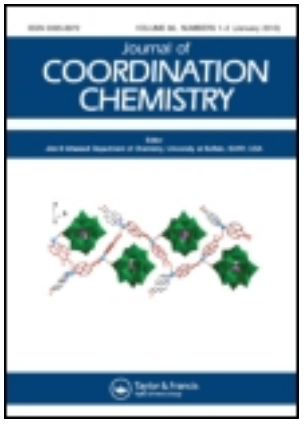


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of 1-phenyl-3-alkylbenzimidazol-2-ylidene salts and their catalytic activities in the Heck and Suzuki cross-coupling reactions

Senem Akkoc [a] & Yetkin Gok [b]

[a] Faculty of Science, Department of Chemistry , Erciyes University , Kayseri , Turkey

[b] Faculty of Science and Arts, Department of Chemistry , Inönü University , Malatya , Turkey

Accepted author version posted online: 18 Mar 2013.Published online: 10 Apr 2013.

To cite this article: Senem Akkoc & Yetkin Gok (2013) Synthesis and characterization of 1-phenyl-3-alkylbenzimidazol-2-ylidene salts and their catalytic activities in the Heck and Suzuki cross-coupling reactions, Journal of Coordination Chemistry, 66:8, 1396-1404, DOI: 10.1080/00958972.2013.786053

To link to this article: http://dx.doi.org/10.1080/00958972.2013.786053

Journal of Coordination Chemistry, 2013
Vol. 66, No. 8, 1396–1404, http://dx.doi.org/10.1080/00958972.2013.786053

Synthesis and characterization of 1-phenyl-3-alkylbenzimidazol-2-ylidene salts and their catalytic activities in the Heck and Suzuki cross-coupling reactions

SENEM AKKOC*† and YETKIN GOK‡

†Faculty of Science, Department of Chemistry, Erciyes University, Kayseri, Turkey;
‡Faculty of Science and Arts, Department of Chemistry, Inönü University, Malatya, Turkey

(*Received 23 October 2012; in final form 15 January 2013*)

The synthesis and characterization of 1-phenyl-3-alkyl-substituted carbene precursors that were prepared from 1-phenyl substituted benzimidazole and various alkyl halides are reported. The new benzimidazolium salts (**1a**–**e**) were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopic methods and elemental analyses. New *in situ* generated palladium-benzimidazolium complexes were tested for catalytic activity in the Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions.

Keywords: *N*-Heterocyclic carbene; Benzimidazolium salts; Alkyl substituent; Mizoroki-Heck reaction; Suzuki-Miyaura reaction

1. Introduction

Heterocyclic salts containing a benzimidazolium group are significant as a carbene ancillary both in catalytic reactions and in the synthesis of carbene complexes. *N*-Heterocyclic carbene (NHC) complexes have high catalytic activities for many organic transformations such as C–C and C–N cross-coupling reactions, C–H bond activation and metathesis [1–7]. Carbon-carbon cross-coupling reactions have played a very important role in organic synthesis [8]. The Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions are two of the modern catalytic carbon-carbon bond-forming reactions. These reactions play an important role in the synthesis of natural products, drug design, and industrially important starting materials [9–12].

Active catalysts in the production of new products with minimal waste are needed. Numerous transition metal complexes containing phosphine ligands have been synthesized and used as catalysts. However, catalytic reactions are carried out in the presence of an excess of these ligands; palladium complexes of NHC ligands offer distinct advantages as alternatives to palladium-phosphine systems in C–C coupling reactions [13–15] and NHCs have attracted the attention of a large number of research groups [7, 16–18]. Some highly

*Corresponding author. Email: senemakkoc@erciyes.edu.tr

active palladium systems with carbene ligands for activation of aryl halides have been developed [19, 20]; *in situ* formation of the NHC complex by deprotonation of the azolium salt led to significantly better results than the use of the preformed complex [21].

Our research group has focused on NHC derivatives and their metal complexes with synthesis, characterization, crystal structure, and catalytic activities such as Mizoroki-Heck, Suzuki-Miyaura, arylation, transfer hydrogenation and amination [6, 8, 22–25]. In order to find more efficient palladium catalysts, we have prepared a series of new benzimidazolium salts and reported here the use of *in situ* generated benzimidazolidin-2-ylidene palladium (II) complexes that are composed of commercially available $Pd(OAc)_2$ and the 1-phenyl-3-alkylbenzimidazolium salts (**1a**–**e**) for Heck and Suzuki cross-coupling reactions in aqueous media. The use of water as a solvent for the Heck and Suzuki cross-coupling reactions clearly has both economical and environmental advantages because it is inexpensive, abundant, nontoxic, nonflammable, and readily separable from organic compounds [26]. The structures of these five new benzimidazolium salts were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopic methods, and elemental analysis.

2. Experimental

2.1. *Materials and methods*

Reactions for the preparation of **1a**–**e** were carried out under argon in flame–dried glassware using standard Schlenk-type flasks and high vacuum-line techniques. Solvents were of analytical grade and distilled under nitrogen from sodium benzophenone (Et_2O, dioxane). Flash chromatography: Merck silica gel 60 (230–400 mesh), eluent ethylacetate/hexane (1 : 5). The 1-phenyl-3-alkylbenzimidazolium salts (**1a**–**e**) were prepared according to known methods [27–29]. All reagents were purchased from Aldrich and Merck. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ and DMSO with 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 and coupling constants (J) are given in Hz. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer and wavenumbers were recorded in cm^{-1}. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by the Technological and Scientific Research Council of Turkey (TÜBİTAK) Microlab.

2.2. *General procedure for the preparation of the benzimidazolium salts (1a–e)*

Alkyl halide (1.0 mM) was added slowly to a solution of 1-phenylbenzimidazole (1.0 mM) in DMF (4 mL) at 25 °C and the resulting mixture was heated to 80 °C for 12 h. Diethylether (15 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethylether (2 × 15 mL) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2–Et_2O at room temperature.

2.2.1. 1-Phenyl-3-(2-hydroxyethyl)benzimidazolium bromide (1a). This compound was prepared from a solution of *N*-phenyl benzimidazole (1.96 g, 10.10 mM) in DMF (4 mL) and 2-bromoethanol (1.27 g, 10.13 mM) was added. The resulting solution was

stirred for 48 h at room temperature. Then Et_2O (15 mL) was added to the reaction mixture. A solid precipitate occurred in this period. The precipitate was then crystallized from CH_2Cl_2/Et_2O (1 : 2). Yield: 83%, m.p.: 189–190 °C, IR $\nu_{(CN)}$: 1554.14 cm^{-1}. ^1H NMR (300.13 MHz, DMSO), δ 3.47 (s, 1H, NCH_2CH_2OH); 3.94 (*t*, 2H, *J*: 4.9 Hz, NCH_2CH_2OH); 4.69 (*t*, 2H, *J*: 5.1 Hz, NCH_2CH_2OH); 7.70–8.27 (m, 9H, Ar–*H*); 10.26 (s, 1H, 2–C*H*). ^{13}C NMR (75.47 MHz, DMSO), δ 50.4 (NCH_2CH_2OH); 59.2 (NCH_2CH_2OH); 113.9, 114.9, 125.7, 127.3, 127.8, 130.9, 131.9, 132.0, 133.6 (Ar–*C*); 143.3 (2–*C*H). Anal. Calcd for $C_{15}H_{15}N_2OBr$ (%): C, 56.44; H, 4.74; N, 8.78; Br, 25.03; O, 5.01. Found: C, 56.48; H, 4.75; N, 8.79; Br, 25.03; O, 5.02.

2.2.2. 1-Phenyl-3-[2-(diethylamino)ethyl]benzimidazolium chloride (1b). This compound was prepared from *N*-phenyl benzimidazole (1.07 g, 5.57 mM) and N-(2-chloroethyl)diethylamine (0.74 g, 5.46 mM) in DMF (4 mL). Yield: 81%, m.p.: 339–340 °C, IR $\nu_{(CN)}$: 1594.82 cm^{-1}. ^1H NMR (300.13 MHz, DMSO), δ 1.78 (*t*, 6H, *J*: 6.9 Hz, $NCH_2CH_2N(CH_2CH_3)_2$; 3.67 (q, 4H, *J*: 6.9 Hz, $NCH_2CH_2N(CH_2CH_3)_2$; 2.51 (m, 2H, $NCH_2CH_2N(CH_2CH_3)_2$; 4.66 (m, 2H, $NCH_2CH_2N(CH_2CH_3)_2$; 7.53–8.58 (m, 9H, Ar–*H*); 10.22 (s, 1H, 2–C*H*). ^{13}C NMR (75.47 MHz, DMSO), δ 12.1, 46.7, 47.6, 51.1 ($NCH_2CH_2N(CH_2CH_3)_2$; 111.1, 120.4, 122.9, 124.2, 125.6, 128.2, 130.6, 131.0, 133.5 (Ar–*C*); 143.8 (2–*C*H). Anal. Calcd for $C_{19}H_{24}N_3Cl$ (%): C, 69.18; H, 7.33; N, 12.74; Cl, 10.75. Found: C, 69.29; H, 7.22; N, 12.69; Cl, 10.75.

2.2.3. 1-Phenyl-3-(N-prophyl phthalimido)benzimidazolium bromide (1c). This compound was prepared from *N*-phenyl benzimidazole (1.0 g, 5.15 mM) and *N*-(3-bromopropyl)-phthalimide (1.31 g, 5.15 mM) in DMF (4 mL). Yield: 86%, m.p.: 206–207 °C, IR $\nu_{(CN)}$: 1556.43 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$), δ 2.64 (*p*, 2H, *J*: 6.7 Hz, $NCH_2CH_2CH_2N$); 3.89 (*t*, 2H, *J*: 6.5 Hz, $NCH_2CH_2CH_2N$); 5.05 (*t*, 2H, *J*: 6.9 Hz, $NCH_2CH_2CH_2N$); 7.58–8.13 (m, 13H, Ar–*H*); 11.21 (s, 1H, 2–C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 28.1, 34.8, and 45.9 ($NCH_2CH_2CH_2N$); 113.5, 113.7, 123.4, 125.0, 127.7, 127.8, 130.8, 130.9, 131.4, 131.8, 131.9, 134.2 (Ar–*C*); 142.6 (2–*C*H). 168.2 (C=O). Anal Calcd. for $C_{24}H_{20}N_3O_2Br$ (%): C, 62.35; H, 4.36; N, 9.09; Br, 17.28; O, 6.92. Found: C, 62.31; H, 4.32; N, 9.05; Br, 17.27; O, 6.92.

2.2.4. 1-Phenyl-3-(2-methyl-1,4-benzodioxano)benzimidazolium bromide (1d). This compound was prepared from *N*-phenyl benzimidazole (1.08 g, 5.57 mM) and 2-bromomethyl-1,4-benzodioxane (1.27 g, 5.55 mM) in DMF (4 mL). Yield: 89%, m.p.: 185–186 °C, IR $\nu_{(CN)}$: 1590.08 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$), δ 4.54 (d, 2H, *J*: 2.5 Hz, $NCH_2CHCH_2O_2C_6H_4$); 5.04 (m, 1H, $NCH_2CHCH_2O_2C_6H_4$); 5.69 (d, 2H, *J*: 2.1 Hz, $NCH_2C_2H_3O_2C_6H_4$); 6.66–7.98 (m, 13H, Ar–*H*); 11.41 (s, 1H, 2–C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 47.9 ($NCH_2CHCH_2O_2C_6H_4$); 64.8 ($NCH_2CHCH_2O_2C_6H_4$); 72.5 ($NCH_2C_2H_3O_2C_6H_4$); 113.3, 114.3, 117.4, 117.8, 122.2, 124.9, 127.6, 127.8, 130.9, 132.5, 132.9, 141.4, 142.4 (Ar–*C*); 142.9 (2–*C*H). Anal. Calcd for $C_{22}H_{18}N_2O_2Br$ (%): C, 62.57; H, 4.30; N, 6.63; Br, 18.92; O, 7.58. Found: C, 62.56; H, 4.21; N, 6.64; Br, 18.91; O, 7.59.

2.2.5. 1-Phenyl-3-(4-vinylbenzyl)benzimidazolium chloride (1e). This compound was prepared from *N*-phenyl benzimidazole (1.35 g, 6.96 mM) and 4-vinylbenzyl chloride (1.06 g, 6.95 mM) in DMF (4 mL). Yield: 87%, m.p.: 165–166 °C, IR $\nu_{(CN)}$: 1593.50 cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 5.31 (d, 2H, J: 7.0 Hz, $NCH_2C_6H_4CH=CH_2$); 6.19 (s, 2H, $NCH_2C_6H_4CH=CH_2$); 6.67 (t, 1H, J: 6.7 Hz, $NCH_2C_6H_4CH=CH_2$); 7.28–7.77 (m, 13H, Ar–*H*); 12.08 (s, 1H, 2–C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 51.4 ($NCH_2C_6H_4CH=CH_2$); 113.7 ($NCH_2C_8H_7$); 114.0 ($C_6H_4CH=CH_2$); 115.2, 124.8, 127.1, 127.5, 129.1, 130.8, 131.4, 132.3, 132.9, 135.9, 138.5 (Ar–*C*); 143.2 (2–*C*H). Anal. Calcd for $C_{22}H_{19}N_2Cl$ (%): C, 76.18; H, 5.52; N, 8.08; Cl, 10.22. Found: C, 76.16; H, 5.48; N, 8.09; Cl, 10.21.

2.3. *General procedure for Heck and Suzuki cross-coupling reactions*

Test reactions for the catalytic activity of the palladium catalysts in the Heck and Suzuki cross-coupling reactions were carried out in the presence of air.

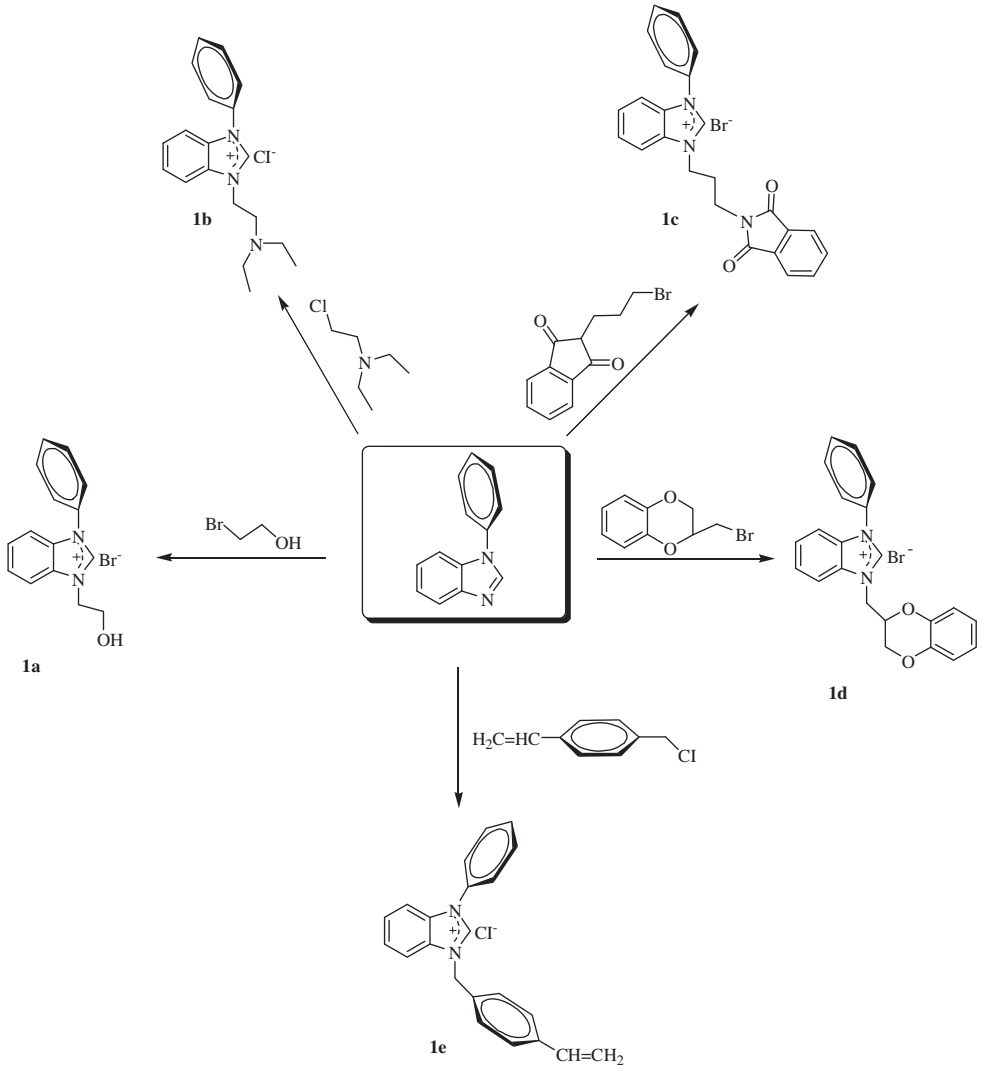
For the Heck reaction, $Pd(OAc)_2$ (1.0 mM), 1-phenyl-3-alkylbenzimidazolium salts (**1a**–**e**) (2.0 mM), aryl bromide (1.0 mM), styrene (1.5 mM), K_2CO_3 (2.0 mM), water (3 mL) and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated to 80 °C for 2 h.

For the Suzuki reaction, $Pd(OAc)_2$ (1.0 mM), 1-phenyl-3-alkylbenzimidazolium salts (**1a**–**e**) (2.0 mM), aryl chloride (1.0 mM), phenylboronic acid (1.5 mM), K_2CO_3 (2.0 mM), water (3 mL) and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated to 80 °C for 2 h. At the end of the Heck and Suzuki cross-coupling reactions, the mixture was cooled, extracted with ethylacetate/hexane (1 : 5), filtered through a pad of silica gel with copious washings, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC. Yields are based on arylbromide for the Heck and arylchloride for the Suzuki. All reactions were monitored by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

3. Results and discussion

3.1. *Synthesis and characterization of phenyl substituted benzimidazolium salts (1a–e)*

During our work in the field of NHC precursors, 1-phenyl-3-alkylbenzimidazol-2-ylidene salts, were isolated. 1-Phenyl-3-alkyl substituted benzimidazolium salts (**1a**–**e**) are conventional NHC precursors. The functionalized benzimidazolium salts were synthesized by alkylation of 1-phenylbenzimidazole, obtained in almost quantitative yield by quaternization of 1-phenylbenzimidazole in DMF with alkyl halides [30, 31] (scheme 1). 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. ^{1}H NMR spectra of the heterocyclic salts containing benzimidazolium further support the assigned structures; the resonances for C(2)–H were sharp singlets at 10.26, 10.22, 11.21, 11.41 and 12.08 ppm for **1a**–**e**, respectively. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbons appeared as singlets at 143.3, 143.8, 142.6, 142.9 and 143.2 ppm for the heterocyclic salts (**1a**–**e**), respectively. FT-IR data for **1a**–**e** clearly indicate the presence of the –C=N– group with $\nu_{(C=N)}$ at 1554, 1594, 1556, 1590 and 1593 cm^{-1}, respectively. The palladium catalysts were prepared *in situ* from $Pd(OAc)_2$ and the appropriate 1-phenyl-3-alkylbenzimidazol-2-ylidene salts in DMF–water mixture. 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



Scheme 1. The synthesis of **1a**–**e**.

arylboronic acid and styrene with various p-substituted aryl halides. The results are summarized in tables 1 and 2.

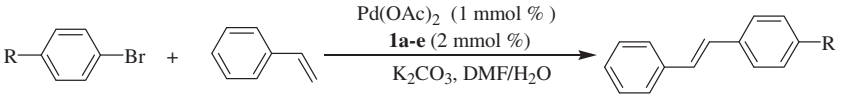
3.2. *Palladium-catalyzed Heck and Suzuki reactions*

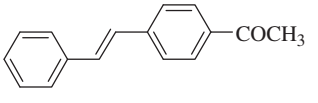
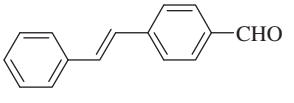
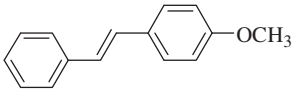
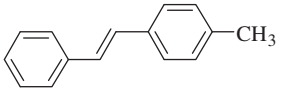
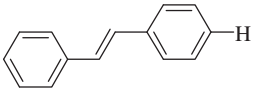
3.2.1. Mizoroki-Heck cross-coupling reaction. Mizoroki-Heck cross-coupling reactions [32–35] have attracted a great deal of attention since its discovery in the early 1970s [36, 37]. The coupling of aryl halides with alkenes has been used in the synthesis of industrially applicable compounds [12] along with a number of natural products [38]. Rates of the Heck and Suzuki cross-coupling reactions are dependent on parameters such as temperature,

solvent, base and catalyst loading. Generally, Heck reactions are conducted with tertiary phosphine [39] or NHC [40] complexes requiring temperatures above 120 °C and polar solvents such as DMAc, DMF or DMA in the presence of base. Both K_2CO_3 and *t*-BuOK were tested as bases for the reactions. For each base, approximately the same results are obtained. So, in the Heck and Suzuki cross-coupling reactions, we prefer K_2CO_3 because it is cheaper than *t*-BuOK. The results are summarized in table 1. We have not conducted control experiments because Özdemir, Yaşar, et al. have made these experiments and the results indicate that the Heck and Suzuki cross-coupling reactions do not occur in the absence of ligand precursors [41, 42].

Under the reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups such as p-bromoacetophenone, p-bromobenzaldehyde, p-bromobenzene, p-bromoanisole, and p-bromotoluene gave excellent yields. These results indicate that the catalytic systems generated *in situ* from these benzimidazolium salts and $Pd(OAc)_2$ have good activities. The yield of Heck coupling reaction is between 80 and 100%. The activities of the catalysts are close to each other. NHC precursor that contains

Table 1. The Heck coupling reaction of styrene by aryl bromides.[a–d]



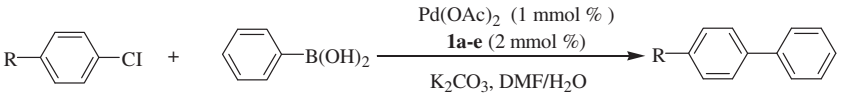
Entry	R	LHX	Product	Yield (%)
1	$COCH_3$	**1a**		98
2	$COCH_3$	**1b**		98
3	$COCH_3$	**1c**		96
4	$COCH_3$	**1d**		98
5	$COCH_3$	**1e**		95
6	CHO	**1a**		98
7	CHO	**1b**		99
8	CHO	**1c**		91
9	CHO	**1d**		94
10	CHO	**1e**		92
11	OCH_3	**1a**		90
12	OCH_3	**1b**		88
13	OCH_3	**1c**		98
14	OCH_3	**1d**		96
15	OCH_3	**1e**		90
16	CH_3	**1a**		97
17	CH_3	**1b**		100
18	CH_3	**1c**		100
19	CH_3	**1d**		99
20	CH_3	**1e**		97
21	H	**1a**		92
22	H	**1b**		80
23	H	**1c**		94
24	H	**1d**		95
25	H	**1e**		95

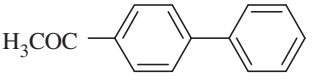
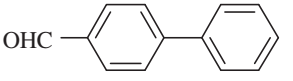
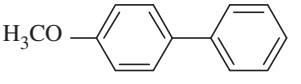
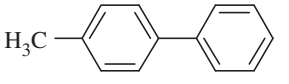
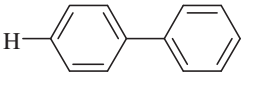
[a]Reaction conditions: p-R-C_6H_4Br (1.0 mM), styrene (1.5 mM), K_2CO_3 (2.0 mM), $Pd(OAc)_2$ (1.0 mM%), **1** (2.0 mM%), water (3 mL)-DMF (3 mL), 80 °C, 2 h. [b]Purity of compounds is checked by NMR. [c]All reactions were monitered by GC spectroscopy and yields are based on arylbromide. [d]Isolated yields.

dioxane substituents (**1d**) is the most effective of the examined salts. Chloroarenes do not react under standard conditions, and the yields are typically less than 5%.

3.2.2. Suzuki-Miyaura cross-coupling reaction. The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halides and pseudohalides represents a powerful method for C–C bond formation [43]. Suzuki reaction of aryl chlorides catalyzed by palladium/tertiary phosphine [39] and palladium/NHC [44–46] systems have been studied owing to the economically attractive nature of the starting materials and production of less toxic by-products (e.g. NaCI instead of NaBr). The coupling of aryl halides with phenyl boronic acid has been used in the synthesis of industrially important compounds along with natural products. Here, various benzimidazolium salts (**1a**–**e**) were compared as ligand precursors under the same reaction conditions. To survey the parameters for the Suzuki reaction, we have found that the reactions performed in DMF/H_2O (1 : 1) with K_2CO_3 or *t*-BuOK at 80 °C appear to be the best within 2 h. The results are summarized in table 2.

Table 2. The Suzuki-Miyaura coupling reaction of phenylboronic acid using aryl chlorides.[a–d]



Entry	R	LHX	Product	Yield (%)
1	$COCH_3$	**1a**		93
2	$COCH_3$	**1b**		86
3	$COCH_3$	**1c**		100
4	$COCH_3$	**1d**		91
5	$COCH_3$	**1e**		88
6	CHO	**1a**		78
7	CHO	**1b**		88
8	CHO	**1c**		87
9	CHO	**1d**		76
10	CHO	**1e**		76
11	OCH_3	**1a**		88
12	OCH_3	**1b**		78
13	OCH_3	**1c**		81
14	OCH_3	**1d**		70
15	OCH_3	**1e**		79
16	CH_3	**1a**		75
17	CH_3	**1b**		71
18	CH_3	**1c**		75
19	CH_3	**1d**		85
20	CH_3	**1e**		78
21	H	**1a**		96
22	H	**1b**		83
23	H	**1c**		93
24	H	**1d**		80
25	H	**1e**		81

[a]Reaction conditions: p-R-C_6H_4Cl (1.0 mM), phenylboronic acid (1.5 mM), $Pd(OAc)_2$ (1.0 mM%), K_2CO_3 (2.0 mM), **1** (2.0 mM%), water (3 mL)-DMF (3 mL), 80 °C, 2 h. [b]Purity of compounds is checked by NMR. [c]All reactions were monitered by GC spectroscopy and yields are based on arylchloride. [d]Isolated yields.

In **1a**–**e**/$Pd(OAc)_2$ catalysts, the Suzuki-Miyaura coupling yields of 4-chloroacetophenone, 4-chlorobenzaldehyde, 4-chloroanisole, 4-chlorotoluene and 4-chlorobenzene with phenylboronic acid were obtained. The 1-phenyl-3-alkylbenzimidazol-2-ylidene salts that contain a wide range of aryl chlorides bearing electron-donating or electron-withdrawing groups react with phenyl boronic acid affording the coupled products in yields of 70–100%. The activities of ligand precursor are close to each other. As a result, synthesized benzimidazolium salts are effective ligands in the Mizoroki-Heck and the Suzuki-Miyaura cross-coupling reactions.

These results are in agreement with other reports on palladium-carbene-catalyzed Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions [8, 21, 23, 27, 29, 41, 42].

4. Conclusions

Air and water stable benzimidazolium salts (**1a**–**e**) were synthesized and characterized by ^1H NMR, ^{13}C NMR, FT-IR and elemental analyses. These salts were active for the Heck and Suzuki reactions in a DMF–water mixture. Only aryl chlorides are reluctant to give the Heck reaction in the presence of $Pd(OAc)_2$/1-phenyl-3-alkylbenzimidazolium salts (**1a**–**e**). The LHX efficiency used in the Mizoroki-Heck and Suzuki-Miyaura coupling reactions were similar with best yields achieved for activated p-bromotoluene and p-chloroacetophenone, respectively.

Acknowledgments

This work was financially supported by Inönü University Research Fund (I.U. B.A.P. 2011/130).

References

[1] E.A.B. Kantchev, C.J. O'Brien, M.G. Organ. *Angew. Chem. Int. Ed.*, **46**, 2768 (2007).
[2] O.H. Winkelmann, A. Riekstins, S.P. Nolan, O. Navarro. *Organometallics*, **28**, 5809 (2009).
[3] S.H. Wiedemann, J.C. Lewis, J.A. Ellman, R.G. Bergman. *J. Am. Chem. Soc.*, **128**, 2452 (2006).
[4] T. Ritter, M.W. Day, R.H. Grubbs. *J. Am. Chem. Soc.*, **128**, 11768 (2006).
[5] X. Zhang, S. Gu, Q. Xia, W. Chen. *J. Organomet. Chem.*, **694**, 2359 (2009).
[6] İ. Özdemir, S. Demir, S. Günal, İ. Özdemir, C. Arıcı, D. Ülkü. *Inorg. Chim. Acta*, **363**, 3803 (2010).
[7] M. Akkurt, S. Akkoç, Y. Gök, Y. Dağdemir, M.N. Tahir. *Acta Crystallogr.*, **E68**, 590 (2012).
[8] S. Demir, İ. Özdemir, B. Çetinkaya. *Appl. Organomet. Chem.*, **23**, 520 (2009).
[9] V. Resch, J.H. Schrittwieser, E. Siirola, W. Kroutil. *Curr. Opin. Biotechnol.*, **22**, 1 (2011).
[10] R.E. Minto, B.J. Blacklock. *Prog. Lipid Res.*, **47**, 233 (2008).
[11] N.T.S. Phan, M. Van Der Sluys, C.W. Jones. *Adv. Synth. Catal.*, **348**, 609 (2006).
[12] J.-P. Corbet, G.R. Mignani. *Chem. Rev.*, **106**, 2651 (2006).
[13] N. Gürbüz, İ. Özdemir, T. Seçkin, B. Çetinkaya. *J. Inorg. Organomet. Polym.*, **14**, 149 (2004).
[14] Q.E. Wang, J. Zhong, J.-H. Xie, K. Li, Q.-L. Zhou. *Adv. Synth. Catal.*, **346**, 595 (2004).
[15] H. Palencia, F. Garcia-Jimenez, J.M. Takacs. *Tetrahedron Lett.*, **45**, 3849 (2004).
[16] B. Yiğit, Y. Gök, İ. Özdemir, S. Günal. *J. Coord. Chem.*, **65**, 371 (2012).
[17] W.A. Herrmann. *Angew. Chem. Int. Ed.*, **41**, 1290 (2002).
[18] F.E. Hahn. *Angew. Chem. Int. Ed.*, **45**, 1348 (2006).
[19] V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann. *J. Organomet. Chem.*, **595**, 186 (2000).
[20] M.S. Viciu, R.F. Germeneau, O. Navarro-Fernandez, E.D. Stevens, S.P. Nolan. *Organometallics*, **21**, 5470 (2002).
[21] Y. Gök, N. Gürbüz, İ. Özdemir, B. Çetinkaya, E. Çetinkaya. *Appl. Organomet. Chem.*, **19**, 870 (2005).
[22] S. Demir, İ. Özdemir, B. Çetinkaya, E. Şahin, C. Arici. *J. Coord. Chem.*, **64**, 2565 (2011).
[23] İ. Özdemir, N. Gürbüz, Y. Gök. *Transition Met. Chem.*, **30**, 367 (2005).
[24] İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, C. Bruneau. *Eur. J. Inorg. Chem.*, **1798**, (2010).

[25] S. Demir, İ. Özdemir, B. Çetinkaya, H. Arslan, D. VanDerveer. *Polyhedron*, **30**, 195 (2011).
[26] C. Li, T.H. Chan. *Organic Ractions in Aqueous Media*, Wiley, New York, NY (1997).
[27] İ. Özdemir, Y. Gök, N. Gürbüz, E. Çetinkaya, B. Çetinkaya. *Heteroat. Chem.*, **15**, 419 (2004).
[28] O.V. Starikova, G.V. Dolgushin, L.I. Larina, P.E. Ushakov, T.N. Komarova, V.A. Lopyrev. *Russ. J. Org. Chem.*, **39**, 1467 (2003).
[29] İ. Ozdemir, Y. Gök, N. Gürbüz, E. Çetinkaya, B. Çetinkaya. *J. Heterocycl. Chem.*, **42**, 303 (2005).
[30] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C.L. Yang, S.P. Nolan. *J. Organomet. Chem.*, **653**, 69 (2002).
[31] C.M. Zhang, M.L. Trudell. *Tetrahedron Lett.*, **41**, 595 (2000).
[32] F. Alonso, I.P. Beletskaya, M. Yus. *Tetrahedron*, **61**, 11771 (2005).
[33] B.M. Bhanage, M. Arai. *Catal. Rev. Sci. Eng.*, **43**, 315 (2001).
[34] G.D. Frey, J. Schutz, E. Herdtweck, W.A. Herrmann. *Organometallics*, **24**, 4416 (2005).
[35] W.A. Herrmann, V.P.W. Böhm. *J. Organomet. Chem.*, **572**, 141 (1999).
[36] T. Mizoroki, K. Mori, A. Ozaki. *Bull. Chem. Soc. Jpn.*, **44**, 581 (1971).
[37] R.F. Heck, J.P. Nolley., Jr. *J. Org. Chem.*, **37**, 2320 (1972).
[38] K.C. Nicolaou, P.G. Bulger, D. Sarlah. *Angew. Chem. Int. Ed.*, **44**, 4442 (2005).
[39] A.F. Littke, G. Angew. *Chem. Int. Ed.*, **41**, 4176 (2002).
[40] J.A. Loch, M. Albrecht, E. Peris, J. Malta, J.W. Faller, R.H. Crabtree. *Organometallics*, **21**, 700 (2002).
[41] İ. Özdemir, Y. Gök, N. Gürbüz, B. Çetinkaya. *Turk. J. Chem.*, **31**, 397 (2007).
[42] S. Yaşar, İ. Özdemir, B. Çetinkaya. *Chin. J. Catal.*, **29**, 185 (2008).
[43] C. Baillie, J.L. Xiao. *Tetrahedron*, **60**, 4159 (2004).
[44] C.M. Zhang, J.K. Huang, M.L. Trudell, S.P. Nolan. *J. Org. Chem.*, **64**, 3804 (1999).
[45] G.A. Grasa, M.S. Viciu, J.K. Huang, C.M. Zhang, M.L. Trudell, S.P. Nolan. *Organometallics*, **21**, 2866 (2002).
[46] G. Altenhoff, R. Goddard, C.W. Lehmann, F. Glorius. *J. Am. Chem. Soc.*, **126**, 15195 (2004).