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# Synthesis and catalytic application of cyclopentadienyl nickel(II) N-heterocyclic carbene complexes

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## ABSTRACT

A series of ester-functionalized benzimidazolium salts **2a–c** were prepared by quaternization of 1-{{ethoxycarbonyl}methyl}benzimidazole (**1**) with 3,5-dimethylbenzyl bromide, 2,5-dimethylbenzyl chloride and 3-methoxybenzyl chloride, respectively. Refluxing **2a–c** with nickelocene in THF yielded the neutral cyclopentadienyl NHC nickel(II) complexes **3a–c**. Their structures were defined by NMR, IR and elemental analysis techniques. Molecular weights of **3a–c** were affirmed by MALDI-TOF mass spectrometry. Catalytic tests of **3a–c** were performed in Kumada coupling of some aryl chlorides with phenylmagnesium bromide at 25 °C.

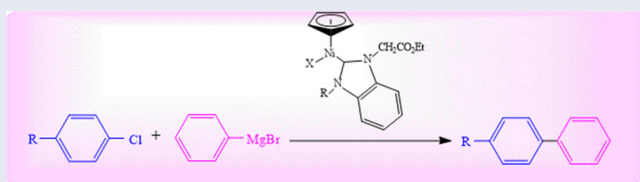
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## KEYWORDS

N-Heterocyclic carbene; benzimidazolium; nickel; Kumada coupling; catalysis



## 1. Introduction

Since metal complexes of N-heterocyclic carbenes (NHCs) having strong  $\sigma$ -donating properties possess robust metal-carbene bonds, NHCs are a favorite ligand in organometallic chemistry since the first isolation of free NHC [1]. NHC-metal complexes exhibiting catalytic activities in many important organic transformations have been used in homogeneous catalysis.

The neutral cyclopentadienylnickel(II) complexes,  $[\text{CpNiX}(\text{NHC})]$  ( $X = \text{Cl, Br, I}$ ), can be prepared by reaction of a suitable NHC precursor with nickelocene. This simple method was first achieved in 2000 for synthesis of the complex containing 1,3-dimesitylimidazol-2-ylidene [2]; since then it has often been applied [3, 4]. NHC complexes of the general formula  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{X})(\text{NHC})]$  ( $\text{R} = \text{H}$  or alkyl;  $X = \text{Cl, Br, or I}$ ) and their cationic derivatives exhibit catalytic activities in transformations such as olefin

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oligomerization and polymerization, Suzuki coupling, Kumada coupling, aryl amination, C-S coupling, hydrosilylation of carbonyls and imines, ketone  $\alpha$ -arylation, hydrothiolation of alkynes and anaerobic oxidation of secondary alcohols [5–21]. These complexes are important in organometallic chemistry.

Cross-coupling reactions in which transition metal complexes have been employed as catalysts are significant reactions to construct carbon-carbon bonds in organic synthesis. Kumada cross-coupling, the reaction of Grignard reagent with aryl or alkenyl halide, was first reported by Kumada and Corriu in 1972 [22, 23]. Biaryls and oligoaryls formed in these reactions have importance in construction of functional materials, medicines and natural products. Numerous catalytic systems have been developed for Kumada cross-coupling reactions using complexes containing nickel, palladium, cobalt and iron [24–38]. Designing of economical catalytic systems have importance, so nickel catalysts are preferable to palladium catalysts.

In the present work, the synthesis of three new benzimidazolium salts and their nickel(II) complexes are reported. Also, findings relevant to the catalytic activities of NHC-Ni(II) complexes in Kumada coupling reactions are reported.

## 2. Experimental

### 2.1. General remarks

Experiments except ligand syntheses were done under an argon atmosphere in flame-dried Schlenk flasks. Organic solvents were dried by distillation over drying agents and stored under argon (THF and Et<sub>2</sub>O over sodium/potassium, toluene and hexane over sodium). **1** was prepared using the literature method [39]. All commercial reagents were utilized as purchased. Elemental analyses were accomplished on a CHNS-932 (LECO) elemental analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Varian 400 MHz spectrophotometer. Mass spectrometric analyses were performed on a Bruker Microflex LT MALDI-TOF spectrometer. IR measurements were achieved with a Perkin-Elmer FT-IR spectrophotometer from 400–4000 cm<sup>-1</sup> using KBr.

### 2.2. Preparation of benzimidazolium salts

The mixture of **1** (1 mmol) and substituted benzyl halide (1.1 mmol) was stirred in DMF (2 mL) at room temperature for 1 h and then at 80 °C for 4 h. After cooling to room temperature, Et<sub>2</sub>O (10 mL) was added. The precipitated white solid was filtered, washed with Et<sub>2</sub>O (2 × 5 mL) and recrystallized from EtOH/Et<sub>2</sub>O.

#### 2.2.1. 1-{(Ethoxycarbonyl)methyl}-3-(3,5-dimethylbenzyl)benzimidazolium bromide, **2a**

Yield: 91%. IR  $\nu_{(\text{NCN})}$ : 1558 cm<sup>-1</sup>,  $\nu_{(\text{CO})}$ : 1736 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.30 (t,  $J$  = 7.24 Hz, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.27 (s, 6H, CH<sub>3</sub>), 4.27 (q,  $J$  = 7.30 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.66 (s, 2H, NCH<sub>2</sub>), 5.75 (s, 2H, NCH<sub>2</sub>), 6.96 (s, 1H, Ar-H), 7.04 (s, 2H, Ar-H), 7.53–7.62 (m, 4H, Ar-H), 11.41 (s, 1H, NCHN) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.01 (CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.17 (CH<sub>3</sub>), 48.12 and 51.72 (NCH<sub>2</sub>), 62.97 (CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 113.19, 113.82, 125.84, 127.31, 127.49, 130.75, 131.03, 131.78, 131.83, 139.17 (Ar-C), 143.50 (NCHN),

165.64 (CO) ppm. Anal. Calcd for  $C_{20}H_{23}N_2O_2Br$  (%): C, 59.55; H, 5.76; N, 6.95. Found: C, 59.20; H, 5.74; N, 6.94.

### 2.2.2. 1-*{(Ethoxycarbonyl)methyl}*-3-(2,5-dimethylbenzyl)benzimidazolium chloride, 2b

Yield: 84%. IR  $\nu_{(N\text{CN})}$ :  $1563\text{ cm}^{-1}$ ,  $\nu_{(\text{CO})}$ :  $1742\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.30$  (t,  $J = 7.17$  Hz, 3H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 2.25 (s, 3H,  $\text{CH}_3$ ), 2.33 (s, 3H,  $\text{CH}_3$ ), 4.27 (q,  $J = 7.40$ , 2H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 5.75 (s, 2H,  $\text{NCH}_2$ ), 5.79 (s, 2H,  $\text{NCH}_2$ ), 6.97 (s, 1H, Ar-H), 7.06–7.12 (m, 2H, Ar-H), 7.44 (d,  $J = 8.32$  Hz, 1H, Ar-H), 7.49–7.53 (m, 1H, Ar-H), 7.60 (d,  $J = 3.70$  Hz, 2H, Ar-H), 11.47 (s, 1H, NCHN) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.98$  ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 18.93 and 20.86 ( $\text{CH}_3$ ), 48.00 and 50.22 ( $\text{NCH}_2$ ), 62.87 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 113.10, 113.76, 127.15, 127.36, 129.14, 129.91, 130.10, 131.00, 131.21, 131.86, 133.39, 136.51 (Ar-C), 144.63 (NCHN), 165.96 (CO) ppm. Anal. Calcd for  $C_{20}H_{23}N_2O_2\text{Cl}$  (%): C, 66.93; H, 6.47; N, 7.81. Found: C, 65.84; H, 6.41; N, 7.60.

### 2.2.3. 1-*{(Ethoxycarbonyl)methyl}*-3-(3-methoxybenzyl)benzimidazolium chloride, 2c

Yield: 91%. IR  $\nu_{(N\text{CN})}$ :  $1563\text{ cm}^{-1}$ ,  $\nu_{(\text{CO})}$ :  $1736\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.31$  (t,  $J = 7.17$  Hz, 3H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 3.79 (s, 3H,  $\text{OCH}_3$ ), 4.28 (q,  $J = 6.94$  Hz, 2H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 5.73 (s, 2H,  $\text{NCH}_2$ ), 5.78 (s, 2H,  $\text{NCH}_2$ ), 6.87 (dd,  $J = 8.09$ , 2.08 Hz, 1H, Ar-H), 6.98–7.03 (m, 2H, Ar-H), 7.25–7.29 (m, 1H, Ar-H), 7.52–7.60 (m, 4H, Ar-H), 11.73 (s, 1H, NCHN) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.97$  ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 48.03 and 51.54 ( $\text{NCH}_2$ ), 55.52 ( $\text{OCH}_3$ ), 62.90 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 113.06, 113.55, 113.83, 114.92, 120.18, 127.16, 127.33, 130.35, 130.81, 131.81, 133.90 (Ar-C), 144.34 (NCHN), 160.20 (Ar-C), 165.87 (CO) ppm. Anal. Calcd for  $C_{19}H_{21}N_2O_3\text{Cl}\cdot 0.5\text{H}_2\text{O}$  (%): C, 61.69; H, 6.01; N, 7.58. Found: C, 61.01; H, 6.02; N, 7.05. The result of elemental analysis was supported by TGA/DTA.

## 2.3. Preparation of NHC-nickel(II) complexes

A solution of nickelocene (1 mmol) in THF (10 mL) was added to a suspension of the benzimidazolium salt (1 mmol) in THF (10 mL). The green suspension was refluxed for 3 h and then THF was removed from the red solution. The residue was washed with n-hexane ( $3 \times 5$  mL). After purification with column chromatography ( $\text{SiO}_2$ , eluent: THF), it was recrystallized from toluene/n-hexane.

### 2.3.1. $\text{CpNi}[1\text{-}\{(\text{ethoxycarbonyl)methyl}\}\text{-3-(3,5-dimethylbenzyl)benzimidazolium-2-ylidene}]\text{Br}$ , 3a

Yield: 66%.  $\nu_{(\text{CN})}$ :  $1404\text{ cm}^{-1}$ ,  $\nu_{(\text{CO})}$ :  $1745\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.40$  (t,  $J = 7.24$  Hz, 3H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 2.27 (s, 6H,  $\text{CH}_3$ ), 4.31–4.44 (m, 2H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 5.20–5.27 (m, 6H, Cp and  $\text{NCH}_2$ ), 6.06 (d,  $J = 16.04$  Hz, 1H,  $\text{NCH}_2$ ), 6.53 (d,  $J = 16.04$  Hz, 1H,  $\text{NCH}_2$ ), 6.85 (s, 2H, Ar-H), 6.90–6.94 (m, 2H, Ar-H and  $\text{NCH}_2$ ), 7.08–7.14 (m, 2H, Ar-H), 7.19–7.23 (m, 2H, Ar-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.30$  ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 21.31 ( $\text{CH}_3$ ), 50.89 and 53.78 ( $\text{NCH}_2$ ), 62.11 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 92.37 (Cp), 109.44, 110.97, 123.00, 123.09, 124.46, 129.59, 135.08, 135.44, 135.78, 138.54 (Ar-C), 168.29 (CO), 182.44 (Ni-C) ppm.

Anal. Calcd for  $C_{25}H_{27}N_2O_2NiBr$  (%): C, 57.07; H, 5.18; N, 5.33. Found: C, 57.72; H, 5.30; N, 5.20. MS (MALDI):  $m/z$  526  $[M]^+$ , 446  $[M-Br]^+$ , 323  $[M-Br-Cp-Ni]^+$ .

### 2.3.2. *CpNi[1-(ethoxycarbonylmethyl)-3-(2,5-dimethylbenzyl)benzimidazolin-2-ylidene]Cl, 3b*

Yield: 57%. IR  $\nu_{(CN)}$ :  $1404\text{ cm}^{-1}$ ,  $\nu_{(CO)}$ :  $1731\text{ cm}^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 1.39 (t,  $J$  = 7.04 Hz, 3H,  $CO_2CH_2CH_3$ ), 2.10 (s, 3H,  $CH_3$ ), 2.56 (s, 3H,  $CH_3$ ), 4.37 (s, br, 2H,  $CO_2CH_2CH_3$ ), 5.10 (s, 5H, Cp), 5.32 (d,  $J$  = 10.56 Hz, 1H,  $NCH_2$ ), 5.88 (d,  $J$  = 12.91 Hz, 1H,  $NCH_2$ ), 6.24 (s, 1H, Ar-H), 6.81 (d,  $J$  = 9.78 Hz, 1H,  $NCH_2$ ), 6.95–7.05 (m, 3H,  $NCH_2$  and Ar-H), 7.13–7.30 (m, 4H, Ar-H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 14.29 ( $CO_2CH_2CH_3$ ), 19.10 and 21.05 ( $CH_3$ ), 50.55 and 51.08 ( $NCH_2$ ), 62.11 ( $CO_2CH_2CH_3$ ), 92.29 (Cp), 109.53, 110.64, 123.16, 123.22, 125.97, 128.33, 130.55, 131.86, 133.52, 135.16, 135.54, 135.93 (Ar-C), 168.30 (CO), 181.43 (Ni-C) ppm. Anal. Calcd for  $C_{25}H_{27}N_2O_2NiCl$ (%): C, 62.33; H, 5.66; N, 5.82. Found: C, 61.98; H, 5.74; N, 5.70. MS (MALDI):  $m/z$  482  $[M]^+$ , 446  $[M-Cl]^+$ , 323  $[M-Cl-Cp-Ni]^+$ .

### 2.3.3. *CpNi[1-(ethoxycarbonylmethyl)-3-(3-methoxybenzyl)benzimidazolin-2-ylidene]Cl, 3c*

Yield: 61%. IR  $\nu_{(CN)}$ :  $1398\text{ cm}^{-1}$ ,  $\nu_{(CO)}$ :  $1756\text{ cm}^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 1.40 (t,  $J$  = 6.85 Hz, 3H,  $CO_2CH_2CH_3$ ), 3.74 (s, 3H,  $OCH_3$ ), 4.37 (s, br, 2H,  $CO_2CH_2CH_3$ ), 5.21 (s, 5H, Cp), 5.29 (d,  $J$  = 16.82 Hz, 1H,  $NCH_2$ ), 6.24 (d,  $J$  = 17.22 Hz, 1H,  $NCH_2$ ), 6.56 (d,  $J$  = 16.82 Hz, 1H,  $NCH_2$ ), 6.79–6.86 (m, 3H, Ar-H), 6.97 (d,  $J$  = 16.04 Hz, 1H,  $NCH_2$ ), 7.12–7.24 (m, 5H, Ar-H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 14.29 ( $CO_2CH_2CH_3$ ), 50.58 and 53.61 ( $NCH_2$ ), 55.39 ( $OCH_3$ ), 62.14 ( $CO_2CH_2CH_3$ ), 92.39 (Cp), 109.50, 110.90, 112.28, 113.71, 118.92, 123.10, 123.22, 129.95, 134.84, 135.67, 137.17, 160.18 (Ar-C), 168.30 (CO), 181.10 (Ni-C). Anal. Calcd for  $C_{24}H_{25}N_2O_3NiCl$  (%): C, 59.60; H, 5.22; N, 5.79. Found: C, 58.93; H, 5.26; N, 5.62. MS (MALDI):  $m/z$  484  $[M]^+$ , 447  $[M-Cl]^+$ , 325  $[M-Cl-Cp-Ni]^+$ .

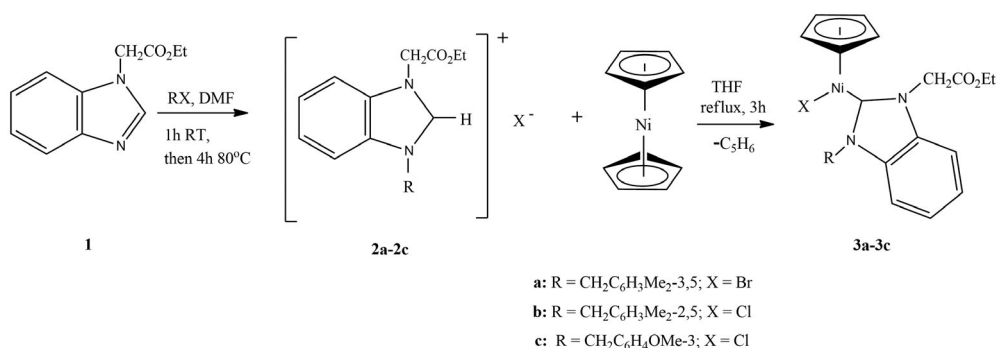
## 2.4. General procedure for Kumada coupling reaction

NHC-Ni(II) complex (0.5% mmol) was dissolved in THF (1 mL). Aryl halide (1 mmol) and  $PhMgBr$  (1.5 mmol) were added to the solution. The mixture was stirred at  $25^\circ C$  for a period of time. The reaction was stopped by the addition of water. After extraction with  $CH_2Cl_2$  ( $3 \times 10\text{ mL}$ ) and drying with  $Na_2SO_4$ , pure cross-coupling product was obtained by column chromatography and analyzed by  $^1H$  NMR.

## 3. Results and discussion

Syntheses of **2a–c** and **3a–c** are shown in Figure 1. Ester-functionalized benzimidazolium salts **2a–c** were synthesized by reaction of **1** with substituted benzyl halides. The colorless solids are stable towards air and moisture and soluble in  $CH_2Cl_2$ , EtOH, MeOH, DMF, DMSO,  $CH_3CN$  and water.

NHC-nickel(II) complexes **3a–c** were prepared by refluxing of **2a–c** with nickelocene in THF for 3 h. This direct method has advantages, since the isolation of the unstable

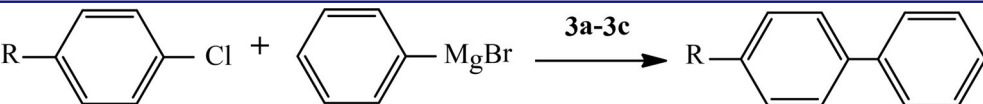


**Figure 1.** Synthesis of **2a–c** and **3a–c**.

NHC ligand is not necessary. After column purification, the neutral NHC-Ni(II) complexes having formula [CpNi(NHC)X] (X = Br, Cl) Ni(II) complexes were isolated as red or violet solids. These compounds are stable towards air and moisture in the solid state. They are soluble in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, THF, toluene and DMSO.

The formulations of the synthesized compounds were affirmed by elemental analysis. In <sup>1</sup>H NMR spectra of **2a–c**, acidic NCHN protons resonate at 11.41–11.73 ppm. The <sup>13</sup>C NMR spectra exhibit signals from 143.50–144.63 ppm for the C2 carbon. In the <sup>1</sup>H NMR spectra of the complexes, the peaks of benzimidazolium protons disappear, evidence of the deprotonation and generation of the Ni(II)-NHC complexes. The signals of carbene carbon atoms are at 181.10–182.44 ppm in the <sup>13</sup>C NMR spectra. For Cp protons and carbons, the signals appear at 5.10–5.21 ppm and 92.29–92.39 ppm in <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, respectively. NMR data are consistent with literature values [10, 40–43]. The singlet signals for the NCH<sub>2</sub> protons in the <sup>1</sup>H NMR spectra of the salts turn into doublets in the <sup>1</sup>H NMR spectra of the complexes, indicating that the methylene protons are diastereotopic as reported earlier [5, 44, 45]. The presence of –C=N– groups is verified by FT-IR spectra with peaks at 1558–1563 cm<sup>-1</sup> for the NHC precursors and at 1398–1404 cm<sup>-1</sup> for the complexes [46, 47]. In mass spectra of the complexes, the peaks support the proposed structures.

The first study of Kumada cross-coupling of aryl halides catalyzed by [CpNiX(NHC)] was published in 2015 [5]. There are limited studies on this subject in the literature [11]. In this article, catalytic activities of the synthesized NHC-Ni(II) complexes were tested for the reaction of some aryl chlorides with phenylmagnesium bromide in THF at 25 °C. The results are listed in Table 1. Catalytic activities of **3a–c** were compared by using 4-chloroanisole as the substrate with 0.5 mol% catalysts in THF for 3 h (Entries 1–3). **3b** and **3c** showed similar moderate activities, and the cross-coupling product 4-methoxybiphenyl was isolated in 66–67% yields. **3a** is much more active than **3b** and **3c**. According to these results, the substituted benzyl groups on benzimidazolin-2-ylidene ligands do not affect the yields. The reason why **3a** is the most active catalyst may be because it contains bromo ligand instead of chloro ligand. The same conclusion was previously reported in Suzuki coupling catalyzed by nickel complexes of similar structure [9]. Increasing time does not change the yield (Entries 3–5). Different solvents were studied for the same reaction. It is concluded, as with other studies, that THF is the best solvent (Entries 1, 6–8) [28, 30]. Increasing the amount of

**Table 1.** Kumada cross-coupling reactions catalyzed by NHC-Ni(II) complexes.<sup>a</sup>


Entry	Catalyst (mol %)	R	Solvent	Time (h)	Yield (%) <sup>b, c</sup>
1	<b>3a</b> (0.5)	OCH <sub>3</sub>	THF	3	80
2	<b>3b</b> (0.5)	OCH <sub>3</sub>	THF	3	66
3	<b>3c</b> (0.5)	OCH <sub>3</sub>	THF	3	67
4	<b>3c</b> (0.5)	OCH <sub>3</sub>	THF	6	67
5	<b>3a</b> (0.5)	OCH <sub>3</sub>	THF	24	68
6	<b>3a</b> (0.5)	OCH <sub>3</sub>	toluene	3	65
7	<b>3a</b> (0.5)	OCH <sub>3</sub>	1,4-dioxane	3	76
8	<b>3a</b> (0.5)	OCH <sub>3</sub>	DMF	3	19
9	<b>3a</b> (1)	OCH <sub>3</sub>	THF	3	80
10	<b>3a</b> (0.5)	H	THF	3	97
11	<b>3a</b> (0.5)	CHO	THF	3	75
12	<b>3a</b> (0.5)	OH	THF	3	81

<sup>a</sup>Reaction conditions: 1 mmol aryl chloride, 1.5 mmol PhMgBr, 1 mL THF, 25 °C.

<sup>b</sup>Isolated yields.

<sup>c</sup>Average of min. two runs.

**3a** to 1 mol % did not affect the catalytic activity (Entry 9). For other substrates, good yields were obtained (Entries 10–12). The results are comparable with previously reported nickel(II) complexes [28, 48, 49]. The catalytic products are known compounds and were characterized by <sup>1</sup>H NMR spectroscopy.

## 4. Conclusion

A new series of ester-functionalized benzimidazolium salts and their neutral cyclopentadienyl NHC nickel(II) complexes were prepared and characterized. The complexes exhibited good catalytic activities in reactions of some aryl chlorides with phenylmagnesium bromide. Complex **3a** containing bromo ligand displayed higher activity than **3b** or **3c**.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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