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Facile synthesis of half-sandwich (NHC)Ni(Cp)X complexes from labile NHC proligands

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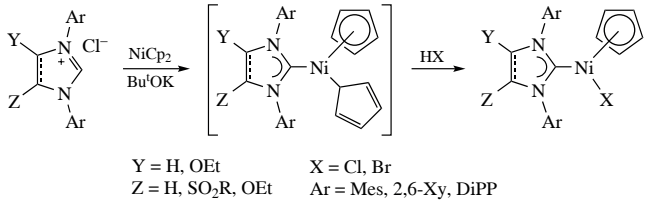
A new approach to the one-pot synthesis of a series of nickel(II) complexes of the general formula (NHC)Ni(Cp)X (NHC = N-heterocyclic carbene, Cp = η^5-coordinated cyclopentadienyl anion, X = Cl, Br) has been developed. The method involves the reaction of *N*,*N*′-diarylimidazolium or imidazolinium salt NHC-precursor with nickelocene in the presence of Bu^{t}OK with subsequent displacement of one Cp ligand in nickel complex by halide anion under the action of HCl or HBr. The method allows one to obtain previously inaccessible complexes with NHC ligands containing alkoxy or RSO$_2$ groups in the NHC backbone, which are unstable under the usual conditions of synthesis of (NHC)Ni(Cp)X complexes.



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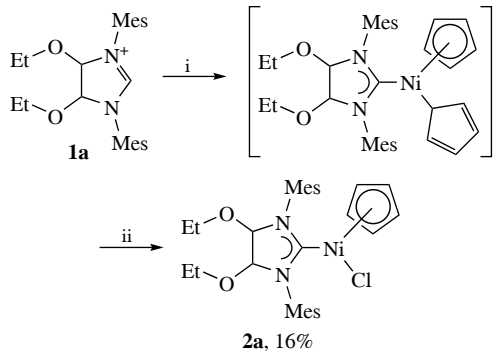
Over the past decade, nickel complexes with N-heterocyclic carbenes (Ni/NHC) have played a significant role in the catalysis of organic reactions.[1–5] Among the various types of Ni/NHC complexes, half-sandwich (NHC)Ni(Cp)X complexes (where Cp refers to the η^5-coordinated cyclopentadienyl anion) have gained widespread use as precatalysts due to their simple preparation.[6–10] These 18 electron nickel(II) complexes are usually diamagnetic and stable in air. The synthesis of (NHC)Ni(Cp)X complexes generally involves the use of *N*,*N*′-diarylimidazolium salts with bulky *N*-aryl substituents, which are reacted with nickelocene.[6] A contemporary trend in tailoring the electronic and steric parameters of NHC ligands involves installation of various substituents into the NHC backbone to influence the electronic and steric properties of the ligand.[11–13] It has been shown that substituents in the NHC backbone can have a significant impact on catalytic activity.[14,15] While the preparation of (NHC)Ni(Cp)X complexes using imidazole-type NHC ligands with alkylamino (NR) substituents in the NHC nucleus has been reported,[14] the synthesis of similar complexes with NHC ligands containing alkoxy (OR) or sulfonyl (RSO$_2$) groups at the 4- and 5-positions of imidazole/imidazoline ring was unsuccessful under the usual conditions of direct metallation of imidazolium or imidazolinium salts with nickelocene under heating, proposedly due to side reactions involving RO and RSO$_2$ groups.[11,13]

In this paper, we present a novel mild approach to the synthesis of various (NHC)Ni(Cp)X complexes, including NHC ligands with labile OR and RSO$_2$ groups in the imidazole and imidazoline rings.

We started our study with attempts to synthesize the complex (NHC)Ni(Cp)X using the most conventional and widely used approach,[16] which involves the reaction of NiCp$_2$ with azolium salts in THF at 65 °C. Notably, under these conditions, the use of **1a** as a model NHC proligand did not yield even trace amounts of the desired complex **2a** (see Online Supplementary Materials, Table S1). According to ^{1}H NMR spectroscopy data and GCMS analysis, only a complex mixture of products was formed. This result may be attributed to the low basicity of the Cp anion in NiCp$_2$, as well as the possibility that NiCp$_2$ induces complex transformations of compound **1a**, which may involve binding of the nickel atom by two OEt groups,[17] leading to imidazole ring cleavage.

Recently it was shown that the similar structure (IMes)Ni(η^5-Cp)(η^1-Cp) complex can be formed by the reaction of the azolium salt IMes·HCl, sodium *tert*-butoxide and NiCp$_2$ in toluene at low temperature (25 °C).[18] Under these conditions, we found that using **1a** results in the appearance of characteristic singlets of one η^1-bonded Cp ring at ~6.0 ppm and one η^5-bonded Cp ring at ~4.4 ppm in ^{1}H NMR spectra (see Online Supplementary Materials, Figure S1). Obviously, under the action of strong base, free NHC is generated *via* a C–H deprotonation of the azolium salt **1a**, which suffers conversion of NiCp$_2$ to the complex [IMes(OEt)$_2$]Ni(η^5-Cp)(η^1-Cp) (Scheme 1). However, attempts to isolate this Ni/NHC complex were unsuccessful. Apparently, this may be explained by the low stability of the [IMes(OEt)$_2$]Ni(η^5-Cp)(η^1-Cp) complex in air, which is predominantly decomposed by oxidizing the NHC ligand with oxygen, resulting in the liberation of the corresponding azolone and initial NiCp$_2$. Interestingly, the



Scheme 1 *Reagents and conditions*: i, azolium salt **1a** (0.25 mmol), $NiCp_2$ (0.26 mmol), Bu^tONa (0.26 mmol), toluene (1 ml), 2 h, 25 °C; ii, 1 M aqueous solution of HCl (280 μl), 5 min, 25 °C.

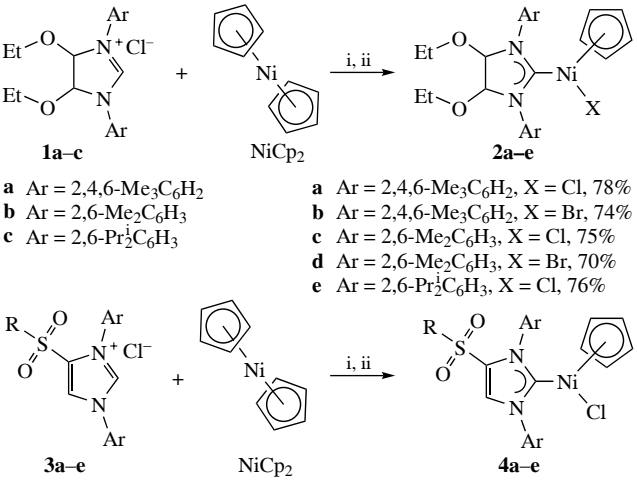
addition of aqueous HCl to the reaction mixture led to the formation of desired and more air stable complex **2a** (see Scheme 1). In order to increase the yield of complex **2a**, the reaction conditions were further optimized (Table 1).

Among the bases studied, the use of *tert*-butoxide bases was crucial. In the presence of weaker bases such as Cs_2CO_3 or K_2CO_3, the formation of the complex [IMes(OEt)$_2$]Ni(η^5-Cp)(η^1-Cp) was not observed in the ^{1}H NMR spectra (entries 1 and 2). Different solvents were also tested, and 1,4-dioxane was found to be the best one (entries 3–8). Among the various well-defined HCl solutions, the 1 M HCl in dioxane was found to be the most suitable (entry 9 *vs*. entry 8). The inefficiency of aqueous HCl solution may be related to the deleterious effect of water on the reaction. Potassium *tert*-butoxide was chosen as a convenient base, compared to Bu^tONa (entries 9–12) or Bu^tOLi (entry 13), the use of Bu^tOK (entries 14–16) significantly reduces the synthesis time to 8 h (entry 15), no increase in yield of **2a** was observed with prolongated reaction time (entry 15 *vs*. entries 14 and 16). Increasing the reaction temperature led to an increase in the formation of by-products

Table 1 Effect of reaction conditions on the yield of complex **2a**.[a]

Entry	Base (mol per 1 mol of **1a**)	Solvent	Time/ h	HCl additive (equiv.)[b]	Yield of **2a** (%)[c]
1	Cs_2CO_3 (3)	Toluene	16	3[d]	0
2	K_2CO_3 (3)	Toluene	16	3[d]	0
3	Bu^tONa (1.05)	Toluene	2	1.1[d]	16
4	Bu^tONa (1.05)	MeCN	2	1.1[d]	0
5	Bu^tONa (1.05)	DMA	2	1.1[d]	0
6	Bu^tONa (1.05)	NMP	2	1.1[d]	0
7	Bu^tONa (1.05)	THF	2	1.1[d]	20
8	Bu^tONa (1.05)	Dioxane	2	1.1[d]	23
9	Bu^tONa (1.05)	Dioxane	2	1.1	34
10	Bu^tONa (1.05)	Dioxane	6	1.1	62
11	Bu^tONa (1.05)	Dioxane	16	1.1	77
12	Bu^tONa (1.05)	Dioxane	24	1.1	74
13	Bu^tOLi (1.05)	Dioxane	16	1.1	58
14	Bu^tOK (1.05)	Dioxane	4	1.1	65
15	Bu^tOK (1.05)	Dioxane	8	1.1	83 (78)
16	Bu^tOK (1.05)	Dioxane	16	1.1	81
17	Bu^tOK (1.05)	Dioxane	8	1.1	63[e]
18	Bu^tOK (2)	Dioxane	8	1.1	48
19	Bu^tOK (1.05)	Dioxane	8	1	76
20	Bu^tOK (1.05)	Dioxane	8	1.5	67

[a] Reaction conditions: **1a** (0.25 mmol), $NiCp_2$ (0.26 mmol), base (1.05–3 equiv.) and solvent (1 ml) were stirred at 25 °C within corresponding time. After cooling to room temperature, 1 M solution of HCl in dioxane was added to the mixture and the resulted solution was stirred within 5 min. [b] Molar quantity of HCl per 1 mol of **1a**. [c] Yields determined by ^{1}H NMR integration relative to a $MeNO_2$ internal standard and isolated yields (in parentheses). [d] 1 M aq. HCl (1.1 equiv.). [e] At 40 °C.



a Ar = 2,4,6-$Me_3C_6H_2$
b Ar = 2,6-$Me_2C_6H_3$
c Ar = 2,6-$Pr^i_2C_6H_3$

a Ar = 2,4,6-$Me_3C_6H_2$, X = Cl, 78%
b Ar = 2,4,6-$Me_3C_6H_2$, X = Br, 74%
c Ar = 2,6-$Me_2C_6H_3$, X = Cl, 75%
d Ar = 2,6-$Me_2C_6H_3$, X = Br, 70%
e Ar = 2,6-$Pr^i_2C_6H_3$, X = Cl, 76%

a Ar = 2,4,6-$Me_3C_6H_2$, R = Ph
b Ar = 2,4,6-$Me_3C_6H_2$, R = *p*-Tol
c Ar = 2,6-$Me_2C_6H_3$, R = Ph
d Ar = 2,6-$Me_2C_6H_3$, R = *n*-Bu
e Ar = 2,6-$Pr^i_2C_6H_3$, R = *p*-Tol

a Ar = 2,4,6-$Me_3C_6H_2$, R = Ph, 72%
b Ar = 2,4,6-$Me_3C_6H_2$, R = *p*-Tol, 79%
c Ar = 2,6-$Me_2C_6H_3$, R = Ph, 65%
d Ar = 2,6-$Me_2C_6H_3$, R = *n*-Bu, 68%
e Ar = 2,6-$Pr^i_2C_6H_3$, R = *p*-Tol, 76%

Scheme 2 *Reagents and conditions*: i, azolium salt **1a–c** or **3a–e** (0.25 mmol), $NiCp_2$ (0.26 mmol), Bu^tOK (0.26 mmol), 1,4-dioxane (1 ml), 25 °C, 8 h; ii, 1 M solution of HX (X = Cl or Br) in dioxane (0.28 mmol HCl or HBr), 25 °C, 5 min.

(entry 17). Further investigation suggested that a 1.1 : 1 molar ratio loading of HCl and 1.05 equiv. of Bu^tOK relative to **1a** was optimal (entry 15 *vs*. entries 18–20). Therefore, the conditions shown in Table 1, entry 15, were accepted as optimal for **2a** complex synthesis.

With the optimized conditions in hand, we explored the substrate scope of several *N*,*N*′-diarylimidazolium or imidazolinium salts as potential NHC proligands for the synthesis of various (NHC)Ni(Cp)X complexes. All reactions proceeded well to give the desired Ni/NHC complexes **2** and **4** in good yields (Scheme 2). Moreover, we discovered that the use of 1 M HBr solution in dioxane instead of HCl was accessible for the synthesis of bromide complexes **2b** and **2d**. Our protocol enables access to Ni/NHC complexes **4a–e** with sulfonyl-substituted NHC ligands, which were previously inaccessible through conventional synthetic methods.[13]

Complexes **2** and **4** were obtained as red-colored, air-stable microcrystalline compounds. The structures of these complexes were confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, high-resolution mass spectrometry (HRMS) and single crystal X-ray studies of compound **2a** (Figure 1).† The NMR spectra of these Ni/NHC complexes are analogous to those of (NHC)Ni(Cp)X complexes reported in the literature[19–21] and contain characteristic Cp ring signals appearing at ~4.5 ppm in ^{1}H NMR and ~92–93 ppm in ^{13}C NMR spectra.

In summary, we have developed a versatile protocol for the synthesis of (NHC)Ni(Cp)X complexes (X = Cl, Br). The method involves the *in situ* generation of

† *Crystal data for* **2a**. $C_{30}H_{39}ClN_2NiO_2$, M = 553.79, tetragonal, $P4_32_12$ at 100 K, a = 12.9909(3), b = 12.9909(3) and c = 33.7830(12) Å, V = 5701.3(3) Å^3, Z = 8, d_{calc} = 1.290 g cm^{-3}, μ(MoKα) = 0.803 mm^{-1}, F(000) = 2352. Total of 140494 reflections were measured and 11954 independent reflections (R_{int} = 0.0522) were used. The refinement converged to wR_2 = 0.0774 and GOF = 1.066 for all independent reflections [R_1 = 0.0310 was calculated against F for 10761 observed reflections with $I > 2\sigma(I)$]. See Online Supplementary Materials for details on the data collection and structure refinement.

CCDC 2402209 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

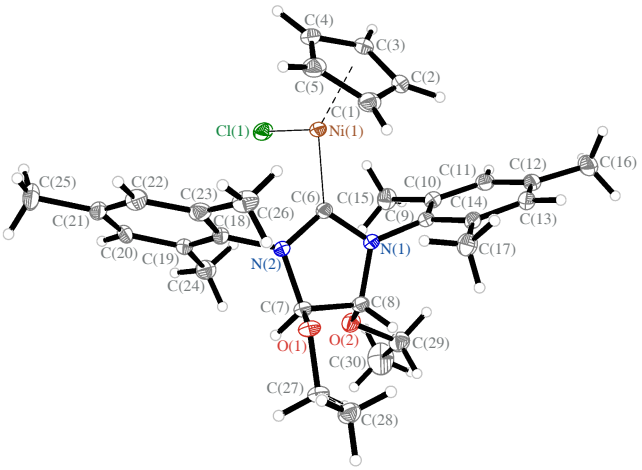


Figure 1 Molecular structure of compound **2a**.

(NHC)Ni(η^5-Cp)(η^1-Cp) complexes, which upon interaction with HCl or HBr yield (NHC)Ni(Cp)X complexes under mild conditions. This approach is compatible with a wide range of NHC proligands, including imidazole-type NHC ligands with RSO_2 or RO groups directly attached to the imidazole nucleus, making it a valuable technique that complements existing methodologies.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7690.

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