N-Heterocyclic Carbene Complexes of Nickel as Efficient Catalysts for Hydrosilylation of Carbonyl Derivatives

Lorena Postigo\textsuperscript{a} and Beatriz Royo\textsuperscript{a,\textordfonna}

\textsuperscript{a} Instituto de Tecnología Química e Biológica, Universidade Nova de Lisboa, Avenida da República, EAN, 2780-157 Oeiras, Portugal

Fax: (+351)-21-441-1277; e-mail: broyo@itqb.unl.pt

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Abstract: Well-defined nickel(II) complexes bearing bidentate tetramethylcyclopentadienyl-functionalised N-heterocyclic carbene ligands (Cp*-NHCMe)NiX (X = Cl, O-t-Bu) have been prepared and applied as efficient catalysts for the hydrosilylation of carbonyl groups. The nickel-alkoxide (Cp*-NHCMe)Ni(O-t-Bu) complex displayed remarkable catalytic activity in the reduction of aldehydes, affording quantitative conversion to the corresponding alcohols in 5 min at 25°C. Mechanistic studies, based on stoichiometric reactions, revealed that the transient nickel hydride (Cp*-NHCMe)NiH complex is the active species in the hydrosilylation of carbonyls.

Keywords: cyclopentadienyl groups; hydrosilylation; N-heterocyclic carbenes; nickel

The reduction of carbonyl functionalities via hydrosilylation processes is an essential transformation in organic synthesis.\textsuperscript{[1]} To date, most of the catalytic systems developed for the reduction of carbonyl groups are based on expensive precious metals such as palladium, rhodium, iridium, and ruthenium.\textsuperscript{[2]} In recent years, replacing noble metal catalysts by readily available, inexpensive first-row transition metals has become an increasingly important area of research in homogeneous catalysis. A perspective article describing the mechanistic aspects of the reduction of carbonyl groups mediated by first-row transition metal complexes has recently been published by Guan and co-workers.\textsuperscript{[3]}

Recently, we described the catalytic activity of a series of piano-stool iron(II) complexes bearing bidentate cyclopentadienyl-functionalised N-heterocyclic carbene (NHC) ligands in the reduction of carbonyl groups and sulfoxides.\textsuperscript{[4–5]} As part of our ongoing research on cyclopentadienyl-functionalised NHCs,\textsuperscript{[6–10]} we became interested in preparing the corresponding nickel complexes containing the fragment “(Cp-NHC)Ni” and exploring their potential application as catalysts for selective reductions.

Half-sandwich nickel complexes containing NHCs have been recently prepared by Chetcuti and co-workers.\textsuperscript{[11]} They described the catalytic efficiency of neutral and cationic cyclopentadienyl derivative of nickel-NHC complexes in Suzuki coupling of aryl halides,\textsuperscript{[12]} and the unprecedented C–C bond activation of a labile acetonitrile ligand on a nickel center, showing the potential of nickel in transition metal-catalysed C–C bond functionalisation.\textsuperscript{[13–17]}

In the last decade, nickel-NHC complexes have been shown to catalyse a vast number of organic transformations,\textsuperscript{[18]} including C–C cross coupling reactions,\textsuperscript{[19]} amination and dehalogenation of aryl halides,\textsuperscript{[20]} oxidation of secondary alcohols,\textsuperscript{[21]} activation of C–F bonds,\textsuperscript{[22]} and hydrosilylation of internal alkynes.\textsuperscript{[23]}

However, no reports are found in the literature regarding the catalytic activity of Ni-NHC complexes in the reduction of carbonyl groups.

The hydrosilylation of carbonyl groups mediated by well-defined Ni(II) complexes is poorly developed,\textsuperscript{[24]} In 2009, Guan and co-workers described a series of nickel PCP-pincer hydride complexes catalysing the hydrosilylation of ketones and aldehydes.\textsuperscript{[25]} In the same year, the catalytic hydrosilylation of ketones via a transient Ni–H complex supported by a monoanionic bidentate amidophosphine ligand was reported by Mindiola and co-workers.\textsuperscript{[26]}

Herein, we describe the first example of a well-defined Ni-NHC complex catalysing the hydrosilylation of aldehydes and ketones. We report the synthesis of the novel Ni complexes bearing the tetramethylcyclopentadienyl-functionalised NHC ligand (Cp*-NHCMe)NiX [Cp*=η\textsubscript{5}-C\textsubscript{5}Me\textsubscript{5}; X = Cl (2), O-t-Bu (3)].
and their catalytic activity in the hydrosilylation of aldehydes and ketones. Reactivity studies of complex 3 with silanes showed the formation of the nickel complexes \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{NiH} \) and \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{Ni} \), with the Ni-hydride being the active catalytic species in the hydrosilylation reaction.

Following the synthetic route previously reported by our group, the tetramethylcyclopentadienyl-functionalised imidazolium proligand \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{I} \) (1) was easily synthesised.\(^6\) Proligand 1 was coordinated to nickel following the synthetic procedure depicted in Scheme 1. Treatment of 1 with two equivalents of BuLi generated the corresponding lithium salt, which was subsequently reacted with NiCl\(_2\) (DME) (DME = dimethoxyethane) to afford \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{NiCl} \) (2) in high yield. Complex 2 was isolated as a crystalline red solid, and characterised by analytical and spectroscopic methods. Its \(^1\)H NMR showed the two doublets due to the protons of the imidazolylidene ligand at \(\delta = 5.91\) and 5.79, and the four distinctive signals at \(\delta = 2.06, 2.00, 1.73, \) and 1.05 of the non-equivalent methyl groups at the cyclopentadienyl ring, as a consequence of the asymmetry of the ligand. The \(^{13}\)C NMR spectrum confirms that coordination of both the NHC and the Cp ring has occurred. The signal at \(\delta = 176\), indicative of a Ni-C\(_{\text{Cyclopentadiene}}\), is in the region of previously reported Ni-NHC complexes \((\delta = 170–180)\).\(^{11–17}\) Unfortunately, we have been unable to obtain X-ray quality crystals of 2. The proposed monomeric structure for 2 is consistent with the X-ray structural analysis of related indenyl-functionalised N-heterocyclic carbenes of Ni(I)\(^27\) and non-linked cyclopentadienyls of Ni-NHC\(^{11}\) that revealed their monomeric composition in the solid state.

We investigated the catalytic activity of 2 in the hydrosilylation of aldehydes using phenylsilane as a reducing agent and 4-trifluoromethylbenzaldehyde as a model substrate (silane:substrate ratio 1:2:1) in the presence of 2 mol% of catalyst. The reaction was carried out at 50°C in toluene over 3.5 h to afford quantitative conversion of the aldehyde to a mixture of the corresponding silylated ether (4-trifluoromethylbenzoyl)silane, and the alcohol (4-trifluoromethylphenol). Subsequent treatment of the mixture with p-toluene sulfonic acid afforded the corresponding alcohol as the only isolated product (Table 1, entry 1). When the reaction was carried out at room temperature, longer reaction times were required to achieve quantitative conversions (72 h in toluene, and 24 h in THF, Table 1, entries 2 and 3, respectively).

The Ni-NHC complex 2 showed good performance under mild conditions (50°C) affording quantitative conversion to the corresponding alcohol in a few hours. To the best of our knowledge, this is the first report of a well-defined Ni-NHC complex catalysing the hydrosilylation of carbonyl functionalities. Remarkably, the addition of base is not needed for this reaction.

Recently, Mindiola and co-workers proposed the formation of a putative nickel alkoxide intermediate in the hydrosilylation of carbonyl functionalities.\(^{26}\) Moreover, copper-NHC alkoxides have been shown to catalyse the hydrosilylation of carbonyl groups with silanes.\(^{28}\) Based on these results, we decided to attempt the synthesis of a nickel alkoxide bearing the \((\text{Cp}^*\text{-NHC}^{\text{Me}})\) ligand, and explore its catalytic applicability in the hydrosilylation reaction. Treatment of 2 with one equivalent of KO-t-Bu in THF at room temperature afforded the corresponding alkoxide complex \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{Ni(O-t-Bu)} \) (3), which was isolated as a brown solid in good yield (55%) (Scheme 2). The

### Table 1. Hydrosilylation of 4-trifluoromethylbenzaldehyde with PhSiH\(_3\) catalysed by \((\text{Cp}^*\text{-NHC}^{\text{Me}})\text{NiCl} \)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>(T(°C))</th>
<th>(t) [h]</th>
<th>Conv(^{b}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>50</td>
<td>3.5</td>
<td>&gt;99 (95)</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>25</td>
<td>72</td>
<td>&gt;99 (94)</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>25</td>
<td>24</td>
<td>&gt;99 (94)</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out with 1.0 mmol of 4-trifluoromethylbenzaldehyde and 1.2 mmol of PhSiH\(_3\) using 2 mol% of catalyst.

\(^b\) Conversion determined by \(^1\)H NMR spectroscopy.

\(^c\) Isolated yield of the corresponding alcohol after treatment with p-toluene sulfonic acid.
identity of 3 was established by elemental analysis and NMR spectroscopy. Complex 3 resulted to be rather stable in solid state, being stored under a nitrogen atmosphere for weeks without noticeable decomposition.

We tested the catalytic activity of 3 in the hydrosilylation of 4-trifluoromethylbenzaldehyde with PhSiH₃. The nickel alkoxide 3 was a very active catalyst, affording quantitative conversion to the corresponding alcohol in 5 min at 25°C in THF or toluene.

**Table 2. Hydrosilylation of 4-trifluoromethylbenzaldehyde with silanes catalysed by the Ni-alkoxide 3.[a]**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Silane</th>
<th>Solvent</th>
<th>t</th>
<th>Conv.[b] (Yield [%][c])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhSiH₃</td>
<td>toluene</td>
<td>5 min</td>
<td>&gt;99 (95)</td>
</tr>
<tr>
<td>2</td>
<td>PhSiH₃</td>
<td>THF</td>
<td>5 min</td>
<td>&gt;99 (95)</td>
</tr>
<tr>
<td>3</td>
<td>PhSiH₂</td>
<td>THF</td>
<td>24 h</td>
<td>95 (90)</td>
</tr>
<tr>
<td>4</td>
<td>Et₃SiH</td>
<td>THF</td>
<td>24 h</td>
<td>80 (73)</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1.0 mmol of 4-trifluoromethylbenzaldehyde and 1.2 mmol of silane using 2 mol% of catalyst.

[b] Conversion determined by ¹H NMR spectroscopy.

[c] Isolated yield of the corresponding alcohol after treatment with p-toluenesulfonic acid.

(Table 2, entries 1 and 2, respectively). The catalyst loading could be lowered to 0.5 mol% (Table 3, entries 1, 2 and 3) without appreciable deterioration of the effectiveness of the catalyst, achieving turnover frequencies of 2304 h⁻¹.

An investigation of the role of different hydrogen sources revealed phenylsilane as the best hydrogen source. Under similar reaction conditions, other silanes such as diphenylsilane and triethylsilane were substantially less effective, and longer reaction times (24 h) were required to achieve quantitative conversion to the corresponding alcohols (Table 2, entries 3 and 4).

In order to investigate the scope of the hydrosilylation of aldehydes catalysed by 3 with phenylsilane, a variety of aldehydes bearing different functional groups were examined. As shown in Table 3, the high efficiency of 3 (reactions are carried out at 25°C) afforded quantitative conversions in 5 min but was suitable for a wide scope of aromatic aldehyde substrates. Benzaldehyde derivatives containing functional groups such as nitro (Table 3, entry 4), cyano (Table 3, entry 5), bromo (Table 3, entry 6) and acyl (Table 3, entry 7) were well tolerated. Aldehydes bearing electron-withdrawing groups were more reactive than aldehydes containing electron-donating substituents such as the ester functionality (Table 3, entry 7). Hexanal was also efficiently reduced under similar reaction conditions.

We also extended our study to the reduction of ketones. Using 4-CF₃-acetophene as substrate under the reaction conditions previously stated for the reduction of aldehydes, no reaction was observed. Heating at 100°C in toluene in the presence of 2 mol% of catalyst 3 and 1.2 equiv. of phenylsilane, afforded quantitative conversion to the corresponding alcohol in 5.5 h. Under these optimised conditions, aromatic and aliphatic, both cyclic and acyclic, ketones were reduced in good to moderate yields (conversions of 50–99%, Table 4, entries 1–8). As an exception, p-nitrobenzophenone was reduced giving only a 25% yield of the corresponding alcohol (Table 4, entry 5).

In order to get an insight into the mechanism of this reaction, the stoichiometric reaction of complex 3 with 0.3 equivalents of phenylsilane was monitored by ¹H NMR spectroscopy. The reaction was performed in a J Young valve NMR tube. Phenylsilane was added to a solution of 3 in deuterated benzene at room temperature. The formation of a Ni-hydride species was
formed in an NMR tube and monitored by NMR spectroscopy. The reaction of a simple labeling experiment which allows to easily distinguish between the conventional hydride mechanism (based on carbonyl insertion into the Ni-hydride bond) or the non-hydride mechanism. In order to check if the mechanism involved with our Ni system implies the insertion of the carbonyl group into the nickel-hydride bond, we performed the stoichiometric reaction of PhCHO with deuterated diphenylsilane Ph₃SiD₂ and A (1:1:1) in C₆D₆. We used.

### Table 4. Hydrosilylation of ketones catalysed by 3[^a][^b]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>t [h]</th>
<th>Conv.[^c] (Yield [%])[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>5.5</td>
<td>95 (90)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>&gt;99 (96)[^e]</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>24</td>
<td>85 (79)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>24</td>
<td>85 (77)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>24</td>
<td>30[^f] (25)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>24</td>
<td>&gt;99 (94)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>24</td>
<td>50 (46)</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>24</td>
<td>50 (43)</td>
</tr>
</tbody>
</table>

[^a]: All reactions were carried out with 1.0 mmol of substrate and 1.2 mmol of PhSiH₃ using 2 mol% of catalyst in toluene at 100°C.
[^b]: Conversion determined by ¹H NMR spectroscopy.
[^c]: Isolated yield after treatment with p-toluenesulfonic acid.
[^d]: Reaction carried out in CD₃CN.
[^e]: Reaction carried out in CD₃CN.

**Scheme 3.** Stoichiometric reactions of (Cp*-NHC⁶⁶⁶⁶⁶⁶)Ni(O-t-Bu) (3) with PhSiH₃ and 4-trifluoromethylbenzaldehyde performed in an NMR tube.
commercially available Ph₂SiD₂ since it is able to perform the catalytic reaction in the presence of A (Table 2, entry 3), and Ph₂SiD₂ does not undergo fast H/D exchange with the nickel hydride A. We observed an immediate formation of PhCHD-SiDPh₂ while the Ni–H complex A remained unchanged, ruling out the conventional hydride mechanism. Similar labelling experiments supported a non-hydride mechanism for the hydrosilylation reaction catalysed by an Fe–H complex recently reported by Guan.[33]

We have developed an efficient Ni-NHC-catalysed hydrosilylation of aldehydes and ketones. This represents the first example using Ni-NHC complexes as catalysts. The Ni-alkoxide (Cp*-NHC²⁶)Ni(O-t-Bu) displayed high catalytic activity in the reduction of aldehydes, affording quantitative conversions to the corresponding alcohols in 5 min at 25 °C (TOF up to 2304 h⁻¹). The high activity and excellent tolerance to functional groups are remarkable features of this catalytic system. Stoichiometric reactions of (Cp*-NHC²⁶)Ni(O-t-Bu) with PhSiH₃ allowed us to characterise by NMR spectroscopic means the intermediate catalytically active Ni-hydride (Cp*-NHC²⁶)NiH species. Isotopic labelling experiments indicate that the hydride ligand does not directly participate in the reduction reaction.[33]

**Experimental Section**

**Hydrosilylation of Aldehydes and Ketones**

A typical procedure was performed as follows. A dried J. Young tube equipped with a Teflon screw cap was flushed with nitrogen and charged with catalyst (1 mol% for aldehydes and 2 mol% for ketones) in 0.5 mL of the corresponding solvent. Then, neat silane (1.20 mmol) and the corresponding carbonyl compound (1.0 mmol) were added. The reaction was completed, the mixture was treated with 1 mL of a 1% solution of p-toluenesulphonic acid in MeOH for 12 h. The solvent was removed under vacuum and the alcohol was extracted in diethyl ether (5 mL). This solution was filtered through silica and the filtrate was concentrated under vacuum to yield the corresponding alcohol.[34] Reaction times and temperatures are indicated in Table 1, Table 2, Table 3, and Table 4. See the Supporting Information for further details as well as for the synthesis of the nickel complexes.

**Acknowledgements**

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[33] We were informed by the editorial office after acceptance of this manuscript that similar work had been submitted to the journal by another group. Both manuscripts were refereed independently and accepted after revision. See: L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais, V. Ritleng, *Adv. Synth. Catal.* **2012**, 354, 2619–2624.