O-Functionalised NHC Ligands for Efficient Nickel-catalysed C–O Hydrosilylation

Simone Bertini and Martin Albrecht*

Abstract: A series of C,O-bidentate chelating mesoionic carbene nickel(i) complexes [Ni(NHC\(^{\text{PhO}}\)] (NHC = imidazolylidene or triazolylidene) were applied for hydrosilylation of carbonyl groups. The catalytic system is selective towards aldehyde reduction and tolerant to electron-donating and -withdrawing group substituents. Stoichiometric experiments in the presence of different silanes lend support to a metal–ligand cooperative activation of the Si–H bond. Catalytic performance of the nickel complexes is dependent on the triazolylidene substituents. Butyl-substituted triazolylidene ligands impart turnover numbers up to 7,400 and turnover frequencies of almost 30,000 h\(^{-1}\), identifying this complex as one of the best-performing nickel catalysts for hydrosilylation and demonstrating the outstanding potential of O-functionalised NHC ligands in combination with first-row transition metals.

Keywords: NHC ligands · Nickel catalysis

Simone Bertini received his BSc and MSc in Chemistry from the University of Rome Tor Vergata. In 2016 he moved to Switzerland for his doctoral studies in the group of Prof. Albrecht, where he earned his PhD as an early stage researcher (ESR) for the Marie Sklodowska-Curie Initial Training Network Non-Noble Metal Catalysis (NoNoMeCat). His research focus is the synthesis, characterisation and catalytic applications of first-row transition metal complexes bearing strong donor ligands such as (mesoionic) N-heterocyclic carbenes.

Martin Albrecht studied Chemistry in Bern and graduated with Gerard van Koten at Utrecht University (NL) in 2000. After postdoctoral work with Bob Crabtree at Yale and with Ciba SC (Basel), he started independent research as an Alfred Werner Assistant Professor in Fribourg, then joined the faculty at University College Dublin and returned in 2015 to his alma mater. His research revolves around ligand-induced control and expansion of the reactivity of metal centres, particularly for catalytic applications. He is fascinated by new ligand classes such as mesoionic N-heterocyclic carbenes, and recently also by their N-donor analogues.

1. Introduction

The use of chelating ligands has become an established methodology for the development of homogeneous catalysts with long lifetime.\(^{[1]}\) This concept has also been implemented to N-heterocyclic carbene (NHC) complexes, which is facilitated by the synthetic versatility and easy accessibility of NHC scaffolds.\(^{[2]}\) Introduction of chelating sites has been successfully employed to tailor properties of the metal centre such as coordination geometry, electron density, and stability of the metal–carbon bond. Among the countless possibilities for NHC functionalisation, a popular approach constitutes the implementation of N-donor groups.\(^{[3]}\) Less common is the introduction of O-donor sites,\(^{[4]}\) despite the attractiveness of this type of donors for selected applications. For example, oxygen sites are fundamental for hydrogen bonding.\(^{[5]}\) In addition, this functionalisation is key for stabilising typically oxophilic first-row transition metals for catalytic applications, one of the major challenges for developing sustainable catalysts based on Earth-abundant metals.\(^{[6]}\) In the absence of chelating stabilization, the M–C\(_{\text{NHC}}\) bond is generally unstable and limits the catalytic application. This instability was demonstrated to be a key issue for the application of triazolylidene-based mesoionic NHC nickel complexes in Suzuki-cross coupling, which takes place with high initial turnover frequencies but rapidly stalls due to Ni–C bond cleavage and ensuing catalyst degradation.\(^{[7]}\) We have therefore become interested in enhancing the stability of these complexes by ligand functionalisation and have developed a new class of O-donor substituted NHC ligands based on the imidazole,\(^{[8]}\) as well as the triazole scaffold. Nickelation under mild conditions afforded the bis-carbene nickel(ii) complexes 1a–c, 2 (Fig. 1).\(^{[9]}\) Here, these complexes were investigated as precursors for the catalytic hydrosilylation of carbonyl groups, providing one of the fastest and most robust nickel-based catalytic systems known to date.\(^{[10,11]}\)

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Fig. 1. Oxygen-functionalized NHC nickel(ii) complexes.
2. Results and Discussion

Hydrosilylation with complexes 1a–c and 2 was initially probed at a 2 mol% catalyst loading using 4-methylbenzaldehyde as model substrate and phenylsilane as hydrosilylation agent. The reaction proceeded to completion with complex 1b in 1,2-dichloroethane, affording 4-methylbenzylsiloxysilane in 99% within 30 h (entry 1, Table 1). Since hydrosilylation with PhSiH₃ afforded mixtures of products, this mixture was subsequently treated with methanolic NaOH (1 M) for 16 h to generate the corresponding alcohol. Analysis of this alcohol provided the actual product yield for each reaction. Increasing the temperature to 40 °C resulted in considerably enhanced activity, affording the product quantitatively in 30 min (entry 2). Replacing phenylsilane by diphenylsilane or triethylsilane under otherwise identical conditions gave only very slow or negligible substrate conversion (entries 3 and 4). Changing the solvent from dichloroethane to THF considerably lowered the catalytic performance (entry 5), whereas conducting the reaction in dichloromethane affected the reaction only slightly (entry 6). A blank experiment under the same conditions but in the absence of the nickel catalyst revealed no detectable activity even over extended reaction time (entry 7), thus confirming the catalytic role of the nickel species.

Table 1. Hydrosilylation of 4-methylbenzaldehyde with complex 1b. *

| entry | solvent | silane | T [°C] | time [min] | conv [%] b | yield [%] c |
|-------|---------|--------|-------|-----------|------------|------------|
| 1     | C₂H₅Cl₂ | PhSiH₃ | 25    | 1,800     | 99         | 97         |
| 2     | C₂H₅Cl₂ | PhSiH₃ | 40    | 30        | 99         | 96         |
| 3     | C₂H₅Cl₂ | Ph₃SiH | 40    | 60        | <1         | <1         |
| 4     | C₂H₅Cl₂ | Et₃SiH | 40    | 60        | <1         | <1         |
| 5     | THF     | PhSiH₃ | 40    | 60        | 73         | 68         |
| 6     | CH₂Cl₂  | PhSiH₃ | 40    | 60        | 84         | 76         |
| 7     | C₂H₅Cl₂ | PhSiH₃ | 40    | 60        | <1         | <1         |

*Reactions were carried out with 4-Me-benzaldehyde (0.5 mmol), PhSiH₃ (0.6 mmol) and Ni complex (2 mol%) in 1,2-dichloroethane (0.4 mL) with C₆Me₆ (0.05 mmol) as internal standard at 40 °C; reaction temperature probed at a 2 mol% catalyst loading using 4-methylbenzaldehyde as model substrate and phenylsilane as hydrosilylation agent. The reaction proceeded to completion with complex 1b in 1,2-dichloroethane, affording 4-methylbenzylsiloxysilane in 99% within 30 h (entry 1, Table 1). Since hydrosilylation with PhSiH₃ afforded mixtures of products, this mixture was subsequently treated with methanolic NaOH (1 M) for 16 h to generate the corresponding alcohol. Analysis of this alcohol provided the actual product yield for each reaction. Increasing the temperature to 40 °C resulted in considerably enhanced activity, affording the product quantitatively in 30 min (entry 2). Replacing phenylsilane by diphenylsilane or triethylsilane under otherwise identical conditions gave only very slow or negligible substrate conversion (entries 3 and 4). Changing the solvent from dichloroethane to THF considerably lowered the catalytic performance (entry 5), whereas conducting the reaction in dichloromethane affected the reaction only slightly (entry 6). A blank experiment under the same conditions but in the absence of the nickel catalyst revealed no detectable activity even over extended reaction time (entry 7), thus confirming the catalytic role of the nickel species.

Based on these results, the activity of catalysts 1a–c and 2 were compared with the model substrate 4-methylbenzaldehyde under the best conditions (phenylsilane, dichloroethane, 40 °C). All complexes reached full conversion in less than 3 h (Table 2, Fig. 2) and show similar time-conversion profiles with high reaction rates with 80–90% conversions. Different C4 substituents on the triazolylidene complexes affected the activity of the metal complexes and the activity is consistent with the electron density on the metal centre as imparted by the ligand, with triazolylidene complexes and the activity is consistent with the electron density on the triazolylidene complexes affected the activity of the metal complexes. We note that the complex configuration has no obvious relevance and both the trans configured complex 1c as well as the cis isomers (1a,b) show catalytic performance that is in line with wingtip substituent effects only. The relatively low activity of complex 2 indicates that the nickel complexes containing mesoionic ligands outperform the imidazolylidene analogue. Perfoeming the reaction in the presence of simple nickel chloride as precatalyst did not lead to any detectable conversion (entry 5), suggesting an essential role of the carbene ligand for enabling catalytic activity.

Table 2. Hydrosilylation of 4-methylbenzaldehyde with complexes 1a-c, 2.

| entry | [Ni] | time [min] | conv [%] | yield [%] | k [h⁻¹] |
|-------|------|------------|----------|-----------|---------|
| 1     | 1a   | 120        | 98       | 94        | 2.4     |
| 2     | 1b   | 30         | 99       | 96        | 6.6     |
| 3     | 1c   | 60         | 98       | 94        | 3.6     |
| 4     | 2    | 180        | 98       | 95        | 1.2     |
| 5     | NiCl₂ | 360         | <1       | <1        |        |

Reactions were carried out with benzaldehyde (0.5 mmol), PhSiH₃ (0.6 mmol) and Ni complex (2 mol%) in 1,2-dichloroethane (0.4 mL) with C₆Me₆ (0.05 mmol) as internal standard at 40 °C; conversion determined by 1H NMR spectroscopy; yield determined by 1H NMR spectroscopy after treatment with NaOH (1 M) in MeOH.

2.1 Substrate Scope

The scope of this catalytic hydrosilylation system was investigated by using the most active nickel complex, 1b, and a variety of functionalised benzaldehydes. These studies revealed a high tolerance of the nickel catalyst towards various functional groups including halides, ethers, and amines (Fig. 3, Table 3). Electron-rich benzaldehydes with substituents such as −NMe₂, −OMe, and −Me, as well as electron-poor ones with substituents such as −F, −Br, and −CF₃, are converted completely within 7–180 min (entries 1–7).
Comparison of the reaction rates as TOF$_{50}$ values with the Hammett parameter $\sigma_p$ shows an inverse correlation, with a lower Hammett parameter inducing faster turnover (Fig. 4). The correlation is satisfactory ($R^2 = 0.98$) and the considerable slope suggests a strong influence of the substituent’s electronic properties on the reaction rate, which provides a rationale also for the very low conversion at this low loading implies turnover numbers as high as 5,000, and maximum turnover frequencies of 27,000 h$^{-1}$ (entry 4). Successively decreasing of the precatalyst to 0.02 mol% does not compromise the yield of the reaction (entries 5–10). Full conversion at this low loading implies turnover numbers as high as 5,000, and maximum turnover frequencies of 27,000 h$^{-1}$ (entry 4). When the loading of complex 1b was lowered even further to 0.01 mol%, conversions were incomplete even when the reaction was run for extended periods of time, yet these conditions allowed to determine the maximum turnover number TON = 7,400 (60 min, 63%; entry 11). In the absence of nickel complex 1b no conversion was detected also at these slightly elevated temperatures (entry 12).

The TOF$_{50}$ values accomplished with complex 1b are higher than other known nickel-based hydrosilylation catalyst with$^{[10]}$ or without a NHC ligand.$^{[11,12]}$ and similar to those of the best-performing iron complexes$^{[13]}$ yet about two-times lower when compared to the best-performing manganese-based catalyst.$^{[14]}$ The high catalytic performance of 1b in terms of turnover numbers and frequencies suggests a marked influence imparted by chelation of the triazolylidene ligand when bound to nickel. Its key role is confirmed when comparing complex 3 as the best nickel catalyst reported so far with the Ni-O(NHC) system 1b (Fig. 5). Under the same catalytic conditions, the O-chelated nickel complex 1b outperforms the N-chelated system 3 and reaches higher TON (7,400 vs 5,500) and higher TOF$_{50}$ values (27,000 vs 23,000 h$^{-1}$).$^{[10]}$

### 2.2 Stoichiometric Experiments

In order to better understand the observed activities of catalyst 1b and more generally the potential role of oxygen chelation during hydrosilylation, a set of stoichiometric experiments was performed. Adding a slight excess (1.2 equiv) of phenylsilane to complex 1b in a CD$_2$Cl$_2$ solution containing SiMe$_3$ as an internal standard resulted in an immediate change in colour of the solution and different sets of new signals appeared in the $^1$H NMR spectrum, suggesting the formation of new species. The resonances of complex 1b disappeared and no triazolium salt formation was detected, while two singlets appeared in the hydride region at $\delta$$_H$ = -7.19 and -8.21 ppm in a 1:1 relative ratio and accounting for turnover numbers and frequencies of hydrosilylation using 4-anisaldehyde as the substrate. When using 2 mol% of the catalyst precursor 1b, the reaction is completed at 40 °C within 12 min (Table 4, entry 1). This reactivity is three times faster when compared to runs using unsubstituted benzaldehyde as substrate (Table 3, entry 4). Quantitative formation of the product alcohol was also observed upon reducing the loading of complex 1b to 1 and 0.5 mol%, although reaction times were slightly longer to reach completion under these conditions (14 and 18 min, respectively, entries 2 and 3). The reaction time is considerably shortened when the reaction temperature was increased to 60 °C, affording full conversion within 6 min with 2 mol% loading of complex 1b (entry 4). Successively decreasing the precatalyst to 0.02 mol% does not compromise the yield of the reaction (entries 5–10). Full conversion at this low loading implies turnover numbers as high as 5,000, and maximum turnover frequencies of 27,000 h$^{-1}$ (entry 4). When the loading of complex 1b was lowered even further to 0.01 mol%, conversions were incomplete even when the reaction was run for extended periods of time, yet these conditions allowed to determine the maximum turnover number TON = 7,400 (60 min, 63%; entry 11). In the absence of nickel complex 1b no conversion was detected also at these slightly elevated temperatures (entry 12).

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Table 4. Hydrosilylation of 4-anisaldehyde with complexes 1b.

| entry | mol% 1b | T [°C] | time [min] | conv [%] | yield [%] | TON | TOF\textsubscript{50} [h\textsuperscript{-1}] |
|-------|--------|--------|------------|----------|-----------|-----|----------------|
| 1     | 2      | 40     | 12         | 99       | 96        | 48  | 340            |
| 2     | 1      | 40     | 14         | 98       | 94        | 96  | 460            |
| 3     | 0.5    | 40     | 18         | 99       | 95        | 192 | 636            |
| 4     | 2      | 60     | 6          | 99       | 96        | 48  | 568            |
| 5     | 1      | 60     | 6          | 99       | 95        | 48  | 960            |
| 6     | 0.5    | 60     | 8          | 98       | 96        | 192 | 2,600          |
| 7     | 0.25   | 60     | 16         | 99       | 93        | 384 | 2,200          |
| 8     | 0.1    | 60     | 20         | 99       | 96        | 892 | 3,800          |
| 9     | 0.05   | 60     | 20         | 99       | 94        | 1,850 | 14,500      |
| 10    | 0.02   | 60     | 20         | 93       | 89        | 4,500 | 27,000      |
| 11    | 0.01   | 60     | 60         | 74       | 63        | 7,400 | 6,500      |
| 12\textsuperscript{d} | 0 | 60 | 120 | <1 |

\textsuperscript{a}Reactions were carried out with 4-anisaldehyde (0.5 mmol), PhSiH\textsubscript{3} (0.6 mmol) and complex 1b in 1,2-dichloroethane (0.4 mL) with C\textsubscript{6}Me\textsubscript{6} (0.05 mmol) as internal standard; \textsuperscript{b}conversion determined by \textsuperscript{1}H NMR spectroscopy; \textsuperscript{c}yield determined by \textsuperscript{1}H NMR spectroscopy after treatment with NaOH (1 M) in MeOH; \textsuperscript{d}in absence of any nickel complex.

almost 80{}\% when compared to the internal standard. These observations suggest the formation of two metal hydride species. The \textsuperscript{13}C NMR signals were less clear, yet, two new resonances at 152 and 154 ppm were observed and attributed to phenolate C–O groups. These resonances are shifted upfield compared to the C–O resonance in 1b (\(\delta_{\text{C–O}} = 160\) ppm) and compatible with the values of free phenol C–O groups that are not metal-coordinated, as for example in the triazolium ligand precursor (\(\delta_{\text{C–OH}} = 150\) ppm). The \textsuperscript{29}Si NMR spectrum supports the formation of two new species as two new signals appeared in the –25 to –30 ppm region (Fig. 6). Their chemical shift is substantially downfield from the signal of PhSiH\textsubscript{3} (\(\delta_{\text{Si}} = –60\)) and indicative of a more electrophilic silicon nucleus. All these data are consistent with cleavage of the Ni–O bond and concomitant formation of the two isomers of a nickel-hydride complex containing a phenylsilylether, cis-5 and trans-5 as a result of the addition of a Si–H bond across the Ni–O bond (Scheme 1).\textsuperscript{[15]}

Interestingly, a identical experiment using stoichiometric amounts of Et\textsubscript{3}SiH instead of PhSiH\textsubscript{3} did not induce any spectroscopic changes of complex 1b according to \textsuperscript{1}H and \textsuperscript{29}Si NMR spectroscopy. Since Et\textsubscript{3}SiH is also catalytically inactive, these data suggesting that the silane addition and formation of the silylether is inhibited, suggesting that this step is essential for catalyst activation. These observations therefore lend support to a met...

Scheme 1. Proposed Ni–O bond cleavage and formation of cis-5 and trans-5 from reaction of complex 1b with phenylsilane.
al–ligand cooperative mechanism for the activation of the Si–H bond and a beneficial role of the anionic oxygen functionality in hydrosilylation catalysis.

Several different mechanisms have been put forward for the hydrosilylation of C=O and C=O bonds over the years.[16–19] Based on our observations, a tentative mechanism is proposed (Scheme 2), involving catalyst activation via Ni–O bond cleavage to form the hydride species 5. This step may be under rigorous steric control due to the bulkiness of the carbene ligand as well as the shielding of the silicon nucleus, thus providing a rationale for the loss in activity when changing the hydrosilylation agent from PhSiH₃ to Ph₂SiH₂ or Et₃SiH. Different pathways are conceivable from this hydride species 5. We propose that the aldehyde substrate is coordinating to the nickel hydride 5 to form the pentacoordinate Ni adduct A. Subsequent activation of the carbonyl unit produces transition state B comprised of a carbon with a strong δ⁺ character, which is in line with the inverse correlation of the Hammett parameter and the reaction rate, as well as the dependence of catalytic activity on the electron density at the nickel centre. The higher the electron density at the metal centre is, the more reactive the hydride. Completing the migratory insertion step affords the alkoxy nickel intermediate C, which is presumed to react with phenylsilane via heterolytic Ni–O bond cleavage to complete the cycle and release the product with concomitant regeneration of the nickel hydride 5. An alternative mechanism consistent with our data involves the formation of a silylene in analogy to the catalytic systems developed by Tilley and coworkers.[20]

3. Conclusions

Nickel(II) complexes with C,O-bidentate chelating mesoionic carbene ligands display remarkable activity in the hydrosilylation of C=O bonds. Complexes supported by mesoionic ligands outperformed non-mesoionic analogues and can be rationally tailored to reach very high turnover frequencies and turnover numbers in the thousands, indicating a reliable control of the catalytic nickel centre through ligand modification. The catalytic system is selective towards aldehyde reduction and tolerant to electron-rich and -poor benzyaldehydes. These results provide useful guidelines for installing O-containing functional groups to promote ligand cooperativity in catalytic systems based on first-row transition metals. Moreover, this work demonstrates that appropriate ligand design provides a powerful methodology for approaching the catalytic activity of noble metal catalysts by using Earth-abundant metal complexes.

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Scheme 2. Proposed mechanistic cycle for hydrosilylation of C=O with complex 1.
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