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# Catalysis of hydrosilylation[☆]

# Part XXXIV. High catalytic efficiency of the nickel equivalent of Karstedt catalyst $[\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}]$

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Dedicated to Professor Stanisław Pasynkiewicz, in recognition of his great contribution to organometallic chemistry

**Abstract**

The nickel equivalent of Karstedt catalyst $[\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}]$ (**1**) appeared to be a very efficient catalyst for dehydrogenative coupling of vinyl derivatives (styrene, vinylsilanes, vinylsiloxanes) with trisubstituted silanes $HSi(OEt)_3$, $HSiMe_2Ph$. The reaction occurs via three pathways of dehydrogenative coupling, involving formation of an unsaturated compound as the main product as well as a hydrogenated olefin (DS-1) pathway, hydrogenated dimeric olefin (DS-2) and dihydrogen (DC), respectively. The reaction is accompanied by side hydrosilylation. Stoichiometric reactions of **1** with styrene and triethoxysilane, in particular synthesis of the bis(triethoxysilyl) (divinyltetramethyldisiloxane) nickel complex **3** and the first documented insertion of olefin (styrene) into Ni–Si bond of complex **3**, as well as all catalytic data have allowed us to propose a scheme of catalysis of this complex reaction by **1**. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Silicon; Dehydrogenative (coupling) silylation; Hydrosilylation; Nickel complexes; Silanes

## 1. Introduction

The use of vinylsilicon compounds as ligands in organometallic chemistry is a relatively recent development. The silicone industry extensively uses highly active platinum catalysts, e.g. the silicone-soluble Karstedt catalyst, which is prepared by the reaction of chloroplatinic acid with vinylsilicon-containing compounds such as divinyltetramethyldisiloxane (LL) [1,2]. According to earlier by Lappert and co-workers, studies (at Sussex) the reaction mixture, obtained by mixing these two components, contained a bridging LL and each platinum had a chelating LL group $[\{Pt(LL)\}_2(\mu\text{-}LL)]$ [3]. The cost of platinum compounds stimulated much research to check other transition metal compounds as potential hydrosilylation catalysts. By analogy to the Karstedt catalyst, the nickel complex $[\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}]$ was obtained in the reaction between (*trans*,*trans*,*trans*-cyclododeca-1,5,9-triene)nickel(0) and LL [4,5]:

$$[Ni(\textit{trans,trans,trans}\text{-}CDT)] + 3LL \rightarrow \underset{\mathbf{1}}{[\{Ni(LL)_2\}(\mu\text{-}LL)]} + 2\text{-}\textit{trans,trans,trans}\text{-}CDT$$

Complex **1** was an orange crystalline solid, extremely soluble in both aliphatic and aromatic solvents, and was initially isolated from the reaction mixture as an oil. The solubility of **1** has thus far inhibited the isolation of single crystals suitable for X-ray diffraction.

Nickel complexes are well known as usually non-selective catalysts for hydrosilylation reactions of olefins [6]. The hydrosilylation is accompanied very often by the reaction of dehydrogenative coupling [7]. The dehy-

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[☆] For Part XXXIII, see Ref. [22].

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drogenative coupling of hydrosilanes with olefins is catalysed mainly by iron and cobalt triad members and proceeds via two pathways yielding unsaturated product (vinylsilane) and dihydrogen (dehydrocondensation) (Eq. (1)) and/or a hydrogenated olefin (dehydrogenative silylation) (Eq. (2)) as shown below:

$$HSiR_3 + CH_2{=}CHR' \rightarrow R'CH{=}CHSiR_3 + H_2 \tag{1}$$

$$HSiR_3 + 2CH_2{=}CHR' \rightarrow R'CH{=}CHSiR_3 + R'CH_2CH_3 \tag{2}$$

Although much data on the competitive hydrosilylation–dehydrogenative coupling reactions have been reported, examples of the exclusive (or at least highly selective) formation of vinylsilanes are still limited [8–10]. Vinylsilanes (alkenylsilanes) exhibit considerable synthetic utility in organic synthesis [11].

Our recent contribution to this field is the first example of the nickel-catalysed dehydrogenative silylation of vinylsubstituted silanes and styrene by triethoxysilane and triethylsilane occurring in the presence of [Ni(acac)$_2$], [Ni(cod)$_2$] and nickel phosphine complexes [12–16]. Besides the two above-mentioned pathways (Eqs. (1) and (2)), in the presence of nickel catalysts the dehydrogenative coupling occurs also via another route giving an unsaturated product and the product of hydrogenative dimerization of olefins, as follows:

$$3CH_2{=}CHR + HSiR'_3 \rightarrow RCH_2CH_2CH_2CH_2R + R'_3SiCH{=}CHR \tag{3}$$

where $R = SiR'_3$, Ph; $R' = OC_2H_5$, Et.

The aim of this work is to examine the catalytic system based on **1** in the reaction of trisubstituted silanes with various vinyl derivatives. We shall also describe a new, very useful method for the synthesis of **1**.

## 2. Experimental

### *2.1. Materials*

All reagents were dried and purified before use by the usual procedures. Triethoxysilane was obtained by alcoholysis of $SiHCl_3$ and purified to avoid the presence of traces of HCl. [Ni(cod)$_2$] was prepared as described in the literature [17]. Other chemicals were purchased as specified: divinyltetramethyldisiloxane $(CH_2{=}CHSiMe_2)_2O$, dimethylphenylsilane $HSiMe_2Ph$, vinyltrimethylsilane $CH_2{=}CHSiMe_3$, vinyltriethoxysilane $CH_2{=}CHSi(OC_2H_5)_3$ and styrene $CH_2{=}CHPh$ from Fluka, vinylmethylbis(trimethylsilyloxy)silane $CH_2{=}CHSiMe(OSiMe_3)_2$ and vinyltris(trimethylsilyloxy)silane, $CH_2{=}CHSi(OSiMe_3)_3$ from ABCR. Benzene (Fluka), *n*-pentane and diethyl ether (Merck) were purified by standard methods and distilled prior to use.

#### *2.1.1. Synthesis of* $[\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}]$ (**1**)

Divinyltetramethyldisiloxane (2 ml) was added slowly to a stirred red suspension of [Ni(cod)$_2$] (0.5 g, 1.8 mmol) in ether (10 ml) at ambient temperature. The suspension was dissolved and a yellow–red solution was obtained. The reaction mixture was stirred overnight. The volatiles were removed in vacuo to give an yellow–orange oil with the deposition of some colloidal nickel metal, which was taken up into pentane and filtered through Celite (2 × 2 ml). After concentration of the solution, the red oil of **1** was obtained (1.15 g, 95% yield).

Analytical data of **1**: $^1$H-NMR ($C_6D_6$, 298 K, 500 MHz); $\delta$ −0.35 (s, 6H, Me), −0.21 (s, 6H, Me), −0.04 (s, 6H, Me), 0.10 (s, 6H, Me), 0.41 (s, 6H, Me), 0.42 (s, 6H, Me), 2.94–3.91 (m, 18H, $CH_2{=}CH$), ${}^2J({}^1H_1-{}^1H_2) = 12.9$, ${}^2J({}^1H_1-{}^1H_3) = 16.8$ Hz. $^{13}C\{^1H\}$-NMR ($C_6D_6$, 298 K, 75.5 MHz); $\delta$ −3.0 (s, Me), −0.5 (s, Me), 0.0 (s, Me), 0.7 (s, Me), 65.5 (s, –CH=), 66.6 (s, =$CH_2$). $^{29}Si\{^1H\}$-NMR ($C_6D_6$, 231 K, 99.4 MHz); $\delta$ 6.4 (s), 1.6 (s), 7.5 (s). EI (MS): *m/z* 186 [27%, $(CH_2{=}CHSiMe_2)_2O^+$], 229 [42%, $Ni(CH_2{=}CHSiMeOSiMe_2CH{=}CH_2)^+$], 244 [34%, $Ni(CH_2{=}CHSiMe_2)_2O^+$], 430 [39%, $\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\text{–}(\mu\text{-}CH_2{=}CHSiMe_2)_2O\}^+$].

### *2.2. Stoichiometric reactions*

#### *2.2.1. Reaction of* **1** *with styrene — synthesis of* $[Ni\{(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}(\eta\text{-}CH_2{=}CHPh)]$ (**2**)

To a stirred solution of **1** (0.67 g, 1 mmol) in 10 ml of benzene (under argon, at room temperature), 0.23 ml (2 mmol) of styrene was added. After 4 h the reaction mixture was analysed by GC–MS and divinyltetramethyldisiloxane was detected. The volatiles were removed from the reaction mixture under reduced pressure and a red oil of **2** was obtained.

Analytical data of **2**: $^1$H-NMR ($C_6D_6$, 298 K, 300 MHz); $\delta$ −0.76 (s, 3H, Me), −0.34 (s, 3H, Me), 0.24 (s, 3H, Me), 0.33 (s, 3H, Me), 2.85–4.25 (m, 6H, $CH_2{=}CH$), 6.81–7.20 (m, Ph). $^{13}C\{^1H\}$-NMR ($C_6D_6$, 298 K, 75.5 MHz); $\delta$ −2.29 (s, Me), −1.28 (s, Me), 69.43 (s, –CH=), 70.28 (s, $CH_2$=), 114.06 (s, $CH_2$=), 137.8 (s, –CH=), 126.21–129.28 (m, Ph).

#### *2.2.2. Reaction of* **2** *with triethoxysilane — synthesis of* $[Ni\{(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}\{Si(OC_2H_5)_3\}_2]$ (**3**)

Triethoxysilane (1 ml) was added to a rapidly stirred red solution of **2** in benzene (15 ml). The reaction mixture was stirred for 4 h at 40°C. The volatiles were removed under reduced pressure. The residual deep-red oil was dissolved in pentane (10 ml) and filtered through Celite (2 × 2.5 ml), then washed with pentane (2 × 5 ml). The combined filtrate and washings were concentrated under reduced pressure and dried in vacuo for 8 h yielding a deep-red oil of **3**.

Analytical data of **3**: $^{1}$H-NMR ($C_6D_6$, 298 K, 300 MHz); $\delta$ 0.21 (s, 6H, Me), 0.35 (s, 6H, Me), 1.15 (t, 18H, Me), 2.26–2.72 (m, 6H), 3.83 (q, 12H, $-OCH_2$). $^{13}C\{^{1}H\}$-NMR ($C_6D_6$, 298 K, 75.5 MHz); $\delta$ −0.24 (s, Me), 1.52 (s, Me), 18.51 (s, Me), 58.78 (s, $-OCH_2$), 71.0 (s, $=CH_2$), 72.26 (s, $-CH=$).

### 2.3. Equipment and analytical measurements

The NMR spectra ($^{1}$H, $^{13}$C, $^{29}$Si) were recorded on a Varian XL 300 spectrometer. In all cases $C_6D_6$ was used as solvent; GC–MS analyses were carried out with a Varian 3300 chromatograph (equipped with a DB-1, 30 m capillary column), connected to a Finnigan Mat 700 mass detector. GC analysis was also carried out with a Varian 3800 chromatograph with a Megabore column (30 m, DB-1).

### 2.4. General procedure for the catalytic test

Catalyst **1** was placed in a glass ampoule (or Schlenk tube) and filled with a mixture of vinyl derivatives and triethoxysilane or dimethylphenylsilane. All manipulations were carried out using standard Schlenk and high vacuum line techniques.

Sealed ampoules (or Schlenk tubes) were heated at a given temperature. The distribution of substrates and products, conversion of substrates and the yield of products were determined by GC–MS and GLC analyses.

## 3. Results and discussion

### 3.1. Synthesis of 1

The new method for synthesis of **1** is based on the reaction of [Ni(cod)$_2$] with vinylsiloxane occurring as follows:

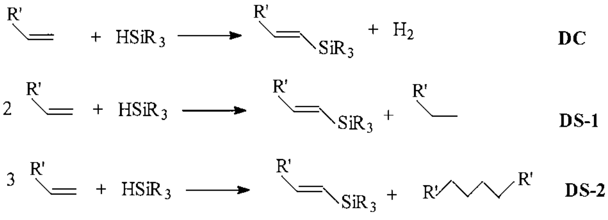
$$[Ni(cod)_2] + 3(CH_2{=}CHSiMe_2)_2O \rightarrow [\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\text{-}\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}] + 4\ cod \quad (4)$$

Cyclooctadiene, which is formed as a co-product, may be very easily removed under vacuum from the reaction mixture, thus a practically pure product is obtained. Moreover, the synthesis of [Ni(cod)$_2$] as a starting substance is relatively simple as compared with the *trans,trans,trans*-cyclododeca-1,5,9-trienenickel(0) — the starting material for synthesis of **1** in the previous method [4,5].

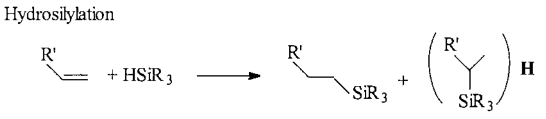
### 3.2. Catalytic examinations

Complex **1** was used as a catalyst in the reactions of some hydrosilanes, mainly $HSiMe_2Ph$ and $HSi(OEt)_3$ with vinyl derivatives, i.e. styrene and vinyltrisubstituted silanes and vinylsiloxanes.

The complex reaction proceeds according to Eqs. (5) and (6):



(5)



(6)

Thus, the three reactions of dehydrogenative coupling DC, DS-1 and DS-2 compete with regular hydrosilylation H. The amount of DS ($RCH{=}CHSiR_3$, mainly *E*-isomer) is equal to the sum of the second products of hydrogenative silylation of olefin DS-1, hydrogenative dimerization of olefin DS-2 and hydrogen evolved (not measured but calculated from DC = DS − (DS-1 + DS-2)). Besides, the presence of small amounts of tetrasubstituted silanes $SiR_4$ and siloxanes, as by-products coming from disproportionation of $HSi(OEt)_3$, and their condensation, are also observed.

Effects of temperature, reaction time and the substrate ratio on the yield and selectivity of this complex competitive process occurring in the presence of **1** and [Ni(cod)$_2$] (for comparison) are compiled in Table 1 (for triethoxysilane) and in Table 2 (for dimethylphenylsilane).

Our previous experience in the reaction of triethoxysilane with vinyltrisubstituted silanes (e.g. $(EtO)_3SiCH{=}CH_2$ and $Me_3SiCH{=}CH_2$) [12,15] and styrene [16] catalysed by [Ni(cod)$_2$] and [Ni(acac)$_2$] showed the preference of dehydrogenative silylation DS-1 and DS-2 over dehydrogenative coupling DC as well as over the hydrosilylation H.

However [Ni(cod)$_2$], [Ni(acac)$_2$] and particularly the latter activated by triethoxysilane complex, characterised as [(acac)Ni($C_2H_5$)PPh$_3$]-intermediate, appeared to be active but not selective catalysts in the dehydrogenative silylation of vinylsilanes, yielding the majority of side reactions such as hydrosilylation, redistribution and oxidation of hydrosilanes and condensation products [14,15].

On the other hand, dehydrogenative coupling of styrene with triethoxysilane occurs in the presence of [Ni(acac)$_2$] and [Ni(cod)$_2$] exclusively via DS-1 and DS-2 pathways and with relatively high selectivity compared to the hydrosilylation H [16]. Yet, application of **1** finds a much more efficient catalyst for dehydrogenative coupling (the yield and selectivity) than any of the reported earlier based on [Ni(acac)$_2$] and [Ni(cod)$_2$].

Similarly to [Ni(acac)$_2$] and [Ni(cod)$_2$] catalysts, the dehydrogenative coupling of vinylsubstituted silanes and siloxanes by triethoxysilane is based on dehydrogenative silylation (DS-1 and DS-2) and there is no direct dehydrocondensation process involved. The dehydrogenative silylation (DS) pathway dominates over hydrosilylation (H) in the case of all vinylsubstituted silanes and particularly siloxanes. The latter results are very promising for possible synthesis of unsaturated (poly)siloxanes, so supposedly under the optimum conditions it would be possible to elaborate procedures for

Table 1
Dehydrogenative coupling versus hydrosilylation of vinyl derivatives $CH_2{=}CHR$ with triethoxysilane catalysed by **1** and [Ni(cod)$_2$] [a]

| R | $T$ (°C) | $t$ (h) | Yield (%) | Product distribution (%) | | | Ratio DC:DS-1:DS-2 |
|---|---|---|---|---|---|---|---|
| | | | | DS | H | Others | |
| Ph | 120 | 0.5 | 92 | 85 | 13 | 2 | 0.55:0.32:0.13 |
| | 120 [b] | 0.5 | 100 | 88 | 10 | 2 | 0.26:0.50:0.24 |
| | 120 [d] | 0.5 | 52 | 79 | 10 | 2 | 0.20:0.46:0.34 |
| | r.t. | 50 | 49 | 79 | 19 | 2 | 0.31:0.50:0.19 |
| | r.t. [d] | 50 | 32 | 83 | 8 | 2 | 0.35:0.46:0.19 |
| | r.t. | 120 | 68 | 81 | 17 | 9 | 0.32:0.49:0.19 |
| $Si(OC_2H_5)_3$ | 120 | 0.5 | 56 | 98 | 0 | 2 | 0.01:0.53:0.46 |
| | 120 | 2 | 95 | 81 | 12 | 7 | 0.16:0.60:0.24 |
| $SiMe_3$ | 120 | 2 | 100 | 91 | 4.5 | 4.5 | 0:0.80:0.20 |
| | 120 [d] | 2 | 61 | 70 | 21 | 9 | 0:0.63:0.37 |
| $Si(OSiMe_3)_3$ | 120 | 0.5 | 100 | 96 | 4 | Trace | 0.10:0.80:0.10 |
| | 120 [d] | 0.5 | 40 | 72 | 19 | 9 | 0.17:0.45:0.38 |
| | r.t. | 24 | 18 | 100 | 0 | Trace | 0:077:0.23 |
| | r.t. | 120 | 74 | 93 | 7 | Trace | 0:0.69:0.31 |
| $SiMe(OSiMe_3)_2$ | 120 | 0.5 | 88 | 92 | 6 | 2 | 0.12:088:0 |
| | 120 [c] | 0.5 | 43 | 85 | 13 | 2 | 0.34:0.66:0 |

[a] $[HSi\equiv]:[CH_2{=}CHR]:[cat] = 1:2:10^{-3}$, argon, glass ampoules.
[b] $[HSi\equiv]:[CH_2{=}CHR] = 1:3$.
[c] $[HSi\equiv]:[CH_2{=}CHR] = 1:1$.
[d] [Ni(cod)$_2$].

Table 2
Dehydrogenative coupling versus hydrosilylation of vinyl derivatives $CH_2{=}CHR$ with dimethylphenylsilane catalysed by **1** and [Ni(cod)$_2$] [a]

| R | $T$ (°C) | $t$ (h) | Yield (%) | Product distribution (%) | | Ratio DC:DS-1:DS-2 |
|---|---|---|---|---|---|---|
| | | | | DS | H | |
| Ph | 120 | 1 | 83 | 91 | 9 | 0.45:0.55:0 |
| | 120 [d] | 1 | 65 | 84 | 16 | 0.24:0.45:0.31 |
| | r.t. | 96 | 18 | 79 | 21 | 0.56:0.44:0 |
| | r.t. [d] | 96 | Trace | Trace | – | – |
| | 120 [b] | 0.5 | 37 | 84 | 16 | 0.71:0.29:0 |
| $Si(OC_2H_5)_3$ | 120 | 2 | 63 | 37 | 63 | 0:0.75:0.25 |
| $SiMe_3$ | 120 | 24 | 100 | 58 | 42 | 0.39:0.33:0.28 |
| | 120 [d] | 24 | 55 | 36 | 57 | 0.25:0.45:0.30 |
| | 120 [c] | 0.5 | 61 | 79 | 21 | 0.43:0.42:0.15 |
| $Si(OSiMe_3)_3$ | 120 | 0.5 | 75 | 72 | 28 | 0:0.16:0.84 |
| | 60 | 24 | 95 | 89 | 11 | 0.02:0.14:0.84 |

[a] $[HSi\equiv]:[CH_2{=}CHR]:[cat] = 1:2:10^{-3}$, argon, glass ampoules.
[b] $[HSi\equiv]:[CH_2{=}CHR] = 1:3$.
[c] $[HSi\equiv]:[CH_2{=}CHR] = 1:1$.
[d] [Ni(cod)$_2$].

highly selective dehydrogenative coupling (silylation) of all vinylsubstituted silanes and siloxanes with quantitative conversion of hydrosilanes (e.g. triethoxysilane).

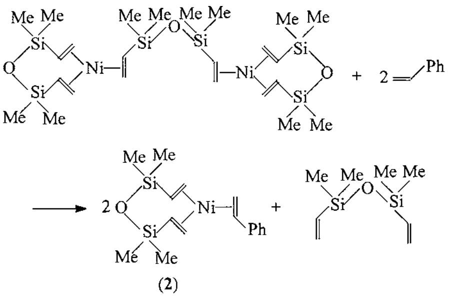
Dehydrogenative coupling of styrene by $HSi(OEt)_3$ occurs in the presence of **1** and in excess of styrene with very high efficiency (0.5 h, 120°C, 100% yield) and also high selectivity (see compared with $[Ni(cod)_2]$ catalyst) but apparently in this case *E*-1-phenyl-2-silyl-ethene is also formed via dehydrocondensation. In the case of all vinylsubstituted silanes and siloxanes, the process is also regioselective (1,2-derivatives of ethene are noted exclusively) but the stereoselectivity *E*/*Z* exceeds ten.

Contrary to triethoxysilane, dimethylphenylsilane reacts with all vinylsubstituted silicon compounds in the presence of **1** with low selectivity, yielding a mixture of dehydrogenative silylation (coupling) and hydrosilylation products, yet, with higher efficiency than those reported earlier in the presence of other nickel catalysts. Interestingly, dehydrogenative coupling of styrene by $HSiMe_2Ph$ is efficiently catalysed (at 120°C) with high selectivity of DS products, but the process proceeds by the pathways DS-1 and DC. There is no 1,3-diphenylbutane (product of hydrogenated dimerization of styrene) observed in the reaction mixture.

Finally, it is worth emphasising that contrary to the case when $[Ni(acac)_2]$- and $[Ni(cod)_2]$-based catalysts are used, there is no precipitation of nickel products after completion of the reaction catalysed by **1**. Apparently, divinylsiloxane chelate keeps Ni(0) molecule in solution, being still active in reactions examined and can be regenerated.

### 3.3. Reactions of 1 with substrates under the conditions of catalysis

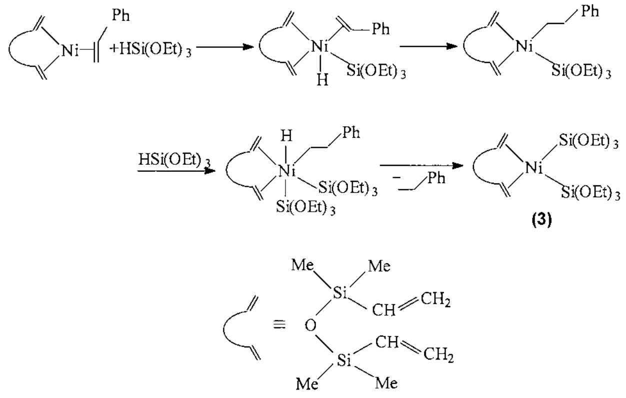
In order to explain the role of **1** in the complex dehydrogenative coupling–hydrosilylation process, a separate study on the reaction of **1** with styrene and $HSi(OEt)_3$ at ambient temperature was undertaken, under oxygen-free conditions; **1** reacts with styrene according to Eq. (7):



(7)

$^1$H- and $^{13}$C-NMR characterisation of the isolated product **2** reveals a formation of trigonal π-complex of nickel(0). The signals from vinyl groups (from styrene and $(CH_2{=}CHSiMe_2)_2O$) in $^1$H-NMR, were observed between 2.85 and 4.25 ppm, which is evidence of coordination of all these groups to the metal centre (see Section 2.2.1).

Complex **2** was subjected to the reaction in excess of triethoxysilane for 4 h at 40°C. In the reaction mixture, ethylbenzene was detected by GC–MS analysis. After removal of volatiles the product was isolated and characterised by $^1$H- and $^{13}$C-NMR. In the NMR spectra, the signals from two triethoxysilyl groups and one molecule of divinyltetramethyldisiloxane were observed (see Section 2.2.2). This experiment permits us to propose Eq. (8) for initiation of active intermediate unisolable under the catalytic conditions.



(8)

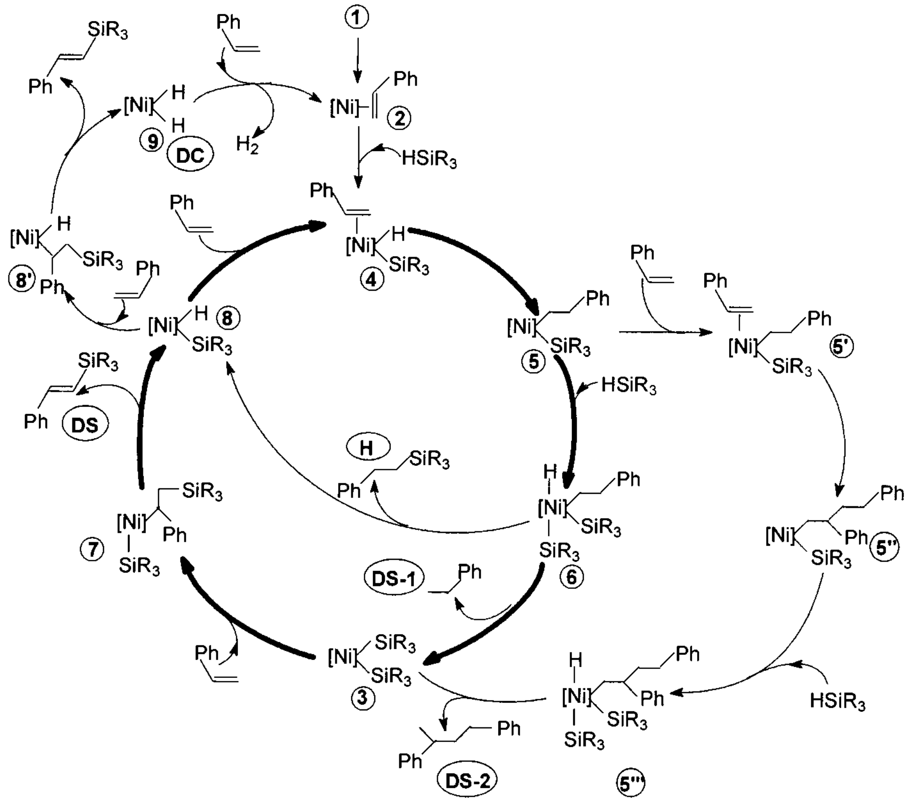
Additionally, the reaction of **3** with excess of styrene, at 40°C for 4 h, was carried out. After the reaction, the product of DS (1-phenyl-2-silylethene) was detected by the GC–MS method, which evidences the insertion of a styrene molecule into the Ni–Si bond

### 3.4. Mechanistic implications

Although the Chalk–Harrod mechanism for hydrosilylation has been widely accepted, the fact that it does not explain the formation of alkenylsilanes led to proposals of alternative mechanisms, e.g. Seitz and Wrighton mechanism [18,19]. The key step of this mechanism involves insertion of an alkene into a metal–silicon bond (or migration of silyl group, to a coordinated alkene molecule). The elimination of vinylsilane and regeneration of the M–H complex may support the dehydrogenative pathway of the hydrosilylation processes [6,19].

However, in the case of nickel-catalysed reactions, a stable complex containing one silyl group bonded to nickel atom has not been isolated yet.

On the other hand, only a few stable bis(silyl)nickel complexes, e.g. $[Ni(SiCl_3)_2(bipy)]$ [19,20] and bis(silyl)nickel complexes with *o*-carboranyl units [21] were evidenced to be intermediates in facile double silylation of alkynes. Our previous study on the reaction of $[Ni(acac)_2]$ with triethoxysilane in the presence of $PPh_3$ under oxygen-free conditions permitted isolation of the



Scheme 1.

intermediate containing no Ni–Si bond (i.e. [Ni(acac)Et(PPh$_3$)]) [15], which is active in the dehydrogenative silylation but only after prior oxygenation of PPh$_3$.

Present examination of a new chelating system of nickel, i.e. **1** with triethoxysilane, afforded a double silyl complex **3**, which appeared to be an active intermediate just in the dehydrogenative coupling (silylation) of olefins. In view of the data from the catalytic and stoichiometric examinations, we propose a mechanistic scheme (Scheme 1) for this complex reaction catalysed by **1**, using the exemplary system of reagents styrene–triethoxysilane.

Initiation occurs via the transformation **1** → **2** and after the next oxidative addition, complex **4** starts the catalytic cycle. The insertion of styrene into the Ni–H bond gives the σ-complex **5**. The two subsequent competitive reactions can proceed: the oxidative addition of the next hydrosilane molecule to yield **6** and/or coordination of the next molecule of styrene followed by its insertion into Ni–C in **5**″ giving finally (after the oxidative addition of HSi≡) the product of hydrogenative dimerization (DS-2). That the insertion of styrene into Ni–C in (**5**′) is favoured over that into the Ni–Si bond is evidenced by the absence of silylbutanes (or silylbutenes) among the products, which if present should be eliminated after the latter rearrangement. According to the stoichiometric studies, **6** → **3** is proposed with elimination of ethylbenzene (DS-1 pathway). Alternatively (competitively) an elimination of 1,2-phenylsilylethane, as the hydrosilylation by-product, can lead to complex **8**. The latter is formed via the main pathway of dehydrogenative silylation **3** → **8** involving a classical insertion of styrene into one of Ni–Si bonds and yielding the main product — silylstyrene. Contrary to the reported data on the insertion of alkenes [18] into such a complex, and in agreement with the results concerning olefin insertion [19], we do not observe any products of bis(silylation).

Coordination of styrene to complex **8** closes the catalytic cycle discussed. Dehydrocondensation (DC) observed in the case of the reaction with styrene can be accounted for by the side cycle involving the preferred insertion of styrene into Ni–Si bond of **8** to give dihydrido-intermediate **9**, very easily decomposed to evolve dihydrogen and regenerate complex **2**.

In the reactions catalysed by other Ni complexes, the appearance of the products of redistribution of trisubstituted silanes, in particular those containing alkoxy groups, and their condensation have been commonly observed as competing to the main reactions, while in the process catalysed by **1**, these side reactions are negligible.

## 4. Conclusions

1. [{Ni(η - $CH_2$=CHSi$Me_2$)$_2$O}$_2${μ - ( - η - $CH_2$=CHSi - $Me_2$)$_2$O}] (**1**) after prior dissociation and olefin coordination appeared to be a very efficient (high yield and selectivity and stability, i.e. non-reduced to the metal under catalysis conditions) catalyst for dehydrogenative coupling of vinyl derivatives (styrene, vinylsilanes, vinylsiloxane) particularly with triethoxysilane.
2. Three pathways of dehydrogenative coupling DS-1, DS-2 and DC of selected olefins (e.g. styrene) are documented, involving the formation of unsaturated product (e.g. *E*-1-phenyl-2-silylethene) as well as hydrogenated olefin (e.g. ethylbenzene) (DS-1), hydrogenated dimeric product (e.g. 1,3-diphenylbutane) (DS-2) and dihydrogen (as a product of dehydrocondensation) (DC), respectively.
3. Catalytic examinations and stoichiometric reactions of **1** with styrene and triethoxysilane have made grounds for the mechanistic scheme proposed.
4. The insertion of styrene into Ni–Si of the bis(silyl)divinyltetramethyldisiloxane) nickel complex is documented as the first evidence for insertion of olefins into a nickel–silicon bond.
5. The first evidence of high catalytic activity of nickel complex **1** in the hydrosilylation and related reactions (dehydrogenative coupling especially of vinyl derivatives) raises hopes that the Karstedt platinum complex might be replaced by nickel complexes of type **1**, used as a catalyst for various reactions, e.g. cross-linking of vinylsubstituted silicones, synthesis of alkenylsilanes and reagents in organic synthesis.

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