

# Dehydrogenative coupling of styrene with trisubstituted silanes catalyzed by nickel complexes <sup>1</sup>

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Received 2 September 1997; accepted 27 November 1997

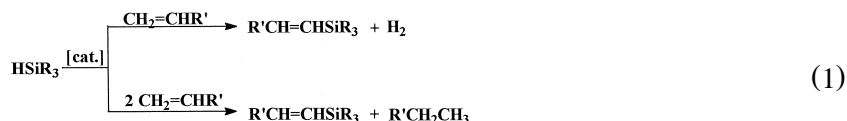
## Abstract

Trisubstituted silanes, e.g.,  $\text{Me}_n(\text{EtO})_{3-n}\text{SiH}$  (where  $n = 0-2$ ) and  $\text{Me}_2\text{PhSiH}$  in the presence of nickel complexes, e.g.,  $[\text{Ni}(\text{acac})_2]$  and  $[\text{Ni}(\text{cod})_2]$ , undergo two reactions of dehydrogenative silylation of styrene to yield in both cases an unsaturated product—*E*-1-phenyl-2-silyl-ethene as well as products of styrene hydrogenation—ethylbenzene DS-1 and of hydrogenative dimerization of styrene—1,3-diphenylbutane—DS-2. The two reactions are accompanied by the hydrosilylation products H as well as redistribution of the silanes containing at least one ethoxy substituent. The catalytic examinations and identification of nickel square planar complexes suggest that the intermediates containing Ni–Si (I), Ni–H (II) and Ni–C (III) bonds are responsible for the catalysis. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Dehydrogenative coupling; Silylation; Styrene; Nickel-complex catalyst

## 1. Introduction

The dehydrogenative coupling of hydrosilanes with olefins proceeds via two pathways yielding unsaturated product (vinylsilane) and hydrogen (dehydrocondensation) and/or a hydrogenated olefin (dehydrogenative silylation) as shown below (Eq. (1)), and is usually accompanied by hydrosilylation products [2];



Complexes of iron- and cobalt-triad members—i.e., Fe, Ru, Os and Co, Rh, Ir—appeared to be extremely favourable catalysts for the heterocoupling of hydrosilanes with olefins [3].

However, the number of examples of exclusive (or highly selective) formation of vinylsilanes is still limited.  $[\text{Ru}_3(\text{CO})_{12}]$ ,  $[\text{Fe}_3(\text{CO})_{12}]$  [4–6] and cationic rhodium complexes [7] catalyzed dehydro-

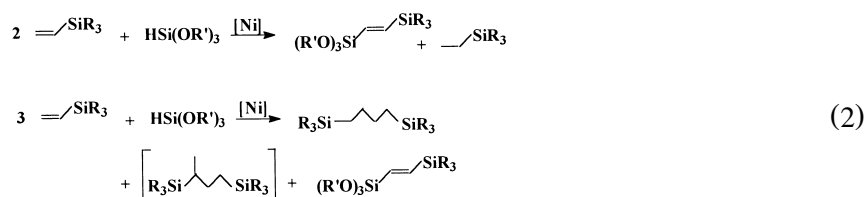
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<sup>1</sup> Part XXXII in the series 'Catalysis of Hydrosilylation', for Part XXXI see Ref. [1].

genative silylation of styrene and of vinylsilane with  $\text{HSiEt}_3$  [8] as well as  $[\text{Fe}(\text{CO})_5]$  [9] and particularly  $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$  [10] catalyzed reaction of ethylene with  $\text{HSiEt}_3$  are the most convincing examples.

Pt [11], Pd [12] and Ni [13,14] complexes are exceptionally applied for catalysis of dehydrogenative coupling as the main direction of the complex reactions. Also, the early transition metal compounds have recently been reported as efficient catalysts of this reaction [15,16].

Our recent contribution to the field is the first successful attempt of nickel(0) and nickel(II) catalyzed dehydrogenative silylation of vinylsubstituted silanes by triethoxysilane and triethylsilane. In the excess of vinylsilanes over triethoxysilane, the reaction catalyzed by  $[\text{Ni}(\text{acac})_2]$ ,  $[\text{Ni}(\text{cod})_2]$  and other Ni-complexes yields in the temperature range 80–120°C predominantly products of dehydrogenative silylation according to the following equations [13,14,17]:



The latter reaction is quite a new pathway of dehydrogenative silylation leading to unsaturated product and the product of hydrogenative dimerization of vinylsilane.

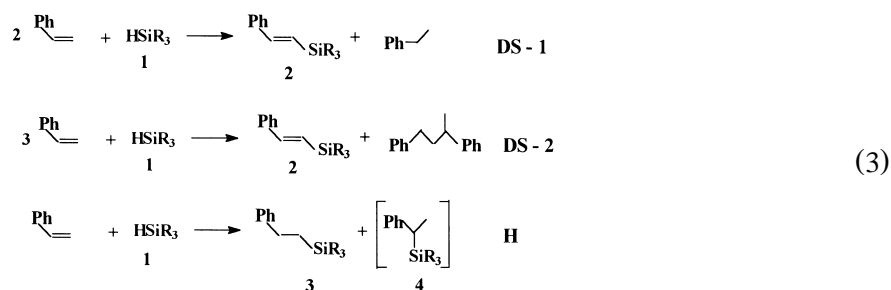
Most side reactions such as regular hydrosilylation, redistribution of hydrosilanes and reactions of unsaturated products with hydrosilanes can be practically excluded under the optimum conditions [17]. Separate study on the reaction of  $\text{Ni}(\text{acac})_2$  with triethoxysilane in the presence of  $\text{PPh}_3$  permitted isolation of  $[\text{Ni}(\text{acac})\text{Et}(\text{PPh}_3)]$  (**A**) [18] which appeared to be an intermediate in the  $[\text{Ni}(\text{acac})_2] + \text{PPh}_3$  catalyzed reaction. The (**A**) is very active at room temperature, but only after preliminary oxygenation of the coordinated triphenylphosphine [19].

All the stoichiometric and catalytic reactions of (**A**) with substrates allow us to propose the catalytic cycle involving competitive insertion of vinylsilane molecule into Ni–Si, Ni–H as well as Ni–C bonds [19].

The aim of this work is to examine the catalytic systems based on  $[\text{Ni}(\text{acac})_2]$  and  $[\text{Ni}(\text{cod})_2]$  in the reaction of trisubstituted silanes, mostly containing at least one alkoxy substituent, with styrene in order to find products of dehydrogenative silylation.

## 2. Results and discussion

The reaction of styrene with trisubstituted silanes containing at least one alkoxy group at silicon, e.g.,  $\text{HSi}(\text{OEt})_3$ , in the presence of Ni(0) and Ni(II) complexes in the range 20–120°C occurs according to the following equations;



The organosilicon products are numbered. Besides, tetrasubstituted silanes  $\text{SiR}_4$  (**5**) and siloxanes are also observed as products of the  $\text{HSiR}_3$  disproportionation as well as oxygenation and hydrolysis of the  $\equiv\text{Si}-\text{O}-\text{C}-$  bond, followed by further condensation.

Thus, two reactions of dehydrogenative silylation DS-1 and DS-2 compete with regular hydrosilylation H. *E*-1-phenyl-2-silyl-ethene (**2**), the main product yielded, comes from the two reactions—DS-1 and DS-2. The amount of (**2**) was almost equal to a sum of the second products of the reactions DS-1 and DS-2, i.e., ethylbenzene and 1,3-diphenylbutane. The latter is an exclusive isomer formed by hydrogenative dimerization of styrene. Our previous experience in the reaction of vinylsilane with hydrosilanes indicated it was worth using triethoxysilane (**1a**) as a initial substance.

It could be expected that the kind of the nickel precursor as well as the ratio of styrene and triethoxysilane affected markedly the selectivity of the above mentioned reactions as well as, finally, their products. The effect is summarized in Table 1.

The hydrogenative silylation pathway DS dominates over the hydrosilylation one H only in the presence of  $[\text{Ni}(\text{acac})_2]$  and  $[\text{Ni}(\text{cod})_2]$  as the initial catalysts. The excess of styrene leads not only to an increase in the total conversion of triethoxysilane (**1a**) but obviously, to increase in the yield of the unsaturated product (**2a**), and also the ratio of (**2a**) to the hydrosilylation products (**3a** + **4a**). Under the optimum conditions, i.e., when  $[\text{SiH}]_o : [\text{styrene}]_o = 1:2 \rightarrow 1:3$  the dehydrogenative silylation takes place along both pathways DS-1 and DS-2. The amounts of ethylbenzene and 1,3-diphenylbutane as the second products of the DS-1 and DS-2 pathways, respectively, (Eq. (3)) are also proportionally increased (see Section 3).  $[\text{NiI}_2(\text{PPh}_3)_2]$  and  $[\text{NiCp}_2]$  are more favourable catalysts of the hydrosilylation H and the redistribution of (**1a**) than the dehydrogenative silylation DS. In the presence of nickel phosphine complexes such as  $[\text{NiCl}_2(\text{PPh}_3)_2]$ ,  $[\text{Ni}(\text{SCN})_2(\text{PPh}_3)_2]$ ,  $[\text{Ni}(\text{NO}_3)_2(\text{PPh}_3)_2]$  and  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  only products of styrene polymerization and the redistribution of silane are observed.

The results of the catalysis by  $[\text{Ni}(\text{acac})_2]$  and  $[\text{Ni}(\text{cod})_2]$  clearly show that styrene acts as a hydrogen acceptor. The dehydrogenative silylation pathways DS-1 and DS-2 are competitive with the hydrosilylation. Thus, we have focused on developing a highly selective dehydrogenative silylation as well as increased total yield of the reaction. The selectivity is slightly sensitive to the reaction temperature (Table 2). However, the reaction occurs effectively even at room temperature although it is accompanied not only by hydrosilylation but also by silane redistribution products.

Table 1

Effect of the kind of nickel catalyst and the molar ratio of substrates on competitive dehydrogenative silylation and hydrosilylation of styrene with triethoxysilane

| Catalyst                         | Styrene (mmol) | Yield <sup>a</sup> (%) | Product distribution <sup>b</sup> (%) |           |           |           |
|----------------------------------|----------------|------------------------|---------------------------------------|-----------|-----------|-----------|
|                                  |                |                        | <b>2a</b>                             | <b>3a</b> | <b>4a</b> | <b>5a</b> |
| $[\text{Ni}(\text{acac})_2]$     | 6              | 55                     | 74                                    | 14        | 3.5       | 3.5       |
|                                  | 12             | 80                     | 76                                    | 8         | 2         | 6         |
|                                  | 18             | 78                     | 81                                    | 9         | 2         | 2         |
| $[\text{NiI}_2(\text{PPh}_3)_2]$ | 6              | 80                     | 51                                    | 31        | 4.5       | 6.5       |
|                                  | 6              | 59                     | 19                                    | 42        | 0         | 30        |
| $[\text{Ni}(\text{cod})_2]$      | 6              | 52                     | 70                                    | 14        | 4.5       | 6.5       |
|                                  | 12             | 76                     | 79                                    | 8         | 2         | 6.5       |
|                                  | 18             | 84                     | 82                                    | 9         | 2         | 2         |
| $[\text{Ni}(\text{Cp})_2]$       | 6              | 69                     | 19                                    | 25        | 0         | 44        |

Reaction conditions: 120°C, 1 h, argon, without solvent,  $[\text{HSi}\equiv]:[\text{Ni}] = 1.5 \times 10^{-3}$ ,  $[\text{HSi}(\text{OEt})_3] = 6$  mmole.

<sup>a</sup>The yield is calculated from the  $\text{HSi}(\text{OEt})_3$  consumed, determined by GLC.

<sup>b</sup>For products notation see text.

Table 2

The effect of temperature on the yield and selectivity of the nickel-complex catalyzed dehydrogenative silylation of styrene with triethoxysilane

| Conditions                    | Yield (%) | Product distribution (%) |     |     |     |
|-------------------------------|-----------|--------------------------|-----|-----|-----|
|                               |           | 2a                       | 3a  | 4a  | 5a  |
| <b>[Ni(acac)<sub>2</sub>]</b> |           |                          |     |     |     |
| 120°C, 4 h                    | 92        | 77                       | 12  | 1   | 6   |
| 80°C, 4 h                     | 86        | 80                       | 11  | 1.5 | 3   |
| 80°C, 6 h                     | 90        | 82                       | 12  | 0   | 3.5 |
| RT, 100 h                     | 0         | 0                        | 0   | 0   | 0   |
| RT, 100 h <sup>a</sup>        | 74        | 64                       | 12  | 2.5 | 16  |
| Reflux, 1 h                   | 66        | 80                       | 7   | 5   | 3.5 |
| <b>[Ni(cod)<sub>2</sub>]</b>  |           |                          |     |     |     |
| 120°C, 4 h                    | 83        | 83                       | 10  | 1.5 | 5   |
| 80°C, 4 h                     | 64        | 83                       | 9.5 | 1.5 | 2   |
| 80°C, 6 h                     | 65        | 83                       | 9.5 | 1.5 | 2.5 |
| RT, 50 h                      | 32        | 83                       | 4   | 1.5 | 9   |
| RT, 50 h <sup>a</sup>         | 8         | 53                       | 12  | 4.5 | 25  |
| Reflux, 1 h                   | 60        | 91                       | 4.5 | 3.5 | 1   |
| Reflux, 2 h                   | 67        | 83                       | 7   | 6   | 5   |

Reaction conditions: [HSi≡]:[styrene]:[Ni] = 1:2:5 × 10<sup>-3</sup>, under argon.

<sup>a</sup>[HSi≡]:[styrene] = 1:1.

It is well known that the reactivity of the Si–H bond in the competitive silylation and hydrosilylation reactions as well as their selectivity can be influenced by substituents at the silicon atom [2]. Therefore, some trisubstituted silanes were used in the reaction studied in the presence of both catalysts [Ni(acac)<sub>2</sub>] and [Ni(cod)<sub>2</sub>]. Results are summarized in Table 3.

Under the conditions studied, triethylsilane causes a reduction of [Ni(acac)<sub>2</sub>] and decomposition of [Ni(cod)<sub>2</sub>] to give metallic nickel, which does not catalyze the hydrosilylation and/or dehydrogenative silylation. The rest of silanes include at least one electronwithdrawing substituent (EtO and Ph) at the silicon. While in the presence of Ni(0) complex there is no change in catalytic activity and

Table 3

The effect of substituents at silicon on the nickel-complex catalyzed dehydrogenative silylation of styrene with trisubstituted silanes (R<sub>3</sub>SiH)

| R <sub>3</sub>                | Yield (%) | Product distribution (%) |    |    |     |
|-------------------------------|-----------|--------------------------|----|----|-----|
|                               |           | 2a                       | 3a | 4a | 5a  |
| <b>[Ni(acac)<sub>2</sub>]</b> |           |                          |    |    |     |
| Et <sub>3</sub>               | 0         | 0                        | 0  | 0  | 0   |
| Me <sub>2</sub> (EtO)         | 10        | 18                       | 0  | 0  | 40  |
| Me(EtO) <sub>2</sub>          | 35        | 92                       | 7  | 1  | 0   |
| (EtO) <sub>3</sub>            | 80        | 76                       | 8  | 2  | 6   |
| Me <sub>2</sub> Ph            | 41        | 71                       | 14 | 15 | 0   |
| <b>[Ni(cod)<sub>2</sub>]</b>  |           |                          |    |    |     |
| Et <sub>3</sub>               | 0         | 0                        | 0  | 0  | 0   |
| Me <sub>2</sub> (EtO)         | 71        | 83                       | 8  | 1  | 4   |
| Me(EtO) <sub>2</sub>          | 76        | 85                       | 8  | 1  | 3.5 |
| (EtO) <sub>3</sub>            | 76        | 79                       | 8  | 2  | 6.5 |
| Me <sub>2</sub> Ph            | 65        | 84                       | 9  | 7  | 0   |

Reaction conditions: 120°C; 1 h; [HSi≡]:[styrene]:[Ni] = 1:2:5 × 10<sup>-3</sup>, under argon.

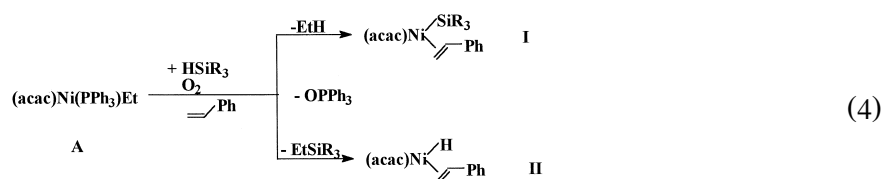
selectivity of products for all trisubstituted silanes (except  $\text{Et}_3\text{SiH}$ ), the total yield of DS and H in  $[\text{Ni}(\text{acac})_2]$  catalyzed reaction strongly depends on the presence of electronegative substituents (e.g., EtO) at the silicon.

Lowering the number of EtO group in the hydrosilane implies a decrease also in their yield in the reaction with styrene. Replacement of ethoxy on phenyl group in  $\text{Me}_2\text{R}'\text{SiH}$  (where  $\text{R}' = \text{EtO}$  and/or Ph) activates particularly  $[\text{Ni}(\text{acac})_2]$  precursor in the reaction examined.

Earlier examinations of  $[\text{Ni}(\text{acac})_2]\text{-HSi}(\text{OEt})_3\text{-PPh}_3$  system, allowed an isolation and identification of the square planar red complex  $[\text{Ni}(\text{acac})(\text{PPh}_3)\text{Et}]$  (**A**) being an active intermediate in dehydrogenative silylation of vinylsilanes [19] (after prior oxygenation of  $\text{PPh}_3$ ).

Regardless of the method used for preparation of complex **A** (**A1** or **A2**) appeared to be an intermediate also in the reaction of trisubstituted silanes containing alkoxy group with styrene, but only after elimination of phosphine by its oxygenation (Table 4).

So, similarly to the mechanism of dehydrogenative silylation of vinylsilanes under catalytic conditions of the reaction of tri(methyl, ethoxy)silanes with styrene, the following complexes (I) and (II) (Eq. (4)) can be generated which are directly responsible for the catalytic cycle postulated in Eq. (6).



Contrary to silylation of vinylsilanes catalyzed by  $[\text{Ni}(\text{acac})_2]$ , such a reaction of trisubstituted silanes with styrene occurs also at room temperature. Apparently a formation of the square planar Ni complex of the (**A**) and/or (I, II) type structure can be generated and this complex can remain in solution even in the absence of  $\text{PPh}_3$ . So, such system can be active even at room temperature (in argon).

Another difference between silylation of vinylsilane and styrene in the presence of  $[\text{Ni}(\text{acac})_2]$  is the inactivity of dimethylphenylsilane with the former and its relatively mild activity with latter one (Table 3). Direct formation of Ni–Si intermediates in the reaction of  $[\text{Ni}(\text{acac})_2]$  with  $\text{HSiR}_3$  seems to

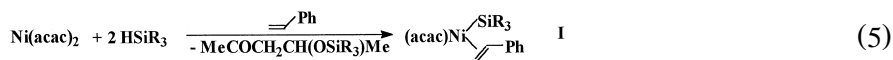
Table 4

The catalytic activity of **A1** and **A2** in the dehydrogenative silylation of styrene with triethoxysilane

| Catalyst  | Time (h)         | Yield (%) | Product distribution [%] |     |     |      |           |
|-----------|------------------|-----------|--------------------------|-----|-----|------|-----------|
|           |                  |           | 2a                       | 3a  | 4a  | 5a   | Siloxanes |
| <b>A1</b> | 1 <sup>a</sup>   | 0         | 0                        | 0   | 0   | 0    | 0         |
|           | 22 <sup>b</sup>  | 20        | 50                       | 4.5 | 1.5 | 14.5 | 29        |
|           | 44 <sup>b</sup>  | 32        | 65                       | 5   | 2.0 | 12.5 | 17        |
|           | 110 <sup>b</sup> | 51        | 72                       | 5   | 2   | 10   | 11        |
|           | 110 <sup>a</sup> | 0         | 0                        | 0   | 0   | 0    | 0         |
| <b>A2</b> | 1 <sup>a</sup>   | 0         | 0                        | 0   | 0   | 0    | 0         |
|           | 18 <sup>b</sup>  | 17        | 64                       | 6   | 3   | 9    | 18        |
|           | 50 <sup>b</sup>  | 25        | 68                       | 8   | 4   | 8    | 12        |
|           | 110 <sup>b</sup> | 36        | 71                       | 8   | 4   | 8    | 9         |
|           | 110 <sup>a</sup> | 0         | 0                        | 0   | 0   | 0    | 0         |

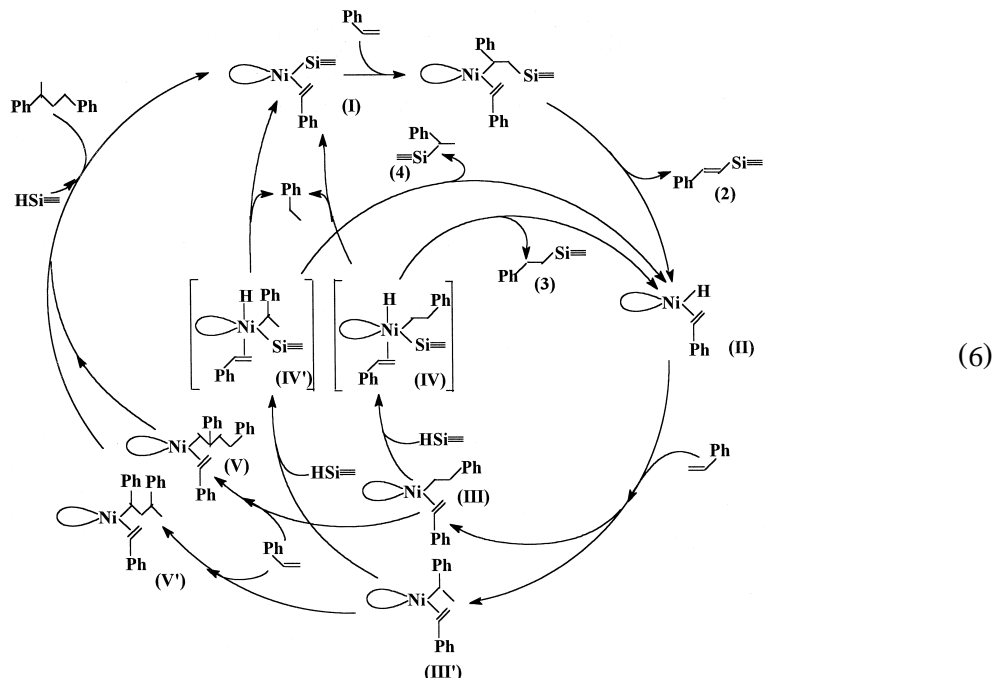
Reaction conditions: RT. <sup>a</sup>argon; <sup>b</sup>air;  $[\text{HSi}\equiv]:[\text{styrene}]:[\text{Ni}] = 1:2:5 \times 10^{-3}$ .

be a key step for all the reactions examined, at least for the silanes containing no alkoxy groups and occurring in the absence of  $\text{PPh}_3$ . It can proceed according to the following equation:



Elimination of  $\text{MeCOCH}_2\text{CH(OSiR}_3\text{)Me}$  is a result of protonation of one acetylacetonate ligand by trisubstituted silane followed by its fast hydrosilylation as was found earlier [18].

The mechanism involving two types of intermediates, i.e., containing  $\text{Ni-Si}$  (I) and  $\text{Ni-H}$  (II), is illustrated in Eq. (6).



The insertion of styrene into the nickel silicon bond of (I) leads to a complex with  $\alpha$ (phenyl) $\beta$ (silyl)ethyl ligand bonded to nickel. Elimination of 1-phenyl-2-silylethene (2)—the product of the dehydrogenative silylation—leads to generation of the active intermediate (II). Insertion of the styrene molecule into  $\text{Ni-H}$  bond gives complex containing  $\sigma$ -(phenyl)ethyl (III) or  $\sigma$ -( $\alpha$ -phenyl)ethyl (III') ligands, respectively. The subsequent step involves an oxidative addition of hydrosilane to form unstable complex (IV) and/or (IV'), respectively, which can undergo elimination of the hydrosilylation products (3) and (4) and to regenerate the hydride complex (II). However, in the reaction with styrene the favoured pathway for (IV) and for (IV') is a reductive elimination of the ethylbenzene and regeneration of the  $\text{Ni-Si}$  intermediate (I). In competition with oxidative addition of  $\text{Si-H}$  (particularly in an excess of olefin) insertion of styrene into  $\text{Ni-C}$  bond occurs to yield the complex (V) and (V') (starting from both (III) and (III') complexes, respectively) and finally—after reductive elimination of only one isomer (1,3-diphenylbutane) to regenerate the active intermediate (I). Pathway (III')  $\rightarrow$  (V') seems to be more probably than (III)  $\rightarrow$  (V) to yield corresponding  $\sigma$ -carbyl-metal intermediate, responsible for selective formation of 1,3-diphenylbutane. It is worth to

emphasize that this is a novel pathway of the dehydrogenative silylation of styrene (olefin) DS-2 occurring via competitive insertion of olefin into Ni–C bond giving the product of hydrogenation of dimeric olefin (e.g., butyl derivatives), beside the unsaturated product. Products of redistribution of trisubstituted silanes containing at least one alkoxy group occur under the reaction conditions studied competitively with main reactions. In oxygen atmosphere catalytic oxygenation of Si–H to Si–OH and hydrolysis of the Si–O–C bond followed by further condensation give siloxanes observed mostly as by-products. The scheme for their formation was presented earlier [19].

### 3. Experimental

#### 3.1. Materials

All reagents were dried and purified before use by the usual procedures. Triethoxysilane, methyldiethoxysilane and dimethylethoxysilane were obtained by alcoholysis of  $\text{SiHCl}_3$ ,  $\text{MeSiHCl}_2$  and  $\text{Me}_2\text{SiHCl}$ , respectively, according to the standard procedure. Alkoxysilanes were thoroughly purified to avoid the presence of traces of HCl.

Bis(2,4-pentanodionato)nickel (II) [20] and bis(cyclooctadiene)nickel(0) [21] were prepared as described in the literature. Bis(2,4-pentanodionato)nickel (II) was dehydrated by maintaining a temperature  $100^\circ\text{C}$  while under vacuum for 24 h. Other chemicals were purchased as follows: triethylsilane, dimethylphenylsilane, triphenylphosphine, styrene, triethylaluminium, tetrakis(triphenylphosphine)nickel(0) and nickelocene from Fluka; nickel trifluoroacetylacetonate from Strem Chemicals. Benzene (Fluka), *n*-pentane, cyclooctadiene (Merck), acetylacetonate and all of used solvents (Aldrich) were purified by standard methods and distilled prior to use.

(2,4-pentanedionato)(triphenylphosphine)ethylnickel(II) was prepared by two methods: **A1**—A solution of diethylaluminium monoethoxide (20 mmol) in hexane was added dropwise to a stirred mixture of nickel acetylacetonate (20 mmol) and triphenylphosphine (20 mmol) in 50 ml of ether cooled to  $-30^\circ\text{C}$ . The temperature was allowed slowly to increase to room temperature and was maintained there for 1 h. The mixture was filtered off and then placed in the freezer overnight. The reddish-yellow crystals were washed with hexane [22,23].  $^1\text{H}$  NMR ( $\delta$ , ppm) ( $\text{C}_6\text{D}_6$ ) 0.79 (s,  $\text{C}_2\text{H}_5$ ); 1.40 (s,  $\text{CH}_3$ ); 1.90 (s,  $\text{CH}_3$ ); 5.27 (s, CH); 6.9–7.8 (m,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\delta$ , ppm) ( $\text{C}_6\text{D}_6$ ) 7.1 ( $\text{CH}_3$ ); 15.0 ( $-\text{CH}_2-$ ); 27.0 ( $\text{CH}_3$ -acac); 27.9 ( $\text{CH}_3$ -acac); 100.9 (CH-acac); 189.6 (CO); 127–129 ( $\text{C}_6\text{H}_5$ ). **A2**—To a stirred mixture, cooled to  $-30^\circ\text{C}$  under argon, of  $\text{Ni}(\text{acac})_2$  (0.1 mmol) and of  $\text{PPh}_3$  (0.3 mmol) in 10 ml of benzene,  $\text{HSi}(\text{OEt})_3$  (0.5 mmol) was added. The solution was concentrated by evaporation and yellow-red crystals were precipitated with pentane. Analytical data showed that this solid contains a mixture of various complexes. Apart from the signals attributed to  $[\text{Ni}(\text{acac})\text{C}_2\text{H}_5(\text{PPh}_3)]$  in  $^1\text{H}$  NMR spectra [0.90 (s,  $\text{C}_2\text{H}_5$ ); 1.32 (s,  $\text{CH}_3$ ); 1.93 (s,  $\text{CH}_3$ ); 5.35 (s, CH)], the signals of  $[\text{Ni}(\text{acac})_2]$  [1.18 (s,  $\text{CH}_3$ ); 1.38 (s,  $\text{CH}_3$ ); 5.30 (s, CH)] and of  $[\text{Ni}(\text{PPh}_3)_3]$  [6.8–7.8 (m,  $\text{C}_6\text{H}_5$ ) and in  $^{31}\text{P}$  NMR ( $-60^\circ\text{C}$ )  $-22$  ppm] and a few other unidentified signals were observed.

#### 3.2. Equipment and analytical measurements

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on Varian XL 300 spectrometer. Samples were dissolved in  $\text{C}_6\text{D}_6$  solutions. GC analysis were performed on Varian 3400 chromatograph equipped with Megabore column (DB-1, 30 m). GC-MS analyses were carried out with Varian 3300

chromatograph (equipped with a DB-1 capillary column, 30 m) connected to a Finnigan Mat 700 mass detector.

### 3.3. General procedure for the dehydrogenative silylation of styrene

The nickel complex precursors were placed in glass ampoules (or in a flask equipped with a condenser) and filled with a mixture of styrene and one of various silanes (in different molar ratio). All manipulations were carried out using standard Schlenk and high vacuum techniques. The reactor was evacuated and filled with argon (or dry air). The mixture was stirred and heated to the required reaction temperature. The progress of the reaction was monitored by GLC analysis. After the reaction, most products were identified by GC-MS analysis, by comparing spectra and the retention time of the peaks with standards. The yield and distribution of the reaction products were detected and calculated by GLC analysis.

Example: The catalyst  $\text{Ni}(\text{cod})_2$  (8 mg, 0.03 mmol) was placed in a flask equipped with a condenser. The reactor was evacuated and filled with argon, and then a mixture of styrene (12 mmol) and triethoxysilane (6 mmol) was added. The reactor was heated at 120°C for 4 h. After the reaction completion, a mixture was analyzed; 5.3 mmol triethoxysilane and 11.5 mmol styrene were consumed. The following products were detected: 4.09 mmol 1-(triethoxysilyl)-2-phenylethene, 0.56 mmol 1-(triethoxysilyl)-2-phenylethane, 0.07 mmol 1-(triethoxysilyl)-1-phenylethane, 0.29 mmol tetraethoxysilane, 0.31 mmol siloxanes, 3.17 mmol ethylbenzene and 1.09 mmol 1,3-diphenylbutane. All products were distilled under vacuum and characterized spectroscopically.

(*E*)-1-(Triethoxysilyl)-2-phenylethene:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) 1.32 (t, 9H), 3.93 (q, 6H), 6.28 (d, 1H), 7.33–7.42 (m, 6H); 1-(Triethoxysilyl)-2-phenylethane:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) 0.91–1.00 (m, 2H), 1.21 (t, 9H), 2.68–2.73 (m, 2H), 3.80 (q, 6H), 7.21–7.52 (m, 5H); 1-(Triethoxysilyl)-1-phenylethane:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) 1.14 (t, 9H), 1.42 (d, 3H), 2.3 (q, 1H), 3.71 (q, 6H), 7.2 (m, 5H); Ethylbenzene:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.23 (t, 3H), 2.6 (q, 2H), 7.1 (s, 5H); 1,3-Diphenylbutane:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.12 (d, 3H), 1.77 (m, 2H), 2.39 (t, 2H), 2.53 (m, 1H), 7.0–7.2 (m, 10H).

## 4. Conclusions

1.  $[\text{Ni}(\text{acac})_2]$  and  $[\text{Ni}(\text{cod})_2]$  are effective precursors of dehydrogenative silylation of styrene with trisubstituted silanes containing electron withdrawing (non-halogen) substituents at silicon, e.g.,  $(\text{EtO})_3\text{SiH}$  and  $\text{PhMe}_2\text{SiH}$ .

2. Two pathways, DS-1 and DS-2, of the dehydrogenative silylation of styrene are observed involving formation of *E*-1-phenyl-2-silyl-ethene as the main (unsaturated) product as well as ethylbenzene and 1,3-diphenylbutane as products of hydrogenation for DS-1 and hydrogenative dimerization for DS-2 of styrene. The reactions are accompanied by two products of the styrene hydrosilylation H and the redistribution of silanes containing alkoxy group(s).

3.  $[\text{Ni}(\text{acac})\text{Et}(\text{PPh}_3)]$  appeared to be an intermediate of the DS-1 and DS-2 with triethoxysilane but only after elimination of phosphine by oxygenation. However, contrary to the corresponding reaction with vinylsilanes [19] effective catalysis by  $[\text{Ni}(\text{acac})_2]$  of the reaction with  $(\text{EtO})_3\text{SiH}$  at room temperature as well as relatively high activity of  $\text{Me}_2\text{PhSiH}$  in this reaction suggest that direct formation of Ni–Si intermediates can be a key step for an initiation of catalytic cycle.

4. All results of the catalytic and analytical studies allow us to propose the general scheme of DS-1, DS-2 and H catalysis by nickel precursors involving the insertion of styrene into Ni–Si, Ni–H and Ni–C bonds.



## Acknowledgements

This work was supported by State Committee for Scientific Research (Poland), Project No. 13T09A074.

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