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Half-sandwich nickel complexes with ring-expanded NHC ligands – synthesis, structure and catalytic activity in Kumada-Tamao-Corriu coupling

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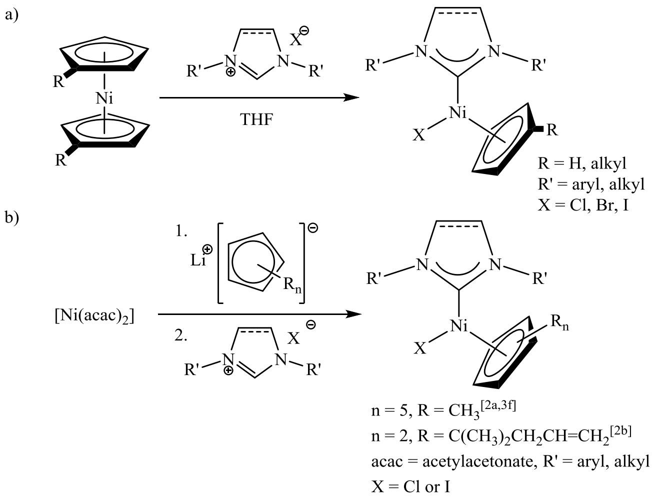
A general synthesis of complexes [Ni(Cp)(X)(NHC)] from a nickel halide, CpLi, and a carbene solution is reported. This procedure yields unprecedented complexes with ring-expanded NHC ligands (RE-NHC) of six- (1a, 1b), seven- (1c), and eight-membered (1d) heterocycles. The NMR spectra of 1a-1d are consistent with hindered rotation of Ni-C$_{carbene}$ and N-C$_{Mes}$ bonds, while X-ray analyses of 1b, 1c, and 1d reveal a pronounced *trans* influence of the RE-NHC ligands. Complexes 1a-1e are efficient pre-catalysts in Kumada-Tamao-Corriucoupling with maximum efficiency observed for complexes bearing the six-membered NHC.

Half-sandwich nickel complexes of the general formula [Ni(η^5-C$_5$H$_4$R)(X)(NHC)] (R = H, alkyl, alkenyl; X = Cl, Br, I; NHC = *N*-heterocyclic carbene) are known only for five-membered NHCs. These complexes are usually synthesized in reactions of nickelocene with imidazolium halides (Scheme 1a).[1] However, for compounds with bulky substituents on the cyclopentadienyl (Cp) ligand, another protocol has to be utilized (Scheme 1b).[2]

Owing to their catalytic activity in many organic transformations, these air- and moisture-stable complexes are currently the object of intensive research.[2-5] Efforts on tuning properties of [Ni(Cp)(X)(NHC)] are focused on the appropriate ligand selection within the scope of synthetic methodologies presented on Scheme 1, *i.e.* for five-membered NHCs only. Since the halide[1a,3b,3c,3d,4] or Cp ligands[5] can be readily displaced from the title complexes, NHC is the ligand of choice for modifications aimed at enhancing their catalytic activity. Recently, it has been shown that increasing the steric demand of NHCs by means of bulky substituents on the nitrogen atoms improved efficiency of the arylamination of aromatic halides catalysed by [Ni(Cp)(X)(NHC)].[3i] Another way to enhance spatial requirements as well as electron-donating strength of NHC ligands is expansion of the carbenic heterocycle.[6] Both of these properties are presumed to influence reactivity of complexes by facilitating formation of the catalytically active intermediate and increasing its stability. On the other hand, ring-expanded NHC (RE-NHC) may enable an intramolecular C-H activation, which can be detrimental for catalytic performance.[7]



Scheme 1. Reported synthetic routes to complexes [Ni(η^5-C$_5$H$_n$R$_{5-n}$)(X)(NHC)].

Although RE-NHC nickel complexes are known, these studies are limited to only a few papers.[7,8] To the best of our knowledge, up to date there have been no reports on [Ni(Cp)(X)(RE-NHC)]. Driven by scientific curiosity to see if [Ni(Cp)(X)(RE-NHC)] complexes are of greater catalytic activity than their congeners with five-membered "classical" NHCs, we decided to develop the synthesis of such complexes.

Our initial attempts to prepare the desired RE-NHC nickel complexes according to the procedure shown in Scheme 1a, *i.e.* from nickelocene and the appropriate carbene precursor, failed. Reactions involving the use of [Ni(acac)$_2$] as the starting material were also unsuccessful (Scheme 1b). A probable reason for this lack of reactivity is the weak acidity of carbene precursors[9] and steric congestion around the reacting centre.[6] Inspired by the synthesis of related complexes with Cp*-functionalized NHC ligands,[3g] we decided to test a similar approach involving addition of the two ligands (Cp and RE-

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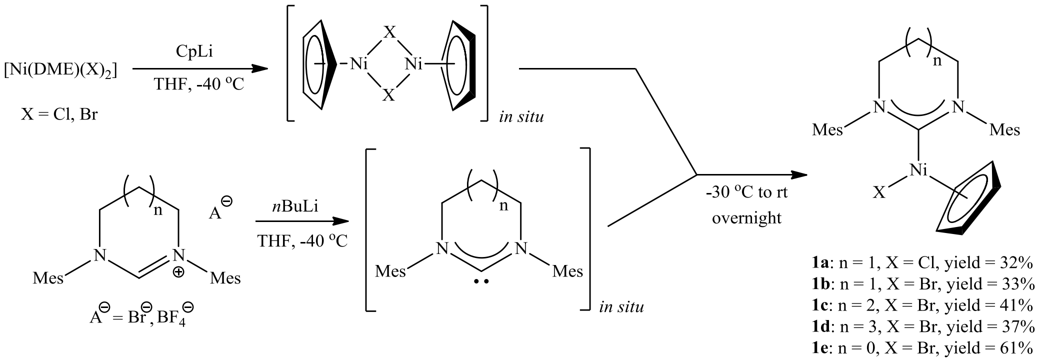

Scheme 2. Synthesis of complexes [Ni(Cp)(X)(NHC)]

NHC) to a nickel halide. Despite plausible formation of different products, *e.g.* nickelocene and $[Ni(X)_2(RE\text{-}NHC)_2]$, the desired [Ni(Cp)(X)(RE-NHC)] complexes were obtained in remarkably good yields as the only isolable products. More specifically, $[Ni(DME)(X)_2]$ (X = Br or Cl, DME = 1,2-dimethoxyethane) was treated first with a CpLi solution in THF to form what we believe is a dinuclear complex $[Ni(Cp)(\mu\text{-}X)]_2$.[10] Subsequently, a freshly prepared RE-NHC solution, obtained by deprotonation of the carbene precursor with BuLi, was injected. After stirring overnight and conventional purification complexes **1a**-**1d** were obtained in 32-41% yields (two steps from the Ni halide) as deep purple solids (Scheme2).[11]

Moreover, to further expand the scope of our method, we have applied it to prepare a complex with a five-membered NHC Thus, [Ni(Cp)(Br)(SIMes)][3c] (SIMes = 1,3-bis(2,4,6-trimethyl-phenyl)-4,5-dihydroimidazol-2-ylidene) (**1e**) was obtained via this simple procedure in 61% yield (two steps from $[Ni(DME)Br_2]$).

The NMR spectra of complexes **1a**-**1d** were conventionally recorded in $CDCl_3$ at ambient temperature. Signals originating from NHC ligands imply restricted Ni-$C_{carbene}$ and N-C_{Mes} bond rotation. Owing to the inequivalence of hydrogen atoms in each NCH_2 group their signals appear in the ^1H NMR spectra as unresolved multiplets. Moreover, as a result of the hindered rotation, all complexes **1a**-**1d** have characteristic set of signals for mesityl wingtips, showing two separated equal singlets (2:2 ratio) for *meta* hydrogens from phenyl rings and three singlets (6:6:6 ratio) for methyl groups, *i.e.* *ortho* methyls and *meta* hydrogens are nonequivalent within each mesityl moiety. Another interesting feature of ^1H NMR spectra concerns the Cp group. While for [Ni(Cp)(X)(NHC)] with five-membered NHCs the Cp singlet appears from 5.2 to 4.6 ppm, its chemical shift for **1a**-**1d** is unusual and strongly influenced by size of the NHC as it varies from 4.21 ppm for **1b** to 3.68 ppm for **1d**. Moreover, all signals in the ^1H NMR spectrum of **1d** are strongly broadened. We tentatively interpret these phenomena in terms of spin equilibrium,[4f,12] *i.e.* increasing content of the high-spin form of the complex which is correlated to the NHC's ring size.

Crystal structure analysis of complexes **1b**-**1d** revealed that they crystallize in the monoclinic crystal system and their molecular geometries are typical for nickel(II) NHC complexes (Figures 1-3).[13] The Ni–C_{Cp} bond lengths exhibit a pronounced *trans* influence of the RE-NHC ligands while the C-C bond lengths in Cp (see Figure captions for selected bond lengths) show variations characteristic of the so-called "diene distortion".[14,15]

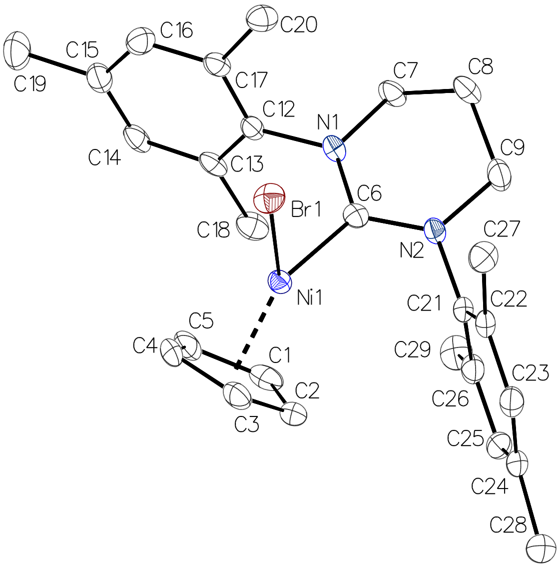

Figure 1. Molecular structure of complex **1b**. Since there are no significant differences in the conformations of four molecules present in the asymmetric unit only one is shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in Å: Ni1–Br1 2.3371(5), Ni1–C1 2.054(3), Ni1–C2 2.193(3), Ni1–C3 2.197(3), Ni1–C4 2.165(3), Ni1–C5 2.151(3), Ni1–C6 1.905(3), C1–C2 1.429(5), C1–C5 1.433(5), C2–C3 1.379(4), C3–C4 1.440(4), C4–C5 1.387(5).

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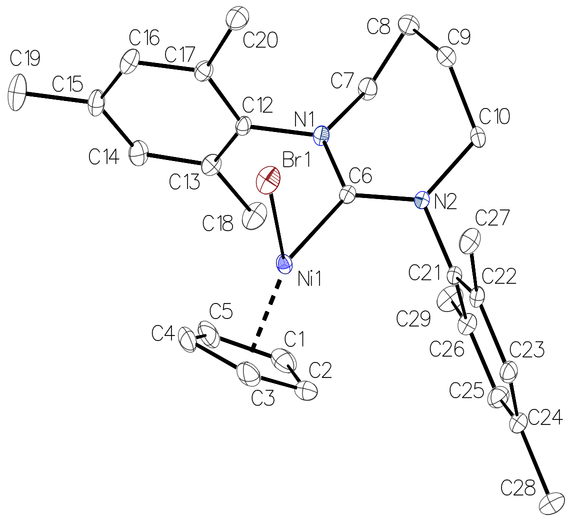


Figure 2. Molecular structure of complex **1c**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in Å: Ni1–Br1 2.3281(3), Ni1–C1 2.0529(17), Ni1–C2 2.1914(17), Ni1–C3 2.1847(17), Ni1–C4 2.1722(18), Ni1–C5 2.1422(17), Ni1–C6 1.8972(15), C1–C2 1.431(3), C1–C5 1.436(3), C2–C3 1.384(3), C3–C4 1.444(2), C4–C5 1.389(3).

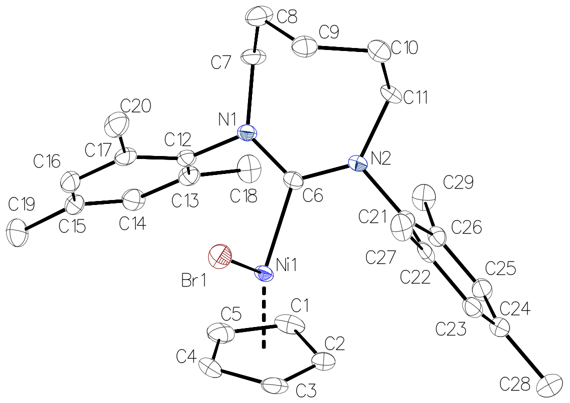
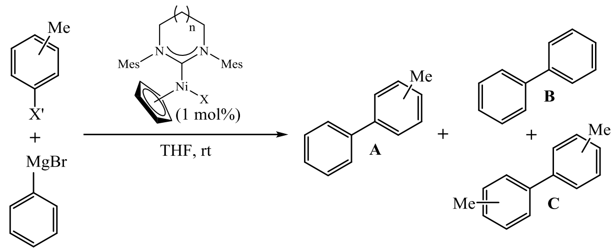


Figure 3. Molecular structure of complex **1d**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in Å: Ni1–Br1 2.3466(4), Ni1–C1 2.074(2), Ni1–C2 2.195(2), Ni1–C3 2.178(2), Ni1–C4 2.150(2), Ni1–C5 2.161(2), Ni1–C6 1.918(2), C1–C2 1.438(3), C1–C5 1.425(4), C2–C3 1.380(3), C3–C4 1.439(3), C4–C5 1.393(4).

Complex [Ni(Cp)(Cl)(IMes)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was reported as an active catalyst in Kumada-Tamao-Corriu (KTC) coupling between *p*-tolylmagnesium bromide and phenyl *O*-sulfamate.[3a] To our surprise, further application of [Ni(Cp)(X)(NHC)] complexes in this reaction are limited.[3l,3p,16] In order to get insight into the influence of NHC ring expansion on the activity of [Ni(Cp)(X)(NHC)] in KTC coupling, we tested complexes **1a**-**1e** in reactions of PhMgBr with halotoluenes (3-bromotoluene, 4-chlorotoluene). Expansion of the NHC ligand from a five- to six-membered ring proved to be beneficial for the catalytic activity (Table 1, entries 1-3, 9,10). Catalyst loading of only 1%$_{mol}$ of **1a** or **1b** is sufficient to achieve conversions over 95% with very good selectivity at room temperature in 90 minutes.[17] Also, the nature of the halogen ligand in the nickel complex appeared to have no influence on the catalytic performance (Table 1, entries 2 and 3). Further expansion of NHC ligand to seven- or eight-membered rings resulted in diminished activity. However, high conversions could be achieved at longer reaction times (Table 1, entries 4-7). Selectivity is another parameter affected by ring expansion beyond the six-membered system (Table 1, entries 4, 5, 7).

Table 1. Kumada-Tamao-Corriu coupling of PhMgBr with halotoluenes catalysed by **1a**-**1e**.[a]



Entry	Catalyst	n	X′	Conversion (%)[b]	Ratio A:B:C[b]
1	**1e**	0	3-Br	78	91:6:3
2	**1a**	1	3-Br	97	92:6:2
3	**1b**	1	3-Br	98	92:7:1
4	**1c**	2	3-Br	36	89:11:0
5[c]	**1c**	2	3-Br	86	85:10:5
6	**1d**	3	3-Br	traces	-
7[c]	**1d**	3	3-Br	97	70:20:10
8	**1a**	1	4-Cl	traces	-
9[c]	**1a**	1	4-Cl	68	65:22:13
10[c]	**1e**	0	4-Cl	42	54:36:10

[a] All reactions in duplicate; reaction conditions: THF (2.8 mL), halotoluene (0.66 mmol), phenylmagnesium bromide solution in THF (0.81 mL, 1.00 mmol, 1.24 mol/L), nickel complex (6.7 μmol, 1 mol%), room temperature, 90 min; See the Supporting Information for details. [b] Determined with GC. [c] Reaction time = 21 h.

Conclusions

We report here a new general synthesis of complexes [Ni(Cp)(X)(NHC)] that is applicable to ring-expanded NHC ligands. Complexes with the six-membered NHC provided the best efficiency in KTC coupling. Further studies will focus on application of [Ni(Cp)(X)(RE-NHC)] in other catalytic reactions, including arylamination of aromatic halides.

Acknowledgements

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