Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 359 (2006) 2989–2997

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Intermediates in nickel(0)–phosphine complex catalyzed dehydrogenative silylation of olefins

Hieronim Maciejewski [a], Agnieszka Sydor [a], Bogdan Marciniec [a,*], Maciej Kubicki [a], Peter B. Hitchcock [b]

[a] *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
[b] *The Chemical Laboratory, University of Sussex, Brighton BN1 9QJ, UK*

Received 24 November 2005; accepted 31 December 2005
Available online 9 March 2006

Dedicated to Professor Brian James on the occasion of his 70th birthday in recognition of his great contribution to homogeneous catalysis.

Abstract

Nickel(0) complexes **1**–**4** containing π-coordinated olefin and triphenylphosphine (tricyclohexylphosphine) (starting from Ni(cod)$_2$) were prepared and the X-ray structures of **1** and **2** were resolved. The complexes appeared as efficient catalysts in dehydrogenative silylation of styrene and vinyltris(trimethylsiloxy)silane, but only after prior oxygenation of phosphine ligand. Stoichiometric studies of Ni(0) complexes with substrates showed that the bis(silyl)nickel(II) complex was a key intermediate in both reactions examined. A scheme of catalysis by Ni(0) complex involving olefin insertion into Ni–Si bond, as a crucial step, is presented.

Keywords: Nickel–silyl complexes; Dehydrogenative silylation; Catalysis

---

1. Introduction

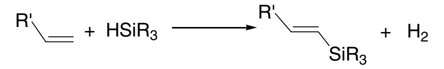
Hydrosilylation is a versatile reaction in organosilicon chemistry and apart from the "direct process," the only industrially used silicon–carbon bond formation method [1–5]. The mechanism of catalysis of hydrosilylation by platinum complexes, later generalized for other transition metal complexes, was proposed by Chalk and Harrod [6]. It involves oxidative addition of trisubstituted silanes to a metal–alkene complex, followed by migratory insertion of alkene to M–H bond and reductive elimination of the hydrosilylation product from the metal center. Although the basic aspects of this mechanism still enjoy wide acceptance, it has failed to explain a number of phenomena, e.g., the formation of an unsaturated organosilicon product. Such unsaturated compounds are formed in the reactions catalyzed not only by complexes of the iron and cobalt triads but also by nickel complexes as a result of the dehydrogenative silylation of olefins, proceeding competitively with hydrosilylation [7–9]. A key step for the dehydrogenative silylation catalyzed by late transition-metal complexes is the insertion of alkene into the M–Si bond (for recent review, see [9]). The first mechanism involving this step was presented by Seitz and Wrighton, on the basis of the photochemical study of the reaction with Co–Si complex [8].

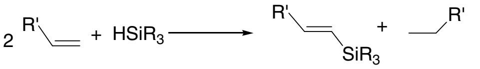
Our previous examination of the reaction between trisubstituted silanes and vinylsilanes [10,11], styrene [11,12] and other olefins [12] has shown that in the presence of nickel complexes the dehydrogenative silylation proceeds via three ways yielding the unsaturated product and the respective hydrogenated product of direct dehydrogenation (**DC**) and olefin hydrogenation (**DS-1**), as well as hydrogenated dimerization (**DS-2**), according to the following equations:

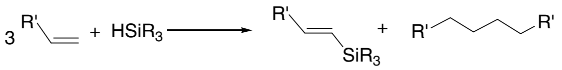
---

[*] Corresponding author. Tel.: +48 61 8291 366; fax: +48 61 8291 508.
E-mail address: marcinb@amu.edu.pl (B. Marciniec).

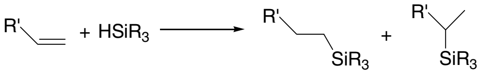
0020-1693/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.12.067


(DC)


(DS-1)


(DS-2)

accompanied by the small amount of hydrosilylation products:


(H) (1)

The Seitz and Wrighton mechanism does not explain the possibility of formation of unsaturated product in the three different reactions. On the other hand, this mechanism involves insertion of alkene into the M–Si bond, but for the nickel catalyzed reactions, a stable complex containing one silyl group bonded to nickel atom has not been isolated yet. However, a few stable bis(silyl)nickel complexes with strong electron withdrawing substituents at silicon atoms have been isolated and characterized [13–22]. Our recent contribution to this field is the first example of nickel–silyl complexes of the type $[Ni(PR_3)_2(SiMe_nCl_{3-n})_2]$, containing at least one alkyl group at silicon, which has been synthesized and fully characterized [22]. Also our earlier study of the reaction between triethoxysilane and olefins, catalyzed by nickel equivalent of Karstedt catalyst $[\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}]$, has led to the isolation of a bis(silyl)nickel complex containing divinyltetramethyldisiloxane as chelating ligands, besides two triethoxysilyl groups [11]. The presence of these chelating ligands stabilizes this complex, so Ni(0) complex under catalytic conditions does not undergo reduction to Ni metal, which is commonly observed in the reaction with hydrosilanes and other nickel complexes. Tertiary phosphines may also stabilize metal complexes and additionally they play a crucial role in many industrially important TM-catalyzed organic reactions [23]; therefore, they could be used for the isolation of complexes forming during the catalytic reactions.

Bis(cyclooctadiene)nickel(0) is a popular catalyst and a good starting material for the synthesis of other nickel complexes. Cyclooctadiene is a very labile ligand which readily undergoes displacement by many olefinic ligands, including vinyl-organosilicon compounds, e.g., vinylsiloxane [11,24], vinylsilazane [25] and vinylsilane [26], and also tertiary phosphine. $[Ni(cod)_2]$ is also an effective precursor of the dehydrogenative silylation reactions [11,12] but due to its high reactivity, the isolation of the "real catalyst" (formed in the course of the catalytic reaction) was unsuccessful. When $[Ni(cod)_2]$-based catalyst was used, after the completion of the reaction, a precipitate of nickel–metal was observed. We used tertiary phosphine to prevent the reduction of the nickel complex.

The aim of the study reported in this paper was to examine the initial species formed in the system $[Ni(cod)_2] + PR_3 +$ substrates in order to identify the active intermediates in the reaction of H–Si species (i.e., hydro-silanes and -siloxanes) and olefins (styrene and vinyl-siloxanes).

2. Experimental

2.1. Materials

All reagents were dried and purified before use by the usual procedures. Triethoxysilane was obtained by alcoholysis of $HSiCl_3$ and thoroughly purified to avoid the presence of traces of HCl. $[Ni(cod)_2]$ was prepared as described in the literature [27]. Other chemicals were purchased from Aldrich.

2.1.1. Synthesis of $[Ni(PPh_3)_2(cod)]$ (**1**)

A solution of 1.05 g (4.0 mmol) PPh_3 in 10 mL of diethyl ether was added to 0.55 g (2 mmol) $[Ni(cod)_2]$ yielding a red suspension. After a few minutes, a yellow solid precipitated. The mixture was stirred for 2 h at room temperature. Then, the solid was filtered and washed with diethyl ether (3×5 mL) and dried under vacuum yielding complex **1** (yield 90%). Yellowish-gold crystals of **1** suitable for X-ray diffraction were grown from benzene at ambient temperature over a period of 24 h.

Anal. Calc. for $C_{44}H_{42}NiP_2$: C, 76.43; H, 6.12. Found: C, 76.21; H, 6.22%.

^1H NMR (C_6D_6, 298 K, 300 MHz); δ (ppm): 1.6 (s, 4H), 1.8 (s, 4H), 4.8 (s, 4H), 6.9–7.6 (m, 30H).

^{31}P NMR (C_6D_6, 298 K, 101.2 MHz); δ (ppm): 42.0 (s).

2.1.2. Synthesis of $[Ni(PPh_3)_2(\eta^2\text{-}CH_2{=}CHC_6H_5)]$ (**2**)

To the suspension of 0.55 g (2 mmol) $[Ni(cod)_2]$ in 10 mL of diethyl ether, 1.05 g (4 mmol) of PPh_3 was added. Next, 1.5 mL of styrene was added to a stirred reaction mixture. Suddenly, the suspension was dissolved and then after 15 min an orange solid started to precipitate. The reaction mixture was stirred for 24 h at room temperature and the solid was filtered and washed by diethyl ether (95% of yield). Yellow crystals of **2** suitable for X-ray diffraction were grown from benzene at ambient temperature over a period of 24 h.

Complex **2** was also independently synthesized at the same conditions but using complexes **1** and **3**, as starting materials and yielded a desired complex **2** with 87% and 82% yield, respectively.

Anal. Calc. for $C_{44}H_{38}NiP_2$: C, 76.88; H, 5.57. Found: C, 76.65; H, 5.69%.

^1H NMR (C_6D_6, 298 K, 300 MHz); δ (ppm): 2.66 (m, $=CH_2$); 2.93 (m, $=CH_2$); 4.13 (m, $-CH=$); 6,52, 7.15, 7.53 (Ph).

^{13}C NMR (C_6D_6, 298 K, 125.8 MHz); δ (ppm): 118.0 (s, $=CH_2$); 127 (m, Ph); 133.2 (d, $-CH=$).

^{31}P NMR (C_6D_6, 298 K, 101.2 MHz); δ (ppm): 37.3 (d); 32.1 (d).

2.1.3. Synthesis of $[Ni(PPh_3)_2C_2H_4]$ (3)

Compound **3** was synthesized as described in the literature [28,29]. Analytical data of **3** are identical with those from the literature.

2.1.4. Synthesis of $[Ni(PCy_3)_2(\eta^2\text{-}CH_2{=}CHC_6H_5)]$ (4)

Compound **4** was prepared in a similar manner as **2**, except that PCy_3 was used instead of PPh_3.

^{1}H NMR (C_6D_6, 298 K, 300 MHz); δ (ppm):1.1–2.2 (m, 66H), 2.4 (m, 2H), 4.04 (t, 1H), 7.00–7.05 (m, 2H), 7.09–7.30 (m, 2H), 7.48 (d, 1H).

^{13}C NMR (C_6D_6, 298 K, 125.8 MHz); δ (ppm): 27.47–37.62 (m, C_6H_{11}-c), 48.81 (s, =CH-), 52.28 (s, $=CH_2$), 131.25, 128.37, 125.82, 121.77 (s, Ph).

^{31}P NMR (C_6D_6, 298 K, 101.2 MHz); δ (ppm): 37.36 (d).

2.2. Stoichiometric reactions

2.2.1. Reaction of 2 with triethoxysilane – synthesis of $[Ni(PPh_3)_2\{Si(OEt)_3\}_2]$ (5)

Triethoxysilane (0.2 mL, 1 mmol) was added under argon, to a rapidly stirred solution of $[Ni(PPh_3)_2\{\eta^2\text{-}(CH_2{=}CHC_6H_5)\}]$ (**2**) (0.30 g, 0.43 mmol) in benzene (5 mL), in a Schlenk tube. The reaction mixture was stirred for 6 h at 60 °C. After this time, some amount of black-red solid precipitated, was filtered off, washed with pentane and dried under vacuum. The GC–MS analysis of filtrate showed the presence of ethylbenzene. The obtained complex **5** was analyzed by NMR method.

^{1}H NMR (C_6D_6, 298 K, 300 MHz); δ (ppm): 0.91–1.18 (m, 18H), 3.69 (q, 12H); 6.90–7.05 (m, 18H); 7.25–7.39 (m, 12H).

^{13}C NMR (C_6D_6, 298 K, 125.8 MHz); δ (ppm): 18.29 (s, CH_3), 56.40 (s, $-OCH_2$); 130.10, 131.57, 132.38, 135.23 (s, –Ph).

2.2.2. Reaction of $[Ni(PCy_3)_2(\eta^2\text{-}CH_2{=}CHC_6H_5)]$ (4) with heptamethyltrisiloxane

0.34 g (0.5 mmol) of **4** was dissolved under argon in 0.6 mL of $C_5D_5CD_3$ in an NMR tube. A portion of 0.25 mL (1 mmol) heptamethyltrisiloxane was added to the solution and the course of the reaction was monitored by ^{1}H NMR at −20 °C.

2.2.3. Reaction of 5 with styrene

1 mL of styrene was added to the solution of **5** (0.2 g, 0.22 mmol) in benzene (5 mL). The reaction mixture was stirred for 2 h at 60 °C. After this time, the mixture was analyzed by GC–MS method, which showed the presence of 1-phenyl-2-silylethene and phosphine oxide.

2.3. Structure determinations

All data were measured using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). For **2**, the measurement was performed at 173(1) K on an Enraf-Nonius CAD4 four-circle diffractometer [30] by the ω–2θ scan technique; for **1** the same scan technique was used on a KUMA KM4 four-circle diffractometer [31], at 293 K. The temperature was controlled by an Oxford Instruments Cryosystem cooling device. The data were corrected for Lorentz-polarization effects [31,32] as well as for absorption [31,33]. Accurate unit-cell parameters were determined by a least-squares fit of 25 (**1**) and 50 (**2**) reflections. The structures were solved with SHELXS-97 [34] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-97 [35]. Scattering factors incorporated in SHELXL-93 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A \cdot P)^2 + BP \;\; (P = [\max(F_o^2, 0) + 2F_c^2] \;/3)$. No empirical extinction corrections were applied. The final values of A and B are listed in Table 1. All non-hydrogen atoms were refined anisotropically. In **1**, hydrogen atoms were put in idealized positions and refined as a 'riding model', with U_{iso} set at 1.2 times U_{eq} of appropriate carrier atom. In **2**,

Table 1
Crystal data, data collection and structure refinement

Compound	1	2
Formula	$Ni(PPh_3)_2(C_8H_{12})$	$Ni(PPh_3)_2(C_8H_8)$
Formula weight	691.43	687.39
Crystal system	monoclinic	orthorhombic
Space group	*Cc*	*Pna*2$_1$
a (Å)	17.504(4)	24.657(3)
b (Å)	11.370(2)	13.009(2)
c (Å)	17.951(4)	10.955(2)
α (°)	90	90
β (°)	102.82(3)	90
γ (°)	90	90
V (Å^3)	3483.6(13)	3514.0(9)
Z	4	4
D_{calc} (g cm^{-3})	1.318	1.299
μ (mm^{-1})	0.680	0.674
Crystal size (mm)	0.4 × 0.2 × 0.15	0.3 × 0.2 × 0.1
θ Range (°)	3–26	3–25
hkl Range	$0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 14$, $-22 \leqslant l \leqslant 21$	$-29 \leqslant h \leqslant 29$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 139$
Number of reflections collected	3544	6251
Number of unique reflections (R_{int})	3540	3172 (0.0352)
Number of reflections with $[I > 2\sigma(I)]$	3086	2738
Number of parameters	424	436
Weighting scheme		
A	0.0511	0.0238
B	1.3389	0.0
$R(F)$ $[I > 2\sigma(I)]$	0.0300	0.0303
$wR(F^2)$ $[I > 2\sigma(I)]$	0.0758	0.0601
$R(F)$ [all data]	0.0452	0.0410
$wR(F^2)$ [all data]	0.0834	0.0640
Goodness-of-fit	1.114	1.035
Maximum/minimum $\Delta\rho$ (e Å^{-3})	0.70/−0.37	0.34/−0.21

hydrogen atoms from terminal CH_2 group were refined, others were treated as in **1**. Relevant crystal data are listed in Table 1, together with refinement details.

2.4. Equipment and analytical measurements

The NMR spectra (^1H, ^{13}C, ^{31}P, ^{29}Si) were recorded on a Varian XL 300 spectrometer. In all cases, C_6D_6 was used as a 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 Megabore column (30 m, DB-1).

2.5. General procedure for catalytic test

The catalyst was placed in a Schlenk tube, equipped with a condenser, and filled with a mixture of styrene and triethoxysilane (or heptamethyltrisiloxane and vinyltris(trimethylsiloxy)silane). All manipulations were carried out using the standard Schlenk and high vacuum line techniques. The Schlenk tubes were heated at a given temperature, under argon (or in the presence of air). The distribution of substrates and products, conversion of substrates and the yield of products were determined by GC–MS and GC analyses.

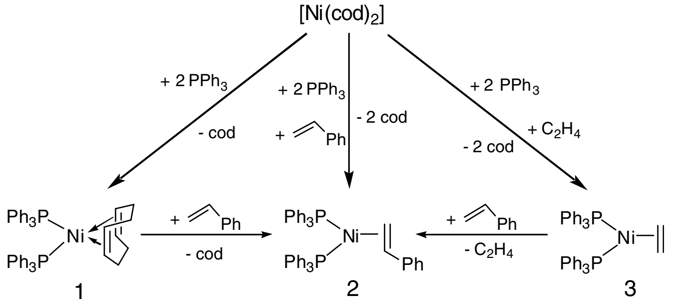
3. Results and discussion

3.1. Synthesis and structure of nickel(0) complexes

The addition of triphenylphosphine to [Ni(cod)$_2$] (in the ratio 2:1) leads to the synthesis of [Ni(PPh$_3$)$_2$(cod)] (**1**) with a high yield. The excess of PPh$_3$ or the presence of other olefins (e.g., styrene, ethylene) in this system causes a displacement of the second molecule of cyclooctadiene yielding [Ni(PPh$_3$)$_4$], [Ni(PPh$_3$)$_2$(η-CH$_2$=CHC$_6$H$_5$)] (**2**) and [Ni(PPh$_3$)$_2$C$_2$H$_4$] (**3**), respectively. Due to a stronger coordination of styrene to the metal center, when compared to the other olefinic ligands, the formation of complex [Ni(PPh$_3$)$_2$(η-CH$_2$=CHC$_6$H$_5$)] (**2**) was observed in all cases when styrene was present in the system. Complexes **1**, **2** and **3** were synthesized and fully characterized. Complex **2** was obtained in the direct reaction from [Ni(cod)$_2$] and PPh$_3$ or from complex **1** or **3** with a high yield (Scheme 1). The replacement of PPh$_3$ by PCy$_3$ permitted the synthesis of the counterpart of complex **2**, [Ni(PCy$_3$)$_2$CH$_2$=CHC$_6$H$_5$] (**4**), in an analogous reaction. The synthetic routes to complexes **1**–**4** are illustrated in Scheme 1.

Complex **3** is well known but the others have not been fully characterized yet, so the crystals of **1** and **2** suitable for X-ray diffraction were used to resolve their crystal structure.

Anisotropic ellipsoid representations of molecules **1** and **2** are presented in Figs. 1 and 2, respectively. Table 2 lists the relevant geometrical parameters.



or **4** (contains PCy$_3$ instead of PPh$_3$)

Scheme 1.

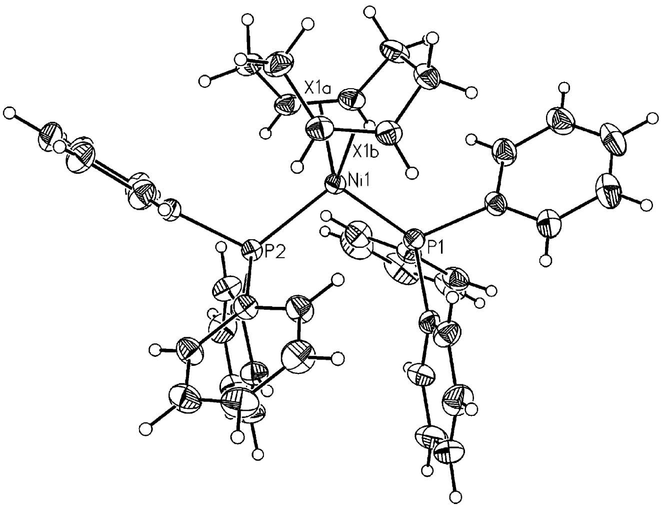


Fig. 1. Anisotropic ellipsoid representation of complex **1**. The ellipsoids are drawn at 33% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. X1a, X1b are the middlepoints of C=C bonds.

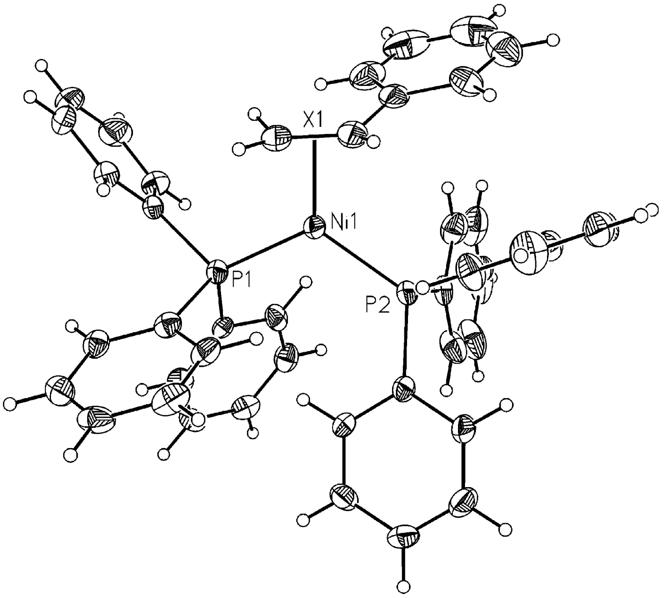


Fig. 2. Anisotropic ellipsoid representation of complex **2**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. X1 is the middlepoint of C=C bonds.

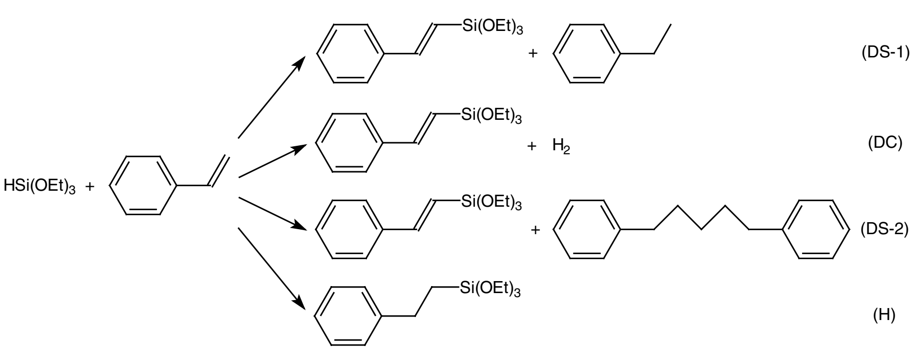
In all cases the middlepoints of the double bonds were assumed as coordination centers. In **1**, the coordination of the Ni atom is close to tetrahedral (cf. Table 2), slightly distorted due to the different ligands (a very similar geometry was found in a closely related bis-ethyldiphenylphosphine complex [36]). On the other hand, in complex **2** the coordination number of the central Ni atom is 3, and nickel lies very close (0.044(1) Å) to the plane defined by P1, P2 and X (middlepoint of the double C=C bond) – in this case, the coordination is therefore trigonal. It was found that Ni–P distances in the crystal structures show bimodal distribution with the mean values around 2.187 and 2.321 Å, without apparent chemical distinction between these two groups [37]. The Ni–P distances in **1** and **2** belong to the group with shorter bond lengths (2.16–2.19 Å).

The phenyl rings are almost ideally planar (maximum deviation from the least squares plane is 0.020(2) Å). Their mutual disposition may be described by the dihedral angles between their planes or by the dihedral angles between the phenyl ring and the P–Ni–P plane. The latter values in **1** are all large, almost close to 90° (65–89°; mean value is 80°), while in **2** these values are significantly smaller (mean values are 64°). In **1**, the cycloocta-1,5-diene fragment adopts a nearly ideal boat conformation. This is confirmed by the values of torsion angles (Table 1) and of ΔC_2 asymmetry parameter of 1.35°. The bond lengths pattern clearly shows a distinction between single and double bonds.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of complexes **1**–**4**, show the signals in the expected region, typical of the phosphine nickel π-complexes.

3.2. Catalytic examinations

The above complexes **1**–**3** were used as catalysts in the reaction between styrene and triethoxysilane:



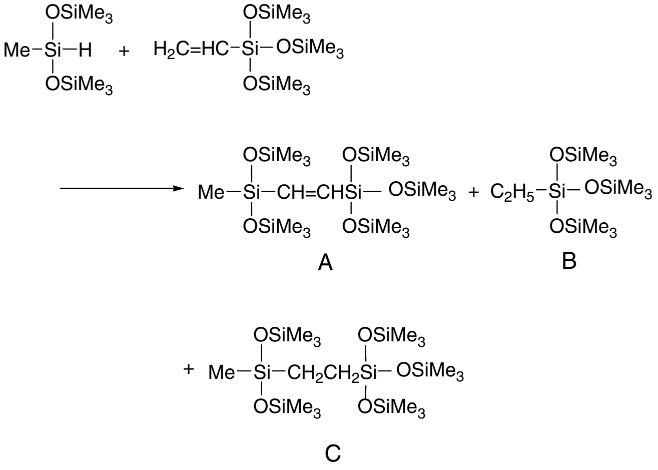
(2)

Besides, the presence of small amounts of tetrasubstituted silanes $Si(OEt)_4$ and siloxanes, as by-products coming from disproportionation of $HSi(OEt)_3$, and their condensation, is also observed. The yields of these reactions and product distributions are presented in Table 3.

The amount of **DS** ($PhCH{=}CHSi(OEt)_3$) is equal to the sum of the second products of hydrogenative silylation (C_2H_5Ph), hydrogenative dimerization ($Ph(CH_2)_4Ph$) and hydrogen evolved.

The reaction that occurred in the presence of air showed the preference of dehydrogenative coupling **DC** over dehydrogenative silylation **DS-1** and particularly **DS-2**. In all cases, the dehydrogenative silylation **DS** pathway dominates over hydrosilylation **H**.

The nickel complexes **1**, **2**, and **4** were also used as catalysts in the reaction of vinyltris(trimethylsiloxy)silane with heptamethyltrisiloxane, which is a model reaction for cross-linking of polysiloxane via hydrosilylation:



(3)

The obtained results are presented in Table 4.

All the obtained results show that tertiary phosphines strongly stabilize nickel complexes; therefore, they are inactive in the atmosphere of argon. However, after stepwise elimination of phosphine via oxygenation in air, these complexes are as active as $[Ni(cod)_2]$, and they catalyzed mainly dehydrogenative silylation of olefins. In the dehydrogenative silylation of styrene by triethoxysilane in air, complex **2** containing styrene as a ligand was the most active.

It is worthy to say that phosphines stabilize Ni complexes (contrary to complexes without phosphines, i.e.,

Table 2
Relevant geometrical parameters (Å, °)

	Compound **1**	Compound **2**
Ni–P	2.182(1) 2.189(1)	2.156(1) 2.168(1)
Ni–X	1.9984(6) 2.0160(5)	1.849(7)
⟨P–C⟩	1.839(4)	1.835(4)
⟨C–Si⟩		
P–Ni–P	107.56(4)	116.67(4)
P–Ni–X	117.13(4) 111.59(3) 112.83(4) 116.99(3)	119.18(3) 124.02(4)
X–Ni–X	90.35(2)	

X denotes the middlepoint of the double bond, regarded as the coordination site.

Table 3
Dehydrogenative silylation vs. hydrosilylation of styrene with triethoxysilane catalyzed by nickel(0) complexes

Catalyst	Yield (%)	Product distribution			Ratio DC:DS-1:DS-2
		DS	H	Other	
$Ni(cod)_2$	83	85	11	4	0.20:0.46:0.34
1	5	80	5	15	0.43:0.38:0.19
1[a]	76	78	10	12	0.64:0.26:0.10
2	7	81	8	11	0.43:0.43:0.14
2[a]	90	90	8	2	0.64:0.33:0.02
3	4	76	4	20	0.41:0.33:0.26
3[a]	79	80	15	5	0.56:0.38:0.06

[HSi≡]: [CH_2=CHPh]:[cat] = 1:2:10^{-3}; T = 120 °C, t = 2 h; in argon.
[a] In air.

Table 4
The reaction of vinyltris(trimethylsiloxy)silane with heptamethyltrisiloxane catalyzed by nickel(0) complexes

Catalyst	Conversion (%)		Yield of product (%)			Ratio DC:DS:H
	HSi≡	CH_2=CHSi	A	B	C	
[$Ni(cod)_2$]	88	91	64	19	5	0.65:0.28:0.07
1	5	6	3	2	trace	
1[a]	54	57	36	15	2	0.55:0.39:0.06
2	2	3	1	1	trace	
2[a]	39	42	27	10	1	0.60:0.36:0.04
4	6	8	4	2	trace	
4[a]	87	90	65	18	3	0.69:0.26:0.05

[HSi≡]:[CH_2=CHSi]:[cat] = 1:2:10^{-3}; T = 120 °C; t = 24 h; in argon.
[a] In air.

[$Ni(cod)_2$]) preferring the dehydrogenative silylation via direct dehydrogenation step (**DC**) over **DS-1** and **DS-2**. On the other hand, in the dehydrogenative silylation of vinyltris(trimethylsiloxy)silane, no hydrogenated dimerization step (**DS-2**) was observed. The catalytic activity of the complexes examined depends on the kind of phosphine, as follows from the observations of the hydrosilylation of vinyltris(trimethylsiloxy)silane by heptamethyltrisiloxane. Oxidation of tricyclohexylphosphine proceeds easier than that of triphenylphosphine; therefore, the complex [$Ni(PCy_3)_2(CH_2$=$CHC_6H_5)$] (**4**) is more active than [$Ni(PPh_3)_2(CH_2$=$CHC_6H_5)$] (**2**) in the examined reaction proceeding in the air.

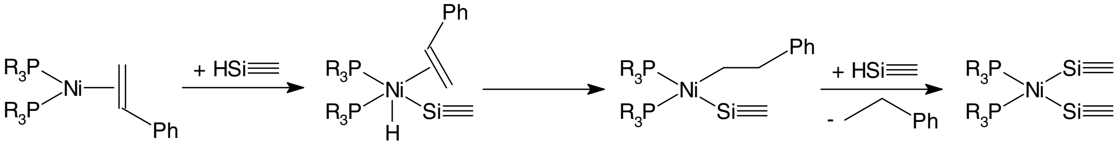
3.3. Stoichiometric reactions

It is obvious that the first step in the catalysis of dehydrogenative silylation of olefins by Ni(0) complexes is the coordination of olefin to nickel (generally by the displacement of ligands) but in order to explain the next steps, a separate study of the reaction of **2** (and **4**) in excess of triethoxysilane at 60 °C was undertaken (see Scheme 2).

After 6 h, in the reaction mixture, ethylbenzene was detected by GC–MS analysis. After the removal of volatiles, the product was characterized by NMR analysis. The location and intensity of signals in NMR spectra confirmed the presence of two triethoxysilyl groups and two molecules of triphenylphosphine at the nickel center. The formation of the same type of bis(silyl)nickel complex was reported previously by us; however, this complex was stabilized by divinyltetramethyldisiloxane [11]. The reaction between **2** and triethoxysilane was very fast, so it was not possible to observe the first complex **5a** – product of oxidative addition of one molecule of triethoxysilane; however, it was possible to observe it in the reaction of **4** with heptamethyltrisiloxane. Low-temperature ^{1}H NMR spectra of the mixture of **4** and trisiloxane showed signals at −15.9 ppm (see Fig. 3), which is the evidence for the presence of hydrido-nickel complex **5a**.

The addition of the next molecule of trisiloxane led to obtaining the bis(silyl)nickel complex with simultaneous elimination of ethylbenzene (observed by GC–MS method).

The bis(silyl)nickel complexes seem to be the real catalyst (the active intermediates) in all reactions between



2, 4 **5a** **5**

where R = Ph, Cy
HSi≡ = HSi$(OEt)_3$, HSiMe$(OSiMe_3)_2$

Scheme 2.

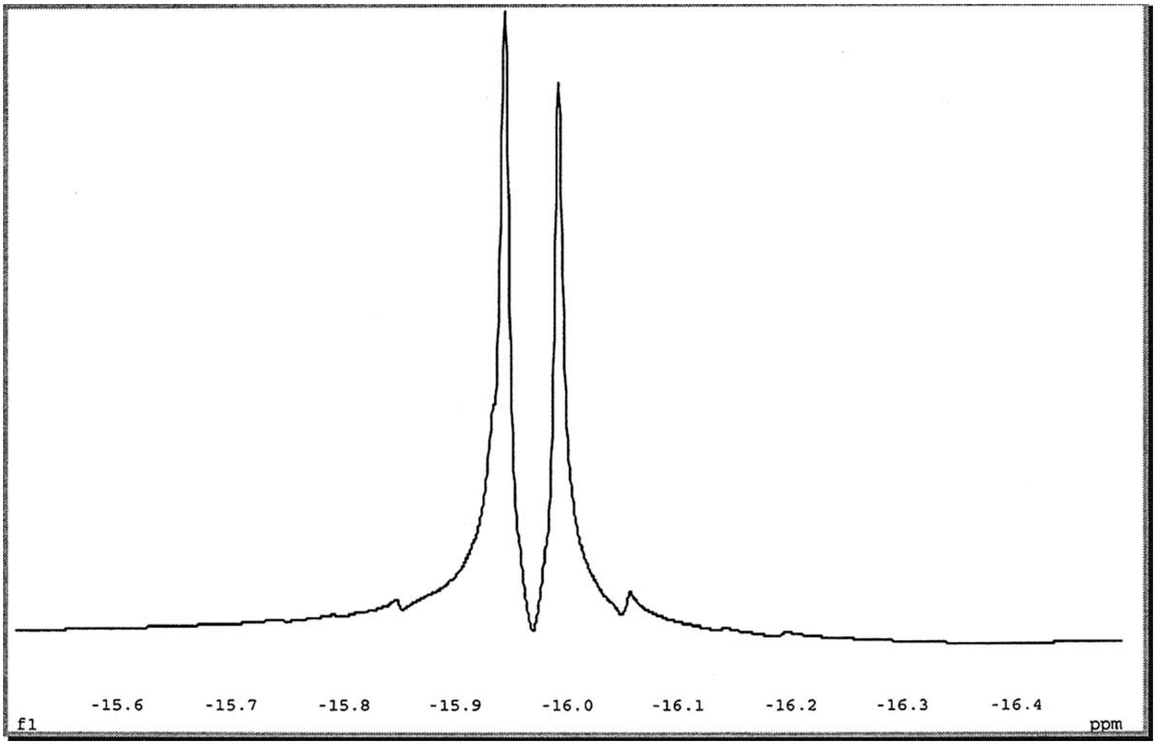


Fig. 3. Low-temperature ^{1}H NMR spectra of the mixture of **4** and heptamethyltrisiloxane.

trisubstituted silanes and olefins catalyzed by nickel complexes. Confirmation of this fact is the reaction (in air) of complex **5** with excess of styrene at 60 °C. After the reaction, similarly as in the previously reported results [11], the product of dehydrogenative silylation (1-phenyl-2-silylethene) was detected by the GC–MS analysis, which evidenced the insertion of styrene molecule into the Ni–Si. Additionally, phosphine oxide was observed.

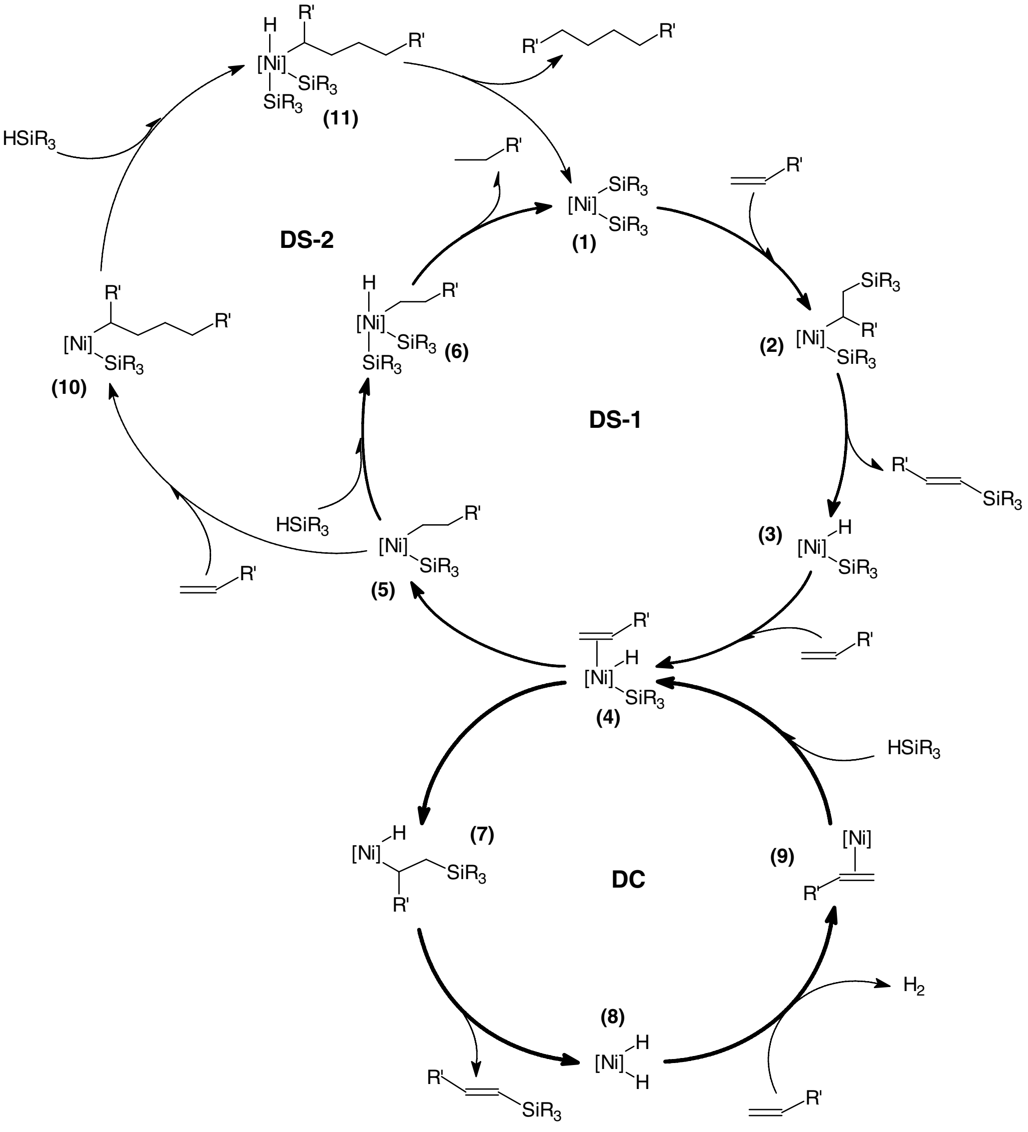
3.4. Mechanistic implications

The key step of catalysis by nickel complexes is the formation of bis(silyl) species depending on the starting nickel precursor. In the case of Ni(0) precursor, at the beginning the coordination of olefins to metal is observed. This coordinated olefin plays the role of a hydrogen acceptor from hydrosilanes; therefore, after elimination of alkane (product of hydrogenation of olefins) the bis(silyl)nickel complex is formed, as a product of oxidative addition of two molecules of silane to the nickel. The formation of bis(silyl)-nickel complex from Ni(II) precursors occurs via the oxidative addition of silane followed by the replacement of an ionic ligand from Ni(II) precursor [22]. Therefore, the differences in the catalytic activity of nickel(0) and nickel(II) precursors are observed. Due to high coordination of tertiary phosphines to nickel center, the complexes obtained are inactive; however, the use of phosphine permitted isolation of the intermediates formed in the course of the catalytic reaction.

On the basis of our experience, we may say that generally the nickel(0) complexes are more active catalysts than the nickel(II) ones in the dehydrogenative silylation processes, because in most cases the formation of bis(silyl)nickel complex proceeds easier from nickel(0) precursor. Regardless of the nickel precursor used, the formed bis(silyl)nickel complex is an active intermediate responsible for the formation of the dehydrogenative silylation products, according to Scheme 3 (side hydrosilylation process is omitted for clarity).

The evidence for this is the insertion of styrene into the Ni–Si bond in complex **5** and $[Ni\{(CH_2{=}CHSiMe_2)_2O\}(CH_2{=}CHC_6H_5)]$ [11] and also ethylene into the complex $[Ni(PBu_3)_2(SiMeCl_2)_2]$ [22]. In all of these reactions, the unsaturated products of dehydrogenative silylation were formed. As follows from analysis of the catalytic data, **DC** competes with **DS-1** cycle in both dehydrogenative silylation processes studied. The insertion of olefin into M–Si bond (silyl migration) proceeds more readily than into M–H bond (hydrid migration), which is a characteristic feature of general Seitz–Wrighton mechanism of dehydrogenative silylation. In the silylation of vinyltris(trimethylsiloxy)silane, the latter molecule can stabilize **8** even in the absence of phosphine. In this reaction, the **DS-2** process is not observed, presumably due to a steric hindrance of vinylsiloxane, preventing its insertion into Ni–C bond (complex **5**).

The isolation and also spectroscopic and crystallographic characterization of bis(silyl)platinum complex have been recently described [38]. On the basis of the results from the catalytic and stoichiometric reactions, the authors postulate that bis(silyl)platinum complex is the truly catalytic species responsible for Pt-catalyzed dehydrogenative silylation processes.



Scheme 3.

4. Conclusions

1. Nickel(0) complexes **1**–**4** containing π coordinated olefins have been prepared starting from $Ni(cod)_2$, olefins and triphenylphosphine (tricyclohexylphosphine) as substrates. The X-ray crystal structures were resolved for two of them **1** and **2**.
2. Complexes **1**–**4** were used as catalysts of dehydrogenative silylation of styrene and vinyltris(trimethylsiloxy)silane, showing high efficiency only after prior elimination of phosphine via oxygenation in air.
3. Equimolar reactions of **2** and **4** with substrates evidenced that bis(silyl)nickel(II) complex is a key intermediate in the reactions examined. A scheme of catalysis of dehydrogenative silylation by all Ni(0) complexes (**1**–**4**) including an insertion of olefin into Ni–Si bonds as a crucial step, is proposed.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 232292 (**1**) and CCDC 232293 (**2**). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgment

This work was supported by the State Committee for Scientific Research (Poland), Project No. 3 T09B 121 26.

References

[1] B. Marciniec (Ed.), Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford, 1992.

[2] B. Marciniec, in: B. Cornils, W.A. Herrman (Eds.), Applied Homogenous Catalysis with Organometallic Compounds, Verlag Chemie, Weinheim, 2002 (Chapter 2.6).

[3] I. Ojima, Z. Li, J. Zhu, in: Z. Rapport, Y. Apehoig (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1998.

[4] M.A. Brook, Organic, Organometallic and Polymer Chemistry, Wiley, New York, 2000.

[5] B. Marciniec, J. Guliński, H. Maciejewski, in: I.T. Horvath (Ed.), Encyclopedia of Catalysis, Wiley, New York, 2003, pp. 107–152.

[6] A.J. Chalk, J.F. Harrod, J. Am. Chem. Soc. 87 (1965) 16.

[7] M.A. Schroeder, M.S. Wrighton, J. Organomet. Chem. 128 (1977) 345.

[8] F. Seitz, M.S. Wrighton, Angew. Chem., Int. Ed. Engl. 27 (1988) 289.

[9] B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374.

[10] B. Marciniec, H. Maciejewski, J. Organomet. Chem. 454 (1993) 45.

[11] H. Maciejewski, B. Marciniec, I. Kownacki, J. Organomet. Chem. 597 (2000) 175.

[12] B. Marciniec, H. Maciejewski, I. Kownacki, J. Mol. Catal. A 135 (1998) 223.

[13] S.K. Janikowski, L.J. Radonowich, T.J. Groshens, K.J. Klabunde, Organometallics 4 (1985) 396.

[14] T.J. Groshens, K.J. Klabunde, J. Organomet. Chem. 259 (1983) 337.

[15] S.T. Lin, T.J. Groshens, K.J. Klabunde, Inorg. Chem. 23 (1984) 1.

[16] T.J. Groshens, K.J. Klabunde, Organometallics 1 (1982) 564.

[17] T.R. Bierschenk, M.A. Guerra, T.J. Juhlka, S.B. Larson, R.J. Lagow, J. Am. Chem. Soc. 109 (1987) 4855.

[18] S.-B. Choe, K.J. Klabunde, J. Organomet. Chem. 359 (1989) 409.

[19] S.-B. Choe, J. Schneider, K.J. Klabunde, L.J. Radonovich, J. Organomet. Chem. 376 (1989) 419.

[20] M. Brzeziński, J. Schneider, L.J. Radonovich, K.J. Klabunde, Inorg. Chem. 28 (1989) 2414.

[21] S. Schimada, M.L. Rao, M. Tanaka, Organometallics 18 (1999) 291.

[22] H. Maciejewski, B. Marciniec, J. Guliński, A. Karolak, N.K. Skvortsov, Inorg. Chem. Commun. 5 (2002) 464.

[23] B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996.

[24] P.B. Hitchcock, M.F. Lappert, H. Maciejewski, J. Organomet. Chem. 605 (2000) 221.

[25] H. Maciejewski, M. Kubicki, B. Marciniec, A. Sydor, Polyhedron 21 (2002) 1261.

[26] H. Maciejewski, A. Sydor, M. Kubicki, J. Organomet. Chem. 689 (2004) 3075.

[27] D.J. Krysan, P.B. Mackenzie, J. Org. Chem. 55 (1990) 4229.

[28] C.A Tolman, W.M. Riggs, W.J. Linn, C.M. King, R.C. Wendt, Inorg. Chem. 12 (1973) 2770.

[29] P. Giannoccaro, A. Sacco, G. Vasapollo, Inorg. Chim. Acta 37 (1979) L455.

[30] CAD-4 Software, Version 5, Enraf-Nonius, Delft, The Netherlands, 1989.

[31] KUMA, KUMA KM4 Software, Version 5.0, KUMA Diffraction, Wrocław, Poland, 1992.

[32] CRYSALISRED: Program for Reduction of the Data from Kuma CCD Diffractometer, Kuma Diffraction, Wrocław, Poland, 1999.

[33] R.H. Blessing, J. Appl. Crystallogr. 22 (1989) 396.

[34] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[35] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

[36] R. Kempe, J. Sieler, D. Walther, Z. Kristallogr. 211 (1996) 565.

[37] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, G. Orpen, R. Taylor, J. Chem. Soc., Dalton Trans. (1987) S1.

[38] A.K. Roy, R.B. Taylor, J. Am. Chem. Soc. 124 (2002) 951.