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Synthesis of inexpensive chiral half-sandwich nickel N-heterocyclic carbene complexes: X-ray diffraction study of the D-menthyl-functionalized complex [Ni(iPr$_2$Ph-NHC-CH$_2$OMent)ClCp]

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This manuscript is dedicated to the late Professor Malcolm H. Chisholm a great chemist, a true mentor and an extraordinary man.

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ABSTRACT

The imidazolium salts, 1-(2,4,6-trimethylphenyl)-3-[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium chloride (Mes-NHC-CH$_2$OMent·HCl) (**1a**) and 1-(2,6-diisopropylphenyl)-3-[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium chloride (iPr$_2$Ph-NHC-CH$_2$OMent·HCl) (**1b**), are readily accessible from inexpensive (1R,2S,5R)-(−)-menthol. They react with nickelocene to give two new chiral nickel-N-heterocyclic carbene (NHC) complexes, [Ni(Mes-NHC-CH$_2$OMent)ClCp] (**2a**) and [Ni(iPr$_2$Ph-NHC-CH$_2$OMent)ClCp] (**2b**), in good yields. The new complexes were fully characterized by standard spectroscopic techniques and by a single crystal X-ray diffraction study on complex **2b**. Complex **2b** crystallizes in the chiral spacegroup *P*1, with two independent molecules in the unit cell, which are slightly different from each other. Preliminary studies show that these complexes are effective catalysts for the hydrosilylation of ketones. However no chiral induction was observed.

1. Introduction

N-heterocyclic carbene (NHC) ligands have greatly expanded the synthetic and catalytic repertoire of organometallic chemists in recent years [1]. Electronically they resemble trialkyl- and triarylphosphine ligands [2], but there are some important stability and reactivity differences: NHC are unlikely to dissociate in catalytic reactions, and metal NHC complexes are often significantly more thermally stable and less oxygen sensitive than their corresponding triarylphosphine complexes [1]. Furthermore, NHC ligands, while retaining the steric and electronic tunability of phosphine ligands, are much more readily accessible and also much less expensive, as in most cases, the precursors to these ligands are imidazolium salts, which are air-stable (though sometimes hydroscopic) species that can be prepared in aerobic conditions [3].

The chemistry and the catalytic applications of nickel-NHC complexes have exploded in recent years, as attested by our results [4] and others [5], and also by a number of recent reviews [6] that have highlighted various aspects of this rapidly emerging field. This has been driven by the unique reactivity patterns exhibited by nickel complexes [7] and also by the huge cost advantage obtained by using nickel species as opposed to their much more expensive palladium and platinum analogs.

Despite the progresses made in the area, chiral nickel NHC complexes are still relatively uncommon and there are few reports of well-characterized species and their applications [8]. Our research in recent years has focused on relatively stable nickel(II)-NHC complexes, with a focus on using inexpensive and readily available NHC ligands [4]. In keeping with this philosophy, we

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wanted to move towards the synthesis of chiral but inexpensive nickel-NHC complexes [8d,8g]: this report describes our first endeavors in the field.

2. Results and discussion

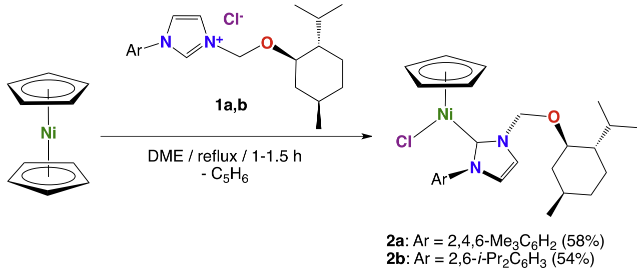
2.1. Synthesis and characterization

A series of chiral imidazolium ionic liquids derived from D-menthol [(1R,2S,5R)-(−)-menthol], which notably demonstrated high anti-microbial activity, was reported in 2007 [9]. D-Menthol was reacted with paraformaldehyde and gaseous HCl at 10 °C to give chloromethyl (1R,2S,5R)-(−)-menthyl ether [10,11]. This, in turn, was used to alkylate 1-alkylimidazoles to obtain the chiral imidazolium ionic liquids [9]. Following the same synthetic strategy, the chiral imidazolium salts, 1-(2,4,6-trimethylphenyl)-3-[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium chloride (**1a**) and 1-(2,6-diisopropylphenyl)-3-[(1R,2S,5R)-(−)-menthoxymethyl] imidazolium chloride (**1b**), were readily synthesized by the reactions of 1-(2,4,6-trimethylphenyl)-1H-imidazole and 1-(2,6-diisopropylphenyl)-1H-imidazole with chloromethyl (1R,2S,5R)-(−)-menthyl ether in toluene at room temperature (Scheme 1).

The imidazolium salts were isolated in good to excellent yields, and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and elemental analyses. The characteristic resonance for the imidazolium protons, observed as an apparent singlet at 11.22 and 11.14 ppm for **1a** and **1b**, respectively, confirmed the formation of the salts. The AB spin system seen for the methylene protons of the two molecules, at different chemical shifts from that of chloromethyl menthyl ether starting material (5.56/5.54 ppm *vs.* 6.39/6.05 ppm (**1a**) and 6.48/6.13 ppm (**1b**)), also provided good evidence that the desired products had been obtained.

The chiral cyclopentadienyl nickel(NHC) complexes **2a** and **2b** were then prepared in better than 50% yields by reacting salts **1a** and **1b** with nickelocene (Scheme 2), following standard synthetic procedures for the syntheses of [NiClCp(NHC)] (Cp = η^5-C_5H_5) species [12]. The products were purified by column chromatography and fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, elemental analyses, and, for complex **2a**, by a single crystal X-ray diffraction study.

Spectroscopic data is fully consistent with the presumed structure of these species (shown in Scheme 2). Thus, for example, the ^{1}H NMR spectra no longer show the imidazolium protons but display the cyclopentadienyl protons as a singlet at 4.73 (**2a**) and 4.70 ppm (**2b**), whilst ^{13}C NMR spectra reveal resonances for the NHC carbene and cyclopentadienyl carbon atoms at 164.5 and 91.8 ppm (**2a**), and 165.5 and 91.6 ppm (**2b**), respectively: these chemical shifts are typical for these carbon atom resonances in [NiClCp(NHC)] species [12].

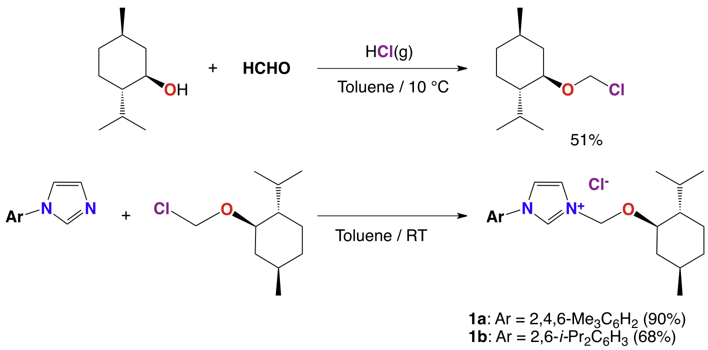


Scheme 2. Synthesis of the enantiomerically pure complexes **2a** and **2b**.

The ^{1}H NMR spectra of **2a** and **2b** feature a number of broad signals (see Figs. S5 and S7 in the Supporting information). Thus, the two *meta*-hydrogens and the two *ortho*-methyl groups of the mesityl ring of **2a** are respectively not equivalent and appear as four broad singlets in a 1:1:3:3 relative integrated ratio. In the case of **2b**, the *meta*-protons of the aromatic ring appear as two relatively broad doublets in a 1:1 integrated ratio, and the two isopropyl groups of the aromatic ring are displayed as three doublets in a 3:3:6 integrated ratio (two doublets are coincidentally isochronous) and two very broad signals in a 1:1 relative integrated ratio. In addition, the three methyl groups of the menthyl moiety appear as three broad doublets in a 3:3:3 relative integrated ratio. Similar broad ^{1}H NMR spectra at room temperature have been previously observed for the closely related [NiXCp(Mes-NHC-*n*Bu)] (X = Br [13], I [14]), [NiICp(*i*Pr_2Ph-NHC-*n*Bu)] [14] and [NiICp{Mes-NHC-$(CH_2)_4$CN}] [15] complexes, as well as for more sterically congested [NiXCp*(NHC)] (Cp* = η^5-C_5Me_5) complexes [12c,14]. This phenomenon has been attributed to restricted rotations about the Ni–carbene and N–C bonds that result from the significant steric congestion in all these species. The same is probably true for **2a** and **2b** (see X-ray diffraction study).

2.2. X-ray diffraction study of **2b**

A single crystal X-ray diffraction study of **2b** corroborated the NMR data and confirmed the molecule's structure. Key bond distances and bond angles are listed in Table 1 and selected crystallographic data and data collection parameters can be found in Table 3. Complex **2b** crystallizes in the triclinic space group *P*1, with two independent molecules (A and B) in the unit cell (Fig. 1). The two molecules are not identical and have slightly different structural parameters. Thus, the Ni–C(1) distances [C(1) = the carbene carbon atom] are 1.896(12) and 1.857(12), while the corresponding Ni–Cl distances are 2.181(4) and 2.195(4) Å for molecules A and B, respectively. When one considers the plane formed by the Cp centroid, C(1), and the chlorine atom, the nickel



Scheme 1. Synthesis of the chiral imidazolium salts **1a** and **1b**.