

[NiX₂(NHC)₂] Complexes in the Hydrosilylation of Internal Alkynes

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A number of nickel(II) dihalide complexes with small monodentate N-heterocyclic carbene ligands was synthesized and tested for their catalytic activity in the hydrosilylation of internal alkynes. The nickel(0) active species was obtained from the starting nickel(II) complex by reduction with diethylzinc. In all cases the catalytic reaction yielded the *syn* product selectively. The fastest catalysts reached full conversion

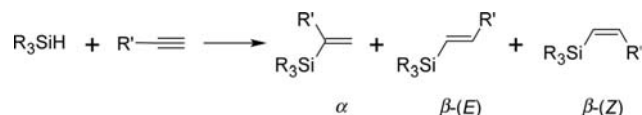
of the symmetric alkyne 3-hexyne in 60 min at 50 °C, with 5 mol-% catalyst loading. The asymmetrically substituted internal alkyne 1-phenyl-1-propyne gave full conversion within 30 min. The major product (83 %) was shown to be the expected (*E*)-1-phenyl-1-(triethylsilyl)propene. The active catalyst was demonstrated to be a homogeneous species.

Introduction

N-Heterocyclic carbenes (NHCs) have been shown to be versatile ligands in organometallic chemistry and catalysis.^[1] The bonding properties of these ligands are often compared to those of well-known trialkylphosphanes, and they may even be better σ -donors than these phosphanes. This makes them good candidates for the stabilization of transition-metal catalysts in various oxidation states during the catalytic cycle. In addition, the shape and size of NHCs can easily be modified by the introduction of various substituents on the heterocycle.

The hydrosilylation of C–C double and triple bonds is one of the most important methods for the formation of C–Si bonds and can be used to functionalize organic molecules.^[2] Vinylsilanes, obtained from the reaction between a silane and an alkyne, are useful reagents in organic synthesis.^[3] A large issue in the direct hydrosilylation of alkynes is the problem of stereoselectivity and regioselectivity, as the use of a terminal alkyne can result in three isomeric vinylsilanes:^[4] the α -silyl product and the β -(*E*)- and the β -(*Z*)-stereoisomers (Scheme 1). Internal alkynes can give rise to regioisomers and (*E*)- and (*Z*)-isomers. The selectivity towards any of these products depends upon several factors, such as the substituents on the alkyne and the silane, the catalyst, and the reaction conditions. The hydrosilylation of alkynes may be catalyzed by a number of different metal complexes, including rhodium,^[5–7] iridium,^[6,8] ruthenium^[9,10] and platinum.^[11–13] Complexes of the less precious metals nickel,^[14] cobalt,^[15] and titanium^[16] have also

been reported to catalyze this reaction. In general, the hydrosilylation of internal alkynes is less explored than the hydrosilylation of terminal alkynes.^[15]



Scheme 1. Products in the hydrosilylation of terminal alkynes.

Recently, Chaulagain et al. reported that a catalyst derived from Ni(COD)₂ (COD = cycloocta-1,5-diene), a bulky 1,3-diarylimidazolium salt and KO^tBu is effective in the hydrosilylation of alkynes.^[17] The active catalyst is assumed to form in situ by deprotonation of the imidazolium salt and formation of the Ni⁰ NHC complex. In contrast, a mixture of Ni(COD)₂ and tributylphosphane was inactive under the same conditions. In order to further investigate the nickel-NHC complex catalyzed reaction we decided to prepare a larger range of ligands, and to develop a protocol starting from preformed and fully characterized nickel(II)-NHC complexes.

In this report the preparation is described of a variety of nickel(II) complexes bearing two monodentate NHC ligands and two halide anions, based on literature syntheses.^[18,19] These complexes are used in the catalytic hydrosilylation of internal alkynes.

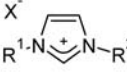
Results and Discussion

Ligand Synthesis

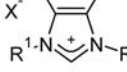
An overview of ligand precursors used in this study is shown in Figure 1. The (benz)imidazolium salts were prepared by the direct alkylation of a number of N-substituted

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imidazoles and benzimidazoles. These quaternization reactions are commonly performed in refluxing THF or acetonitrile. However, to reduce reaction times the higher boiling 1,4-dioxane was used in a number of cases. The salts were obtained in good yields as white to off-white solids and most were found to be hygroscopic. These carbene precursors were characterized by ^1H and ^{13}C NMR and IR spectroscopy, elemental analysis and mass spectrometry (ESI-MS). The NMR spectra of the (benz)imidazolium salts in deuterated DMSO showed a downfield shifted signal at around 10 and 140 ppm, characteristic of the imidazolium NCHN proton and carbon, respectively.^[20]



1



2

	R ¹	R ²	X		R ¹	R ²	X
1a	Me	Me	I	2a	Me	Me	I
1b	Me	Et	I	2b	Me	<i>i</i> Pr	Br
1c	Me	Pr	I	2c	Me	<i>i</i> Pr	I
1d	Me	<i>i</i> Pr	I	2d	Me	Ph	I
1e	Me	Ph	I	2e	<i>i</i> Pr	<i>i</i> Pr	I
1f	Bn	Bn	Br	2f	Bn	Bn	Br

Figure 1. Overview of ligand precursors used in this study.

Synthesis of Nickel(II) Complexes Bearing Two Monodentate NHC Ligands

Following literature procedures,^[19] the (benz)imidazolium salts, with the exception of **1f**, were reacted at high temperatures with $\text{Ni}(\text{OAc})_2$ to yield the $[\text{NiX}_2(\text{NHC})_2]$ complexes depicted in Figure 2. In the cases in which the melting point of the imidazolium salt was too high for the reaction to occur successfully an additional low-melting salt, tetrabutylammonium halide, was added as a solvent, in an adaptation of the original procedure reported by Huynh et al.^[18] After aqueous work-up and purification, the $[\text{NiX}_2(\text{NHC})_2]$ complexes were obtained as stable, orange-red to purple powders. Complexes **3c**, **3d**, **4a** and **4f** have been synthesized before, following these literature procedures.^[18,19,21] Complex **3a** has been synthesized before, by an analogous reaction in nitromethane.^[22] Complex **3f** was obtained by transmetalation of the ligand from the silver(I) complex to $\text{NiBr}_2(\text{PPh}_3)_2$. The silver(I) complex was prepared in situ from ligand precursor **1f** and Ag_2O in dichloromethane.^[23]

The ^1H NMR spectra of all nickel complexes lacked the characteristic imidazolium NCHN resonance at around 10 ppm, indicating successful carbene generation. The other peaks present in the NMR spectra of the starting imidazolium salts could successfully be identified, albeit shifted slightly from their original position. The carbene carbon atom of the novel complexes **3e**, **3f** and **4b** is observed in their ^{13}C NMR spectra at 174.7, 169.0 and 188.0 ppm, respectively. The carbene carbon atoms of complexes **3b**,



Figure 2. Nickel complexes prepared in this study. R¹ and R² are as given in Figure 1 for **1** and **2**, respectively.

4d and **4e** could not be observed, probably due to peak broadening. Due to its poor solubility in common solvents, a ^{13}C NMR spectrum could not be recorded for complex **4e**. The NMR spectra of **3b**, **3e**, **4b**, **4c** and **4d** showed splitting of a number of resonances, indicating the presence of two rotamers in solution, due to restricted rotation about the Ni–C bond. This behaviour has been reported before for complex **3d**.^[19] The NMR spectra of **4b** and **4c**, which only differ in halide, are quite similar, as expected. Interestingly, however, the isopropyl-CH and the NCH_3 resonances are shifted more downfield in the case of the bromide complex **4b**. The isopropyl-CH resonances of **4b** are obscured by resonances of the aromatic protons, but could be assigned with the aid of a ^1H COSY NMR spectrum. The isopropyl-CH resonances of the iodide complex **4e** are also shifted less downfield than those reported for the bromide analogue,^[21] indicating a trend in the electronic properties of the complexes depending on the halide anion. This phenomenon has also been observed for the corresponding Pd^{II} compounds.^[24]

Catalytic Studies: General Remarks

Complexes **3a–f** and **4a–f** were tested for their catalytic activity in the hydrosilylation of internal alkynes with triethylsilane. As a benchmark, the symmetric 3-hexyne was chosen as the internal alkyne. The results of the catalytic studies are given in Table 1 and Table 2. The activity is reported as the time needed to consume all alkyne substrate (t_{99}), i.e. the time after which the alkyne could no longer be detected by GC. As full conversion is reached asymptotically, exact determination of t_{99} is difficult, and therefore the time at which 50% of the alkyne was consumed (t_{50}) is reported as well. A typical example of the evolution of the substrate and the product in time for an active catalyst is shown in Figure 3, for a nickel compound that is preactivated with diethylzinc (Table 2, entry 12; see next section).

Two different isomers of the product may be obtained from the hydrosilylation of 3-hexyne (Figure 4), i.e. the (*E*)- and the (*Z*)-isomer. In the current experiments, however, only one isomer was observed. Isolation and characterization revealed it to be the (*E*)-isomer, in which the H and

Table 1. The use of different compounds for the activation of complex **3a** in the hydrosilylation of 3-hexyne.^[a]

Entry	Activator ^[b]	Amount ^[c]	<i>t</i> ₅₀ [min] ^[d]	<i>t</i> ₉₉ [min] ^[e]
1	none ^[f]	—	—	—
2	BuLi (0 °C) ^[g]	2	10–50	30–250
3	BuLi (–78 °C)	2	40	140
4	PhMgCl ^[f]	4	—	—
5	PhMgCl	10	200	n.d.
6	AlEt ₃ ^[f]	8	—	—
7	ZnEt ₂	2	70	240
8	ZnEt ₂	4	40	140

[a] Reagents and conditions: 0.05 mmol **3a**, 1.0 mmol 3-hexyne, activator, 2.0 mmol triethylsilane, 5 mL of THF, 50 °C. All catalytic runs were performed in duplicate. The (*E*)-product is obtained selectively. [b] Activator was added at room temp. unless noted otherwise. [c] Equivalents of activator relative to nickel. [d] Time needed to reach 50% conversion of 3-hexyne. [e] Time needed to reach full conversion. [f] No conversion was observed after 5 h. [g] The experiment was difficult to reproduce, and was performed 4 times. In one run no activation occurred.

Table 2. Nickel-catalyzed hydrosilylation of 3-hexyne using complexes **3** and **4**.^[a]

Entry	Catalyst	Standard procedure ^[b]		With pre-activation ^[c]	
		<i>t</i> ₅₀ [min] ^[d]	<i>t</i> ₉₉ [min] ^[e]	<i>t</i> ₅₀ [min] ^[d]	<i>t</i> ₉₉ [min] ^[e]
1	3a	40	140	40	160
2	3b	40	120	45	150
3	3c	40	100	35	120
4	3d	60	150	40	140
5	3e	40	120	14	60
6	3f	25	70	22	80
7	4a	40	160	45	180
8	4b	20	60	25	80
9	4c	60	130	25	80
10	4d	50	140	25	120
11	4e	300	n.d.	200 (45) ^[f]	n.d. (150) ^[f]
12	4f	25	80	20	60
13	— ^[g]	—	—	—	—

[a] Reagents and conditions: 0.05 mmol Ni, 5 mL of THF, 0.2 mmol ZnEt₂, 1.0 mmol 3-hexyne, 2.0 mmol triethylsilane, 50 °C. All catalytic runs were performed in duplicate. The (*E*)-product is obtained selectively. [b] All reagents were mixed at room temp. before heating to 50 °C. [c] Reaction mixture was stirred 10 min at 50 °C, before the alkyne and the silane were added. [d] Time needed to reach 50% conversion. [e] Time needed to reach full conversion. [f] Reaction mixture was stirred 30 min at 50 °C, before the alkyne and the silane were added. [g] No nickel complex was added. No conversion was observed after 5 h in the presence of 0.2 mmol ZnEt₂.

the SiEt₃-group are located on the same face of the double bond, in agreement with the results of other nickel catalysts.^[12] In contrast, the Lewis acid-catalyzed hydrosilylation of alkynes has been reported to yield the (*Z*)-isomer selectively.^[25]

Catalyst Activation Procedures

The starting point of the catalytic cycle of the hydrosilylation of alkynes is a nickel(0) species. The nickel(II)-NHC compounds indeed are not active in the hydrosilylation reaction under the conditions used in our study (Table 1, entry 1). It has been shown that nickel(II) com-

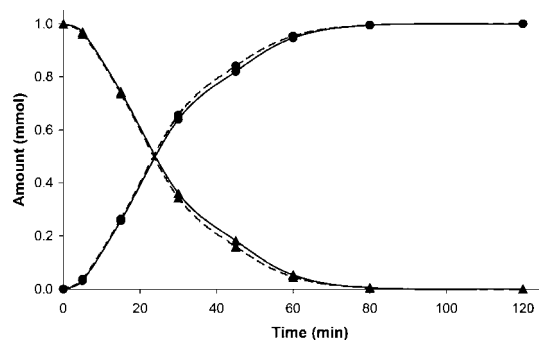


Figure 3. Typical example of the consumption of the substrate 3-hexyne (▲) and the evolution of the product (●) in time using complex **4f** (Table 2, entry 12). Solid line: regular run; dashed line: with 100 equiv. Hg added after 30 min.

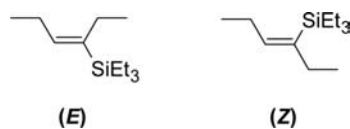


Figure 4. Possible isomers of the product of the hydrosilylation of 3-hexyne.

plexes may be activated by reaction with an appropriate silane, however, this process requires high temperatures.^[26] As a reducing agent butyllithium was considered, although it was unclear whether this reagent could be used to activate nickel(II) complexes, rather than nickel(II) salts.^[27–29] In addition, triethylaluminum, diethylzinc and phenylmagnesium chloride were evaluated. Trialkylaluminum compounds are known for the activation of Ni(acac)₂ in Ziegler-type catalysts, the zinc reagent is anticipated to have similar alkylating properties,^[30] and the Grignard reagent is used for the activation of nickel dihalide complexes in the Kumada coupling reaction.^[31–34] The results of the catalytic hydrosilylation of 3-hexyne with triethylsilane using complex **3a** in combination with these activators are summarized in Table 1.

Initially, in the butyllithium-activated experiments, the activator was added to the nickel(II) complex at 0 °C (entry 2), which caused a rapid color change of the solution from red to yellow. As the catalytic results were difficult to reproduce, it was suspected that this activation method was too vigorous. It was decided to moderate the activation, by adding the butyllithium at –78 °C, and allowing the reaction mixture to slowly warm up to room temperature (entry 3). This modified procedure greatly improved the reproducibility of the catalytic experiments. In the case of the activation using AlEt₃, PhMgCl or ZnEt₂, no rapid color change was observed during the addition of the activator to the solution of the nickel(II) complex at room temperature, and cooling was not employed in these experiments. Unfortunately, no catalytic activity was observed after the addition of AlEt₃ (entry 6), and even an excess of PhMgCl (entry 5) gave only partial activation.

In the catalytic experiments in which butyllithium was employed as activating agent, small amounts of two side-

products were observed. These were identified as butyltriethylsilane and ethoxytriethylsilane (Figure 5). The first may be formed by a reaction between butyllithium and triethylsilane, while the latter is most likely derived from butyllithium, triethylsilane and ethanol used in the work-up procedure. In addition, it was observed that the use of a larger excess of butyllithium resulted in larger amounts of these side products. As both side products are derived from the silane reagent, which is used in excess, they are not taken into consideration for the calculation of the selectivity of the catalyst, which is based on conversion of the alkyne.



Figure 5. Side products observed in the butyllithium-activated catalytic experiments.

The catalyst activation with butyllithium at low temperature and the activation with 4 equiv. diethylzinc yielded a catalyst of equal activity. Because of the formation of side products and the laborious activation (cooling to -78°C) when using butyllithium, and the insufficient activating properties of phenylmagnesium chloride and triethylaluminum, it was decided to use 4 equiv. of diethylzinc as activator for the remainder of catalytic experiments.

Catalytic Activity: Effect of Different NHC Ligands

The results of the diethylzinc-activated, nickel-catalyzed hydrosilylation of 3-hexyne using complexes **3a–f** and **4a–f** are summarized in Table 2. In all cases the catalytic reaction was performed using the following procedure: the nickel complex is dissolved/suspended in THF and 3-hexyne is added, followed by diethylzinc. Next, the silane is added and the reaction vessel is immediately placed in a preheated oil bath. All nickel complexes bearing monodentate N-heterocyclic carbenes tested in this study are active hydrosilylation catalysts after activation with diethylzinc.

The t_{50} and t_{99} values given in Table 2 are an indication the activity of the catalyst. However, if the activation is a slow process, the nickel complex is not activated immediately after the starting point of the catalytic run and the true activity of the catalyst may be underestimated. Therefore, the *overall* activity of the catalyst is dependent on the rate of the activation of the initial nickel(II) complex. The activation of the catalyst may be influenced by (a) the halide ion and (b) the solubility of the starting complex.

It is often assumed that the activity of a complex is independent on the halide of the starting compound, as this halide is removed during the activation process. However, it is clear (Table 2, entries 8 and 9) that the halide does have an effect on the overall activity, as the substrate is consumed faster when starting from the bromide complex **4b**, than from the iodide complex **4c**. This indicates that in the case of the iodide complexes the activation is rather sluggish. Complexes **4a**, **4c**, and especially **4e** are poorly soluble in THF, which may cause slow catalyst activation. Indeed,

in a number of cases an induction time of 5 to 10 min is observed before full catalytic activity starts and with complex **4e** no conversion is observed in the first 45 min.

To eliminate the influence of the slow activation on the overall activity, all catalytic runs were repeated with an alternative procedure in which the nickel(II) complex is activated prior to the addition of the two reagents. Preactivation is accomplished by stirring the mixture of the nickel complex with diethylzinc at 50°C for 10 min, before the alkyne and the silane are added. The results obtained with this alternative procedure are included in Table 2.

In a number of cases the preactivation of the nickel(II) complex significantly decreases the time needed to bring the reaction to full conversion. For instance, using complex **3e** with pre-activation the time needed to reach full conversion is halved compared to the regular procedure. Nickel iodide complexes with isopropyl- and phenyl-substituted ligands appear to benefit the most from the preactivation procedure. In some runs the catalytic activity appears to have decreased slightly, possibly due to catalyst decomposition in the absence of substrate, although this may be within experimental error. However, as expected, the halide of the nickel(II) starting complex no longer has an influence on the catalytic activity, as it is now removed at the activation step before the catalytic reaction starts (Table 2, entries 8 and 9). Complex **4e** is highly insoluble and even after preactivation for 30 min, some undissolved starting complex is still present in the reaction mixture. Therefore, the results shown for this complex are an underestimation of the true catalytic activity of the nickel(0) species.

Comparison of the Catalysts

The catalytic activity of the various nickel complexes is dependent on the ligand substituents. For instance, an increase in the length of the alkyl chain from methyl to propyl in complexes **3a–3c**, leads to a decrease in the time needed to reach full conversion, although the more bulky isopropyl substituent leads to a less active catalyst in the case of the imidazole-based carbene ligands. In the case of the benzimidazole-based carbene ligands, an increase in bulk around the metal center clearly leads to enhanced catalytic activity, although this is not apparent for complex **4e**, which was only partly activated.

The most active catalysts found in this study are the *N*-methyl-*N'*-phenyl-substituted imidazole-based complex **3e** and *N,N'*-dibenzyl-substituted benzimidazole-based complex **4f**, which both reach full conversion within 60 min. The highest turnover frequency was observed with complex **3e**, as it reached 50% conversion in 14 min, which is equal to $43 \text{ mol}(\text{mol cat})^{-1} \text{ h}^{-1}$. In the case that no catalyst preactivation is performed, the bromide complexes (**3f**, **4b** and **4f**) are the most active.

To confirm that the nickel complex is the source of the catalytic activity, one experiment was performed without addition of the nickel complex. As expected, after 5 h of stirring at 50°C no product could be observed (Table 2, entry 13).

The hydrosilylation of 3-hexyne with triethylsilane has been reported a number of times in the literature. For instance, 0.5 mol-% of a cationic rhodium complex in an aqueous micellar system yielded 53% of the (*E*)-product in 3 h at room temperature.^[35] A cobalt(I) complex was shown to yield 71% of the (*E*)-product in 10 h, using 5 mol-% catalyst loading at 40 °C.^[15] However, using heterogeneous platinum on carbon, the same product could be obtained in 95% yield in 3 h using only 0.02 mol-% Pt at 80 °C.^[12] Although the latter catalyst is clearly the most efficient, the nickel catalyst under study may be an attractive alternative as it does not make use of the rather scarce and expensive platinum or rhodium.

In addition to the benchmark substrate 3-hexyne, the reactivity and selectivity of a small series of other internal alkynes was investigated as well. The results of this survey using complex **3a** under the standard conditions are shown in Table 3. For example, the more sterically hindered diphenylacetylene was fully converted into 1,2-diphenyl-1-triethylsilyl-*cis*-ethene (**5**) in 150 min (entry 1). In contrast, no activity was observed using the even larger bis(triethylsilyl)-substituted acetylene (entry 3). Within 2 h the substrate 1,4-dimethoxy-2-butyne was fully and cleanly converted into (*E*)-1,4-dimethoxy-2-triethylsilyl-2-butene (**6**). The asymmetrically substituted internal alkyne 1-phenyl-1-propyne gave full conversion within 30 min. However, two products could be detected by GC. The major product was shown to be the expected (*E*)-1-phenyl-1-(triethylsilyl)propene (**7a**). NMR measurements indicate that the minor product is the regioisomer (*E*)-1-phenyl-2-(triethylsilyl)propene.

Table 3. Catalytic hydrosilylation of various internal alkynes using complex **3a**.^[a]

Entry	Alkyne R–C≡C–R'	Product (yield) ^[b]	<i>t</i> ₅₀ [min] ^[c]	<i>t</i> ₉₉ [min] ^[d]
1	Ph Ph	5 (quant.)	50	150
2	CH ₃ OCH ₂ CH ₃ OCH ₂	6 (quant.)	40	120
3	(Et) ₃ Si (Et) ₃ Si	– ^[e]	–	–
4	Ph Me	7a (83%) ^[f]	10	30

[a] Reagents and conditions: 0.05 mmol **3a**, 5 mL of THF, 0.2 mmol ZnEt₂, 1.0 mmol alkyne, 2.0 mmol triethylsilane, 50 °C. All catalytic runs were performed in duplicate. All reagents were mixed at room temp. before heating to 50 °C. [b] GC yield; isolated yields are given in the experimental section. [c] Time needed to reach 50% conversion. [d] Time needed to reach full conversion. [e] No conversion was observed after 5 h. [f] 17% minor product (**7b**).

Homogeneous vs. Heterogeneous Catalysis

A continuing discussion in homogeneous catalysis involving zero-valent transition-metal intermediate species is the question whether the active catalyst is indeed the homogeneous zero-valent metal complex, or that heterogeneous metal nanoparticles or clusters are catalytically active. This is of importance, especially since nanoparticles have been shown to be catalytically active in a number of related nickel-catalyzed reactions, such as hydrogenation^[36] and the Heck reaction.^[37]

One method for excluding the observed catalytic activity to be due to nickel nanoparticles is the so called “mercury test”. During the catalytic run a drop of metallic mercury is added to the reaction mixture, which, in the case of nickel nanoparticles, should quench the reaction due to the formation of an HgNi₃ or HgNi₄ amalgam.^[38] If, on the other hand, the reaction continues, it is generally accepted that the catalyst must be a homogeneous species. In the present study, 100 equiv. of mercury on nickel were added after 30 min of reaction time. To ensure a large contact surface, the reaction mixtures were stirred vigorously to create small mercury droplets. To exclude the possibility of an unintended active heterogeneous catalyst being present, the mercury test was performed with all catalysts. In all cases the addition of mercury had no noticeable effect on the outcome of the catalytic reaction, in terms of rate or selectivity. A comparative example of the evolution of 3-hexyne and the product in time during the mercury test is included in Figure 3.

Although the mercury test is a fast and easy-to-perform method for distinguishing homogeneous and heterogeneous catalysts, it is not always conclusive.^[39] For instance, poisoning may be incomplete if the contact between the mercury drop and the catalyst solution is not sufficient, the mercury may cause side reactions, or there simply may not be enough mercury present to bind all nanoparticles.^[40] Therefore, it was decided to perform a kinetic study on selected catalytic systems. In theory, in the case of a homogeneous catalyst an increase in catalyst concentration should lead to a proportional increase in the overall rate of the reaction, while for heterogeneous catalysts this is not necessarily the case, due to the formation of different sizes of metal clusters. The results of this kinetic study using complex **3e** are shown in Figure 6. Using different catalyst concentrations, the product yield was determined after 15, 30 and 60 min. Clearly, an increase in catalyst concentration gives a linear increase in the conversion within experimental error and thus it may be concluded that the ZnEt₂-activated catalyst is truly homogeneous. Comparable results were obtained using complex **3a**.

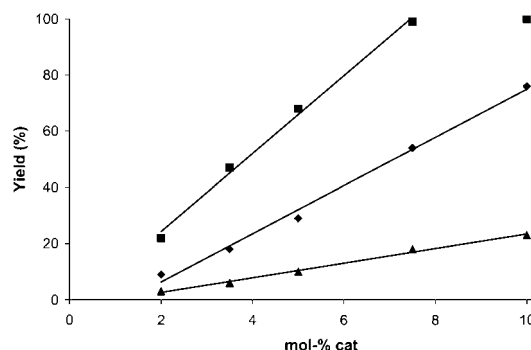


Figure 6. Product yield as a function of catalyst concentration after a fixed time: (■) 60 min; (◆) 30 min; (▲) 15 min.

As a final check for homogeneity it was attempted to deliberately prepare a heterogeneous catalyst and to test its activity in the hydrosilylation of internal alkynes. The

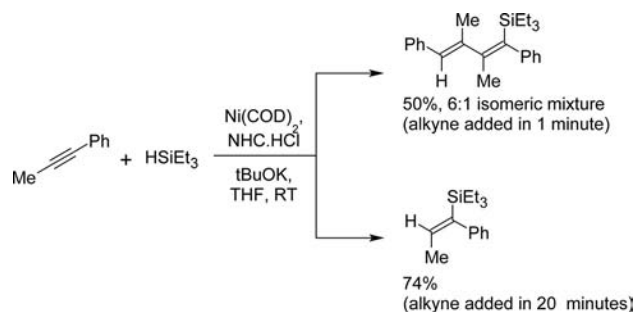
heterogeneous nickel-catalyzed hydrosilylation of terminal olefins has been reported.^[41] However, to the best of our knowledge, no internal alkynes have been used in these studies, except one: Lappert et al. reported that Ni(acac)₂, reduced by AlEt₃, was inactive for the hydrosilylation of 2-hexyne and 4-octyne,^[42] although with terminal alkynes a 2:1 adduct could be obtained (Scheme 2).^[43] Indeed, using Ni(acac)₂ and AlEt₃ under the conditions of the present study did not result in any conversion of 3-hexyne. Therefore, it is concluded that the activity observed with complexes **3a–f** and **4a–f** must arise from a homogeneous catalyst.



Scheme 2. Hydrosilylation and dimerization of terminal alkynes with a Ziegler-type catalyst.^[42]

Mechanistic Considerations

Chaulagain et al.^[17] reported that a mixture of 10 mol-% Ni(COD)₂, 10 mol-% of a bulky *N,N'*-diarylimidazolium salt, such as *N,N'*-dimesitylimidazolium chloride, and 10 mol-% KO^tBu in THF is active in the hydrosilylation of internal alkynes, when using 2 equiv. of silane at room temperature. However, slow addition of the alkyne was required to obtain the 1:1 adduct in good yield. Fast addition of the alkyne led to the formation of a 2:1 adduct (Scheme 3). In contrast, our catalytic system with two carbene ligands is less active, and requires elevated temperatures in order to proceed at an appreciable rate. In this case, only the (*E*)-alkene product is observed and may be isolated quantitatively.



Scheme 3. Hydrosilylation of an internal alkyne using Ni(COD)₂ and a bulky imidazolium salt (NHC·HCl is *N,N'*-dimesitylimidazolium chloride).^[17]

The differences between the two systems may be explained by the different ligand-to-metal ratio applied. In the case of the 1:1 ligand-to-metal ratio, the nickel center is highly coordinatively unsaturated, which enables the coordination of two alkynes and one silane substrate, leading to the 2:1 adduct. The lack of steric bulk around the metal center may also account for the high reactivity of this system. In contrast, the use of a 2:1 ligand-to-metal ratio – as in the current paper – leads to a catalyst to which only one alkyne and one silane may be bound simultaneously,

resulting in the 1:1 adduct. Although there is no direct experimental evidence for this hypothesis, it is supported by reports of the isolation and characterization of nickel complexes with one NHC ligand and two coordinated alkenes as well as nickel complexes with two NHC ligands and only one coordinated alkene or alkyne.^[44,45]

Conclusions

In conclusion, the synthesis and characterization of twelve monodentate *N*-heterocyclic carbene complexes of nickel(II) and their activity in the catalytic hydrosilylation of internal alkynes is reported. Four activating agents were evaluated, from which diethylzinc was selected as being the most efficient. Using a procedure in which the nickel catalyst is preactivated, *N*-methyl-*N'*-phenyl-substituted complex **3e** and *N,N'*-dibenzyl-substituted complex **4f** show the highest activity in the hydrosilylation of 3-hexyne with triethylsilane, giving the desired (*E*)-product in quantitative yield within 60 min at 5 mol-% catalyst loading.

Using the mercury test and kinetic studies, it was unambiguously shown that the active catalyst is a homogeneous species.

Experimental Section

General Considerations: All experiments were performed under air and moisture-free conditions under an argon atmosphere, unless indicated otherwise. All chemicals were obtained from commercial sources and used as received. THF and 1,4-dioxane were distilled under an argon atmosphere from CaH₂ and stored on molecular sieves. Dry Ni(OAc)₂ was obtained by heating the hydrate at 165 °C under a stream of argon. Triethylsilane and 3-hexyne were degassed and stored under argon on activated molecular sieves. *N*-Isopropylimidazole,^[20] *N*-phenylimidazole,^[46] *N*-isopropylbenzimidazole,^[20] *N*-phenylbenzimidazole,^[47] **1a**,^[48] **1b**,^[49] **1f**,^[23] **2e**,^[24] **3c**,^[19] **3d**,^[19] **4a**,^[18] and **4f**^[21] were synthesized according to literature procedures.

¹H and ¹³C NMR spectra were recorded on a Bruker DPX300. Chemical shifts are reported as referenced against residual solvent signals and quoted in ppm relative to tetramethylsilane. IR spectra were recorded with a Perkin–Elmer FT-IR Paragon 1000 spectrophotometer equipped with a golden-gate ATR device, using the reflectance technique. C, H, N determinations were performed on a Perkin–Elmer 2400 Series II analyzer. Electrospray mass spectra were recorded on a Finnigan TSQ-quantum instrument using an electrospray ionization technique (ESI-MS). GC measurements were performed on a Varian CP3800 with a 25 m WCOT fused silica column and an autosampler, calibration lines were made using heptane as internal standard. Peaks were identified by comparison with the pure compound (3-hexyne, Et₃SiH, 3-triethylsilyl-*cis*-hex-3-ene, butyltriethylsilane,^[50] ethoxytriethylsilane,^[50] 1,2-diphenyl-1-triethylsilyl-*cis*-ethene) and by GC-MS analysis (butyltriethylsilane, ethoxytriethylsilane). Diethylzinc was added as a 1.0 M solution in hexanes, *n*-butyllithium was added as a 1.6 M solution in hexanes, triethylaluminum was added as a 0.6 M solution in heptane and phenylmagnesium chloride was added as a 25 wt.-% solution in THF.

General Reaction for the Synthesis of (Benz)imidazolium Salts: A solution of *N*-substituted (benz)imidazole and about 1.1 equiv. of

haloalkane in dry THF or 1,4-dioxane was placed under an argon atmosphere and stirred at 80 or 100 °C, respectively, for 24 h. When using iodomethane as alkylating agent, the reaction mixture was stirred at room temperature. The off-white precipitate was collected by filtration and recrystallized from methanol/diethyl ether to yield a white solid, which was dried in vacuo.

***N*-Methyl-*N'*-phenylimidazolium Iodide (1e):** The synthesis was performed according to the general procedure, starting from 2.16 g of *N*-phenylimidazole (15 mmol) and 2.42 g of iodomethane (17 mmol) in 20 mL of THF; yield 4.21 g (98%). ¹H NMR (300 MHz, 300 K, [D₆]DMSO): δ = 9.80 (s, 1 H, NCHN), 8.31 (s, 1 H, NCH), 7.98 (s, 1 H, NCH), 7.79 (m, 2 H, Ar-H), 7.68–7.58 (m, 3 H, Ar-H), 3.96 (s, 3 H, NCH₃) ppm. ¹³C NMR (75 MHz, 300 K, [D₆]DMSO): δ = 137.2 (NCHN), 136.0 (C_q), 131.5 (C_{Ar}), 131.0 (C_{Ar}), 125.7 (NCH), 123.1 (C_{Ar}), 122.2 (NCH), 37.6 (NCH₃) ppm. IR (neat): ν̄ = 3447 (m), 3371 (m), 3094 (m), 3029 (m), 1599 (w), 1576 (m), 1553 (m), 1496 (m), 1423 (w), 1222 (m), 1068 (m), 813 (w), 758 (s), 682 (s), 611 (s) cm⁻¹. C₁₀H₁₁IN₂·0.5H₂O (295.12): calcd. C 40.70, H 4.10, N 9.49; found C 40.69, H 4.01, N 9.48. MS (ESI): *m/z* (%) = 159 (100) [[M – I]⁺].

***N*-Methyl-*N'*-isopropylbenzimidazolium Bromide (2b):** Following the general procedure, the compound was obtained from 1.06 g of *N*-methylbenzimidazole (8.0 mmol) and 1.23 g of 2-bromopropane (10.0 mmol) in 30 mL of 1,4-dioxane and isolated as a white solid; yield 1.41 g (69%). ¹H NMR (300 MHz, 300 K, [D₆]DMSO): δ = 9.93 (s, 1 H, NCHN), 8.12 (m, 1 H, Ar-H), 8.03 (m, 1 H, Ar-H), 7.69 (m, 2 H, Ar-H), 5.06 (sept, *J* = 7 Hz, 1 H, NCH), 4.07 (s, 3 H, NCH₃), 1.60 (d, *J* = 7 Hz, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, 300 K, [D₆]DMSO): δ = 141.1 (NCHN), 132.0 (C_q), 130.3 (C_q), 126.4 (C_{Bim}), 126.3 (C_{Bim}), 113.8 (C_{Bim}), 113.6 (C_{Bim}), 50.3 (NCH₃), 33.2 (NCH), 21.6 (CH₃) ppm. IR (neat): ν̄ = 3080 (w), 2978 (w), 1564 (m), 1456 (m), 1436 (m), 1349 (m), 1262 (m), 1216 (m), 1100 (m), 1016 (w), 830 (w), 759 (s), 615 (m), 552 (m) cm⁻¹. C₁₁H₁₅BrN₂ (255.16): calcd. C 51.78, H 5.93, N 10.98; found C 51.98, H 6.15, N 10.85. MS (ESI): *m/z* (%) = 175 (100) [[M – Br]⁺], 133 [[M – Br – C₃H₇ + H]⁺].

***N*-Methyl-*N'*-isopropylbenzimidazolium Iodide (2c):** According to the general synthesis, 2.64 g of *N*-methylbenzimidazole (20 mmol) was treated with 4.25 g of 2-iodopropane (25 mmol) in 25 mL of THF. The compound was obtained as a white solid; yield 3.87 g (64%). ¹H NMR (300 MHz, 300 K, [D₆]DMSO): δ = 9.81 (s, 1 H, NCHN), 8.12 (m, 1 H, Ar-H), 8.02 (m, 1 H, Ar-H), 7.69 (m, 2 H, Ar-H), 5.05 (sept, *J* = 7 Hz, 1 H, NCH), 4.06 (s, 3 H, NCH₃), 1.60 (d, *J* = 7 Hz, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, 300 K, [D₆]DMSO): δ = 141.2 (NCHN), 131.9 (C_q), 130.3 (C_q), 126.4 (C_{Bim}), 126.3 (C_{Bim}), 113.7 (C_{Bim}), 113.6 (C_{Bim}), 50.3 (NCH₃), 33.3 (NCH), 21.6 (CH₃) ppm. IR (neat): ν̄ = 3022 (w), 2979 (w), 1610 (w), 1567 (m), 1456 (m), 1431 (m), 1352 (w), 1260 (m), 1215 (m), 1135 (m), 760 (s), 618 (m), 603 (m), 425 (m) cm⁻¹. C₁₁H₁₅IN₂ (302.16): calcd. C 43.73, H 5.00, N 9.27; found C 43.88, H 5.39, N 9.37. MS (ESI): *m/z* (%) = 175 (100) [[M – I]⁺], 133 [[M – I – C₃H₇ + H]⁺].

***N*-Methyl-*N'*-phenylbenzimidazolium Iodide (2d):** Following the general procedure, the compound was obtained as a white solid from 1.17 g of *N*-phenylbenzimidazole (6.0 mmol) and 0.85 g of iodomethane (7.0 mmol) in 15 mL of THF; yield 1.67 g (83%). ¹H NMR (300 MHz, 300 K, [D₆]DMSO): δ = 10.12 (s, 1 H, NCHN), 8.15 (m, 1 H, Ar-H), 7.87–7.68 (m, 8 H, Ar-H), 4.17 (s, 3 H, NCH₃) ppm. ¹³C NMR (75 MHz, 300 K, [D₆]DMSO): δ = 143.1 (NCHN), 133.1 (C_q), 131.8 (C_q), 130.8 (C_q), 130.4 (2 × C_{Ph}), 127.4 (C_{Bim}), 126.9 (C_{Bim}), 125.1 (C_{Ph}), 113.9 (C_{Bim}), 113.3 (C_{Bim}), 33.5 (NCH₃) ppm. IR (neat): ν̄ = 3021 (w), 1563 (m), 1557 (s), 1487 (m), 1424 (w), 1308 (w), 1263 (m), 1239 (m), 1161 (m), 1133 (m),

1080 (m), 828 (m), 785 (m), 747 (s), 697 (s), 600 (s), 484 (m) cm⁻¹. C₁₄H₁₃IN₂ (336.18): calcd. C 50.02, H 3.90, N 8.33; found C 50.11, H 3.92, N 8.39. MS (ESI): *m/z* (%) = 209 (100) [[M – I]⁺].

General Procedure for the Synthesis of Nickel Complexes: A mixture of (benz)imidazolium halide, 0.5 equiv. anhydrous Ni^{II} acetate and about 50% of the combined weight of the two reagents of the corresponding tetrabutylammonium halide was dried in vacuo at 60 °C for 1 h. The temperature was then raised to 130 °C (bromide salts) or 155 °C (iodide salts) and kept at this temperature in vacuo for several hours. After cooling, water was added and the mixture was triturated thoroughly. After isolation of the crude product by filtration, the pure compound was obtained either by repeated washing of a dichloromethane solution of the crude product with water, evaporation of the solvent and precipitation with diethyl ether (compounds **3a,b,e** and **4b**), or by recrystallization from hot DMF (compounds **4c,d,e**), and were isolated as red-orange to purple solids.

Bis(*N,N'*-dimethylimidazol-2-ylidene)diiodidonickel(II) (3a): Following the general procedure, the complex was obtained from 1.12 g of imidazolium iodide **1a** (5.0 mmol) and 0.44 g of nickel(II) acetate (2.5 mmol), without the addition of tetrabutylammonium iodide, at 155 °C; yield 0.69 g (55%). NMR spectra are identical to those reported in the literature.^[22]

Bis(*N*-ethyl-*N'*-methylimidazol-2-ylidene)diiodidonickel(II) (3b): Following the general procedure, 1.19 g of imidazolium iodide **1b** (5.0 mmol) and 0.44 g of nickel(II) acetate (2.5 mmol) were reacted in 0.8 g of tetrabutylammonium iodide at 155 °C; yield 0.47 g (35%). ¹H NMR (300 MHz, 300 K, CDCl₃): δ = 6.77 (m, 4 H, NCH), 4.84 (2 × q, *J* = 7 Hz, 4 H, NCH₂), 4.26 (s, 6 H, NCH₃), 1.69 (2 × t, *J* = 7 Hz, 6 H, CH₃) ppm. ¹³C NMR (75 MHz, 300 K, CDCl₃): δ = 123.2 (NCH), 120.5 (NCH), 45.6 (NCH₂), 37.9 (NCH₃), 15.2 (CH₃) ppm. IR (neat): ν̄ = 3098 (w), 2972 (w), 1558 (w), 1455 (m), 1401 (m), 1256 (m), 1219 (s), 1085 (m), 954 (m), 796 (m), 732 (s), 697 (s) cm⁻¹. C₁₂H₂₀I₂N₄Ni (532.84): calcd. C 27.05, H 3.78, N 10.52; found C 27.27, H 3.49, N 10.44. MS (ESI): *m/z* (%) = 446 (100) [[M – I + MeCN]⁺].

Bis(*N*-methyl-*N'*-phenylimidazol-2-ylidene)diiodidonickel(II) (3c): Following the general procedure, the compound was obtained starting from 2.28 g of imidazolium salt **1e** (8.0 mmol) and 0.71 g of nickel(II) acetate (4.0 mmol) in 1.5 g of tetrabutylammonium iodide at 155 °C; yield 0.73 g (29%). ¹H NMR (300 MHz, 300 K, CDCl₃): δ = 8.28 (d, *J* = 8 Hz, 4 H, Ar-H), 7.61 (t, *J* = 8 Hz, 4 H, Ar-H), 7.49 (t, *J* = 8 Hz, 2 H, Ar-H), 7.00 (d, *J* = 2 Hz, 2 H, NCH), 6.84 (d, *J* = 2 Hz, 2 H, NCH), 4.01 (s, 6 H, NCH₃) ppm. ¹³C NMR (75 MHz, 300 K, CDCl₃): δ = 174.7 (Ni-C), 140.8 (C_q), 128.8 (C_{Ar}), 128.1 (C_{Ar}), 126.4 (C_{Ar}), 123.6 (NCH), 122.6 (NCH), 38.2 (NCH₃) ppm. IR (neat): ν̄ = 3129 (w), 1598 (w), 1497 (s), 1444 (m), 1403 (w), 1229 (m), 1069 (m), 915 (m), 759 (m), 724 (m), 690 (s), 623 (m), 547 (m) cm⁻¹. C₂₀H₂₀I₂N₄Ni (628.93): calcd. C 38.20, H 3.21, N 8.91; found C 38.23, H 3.00, N 8.86. MS (ESI): *m/z* (%) = 542 [[M – I + MeCN]⁺], 501 (100) [[M – I]⁺], 228 [[M – 2I + MeCN]²⁺].

Bis(*N,N'*-dibenzylimidazol-2-ylidene)dibromidonickel(II) (3f): A mixture of 0.23 g of ligand precursor **1f** (1.0 mmol) and 0.14 g of silver(I) oxide (0.5 mmol) in 10 mL of dichloromethane was stirred in the absence of light at room temperature for 2 h. The resulting solution was filtered with the aid of a membrane filter and added to a solution of 0.34 g of Ni(PPh₃)₂Br₂ (0.5 mmol) in dichloromethane. A rapid color change from green to red occurred and stirring was continued for 30 min. The off-white precipitate that had formed was removed by filtration to give an orange solution, which was concentrated in vacuo until a red solid started to precipitate.

After filtration and washing with hexane the red product was recrystallized from DMF/diethyl ether; yield 0.15 g (42%). ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 300 K): δ = 7.55 (d, J = 4 Hz, 4 H, Ar-H), 7.29 (m, 16 H, Ar-H), 6.94 (s, 4 H, NCH), 6.09 (s, 8 H, NCH₂) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$, 300 K): δ = 169.0 (Ni-C), 136.9 (C_q), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 127.7 (C_{Ar}), 122.0 (NCH), 53.3 (NCH₂) ppm. IR (neat): $\tilde{\nu}$ = 3134 (w), 2930 (w), 1494 (w), 1452 (m), 1417 (m), 1342 (w), 1228 (m), 1150 (w), 1028 (w), 769 (w), 728 (m), 692 (s), 594 (m) cm^{-1} . $\text{C}_{34}\text{H}_{32}\text{Br}_2\text{N}_4\text{Ni}\cdot 0.25\text{DMF}$ (733.45): calcd. C 56.91, H 4.64, N 8.12; found C 57.01, H 5.06, N, 8.07. MS (ESI): m/z (%) = 676 (100) $[[\text{M} - \text{Br} + \text{MeCN}]^+]$.

Bis(*N*-methyl-*N'*-isopropylbenzimidazol-2-ylidene)dibromidonickel(II) (4b): Following the general synthesis, the complex was obtained from 1.28 g of benzimidazolium bromide **2b** (5.0 mmol) and 0.44 g of nickel(II) acetate (2.50 mmol) in 0.8 g of tetrabutylammonium bromide at 130 °C; yield 0.57 g (40%). ^1H NMR (300 MHz, 300 K, CDCl_3): δ = 7.50 (m, 2 H, Ar-H), 7.33–7.14 (m, 8 H, Ar-H + NCH), 4.72 (2 \times s, 6 H, NCH₃), 1.95 (2 \times d, J = 7 Hz, 12 H, CH₃) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl_3): δ = 183 (Ni-C), 136.7 (C_q), 132.7 (C_q), 122.0 (C_{Ar}), 121.8 (C_{Ar}), 111.7 (C_{Ar}), 109.7 (C_{Ar}), 54.0 (NCH₃), 34.2 (NCH), 21.2 (CH₃) ppm. IR (neat): $\tilde{\nu}$ = 2974 (w), 1484 (m), 1435 (m), 1386 (m), 1344 (m), 1293 (m), 1135 (m), 1092 (m), 780 (w), 744 (s), 564 (m) cm^{-1} . $\text{C}_{22}\text{H}_{28}\text{Br}_2\text{N}_4\text{Ni}$ (567.01): calcd. C 46.60, H 4.98, N 9.88; found C 46.55, H 4.97, N 9.79. MS (ESI): m/z (%) = 528 (100) $[[\text{M} - \text{Br} + \text{MeCN}]^+]$.

Bis(*N*-methyl-*N'*-isopropylbenzimidazol-2-ylidene)diiodidonickel(II) (4c): This complex was obtained following the general synthesis, starting from 0.50 g of benzimidazolium salt **2c** (1.65 mmol) and 0.14 g of nickel(II) acetate (0.82 mmol) in 0.4 g of tetrabutylammonium iodide at 155 °C; yield 0.25 g (46%). ^1H NMR (300 MHz, 300 K, CDCl_3): δ = 7.48 (m, 2 H, Ar-H), 7.31 (m, 2 H, Ar-H), 7.18 (m, 4 H, Ar-H), 6.90 (m, 2 H, NCH), 4.47 (2 \times s, 6 H, NCH₃), 1.91 (d, J = 7 Hz, 12 H, CH₃) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl_3): δ = 188.0 (Ni-C), 137.4 (C_q), 133.1 (C_q), 121.8 (C_{Ar}), 121.7 (C_{Ar}), 111.7 (C_{Ar}), 109.5 (C_{Ar}), 54.0 (NCH₃), 34.4 (NCH), 20.4 (CH₃) ppm. IR (neat): $\tilde{\nu}$ = 2975 (w), 1483 (w), 1436 (w), 1392 (m), 1351 (m), 1294 (m), 1137 (w), 1090 (m), 744 (s), 563 (m), 427 (m) cm^{-1} . $\text{C}_{22}\text{H}_{28}\text{I}_2\text{N}_4\text{Ni}$ (661.01): calcd. C 39.98, H 4.27, N 8.48; found C 39.85, H 4.36, N 8.26. MS (ESI): m/z (%) = 574 (100) $[[\text{M} - \text{I} + \text{MeCN}]^+]$.

Bis(*N*-methyl-*N'*-phenylbenzimidazol-2-ylidene)diiodidonickel(II) (4d): This complex was obtained following the general complex synthesis, starting from 0.20 g of benzimidazolium salt **2d** (0.6 mmol) and 53 mg of nickel(II) acetate (0.3 mmol) in 0.2 g of tetrabutylammonium iodide at 155 °C; yield 0.14 g (63%). ^1H NMR (300 MHz, 300 K, CDCl_3): δ = 8.17 (m, 4 H, CH_{Ph}), 7.75 (m, 4 H, CH_{Ph}), 7.67 (m, 2 H, CH_{Ph}), 7.21 (m, 4 H, CH_{Bim}), 7.13 (m, 4 H, CH_{Bim}), 4.06 (s, 6 H, NCH₃) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl_3): δ = 138.2 (C_q), 136.8 (C_q), 136.7 (C_q), 129.1 (C_{Ph}), 128.8 (C_{Ph}), 127.9 (C_{Ph}), 122.5 (C_{Bim}), 122.4 (C_{Bim}), 110.2 (C_{Bim}), 109.1 (C_{Bim}), 34.5 (NCH₃) ppm. IR (neat): $\tilde{\nu}$ = 3054 (w), 1597 (w), 1500 (m), 1435 (m), 1389 (m), 1339 (m), 1231 (m), 1090 (m), 917 (w), 750 (s), 695 (s), 613 (m), 554 (m), 490 (m) cm^{-1} . $\text{C}_{28}\text{H}_{24}\text{I}_2\text{N}_4\text{Ni}$ (729.05): calcd. C 46.13, H 3.32, N 7.69; found C 46.07, H 3.46, N 7.72. ESI (MS): m/z (%) = 642 (100) $[[\text{M} - \text{I} + \text{MeCN}]^+]$.

Bis(*N,N'*-diisopropylbenzimidazol-2-ylidene)diiodidonickel(II) (4e): The compound was prepared following the general procedure, from 3.90 g of *N,N'*-diisopropylbenzimidazolium iodide (11.8 mmol) and 1.04 g of nickel(II) acetate (5.9 mmol) in 2.0 g of tetrabutylammonium iodide at 155 °C; yield 1.26 g (30%). ^1H NMR (300 MHz, 300 K, CDCl_3): δ = 7.48 (m, 4 H, Ar-H), 7.12 (m, 4 H, Ar-H), 6.93 (sept, J = 7 Hz, 4 H, NCH), 1.88 (d, J = 7 Hz, 24 H, CH₃)

ppm. Due to the poor solubility, no ^{13}C NMR spectrum was recorded. IR (neat): $\tilde{\nu}$ = 2976 (w), 1472 (m), 1417 (m), 1385 (m), 1343 (m), 1306 (m), 1139 (m), 1095 (m), 745 (s), 551 (m) cm^{-1} . $\text{C}_{26}\text{H}_{36}\text{I}_2\text{N}_4\text{Ni}\cdot 2\text{H}_2\text{O}$ (753.15): calcd. C 41.46, H 5.35, N 7.44; found C 41.45, H 5.01, N 7.55. ESI (MS): m/z (%) = 630 (100) $[[\text{M} - \text{I} + \text{MeCN}]^+]$.

Typical Procedure for the Nickel-Catalyzed Hydrosilylation of Internal Alkynes: In a Schlenk tube at room temperature, 0.050 mmol nickel complex **3a** (25.2 mg) was dissolved/suspended in 5.0 mL of dry THF and 1.0 mmol 3-hexyne (82.1 mg) was added. Then, 0.20 mmol diethylzinc (1.0 M in hexanes, 0.20 mL) was added with stirring, followed by 2.0 mmol triethylsilane (232.5 mg). The tube was then placed in an oil bath, preheated to 50 °C and the mixture was kept at this temperature. The reaction was followed by taking samples at regular intervals, which were quenched by the addition of ethanol and which were analyzed by GC. In the initial studies heptane was added to the reaction mixture as an internal standard; as it appeared that only one product was obtained in all cases, for monitoring the conversion in time in the screening studies the relative intensities of the substrate and product were used.

To isolate the product after full conversion was reached, water was added to the reaction mixture and the product was extracted using ethyl acetate. After drying of the organic layer with magnesium sulfate, and removal of the solvents in vacuo, the residue was purified by column chromatography (silica gel, hexanes) to give the product, which analyzed as 3-triethylsilyl-*cis*-hex-3-ene, as a colorless oil;^[12] yield 186 mg (94%).

The mercury test was performed by the addition of 5.0 mmol mercury (1.0 g) to the reaction mixture, 30 min after the tube was transferred to the oil bath.

1,2-Diphenyl-1-triethylsilyl-*cis*-ethene (5): Following the procedure described above, the product was obtained from 178.2 mg of diphenylacetylene (1.0 mmol) and 232.5 mg of triethylsilane (2.0 mmol). The product was purified by column chromatography (silica gel, petroleum ether), and obtained as a colorless oil, which analyzed as 1,2-diphenyl-1-triethylsilyl-*cis*-ethene;^[12] yield 283 mg (96%).

(*E*)-1,4-Dimethoxy-2-triethylsilyl-2-butene (6): Following the procedure described above, the product was obtained starting from 114.1 mg of 1,4-dimethoxy-2-butyne (1.0 mmol) and 232.5 mg of triethylsilane (2.0 mmol). The product was purified by chromatography (silica gel, petroleum ether), and obtained as a colorless oil, which analyzed as (*E*)-1,4-dimethoxy-2-triethylsilyl-2-butene;^[15] yield 219 mg (95%).

(*E*)-1-Phenyl-1-(triethylsilyl)propene (7a): Following the procedure described above, the product was obtained starting from 116.2 mg of 1-phenyl-1-propyne (1.0 mmol) and 232.5 mg of triethylsilane (2.0 mmol). The product was purified by chromatography (silica gel, petroleum ether), and obtained as a colorless oil, which analyzed as (*E*)-1-phenyl-1-(triethylsilyl)propene;^[17] yield 167 mg (72%).

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