



Competitive dehydrogenative silylation and hydrogenative dimerization of vinyltriethoxysilane catalyzed by the $[\text{Ni}(\text{acac})_2] + \text{PPh}_3$ system, intermediate and mechanistic implications ¹

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Abstract

[Ni(acac)C₂H₅(PPh₃)] (C) has been shown to be an essential intermediate in the reaction between HSi(OC₂H₅)₃ and vinyltrisubstituted silanes catalyzed by the system [Ni(acac)₂] + PPh₃ at room temperature, but only after oxygenation of the coordinated triphenylphosphine. The stoichiometric and catalytic reactions of complex C with the substrates lead to catalysed, competitive dehydrogenative silylation and hydrogenative dimerization of vinylsilane, which occur following insertion of the latter into Ni-H, Ni-Si \equiv and Ni-C bonds.

Keywords: Silicon; Dehydrogenative silylation; Hydrogenative dimerization of vinylsilanes; Silane; Acetylacetonate

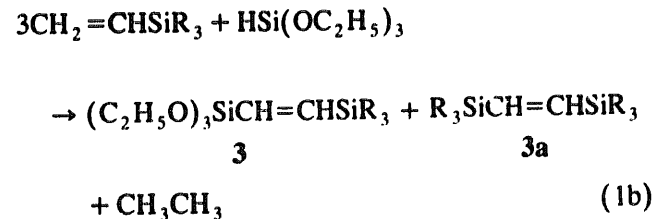
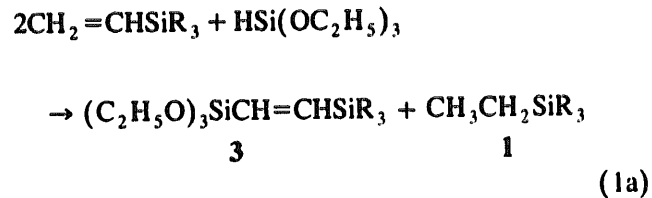
1. Introduction

Dehydrogenative silylation (DS) of olefins in competition with their hydrosilylation catalyzed by complexes of Ru, Fe, Rh, Ir, Os and Pt has been the subject of extensive examinations in the past decade [1]. This great interest in DS is due to the formation of unsaturated organosilicon compounds of the general formula $X_3SiCH=CHR$ (where $R = H$, alkyl, fluoroalkyl, phenyl or silyl, and $X =$ phenyl, alkyl or alkoxy groups), which can provide a very good method for their synthesis. Moreover, an alternative mechanism of DS, different from Chalk and Harrod's concept of hydrosilylation and involving the insertion of an olefin into a metal-silicon bond, has been suggested.

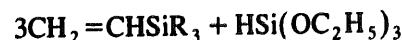
In contrast to the above-mentioned transition metal complexes, nickel compounds catalyze the hydrosilylation of olefins, yielding predominantly a mixture of α - and β -adducts [2,3]. However, Ziegler type complexes based on $[\text{Ni}(\text{acac})_2]$ are also active in catalytic dimerization of vinyltrisubstituted silanes [4,5].

Our previous study of the reaction of vinyltrisubstituted silanes with $\text{HSi}(\text{OC}_2\text{H}_5)_3$ (and also with $\text{HSi}(\text{C}_2\text{H}_5)_3$) catalyzed by nickel acetylacetonate [6,7], nickel-phosphine and other nickel complexes [8], at a temperature of 80–120°C, revealed the formation of bis(silyl)ethenes (products of the DS) and bis(silyl)butanes (products of hydrogenative dimerization (HD)), according to the following equations:

DS

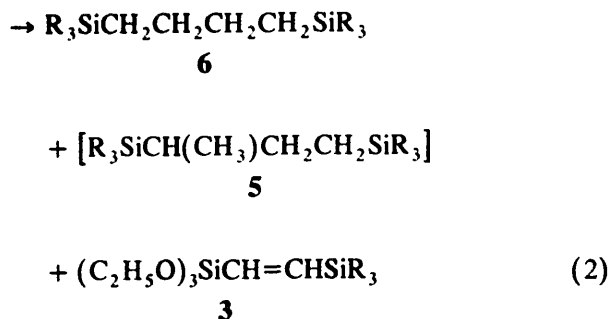


HD



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¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry. Part XXX in the series Catalysis of Hydrosilylation, for Part XXIX see Ref. [16].



For an equimolar ratio of vinylsilane to hydrosilane, the two main processes (DS and HD) are accompanied by side and consecutive reactions, e.g. normal hydrosilylation of vinylsilane, yielding $\text{R}_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ (**4**), disproportionation of substrates (giving tetraethoxysilane (**2**) and siloxanes (**7**)), as well as dehydrogenative silylation and normal hydrosilylation of the unsaturated products [7,8].

In order to identify the intermediates in the process, a separate study on the reaction of $\text{Ni}(\text{acac})_2$ with triethoxysilane in the presence of PPh_3 was undertaken, and under optimal conditions allowed isolation of $[\text{Ni}(\text{acac})\text{C}_2\text{H}_5(\text{PPh}_3)]$ (**C**), which was the subject of a preliminary communication [9].

The aim of the work described in this paper was to examine in detail the initial species formed in the system $[\text{Ni}(\text{acac})_2] + \text{PPh}_3 + \text{substrates}$ in order to evaluate the catalytic activity of the isolated intermediates in the reaction of vinyltrisubstituted silanes with triethoxysilane. In the light of the available experimental data, a general scheme for catalysis of the competitive reactions examined is proposed.

2. Experimental

2.1. Materials

Bis(2,4-pentanedionato)nickel(II) and (2,4-pentanedionato)(triphenylphosphine)ethylnickel(II) were prepared as previously described [9–11]. Vinyltriethoxysilane was obtained from Fluka, and triethoxysilane was made from Cl_3SiH by the usual method. Both silanes were thoroughly purified to avoid the presence of traces of HCl . Triphenylphosphine and triethylaluminium were from Fluka, and used without any purification. Benzene (Fluka), n-pentane (Merck), and acetylacetone (Fluka) were purified by standard methods and distilled prior to use.

2.2. Equipment and analytical measurements

The NMR spectra (^1H , ^{13}C , ^{31}P) were recorded on a Varian XL 300 spectrometer. In all cases C_6D_6 was

used as solvent; for ^{31}P NMR spectroscopy 85% H_3PO_4 was used as external standard. An FT-IR Bruker IFS 113v was used for recording IR spectra (CsBr pellets) and a Perkin Elmer 2400 instrument for elemental analysis. Vis-spectrophotometric investigations were performed on a Specord UV-vis using 0.04 cm cells. GLC-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. GLC analysis was also carried out with a Varian 3300 chromatograph with a Megabore column (30 m, DB-1).

2.3. Typical procedure for stoichiometric reactions

2.3.1. Reaction of $[\text{Ni}(\text{acac})_2]$ with triethoxysilane in the presence of PPh_3 in benzene solution

To a stirred mixture under argon of 0.26 g of $[\text{Ni}(\text{acac})_2]$ (0.1 mmol) and 0.26 g of PPh_3 (0.1 mmol) in 10 ml of C_6H_6 was added 0.93 ml of $\text{HSi}(\text{OEt})_3$ (0.5 mmol). The solution turned red after a few minutes. Samples were examined by GLC-MS and ^1H NMR spectroscopy. These solutions, containing various concentrations of PPh_3 , were used at 20°C for spectrophotometric studies (vis), involving repetitive scanning of the spectrum at suitable times. After introduction of traces of oxygen, the solution turned green and was analysed by GLC-MS, and by ^1H and ^{31}P NMR spectroscopy.

2.3.2. Isolation of complex **C**

After the procedure described above, the solution was concentrated by evaporation, and a yellow-red complex **C** was precipitated by addition of n-pentane. The solid was washed carefully with pentane several times and kept under argon, and subsequently identified spectroscopically [9] as $[\text{Ni}(\text{acac})/\text{C}_2\text{H}_5/(\text{PPh}_3)]$.

2.3.3. Attempts to isolate complex **D**

The procedure described above up to the isolation of complex **C** was repeated but 1.05 ml of $\text{CH}_2=\text{CHSi}(\text{OEt})_3$ (0.5 mmol) was then added. The red solution turned yellow. It was concentrated by evaporation of benzene to leave a yellow oil.

2.3.4. Isolation of complex **A** $[(\text{Ni}(\text{acac})_2)]$

The procedure described above up to the isolation of complex **C** was repeated but without PPh_3 present and under air. The green solution was concentrated and complex **A** was precipitated by adding pentane, it was then characterized by IR, ^1H and ^{13}C NMR spectra as $[\text{Ni}(\text{acac})_2]$.

2.3.5. Isolation of **B** (Ni metal)

The same procedure was used to isolate **B** after the original mixture had been kept either under argon at

room temperature or under air at an elevated temperature. A black solid was precipitated from the green solution and found to show no absorption in the IR.

2.4. Catalytic tests

The catalyst (**B** or **C**) was placed in a glass ampoule under argon and a mixture of vinyltriethoxysilane and triethoxysilane was added. The product distribution and degree of conversion of the substrates were monitored by GLC-MS and GLC analysis.

3. Results and discussion

3.1. The reaction of $[\text{Ni}(\text{acac})_2]$ with PPh_3 , $\text{HSi}(\text{OC}_2\text{H}_5)_3$ and $\text{CH}_2=\text{CHSiR}_3$

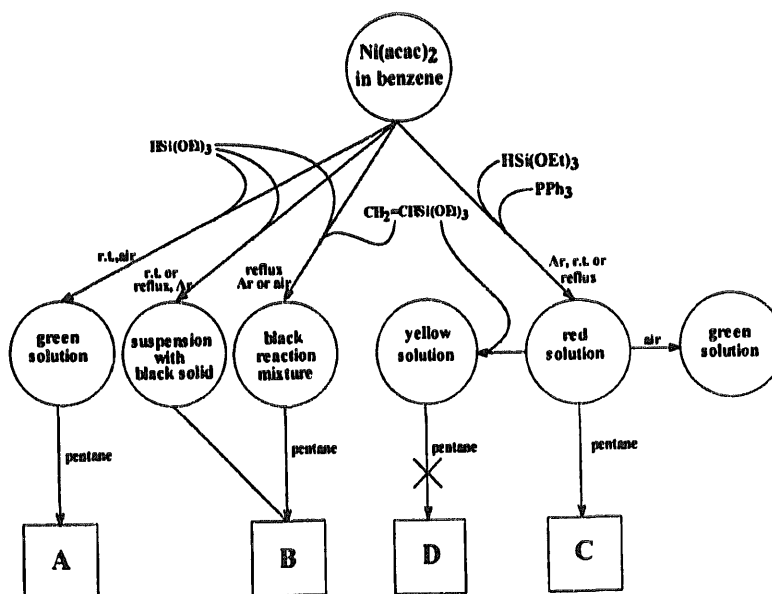
The reaction of vinyltriethoxysilane with triethoxysilane was selected as the standard one for determining the role of the phosphine ligands introduced into the $[\text{Ni}(\text{acac})_2]$ catalyst [8]. In the absence of a tertiary phosphine under the reaction conditions (120°C, or in reflux ca. 160°C) reduction of nickel acetylacetonate to nickel precipitate was observed to take place within a few minutes, i.e. when the main stage of reaction was almost complete. In order to stabilize the catalyst precursor and at the same time keep it in solution, triphenylphosphine was added. For $[\text{Ni}]:[\text{PPh}_3] = 1:2$, the catalytic activity after 72 h at 120°C was the same as for the precursor alone after 24 h [8]. For $[\text{Ni}]:[\text{PPh}_3] = 1$, the nickel complex still remained in solution, but the yield of the main products was much lower than that observed in the absence of phosphine. Drastic inhibition

by triphenylphosphine has been reported for reactions under reflux [8].

Although the addition of PPh_3 reduces the catalytic activity of $[\text{Ni}(\text{acac})_2]$, it still keeps it effective and allows the formation of nickel intermediates to be monitored. The results of reactions involving nickel acetylacetonate in the presence of triphenylphosphine, the substrates, and dioxygen are summarized in Scheme 1. Three types of precipitate were finally isolated from the solutions, and were identified as **A–C**.

It is known that nickel acetylacetonate (green) has a trimeric structure with octahedral geometry. A monomeric form can be obtained at elevated temperatures (above 200°C) or in dilute donor solvents. Reaction of $[\text{Ni}(\text{acac})_2]$ with triethoxysilane leads either to metallic nickel deposition **B** (benzene solution, Ar room temperature, or Ar (air) at elevated temperature) or to isolation of the unchanged complex **A** (room temperature, air). It should be noted that heating of the $[\text{Ni}(\text{acac})_2]$ solution with triethoxysilane gives a transient red species (probably caused by protonation of the initial trimer and subsequent dissociation to the monomer), but this decomposes to give a black Ni precipitate very quickly. It was also shown that no reaction between $[\text{Ni}(\text{acac})_2]$ and vinyltrialkoxysilane takes place at room or elevated temperature.

Reaction of $[\text{Ni}(\text{acac})_2]$ with triethoxysilane in the presence of PPh_3 at room temperature in benzene solution was studied. Since the reduction of $[\text{Ni}(\text{acac})_2]$ to $\text{Ni}(0)$ is very rapid in an oxygen-free atmosphere [9], triethoxysilane was introduced under argon to a benzene solution of Ni complex containing a small excess of triphenylphosphine (1–2 mol PPh_3 per mol Ni). After several seconds the solution turned from yellowish-green to an intense blood red. No reduction to metallic Ni was



Scheme 1.

observed. GLC-MS analysis of the solution showed that the colour change is accompanied by loss of PPh_3 from the solution (which becomes attached to the Ni centre) and the formation of silylation and reduction products of the acetylacetonate ligand. It is known that acetylacetonate itself reacts with triethoxysilane (in the presence of $[\text{Ni}(\text{acac})_2]$ or without any catalyst), yielding $\text{CH}_3\text{COCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{CH}_3\text{COCH}_2\text{CH}[\text{OSi}(\text{OC}_2\text{H}_5)_3]\text{CH}_3$. The ^1H NMR spectrum of the reaction mixture (in C_6D_6) supports the presence of new " $\text{Ni}(\text{acac})\text{PPh}_3$ " species and silylated acac derivatives. The red solution is very sensitive and turns green immediately when exposed to traces of oxygen (air). The formation of OPPh_3 , ethyltriethoxysilane and several siloxanes, monitored by GLC-MS and ^1H NMR spectra, accounts for the role of oxygen in this system: it oxidizes PPh_3 ligands on the Ni to free OPPh_3 molecules, thus removing them from the complex. In addition, the Si–H bond is oxidized to give some siloxanes. In the presence of an excess of triethoxysilane and PPh_3 in the solution, after all the oxygen present has been consumed, the mixture turns red again, the time intervals depending on the concentrations of PPh_3 and hydrosilane. Subsequent exposure to air causes the next colour change to green.

Spectrophotometric studies (vis) of the system $[\text{Ni}(\text{acac})_2] + n\text{PPh}_3 + n\text{HSi}(\text{OC}_2\text{H}_5)_3 + \text{C}_6\text{H}_6$ under oxygen-free conditions showed that the absorbance at $26 \times 10^3 \text{ cm}^{-1}$ increases with increasing PPh_3 concentration, up to the value observed for a solution of $[\text{Ni}(\text{PPh}_3)_4]$ in benzene. It is known that tetrakis(triphenylphosphine)nickel(0) dissociates in benzene to give practically 100% of the $[\text{Ni}(\text{PPh}_3)_3]$ species [12]. The shape of the band and the absorbance in the electronic spectra of the complexes formed in the C_6H_6 solutions, starting from various $[\text{Ni}]/[\text{P}]$ ratios, are closely similar to those for $[\text{Ni}(\text{PPh}_3)_n]$, and so the geometry (square-

planar) of the complexes involved should also be close. It is noteworthy that the red colour for the Ni complexes is characteristic of the square-planar geometry, whereas the green–blue colour is characteristic of the tetrahedral geometry or a higher coordination (namely 6) [13]. In addition, the high values of the molar absorbance coefficients observed are characteristic of a complex with low symmetry and/or charge transfer spectra.

Fig. 1 shows the dependence on phosphine concentration of the proportions of the various complexes present in the solution for the system $[\text{Ni}(\text{acac})_2] + \text{PPh}_3 + \text{HSi}(\text{OEt})_3$ at various molar ratios of the components. It may be concluded that the Ni complex with one PPh_3 molecule is initially formed and then, with a large excess of PPh_3 , even $[\text{Ni}(\text{PPh}_3)_3]$ is present. The other measurements revealed that the presence of an excess of acetylacetonate shifts the equilibrium to the left (i.e. towards the starting material).

Synthetic studies were carried out for the solution with $[\text{Ni}(\text{acac})_2]$, PPh_3 and $\text{HSi}(\text{OC}_2\text{H}_5)_3$ in the 1 : 1 : 5. The solution was concentrated by evaporation of benzene and the yellow–red complex C was precipitated by addition of n-pentane (52% yield) [9]. All spectroscopic data (IR, ^1H , ^{13}C , ^{31}P NMR) for the isolated complex C point to the formulation $[\text{Ni}(\text{acac})\text{C}_2\text{H}_5(\text{PPh}_3)]$, having square-planar geometry. As we reported previously [9], this procedure appears to provide a new, efficient method for synthesis of C, which is an example of a nickel complex with a bidentate ligand, a type of species very active in oligomerization of olefins by Ziegler–Natta type catalysts. Triethoxysilane can be used successfully in place of the organoaluminium reagent $[\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)]$ used previously [11], and the reaction proceeds according to the scheme presented earlier [9].

A solution of complex C in benzene containing triethoxysilane is extremely sensitive to traces of oxygen, irreversibly yielding OPPh_3 and an octahedral (green/white) " $\text{Ni}(\text{acac})$ " species; disiloxanes were detected by GLC-MS as by-products. This represents the first observed cleavage of an oxygen–carbon bond in a triethoxysilyl group involving transfer of an ethyl group to Ni.

Under oxygen-free conditions, C reacts with vinyltri-alkoxysilane almost immediately to yield a yellow solution. Vinylsilane molecules apparently coordinate to a metal centre without phosphine dissociation (GLC-monitoring). The change in the red colour of the solution of C to yellow suggests the presence of an octahedral or pentacoordinate complex $[\text{Ni}/\text{acac}/\text{C}_2\text{H}_5(\text{PPh}_3)/\cdot n\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3]$ ($n = 1, 2$) in the solution, but owing to the paramagnetic character of the Ni species the resolution in NMR spectra is very limited, and it was not possible to isolate any pure vinylsilane–nickel complexes, probably because of their high lability.

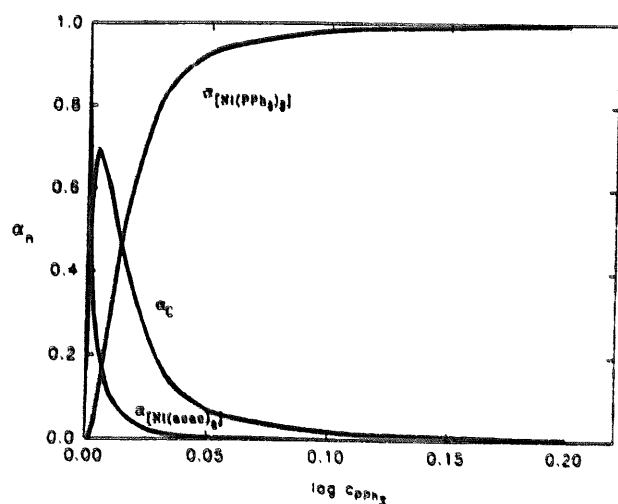


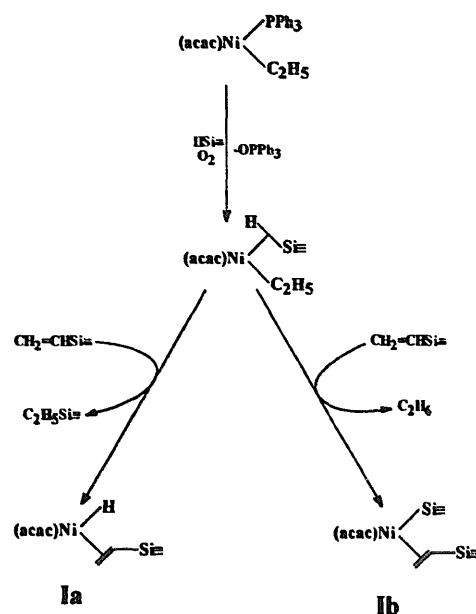
Fig. 1. Fractions of different complexes in a benzene solution of $\text{Ni}(\text{acac})_2 + \text{HSi}(\text{OC}_2\text{H}_5)_3 + \text{PPh}_3$.

3.2. Reactions of complex C with substrates under conditions of catalysis

The reaction of vinyltriethoxysilane with triethoxysilane in the presence of any nickel complex used previously occurs only at elevated temperatures (above 80°C) [6–8]. That of complex C was tried at room temperature. Under oxygen-free conditions no product formation was observed, either after three weeks or at elevated temperatures; a subsequent exposure of the reaction mixtures to air at room temperature led the reaction to complete within 15 min.

The results presented in Table 1 show that conversion of vinylsilane and hydrosilane, present in a ratio 2:1 or even 1:1 goes to completion to yield products of dehydrogenative silylation and hydrogenative dimerization of vinylsilane accompanied by traces of normal hydrosilylation products (see reactions 1 and 2). The $\text{Si}(\text{OC}_2\text{H}_5)_4$ and siloxanes are the products of $\text{HSi}(\text{OC}_2\text{H}_5)_3$ redistribution and subsequent oxygenation and condensation reactions, but particularly when an excess of hydrosilane is present. No secondary hydrosilylation or dehydrogenative silylation of products was observed, even in the presence of an excess of hydrosilane. Complex C became active again when further portions of substrates were added. It is noteworthy that complex C is the first highly efficient complex for dehydrogenative silylation of olefins, and also for hydrogenative dimerization of silyl olefins.

As has been mentioned, complex C is not active under oxygen-free conditions. When preparing a similar type of nickel complex (involving a bidentate ligand), Keim and coworkers [14] also reported that addition of tertiary phosphine stabilizes the intermediate and allows its isolation, yet simultaneously results in catalytic deactivation. Since our system seems to react in a very similar way, the experiment was performed following the treatment of C in benzene in air (i.e. release of the



Scheme 2.

phosphine and its oxidation to phosphine oxide) with triethoxysilane and vinyltriethoxysilane.

This experiment, and stoichiometric data on the reaction of C with the various substrates, permits us to propose the following scheme (Scheme 2) for initiation of active intermediates, unisolable under catalytic conditions. The products of the reaction of C with substrates and O_2 were confirmed by GLC-MS (i.e. OPPh_3 , C_2H_6 and/or $\text{C}_2\text{H}_5\text{Si}\equiv$).

3.3. Catalytic cycles of the reaction between vinyltrisubstituted silanes and triethoxysilane

The reaction pathways in the presence of C in Scheme 2 are the basis of our analysis of the reaction mecha-

Table 1

Effect of oxygen on conversion and yield of the reaction of vinyltriethoxysilane with triethoxysilane catalyzed by nickel complexes

Substrates and products	Argon			Air, 15 minutes			
	Three weeks, room temperature 0.5 h, 120°C			[Ni(acac) ₂]	C	C ^{••}	C [•]
	[Ni(acac) ₂]	C	C [•]				
<i>Conversion (%)</i>							
HSi(OEt) ₃	0.8	5.0	4.0	1.6	55	24	48
CH ₂ ≡CHSi(OEt) ₃	1.5	6.4	5.8	4.6	98	90	95
<i>Yield (%)</i>							
1 EtSi(OEt) ₃ (DS)	0.5	1.0	0.8	1.0	10.0	8.0	11.0
2 Si(OEt) ₄	0.5	4.0	3.8	1.5	16.0	19.0	17.0
3 ≡SiCH=CHSi≡ (DS)	—	—	—	0.3	31.0	25.0	32.0
4 ≡SiCH ₂ CH ₂ Si≡ (H)	—	—	—	—	3.0	4.0	2.0
5 ≡SiCH(CH ₃)CH ₂ CH ₂ Si≡	—	—	—	—	3.0	1.0	1.0
6 ≡Si(CH ₂) ₄ Si≡ (HD)	—	—	—	0.3	34.0	24.0	28.0
7 Siloxanes	0.2	0.4	0.4	1.0	2.0	8.0	4.0

$[\text{CH}_2=\text{CHSi}\equiv]:[\text{HSi}\equiv]:[\text{cat}] = 1:1:5 \times 10^{-3}$, room temperature.

^{*} After conditioning at 120°C, 0.5 h in argon.

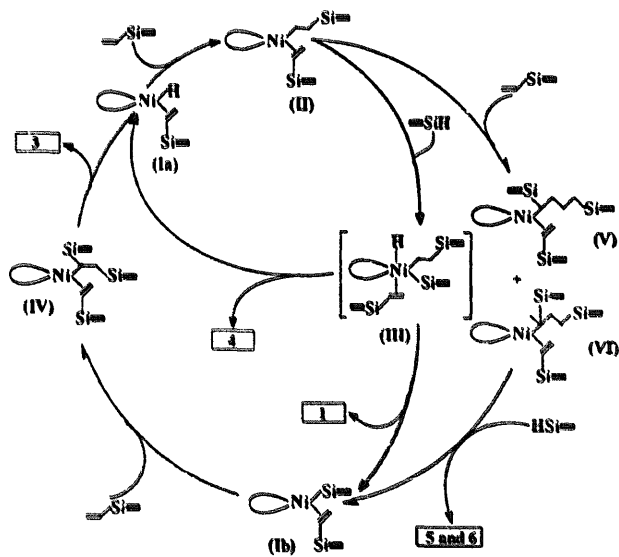
^{**} Next portion of substrates added.

nism. We also note the ability of **C** to form **Ia** and **Ib** intermediates, which could be responsible for the catalytic cycles in the DS and HD.

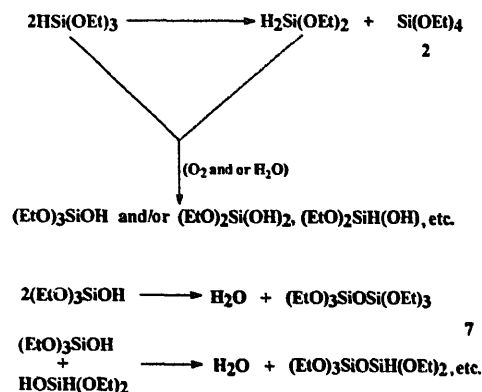
The mechanism involving these two intermediates is illustrated in Scheme 3. The cycle is initiated by the insertion of the vinylsilane molecule into an Ni–H bond to form a complex **II** containing a σ -ethylsilyl ligand. There is much evidence that with Ni complexes containing bidentate ligands in the oligomerization of ethylene, this step is very fast [15], although only at elevated temperatures.

The main catalytic cycle involves oxidative addition of hydrosilane to form an unstable intermediate **III** which undergoes elimination of the hydrosilylation product **4** to regenerate the hydrido complex **Ia**. However, the favoured pathway for **III** involves reductive elimination of the ethylsilane **1** from **III** and formation of the Ni–Si intermediate **Ib**. In competition with oxidative addition of Si–H (particularly in the presence of an excess of olefin), insertion of vinylsilane into the Ni–C bond also occurs, in both fashions (yielding finally, after reductive eliminations, the two isomers of bis(silyl)butanes **5**, **6**), regenerating the nickel–silyl intermediate **Ib**. The insertion of the vinylsilane molecule coordinated into the Ni–Si bond of **Ib** leads to a complex with an α -silyl- and a β -ethylsilyl ligand both bonded to nickel. In the next step, elimination of bis(silyl)ethene **3** from **IV** leads to regeneration of the active intermediate **Ia**.

The operation of these two catalytic cycles can account for the stoichiometric and catalytic examinations of the reactions studied. But for $[H-Si\equiv]:[CH_2=CHSi\equiv]=1:1$ (i.e. (see Eq. (1a)) with an excess of hydrosilane so that the main reactions go to completion), secondary reactions of hydrosilane with bis(silyl)ethene cannot occur, as we tried to prove previously using $[Ni(cod)_2]$ as standard catalyst [8]. The



Scheme 3.



Scheme 4.

subsequent dehydrogenative silylation of bis(silyl) ethene, observed also in the case of $[Ni(acac)_2]$ [7], can take place only if both olefins, i.e. vinylsilane and bis(silyl)ethene, are present, in addition to hydrosilane, in the catalytic system. Apparently, at room temperature the primary reactions are much faster, using up all the vinylsilane, which is necessary for further transformations.

Normal hydrosilylation of vinylsilane, which is the side reaction in this complex process is accounted for by this mechanism, but the high yield of tetraethoxysilane observed in the presence of an excess of hydrosilane with exposure to oxygen can be explained in terms of Scheme 4, involving disproportionation of $HSi(OC_2H_5)_3$ as well as oxygenation of the $\equiv Si-H$ bond and hydrolysis of the $\equiv Si-O-C$ bond, followed by further condensation. All the products shown in Scheme 4 were confirmed by GLC-MS examination.

The above reactions can occur spontaneously, but nickel complexes catalyze the oxygenation of the $\equiv Si-H$ bond.

4. Conclusions

(1) The isolated and identified complex **C** $[Ni(acac)_2C_2H_5(PPh_3)]$ has been shown to be an intermediate in the $[Ni(acac)_2] + PPh_3$ catalyzed reaction between vinylsubstituted silanes and $HSi(OC_2H_5)_3$; the catalyst system is very active at room temperature, but only after elimination of phosphine by oxygenation. This is the first example of a very effective catalysis of dehydrogenative silylation of olefins by nickel complexes under such mild conditions.

(2) The information from stoichiometric and catalytic reactions of **C** with substrates in air allows us to conclude that formation of intermediates containing Ni–H (**Ia**) and Ni–Si (**Ib**) bonds is responsible for the catalysis.

(3) All results of the studies on the intermediates and their catalytic properties allow us to analyse the nature of the competitive pathways. DS and HD of vinylsilanes

proceed in the presence of **C** by insertion of a vinylsilane molecule into Ni–Si \equiv , Ni–H as well as Ni–C bonds, and these main reactions can be followed by side reactions such as normal hydrosilylation, as well as redistribution and oxygenation of HSi(OC₂H₅)₃.

(4) The nature of complex **C**, which is a Ziegler-type catalyst, accounts for the mechanism of the two main reactions similar to the oligomerization of alkenes. It should be noted that triethoxysilane can be used successfully in place of organoaluminium (AlR₃) or other organometallic reagents usually used for the synthesis of type **C** complexes.

(5) The very high effectiveness of **C** in the reaction of hydrosilanes with vinyltrisubstituted silanes holds out hope that use of platinum might be replaced by that of nickel complexes in hydrosilylation (e.g. cross-linking of vinylsubstituted silicones) and/or related reactions.

Acknowledgements

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