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Synthesis of rhodium complexes derived from benzimidazolin-2-ylidene ligands and first used for the addition of arylboron to benzonitriles

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ABSTRACT

Benzimidazolium salts and their new rhodium complexes ([Rh(COD)(NHC)Cl]) were synthesized and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. The addition of arylboron to benzonitriles in the presence of a catalytic amount of rhodium NHC complexes was examined. Corresponding carbonyl compounds were obtained in good yields. This method allows for the preparation of a wide variety of carbonyl compounds in moderate to excellent yields and displays a high level of activity for the addition of arylboron to nitriles.

1. Introduction

N-Heterocyclic carbenes (NHCs) and their metal complexes are prevalent in modern organometallic chemistry [1]. The history of the NHC family of ligands is rich but began with little fanfare in 1968 with simultaneous reports of new Cr-NHC and Hg-NHC complexes by Öfele [2] and Wanzlick and Schonherr [3], respectively. In 1991, Arduengo et al successfully isolated a free NHC [4], but by that time the coordination chemistry of NHCs was already well-developed. Lappert et al. exploited electron rich olefins (ero), which act as masked NHCs, and significantly advanced the synthetic methodologies for building complexes [5]. Key work by Herrmann and co-workers has led to the widespread use of NHC complexes in catalysis [6]. Different types of NHCs derived from imidazole [7], benzimidazole [8], imidazolidine [9,10], and triazole [11] have been reported during the last decade. Studies involving NHCs are, in general, dominated by NHCs based on the imidazole ring [12,13]. Benzimidazolin-2-ylidenes have received considerably less interest, though in recent years this area has been developed by Hahn and co-workers [14–16]. The benzimidazole skeleton is found in a variety of natural products. Dimethylbenzimidazole, for example, is a key component in vitamin B12 and its derivatives. Besides its prominent role in pharmaceutical chemistry, the benzimidazole moiety also serves as a basis for ionic liquids [17] and as precursor for NHCs [18,19]. In addition, NHC ligands can be easily derived by changing the substituents on nitrogen atoms and the backbone of carbenes, which provides various ligands for metal-organic materials. NHCs resemble the widely used donor phosphine ligands [20–22]. Binding a transition metal to the carbene carbon atom of the NHC ligand leads to the formation of a very strong metal-carbon bond, which endows the NHC metal complexes to possess higher stability toward heat, moisture and oxygen. So far, a variety of NHC transition metal complexes have been synthesized, and some of them have been applied to a broad spectrum of catalytic reactions including cross couplings, olefin metathesis and hydroformylation of olefins [23–26].

The transition metal-catalyzed addition of aryl groups to a carbon-heteroatom double bond remains a relatively undeveloped process compared to the related addition to carbon–carbon double bonds [27]. In the past decades, addition of carbon–metal species to carbon-heteroatom multiple bonds, such as the carbonyl, imino, and nitrile groups, is an important reaction for organic synthesis, and the addition products are important precursors for the synthesis of biologically active compounds [28,29]. In recent years, the transition metal catalyzed addition reactions provide for the synthesis of aryl ketones from nitriles. Larock and Zhou indicated synthesis of aryl ketones by the palladium catalyzed C–H activation of arenes and intermolecular carbopalladation of nitriles [30]. Later, Lu and Zhao

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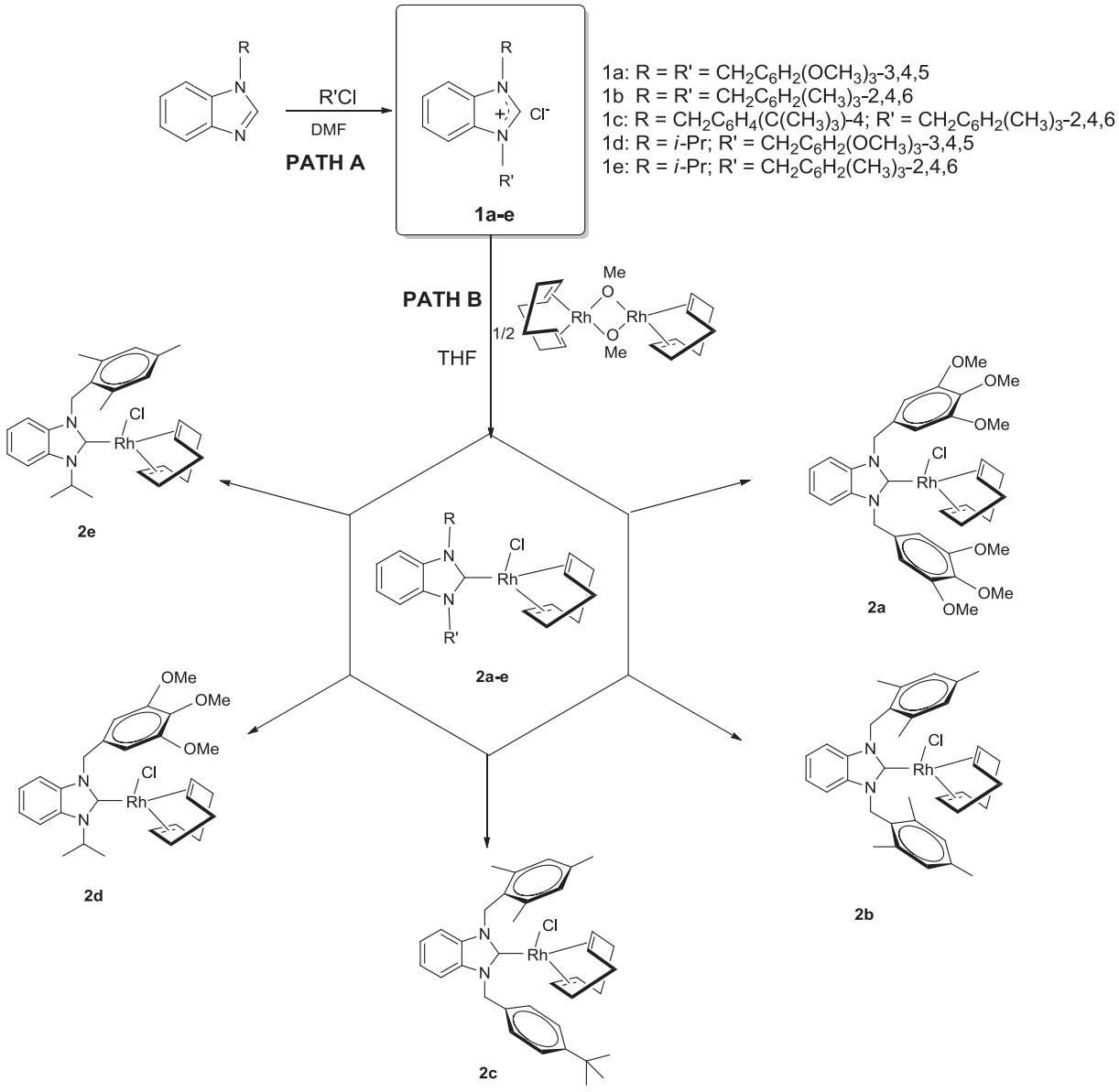
developed a cationic palladium catalyzed addition of arylboronic acids to nitriles [31]. In 2010, Nickel catalyzed addition of arylboronic acids to nitriles has reported by Cheng et al. [32]. Recent publications describing the rhodium catalyzed addition of organoboron reagents to aldehydes have attracted many chemists' interest [33–38]. In 2001 Fürstner and Krause developed an efficient protocol to perform the arylation of aldehydes using catalytic systems based on N-heterocyclic ligands and rhodium complexes [39]. The rhodium-catalyzed nucleophilic addition reactions of organoboron and -stannane reagents to carbon-heteroatom multiple bonds are now recognized to be highly useful tools for C–C bond formation [40–43]. Recently, arylboron compounds including arylboronic acids and tetraaryl borates have proved to be effective arylating reagents in rhodium catalysis. The treatment of benzonitrile with sodium tetraphenylborate was reported by Miura et al. [36]. In this type reaction, the use of NHC as a ligand are not specified to the present. We previously reported catalytic reactions that hydrosilylation and the addition to aldehyde of phenylboronic acid in the presence of a catalytic amount of rhodium NHC complex [44,45]. In this letter, we report the first use of Rh-NHC complex as a catalyst for the efficient addition of the sodium tetraphenylborate to the C–N triple bond to produce diaryl ketones. For this purpose, our team has focused on the synthesis, characterization of a series benzimidazolium salts as NHC precursor and their rhodium complexes.

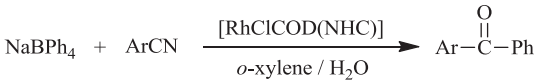
2. Results and discussion

2.1. Synthesis and characterization

Benzimidazolium salts (**1**) as NHC precursors were readily accessible by reaction of alkyl halides with 1-alkyl benzimidazole derivatives in heating DMF (Scheme 1-Path A). These salts were characterized by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis techniques which support the proposed structures. All compounds showed good solubility in water and common organic solvents, such as dichloromethane, chloroform, methanol, acetonitrile, and N,N-dimethylformamide. The ^{1}H NMR spectra of the benzimidazolium salts (**1a**–**e**) in $CDCl_3$ exhibit as a singlet in the range



Scheme 1. Synthesis of rhodium NHC complexes.



Scheme 2. The reaction of sodium tetraphenylborate with benzonitrile.

δ 10.44–11.93 ppm, characteristic of the NC*H*N benzimidazolium proton. The chemical shift of the C2 carbon and IR spectra showed strong C–N bands are in agreement with data reported for other benzimidazolium salts [46–49].

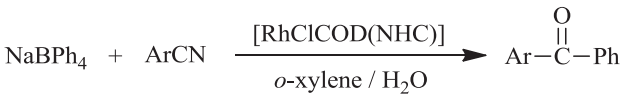
To form carbene rhodium (COD) complexes three different synthesis routes are well established [50]. First the reaction of a free carbene with the dimeric precursor $[Rh(COD)Cl]_2$. This method is used for both imidazolium/imidazolidinium and benzimidazolium groups to give carbene rhodium complexes by cleaving the chloro bridge of the dimeric COD complexes during the reaction [51–55]. Another method for prepare carbene complexes of rhodium is in situ deprotonation of the azolium salts [56–59]. Substituting the halide bridge in the precursor dimer by an alkoxy bridge, this "internal base" deprotonates the azolium salt in situ, leading to the desired complexes [60]. The third preparation pathway for carbene substituted COD complexes is transmetallation from the silver intermediate [61]. We chose the second preparation pathway that we obtained excellent yields by in situ deprotonation with $[Rh(OMe)COD]_2$ in this work. (Scheme 1-Path B) The reaction of benzimidazolium salts with the binuclear $[Rh(OMe)COD]_2$ complex proceeded smoothly in refluxing THF to give the RhCl(COD)(NHC) complexes as crystalline solids in 59–82% yields.

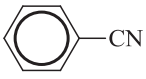
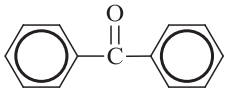
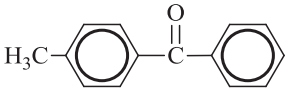
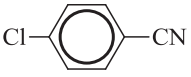
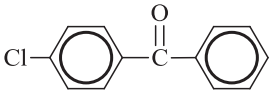
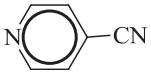
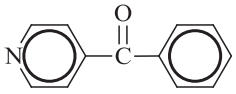
New Rh complexes which are very stable in the solid state have been characterized by analytical and spectroscopic techniques. The complexes appear to be spectroscopically pure, and exhibit signals slightly upfield in comparison with the parent carbene precursors (**1**); as expected, the C_2–H signal is absent. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that $C_{carbene}$ is substantially deshielded. The signal for the carbene carbon of Rh-NHC complexes was doubled with peaks observed in the δ 196.1–198.0 ppm range ($J_{Rh\text{-}C_{carbene}}$ = 50.0–51.1 Hz), upfield relative to the free carbene and with the characteristic doublet from coupling to Rh. Coupling constants $J(^{103}Rh–^{13}C)$ for the new rhodium complexes (**2a**–**e**) are comparable with those found for carbene rhodium(I) complexes [62]. In 2012, Herrmann et al. reported a water soluble carbene complexes of Rh, Ir and Ru from benzimidazolin-2-ylidene ligand [63]. Rhodium complex exhibits peak in δ 195.5 ppm, which was reported in the same paper. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other RhCl(COD)(1,3-dialkylbenzimidazole-2-ylidene) complexes.

2.2. Catalytic application of Rh-NHC complexes

In 2006 Miura et al. developed an efficient protocol to perform the arylation of benzonitrile using rhodium complexes. They first

Table 1
Rhodium-NHC catalyzed reaction of sodium tetraphenylborate with nitriles.

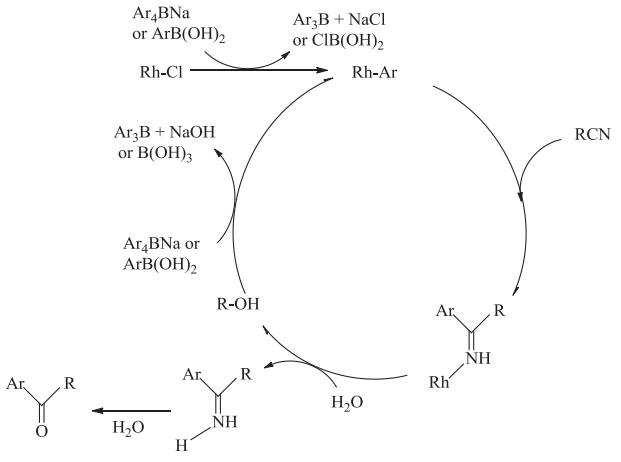


Entry	ArCN	Product	Catalyst	Yield %[a]
1			2a	95
2			2b	97
3			2c	94
4			2d	97
5			2e	96
6			2a	96
7			2b	98
8			2c	93
9			2d	97
10			2e	98
11			2a	83
12			2b	83
13			2c	72
14			2d	81
15			2e	78
16			2a	93
17			2b	86
18			2c	84
19			2d	89
20			2e	96

[a] Reaction conditions: benzonitrile (2 mmol), sodium tetraphenylborate (0.5 mmol), [RhClCOD(NHC)] (0.005 mmol), *o*-xylene/H_2O (9/1.5 mL), 120 °C, 1 h. isolated yield (purity of yield checked by NMR and GC and GC–MS). Yields are based on sodium tetraphenylborate.

indicated the reaction using phenylboronic acid, potassium phenyl(trifluoro)borate and sodium tetraphenylborate as phenylating reagents in the presence of acetic anhydride [64]. Miura has reported that the treatment of sodium tetraphenylborate with benzonitrile in the presence of $[RhCl(cod)]_2$ –dppp catalytic system (cod = 1,5-cyclooctadiene, and dppp (1,3-bis(diphenylphosphino) propane, in *o*-xylene at 120 °C for 44 h under nitrogen gave benzophenone imine in 21% yield. The addition of H_2O (0.5 mL) completely suppressed the ortho-phenylation and significantly promoted the reaction to afford benzophenone imine in 91% yield within 1 h. Under the conditions with H_2O, part of benzophenone imine was hydrolyzed to benzophenone. The omission of dppp or the use of PPh_3 in place of it resulted in low efficiency of the phenylation. These results have shown that ligand is important this catalytic system. N-heterocyclic carbenes have emerged as an extremely useful class of ligands for use in transition-metal complexes. It is well recognized that replacement of phosphines by NHCs can provide complexes with enhanced stability and catalytic performance due to the high electron-donor ability. With the introduction of N-heterocyclic carbenes novel class of ligands have been developed that display similar binding properties than phosphines. They act also as very strong σ-donors and very poor π-acceptors but form at the same time much more stable metal–NHC-bonds in many cases. Two nitrogen atoms within the heterocycle stabilize the carbene carbon through inductive and mesomeric effects, allocating strong σ-donation to a metal ion. As a result, M-NHC complexes are often thermally robust and electron-rich, ideal for catalytic application. So far, NHC ligand has not used in the above mentioned reaction, therefore we firstly used Rh-NHC catalyst at the arylation of benzonitrile with sodium tetraphenylborate (Scheme 2).

In an initial attempt, benzonitrile (2 mmol) was treated with sodium tetraphenylborate (0.5 mmol) in the presence of [RhClCOD(NHC)] (0.005 mmol) in *o*-xylene/H_2O at 120 °C for 1 h under nitrogen. All the four aryl groups of the $NaBPh_4$ were added to the nitrile. As a result, benzophenone was formed in good yields for all Rh complexes (Entries 1–5 in Table 1). The reaction using other nitriles with sodium tetraphenylborate as phenyl source was next examined. 4-Methylbenzonitrile under went phenylation to give the corresponding ketone in 84–96% isolated yield (Entries 6–10 in Table 1). The reaction of 4-chlorobenzonitrile also proceeded efficiently (Entries 11–15 in Table 1). The reactions of 4-pyridine carbonitrile with sodium tetraphenylborate also proceeded smoothly *o*-xylene/H_2O at 120 °C for 1 h, affording the corresponding ketone in good isolated yields (93–98%; Entries 16–20 in Table 1). Under the same reaction conditions, Miura investigated treatment of 4-methylbenzonitrile with sodium tetraphenylborate to give the related ketone in 98% yield. We have obtained same conversion for 4-methylbenzonitrile while achieving better results for 4-chlorobenzonitrile [36]. We have found that arylboron compound can be additioned efficiently with various nitriles in the presence of an appropriate rhodium-NHC based catalyst. Corresponding ketone was observed in *o*-xylene/water reaction mixture. The good yields were observed in the reaction using all Rh-NHC complexes which has substituted phenyl groups on N-atoms. These results imply that Rh complex with benzimidazolin-2-ylidene ligand shows the excellent catalytic activity.



Scheme 3. The mechanism proposed by Miura.

Many transition-metal complexes catalyze the addition reactions of main metal reagents, but their mechanism has not yet been studied in detail. However, the transmetalation between the main metal reagents and transition-metal complexes has been proposed as a key step of the catalytic cycle. A plausible mechanism for the reaction of nitrile with borate which reported by Miura has shown in Scheme 3 [36].

3. Conclusion

In summary, a series of NHC precursors and their rhodium complexes have been synthesized and characterized. All complexes are stable toward light and air in the both solid state and solution. We have developed a first Rh-NHC catalyst for the addition reaction of sodium tetraphenylborate to nitriles. Further studies on this chemistry and its application of rhodium catalyzed addition protocol are currently underway.

4. Experimental

4.1. General procedures

All reactions for the preparation of benzimidazolium salts and their rhodium complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and Fluka. $[Rh(OMe)(cod)]_2$ was prepared according to the published method [65]. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a Perkin Elmer Spectrum 100. ^1H- and ^{13}C NMR spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, hept = heptet and m = multiplet signal. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

4.2. Synthesis and characterization of benzimidazolium salts

Benzimidazolium salt (**1a**) was prepared according to the literature [46]. Other *N*-heterocyclic carbene precursors (**1b**–**1e**) were prepared according to general pathway depicted in Scheme 1. 1-alkyl benzimidazole (1.0 mol) was treated with an alkyl halide (1.0 mol) in DMF at 80 °C. Upon cooling to room temperature, a colorless solid precipitated when was added diethylether. Crude product was filtered, dried under vacuum and then was recrystallized from absolute ethanol to give colorless needles, and the solid was washed with diethylether (2 × 10 mL) and dried under vacuum led to the formation of the corresponding benzimidazolium salts.

*4.2.1. 1,3-Bis-(2,4,6-trimethylbenzyl)benzimidazolium chloride (**1b**)*

Yield: 3.85 g (92%). M.p.: 200–201 °C. FT-IR $\upsilon_{(CN)}$: 1592 cm^{-1}. Anal. Calc. for $C_{27}H_{31}N_2Cl$: C, 77.40; H, 7.46; N, 6.69. Found: C, 77.42; H, 7.45; N: 6.70%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 2.03 and 2.00 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.64 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.64 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.16 (s, 4H, NC_6H_4N), 10.59 (s, 1H, NCHN). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 20.0 and 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 47.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 125.1, 129.9, 137.6 and 139.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 113.7, 127.1 and 131.4 (NC_6H_4N), 142.8 (NCHN).

*4.2.2. 1-(2,4,6-Trimethylbenzyl)-3-(4-ter-butylbenzyl) benzimidazolium bromide (**1c**)*

Yield: 4.23 g (89%). M.p.: 219–220 °C. FT-IR $\upsilon_{(CN)}$: 1601 cm^{-1}. Anal. Calc. for $C_{28}H_{33}N_2Br$: C, 70.43; H, 6.97; N, 5.87. Found: C, 70.45; H, 6.94; N: 5.88. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.24 (s, 9H, $CH_2C_6H_4C(CH_3)_3$-*p*), 2.27 and 2.30 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.85 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_4C(CH_3)_3$-*p*), 6.91 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.36 and 7.41 (m, 8H, NC_6H_4N and $CH_2C_6H_4C(CH_3)_3$-*p*), 11.21 (s, 1H, NCHN). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 20.7 and 21.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 31.6 ($CH_2C_6H_4C(CH_3)_3$-*p*), 35.0 ($CH_2C_6H_4C(CH_3)_3$-*p*), 47.8 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 51.5 ($CH_2C_6H_4C(CH_3)_3$-*p*), 125.4, 130.2, 138.3 and 140.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 114.2, 114.3, 126.6, 127.5, 127.6, 128.3, 130.6, 130.8, 131.9, and 152.7 ($CH_2C_6H_4C(CH_3)_3$-*p* and NC_6H_4N), 143.1 (NCHN).

*4.2.3. 1-Izo propyl-3-(3,4,5-trimethoxybenzyl)benzimidazolium chloride (**1d**)*

Yield: 2.82 g (75%). M.p.: 198–199 °C. FT-IR $\upsilon_{(CN)}$: 1568 cm^{-1}. Anal. Calc. for $C_{20}H_{25}N_2O_3Cl$: C, 63.74; H, 6.69; N, 7.43. Found: C, 63.76; H, 6.65; N, 7.42%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.83 (d, J = 6.4 Hz, 6H, $CH(CH_3)_2$), 4.97 (hept., J = 6.4 Hz, 1H, $CH(CH_3)_2$), 3.79 and 3.81 (s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.84 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.94 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 7.59–7.60 and 7.71-7.73 (m, 4H, NC_6H_4N), 11.93 (NCHN). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 22.5 ($CH(CH_3)_2$), 51.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 52.1 ($CH(CH_3)_2$), 56.9 and 60.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 106.6, 113.6, 114.1, 127.1, 127.3, 128.9, 130.9, 131.8, 138.7 and 153.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5 and NC_6H_4N), 142.5 (NCHN).

*4.2.4. 1-Izo propyl-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride (**1e**)*

Yield: 2.69 g (82%). M.p.: 216–217 °C. FT-IR $\upsilon_{(CN)}$: 1565 cm^{-1}. Anal. Calc. for $C_{20}H_{25}N_2Cl$: C, 73.04; H, 7.66; N, 8.52. Found: C, 73.07; H, 7.63; N, 8.55%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.77 (s, 6H, $CH(CH_3)_2$), 2.21 and 2.23 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.99 (hept., J = 6.7 Hz, 1H, $CH(CH_3)_2$), 5.96 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.82 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.97 (d, J = 8.4 Hz, 1H, NC_6H_4N), 7.31 (t, J = 7.6 Hz, 1H, NC_6H_4N), 7.48 (t, J = 7.6 Hz, 1H, NC_6H_4N), 7.71 (d, J = 8.4 Hz, 1H, NC_6H_4N), 11.78 (NCHN). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 20.5 and 21.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 22.7 ($CH(CH_3)_2$), 48.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 52.1 ($CH(CH_3)_2$), 114.5, 125.9, 127.1, 127.4, 130.4, 130.5, 131.2, 131.9, 138.2 and 139.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and NC_6H_4N), 143.1 (NCHN).

4.3. Synthesis and characterization of rhodium NHC complexes

To a solution of benzimidazolium salts (10 mmol) in THF (15 mL) was added rhodium dimer $[Rh(OMe)COD]_2$ (5 mmol) and the resulting mixture was stirred at reflux for 5 h. After removal of the solvent, the residue was washed twice with diethylether (5 mL) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O.

*4.3.1. 1,3-Bis[(3,4,5-trimethoxybenzyl)]-benzimidazolin-2-ylidene-[(1,2,5,6-η^4)-1,5-cyclooctadiene]chlororhodium(I)(**2a**)*

Yield: 0.48 g (67%). M.p.: 215–216 °C. FT-IR $\upsilon_{(CN)}$: 1592 cm^{-1}. Anal. Calc. for $C_{35}H_{42}N_2O_6RhCl$: C, 57.98; H, 5.84; N, 3.86. Found: C, 57.94; H, 5.86; N, 3.82%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.96–1.99 (m, 4H, CH_2COD), 2.36–2.39 (m, 4H, CH_2COD), 3.37 (m, 2H, CHCOD), 3.79 and 3.81 (s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.18 (m, 2H, CHCOD), 5.58 (d, J = 14.8 Hz, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.73 (d, J = 15.2 Hz, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.86 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 7.05 (m, 4H, NC_6H_4N). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 28.9 and 33.1(CH_2COD), 53.6 and 53.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 56.8 and 61.0 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 69.3 and 100.9 (d, J = 13.7 Hz and J = 6.1 Hz, CHCOD), 105.6, 111.2, 122.7, 131.6, 135.1, 138.1 and 153.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5 and NC_6H_4N), 197.4 (d, J = 51.1 Hz, Rh-$C_{carbene}$).

*4.3.2. 1,3-Bis[(2,4,6-trimethylbenzyl)]-benzimidazolin-2-ylidene-[(1,2,5,6-η^4)-1,5-cyclooctadiene]chlororhodium(I)(**2b**)*

Yield: 0.47 g (75%). M.p.: 184–185 °C. FT-IR $\upsilon_{(CN)}$: 1681 cm^{-1}. Anal. Calc. for $C_{35}H_{42}N_2RhCl$: C, 66.82; H, 6.73; N, 4.45. Found: C, 66.85; H, 6.76; N, 4.42%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.96–2.02 (m, 4H, CH_2COD), 2.31 and 2.32 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.42–2.46 (m, 4H, CH_2COD), 3.51 (m, 2H, CHCOD), 5.18 (m, 2H, CHCOD), 5.95 (d, J = 14.8 Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.54 (d, J = 15.2 Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.28–6.31 (m, 2H, NC_6H_4N), 6.72–6.75 (m, 2H, NC_6H_4N), 6.90 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 21.0 and 21.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 28.9 and 33.1(CH_2COD), 50.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 69.1 and 100.1 (d, J = 14.5 Hz and J = 6.8 Hz, CHCOD), 110.8, 122.1, 128.4, 129.9, 135.4, 138.4 and 138.6 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and NC_6H_4N), 197.7 (d, J = 50.4 Hz, Rh-$C_{carbene}$).

*4.3.3. [1-(2,4,6-Trimethylbenzyl)-3-(4-ter-butylbenzyl)]-benzimidazolin-2-ylidene-[(1,2,5,6-η^4)-1,5-cyclooctadiene] chlororhodium(I)(**2c**)*

Yield: 0.38 g (59%). M.p.: 171–172 °C. FT-IR $\upsilon_{(CN)}$: 1471 cm^{-1}. Anal. Calc. for $C_{36}H_{44}N_2RhCl$: C, 67.23; H, 6.90; N, 4.36. Found: C, 67.27; H, 6.93; N, 4.32%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.31 (s, 9H, $CH_2C_6H_4C(CH_3)_3$-4), 1.78–2.05 (m, 4H, CH_2COD), 2.18–2.32 (m, 4H, CH_2COD), 2.36 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.42 (m, 2H, CHCOD), 5.21 (m, 2H, CHCOD), 6.01 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.28 (s, 2H, $CH_2C_6H_4C(CH_3)_3$–4), 6.79–6.92 (m, 3H, $CH_2C_6H_4C(CH_3)_3$-4 and NC_6H_4N), 6.97 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 7.29–7.36 (m, 5H, $CH_2C_6H_4C(CH_3)_3$-4 and NC_6H_4N). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 21.4 and 21.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 29.1, 29.4, 32.9 and 33.1(CH_2COD), 31.7 ($CH_2C_6H_4C(CH_3)_3$–4), 34.9 ($CH_2C_6H_4C(CH_3)_3$–4), 50.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 53.3 ($CH_2C_6H_4C(CH_3)_3$–4), 69.7 and 71.1 (d, J = 14.3 Hz and J = 14.1 Hz, CHCOD), 99.6 and 99.9 (d, J = 6.5 Hz and J = 6.7 Hz, CHCOD), 111.1, 111.3, 122.3, 122.8, 126.1, 127.1, 128.7, 130.1, 133.6, 135.4, 135.9, 138.8, 139.0 and 151.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6, $CH_2C_6H_4C(CH_3)_3$-4 and NC_6H_4N), 198.0 (d, J = 50.4 Hz, Rh-$C_{carbene}$).

*4.3.4. [1-(3,4,5-Trimethoxybenzyl)-3-(i-propyl)]-benzimidazolin-2-ylidene-[(1,2,5,6-η^4)-1,5-cyclooctadiene]chlororhodium(I)(**2d**)*

Yield: 0.48 g (82%). M.p.: 154–155 °C. FT-IR $\upsilon_{(CN)}$: 1600 cm^{-1}. Anal. Calc. for $C_{28}H_{36}N_2O_3RhCl$: C, 57.30; H, 6.18; N, 4.77. Found: C, 57.27; H, 6.15; N, 4.82%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.75 and 1.84 (d, J = 7.1 Hz, 6H, $CH(CH_3)_2$), 1.87–2.13 (m, 4H, CH_2COD), 2.22–2.59 (m, 4H, CH_2COD), 3.28 (m, 2H, CHCOD), 3.54 (hept., J = 7.1 Hz, 1H, $CH(CH_3)_2$), 3.82 and 3.83 (s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.15 (m, 2H, CHCOD), 5.58 (d, J = 15.0 Hz, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.79 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.59–7.53 (m, 4H, NC_6H_4N). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 28.6 and 32.6 (CH_2COD), 29.9 and 34.0 ($CH(CH_3)_2$), 53.5

($CH_2C_6H_2(OCH_3)_3$-3,4,5), 54.7 ($CH(CH_3)_2$), 57.1 and 61.3 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 68.8 and 69.2 (d, J = 14.4 Hz, *C*HCOD), 100.1 and 100.7 (d, J = 6.65 Hz, *C*HCOD), 105.5, 111.7, 112.2, 122.5, 122.6, 132.0, 133.4, 135.9, 138.1 and 153.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5 and NC_6H_4N), 196.1 (d, J = 50.45 Hz, Rh-$C_{carbene}$).

4.3.5. [1-(2,4,6-Trimethylbenzyl)-3-(i-propyl)]-benzimidazolin-2-ylidene-[(1,2,5,6-η^4)-1,5-cyclooctadiene]chlororhodium(I)(**2e**)

Yield: 0.42 g (78%). M.p.: 231–232 °C. FT-IR $\upsilon_{(CN)}$: 1477 cm^{-1}. Anal. Calc. for $C_{28}H_{36}N_2RhCl$: C, 62.40; H, 6.73; N, 5.20. Found: C, 62.44; H, 6.76; N, 5.22%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 1.75 and 1.84 (d, J = 7.1 Hz, 6H, $CH(CH_3)_2$), 2.05–2.11 (m, 4H, CH_2COD), 2.31 and 2.34 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.48–2.55 (m, 4H, CH_2COD), 3.47 (m, 2H, *CH*COD), 3.52 (hept., J = 7.1 Hz, 1H, $CH(CH_3)_2$), 5.11 (m, 2H, *CH*COD), 5.89 (d, J = 14.9 Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.91 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.54–7.15 (m, 4H, NC_6H_4N). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 21.4 and 21.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 28.3 and 32.3 (CH_2COD), 30.0 and 34.3 ($CH(CH_3)_2$), 49.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 54.9 ($CH(CH_3)_2$), 67.9 and 69.7 (d, J = 14.5 Hz and J = 14.3 Hz, *C*HCOD), 99.5 and 100.3 (d, J = 6.8 Hz and J = 6.5 Hz, *C*HCOD), 111.6, 112.0, 121.9, 122.3, 128.6, 130.1, 133.2, 136.5, 138.7 and 138.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and NC_6H_4N), 196.2 (d, J = 50.0 Hz, Rh-$C_{carbene}$).

4.4. General procedure for the rhodium-catalyzed reaction of sodium tetraphenylborate with nitrile

A mixture of sodium tetraphenylborate (0.5 mmol), nitrile (2 mmol), Rh-NHC complex (0.005 mmol) was stirred in *o*-xylene/H_2O (9/1.5 mL) at 120 °C under N_2 for 1 h. After cooling, the reaction mixture was extracted with Et_2O and dried over anhydrous $MgSO_4$ and filtered. Solvent was removed under reduced pressure and concentrated in vacuum to give the crude product. The crude product was purified by column chromatography on silica gel (60–120 mesh) using ethyl acetate/*n*-hexane as eluent to afford the ketone. The purity of the compounds was checked by NMR and yields are based on $NaBPh_4$. We determined conversion of starting material to product by gas chromatography and molecule weight of product by gas chromatography-mass spectrometry.

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