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In Situ Generated Rhodium-Based Catalyst for Addition of Phenylboronic Acid to Aldehydes

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ABSTRACT: *New 1,3-dialkylperhydrobenzimidazolinium and 1,3-dialkylimidazolinium salts (**2,4**) as NHC precursors have been synthesized and characterized. These salts in combination with [RhCl(COD)]$_2$ provided active catalysts for the addition of phenylboronic acid to aldehydes under mild conditions. The in situ prepared three-component system [RhCl(COD)]$_2$/imidazolinium salts (**2,4**) and KOBu^t catalyse the addition of phenylboronic acid to sterically hindered aldehydes affording the corresponding arylated secondary alcohols in good yields*. © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:461–465, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20132

INTRODUCTION

The number of synthetic applications of homogeneous catalysts has increased enormously during the last decade. Highly active and selective catalysts have been prepared to activate a large variety of bonds, thus providing efficient methods to obtain new products with important industrial and pharmaceutical applications. Homogeneous organometallic catalysis has long depended on phosphine ligands [1]. Despite their effectiveness in controlling reactivity and selectivity, phosphine catalysts require air-free handling to prevent the oxidation of the ligand and are subjected to P-C activation at elevated temperatures [2]. Therefore, in view of practical use, the development of more reactive and stable ligands is of importance for the homogeneous catalytic system. Recently, nucleophilic *N*-heterocyclic carbenes (NHCs) [3], with a strong σ-donor electronic property than bulky tertiary phosphines [4], have emerged as a new family of ligands. In contrast to metal complexes of phosphines, the metal-NHC complexes appeared to be extraordinarily stable toward heat, air, and moisture due to their high dissociation energies of the metal-carbon bond [5]. The precursor imidazolium salts are often easier to obtain than phosphines but preparation of the metal compounds from these salts can be more difficult [6]. The most common method is direct complexation of the free NHC, either isolated [7], or generated in situ [8] formed by deprotonation of the imidazolium salts. These methods require that the free NHC be stable and may be fatally complicated by the presence of other acidic protons in the ligand precursor. Oxidative addition of an imidazolinium carbon–hydrogen bond [9] to a low valent metal center and addition of an electron-rich olefin with C=C bond cleavage [10] can also lead to metal-NHC complexes in certain cases.

Transition-metal complexes with *N*-heterocyclic carbene ligands show considerable potential as

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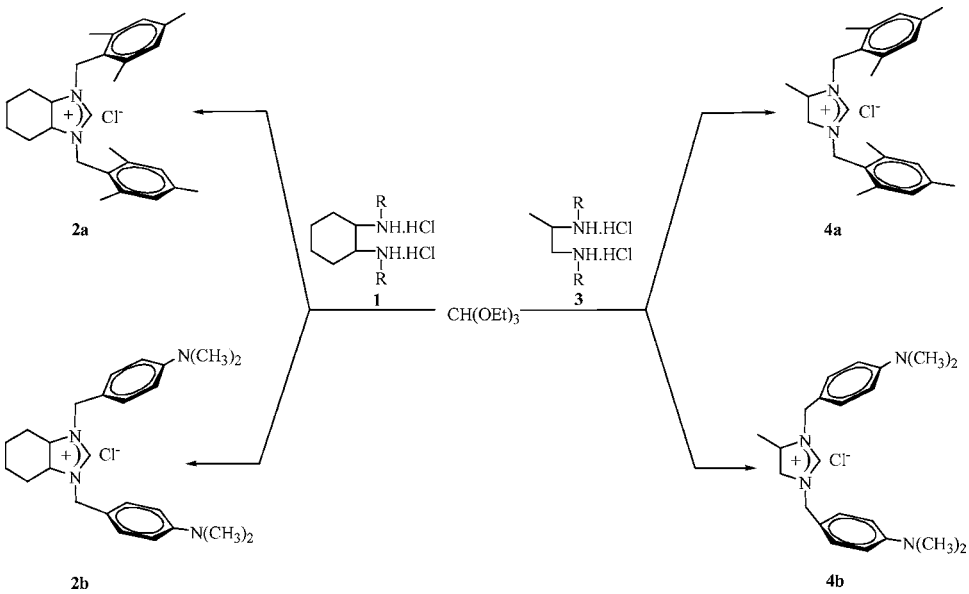


SCHEME 1

catalysts for organic synthesis and fine chemical production [11], for example, hydrogenation reactions [12], C—C coupling [13], olefin metathesis [14], amination of aryl halides [15], cyclopropanation [16], and cycloisomerisation [17] reactions.

Our contribution to this field has started with syntheses of imidazolidin-2-ylidenes complexes of Rh(I) and Ru(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate [16] and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran and addition of phenylboronic acid to aldehydes in good yields [18,19]. A highly effective, easy to handle, and environmentally benign process for palladium-mediated Suzuki cross-coupling was developed [20].

Rhodium-carbene complexes have been extensively studied. However, there are few reports on the catalytic activity of rhodium-carbene complexes in rhodium-mediated processes [21,22]. 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 [23]. 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 in combination with rhodium salt, 1,3-dialkylimidazolium chloride, and base [24].

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 imidazolinium chlorides LHX, **2a,b–4a,b** (Scheme 1), containing a saturated imidazole ring and we report here in situ rhodium-carbene based catalytic system for the addition of phenylboronic acid to aldehydes.

RESULTS AND DISCUSSION

Dialkylperhydrobenzimidazolinium and imidazolinium salts, (**2a,b** and **4a,b**) are conventional NHC precursors. The reaction of **1** and **3** [25] with triethyl orthoformate yielded the symmetrical perhydrobenzimidazolidinium **2a,b** and imidazolidinium **4a,b** salts (Scheme 1). The salts are air and moisture stable both in the solid state and in solution. The structures of **2** and **4** were determined by their characteristic spectroscopic data and elemental analyses.

^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 161.2, 161.8, 157.3, and 157.5 ppm respectively for imidazolinium salts **2a,b–4a,b**. The

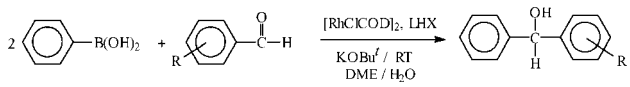
^{1}H NMR spectra of the perhydrobenzimidazolinium and imidazolinium salts furher supported the assigned structures; the resonances for C(2)-H were observed as sharp singlets in the 9.10, 10.70, 9.21, and 10.80 ppm respectively for **2a,b–4a,b**. The IR data for perhydrobenzimidazolinium and imidazolinium salts **2a,b–4a,b** clearly indicate the presence of the —C=N— group with a ν(C=N) vibration at 1616, 1603, 1649, and 1622 cm^{-1} respectively for **2a,b–4a,b**. The NMR and IR values are similar to those found for other 1,3-dialkylimidazolinium salts [25].

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 [23,24]. 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 [26].

Here, various perhydrobenzimidazolinium and imidazolidinium salts (**2a,b–4a,b**) 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 examine Cs_2CO_3, K_2CO_3, and KOBu^t as a base and DME/H_2O (3:1) as a 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 the best. We started our investigation with the addition of phenylboronic acid to *p*-chlorobenzaldehyde, in the presence of [RhCl(COD)]$_2$/**2–4**. Table 1 summarizes the results obtained in the presence of **2a,b–4a,b** (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 **2a**. 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, 9, 13, 17, and 21). A systematic study on the substituent effect in the imidazolidinium salts **2a, 4a** indicated that the introduction of 2,4,6-trimethybenzyl substituent on the N-atoms notably increased the reaction rate and the yield of the product. In summary, we have demonstrated that in situ generated imidazolidin-2-ylidene complexes of rhodium are very effective for the addition of phenylboronic acid to aldehydes.

TABLE 1 Rhodium-Carbene Catalyzed Addition of Phenylboronic Acid to Aldehydes



Entry	*R*	*LHX*	*Yield* [a–c]
1	*p*-Cl	2a	96
2	*p*-Cl	2b	92
3	*p*-Cl	4a	92
4	*p*-Cl	4b	90
5	H	2a	88
6	H	2b	85
7	H	4a	83
8	H	4b	80
9	*p*-OCH_3	2a	89[d]
10	*p*-OCH_3	2b	88[d]
11	*p*-OCH_3	4a	85[d]
12	*p*-OCH_3	4b	81[d]
13	2,4,6$(CH_3)_3$	2a	88[d]
14	2,4,6$(CH_3)_3$	2b	84[d]
15	2,4,6$(CH_3)_3$	4a	86[d]
16	2,4,6$(CH_3)_3$	4b	81[d]
17	3,4,5$(OCH_3)_3$	2a	85[d]
18	3,4,5$(OCH_3)_3$	2b	79[d]
19	3,4,5$(OCH_3)_3$	4a	80[d]
20	3,4,5$(OCH_3)_3$	4b	78[d]
21	2,4,6$(OCH_3)_3$	2a	81[d]
22	2,4,6$(OCH_3)_3$	2b	77[d]
23	2,4,6$(OCH_3)_3$	4a	78[d]
24	2,4,6$(OCH_3)_3$	4b	70[d]

[a]Isolated yield (purity of yield checked by NMR).
[b]Yields are based on aldehydes.
[c]All reactions were monitored by TLC.
[d]60°C, 5 h.

CONCLUSION

We are pleased to find that among the various NHC precursurs, perhydrobenzimidazolinium, and imidazolidinium salts (**2,4**) 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 toward various aryl aldehydes and does not require induction periods. Detailed investigations, focusing on imidazolidin-2-ylidene and benzimidazolin-2-ylidene substituent effects, functional group tolerance, and catalytic activity in this and other addition reactions are ongoing.

EXPERIMENTAL

All reactions for the preparation of perhydrobenzimidazolinium and imidazolinium salts (**2a,b–4a,b**) 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 $[RhCl(COD)]_2$[27] and **1** and **3** were prepared according to known methods [25]. All reagents were purchased from Aldrich Chemical Co. All ^{1}H and ^{13}C-NMR were performed in DMSO-d_6. ^{1}H NMR and ^{13}C NMR spectra were recorded 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 Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. Melting points were measures in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

*Preparation of 1,3-bis(2,4,6-trimethylbenzyl)per hydrobenzimidazolinium) chloride (**2a**)*

A mixture of *N,N′*-bis(2,4,6-trimethylbenzyl)-1,2-cyclohexanediamine dihydrochloride (6 g, 1.33 mmol), in triethylorthoformate (50 mL) was heated in a distillation apparatus until the distillation of ethanol ceased. The temperature of the reaction mixture reached 110°C. Upon cooling to RT a colorless solid precipitated which was collected by filtration, and dried in vacuum. The crude product was recrystallized from absolute ethanol to give colourless needles, and the solid was washed with diethyl ether (2× 10 mL), dried under vacuum, and the yield was 4.40 g, 78%, mp 248-249°C. IR, ν: 1616 cm^{-1} (N—C—N). ^{1}H-NMR($CDCl_3$) δ: 1.00–1.44 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.60–1.90 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.35–3.45 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 4.82 (s, 4H, C*H*$_2$Ar), 2.20, 2.25 (s, 18H, C_6H2(C*H*$_3$)$_3$), 6.80 (s, 4H, Ar-*H*), 9.10 (s, 1H, 2-C*H*). ^{13}C-NMR($CDCl_3$) δ: 24.10 (NCH CH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.11 (NCH*C*H$_2$CH$_2$ CH$_2$*C*H$_2$CHN), 46.42 (N*C*HCH$_2$CH$_2$ CH$_2$CH$_2$*C*HN), 20.51, 21.41 (C_6H$_2$(*C*H$_3$)$_3$), 125.90, 130.23, 137.92, 139.33 (Ar-*C*), 69.00 (*C*H$_2$Ar), 161.20 (2-*C*H). Found: C,76.39; H,8.74; N,6.50%. Calcd for $C_{27}H_{37}N_2CI$: C,76.32; H,8.71; N,6.59%.

*Preparation of 1,3-bis(p-dimethylaminobenzyl)-perhydrobenzimidazolinium) chlorid (**2b**)*

Compound **2b** was prepared in the same way as **2a** from *N,N′*-bis(*p-dimethylaminobenzyl*) -1,2-cyclohexanediamine dihydrochloride (4.34 g, 10 mmol) in triethyl orthoformate (50 mL) to give white crystals of **2b**. Yield: 3.64 g, 73%, mp 223–224 °C. IR, ν: 1603 cm^{-1} (N—C—N). ^{1}H-NMR($CDCl_3$) δ: 1.00–1.14 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.61–1.82 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.05–3.15 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 4.45, 4.95 (d, 4H, J = 14.5 Hz, C*H*$_2$Ar), 2.95 (s, 12H, N(C*H*$_3$)$_2$), 6.65, 7.25 (d, 8H, J = 8.8 Hz, Ar-*H*), 10.70 (s, 1H, 2-C*H*). ^{13}C-NMR($CDCl_3$) δ: 24.04 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 27.79 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 50.80 (N*C*HCH$_2$ CH$_2$CH$_2$CH$_2$*C*HN), 40.71 (N(*C*H$_3$)$_2$), 112.86, 120.28, 130.06, 150.94 (Ar-*C*), 66.65 (*C*H$_2$Ar), 161.80 (2-*C*H). Found: C,70.38; H,8.22; N,13.21%. Calcd. for $C_{25}H_{35}N_4CI$: C,70.33; H,8.20; N,13.13%.

*Preparation of 1,3-bis(2,4,6-trimethylbenzyl)-4-methylimidazolinium chloride (**4a**)*

Compound **4a** was prepared in the same way as **2a** from 1,2-bis(*2,4,6-trimethylbenzylamino)propane* dihydrochloride (4.34 g, 10 mmol) in triethyl orthoformate (50 mL) to give white crystals of **4a**. Yield: 3.52 g, 75%, mp 224–224.5°C. IR, ν: 1649 cm^{-1} (N—C—N). ^{1}H-NMR($CDCl_3$) δ: 4.10–4.25 (m, 1H, NC*H*(CH$_3$)CH$_2$N), 3.20, 3.90 (t, 2H, J = 10 Hz, NCH(CH$_3$)C*H*$_2$N), 1.22 (d, 3H, J = 6.2 Hz, NCH(C*H*$_3$)CH$_2$N), 2.20, 2.25, 2.26 (s, 18H, C_6H_2(C*H*$_3$)$_3$), 4.60, 4.85 (d, 4H, J = 14.9 Hz, C*H*$_2$Ar), 6.8 (s, 4H, Ar-*H*), 9.21 (s, 1H, 2-C*H*). ^{13}C-NMR($CDCl_3$) δ: 55.29 (N*C*H(CH$_3$)CH$_2$N), 46.76 (NCH(CH$_3$)*C*H$_2$N), 45.00 (NCH(*C*H$_3$)CH$_2$N), 19.59, 20.36, 20.48, 21.31 (C_6H_2(*C*H$_3$)$_3$), 56.17, 57.91 (*C*H$_2$Ar), 125.76, 125.88, 130.13, 137.96, 138.04, 139.34, 139.42 (Ar-*C*), 157.30 (2-*C*H). Found: C,74.86; H,8.64; N,7.36%. Calcd for $C_{24}H_{33}N_2CI$: C,74.90; H,8.58; N,7.28%.

*Preparation of 1,3-bis(p-dimethylaminobenzyl)-4-methylimidazolinium chloride (**4b**)*

Compound **4b** was prepared in the same way as **2a** from 1,2-bis(*p-dimethylaminobenzylamino)propane* dihydrochloride (5.5 g, 1.33 mmol) in triethyl orthoformate (50 mL) to give white crystals of **4b**. Yield: 3.38 g, 70%, mp 215–215.5°C. IR, ν: 1622 cm^{-1} (N—C—N). ^{1}H-NMR($CDCl_3$) δ: 3.50–3.70 (m, 1H, NC*H*(CH$_3$)CH$_2$N), 2.90, 3.40 (t, 2H, J = 9.8 Hz, NCH(CH$_3$)C*H*$_2$N), 1.20 (d, 3H, J = 6.1 Hz, NCH(C*H*$_3$)CH$_2$N), 4.20, 4.92 (d, 4H, J = 14.7 Hz, C*H*$_2$Ar), 6.60, 7.80 (d, 8H, J = 6.7 Hz, Ar-*H*), 2.86 (s, 12H, N(C*H*$_3$)$_2$), 10.80 (s, 1H, 2-C*H*). ^{13}C-NMR($CDCl_3$): 46.33 (N*C*H(CH$_3$)CH$_2$N), 28.19 (NCH(CH$_3$)*C*H$_2$N), 24.05 (NCH(*C*H$_3$)CH$_2$N), 60.52 (*C*H$_2$Ar), 112.71, 112.80, 127.30, 127.78, 128.07, 128.26, 129.30, 129.69 (Ar-*C*), 157.50 (2-*C*H). Found: C,68.39; H,8.12; N,14.51%. Calcd. for $C_{22}H_{31}N_4Cl$: C,68.30; H,8.02; N,14.48%.

General Procedure for Rhodium-Carbene Catalyzed Addition of Phenylboronic Acid to Aldehydes

Phenylboronic acid (1.20 g, 9.8 mmol), KO*t*Bu (4.9 mmol), substituted aldehydes (4.9 mmol), $[RhCl(COD)]_2$ (1 mmol%), imidazolinium salts (**2** and **4**) (2 mmol), dimethoxyethane (15 mL) were introduced in to Schlenk tube and then water (5 mL) was added. The resulting mixture was stirred room temperature or heated for 5 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, all reactions were monitored by TLC.

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