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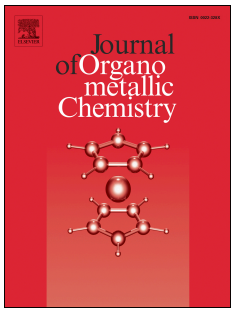

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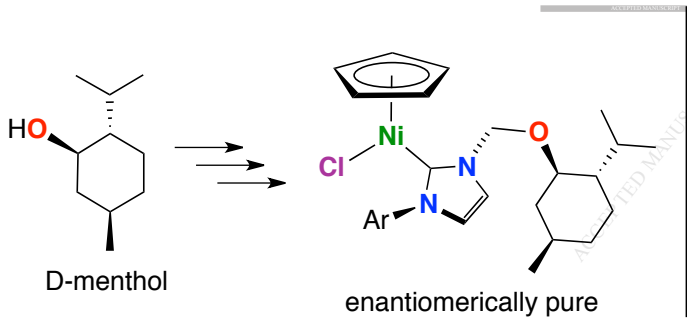
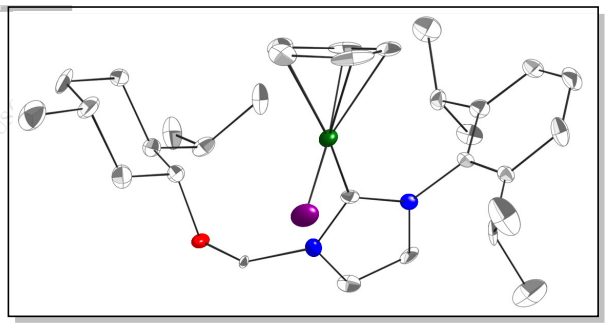

HO
Cl
Ni
N
O
N
Ar
D-menthol
enantiomerically pure



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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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 space-group *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.

Keywords

(1R,2S,5R)-(–)-menthol, chiral imidazolium salt, N-heterocyclic carbene, nickel, hydrosilylation

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.

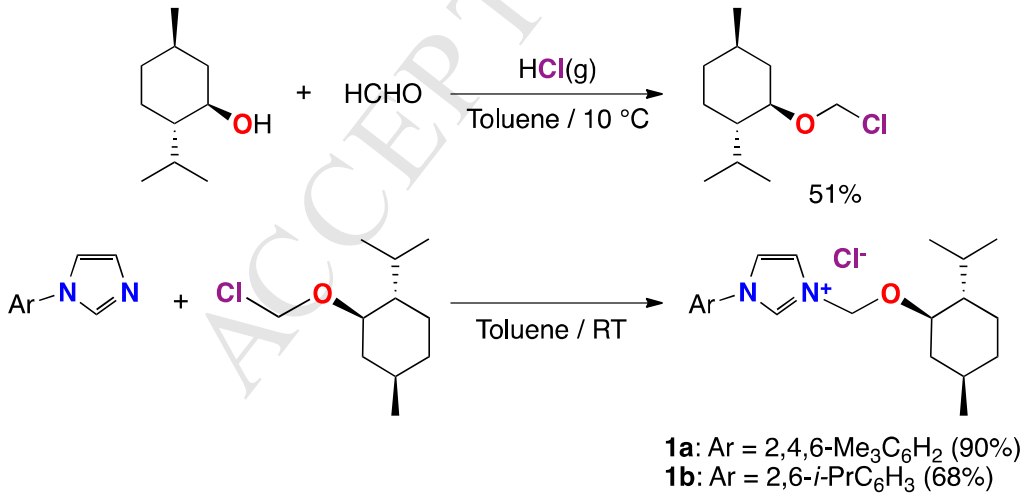
Despite the progresses made in the area, chiral nickel NHC complexes are still relatively uncommon and there are few reports of well-characterized species and their applications [8]. Our research in recent years has focused on relatively stable nickel(II)-NHC complexes, with a focus on using inexpensive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

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

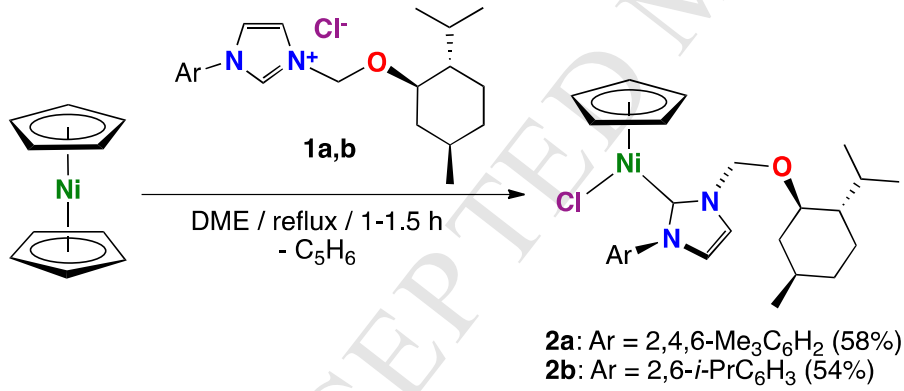
A series of chiral imidazolium ionic liquids derived from D-menthol [(1R,2S,5R)-(–)-menthol], which notably demonstrated high anti-microbial activity, was reported in 2007 [9]. D-Menthol was reacted with paraformaldehyde and gaseous HCl at 10 °C to give chloromethyl (1R,2S,5R)-(–)-menthyl ether [10],[11]. 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).



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

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.



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

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].

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$_2$Ph-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$_5$Me$_5$) 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).

*3.2. 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 (Figure 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 atom is essentially in a planar environment, as is seen from its tiny

displacements, in both molecules A and B, from this plane (Table 1, last entry). Finally, it is noteworthy that in both molecules, the menthyl group seems to exert a significant steric footprint and is pushed away from the nickel atom, the plausible reaction site in catalysis.

Table 1. Selected bond distances (Å) and angles (°) in molecules A and B of **2b** with Esd's in parentheses.

	Molecule A	**Molecule B**
Ni–C(1)	1.896(12)	1.857(12)
Ni–Cl	2.181(4)	2.195(4)
Ni–Cp_{cent} [a]	1.780	1.763
Ni–C_{Cp} av [b]	2.146	2.133
C(1)–Ni–Cl	96.3(3)	95.4(4)
C(1)–Ni–Cp_{cent}	136.5	134.9
Cl–Ni–Cp_{cent}	127.0	129.7
(NHC)[c]–(Cl–Ni–Cp_{cent})	56.5	58.3
Ni–(C(1)–Cp_{cent}–Cl)	0.043	0.011

[a] Cp_{cent} = centroid of the Cp group. [b] Average Ni–C distance to the Cp ring. [c] (NHC) = best least-squares plane through the five-membered imidazol-2-ylidene ring.

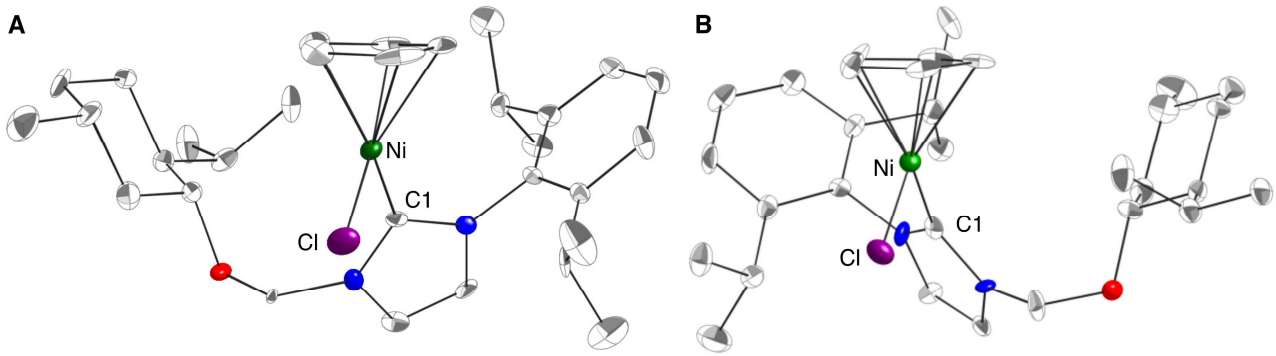
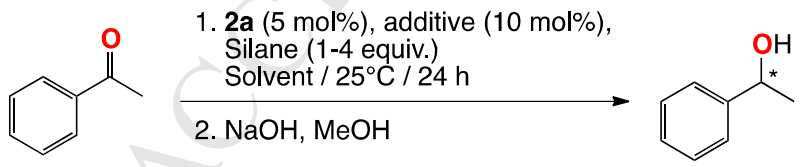


Fig. 1. Molecular structures of molecules A and B of **2b** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labeled.

3.3. Catalytic study

The high activity of the closely related [NiClCp(IMes)] complex for the hydrosilylation of aldehydes, ketones or imines at room temperature [16] prompted us to check whether complex **2a** bearing both a mesityl substituent and a (1R,2S,5R)-(–)-menthoxymethyl group could be both highly active and exert an asymmetric induction to provide entiomerically enriched reduction products (Note that [NiClCp(IPr)] proved to be a poor catalyst for this reaction [16a]). To this end, complex **2a** was used as catalyst precursor for the reduction of acetophenone with Ph_2SiH_2 as the hydrogen source, under the standard conditions established with [NiClCp(IMes)] for the reduction of ketones, *i.e.*: with a loading of 5 mol% in THF at room temperature in the presence of 10 mol% of $NaHBEt_3$ to generate the active nickel–hydride species [16]. Gratifyingly, full conversion to the corresponding alcohol was observed after 24 h reaction and a methanolysis step (Table 2, entry 1). However no chiral induction was observed by HPLC, and furthermore, replacing Ph_2SiH_2 with the milder reducing agent, PMHS, gave no improvement (Table 2, entry 2). This absence of chiral induction may be due to both the distant location of the chiral menthyl auxiliary and its orientation away from the metallic center (as shown by the X-ray structure of **2b**). Use of a directly N-bounded D-menthyl substituent in an amido-functionalized NHC-Ni catalyst was indeed recently demonstrated to induce relatively high *ee*'s in base-free Michael addition reactions [8g].

Table 2. Hydrosilylation of acetophenone catalyzed by **2a**.[a]



Entry	Additive	Silane [equiv.]	Solvent	Conv. [%] [b]	*ee* [%] [c]
1	$NaHBEt_3$	Ph_2SIH_2 (1)	THF	> 99	0
2	$LiHBEt_3$	PMHS (4)	Toluene	> 99	0

[a] *Typical procedure:* activation of **2a** with the additive was followed by the addition of acetophenone and silane, and the reaction was stirred at 25 °C for 24 h. [b] Conversions determined

by GC after methanolysis (MeOH, 2M NaOH) and extraction with Et_2O. [c] *ee* determined by HPLC after methanolysis and extraction with Et_2O.

3. Experimental

3.1. General comments

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon. Solution NMR spectra were recorded at 298 K on a FT-Bruker Ultra Shield 300 instrument operating at 300.13 MHz for ^{1}H, and at 75.47 MHz for $^{13}C\{^{1}H\}$. 2D COSY, $^{1}H/^{13}C$ HSQC and DEPT 135 ^{13}C spectra were recorded to help in the ^{1}H and ^{13}C signal assignments of all new compounds. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. GC analyses were performed with a Shimadzu GC-2014 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M×0.25 mm×0.25 mm film thickness) with N_2/air as the vector gas. The following GC conditions were used: initial temperature 80 °C, for 2 min, then rate 10 °C/min. until 220 °C and 220 °C for 15 min. HPLC analyses were performed with a Waters 1515 isocratic HLPC pump equipped with a Waters 2487 dual wavelength absorbance detector and a chiral OD-H column using *n*-hexane/*i*-propanol (98.5/1.5) as the eluent at a flow rate of 0.85 mL/min (λ = 256 nm). Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. Commercially available chemicals (Aldrich) were used as purchased. 1-(2,4,6-Trimethylphenyl)-1H-imidazole [17], 1-(2,6-diisopropylphenyl)-1H-imidazole [17], and chloromethyl (1R,2S,5R)-(–)-menthyl ether [10] were synthesized according to literature methods.

*3.2. Synthesis of 1-(2,4,6-trimethylphenyl)-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chloride (**1a**)*

1-(2,4,6-Trimethylphenyl)-1H-imidazole (0.971 g, 5.30 mmol) was dissolved in toluene (30 mL) at room temperature, and chloromethyl (1R, 2S, 5R)-(–)-menthyl ether (1.10 mL, 5.30 mmol) was drop-wise added over 15 min with rapid stirring. A whitish precipitate quickly started to appear. After 2 h, the reaction medium was filtered, and the collected solid (1.47 g) washed with toluene (2 × 15 mL), and dried under vacuum for 4 h. Concentration of the mother liquor allowed crystallization of a second crop (0.390 g), that was also collected by filtration, washed with toluene (2 × 5 mL) and dried under vacuum. The combined solids yielded **1a** as a white solid (1.86 g, 4.76 mmol, 90%). Anal. Calcd for $C_{23}H_{35}ClN_2O$: C, 70.65; H, 9.02; N, 7.16. Found: C, 70.64; H, 8.85; N, 7.37. ^{1}H NMR ($CDCl_3$): δ 11.22 (s, 1H, NC*H*N), 7.68 (t, ^3J = 1.8, 1H, C*H*N), 7.16 (t, ^3J = 1.8, 1H, C*H*N), 7.00 (s, 2H, m-*H*), 6.39 and 6.05 (AB, ^2J = 10.5, 2H, NCH_2), 3.62 (td, ^3J = 10.7, ^3J = 4.5, 1H, H1), 2.34 (s, 3H, *p*-Me), 2.17 (bd, ^3J = 11.5, 1H, H6), 2.08 (s, 6H, *o*-Me), 2.05 (m, ^3J = 7.2, ^3J = 2.4, 1H, C*H*Me$_2$), 1.63 (m, 2H, H3 and H4), 1.48 (m, 1H, H5), 1.23 (tt, ^3J = 10.9, ^3J = 3.2, 1H, H2), 0.88 (d, ^3J = 6.6, 6H, Me and CH*Me*$_2$), 0.88 (m, 3H, H3, H4 and H6), 0.63 (d, ^3J = 6.9, 3H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.4 (*ipso*-C_{Ar} or *p*-C_{Ar}), 139.1 (N*C*HN), 134.2 and 134.1 (*o*-C_{Ar}), 130.8 (*p*-C_{Ar} or *ipso*-C_{Ar}), 130.0 (*m*-C_{Ar}), 123.5 and 121.7 (N*C*H=*C*HN), 80.6 (C1), 77.8 (N*C*H$_2$), 47.9 (C2), 40.9 (C6), 34.1 (C3 or C4), 31.1 (C5), 25.7 (*C*HMe$_2$), 23.0 (C3 or C4), 22.2 (CH*Me*$_2$ or Me), 21.1 (*p*-Me), 21.0 (Me or CH*Me*$_2$), 17.7 (*o*-Me), 16.1 (CH*Me*$_2$).

*3.3. Synthesis of 1-(2,6-diisopropylphenyl)-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chloride (**1b**)*

1-(2,6-Diisopropylphenyl)-1H-imidazole (1.20 g, 5.30 mmol) was dissolved in toluene (30 mL) at room temperature, and chloromethyl (1R, 2S, 5R)-(–)-menthyl ether (1.10 mL, 5.30 mmol) was drop-wise added over 15 min with rapid stirring. A whitish precipitate quickly started to appear. After 2 h reaction, the reaction medium was filtered, and the collected solid washed with toluene (2 × 10 mL), and dried under vacuum overnight to yield **1b** as a white solid (1.56 g, 3.60 mmol, 68%). Anal. Calcd for $C_{26}H_{41}ClN_2O$: C, 72.11; H, 9.54; N, 6.47. Found: C, 71.80; H, 9.28; N, 6.64. ^{1}H

NMR ($CDCl_3$): δ 11.14 (s, 1H, NC*H*N), 7.79 (s, 1H, C*H*N), 7.54 (t, ^3J = 8.1, 1H, *p*-H), 7.31 (d, ^3J = 8.1, 2H, *m*-H), 7.16 (s, 1H, C*H*N), 6.48 and 6.13 (AB, ^2J = 10.4, 2H, NCH_2), 3.66 (td, ^3J = 10.1, ^3J = 5.0, 1H, H1), 2.30 (sept, ^3J = 7.2, 2H, *o*-C*H*Me_2), 2.21 (bd, ^3J = 12.0, 1H, H6), 2.07 (sept, ^3J = 7.2, 1.8, 1H, C*H*Me_2), 1.67 (m, 2H, H3 and H4), 1.48 (m, 1H, H5), 1.28 (tt, ^3J = 11.0, 3.0, 1H, H2), 1.27 (t, ^3J = 7.2, 6H, *o*-CH*Me*$_2$), 1.15 (d, ^3J = 7.2, 6H, *o*-CH*Me*$_2$), 0.91 (d, ^3J = 6.9, 6H, Me and CH*Me*$_2$), 0.91 (m, 3H, H3, H4 and H6), 0.68 (d, ^3J = 7.2, 3H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.3 and 145.2 (*o*-C_{Ar}), 139.3 (N*C*HN), 131.9 (*p*-C_{Ar}), 130.2 (*ipso*-C_{Ar}), 124.7 and 124.6 (*m*-C_{Ar}), 124.4 and 121.7 (N*C*H=*C*HN), 80.6 (C1), 78.0 (N*C*H_2), 47.8 (C2), 40.9 (C6), 34.1 (C3 or C4), 31.1 (C5), 28.8 and 28.7 (*o*-*C*HMe_2), 25.7 (*C*HMe_2), 24.3 and 24.2 (*o*-CH*Me*$_2$), 22.9 (C3 or C4), 22.2 (CH*Me*$_2$ or Me), 21.0 (Me or CH*Me*$_2$), 15.9 (CH*Me*$_2$).

*3.4. Synthesis of [Ni(Mes-NHC-CH_2OMent)ClCp] (**2a**)*

Nickelocene (496 mg, 2.65 mmol) and 1-(2,4,6-trimethylphenyl)-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chloride **1a** (1.04 g, 2.65 mmol) were refluxed in DME (30 mL) for 1 h. The resulting red solution was cooled to room temperature, and the solvent removed *in vacuo*. The residue was extracted with THF (30 mL), and the extract was filtered through Celite, which was rinsed with THF (3 × 15 mL). The collected red solution was then concentrated under vacuum to give a red oil, which was re-dissolved in CH_2Cl_2 (3 mL), passed through a neural silica chromatography column (15 × 3 cm), and eluted with dichloromethane. The eluted red solution was concentrated to an oil that was triturated with *n*-pentane to afford **2a** as a red solid that was washed with *n*-pentane and dried under vacuum (796 mg, 1.50 mmol, 58%). Anal. Calcd for $C_{28}H_{39}ClN_2NiO$: C, 65.46; H, 7.65; N, 5.45. Found: C, 65.53; H, 7.61; N, 5.50. ^1H NMR ($CDCl_3$): δ 7.40 (d, 1H, C*H*N), 7.10 and 7.06 (2s, 2H, *m*-H), 6.86 (d, 1H, C*H*N), 6.67 and 6.20 (2 br., 2 × 1H, NC*H*$_2$), 4.73 (s, 5H, Cp), 3.69 (td, ^3J = 10.4, ^3J = 3.8, 1H, H1), 2.43 (s, 3H, *p*-Me), 2.33 (br., 1H, H6), 2.21 (m, 1H, C*H*Me_2), 2.20 (br. s, 3H, *o*-Me), 2.08 (br. s, 3H, *o*-Me), 1.69 (m, 2H, H3 and H4), 1.45 (m, 1H, H5), 1.35 (tt, ^3J = 10.5, 2.5, 1H, H2), 0.96 (m, 3H, H3, H4 and H6), 0.96 (d, ^3J =

6.6, 3H, CH*Me*$_2$), 0.93 (d, ^3J = 6.6, 3H, Me), 0.65 (d, ^3J = 6.6, 3H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.5 (N*C*N), 139.4 (*ipso*-C_{Ar} or *p*-C_{Ar}), 136.7 (*p*-C_{Ar} or *ipso*-C_{Ar}), 136.3 and 135.7 (*o*-C_{Ar}), 129.4 and 129.2 (*m*-C_{Ar}), 124.1 and 122.8 (NC*H*=*C*HN), 91.8 (Cp), 79.7 (N*C*H$_2$), 78.3 (C1), 48.2 (C2), 41.0 (C6), 34.4 (C3 or C4), 31.8 (C5), 25.6 (*C*HMe$_2$), 23.3 (C3 or C4), 22.4 (CH*Me*$_2$), 21.3 (*p*-Me), 21.1 (Me), 18.6 and 18.3 (*o*-Me), 16.1 (CH*Me*$_2$).

*3.5. Synthesis of [Ni(iPr$_2$Ph-NHC-CH$_2$OMent)ClCp] (**2b**)*

Nickelocene (300 mg, 1.59 mmol) and 1-(2,6-diisopropylphenyl)-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chloride **1b** (0.717 g, 1.66 mmol) were refluxed in DME (30 mL) for 1.5 h. The resulting red solution was cooled to room temperature, and the solvent removed *in vacuo*. The residue was extracted with THF (30 mL), and the extract was filtered through Celite, which was rinsed with THF until the washings were colorless. The collected red solution was then concentrated under vacuum to give a red oil, which was re-dissolved in CH_2Cl_2 (5 mL), passed through a neural silica chromatography column (15 × 3 cm), and eluted with dichloromethane. The eluted red solution was concentrated to a sticky solid that was triturated with *n*-pentane (3 mL) to afford **2b** as a red solid that was washed with pentane (3 × 5 mL) and dried under vacuum (474 mg, 0.853 mmol, 54%). Anal. Calcd for $C_{31}H_{45}ClN_2NiO$: C, 66.98; H, 8.16; N, 5.04. Found: C, 67.31; H, 8.25; N, 5.07. ^{1}H NMR ($CDCl_3$): δ 7.57 (t, ^3J = 7.7, 1H, *p*-H), 7.44 (d, ^3J = 6.7, 1H, *m*-H), 7.41 (d, ^3J = 1.8, 1H, NC*H*), 7.35 (d, ^3J = 6.7, 1H, *m*-H), 6.91 (d, ^3J = 1.8, 1H, NC*H*), 6.85 and 6.15 (2 vbr., 2 × 1H, NC*H*$_2$), 4.70 (s, 5H, Cp), 3.60 (br. t, 1H, H1), 2.86 (vbr., 1H, *o*-C*H*Me$_2$), 2.45 (vbr., 2H, *o*-C*H*Me$_2$ and H6), 2.21 (br. sept, 1H, C*H*Me$_2$), 1.71 (m, 2H, H3 and H4), 1.45 (br. d, 3H, Me or CH*Me*$_2$), 1.37 (m, 2H, H5 and H2), 1.28 (br.d, 3H, CH*Me*$_2$ or Me), 1.03 (t, ^3J = 6.9, 6H, *o*-CH*Me*$_2$), 1.03 (m, 3H, H3, H4 and H6), 0.94 (d, ^3J = 7.0, 6H, *o*-CH*Me*$_2$), 0.63 (br. d, 3H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.5 (N*C*N), 147.1 and 146.3 (*o*-C_{Ar}), 136.2 (*ipso*-C_{Ar}), 130.3 (*p*-C_{Ar}), 125.6 (N*C*H), 124.3 and 123.8 (*m*-C_{Ar}), 122.2 (N*C*H), 91.6 (Cp), 79.5 (N*C*H$_2$), 77.2 (C1), 48.0 (C2), 40.8 (C6), 34.3 (C3 or C4), 31.8 (C5), 28.3 and 28.1 (*o*-*C*HMe$_2$), 26.2 and 26.1 (*o*-CH*Me*$_2$),

25.4 (*C*HMe$_2$), 23.2 (C3 or C4), 22.7 and 22.5 (CH*Me*$_2$ and Me), 22.3 (*o*-CH*Me*$_2$), 21.0 (*o*-CH*Me*$_2$), 15.7 (CH*Me*$_2$).

3.6. Catalytic study: hydrosilylation of acetophenone

General procedure: A 10 mL oven dried Schlenk tube containing a stirring bar was loaded with **2a** (13.5 mg, 0.0262 mmol) and THF or toluene (4 mL). The resulting red solution was stirred for 5 min. A solution of 1.0 M NaHBEt$_3$ or LiHBEt$_3$ in THF (0.0524 mmol) was added dropwise, and the solution was stirred until the colour turned dark red. Acetophenone (61 µL, 0.524 mmol) and the silane (1-4 equiv.) were then added, in this order, and the reaction mixture was stirred in a preheated oil bath at 25 °C for 24 h. The reaction mixture was then quenched by the addition of methanol (2 mL) and 2M NaOH (2 mL) and stirred for 2 h. After the addition of water (5 mL), the product was extracted with diethylether (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The conversion was determined by GC, and the enantiomeric excess by HPLC.

3.7. Crystallographic studies

Single crystals of **2b** suitable for an X-ray analysis were grown by slow evaporation of an *n*-pentane solution of **2b**. The crystals were covered with polyfluoroether oil and a single crystal was mounted on a nylon loop. The data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker APEX II CCD diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS [18]. The structure was solved and refined using direct methods with SIR2004 [19] using WINGX-Version 1.80.01 [20] and SHELXL [21] systems of programs. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Molecular diagrams were drawn with

CrystalMaker 7.0.4 for Mac OS X. Distances and angles measurements involving the Cp centroid were obtained using Olex2 [22]. Data collection and structure refinement parameters, and crystallographic data are collected in Table 3.

Table 3. Crystal data and refinement details of compound **2b**.

Compound	**2b**
Molecular formula	$C_{31}H_{45}ClN_2NiO$
Formula weight	555.85
Crystal system	Triclinic
Data collection temperature (K)	150(2)
Crystal size (mm)	$0.40 \times 0.20 \times 0.10$
Crystal form, color	Prism, orange
Space group	*P*1
a (Å)	10.0250(8)
b (Å)	12.6160(12)
c (Å)	13.3170(12)
α (°)	66.416(3)
β (°)	78.758(3)
γ (°)	72.365(3)
V (Å3)	1465.8(2)
Z	2
*D*calc (g cm^{-3})	1.259
μ (mm^{-1})	0.778
Reflections collected	15601
Independent reflections, R_{int}	8078, 0.0323

No. of data with I > 2σ(I)	7031
R1, wR2 with I > 2σ(I)	0.0665, 0.1819
Goodness-of-fit (GOF) on F^2	1.115
Flack's param.	0.07(3)

4. Conclusion

A couple of inexpensive (1R,2S,5R)-(–)-menthoxymethyl-*N*-functionalized nickel(NHC) complexes **2a,b** were effectively synthesized and characterized. The *N*-mesityl derivative **2a** was used as pre-catalyst for the hydrosilylation of acetophenone at room temperature. Though it efficiently catalyzed its reduction to the corresponding alcohol after methanolysis, no chiral induction was observed. The dangling chiral D-menthyl auxiliary is at a distant location and is orientated away from the nickel center and we suggest these two factors as the possible causes for this absence of chiral induction.

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Dedication

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

Appendix A. Supplementary data

CCDC 1442853 contains the supplementary crystallographic data for compound **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article (NMR spectra of **1a**, **1b**, **2a** and **2b**) can be found, in the online version, at http://dx.doi.org/10.1016/j.jorganchem.201X.XX.XXX.

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Highlights

- Chiral Cp-Ni(NHC) complexes bearing menthoxymethyl arms are readily accessible from inexpensive D-menthol.
- One complex has been structurally characterized.
- The complexes are effective catalysts for the hydrosilylation of ketones.
- No chiral induction was observed.