In situ Preparation of Rhodium/*N*-Heterocyclic Carbene Complexes and use for Addition of Arylboronic Acids to Aldehydes

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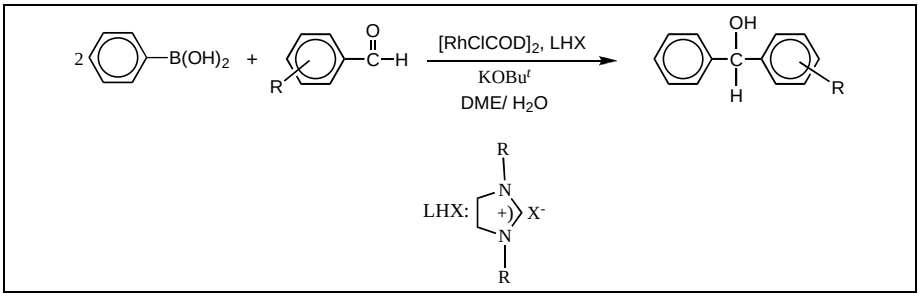

The *in situ* prepared three component system [RhCl(COD)]$_2$/imidazolidinium salts (**2, 4**) and KOBu^t catalyses the addition of phenylboronic acid to sterically hindered aldehydes affording the corresponding arylated secondary alcohols in good yields. Four novel 1,3-dialkylimidazolidinium (**2-4**) salts as NHC precursors were synthesized from *N*,*N*'-dialkylethylenediamine.

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INTRODUCTION

N-Heterocyclic carbenes (NHCs) are currently receiving much research attention for their wide applicability in coordination chemistry and catalysis [1]. Access to new ligand types is a critical component of the design of novel homogeneous transition metal catalysts. Because drastic changes in catalytic activity can result from apparently minor modifications of ligand structure [2], ligand designs that allow systematic variation of steric and electronic properties are particularly valuable.

Since Arduengo's discovery of stable imidazol-2-ylidenes in 1991 [3], substantial efforts have focused on the design and catalytic application of diaminocarbene ligands [4], primarily "*N*-heterocyclic carbenes" (NHCs) derived from imidazolium cations [5]. Diaminocarbenes function as exceptionally strong σ-donors to late transition metals, with binding energies exceeding those of the most basic phosphines by as much as 10 kcal/mol [6], and they lack the electrophilic reactivity of Fischer-type carbenes [4]. The high catalytic activities achieved by a number of NHC-based catalysts have been attributed in part to this strong donor ability, in combination with the unique steric demands [6,7] and enhanced thermal stability [8] of these ligands compared with phosphines. Catalyst advances with particular promise for synthetic applications have been achieved using NHC ligands in ruthenium-catalyzed ring-closing olefin metathesis [8], intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran [9,10], cycloisomerisation [11], amination of aryl halides [12], palladium-catalyzed Suzuki-Miyaura cross coupling [13], rhodium catalyzed hydrosilylation [14], arylation of aromatic aldehydes [15], palladium catalyzed arylation of benzaldehyde [16], aerobic alcohol oxidation [17] and allylic alkylation and etherification [18].

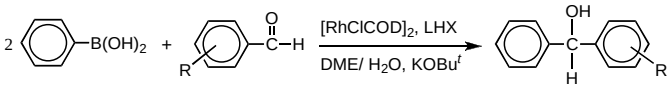
In general, metal complexes of "saturated" (nonaromatic) imidazolidin-2-ylidenes [19] reveal higher catalytic activity than the analogous complexes of "unsaturated" (aromatic) imidazolin-2-ylidenes [20] or benzannulated benzimidazol-2-ylidenes [21]. This is regarded as a consequence of the stronger basicity and nucleophilicity of the nonaromatically stabilized carbene ligands.

Diarylmethanols are important intermediates for the synthesis of biologically and pharmaceutically active substances [22,23].

Miyaura reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes giving secondary alcohols. The reactions were facilitated by the presence of an electron withdrawing group on the aldehyde and an electron donating group on the arylboronic acid, suggesting that the mechanism involves a nucleophilic attack of the aryl group on the aldehyde [24]. The finding that these reactions were run with sterically hindered and strongly basic ligands attracted the attention of Fürstner who subsequently applied *N*-heterocyclic carbene ligands. A *in-situ* generated catalytic system for the addition of phenylboronic acid to aldehydes is prepared combination of rhodium salt, 1,3-dialkylimidazolium chloride and base [25].

Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of saturated NHC ligands in addition of

phenylboronic acid to aldehydes reaction is a neglected area. In order to find more efficient rhodium catalysts we have prepared a series of new 1,3-dialkylimidazolidinium chlorides LHX, **2-5** containing a imidazolidine ring and we report here the synthesized of rhodium-carbene based catalytic system generated *in-situ* in the presence of base for the addition of phenylboronic acid to aldehydes (Scheme 1).



Scheme 1. Addition of phenylboronic acid to aldehydes.

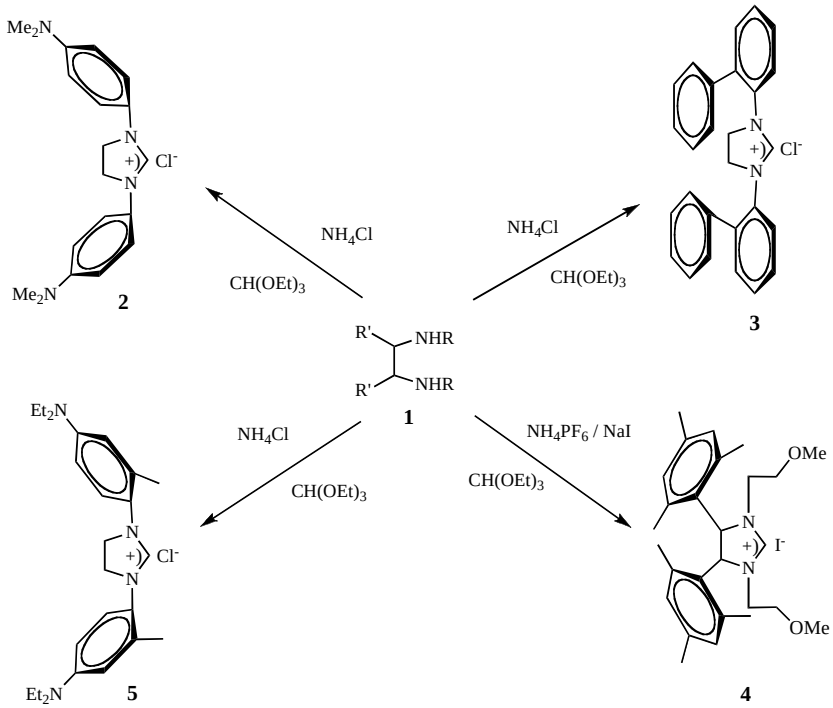
RESULTS AND DISCUSSION

Imidazolidinium salts, (**2-5**) are conventional NHC precursors. The reaction of **1** [26,27] with triethyl orthoformate yielded the **2-5** salts (Scheme 2). The salts are air- and moisture stable both in the solid state and in solution. The structures of **2-5** were determined by their characteristic spectroscopic data and elemental analyses.

resonances for C(2)-H were observed as sharp singlets in the 8.17, 8.53, 9.32 and 7.94 respectively for **2-5**. The IR data for imidazolidinium salts **2-5** clearly indicate the presence of the –C=N- group with a ν(C=N) vibration at 1667, 1610, 1624 and 1608 cm^{-1} respectively for **2-5**. The NMR and IR values are similar to those found for other 1,3-dialkylimidazolidinium salts [26,27].

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that functionalized organometallic reagents required. Recent publications describing the addition of arylboronic acid derivatives to aldehydes in the presence of the catalytic amounts of Rh(I) and phosphine derivatives deserve particular mention [24,25]. Originally $[Rh(acac)(CO)_2]$ in combination with bidentate phosphine ligand such as dppf [1,1'-bis(diphenylphosphino)-ferrocene] has been recommended for the *in situ* preparation of the yet elusive catalyst [28].

Here, various imidazolidinium salts (**2-5**) were compared as ligand precursors under the same reaction conditions. To survey the reaction parameters for the addition of phenylboronic acid to aldehydes, we chose to



Scheme 2. Synthesis of 1,3-dialkylimidazolidinium salts.

^{13}C NMR chemical shifts are consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 163.7, 157.9, 160.8, and 157.4 ppm respectively for imidazolidinium salts **2-5**. The ^{1}H NMR spectra of the imidazolidinium salts further supported the assigned structures; the

examine Cs_2CO_3, K_2CO_3, and $KOBu^t$ as base and DME/H_2O (3:1) as solvent. We found that the reactions performed in DME/H_2O (3:1) with Cs_2CO_3 or $KOBu^t$ as the base at 25 °C and 60 °C appeared to be best. We started our investigation with the addition of phenyl-boronic acid to *p*-chlorobenzaldehyde, in the presence of

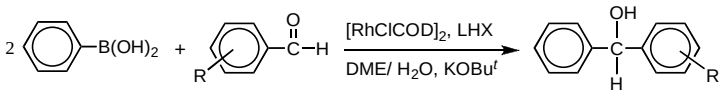
$[RhCl(COD)]_2$/**2**-**5**. Table 1 summarizes the results obtained in the presence of 2-**5** (Table 1, entries 1-4).

Control experiment indicated that the addition of phenylboronic acid to *p*-chlorobenzaldehyde reaction did not occur in the absence of **2**. Under the determined reaction conditions, a wide range of aryl aldehydes bearing electron-donating or electron-withdrawing groups can react with phenylboronic acid affording the addition products in excellent yields (Table 1 entries 1, 5, 6, 9, 13, 17 and 21).

In conclusion, four 1,3-dialkylimidazolidinium salts (**2-5**) have been prepared and characterized. We are pleased to find that among the various NHC precursurs, imidazolidinium salts (**2-5**) are excellent ligand precursors for the addition of phenylboronic acid to aldehydes reaction. Also a convenient and highly user-friendly method for the addition of phenylboronic acid to aldehydes is presented. The procedure is simple and efficient towards various aryl aldehydes and does not require induction periods. 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.

Table 1

Rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes.



Entry	R	LHX	Yield[a-d](%)	Entry	R	LHX	Yield[a-d](%)
1	*p*-Cl	2	96	13	*p*-$C(CH_3)_3$	2	81
2	*p*-Cl	3	95	14	*p*-$C(CH_3)_3$	3	79
3	*p*-Cl	4	92	15	*p*-$C(CH_3)_3$	4	73
4	*p*-Cl	5	89	16	*p*-$C(CH_3)_3$	5	70
5	H	2	87	17	2,5$(OCH_3)_2$	2	84
6	H	3	87	18	2,5$(OCH_3)_2$	3	80
7	H	4	85	19	2,5$(OCH_3)_2$	4	76
8	H	5	83	20	2,5$(OCH_3)_2$	5	72
9	2,4,6$(CH_3)_3$	2	76	21	3,4,5$(OCH_3)_3$	2	73
10	2,4,6$(CH_3)_3$	3	74	22	3,4,5$(OCH_3)_3$	3	70
11	2,4,6$(CH_3)_3$	4	73	23	3,4,5$(OCH_3)_3$	4	64
12	2,4,6$(CH_3)_3$	5	71	24	3,4,5$(OCH_3)_3$	5	66

[a] Phenylboronic acid (9.8 mmol), aldehydes (4.9 mmol), $[RhCl(COD)]_2$ (1 mmol%), LHX (2 mmol), KO*t*Bu (4.9 mmol), dimethoxyethane (15 mL), [a] Isolated yield (purity of yield checked by NMR and GC). [b]Yields are based on aldehydes. [c] All reactions were monitored by TLC. [d] 60°C.

EXPERIMENTAL

All reactions for the preparation of imidazolidinium salts (**2-5**) were carried out under argon using standart Schkenk-type flasks. Test reactions for the catalytic activity of catalysts in the addition of phenylboronic acid to aldehydes reactions were carried out in air. The complex $[RhCl(COD)]_2$ [29] and **1** were prepared according to known methods [26,27]. All reagents were purchased from Aldrich Chemical Co. All ^1H and ^{13}C-NMR were performed in DMSO-d_6. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. Infrared spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on an ATI UNICAM 1000 spectrometer. Melting points were measures 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 1,3-Bis(4-dimethylaminophenyl)imidazolidinium chloride (2). Triethyl orthoformate (10 ml) was added onto *N,N'*-bis(4-dimethylaminophenyl)ethane-1,2-diamine (1.49 g, 5 mmol) and NH_4Cl (0.27 g, 5 mmol). The mixture was stirred for 6 h in oil bath at 140 °C under argon atmosphere. Meanwhile EtOH, formed as a by product, removed from the medium *via* distillation. The resulting yellow solid was collected by filtration, dissolved in MeOH (10 ml) and treated with Na_2CO_3 (0.5 *M*, 20 ml). The resulting colorless solid was collected by filtration and was crystallized from methanol/ diethyl ether to give colourless needles, and the solid was washed with diethyl ether (2x10 mL), dried under vacuum, and the yield was 1.47 g (85 %), mp 221-223 °C; ir: 1667 cm^{-1} (N-C-N). ^1H-NMR($CDCl_3$): δ 2.79 (s,12H, 4-N(CH_3)$_2$$C_6H_4$), 3.89 (s, 4H, N$CH_2CH_2$N), 6.67, 6.97 (d, 8H, *J*=8.8 Hz, 4-N$(CH_3)_2C_6H_4$), 8.17 (s, 1H, 2-C*H*). ^{13}C- NMR ($CDCl_3$): δ 40.8 (4-N(CH_3)$_2$$C_6H_4$), 43.8 (N$CH_2CH_2$N), 113.0, 126.9, 129.7, 150.1 (4-N$(CH_3)_2C_6H_4$), 163.7 (2-*C*H). *Anal.* Calcd. for $C_{19}H_{25}N_4Cl$: C, 66.17, H, 7.31, N, 16.25. Found C, 66.22, H, 7.39, N, 16.20.

Preparation of 1,3-Bis(2-biphenyl)imidazolidinium chloride (3). This compound was prepared in the same manner as **2** using *N,N'*-bis(2-biphenyl)ethane-1,2-diamine (1.82 g, 5 mmol) and NH_4Cl (0.27 g, 5 mmol), in triethyl orthoformate (10 ml) to give colorless crystals of **3**. Yield: 1.78 g (87 %), mp 254-256 °C; ir: 1610 cm^{-1} (N-C-N). ^1H-NMR($CDCl_3$): δ 3.90 (s, 4H,

NCH_2CH_2N), 7.20-7.29, 7.37-7.46 (m, 16H, 2-C$_6H_5$C$_6H_4$), 8.12 (d, 2H, J=8.2 Hz, 2-C$_6H_5$C$_6H_4$), 8.53 (s, 1H, 2-C*H*). ^{13}C-NMR($CDCl_3$): δ 52.3 (N*C*H$_2$*C*H$_2$N), 127.5, 128.7, 128.9, 129.5, 129.9, 130.0, 131.4, 133.6, 137.3, 137.9 (2-*C*$_6$H$_5$*C*$_6$H$_4$), 157.9 (2-*C*H). *Anal*. Calcd. for $C_{27}H_{23}N_2Cl$: C, 78.91, H, 5.64, N, 6.82. Found C, 78.96, H, 5.69, N, 6.79.

Preparation of 1,3-Bis(2-methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)imidazolidinium iodide (4). To a solution of 1,3-bis(2-methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)imidazolidinium hexafluorophosphate (2.84 g, 5 mmol), in acetone (15 ml) was added NaI (0.75 g, 5 mmol). The reaction mixture was refluxed for 3 h. The solvent was removed under vacuum. CH_2Cl_2 (5 ml) was added to the resulting crude and filtered. Volume of the solution was reduced to *ca* 2-3 ml under vacuum and diethy ether (15 ml) was added to complete precipitation. The resulting colorless solid was collected by filtration and was crystallized from methanol/diethyl ether to give colourless needles, and the solid was washed with diethyl ether (2x10 mL), dried under vacuum, and the yield was 2.25 g (82 %), mp 173-175 °C; ir: 1624 cm^{-1} (N-C-N). ^{1}H-NMR ($CDCl_3$): δ 2.13, 2.14 (s, 18H, 2,4,6-(C*H*$_3$)$_3$C$_6$H$_2$), 3.34-3.37, 3.93-3.98 (m, 4H, NC*H*$_2$CH$_2$OCH$_3$), 3.72-3.77 (m, 4H, NCH$_2$C*H*$_2$OCH$_3$), 6.05 (s, 2H, NC*H*C*H*N), 6.61, 6.66 (s, 4H, 2,4,6-(CH$_3$)$_3$C$_6$*H*$_2$), 9.32 (s, 1H, 2-C*H*). ^{13}C- NMR ($CDCl_3$): δ 20.9, 21.3, 21.6 (2,4,6-(*C*H$_3$)$_3$C$_6$H$_2$), 46.9 (N*C*H$_2$CH$_2$OCH$_3$), 69.6 (NCH$_2$*C*H$_2$OCH$_3$), 59.3 (NCH$_2$CH$_2$O*C*H$_3$), 124.2, 130.4, 132.0, 137.3, 139.1 (2,4,6-(CH$_3$)$_3$*C*$_6$H$_2$), 160.8 (s, 1H, 2-*C*H). *Anal*. Calcd. for $C_{27}H_{39}N_2O_2I$: C, 58.91, H, 7.14, N, 5.09. Found C, 58.89, H, 7.18, N, 5.12.

Preparation of 1,3-Bis(2-methyl-4-dethylaminophenyl)-imidazolidinium chloride (5). This compound was prepared in the same manner as 2 using *N,N'*-bis(2-methyl-4-dethylaminophenyl)ethane-1,2-diamine (1.91 g, 5 mmol) and NH_4Cl (0.27 g, 5 mmol), in triethyl orthoformate (10 ml). The colorless crystals 5 formed were stored under argon since they were sensitive toward air. Yield: 0.94 g, 84%, mp 163-165 °C; ir: 1608 cm^{-1} (N-C-N). ^{1}H-NMR($CDCl_3$) δ: 1.07 (t, 12H, J=6.81 Hz, N(CH$_2$C*H*$_3$)$_2$C$_6$H$_3$), 3.22 (q, 8H, J=6.41 Hz, N(C*H*$_2$CH$_3$)$_2$C$_6$H$_3$), 2.28 (s, 6H, 2-C*H*$_3$-4-N(CH$_2$CH$_3$)$_2$C$_6$H$_3$), 4.53 (s, 4H, NC*H*$_2$C*H*$_2$N), 6.37 (s, 2H, N(CH$_2$CH$_3$)$_2$C$_6$*H*$_3$), 6.43 (d, 2H, *J*=8.65 Hz, N(CH$_2$CH$_3$)$_2$C$_6$*H*$_3$), 7.46.43 (d, 2H, *J*=8.66 Hz, N(CH$_2$CH$_3$)$_2$C$_6$*H*$_3$), 7.94 (s, 1H, 2-C*H*). ^{13}C- NMR($CDCl_3$): δ 12.7 (N(CH$_2$*C*H$_3$)$_2$C$_6$H$_3$), 44.7 (N(*C*H$_2$CH$_3$)$_2$C$_6$H$_3$), 18.8 (2-*C*H$_3$-4-N(CH$_2$CH$_3$)$_2$C$_6$H$_3$), 53.7 (N*C*H$_2$*C*H$_2$N), 110.4, 113.3, 122.5, 128.3, 134.7, 148.8 (N(CH$_2$CH$_3$)$_2$*C*$_6$H$_3$), 157.4 (2-*C*H). *Anal*. Calcd. for $C_{25}H_{37}N_4Cl$: C, 66.99, H, 8.69, N, 13.06. Found C, 69.91, H, 9.8.79, N, 13.01.

General Procedure for Rhodium-Carbene Catalyzed Addition of Phenylboronic Acid to Aldehydes. Phenylboronic acid (1.20 g, 9.8 mmol), KOBu^t (4.9 mmol), substituted aldehydes (4.9 mmol), [RhCl(COD)]$_2$ (1 mol%) (with respect to aldehyde), imidazolidinium salts (**2-5**) (2 mol%), dimethoxyethane (15 mL) were introduced in to Schlenk tube and then water (5 mL) was added. The resulting mixture was heated for 6 h at 60 °C, cooled to ambient temperature, exracted with ethyl acetate (30 mL). After drying over $MgSO_4$ the organic phase was evaporated and the residue was purified by flash chromatography. Isolated yield (yields based on aldehydes) is checked by NMR and GC, all reactions were monitored by TLC.

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