,c,d] (%)
1	OCH ₃	1a	87	14	"	1d	96
2	"	1b	91	15	"	1e	71
3	"	1c	89	16	COCH ₃	1a	93
4	"	1d	93	17	"	1b	95
5	"	1e	73	18	"	1c	95
6	CHO	1a	88	19	"	1d	95
7	"	1b	97	20	"	1e	81
8	"	1c	84	21	H	1a	90
9	"	1d	94	22	"	1b	94
10	"	1e	84	23	"	1c	84
11	CH ₃	1a	85	24	"	1d	83
12	"	1b	89	25	"	1e	76
13	"	1c	87				

[a] Reactions conditions: 1.0 mmol of R-C₆H₄Cl-*p*, 1.2 mmol of phenylboronic acid, 2 mmol *t*-BuOK, 1.5 mmol % Pd(OAc)₂, 3 mmol % 1,3-dialkylbenzimidazolium salt, dioxane (3 mL); [b] Purity of compounds is checked by NMR and yields are based on arylchlorides; [c] All reactions were monitored by TLC; [d] 60 °C, 2 hours.

In conclusion, five 1,3-dialkylbenzimidazolium salts (**1a-e**) have been prepared and characterized. We have demonstrated that simple method for Suzuki cross-coupling reaction is presented which employs a catalyst formed *in situ* from Pd(OAc)₂, the readily accessibly and fully air stable benzimidazolium salts. 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.

Detailed investigations, focusing on imidazolin-2-ylidene and benzimidazolin-2-ylidene substituent effects, functional group tolerance and catalytic activity in this and other coupling reactions are ongoing.

EXPERIMENTAL

All reactions were carried out under argon and standard high vacuum-line techniques. Solvents were analytical grade and distilled under nitrogen from sodium benzophenone (Et₂O, dioxane). ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 75.47 MHz (¹³C). Chemical shifts (δ) 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. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

Synthesis of 1,3-Di(2-methoxyethyl)benzimidazolium Chloride (**1a**).

To a solution of 1-(2-methoxyethyl)benzimidazole (2 g, 11.36 mmol) in DMF (1 mL) 2-methoxyethyl chloride (1.03 mL, 11.42 mmol) was added and the resulting solution was stirred for 1 h at room temperature and heated for 5 h at 80 °C. Then, Et₂O (10 mL) was added the reaction mixture. A white solid precipitated in this period. The precipitate was then crystallised from EtOH/Et₂O (1:2). 2.80 g (91 %), mp 134-135°C; IR, ν_(CN): 1564 cm⁻¹; ¹H NMR (CDCl₃): δ 3.27 (s, 6H, CH₃); 3.87 (t, *J* 1.2, 4H, CH₂CH₂); 4.80 (t, *J* 1.2, 4H, CH₂CH₂); 7.53-7.84 (m, 4H, Ar-H); 11.01 (s, 1H, 2-CH); ¹³C NMR (CDCl₃): δ 48.0 (CH₃); 59.3, 70.5 (CH₂CH₂); 114.0, 114.1, 127.2, 132.1 (Ar-C); 143.60 (2-CH).

Anal. Calcd. For C₁₃H₁₉N₂O₂Cl: C, 57.67, H, 7.02, N, 10.35. Found C, 57.52, H, 7.00, N, 10.31.

Synthesis of 1-(2-Methoxyethyl)-3-diphenylmethylbenzimidazolium Chloride (**1b**).

Compound **1b** was prepared in the same way as **1a** from 1-(2-methoxyethyl)benzimidazole (2 g, 11.36 mmol) and diphenylmethyl chloride (2.03 mL, 11.39 mmol) to give white crystals of **1b**, 3 g (70 %), mp 254-255 °C; IR, ν_(CN): 1550 cm⁻¹; ¹H NMR (CDCl₃): δ 3.19 (s, 3H, CH₃); 3.80 (t, *J* 4.2, 2H, CH₂CH₂); 4.89 (t, 2H, CH₂CH₂); 7.12-7.49 (m, 14H, Ar-H); 10.59 (s, 1H, 2-CH); ¹³C NMR (CDCl₃): δ 48.3 (CH₃); 59.2, 70.5 (CH₂CH₂); 114.7, 114.9, 127.3, 127.4, 128.7, 129.6, 129.7, 129.7, 131.2 (Ar-C); 132.8, 135.7, (CH(C₆H₅)₂); 135.8 (2-CH).

Anal. Calcd. For C₂₃H₂₃N₂OCl: C, 72.91, H, 6.07, N, 7.39. Found C, 72.68, H, 6.08, N, 7.42.

Synthesis of 1-(2-Methoxyethyl)-3-isopropylbenzimidazolium Chloride (**1c**).

Compound **1c** was prepared in the same way as **1a** from 1-(2-methoxyethyl)benzimidazole (1.78 g, 11.12 mmol) and isopropyl chloride (1.02 mL, 11.16 mmol) to give white crystals of **1c**, 2.12 g (75), mp 96-98 °C; IR, ν_(CN): 1562 cm⁻¹; ¹H NMR (CDCl₃): δ 1.85 (d, *J* 6.6, 6H, CH(CH₃)₂); 3.19 (s, 3H, CH₃); 3.82 (t, *J* 3.2, 2H, CH₂CH₂); 4.79 (t, *J* 3.2, 2H, CH₂CH₂); 5.09 (sept, *J* 6.6, 6H, CH(CH₃)₂); 7.49-7.74 (m, 4H, Ar-H); 10.11 (s, 1H, 2-CH). ¹³C NMR (CDCl₃): δ 18.2 (CH(CH₃)₂); 30.5 (CH(CH₃)₂); 47.9 (CH₃); 59.3, 70.5 (CH₂CH₂); 113.9, 114.0, 127.1, 129.7, 131.8 (Ar-C); 142.8 (2-CH).

Anal. Calcd. For C₁₃H₁₉N₂OCl: C, 61.29, H, 7.46, N, 11.00. Found C, 61.42, H, 7.49, N, 11.04.

Synthesis of 1-(2-Phenylethyl)-3-(2-methoxyethyl)benzimidazolium Bromide (**1d**).

Compound **1d** was prepared in the same way as **1a** from 1-(2-methoxyethyl)benzimidazole (0.8 g, 4.54 mmol) and 2-phenylethyl bromide (0.62 mL, 4.58 mmol) to give white crystals of **1d**, 1.12 g (86 %), mp 90-92 °C; IR, ν_(CN): 1564 cm⁻¹; ¹H NMR (CDCl₃): δ 3.21 (s, 3H, CH₃); 3.82 (m, 2H, PhCH₂CH₂); 4.00 (t, *J* 3.2, 2H, CH₂CH₂O); 4.72 (m, 4H, CH₂CH₂O, CH₂CH₂Ph); 6.73-7.64 (m, 9H, Ar-H); 9.34 (s, 1H, 2-CH); ¹³C NMR (CDCl₃): δ 48.3 (CH₃); 36.1, 49.5, 59.3, 70.5 (CH₂CH₂); 114.1, 114.1, 127, 129.6, 129.7, 131.2, 32.1, 135, 135.4 (Ar-C); 143.6 (2-CH).

Anal. Calcd. For C₁₈H₂₁N₂OBr: C, 59.83, H, 5.81, N, 7.75. Found C, 60.04, H, 5.84, N, 7.78.

Synthesis of 1,3-Di(2-phenylethyl)benzimidazolium Bromide (**1e**).

Compound **1e** was prepared in the same way as **1a** from 1-(2-phenylethyl)benzimidazole (3.3 g, 15.00 mmol) and 2-phenylethyl bromide (2.03 mL, 15.00 mmol) to give white crystals of **1e**, 5 g (82 %), mp 164-166 °C; IR, ν_(CN): 1565 cm⁻¹; ¹H NMR (CDCl₃): δ 2.74 (t, *J* 7.1, 4H, PhCH₂CH₂); 4.23 (t, *J* 7.1, 4H, PhCH₂CH₂); 6.58-7.43 (m, 9H, Ar-H); 9.89 (s, 1H, 2-CH); ¹³C NMR (CDCl₃): δ 35.2, 49.1 (PhCH₂CH₂); 113.4, 127.4, 129.2, 129.3, 131.2, 136.4 (Ar-C); 143.0 (2-CH).

Anal. Calcd. For C₂₃H₂₃N₂Br: C, 67.81, H, 5.65, N, 6.88. Found C, 68.05, H, 5.63, N, 6.90.

General Procedure for the Suzuki Type Coupling Reactions.

Pd(OAc)₂ (1.5 % mmol), 1,3-dialkylbenzimidazolium salt, **1a-e**, (3 % mmol), aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), *t*-BuOK (2 mmol) dioxane (3 mL) were added in a small Schlenk tube under argon and the mixture was heated at 60 °C for 2 h. At the conclusion of the reaction, the mixture was cooled, diluted with Et₂O, filtered through a pad of silicagel with copious washings, concentrated and purified by flash chromatography on silicagel. Purity of compounds is checked by NMR and yields are based on arylchloride.

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