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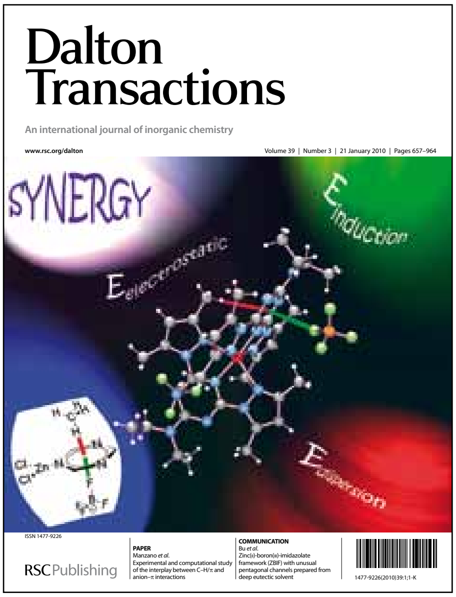
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Dehydrogenative Coupling of Aromatic Thiols with Et_3SiH Catalysed by N-Heterocyclic Carbene Nickel Complexes

Lorena Postigo, Rita Lopes, and Beatriz Royo[*]

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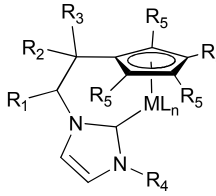
A series of new tetramethylcyclopentadienyl-functionalised N-heterocyclic carbene ligands with different wingtip substituents have been prepared and characterised. These ligands have been successfully coordinated to nickel affording complexes of the general type (Cp*-NHC^R)NiX (X = Cl, I). These well-defined nickel complexes selectively catalysed the coupling of aromatic thiols with Et_3SiH to give the corresponding silylthioethers ($RSSiEt_3$). The nickel complexes bearing ethyl, *iso*-butyl, and *n*-butyl wingtips displayed comparable catalytic efficiency, while the nickel complex bearing a methyl substituent on the wingtip resulted to be the worst performing catalyst.

Introduction

N-Heterocyclic carbene ligands (NHCs) have become one of the most popular ligands in organometallic chemistry and catalysis.[1,2] The easy access to NHCs and their potential application in a large number of catalytic processes, has led to a rapid development in the design of a wide variety of NHC-containing architectures.[3]

During the last few years, our research group in collaboration with Peris and co-workers have developed a new class of bidentate cyclopentadienyl ligands tethered to N-heterocyclic carbenes (NHCs) (**A**, Scheme 1).[4-12] Related indenyl-functionalised NHCs were described by Danopoulos,[13-16] Wang[17] and others.[18] An important feature of these Cp-NHC chelating ligands is the possibility of independently vary their stuctural components, namely the cyclopentadienyl ring, the spacer, and the imidazolium ring in order to fine tuning the steric and electronic properties of ligand. The introduction of chelating NHC ligands to the coordination sphere of a metal catalyst have interesting consequences in terms of enhancement of thermal stability and rigidity. In addition, the introduction of chirality elements in this system may assist in controlling the stereochemistry of reactions taking place at the metal center. The versatile coordination chemistry of these new ligands to a variety of metals ranging from early to late transition metals is also an interesting feature that we are exploring in our group.[10] So far, we have demonstrated the applicability of complexes of general type **A** to a variety of catalytic applications such as hydrogen transfer,[4,8] hydrosilylation,[8,11,12] epoxidation,[6] amination of alcohols with primary amines,[4] β-alkylation of secondary alcohols,[4,5] and isomerisation of allylic alcohols.[7] We showed that the introduction of different substituents on the cyclopentadienyl ring have a direct implication in catalysis.[6] Moreover, the introduction of a chiral center in the Cp-NHC tether have provided an easy access to chiral metal complexes.[7,9]



A

Scheme 1 Functionalised-cyclopentadienyl N-heterocyclic carbenes

One of the structural parameters that can be modified to tune the stereoelectronic properties of the Cp-NHC ligand is the N-subsituent of the imidazolium ring. In this work, we have prepared a new series of bidentate Cp-NHC ligands containing different substituents in the wingtip (R_4) of the imidazolium ring with the aim to investigate the consequences that smooth modifications may have in catalysis. As a part of our ongoing research into the development of new catalytic applications of nickel complexes containing the fragment "(Cp*-NHC)Ni",[12] we decided to prepare a series of (Cp*-NHC^R)NiI (R = ^{i}Bu, ^{n}Bu, Et, Me) complexes and apply them as catalysts for the dehydrogenative coupling of thiols with silanes.

Results and discussion

Compound **1** was prepared following the procedure previously described by us.[4] Alkylation of **1** with the appropriate alkyl halide in THF at 50 °C affords the corresponding imidazolium pro-ligands **2a-2e** with an overall yield of 70-87% (Scheme 2). Compounds **2** are obtained as a mixture of tautomers resulting from the different position of the double bonds in the cyclopentadienyl ring. Alkylation of **1** was limited to primary alkyl halides as secondary and tertiary alkyls gave unwanted elimination reactions. This is a general limitation for the synthesis of unsymmetrical substituted NHCs.[3a]

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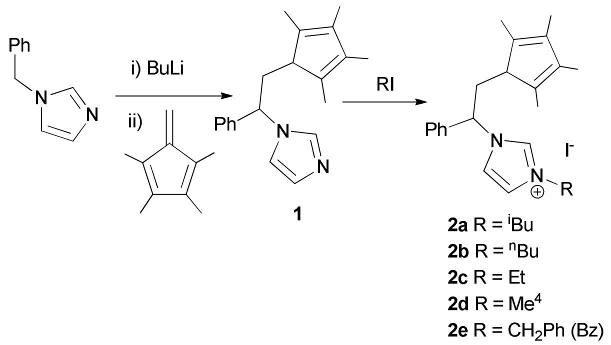
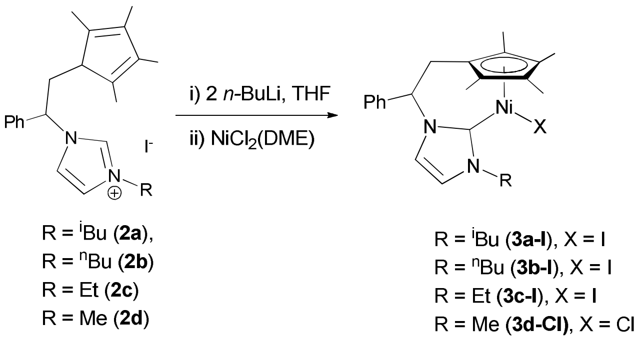


Scheme 2 Synthesis of proligands **2a**-**2e**

Proligands **2a**, **2b** and **2c** were coordinated to nickel following a similar method to that described for the synthesis of (Cp*-NHC^{Me})NiCl (**3d-Cl**) (Scheme 3), recently reported by us.[12] Treatment of **2a**-**2c** with two equivalents of *n*-BuLi generated *in situ* the corresponding (Cp*-NHC^{R})Li (R = ^{i}Bu, ^{n}Bu, Et) lithium salts, which were subsequently reacted with NiCl$_2$(DME) (DME = dimethoxyethane) to afford the novel complexes (Cp*-NHC^{R})NiI [R = ^{i}Bu (**3a-I**), ^{n}Bu (**3b-I**), Et (**3c-I**)] in good yields (Scheme 3). All **3a-I**-**3c-I** complexes were isolated as crystalline red solids. The identity of all compounds was established by analytical and spectroscopic methods. The ^{1}H NMR spectra of **3a-I, 3b-I** and **3c-I** show the signals due to the non-equivalent protons of the methyl substituents of the cyclopentadienyl ring at δ 2.02, 1.93, 1.70 and 1.08 for **3a-I** (similar set of signals are displayed for **3b-I** and **3c-I**) confirming that coordination of the cyclopentadienyl ring has occurred. Their ^{13}C NMR spectra provide a direct evidence of metalation as seen by the signal at δ 174 (for complexes **3a-I**, **3b-I** and **3c-I**), assigned to the Ni-C_{Carbene}, which is in the region of the previously reported (Cp*-NHC^{Me})NiCl (**3d-Cl**) complex (δ 176),[12] and other half-sandwich Ni-NHC complexes described in the literature.[19] Elemental analysis indicated that the corresponding iodide complexes **3a-I**-**3c-I** were formed. The formation of the iodides **3a-I**-**3c-I** instead of the corresponding chlorides was unexpected because similar reaction of proligand **2d** with NiCl$_2$(DME) afforded the chloride complex (Cp*-NHC^{Me})NiCl (**3d-Cl**) instead of the corresponding iodide.[12] However, this halide exchange has been already observed by us in the coordination reaction of proligand **2d** to other transition metals.[6] The iodide complex (Cp*-NHC^{Me})NiI (**3d-I**) was obtained by treating **3d-Cl** with KI in THF under reflux for several hours.

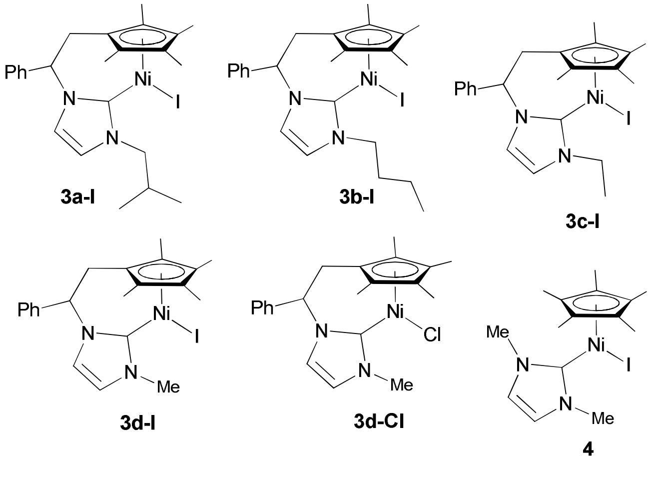
Attempts to coordinate proligand **2e** to nickel failed. The reaction of proligand **2e** with two equivalents of BuLi did not afford the expected imidazolium salt as a pure sample. A mixture of undentified compounds was obtained, probably as a consequence of deprotonation of CH$_2$ protons of the benzyl wingtip, revealing that **2e** is not tolerant to a strong base such as BuLi.



Scheme 3 Synthesis of nickel complexes **3a-I**-**3c-I**. Complex **3d-Cl** has been already published by us.[12]

With these nickel complexes in our hands, we decided to investigate the catalytic efficiency of complexes **3a-I**-**3d-I** (Scheme 4) in the dehydrogenative coupling of thiols (RSH) with triethylsilane (Et$_3$SiH). This reaction represents a useful catalytic process for the preparation of thiosilanes (RSSiEt$_3$).[20] To date, the are only very few reported examples of metal complexes catalysing the coupling of thiols with silanes.[21-23] In 2011, Nakazawa described the unprecedented dehydrogenative coupling of thiol with silanes catalysed by an iron complex, the half-sandwich CpFe(CO)$_2$Me.[24] In view of these results, we became interested in exploring the reactivity of our half-sandwich Ni-NHC complexes in this reaction.

The catalytic activity of complexes **3a-I**-**3d-I** (Scheme 4) was explored using thiophenol (PhSH) as a model substrate with Et$_3$SiH. The reaction was carried out in toluene at 80ºC over 18 h, in the presence of 1 mol% of catalyst, and using a Et$_3$SiH: substrate ratio of 4:1.



Scheme 4 Nickel complexes investigated as catalysts for the dehydrogenative coupling of thiols with Et$_3$SiH

As shown in Table 1, the nickel complexes **3a-I**-**3d-I** catalysed the dehydrogenation of thiophenol affording the corresponding silylthioether (PhSSiEt$_3$) in good yields. The reaction was selective to the formation of the silylthioether; no homo-dehydrogenative coupling products such as disulfide or disilane were detected in the reaction. No coupling was observed in the absence of catalyst. The catalytic activity of

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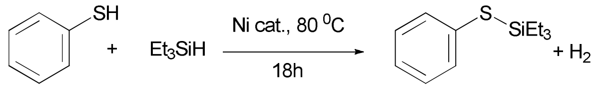
complexes **3a-I**, **3b-I**, and **3c-I** containing the ^{i}Bu, ^{n}Bu, and Et wingtips displayed similar catalytic activities, achieving good yields of the corresponding $PhSSiEt_3$ after 18 h at 80 °C (Table 1, entries 1-3). In contrast, the nickel complex **3d-I** containing the methyl group in the wingtip, resulted to be less active, affording 45 % yield of the corresponding silylthioether under similar reaction conditions.

Table 1. Dehydrogenative coupling of PhSH with Et_3SiH catalysed by **3a-I-3d-I**, **3d-Cl**, and **4**[a]



Entry	Catalyst	%Yield[b]	TON[c]
1	**3a-I**	84	84
2	**3b-I**	81	81
3	**3c-I**	82	82
4	**3d-I**	45	45
5	**3d-Cl**	42	42
6	**4**	62	62

[a]All reactions were carried out with 1.0 mmol of PhSH and 4 mmol of Et_3SiH using 1 mol% of catalyst in toluene at 80°C for 18h. [b]Yield determined by ${}^{1}H$ NMR spectroscopy using Ph_2CH_2 (0.5 mmol) as internal standard. [c]TON (turnover number) calculated from mol product/mol catalyst.

In order to investigate the effect of linking the cyclopentadienyl ring to the NHC in the catalytic performance, the catalytic activity of the related non-linked $Cp^*Ni(NHC^{Me})I$[19a] (**4**) was determined using similar reaction conditions (in toluene at 80 ºC, 18 h). Complex **4** displayed moderate catalytic activity (62% yield, Table 1, entry 6), slighlty higher than that obtained by **3d-I** (45% yield). Additionally, the chloride complex $(Cp^*\text{-}NHC^{Me})NiCl$ (**3d-Cl**) was applied as catalyst under similar conditions to check the influence of the halide in the performance of the catalyst. As shown in Table 1, entries 4 and 5, no influence of the halide was observed.

Under similar reaction conditions, the catalyst loading of complex **3a-I** could be lowered to 0.1 mol % achieving turnover numbers of 650 (Table 2, entry 4), showing better catalytic performance than the previously reported iron complex $CpFe(CO)_2Me$ (TON 5.8 after 24 h in toluene at 80 ºC and using 1:10 PhSH:Et_3SiH ratio).[24]

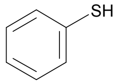
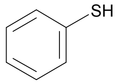
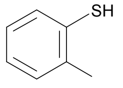
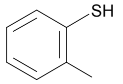
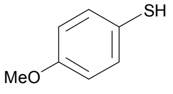
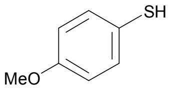
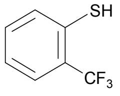
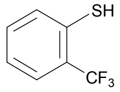
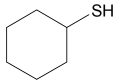
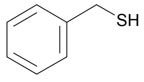
Table 2. Dehydrogenative coupling of PhSH with Et_3SiH catalysed by $(Cp^*\text{-}NHC^{iBu})NiI$ (**3a-I**).[a]

Entry	%mol cat.	%Yield[b]	TON[c]
1	1	84	84
2	0.5	80	160
3	0.25	78	312
4	0.1	65	650

[a]All reactions were carried out with 1.0 mmol of PhSH and 4 mmol of Et_3SiH in toluene at 80ºC for 18h. [b]Yield determined by ${}^{1}H$ NMR spectroscopy using Ph_2CH_2 (0.5 mmol) as internal standard. [c]TON (turnover number) calculated from mol product/mol catalyst.

The catalytic scope was evaluated with catalysts **3a-I** and **3b-I** using different aromatic thiols (Table 3). Thiophenol derivatives containing functional groups such as methyl (Table 3, entries 3 and 4) and methoxy (Table 3, entries 5 and 6) were well tolerated for both **3a-I** and **3b-I** catalysts. A detrimental in the yield was observed for the coupling of 2-(trifluoromethyl)benzenethiol with silane, showing that thiols having electron-withdrawing groups display lower yields than those containing electron-donating groups (Table 3, entries 7 and 8). Low yields were obtained in the coupling of cyclohexanethiol (26%) and benzyl mercaptan (14%) (Table 3, entries 9 and 10). Similar findings were reported for the iron catalyst $CpFe(CO)_2Me$.[24]

Table 3. Dehydrogenative coupling of thiols with Et_3SiH catalysed by $(Cp^*\text{-}NHC^{R})NiI$ (R = ^{i}Bu (**3a-I**), ^{n}Bu (**3b-I**)).[a]

Entry	Substrate	Catalyst	%Yield[b]
1		**3a-I**	84
2		**3b-I**	81
3		**3a**-I	80
4		**3b-I**	75
5		**3a**-I	73
6		**3b-I**	96
7		**3a**-I	60
8		**3b-I**	38
9		**3a-I**	26
10		**3a-I**	14

[a]All reactions were carried out with 1.0 mmol of PhSH and 4 mmol of Et_3SiH using 1 mol% of catalyst in toluene at 80°C for 18h. [b]Yield determined by ${}^{1}H$ NMR spectroscopy using Ph_2CH_2 (0.5

mmol) as internal standard.

Conclusions

In summary, we have described the preparation of new bidentate Cp*-NHC$^{\mathrm{R}}$ ligands and their coordination to nickel. A series of (Cp*-NHC$^{\mathrm{R}}$)NiX (X = Cl, I) complexes bearing different substituents on the wingtip have been applied as catalysts for the dehydrogenative coupling of aromatic thiols with $\mathrm{Et_3SiH}$. Interestingly, nickel complexes bearing ethyl, *iso*-butyl and *n*-butyl wingtips displayed comparable catalytic activity, while the nickel complex containing the methyl substituent on the wingtip resulted to be the worst performing catalyst. This is the first report of well-defined nickel(II) complexes catalysing the coupling of thiols with $\mathrm{Et_3SiH}$.

Experimental Section

Materials and methods

Compounds **1**,[4] **3d-Cl**[12] and **4**[19a] were synthesised according to the methods described in the literature. All other reagents were used as received from commercial suppliers without further purification. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and solvents were purified from appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Avance III 400 MHz. Assigment of resonances was made from HSQC and HMBC experiments. Electrospray mass spectra (ESIMS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulising gas.A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electr-spray interface (Micromass, Manchester, UK) was used for high-resolution mass spectrometry (HRMS). The drying gas as well as nebulizing gas nitrogen at a flow of 400 and 80 L/h, respectively. Elemental analyses were performed in our laboratories at ITQB.

Synthesis of Cp*-NHC$^{\mathbf{iBu}}$I, 2a. 1-Iodo-2-methylpropane (1mL, 8.54 mmol) was added to a solution of **1** (0.56 g, 1.19 mmol) in 10 mL of THF. The mixture was stirred at 50ºC for 3 days. All volatiles were removed under vacuum to afford a yellow solid which was washed several times with ethyl ether and hexane to yield compound **2a** as a yellow solid. Yield: 0.56 g (70%). ^{1}H-NMR ($\mathrm{CDCl_3}$): 10.68, 10.55, 10.49, 10.26, 10.20, 10.16 (s, N=C*H*-N), 7.66-7.01 (m, $\mathrm{C}H_{\mathrm{Ph}}$, $\mathrm{C}H_{\mathrm{Imid}}$), 5.97-5.73 (m, $\mathrm{C}H_{\mathrm{linker}}$), 4.23-4.00 (m, $\mathrm{C}H_{2\mathrm{linker}}$, $\mathrm{C}H_{2\mathrm{iBu}}$)), 3.46- 2.98 (m, $\mathrm{C}H_{2\mathrm{linker}}$, $\mathrm{C}H_{2\mathrm{iBu}}$), 2.15 (m, $\mathrm{C}H_{\mathrm{Cp*}}$, $\mathrm{C}H_{\mathrm{iBu}}$), 1.82-1.76 ($\mathrm{C}_5Me_4$), 1.05-0.84 ($\mathrm{C}_5Me_4$, ^{i}Bu). ^{13}C{^{1}H}-NMR ($\mathrm{CDCl_3}$): 140.0 (N=*C*H-N), 131.3-128.1 ($C\mathrm{H}_{\mathrm{Ph}}$, $C\mathrm{H}_{\mathrm{Imid}}$), 63.9 ($C\mathrm{H}_{\mathrm{linker}}$) 57.2 ($C\mathrm{H}_{2\mathrm{linker}}$, $C\mathrm{H}_{2\mathrm{iBu}}$), 49.0 (*C*H, ^{i}Bu), 31.6 ($C\mathrm{H}_{2\mathrm{linker}}$, $C\mathrm{H}_{2\mathrm{iBu}}$), 29.7-29.6 ($C\mathrm{H}_{\mathrm{Cp*}}$, $C\mathrm{H}_{\mathrm{iBu}}$), 19.5-10.8 ($\mathrm{C}_5Me_4$, ^{i}Bu). Anal. Calc for $\mathrm{C_{24}H_{33}N_2I}$ (476.44): C, 60.50; H, 6.98; N, 5.88. Found: C, 60.70; H, 6.97; N, 5.81. HRMS (ESI-TOF): *m/z* $[\mathrm{M\text{-}I}]^+$ calcd for $\mathrm{C_{24}H_{33}N_2}$, 349.2644; found: 349.2642 $[\mathrm{M\text{-}I}]^+$.

Synthesis of Cp*-NHC$^{\mathbf{nBu}}$I, 2b. A procedure similar to that used for the preparation of **2a** was applied by using iodobutane (0.98 mL, 8.54 mmol) and **1** (0.50 g, 1.70 mmol) Yield: 0.69g (86%). ^{1}H-NMR ($\mathrm{CDCl_3}$): 10.55, 10.43, 10.17, 10.12, 10.08, 9.62, 9.58 (s, N=C*H*-N), 7.80-7.01 ($\mathrm{C}H_{\mathrm{Ph}}$, $\mathrm{C}H_{\mathrm{Imid}}$), 5.90-5.57 ($\mathrm{C}H_{\mathrm{linker}}$), 4.37-3.99 (m, $\mathrm{C}H_{2nBu}$), 3.43-2.98 (m, $\mathrm{C}H_{2\mathrm{linker}}$, $\mathrm{C}H_{2\mathrm{iBu}}$, $\mathrm{C}H_{\mathrm{Cp*}}$), 1.80-0.88 ($\mathrm{C}_5Me_4$, ^{n}Bu). ^{13}C{^{1}H}-NMR ($\mathrm{CDCl_3}$): 135.2 (N=*C*H-N), 131.0-120.3 ($C\mathrm{H}_{Ph}$, $C\mathrm{H}_{\mathrm{Imid}}$), 64.5-62.1 ($C\mathrm{H}_{\mathrm{linker}}$) 51.8-48.9 ($C\mathrm{H}_{\mathrm{Cp*}}$), 49.9-49.7 ($C\mathrm{H}_{2\mathrm{linker}}$, $C\mathrm{H}_{2\mathrm{nBu}}$), 32.3-31.7 ($C\mathrm{H}_{2\mathrm{linker}}$, $C\mathrm{H}_{2\mathrm{nBu}}$), 14.7-10.8 ($\mathrm{C}_5Me_4$, ^{n}Bu). Anal. Calc for $\mathrm{C_{24}H_{33}N_2I}$ (476.44): C, 60.50; H, 6.98; N, 5.88. Found: C, 60.35; H, 6.72; N, 5.54. MS (ESI-TOF): *m/z* $[\mathrm{M\text{-}I}]^+$ calcd for $\mathrm{C_{24}H_{33}N_2}$, 349; found: 349 $[\mathrm{M\text{-}I}]^+$.

Synthesis of Cp*-NHC$^{\mathbf{Et}}$I, 2c. A procedure similar to that used for the preparation of **2a** was applied by using iodoethane (0.55 mL, 6.84 mmol) and **1** (0.40 g, 1.36 mmol). Yield: 0.42 g (70%). ^{1}H NMR ($\mathrm{CDCl_3}$): 10.47, 10.40, 10.06, 10.03, 9.43 (s, N=C*H*-N), 7.75-7.01 ($\mathrm{C}H_{\mathrm{Ph}}$, $\mathrm{C}H_{\mathrm{Imid}}$), 5.83-5.53 (m, $\mathrm{C}H_{\mathrm{linker}}$), 4.43-4.10 (m, $\mathrm{C}H_{2\mathrm{Et}}$), 3.47- 2.29 (m, $\mathrm{C}H_{2\mathrm{linker}}$, $\mathrm{C}H_{\mathrm{Cp*}}$), 1.81-0.83 ($\mathrm{C}_5Me_4$, *Et*). ^{13}C{^{1}H}-NMR ($\mathrm{CDCl_3}$): 140.0 (N=*C*H-N), 131.0-119.5 ($C\mathrm{H}_{\mathrm{Ph}}$, $C\mathrm{H}_{\mathrm{Imid}}$), 69.4-64.0 ($C\mathrm{H}_{\mathrm{linker}}$) 57.2-49.1 ($C\mathrm{H}_{\mathrm{Cp*}}$), 45.6-45.4 ($C\mathrm{H}_{2\mathrm{Et}}$), 32.6-31.4 ($C\mathrm{H}_{2\mathrm{linker}}$), 15.7-11.5 ($\mathrm{C}_5Me_4$, *Et*). Anal. Calc for $\mathrm{C_{22}H_{29}N_2I}$ (448.38): C, 58.93; H, 6.51; N, 6.24. Found: C, 58.61; H, 6.24; N, 5.86.

Synthesis of Cp*-NHC$^{\mathbf{Bz}}$I, 2d. A procedure similar to that used for the preparation of **2a** was applied by using benzylbromide (1.05 mL, 8.85 mmol), NaI (1.32 g, 8.85 mmol) and **1** (0.52 g, 1.77 mmol). Yield: 0.77 g (86%). ^{1}H NMR ($\mathrm{CDCl_3}$): 10.50, 10.50, 10.37, 10.05, 10.02, 9,81 (s, N=C*H*-N), 7.63-6.92 ($\mathrm{C}H_{\mathrm{Ph}}$, $\mathrm{C}H_{\mathrm{Imid}}$), 5.74-5.40 ($\mathrm{C}H_{\mathrm{linker}}$, $\mathrm{C}H_{2\mathrm{Bz}}$), 3.46-2.20 (m, $\mathrm{C}H_{2linker}$, $\mathrm{C}H_{\mathrm{Cp*}}$), 1.82-0.81 ($\mathrm{C}_5Me_4$). ^{13}C{^{1}H}-NMR ($\mathrm{CDCl_3}$): 136.4 (N=*C*H-N), 133.2-120.2 ($C\mathrm{H}_{Ph}$, $C\mathrm{H}_{\mathrm{Imid}}$), 64.5 ($C\mathrm{H}_{\mathrm{linker}}$), 53.8-51.8 ($C\mathrm{H}_{2\mathrm{Bz}}$), 49.0 ($C\mathrm{H}_{\mathrm{Cp*}}$), 31.8-31.4 ($\mathrm{C}H_{2linker}$), 15.2-10.9 ($\mathrm{C}_5Me_4$). Anal. Calc for $\mathrm{C_{27}H_{31}N_2I}$ (510.15): C, 63.53; H, 6.12; N, 5.49. Found: C, 63.20; H, 5.84; N, 5.25. MS (ESI-TOF): (*m/z*) $[\mathrm{M\text{-}I}]^+$ calcd for $\mathrm{C_{27}H_{31}N_2}$ 383; found: 383 $[\mathrm{M\text{-}I}]^+$.

Synthesis of (Cp*-NHC$^{\mathbf{iBu}}$)NiI, 3a-I. Two equivalents of *n*-BuLi (0.86 mL, 1.36 mmol) were added to a solution of **2a** (0.30 g, 0.62 mmol) in THF (10 mL) at -60ºC. The mixture was stirred for 1 h at room temperature, and a suspension of $\mathrm{NiCl_2(DME)}$ (0.14 g, 0.62 mmol) in THF (5 mL) was added at once. The reaction mixture was then stirred overnight at room temperature. The solvent was removed under vacuum, and the remaining solid was extracted in a mixture of toluene/hexane (15 mL/5 mL), yielding **3** as a red crystalline solid. Yield: 0.20 g (74%). ^{1}H-NMR ($\mathrm{C_6D_6}$): 7.07-6.90 (m, 5 H, $\mathrm{C}H_{\mathrm{Ph}}$), 6.05 (s, 1 H, $\mathrm{C}H_{\mathrm{Imid}}$), 5.85 (s, 1 H, $\mathrm{C}H_{\mathrm{Imid}}$), 5.19 (dd, J^{3} = 8.84, 5.60 , 1 H, $\mathrm{C}H_{\mathrm{linker}}$), 5.08 (dd, 1 H, ^{i}Bu, ^{2}J = 13 Hz, ^{3}J = 6 Hz), 3.59 (dd, 1 H, ^{i}Bu, ^{2}J = 13 Hz, ^{3}J = 6 Hz), 2.90 (m, 1 H, ^{i}Bu), 2.02 (s, 3 H, C_5Me_4), 2.12 (m, 2 H, $\mathrm{C}H_{2linker}$) 1.93 (s, 3 H, C_5Me_4), 1.70 (s, 3 H, C_5Me_4), 1.08 (s, 3 H, C_5Me_4), 0.99 (d, 3 H, ^{3}J = 7.2 Hz, ^{i}Bu), 0.80 (d, 3 H, ^{3}J = 7.2 Hz, ^{i}Bu). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$): 174.5 (Ni-C_{Carbene}), 137.9 ($C_{i\mathrm{Ph}}$),

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130.8 (CH_{Ph}), 129.5 (CH_{Ph}), 128.4 (CH_{Ph}), 126.1 (CH_{Ph}), 122.9 (CH_{Imid}), 119.7 (CH_{Imid}), 105.1 (C_5Me_4), 104.4 (C_5Me_4), 102.8 (C_5Me_4), 101.2 (C_5Me_4), 89.1 (C_5Me_4), 66.6 (CH_{linker}), 60.1 (CH_2, ^iBu), 30.2 ($CH_{2linker}$), 30.1 (CH, ^iBu), 20.1 (Me, ^iBu), 20.0 (Me, ^iBu), 12.4 (C_5Me_4), 10.7 (C_5Me_4), 10.6 (C_5Me_4), 10.0 (C_5Me_4). Anal. Calc for $C_{24}H_{31}N_2NiI$ (533.11): C, 54.07; H, 5.86; N, 5.25. Found: C, 53.80; H, 5.52; N, 4.86. HRMS (ESI-TOF): *m/z* $[M-I]^+$ calcd for $C_{24}H_{31}N_2Ni$, 405.1841; found: 405.1841 $[M-I]^+$.

Synthesis of (Cp*-NHC^{nBu})NiI, 3b-I. A procedure similar to that used for the preparation of **3a-I** was applied by using proligand **2b** (0.30 g, 0.62 mmol), *n*-BuLi (0.86 mL, 1.36 mmol), and $NiCl_2(DME)$ (0.14 g, 0.62 mmol). Yield: 0.21 g (78%). ^1H-NMR (C_6D_6): 7.17-6.94 (m, 5 H, CH_{Ph}), 6.05 (s, 1 H, CH_{Imid}), 5.85 (s, 1 H, CH_{Imid}), 5.19 (m, 1 H, CH_{linker}), 5.08 (m, 1 H, *Bu*), 4.04 (m, 1 H, *Bu*), 2.02 (s, 3 H, C_5Me_4), 2.01 (m, 2 H, $CH_{2linker}$), 1.97 (s, 3 H, C_5Me_4), 1.90 (m, 2H, *Bu*), 1.70 (s, 3 H, C_5Me_4), 1.08 (s, 3 H, C_5Me_4), 1.29 (q, 2 H, *Bu*), 0.97 (m, 3 H, *Bu*). $^{13}C\{^1H\}$-NMR (C_6D_6): 174.3 (Ni-$C_{Carbene}$), 137.9 (C_{iPh}), 129.8 (CH_{Ph}), 128.35 (CH_{Ph}), 127.2 (CH_{Ph}), 121.9 (CH_{Imid}), 120.2 (CH_{Imid}), 104.9 (C_5Me_4), 104.4 (C_5Me_4), 102.7 (C_5Me_4), 100.8 (C_5Me_4), 89.2 (C_5Me_4), 66.7 (CH_{linker}), 52.7 (CH_2, *Bu*), 33.5 ($CH_{2linker}$), 30.2 (CH, *Bu*), 19.7 (Me, *Bu*), 12.4 (Me, *Bu*), 11.9 (C_5Me_4), 11.3 (C_5Me_4), 11.1 (C_5Me_4), 10.7 (C_5Me_4). Anal. Calc for $C_{24}H_{31}N_2NiI\cdot C_7H_8$ (625.25): C, 59.55; H, 6.29; N, 4.48. Found: C, 59.30; H, 6.27; N, 4.88. HRMS (ESI-TOF): *m/z* $[M-I]^+$ calcd for $C_{24}H_{31}N_2Ni$, 405.1841; found: 405.1836 $[M-I]^+$.

Synthesis of (Cp*-NHC^{Et})NiI, 3c-I. A procedure similar to that used for the preparation of **3a-I** was applied by using proligand **2c** (0.20 g, 0.44 mmol), *n*-BuLi (0.63 mL, 0.98 mmol), and $NiCl_2(DME)$ (0.10 g, 0.44 mmol). Yield: 0.15 g (72%). ^1H-NMR (C_6D_6): 7.08-6.88 (m, 5 H, CH_{Ph}), 6.97 (s, 1 H, CH_{Imid}), 5.82 (s, 1 H, CH_{Imid}), 5.22 (dd, 1 H, $^3J = 10.6$ Hz, $^3J = 3.5$ Hz, CH_{linker}), 4.85 (sex, 1 H,CH_2^{Et}), 4.17 (sex, 1 H,CH_2^{Et}), 2.10 (m, 2 H, $CH_{2linker}$), 2.07 (s, 3 H, C_5Me_4), 1.99 (s, 3 H, C_5Me_4), 1.73 (s, 3 H, C_5Me_4), 1.30 (t, 3 H, Me^{Et}), 1.05 (s, 3 H, C_5Me_4). $^{13}C\{^1H\}$-NMR (C_6D_6): 174.5 (Ni-$C_{Carbene}$), 137.7 (C_{iPh}), 129.8 (CH_{Ph}), 129.1 (CH_{Ph}), 128.9 (CH_{Ph}), 128.5 (CH_{Ph}), 121.0 (CH_{Imid}), 120.4 (CH_{Imid}), 105.0 (C_5Me_4), 104.5 (C_5Me_4), 102.8 (C_5Me_4), 100.2 (C_5Me_4), 89.3 (C_5Me_4), 66.3 (CH_{linker}), 47.8 (CH_2, *Et*), 30.2 ($CH_{2linker}$), 16.4 (*Me*, *Et*), 12.4 (C_5Me_4), 11.1 (C_5Me_4), 10.7 (C_5Me_4), 9.9 (C_5Me_4). Anal. Calc for $C_{22}H_{27}N_2NiI$ (505.05): C, 52.31; H, 5.39; N, 5.55. Found: C, 51.97; H, 5.08; N, 5.16.

Synthesis of (Cp*-NHC^{Me})NiI, 3d-I. Complex **3d-Cl** (0.15 g, 0.37 mmol) was treated with KI (0.31 g, 1.88 mmol) and the mixture refluxed in THF (15 mL) mixture for 16 h. After cooling, all volatiles were removed in vacuum and the remaining solid was extracted in a mixture of toluene/hexane (10 mL/5 mL), yielding **3d-I** as a red solid. Yield: 0.12 g (65%).^1H-NMR (C_6D_6): 7.09-6.87 (m, 5 H, CH_{Ph}), 5.91 (d, 1 H, $^3J = 1.8$ Hz, CH_{Imid}), 5.79 (d, 1 H, $^3J = 1.8$ Hz, CH_{Imid}), 5.22 (dd, 1 H, $^3J = 10.8$ Hz, $^3J = 3.3$ Hz, CH_{linker}), 3.80 (s, 3 H, NMe), 2.07-2.05 (m, 2 H, $CH_{2linker}$), 2.06 (s, 3 H, C_5Me_4), 2.00 (s, 3 H, C_5Me_4), 1.73 (s, 3 H, C_5Me_4), 1.04 (s, 3 H, C_5Me_4). $^{13}C\{^1H\}$-NMR (C_6D_6): 176.1 (Ni-$C_{Carbene}$), 137.7 (C_{iPh}), 129.0 (CH_{Ph}), 128.9 (CH_{Ph}), 128.3 (CH_{Ph}), 122.4 (CH_{Imid}), 120.2 (CH_{Imid}), 104.8 (C_5Me_4), 104.5 (C_5Me_4), 103.1 (C_5Me_4), 100.0 (C_5Me_4), 89.0 (C_5Me_4), 66.8 (CH_{linker}), 40.9 (NMe), 30.3 ($CH_{2linker}$), 12.4 (C_5Me_4), 10.8 (C_5Me_4), 10.6 (C_5Me_4), 9.7 (C_5Me_4). Anal. Calc for $C_{21}H_{25}N_2NiI\cdot C_7H_8$ (582.10): C, 57.67; H, 5.70; N, 4.80. Found: C, 57.60; H, 5.52; N, 5.15.

Catalytic dehydrogenative coupling of thiols with Et_3SiH. Toluene (0.5 mL), (Cp*-NHC^R)NiX (1 mol%), thiol (1 mmol), Et_3SiH (4 mmol), and Ph_2CH_2 (0.5 mmol) used as internal standard, were charged in a vial. The vial was tight closed under nitrogen, and the solution was heated at 80ºC for 18 h. All volatiles were then removed under vacuum, and the residue was dissolved in $CDCl_3$. The amount of the corresponding triethylsilylthioether formed was determined by ^1H NMR by the relative intensity of signals of the product and the Ph_2CH_2 used as internal standard. The triethylsilylthioether produced was identified by comparison of the NMR spectra with reported data.[21e,24]

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Notes and references

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† Electronic Supplementary Information (ESI) available: NMR and HRMS spectra of coumpounds.

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Dehydrogenative Coupling of Aromatic Thiols with Et$_3$SiH catalysed by N-Heterocyclic Carbene Nickel Complexes

A series of well-defined nickel(II) complexes, (Cp*-NHC^{R})NiX (R = ^{i}Bu, ^{n}Bu, Et, Me; X = I, Cl), effciently catalysed the selective dehydrogenative coupling of thiols with Et$_3$SiH affording the corresponding silylthioethers in good yields.

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