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New Bisbenzimidazolin-2-Ylidene Salts as *N*-Heterocyclic Dicarbene Precursors: Synthesis, Characterization, and Involvement in Palladium-Catalyzed Suzuki Reactions

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ABSTRACT: *A new series of bis-N-heterocyclic carbene precursors, LHX (***3a–d***), have been synthesized and characterized by appropriate spectroscopic techniques and microanalyses. In situ prepared* $Pd(OAc)_2$*/bis-N-heterocyclic carbene precursors catalysts have catalyzed unactivated aryl chlorides on the Suzuki cross-coupling reaction under mild reaction conditions in aqueous media.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:157–162, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21148

INTRODUCTION

The Suzuki coupling reaction is one of the most common and preferred reaction for C—C bond formation of aryl and alkyl halogens in the presence of aryl boronic acid and has attracted much interest [1–7]. Although there are numerous existing methods for the synthesis of biaryls via cross-coupling reactions, the Suzuki reaction has been the most used over the course of the last few decades because of its several useful advantages compared to other available methods. One of the advantages of the Suzuki reaction is the use of nontoxic, thermally, air- and moisture-stable phenyl boronic acid and its derivatives.

Research have focused on developing a new catalyst precursor that can catalyze less reactive and cheaper aryl chlorides with low catalyst loading [8–10]. At the same time, the use of additives, design of catalyst, and changing of solvents are a couple of efforts for creating the best catalysis system. The use of water as a solvent for reactions has economical and environmental advantages as it is inexpensive, abundant, nontoxic, nonflammable, and easily separable from organic compounds. A number of studies of the Suzuki reaction have been performed in water as a solvent [11–14].

Lately, many bulky and electron-rich phosphines have been synthesized and promoted the Suzuki cross-coupling reaction [15, 16]. Substitution of commonly used triarylphosphines and phosphines ligands with sterically and electronically superior *N*-heterocyclic carbene (NHC) ligands generates more active catalyst for the Suzuki reaction of aryl chlorides and unactivated substrates [10]. Buchwald [17], Fu [18], Herrmann [19], and other groups have carried out pioneer studies with unactivated aryl chlorides.

NHCs have become the most preferable ligand for numerous transition metal–catalyzed reactions

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since the first stable free NHC was reported by Arduengo et al. [20, 21]. NHCs complexes are generally highly stable complexes. They have strong σ-donor [22] and weak π-acceptor [23] or sometimes weak π-donor [24] character and have an unrivalled form that may be used to generate sterically demanding ligands. The basicity of NHCs can be related to their σ-donor abilities [25]. σ-Donor abilities and basicity of NHCs increase with expanding N—C—N angles. Recently, ring-expanded NHCs have been synthesized, and catalytic features have been investigated by Cavell et al. [26–29]. Electronic properties of catalysts are more important for an oxidative addition step of the Suzuki reaction. Numerous NHC ligands, which have different electronic properties and similar steric demand, have been synthesized and used as a ligand for the Suzuki cross-coupling reaction of aryl chlorides. As expected, the highest yield was obtained by a palladium catalyst bearing electron-reach ligands [30]. However, electron-drawing group substitute ligands showed close reactivity to electron-rich group substitute ligands for aryl chlorides with arylboronic acid. Thus, reaching to a level of electron richness required for oxidative addition, a sterical modification of ligands becomes more important than an electrical modification [31]. Bulky NHC ligands can provide several advantages for a sterically demanding substrate for the Suzuki coupling reaction. Sterically big NHCs can simplify formation of catalytically active species, as well as make the reductive elimination step easy. Besides, oxidative addition or transmetalation steps might slow down because of the steric effect of NHCs [32, 33].

It has been found that in situ formation of the active catalyst by deprotonation of the imidazolinium chlorides with appropriate base leads to significantly better results than the use of the preformed palladium carbene complexes [34]. Encouraged by these results and to find a more efficient Suzuki catalysis system, we have synthesized a series of new bis-1,3-dialkylbenzimidazolium halides that have different steric properties (**3a–d**). We report a mild, practical in situ generated catalytic system composed of using $Pd(OAc)_2$ as the palladium source, bis-1,3-dialkylbenzimidazolium chlorides (**3a–d**) as carbene precursors, KO*t*Bu as a base, and water–N,N-dimethylformamide (DMF) as a solvent for Suzuki cross-coupling of aryl chlorides.

RESULTS AND DISCUSSION

Bisdialkylbenzimidazolinium salts, LHX (**3a–d**) are classic bis-NHC precursors. The salts, **3a–c**, were obtained in almost quantitative yield by quaternazition of 1-alkyl-benzimidazoline [35–37] in DMF with alkyl halides (Fig. 1). The structures of **3a–d** were determined by their characteristic spectroscopic data and elemental analyses (see the Experimental section). ^{13}C NMR chemical shifts were consistent with the proposed structures; the imino carbon appeared as a typical singlet in the ^1H-decoupled mode in the 144.0, 143.5, 143.8, and 145.6 ppm, respectively, for imidazolinium salts **3a–d**. The ^1H NMR spectra of the imidazolinium salts further supported the assigned structures; the resonances for C(2) protons were observed as a sharp singlet in the 11.39, 11.13, 10.09, and 10.05 ppm, respectively, for imidazolinium salts **3a–d**. The IR data for imidazolinium salts **3a–d** clearly indicate the presence of the C—N group with a ν(C—N) vibration at 1615, 1645, 1632, and 1636 cm^{-1}, respectively, for **3a–d**. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolinium salts [12].

In this study, a series of related ligands with similar electronic character and different steric demand have been used for a systematic optimization of the Suzuki reaction.

Before finding optimum conditions, we investigated the role of NHCs ligand precursors with a couple of test reactions (Table 1, entries 1, 6, 11, 16, 21). The results obtained from test reactions were as expected. Then to find optimum conditions, a series of experiments were carried out with 4-chloroacetophenone and phenylboronic acid as role model compounds. Different bases such as Cs_2CO_3, K_2CO_3, NaOH, and KO*t*Bu were tested, and KO*t*Bu was found as the best base in water/DMF systems. In addition, the reactions were performed in air and without degassing the water with N_2 gas prior to use. After determining the optimum cross-coupling reaction condition, the scope of the reaction and efficiency of the NHCs were evaluated by investigating the coupling of phenylboronic acid with *p*-substituted aryl chlorides. The results are shown in Table 1. Both the electron-rich and the electron-poor unactivated aryl chlorides (*p*-chloroacetophenone, *p*-chlorotoluene, *p*-chlorobenzaldehyde, *p*-chloroanisole, and chlorobenzene) were coupled successfully with boronic acid in good yields to give desirable products by $Pd(OAc)_2$/**3a–d** on a mild reaction condition. But still, we observed that electron attracting aryl chlorides are more appropriate substrate for this catalyzed system as suggested by our results (Table 1, entries 1–10). However, NHC precursors (**3c–d**), which contain an aromatic ring on a bridge position, are the more active ligands than others. In all entries, on average

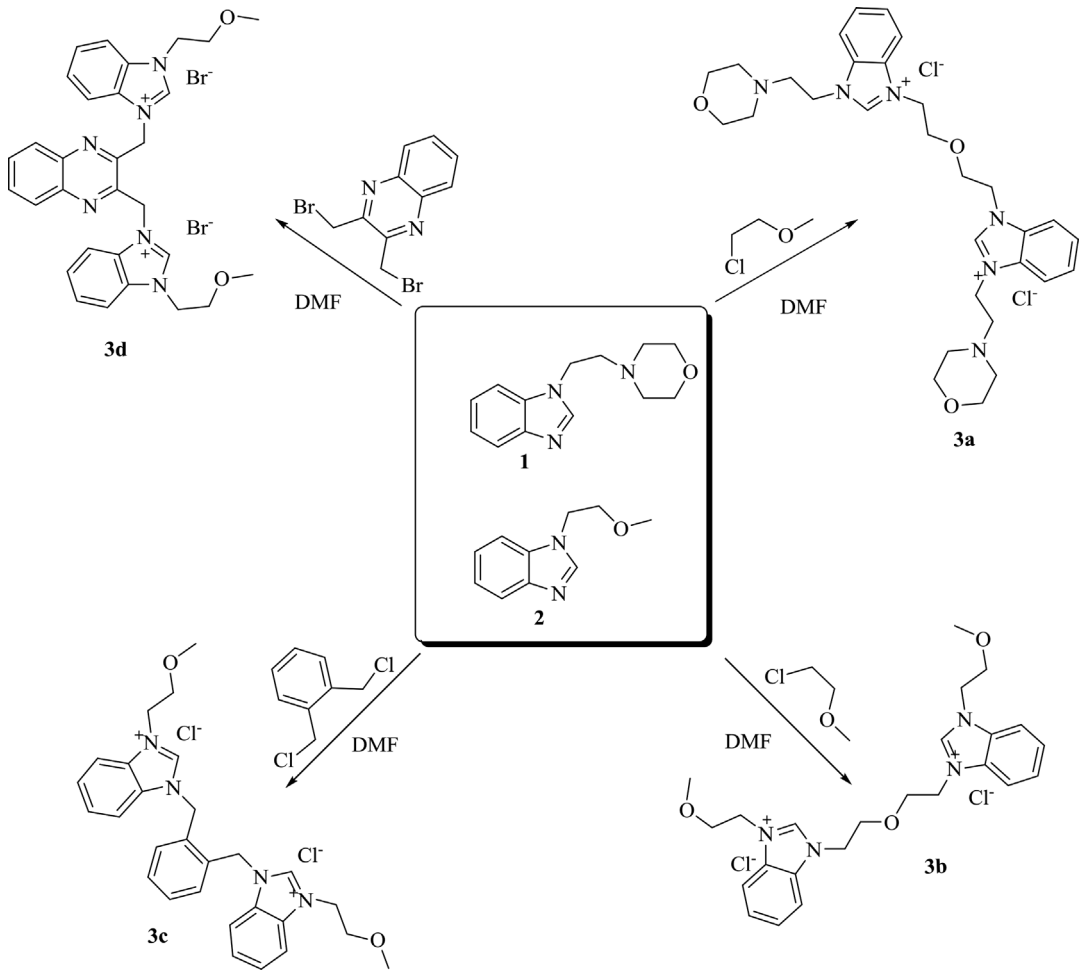


FIGURE 1 Preparation of bis-1,3-dialkylbenzimidazolium halogens, LHX (**3a–d**).

10–15% homocoupling product of the boronic acid (biphenyl), probably originating from the reduction of the Pd(II) precatalyst, was acquired. When 0.5 mol% $Pd(OAc)_2$/0.75 mol% LHX was used for *p*-chloroacetophenone and *p*-chlorobenzaldehyde, the quantity of homocoupling products (diphenyl and *o*-terphenyl) increased to 40–45% and quantity of desired product decreased (Table 1, entries 26–29) . As a result, these bisbenzimidazolium salts were found to be useful NHC ligand precursors for the difficult formation of biaryls from unactivated aryl chlorides.

CONCLUSIONS

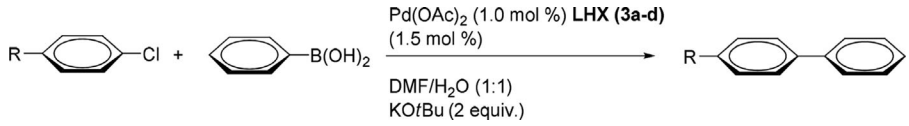
New bisbenzimidazolium salts have been prepared and fully characterized. After deprotonation with KO*t*Bu, the resulting species are associated with a $Pd(OAc)_2$ center to generate catalyst precursors for the Suzuki reactions of unactivated aryl chloride derivatives with phenylboronic acid.

All the catalytic systems are successful for unactivated chlorine substrates, and most of them lead to the formation of products in good yields. However, chelating carbene ligands do not bring catalytically significant improvement with respect to monodentate ligands. This study has supported the fact that aromatic ring bridged sterically demanding NHCs showed more catalytic activity than alkyl-bridged sterically NHCs. We have developed a highly active, easy to producible, and environmentally friendly ligands and catalysis process for palladium-mediated Suzuki cross-coupling in aqueous media using bis-1,3-dialkylbenzimidazolidin-2-ylidene ligands. The catalysis system is simple and efficient for various aryl chlorides without preactivated.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AC400P FT spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C). Chemical shifts (δ)

TABLE 1 The Suzuki Coupling Reaction of Aryl Chlorides with Phenylboronic Acid Catalyzed by $Pd(OAc)_2$/LHX (**3a–d**)



Entry	*R*	*LHX*	*Yield*[a,b,c] *(%)*
1	$COCH_3$	–	25[d]
2	$COCH_3$	**3a**	100
3	$COCH_3$	**3b**	99
4	$COCH_3$	**3c**	98
5	$COCH_3$	**3d**	95
6	CHO	–	30[d]
7	CHO	**3a**	100
8	CHO	**3b**	100
9	CHO	**3c**	99
10	CHO	**3d**	99
11	CH_3O	–	20[d]
12	CH_3O	**3a**	80
13	CH_3O	**3b**	75
14	CH_3O	**3c**	100
15	CH_3O	**3d**	65
16	CH_3	–	15[d]
17	CH_3	**3a**	80
18	CH_3	**3b**	75
19	CH_3	**3c**	90
20	CH_3	**3d**	65
21	H	–	15[d]
22	H	**3a**	95
23	H	**3b**	90
24	H	**3c**	90
25	H	**3d**	100
26	$COCH_3$	**3a**	65[e]
27	$COCH_3$	**3b**	59[e]
28	CHO	**3a**	73[e]
29	CHO	**3b**	70[e]

[a]Reaction conditions: 1.0 mmol of *p*-R–C_6H_4Cl, 1.5 mmol of phenylboronic acid, 2 mmol KO*t*Bu, 1 mmol% $Pd(OAc)_2$, 1.5 mmol% **3a–d**, 50°C, 3 h, water (3 mL)–DMF (3 mL).
[b]Purity of compounds was checked by NMR, and yields are based on arylchloride.
[c]All reactions were monitored by thin-layer chromatography (TLC).
[d]No LHX (**3a–d**).
[e]$Pd(OAc)_2$ (0.5 mol%), LHX (0.75 mol%).

are given in parts per million relative to tetramethylsilane (TMS), coupling constants (*J*) in hertz. 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 at TUBITAK (Ankara, Turkey) Microlab.

2,2′-Bis-(N-2-morpholinethylbenzimidazolium)-ethylether Dichloride, **3a**

To a solution of 1-(2-morpholinethyl)benzimidazoline (**1**; 2.02 g, 10 mmol) in DMF (5 mL), 2-chloroethylether (1.5 g, 10.07 mmol) was added slowly at 25°C, and the resulting mixture was stirred at 100°C for 3 days. Diethyl ether (30 mL) was added to obtain red sticky oil. The red sticky oil was washed with diethyl ether (3 × 10 mL), dried under vacuo, and the crude product was recrystallized from ethanol/diethyl ether (1:3) to obtain hygroscopic yellow crystals.

Yield: 4.48 g; 70%. $\nu_{(CN)}$ = 1615 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 2.59 (m, 8H, $N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$, 3.65 (m, 8H, $N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$, 3.77 (m, 4H, $N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$, 4.12 (m, 4H, $N(CH_2CH_2O)$), 4.71 (m, 4H, $N(CH_2CH_2O)$), 4.89 (m, 4H, $N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$), 7.89–7.61 (m, 8H, aromatic protons), 11.39 (s, 1H, NCHN). ^{13}C NMR (δ, $CDCl_3$): 47.6 ($N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$), 53.5 ($N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$), 56.5 ($N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$), 66.9 ($N(CH_2CH_2O)$), 69.2 ($N(CH_2CH_2O)$), 71.2 ($N(CH_2CH_2)(N(CH_2)_2(CH_2)_2O)$),

132.1; 131.1; 126.9; 126.8; 114.3; 112.5 (***C*****$_6$**H_4, aromatic carbons), 144.0 (N*C*HN). Microanalyses found: C, 59.65; H, 7.25; N, 14.20. Calcd. for $C_{30}H_{42}N_6Cl_2O_3$: C, 59.50; H, 6.99; N, 13.88.

2,2′-Bis-(N-2-methoxyethylbenzimidazolium)-ethylether Dichloride, **3b**

1-(2-Methoxyethyl)-benzimidazole (3.52 g, 20 mmol) and 2-chloroethyl ether (1.43 g, 10 mmol) were dissolved in 5 mL and heated at 100°C for 3 days. Thirty milliliters of dried diethyl ether was added to a dark brown solution and stirred. Sticky oily brown gel was obtained and dried under vacuo.

Yield: 3.5 g; 70%. $\nu_{(CN)}$ = 1645 cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 3.31 (s, 6H, N($CH_2CH_2OCH_3$)), 3.93 (t, J = 4 Hz, 4H, N($CH_2CH_2OCH_3$)), 4.09 (t, J = 4 Hz, 4H, N(CH_2CH_2O)), 4.96 (m, 4H, N(CH_2CH_2O)), 4.96 (m, 4H, N($CH_2CH_2OCH_3$)), 7.96–7.58 (m, 8H, aromatic protons), 11.13 (s, 2H, NC*H*N), ^{13}C NMR (δ, $CDCl_3$): 47.2 (N($CH_2CH_2OCH_3$), 47.8 (NCH_2CH_2O), 58.1(N($CH_2CH_2OCH_3$), 59.1 (NCH_2CH_2O), 70.8 (N($CH_2CH_2OCH_3$), 132.9; 131.2; 127.1; 126.9;114.0;113.2; (aromatic carbons), 143.5 (N*C*HN). Microanalyses found: C, 58.32; H, 6.75; N, 11.40. Calcd. for $C_{24}H_{32}N_4Cl_2O_3$: C, 58.18; H, 6.51; N, 11.31.

1,2-Di-(N-2-methoxyethylbenzimidazolium-methyl)-benzene Dichloride, **3c**

1-(2-Methoxyethyl)-benzimidazole (3.52 g, 20 mmol) and 1,2-bis(chloromethyl) (2.1 g, 12 mmol) were dissolved in 5 mL DMF and heated at 100°C for 2 days. Thirty milliliters of dried diethyl ether was added to a dark brown solution and stirred. Sticky oily brown gel was obtained and dried under vacuo.

Yield: 2.5 g; 50%. $\nu_{(CN)}$ = 1632 cm^{-1}. ^{1}H NMR (δ, DMSO-d_6): 3.27 (s, 6H, N($CH_2CH_2OCH_3$), 3.82 (t, J = 4 Hz, 4H, N($CH_2CH_2OCH_3$)), 4.78 (t, J = 4 Hz, 4H, N($CH_2CH_2OCH_3$)), 6.21 (s, 4H, $(CH_2)_2C_6H_4$), 8.18–7.10 (m, 12H, aromatic protons), 10.09 (s, 2H, NC*H*N). ^{13}C NMR (δ, DMSO-d_6): 48.0 (N($CH_2CH_2OCH_3$), 56.5 (N($CH_2CH_2OCH_3$), 58.7 (N($CH_2CH_2OCH_3$), 69.5 ($C_6H_4(CH_2)_2$), 132.7; 132.0; 131.5; 129.7; 128.6; 127.3;127.2; 114.7; 114.6 (aromatic carbons), 143.8 (N*C*HN). Microanalyses found: C, 64.02; H, 6.80; N, 11.32. Calcd. for $C_{16}H_{24}N_3ClO_2$: C, 63.76; H, 6.11; N, 10.62.

1,1′-[2,3-Quinoxalinyldiylbis(methylene)]bis[3-(2-methoxyethyl)-1H-benzimidazolium] dibromide, **3d**

1-(2-Methoxyethyl)-benzimidazole (3.52 g, 20 mmol) and 2,3-bis(bromomethyl)quinoxalin (3.16 g, 10 mmol) were dissolved in 5 mL DMF at room temperature and heated at 100°C for 2 days. White solid was filtrated and washed with ether (3 × 10 mL). Dried under vacuo and white solid was crystallized with methanol–ether (1:2).

mp: 224–226°C. Yield: 4 g; 60%. $\nu_{(CN)}$ = 1536 cm^{-1}.^{1}H NMR (δ, DMSO-d_6): 3.34 (s, 6H, N($CH_2CH_2OCH_3$)), 3.91 (t, J = 4 Hz, 4H, N($CH_2CH_2OCH_3$)), 4.94 (t, J = *4* Hz, 4H, N($CH_2CH_2OCH_3$)), 6.69 (s, 4H, $C_6H_4N_2C_2(CH_2)_{2)}$, 8.27–7.70 (m, 12H, aromatic protons), 10.05 (s, 2H, NC*H*N). ^{13}C NMR (δ, DMSO-d_6): 48.6 (N($CH_2CH_2OCH_3$) 57.3 (N($CH_2CH_2OCH_3$), 59.4 (N($CH_2CH_2OCH_3$), 71.5 ($C_6H_4(CH_2)_2$), 136.5; 133.2; 132.2; 129.9; 128.9; 128.3; 127.8; 115.9; 115.6 (aromatic carbons) and 145.6 (N***C***HN). Microanalyses found: C, 54.01; H, 5.10; N, 12.76. Calcd. for $C_{30}H_{33}N_6Br_2O_2$: C, 53.83; H, 4.97; N, 12.55.

General Procedure for the Suzuki Cross-Coupling Reactions

$Pd(OAc)_2$ (1.0 mmol%), 1,3-dialkylimidazoliumsalts, **3a–c** (3 mmol%), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), KO*t*Bu (2 mmol) and water (3 mL)–DMF (3 mL) were added to a small round-bottomed flask in air, 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 silica with copious washings, and concentrated and purified by flash chromatography on silica. The purity of the compounds was checked by NMR, and yields are based on aryl chloride.

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