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THE SYNTHESIS OF SOME BENZIMIDAZOLIUM SALTS AND USE AS CARBENE PRECURSORS IN THE HECK AND SUZUKI REACTIONS

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Abstract- Novel 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium salts as *N*-heterocyclic carbene precursors **2a-g** were prepared by quarternazition of 1-(2-diisopropylaminoethyl)benzimidazoles in DMF with alkyl halides. The salts were characterized spectroscopically and in situ formed complexes from $Pd(OAc)_2$ and **2** have been tested as catalyst in homogenous Heck and Suzuki reactions.

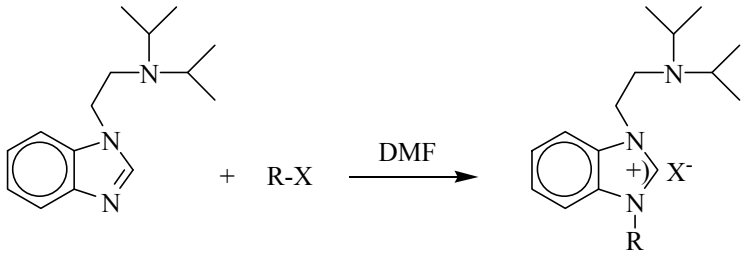
INTRODUCTION

Palladium-catalyzed Heck and Suzuki cross coupling reactions are among the most powerfull tools for the formation of C-C bonds in modern synthetic chemistry.[1-6] For many years, phosphines have been the most commonly used as ligands for these reactions. The phosphine ligands are expensive, toxic and unrecoverable, which needs high temperatures and bases, and have limited substrate generality and selectivity.[7-10] N-Heterocyclic carbenes have proven to be electron rich donors which provide higher reactivity and stability toward heat, air and moisture than phosphines. Typical N-Heterocyclic carbene complexes, formed by treatment of an imidazolium, imidazolinium or benzimidazolium salt with base and metal, are air-stable and have recently been used for several catalytic applications including Heck and Suzuki cross-coupling, olefin metathesis, hydrogenation, arylation and hydrosilylation reactions.[11-20] The Heck and Suzuki couplings are fascinating reactions from a catalysis science perspective. Initially,

water-soluble phosphines were used as ligands for the cross-coupling reactions in aqueous media,[21] but in recent years, other hydrophilic phosphine-free systems[22] and soluble palladium nanoparticles[23-25] have also been found to be higly efficient catalysts for this transformation. 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.[26] There have been a number of reports of the palladium-mediated Heck and Suzuki reaction being performed using water as solvent.[27-35] Due to the large number of Suzuki and other coupling reactions that are carried out in aqueous[27] or biphasic systems, there has been an increased interest in the development of water-soluble ligands for these reactions. Shaughnessy and co-workers utilized both sterically demanding water-soluble alkylphosphines[36] and triarylphosphines[37] in Suzuki and Heck couplings of aryl bromides, respectively. In general, NHC chemistry is dominated by imidazole and imidazoline based carbene ligands. On the other hand, benzimidazole carbene ligands have been less explored than imidazole and imidazoline. We have previously reported the use of the various catalytic systems, such as palladium-catalyzed cross-coupling, ruthenium-catalyzed hydrogenation and rhodium-catalyzed arylation or hydrosilylation.[38-43] 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 catalyst, we have prepared a series of new benzimidazolium chlorides and bromide, **2a-g** (Scheme 1), and we report here in situ palladium-carbene based catalytic system for Heck and Suzuki cross-coupling from aryl halides. The catalysts were prepared in situ by mixing $Pd(OAc)_2$ and NHC yield probably a mixture of palladium-NHC complex and palladium nanoparticles.[44]

RESULTS AND DISCUSSION

As shown in Scheme 1, 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium salts were readily prepared by quarternazition of 1-(2-diisopropylaminoethyl)benzimidazoles in DMF with alkyl halides. After purification, the 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium salts **2a-g** were obtained in good yields of 72-84%. The salts are soluble in common polar solvents and are stable under air and in the presence of moisture. The structures of **2** were determined by their spectroscopic data and elemental analyses (see experimental section). The ^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet at 144.10, 144.40, 143.90, 143.90, 144.28, 143.24 and 143.91 ppm respectively for 1,3-dialkylbenzimidazolium salts **2a-g**. The ^{1}H NMR spectra of perhydrobenzimidazolinium salts further supported the assigned structures. The resonances of the C(2)-H were observed as sharp singlets at δ = 10.72, 11.20, 11.14, 11.18, 11.36, 10.92 and 10.84 ppm for **2a-g**, respectively. The IR data for benzimidazolinium **2a-g** salts clearly indicate the presence of the –C=N- group with a ν(C=N) vibration at 1558, 1565, 1554, 1560, 1556, 1562 and 1552 cm^{-1} for **2a-g** respectively. These NMR and IR values were similar to other 1,3-dialkylbenzimidazolium salts.[14,45]



1 **2**

2a R= $CH_2C_6H_2Me_3$-2,4,6 X= Cl^-

2b R= $CH_2C_6H_4Me$-2 X= Cl^-

2c R= $CH_2C_6H_4Me$-3 X= Cl^-

2d R= $CH_2C_6H_4Me$-4 X= Cl^-

2e R= $CH_2C_6H_5$ X= Cl^-

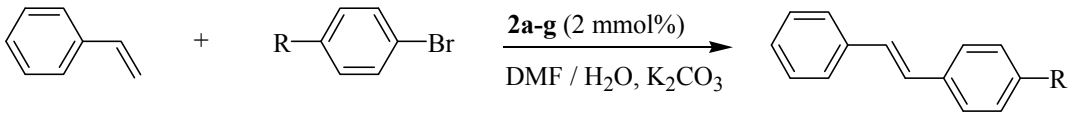
2f R= $CH_2CH_2C_6H_5$ X= Br^-

2g R= $CH(C_6H_5)_2$ X= Cl^-

Scheme 1. Synthesis of 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium salts.

Pd-catalyzed Heck reaction is an efficient way to prepare styrene derivatives, which are important chemicals for many applications. The Heck C-C coupling reactions of aryl halides with styrene were carried out homogenously with $Pd(OAc)_2$/**2a-g** as catalysts in the presence of a base in air. For optimal reaction conditions, the $Pd(OAc)_2$-catalyzed cross coupling of brombenzene with styrene was employed as the model reaction using ligand **2a** at 80 °C, as the base commonly used bases Cs_2CO_3, K_2CO_3, K_3PO_4 and *t*-BuOK were tested. The coupling reactions of aryl bromides and styrene were carried out in DMF/H_2O (3:3 mL) with 1 mol% $Pd(OAc)_2$, 2 mol% **2** and 2 equiv. K_2CO_3 for 2 h at 80 °C. The reactions in this conditions gave the coupling products in good yields (79-95) and the coupling reaction did not occur in the absence of benzimidazolium salt. The results are summarized in Table 1.

Table 1. The Heck coupling reaction of aryl bromides with styrene



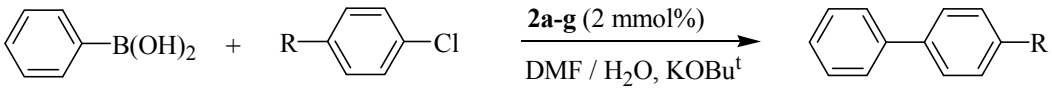
Entry	R	Catalyst	Yield[a,b,c,d] (%)
1	COMe	**2a**	96
2	COMe	**2b**	94
3	COMe	**2c**	94
4	COMe	**2d**	95

5	COMe	**2e**	92
6	COMe	**2f**	90
7	COMe	**2g**	96
8	Me	**2a**	92
9	Me	**2b**	92
10	Me	**2c**	90
11	Me	**2d**	93
12	Me	**2e**	83
13	Me	**2f**	85
14	Me	**2g**	94
15	CHO	**2a**	82
16	CHO	**2b**	80
17	CHO	**2c**	88
18	CHO	**2d**	79
19	CHO	**2e**	90
20	CHO	**2f**	92
21	CHO	**2g**	89
22	OMe	**2a**	93
23	OMe	**2b**	92
24	OMe	**2c**	90
25	OMe	**2d**	89
26	OMe	**2e**	87
27	OMe	**2f**	84
28	OMe	**2g**	94
29	H	**2a**	94
30	H	**2b**	92
31	H	**2c**	93
32	H	**2d**	91
33	H	**2e**	89
34	H	**2f**	87
35	H	**2g**	95

[a] *Reaction conditions*: 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2 mmol K_2CO_3, 1 mmol $Pd(OAc)_2$, 2 mmol% **2a-g**, DMF/H_2O (3 / 3 mL), [b] purity of compounds is checked by NMR and yields are based on aryl halide. [c] All reactions were monitored by TLC, [d] temperature 80 °C, 2h.

Under these reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups react with styrene affording the coupled products in excellent yields (Table 1, entries 1, 14, 20, 28 and 35). We observed that the benzimidazolium salts bearing methyl groups (**2a**, **2b**, **2c**, **2d**) and benzhydryl group (**2g**) were the most effective of the salts than nonsubstituted counterparts for the Heck reactions (**2e**, **2f**). The Suzuki coupling of phenylboronic acid with aryl chlorides to form biaryls were undertaken with $Pd(OAc)_2$/**2a-g** as catalysts. Similar reaction conditions were employed to the Suzuki reactions. As the base $KOBu^t$ was used. The coupling reactions of aryl chlorides and phenylboronic acid were carried out in DMF/H_2O (3:3 mL) with 1 mol% $Pd(OAc)_2$, 2 mol% **2** and 2 equiv. $KOBu^t$ for 2 h at 80 ^oC. We started our investigation on the coupling of 4-chloroacetophenone and phenylboronic in the presence of $Pd(OAc)_2$/**2**. The results are summarized in Table 2.

Table 2. The Suzuki coupling reaction of aryl chlorides with phenylboronic acid



Entry	R	Catalyst	Yield[a,b,c,d] (%)
1	COMe	**2a**	96
2	COMe	**2b**	94
3	COMe	**2c**	93
4	COMe	**2d**	91
5	COMe	**2e**	92
6	COMe	**2f**	90
7	COMe	**2g**	95
8	Me	**2a**	85
9	Me	**2b**	80
10	Me	**2c**	82
11	Me	**2d**	81
12	Me	**2e**	75
13	Me	**2f**	72
14	Me	**2g**	87
15	CHO	**2a**	93

16	CHO	**2b**	86
17	CHO	**2c**	89
18	CHO	**2d**	84
19	CHO	**2e**	82
20	CHO	**2f**	80
21	CHO	**2g**	91
22	OMe	**2a**	88
23	OMe	**2b**	82
24	OMe	**2c**	84
25	OMe	**2d**	81
26	OMe	**2e**	78
27	OMe	**2f**	76
28	OMe	**2g**	85

[a] *Reaction conditions*: 1.0 mmol of R-C_6H_4Cl-*p*, 1.5 mmol of phenylboronic acid, 2 mmol $KOBu^t$, 1 mmol $Pd(OAc)_2$, 2 mmol% **2a-g**, DMF/H_2O (3 / 3 mL), [b] purity of compounds is checked by NMR and yields are based on aryl chloride. [c] All reactions were monitored by TLC, [d] temperature 80 ^oC, 2h.

As seen the Heck reactions, the **2a** catalyst system is more effective for the Suzuki reactions. It can be show these salts are an effective ligand precursor for the coupling of unactivated, activated and deactivated chlorides. These results are in agreement with other reports.[14,45,46]

CONCLUSION

In conclusion, we have synthesized seven 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium chloride and bromide salts and have investigated their catalytic activity in the Heck and Suzuki coupling reactions. In this study, the **2a** catalyst system is seen to be the most effective both the Heck reactions of aryl bromides with styrene and the Suzuki reactions of aryl chlorides with phenylboronic acid. The procedure is simple and efficient toward various types of aryl halides and does not require induction period. The advandage of the catalyst is that it has low-loading capabilities, and it is useable in air. Detailed investigations, focusing on imidazolidin-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 for the preparation of 1-(2-diisopropylaminoethyl)-3-alkylbenzimidazolium salts (**2a-g**) were carried out under argon using standart Schlenk-type flasks. Heck and Suzuki coupling reactions

were carried out in air. All reagents were purchased from Aldrich Chemical Co., Turkey. All ^{1}H and ^{13}C NMR were performed in $CDCI_3$ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. FT-IR spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC were measured on a Agilent 6890N gas chromatograph by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at TUBITAK (Ankara, Turkey) Microlab.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride (2a).
To a solution of 1-(2-diisopropylaminoethyl)benzimidazole (1.5 g, 6.11 mmol) in DMF (2 mL), 2,4,6-trimethylbenzyl chloride (1.03 g, 6.11 mmol) was added; the resulting solution was stirred for 1 h at room temperature and heated for 12 h at 80 ^{o}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: 1.99 g, 79%, mp 270-272 ^{o}C. IR, ν: 1558 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.69 (d, 12H, J = 5.6 Hz, NCH(CH_3)$_2$); 2.95 (m, 2H, NCH(CH$_3$)$_2$); 2.86 (m, 2H, CH$_2$CH_2N(Pr^i)$_2$); 4.66 (s, 2H, CH_2CH$_2$N(Pr^i)$_2$); 5.72 (s, 2H, CH_2C$_6$H$_2$(CH$_3$)$_3$-2,4,6); 2.24, 2.29 (s, 9H, CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6); 6.88 (s, 2H, CH$_2$C$_6H_2$(CH$_3$)$_3$-2,4,6); 7.32, 7.73 (d, 2H, J = 8.4 Hz, Ar-H); 7.42, 7.52 (t, 2H, J = 7.6 Hz, Ar-H); 10.72 (s, 1H, 2-CH). $^{13}C\{1H\}$-NMR ($CDCl_3$) δ: 20.42 (NCH(CH_3)$_2$); 47.32 (NCH(CH$_3$)$_2$); 43.98 (CH$_2$CH_2N(Pr^i)$_2$); 46.86 (CH_2CH$_2$N(Pr^i)$_2$); 47.61 (CH_2C$_6$H$_2$(CH$_3$)$_3$-2,4,6); 20.78, 21.25 (CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6); 96.33, 113.57, 125.42, 126.83, 127.00, 130.32, 131.49, 132.00, 138.30, 139.95 (Ar-C); 144.10 (2-CH). Anal. Calcd for $C_{25}H_{36}N_3Cl$: C, 72.55; H, 8.71; N, 10.15. Found: C, 72.33; H, 8.78; N, 10.11.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(2-methylbenzyl)benzimidazolium chloride (2b).
This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.18 g, 4.81 mmol) and 2-methylbenzyl chloride (0.68 g, 4.81 mmol) in DMF (2 mL). Yield: 1.52 g, 82%, mp 198-199 ^{o}C. IR, ν: 1565 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.72 (s, 12H, NCH(CH_3)$_2$); 2.95 (m, 2H, NCH(CH$_3$)$_2$); 2.90 (m, 2H, CH$_2$CH_2N(Pr^i)$_2$); 4.58 (s, 2H, CH_2CH$_2$N(Pr^i)$_2$); 5.88 (s, 2H, CH_2C$_6$H$_4$CH$_3$-2); 2.36 (s, 3H, CH$_2$C$_6$H$_4$CH_3-2); 7.07-7.56 (m, 8H, Ar-H); 11.20 (s, 1H, 2-CH). $^{13}C\{1H\}$-NMR ($CDCl_3$) δ: 18.62, 19.74 (NCH(CH_3)$_2$); 49.63 (NCH(CH$_3$)$_2$); 44.22 (CH$_2$CH_2N(Pr^i)$_2$); 47.86 (CH_2CH$_2$N(Pr^i)$_2$); 58.08 (CH_2C$_6$H$_4$CH$_3$-2); 20.81 (CH$_2$C$_6$H$_4$CH_3-2); 113.55, 113.77, 126.94, 127.14, 128.74, 129.45, 131.03, 131.38, 131.46, 131.81, 136.68 (Ar-C); 144.40 (2-CH). Anal. Calcd for $C_{23}H_{32}N_3Cl$: C, 71.59; H, 8.30; N, 10.89. Found: C, 71.65; H, 8.46; N, 10.95.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(3-methylbenzyl)benzimidazolium chloride (2c).

This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.18 g, 4.81 mmol) and 3-methylbenzyl chloride (0.68 g, 4.81 mmol) in DMF (2 mL). Yield: 1.57 g, 84%, mp 190-192 ^{o}C. IR, ν: 1554 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.69 (d, J = 6.4 Hz, 12H, NCH(CH_3)$_2$); 2.97 (m, 2H, NCH(CH$_3$)$_2$); 2.88 (m, 2H, CH$_2$CH_2N(Pr^i)$_2$); 4.56 (s, 2H, CH_2CH$_2$N(Pr^i)$_2$); 5.77 (s, 2H, CH_2C$_6$H$_4$CH$_3$-3); 2.24 (s, 3H, CH$_2$C$_6$H$_4$CH_3-3); 7.04-7.71 (m, 8H, Ar-H); 11.14 (s, 1H, 2-CH). ^{13}C{1H}-NMR ($CDCl_3$) δ: 20.78 (NCH(*C*H$_3$)$_2$); 47.86 (N*C*H(CH$_3$)$_2$); 44.12 (CH$_2$*C*H$_2$N(Pr^i)$_2$); 47.45 (*C*H$_2$CH$_2$N(Pr^i)$_2$); 51.35 (*C*H$_2$C$_6$H$_4$CH$_3$-3); 21.45 (CH$_2$C$_6$H$_4$*C*H$_3$-3); 113.42, 113.80, 125.71, 126.97, 127.03, 129.12, 129.27, 130.05, 131.20, 131.82, 133.17, 139.31 (Ar-*C*); 143.90 (2-*C*H). Anal. Calcd for $C_{23}H_{32}N_3Cl$: C, 71.59; H, 8.30; N, 10.89. Found: C, 71.46; H, 8.25; N, 10.76.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(4-methylbenzyl)benzimidazolium chloride (2d).

This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.06 g, 4.32 mmol) and 4-methylbenzyl chloride (0.61 g, 4.32 mmol) in DMF (2 mL). Yield: 1.33 g, 80%, mp 188-189 ^{o}C. IR, ν: 1560 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.71 (d, J = 6.4 Hz, 12H, NCH(CH_3)$_2$); 2.96 (m, 2H, NCH(CH$_3$)$_2$); 2.88 (m, 2H, CH$_2$CH_2N(Pr^i)$_2$); 4.55 (m, 2H, CH_2CH$_2$N(Pr^i)$_2$); 5.76 (s, 2H, CH_2C$_6$H$_4$CH$_3$-4); 2.20 (s, 3H, CH$_2$C$_6$H$_4$CH_3-4); 7.06, 7.33 (d, 4H, J = 8.0 Hz, CH$_2$C$_6$$H_4CH_3$-4); 7.52 (m, 4H, Ar-$H$); 11.18 (s, 1H, 2-C$H$). ^{13}C{1H}-NMR ($CDCl_3$) δ: 20.76 (NCH(*C*H$_3$)$_2$); 48.07 (N*C*H(CH$_3$)$_2$); 44.24 (CH$_2$*C*H$_2$N(Pr^i)$_2$); 47.47 (*C*H$_2CH_2$N(Pr^i)$_2$); 51.22 (*C*H$_2C_6H_4CH_3$-4); 21.32 (CH$_2C_6H_4$*C*H$_3$-4); 113.40, 113.83, 126.95, 126.99, 128.67, 130.04, 130.22, 131.16, 131.87, 139.26 (Ar-*C*); 143.90 (2-*C*H). Anal. Calcd for $C_{23}H_{32}N_3Cl$: C, 71.59; H, 8.30; N, 10.89. Found: C, 71.63; H, 8.48; N, 10.76.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(benzyl)benzimidazolium chloride (2e).

This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.50 g, 6.11 mmol) and benzyl chloride (0.77 g, 6.11 mmol) in DMF (2 mL). Yield: 1.83 g, 81%, mp 194-195 ^{o}C. IR, ν: 1556 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.73 (s, 12H, NCH(CH_3)$_2$); 2.94 (m, 2H, NCH(CH$_3$)$_2$); 2.55 (m, 2H, CH$_2$CH_2N(Pr^i)$_2$); 4.57 (m, 2H, CH_2CH$_2$N(Pr^i)$_2$); 5.83 (d, 2H, J = 12.8 Hz, CH_2C$_6$H$_5$); 7.35-7.71 (m, 9H, Ar-H); 11.36 (s, 1H, 2-CH). ^{13}C{1H}-NMR ($CDCl_3$) δ: 20.71 (NCH(*C*H$_3$)$_2$); 47.92 (N*C*H(CH$_3$)$_2$); 44.38 (CH$_2$*C*H$_2$N(Pr^i)$_2$); 47.56 (*C*H$_2$CH$_2$N(Pr^i)$_2$); 51.44 (*C*H$_2$C$_6$H$_5$); 96.32, 113.78, 114.03, 127.02, 128.55, 128.73, 129.31, 129.45, 129.53, 131.19, 131.87, 133.29 (Ar-*C*); 144.28 (2-*C*H). Anal. Calcd for $C_{22}H_{30}N_3Cl$: C, 71.06; H, 8.07; N, 11.30. Found: C, 71.13; H, 8.16; N, 11.37.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(phenethyl)benzimidazolium bromide (2f).

This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.02 g, 4.16 mmol) and

phenethyl bromide (0.77 g, 4.16 mmol) in DMF (2 mL). Yield: 1.29 g, 72%, mp 196-197 °C. IR, ν: 1562 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 0.78 (d, 12H, J = 6.4 Hz, $NCH(CH_3)_2$); 2.97 (m, 2H, $NCH(CH_3)_2$); 2.87 (m, 2H, $CH_2CH_2N(Pr^i)_2$); 4.51 (m, 2H, $CH_2CH_2N(Pr^i)_2$); 3.34 (t, 2H, J = 7.6 Hz, $CH_2CH_2C_6H_5$); 4.87 (t, 2H, J = 7.6 Hz, $CH_2CH_2C_6H_5$); 7.21 (m, 5H, $CH_2CH_2C_6H_5$); 7.58 (m, 4H, Ar-*H*); 10.92 (s, 1H, 2-C*H*). ^{13}C{1H}-NMR ($CDCl_3$) δ: 20.92 ($NCH(CH_3)_2$); 48.26 ($NCH(CH_3)_2$); 44.38 ($CH_2CH_2N(Pr^i)_2$); 47.75 ($CH_2CH_2N(Pr^i)_2$); 48.77 ($CH_2CH_2C_6H_5$); 35.99 ($CH_2CH_2C_6H_5$); 113.11, 113.44, 127.06, 127.09, 127.52, 129.11, 129.15, 131.31, 131.48, 136.28 (Ar-*C*); 143.24 (2-*C*H). Anal. Calcd for $C_{23}H_{32}N_3Br$: C, 64.18; H, 7.44; N, 9.76. Found: C, 64.21; H, 7.56; N, 9.71.

Synthesis of 1-(2-diisopropylaminoethyl)-3-(benzhydryl)benzimidazolium chloride (2g).

This compound was prepared from 1-(2-diisopropylaminoethyl)benzimidazole (1.20 g, 4.90 mmol) and benzhydryl chloride (0.99 g, 4.90 mmol) in DMF (2 mL). Yield: 1.66 g, 76%, mp 215-216 °C. IR, ν: 1552 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) δ: 1.45, 1.51 (d, 12H, J = 6.8 Hz, $NCH(CH_3)_2$); 3.62 (m, 2H, $NCH(CH_3)_2$); 2.30 (m, 2H, $CH_2CH_2N(Pr^i)_2$); 4.01 (m, 2H, $CH_2CH_2N(Pr^i)_2$); 5.56 (m, 1H, $CH(C_6H_5)_2$); 7.27, 7.63 (t, 6H, J = 8.0 Hz, $CH(C_6H_5)_2$); 8.76 (d, 4H, J = 8.4 Hz, $CH(C_6H_5)_2$); 7.40 (m, 4H, Ar-*H*); 10.84 (s, 1H, 2-C*H*). ^{13}C{1H}-NMR ($CDCl_3$) δ: 18.05, 18.92 ($NCH(CH_3)_2$); 55.31 ($NCH(CH_3)_2$); 43.95 ($CH_2CH_2N(Pr^i)_2$); 45.42 ($CH_2CH_2N(Pr^i)_2$); 67.42 ($CH(C_6H_5)_2$); 114.54, 115.51, 127.77, 128.43, 128.63, 129.88, 129.95, 131.10, 131.91, 135.05 (Ar-*C*); 143.91 (2-*C*H). Anal. Calcd for $C_{28}H_{34}N_3Cl$: C, 75.08; H, 7.59; N, 9.38. Found: C, 75.22; H, 7.74; N, 9.26.

General Procedure for the Heck-Type Coupling Reactions

$Pd(OAc)_2$ (1 mmol%), 1,3-dialkylbenzimidazolium salt, **2a-g** (2 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol) and water (3 mL)-DMF (3 mL) were added in a Schlenk tube under argon and mixture was heated at 80 °C for 2 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 GC. The yields are based on aryl bromide.

General Procedure for the Suzuki-Type Coupling Reactions

$Pd(OAc)_2$ (1 mmol%), 1,3-dialkylbenzimidazolium salt, **2a-g** (2 mmol%), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), $KOBu^t$ (2 mmol) and water (3 mL)-DMF (3 mL) were added in a Schlenk tube under argon and mixture was heated at 80 °C for 2 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 GC. The yields are based on aryl chloride.

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REFERENCES

1. T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jpn*., 1971, **44**, 581.
2. R. F. Heck and J. F. Nolley, Jr., *J. Org. Chem*., 1972, **37**, 2320.
3. N. Miyaura, T. Tanagi, and A. Suzuki, *Synth. Commun*., 1981, **11**, 513.
4. N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457.
5. A. Suzuki, *J. Organomet. Chem*., 1999, **576**, 147.
6. A. Suzuki, *J. Organomet. Chem*., 2002, **653**, 83.
7. W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, and H. Fischer, *Angew. Chem., Int. Ed. Engl*., 1995, **34**, 1844.
8. W. A. Herrmann, V. P. W. Böhm, and C.-P. Reisinger, *J. Organomet. Chem*., 1999, **576**, 23.
9. A. F. Littke and G. C. Fu, *J. Am. Chem. Soc*., 2001, **123**, 6989.
10. I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev*., 2000, **100**, 3009.
11. H. Türkmen, S. Denizaltı, İ. Özdemir, E. Çetinkaya, and B. Çetinkaya, *J. Organomet. Chem*., 2008, **693**, 425.
12. A. Dallas, H. Kuhtz, A. Farrell, B. Quilty, and K. Nolan, *Tetrahedron Lett*., 2007, **48**, 1017.
13. Y. Han, H. V. Huynh, and L. L. Koh, *J. Organomet. Chem*., 2007, **692**, 3606.
14. W. Huang, J. Guo, Y. Xiao, M. Zhu, G. Zou, and J. Tang, *Tetrahedron*, 2005, **61**, 9783.
15. C. W. Bielowski and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2000, **39**, 2903.
16. A. Fürstner, M. Picquet, C. Bruneau, and P. H. Dixneuf, *Chem. Commun*., 1998, 1315.
17. A. C. Hillier, H. M. Lee, E. D. Stevens, and S. P. Nolan, *Organomeallics*, 2001, **20**, 4246.
18. S. Enthaler, R. Jackstell, B. Hagemann, K. Junge, G. Erre, and M. Beller, *J. Organomet. Chem*., 2006, **691**, 4652.
19. M. Sakai, M. Ueda, and N. Miyaura, *Angew. Chem. Int. Ed*., 1998, **37**, 3279.
20. D. Enders and H. Gielen, *J. Organomet. Chem*., 2001, **70**, 617.
21. A. L. Casalnuova and J. C. Calabrese, *J. Am. Chem. Soc*., 1990, **112**, 4324.
22. F. Churruca, R. SanMartin, B. Ines, I. Tellitu, and E. Dominquez, *Adv. Synth. Catal*., 2006, **348**, 1836.

23. A. Alimardanov, L. Schmieder-Van de Vondervoort, A. H. M. de Vries, and J. G. de Vries, *Adv. Synth. Catal*., 2004, **346**, 1812.
24. J. G. de Vries, *Dalton Trans*., 2006, 421.
25. D. Saha, K. Chattopadhyay, and B. C. Ranu, *Tetrahedron Lett*., 2009, **50**, 1003.
26. C. J. Li and T. H. Chan, "Organic Reactions in Aqueous Media", John Wiley & Sons, New York, 1997.
27. J. P. Genet and M. Savignac, *J. Organomet. Chem*., 1999, **576**, 305.
28. H. Sakurai, T. Tsukuda, and T. Hirao, *J. Org. Chem.*, 2002, **67**, 2721.
29. S. Parisot, R. Kolodziuk, C. G. Henry, A. Iourtchenko, and D. Sinou, *Tetrahedron Lett*., 2002, **43**, 7397.
30. D. Schönfelder, O. Nuyken, and R. Weberskirch, *J. Organomet. Chem*., 2005, **690**, 4648.
31. J. Zhou, X. Guo, C. Tu, X. Li, and H. Sun, *J. Organomet. Chem*., 2009, **694**, 697.
32. J. Ma, X. Cui, L. Gao, and Y. Wu, *Inorg. Chem. Commun*., 2007, **10**, 762.
33. Y. J. Shang, J. W. Wu, C. L. Fan, J. S. Hu, and B. Y. Lu, *J. Organomet. Chem*., 2008, **693**, 2963.
34. V. Vashchenko, A. Krivoshey, I. Knyazeva, A. Petrenko, and J. W. Goodby, *Tetrahedron Lett*., 2008, **49**,1445.
35. I. D. Kostas, A. G. Coutsolelos, G. Charalambidis, and A. Skondrab, *Tetrahedron Lett*., 2007, **48**, 6688.
36. K. H. Shaughnessy and R. S. Booth, *Org. Lett*., 2001, **3**, 2757.
37. L. R. Moore and K. H. Shaughnessy, *Org. Lett*., 2004, **6**, 225.
38. İ. Özdemir, M. Yiğit, E. Çetinkaya, and B. Çetinkaya, *Appl. Organometal. Chem*., 2006, **20**, 187.
39. M. Yiğit, *Molecules*, 2009, **14**, 2032.
40. M. Yiğit, B. Yiğit, İ. Özdemir, E. Çetinkaya, and B. Çetinkaya, *Appl. Organometal. Chem*., 2006, **20**, 322.
41. M. Yiğit, İ. Özdemir, E. Çetinkaya, and B. Çetinkaya, *Trans. Met. Chem*., 2007, **32**, 536.
42. İ. Özdemir, M. Yiğit, E. Çetinkaya, and B. Çetinkaya, *Heterocycles*, 2006, **68**, 1371.
43. M. Yiğit, İ. Özdemir, B. Çetinkaya, and E. Çetinkaya, *J. Mol. Catal. A*., 2005, **241**, 88.
44. N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, and S. P. Nolan, *J. Am. Chem. Soc*., 2006, **128**, 4101.
45. İ. Özdemir, Y. Gök, E. Çetinkaya, and B. Çetinkaya, *Heteroatom Chem*., 2004, **15**, 419.
46. N. Hadei, E. A. B. Kantchev, C. J. O'Brien, and M. G. Organ, *Org. Lett*., 2005, **7**, 1991.