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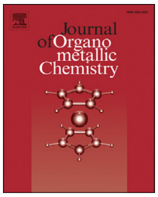

Hydrosilylation *vs.* dehydrogenative silylation of styrene catalysed by iron(0) carbonyl complexes with multivinylsilicon ligands – Mechanistic implications

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ABSTRACT

Well-defined iron(0) complexes with multivinylsilicon ligands of the formula $[Fe(CO)_3L]$ and $\{[Fe(CO)_3]_2L'\}$, where L = dienes, trienes or vinylfunctional silicones and L′ = tetraenes, are new very active and effective catalysts for hydrosilylation and/or dehydrogenative silylation of styrene with trisubstituted silanes and hydrosiloxanes. All catalytic data and selected kinetic measurements as well as the information on stoichiometric reactions of the new precursor catalysts with model substrates (followed by NMR and GC–MS techniques), supported by the relative energies of transition states and intermediates obtained by DFT calculations, permitted proposing a rational mechanism for the catalysis in alkene hydrosilylation, proceeding according to the Chalk-Harrod and/or modified Chalk-Harrod mechanisms.

Introduction

The hydrosilylation reaction of carbon–carbon multiple bonds is commonly used as an efficient tool for the synthesis of a wide range of organosilanes and polysiloxanes as well as for the addition curing of silicone fluids. However, literature and patented data indicate that in the industrial processes, general application of catalytic systems is limited to compounds of noble metals, particularly platinum, e.g. Speier, Karstedt catalysts [1]. The possibility of replacing expensive platinum catalysts with catalytically active derivatives of cheaper transition metals such as Ru or Fe, is a promising alternative and a challenge for many research teams. Recently, Chirik, Ritter groups published results on the application of bis(imino)pyridine and terpyridine and iminopyridine iron complexes in the hydrosilylation of alkenes by primary, secondary [2], and tertiary silanes [3] as well as dienes [4]. On the other hand, $[FeCp(CO)_2Me]$ as reported by Nakazawa, appears to be an efficient catalyst for the dehydrogenative silylation at one vinyl group and hydrogenation at the second one in 1,3-divinyldisiloxane [5]. The iron triad (Fe, Ru and also Os) complexes including carbonyls, competitively catalyse hydrosilylation and dehydrogenative silylation [1]. The key step of this mechanism is the insertion of an olefin into M–H or M–Si bonds to give products of hydrosilylation and/or dehydrogenative silylation [1b] and references therein]. The desired step of the two alternative reactions is actually the competitive β-H transfer from the two ligands (σ-alkyl and σ-silylalkyl) in the complex formed during the reaction (see Scheme 1). A theoretical study has recently explained that the complexes of Ni, Pd, Pt are preferred in the hydrosilylation of olefins, while the complexes of Fe (also to some extent Co) have been shown to be extremely favourable catalysts for the dehydrogenative silylation of olefins, particularly with electron withdrawing substituents [1,6,7]. It is well-recognized that iron complexes such as $[Fe(CO)_5]$ at high temperature and/or upon UV irradiation under mild conditions catalyse both reactions, i.e. dehydrogenative silylation and hydrosilylation [8]. The mechanism proposed by

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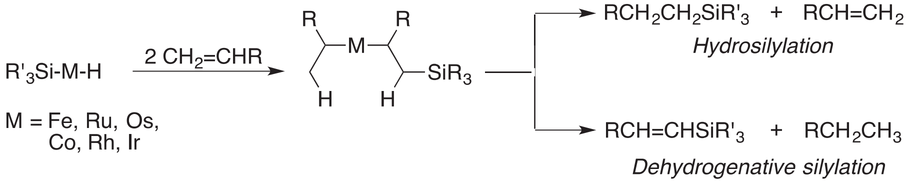


Scheme 1. Mechanism of hydrosilylation *vs.* dehydrogenative silylation reaction.

Randolph and Wrighton assumed important role of irradiation in the formation of catalytically active [Fe(CO)$_3$] species *via* photodissociation of the Fe–CO bond [9].

We have recently developed a general strategy for the synthesis of well-defined iron(0) carbonyl complexes ([Fe(CO)$_3$(L)]) or [{Fe(CO)$_3$}$_2$L] stabilized by multivinylsilicon ligands (where L = diene, triene, tetraene, polyvinyl silicon derivatives) (Scheme 2). Their structures were determined by spectroscopic and X-ray methods [10a,b].

The aim of this paper is to present a full picture of the catalysis of hydrosilylation *vs.* dehydrogenative silylation of styrene by these new Fe(0) complexes (**1**–**9**) (Scheme 2). [Fe(CO)$_3$(cod)] (**10**) and [Fe(CO)$_5$] (**11**) were used for comparison.

Experimental

All syntheses and manipulations were carried out under argon using standard Schlenk and vacuum techniques. The ^{1}H NMR spectra were recorded using a Bruker Ultra Shield NMR spectrometer (600 MHz) in toluene-d$_8$ and referred to the residual protonated solvent peaks (^{1}H δ_H = 2.09 ppm (–Me), ^{13}C δ_C = 20.05 ppm (–Me) for toluene-d$_8$). The volatile compounds were determined by GC–MS (Varian Saturn 2100T equipped with capillary column Varian VF-1 Factor Four, 0.26 mm, 30 m). GC analyses were carried out on a Varian 3400 CX series gas chromatograph equipped with a capillary column Varian VF-5 Factor Four, 30 m and TCD. Yield was calculated on the basis of HSiR$_3$ conversion, using the internal standard calculation method according to the formula $Y(\%) = S \cdot C_{HSi\equiv}$ (S = selectivity of the product obtained, $C_{HSi\equiv}$ = conversion of trisubstituted silane (%)). The chemicals were obtained from the following sources: HSiEt$_3$, HSiMe$_2$Ph and heptamethyltrisiloxane (HSiMe(OSiMe$_3$)$_2$) from ABCR, decane, styrene, toluene-d$_8$ from Sigma Aldrich Co., pentane, toluene, benzene from POCH Gliwice (Poland). All solvents and liquid reagents were dried and distilled under argon prior to use. The iron(0) complexes used for catalytic examinations were synthesized according to published method [10].

Catalytic examinations

The tests on the catalytic activity of iron(0) complexes were conducted in glass ampoules (or Schlenk tubes) filled with a mixture of styrene (3.6 mmol, 0.42 mL), trisubstituted silane (1.8 mmol or 3.6 mmol), toluene 1 mL and decane (5% of initial liquid substrates volume) as an internal standard, under argon atmosphere. Then to the initial mixture iron(0) catalyst ($1.8 \cdot 10^{-2}$ mmol) was added. The ampoules (or Schlenk tubes) were heated to a desired temperature in oil bath. The catalytic reactions at low temperature were carried out using the kinetic reactor cooled with chiller cooling system.

The distribution of substrates and products, conversion of substrates and the yield of products in all tests were determined by GC and GC–MS analysis.

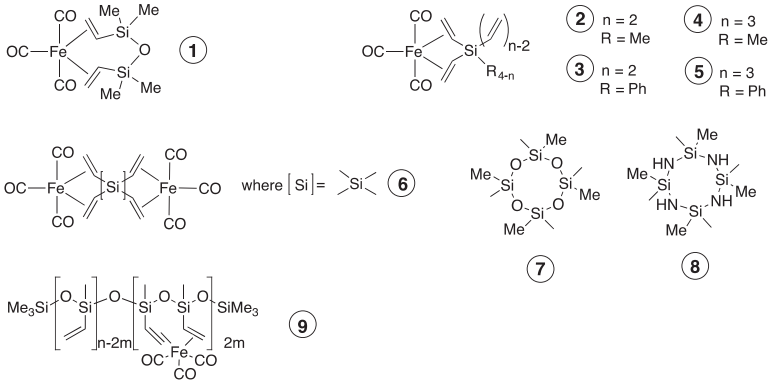
Kinetic examinations

Kinetic measurements were carried out in a reactor (4 mL) equipped with a reflux condenser, inlet for inert gasses and a magnetic stirrer. Appropriate amounts of the catalyst and reagents were placed in the reactor. GC and GCMS analyses were carried out during the reaction. The conversion of substrates and the yield of products were calculated using the internal standard method (see Supplementary Information).

Selected kinetic curves of the dehydrogenative silylation of styrene at the molar ratio [HSiMe$_2$Ph]: [PhCH = CH$_2$] = 1: 2 and hydrosilylation of styrene at the molar ratio [HSiMe$_2$Ph]: [PhCH = CH$_2$] = 1: 1, in the presence of iron(0) complex **1** were used to determine k_{obs}^{HD} and k_{obs}^{H}, respectively. The rate constants were calculated by fitting the experimental concentration 2.303log $[1-c_{HSi\equiv}]$ *vs.* time to an exponential function using the nonlinear least-squares procedures. The activation energy for both reaction was calculated from the Arrhenius plot.

Theoretical calculations

Quantum-chemical calculations were performed with the Gaussian 03 program [11]. Initial geometries of substrates and



Scheme 2. Formulae of iron(0) complexes with multivinyl silicon ligands used for the catalytic examinations.

products were built on the basis of the averaged values of bonds lengths and valence angles with the help of Marvin package [12] and were subjected to full geometry optimization. The calculations were carried out at the most popular for such systems and probably that is why most often criticized [13] B3LYP/LANL2DZ level [14,15] being a compromise between the quality of obtained results and the computation time needed. Vibrational analyses were undertaken to verify if the optimized stationary point was indeed a minimum or a saddle point (transition state) [16]. In the case of transition state (one imaginary frequency) the IRC [17] calculations were carried out to identify the energy minima on both sides of the transition state. Interaction energies between the Fe catalyst and the alkene were calculated with the usual counterpoise correction to account at least in some part for basis set superposition error [18].

Stoichiometric reaction of complex 1 with $HSiMe_2Ph$ and styrene

In the NMR Young's tube, 45 mg ($1.38\cdot10^{-4}$ mol) of iron complex (**1**) and 0.6 mL of toluene-d_8 were placed under an argon atmosphere. The solution obtained was cooled to −60 °C, and then the tube was placed in a spectrometer. The first ^{1}H NMR spectrum was recorded at −40 °C. In the next step, 18.80 mg ($1.38\cdot10^{-4}$ mol) $HSiMe_2Ph$ was added to the solution of the complex at −60 °C. The NMR spectra were recorded starting from −40 °C on increasing temperature by about 10 °C in each 30 min to reach −10 °C. Thirty minutes after reaching the desired temperature, the next ^{1}H NMR spectrum was recorded, and then at this temperature 15 mg ($1.38\cdot10^{-4}$ mol) of styrene was introduced to the NMR tube. The subsequent spectra were recorded after each 30 min on raising temperature at a rate of 10 °C per 30 min, up to room temperature.

Stoichiometric reaction of complex 1 with styrene

In the NMR Young's tube, 32.6 mg ($9.2\cdot10^{-5}$ mol) of iron complex (**1**) and 0.6 mL of toluene-d_8 were placed under an argon atmosphere, then the first ^{1}H and ^{13}C NMR spectra were recorded at room temperature. At the next step 38.3 mg ($3.68\cdot10^{-4}$ mol) of styrene was introduced to the NMR tube and the reaction was carried out for 24 h at room temperature. After this time, ^{1}H and ^{13}C NMR spectra were recorded again.

Results and discussion

Catalytic study

All the iron(0)carbonyl complexes (**1**–**11**) were tested in the reaction of styrene with trisubstituted silanes Et_3SiH, Me_2PhSiH and $Me(OSiMe_3)_2SiH$. Here it should be mentioned that in the case of binuclear complexes, particularly those stabilized by tetravinyl substituted cyclosilicon derivatives such as 1,3,5,7-tetravinyl-1,3,5,7-tetramethyl- cyclotetrasiloxane or cyclotetrasilazane more geometrically matched isomeric molecules, present in the initial silicon reagent, should be involved in the formation of more thermodynamically stable iron(0) carbonyl complexes. Therefore, when in the synthesis of complex **7**, the compound 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane was used as a ligand only one isomer in which all vinyl groups are in axial position, can be involved in the formation of binuclear complex. However, when 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasilazane was used instead of cyclosiloxane, the solid material used in catalytic tests can contain two isomeric complexes **8**, namely those formed with the employment of two isomeric cyclosilazanes, in which all vinyl groups are in axial position or three vinyl groups are in axial position and one nitrogen atom is involved in stabilization of iron centre, as reported in our previous paper [10b].

The catalytic results (Fig. 1) illustrate high effectiveness of most of these new iron complexes in the dehydrogenative silylation of styrene at 80 °C leading to the exclusive formation of unsaturated organosilicon product.

In the presence of some catalysts (**1**, **4**, **5**, **9**) the total conversion of substrates was observed already after a few hours. In all experiments performed, complexes **1**, **4**, **5** and **9** were good catalysts with **1** being the most effective and selective for dehydrogenative silylation at temperature 80 °C, while $[Fe(CO)_3(cod)]$ (**10**) and $[Fe(CO)_5]$ (**11**) have proven to be moderately active in the studied systems. However, on decreasing temperature to the range −15 to +20 °C under equimolar substrate concentrations, complex **1** turned out to be active for the hydrosilylation reaction leading to selective formation of saturated hydrosilylation product (**A**) (Scheme 3 and Table 1) with good yield, whereas at double excess of olefin, both reactions occurred.

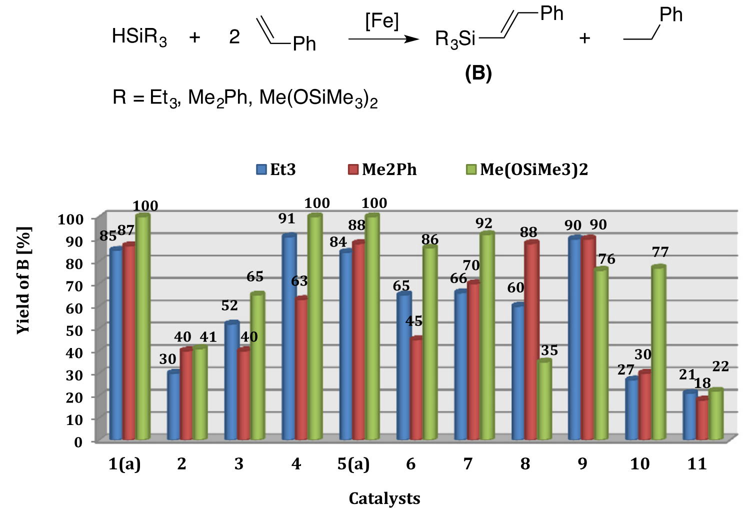
Comparing the catalytic results presented in Fig. 1 with the data of DFT computational study, in particular the calculated interaction energies (see Table 1) of the systems composed of the vinylsilicon ligand and the $Fe(CO)_3$ core, confirmed that complex **1** with $(H_2C{=}CHSiMe_2)_2O$ molecule bonded to iron is the most active catalyst. In this compound, 1,3-divinyltetramethyldisiloxane molecule interacts with metallic centre weaker than the other divinylsubstituted silicon derivatives such as $(H_2C{=}CH)_2SiMe_2$, $(H_2C{=}CH)_2SiPh_2$. Lower compliance of catalytic results with theoretical calculations was found for the complexes stabilized by trivinylsilanesilanes such as $(H_2C{=}CH)_3SiMe$, $(H_2C{=}CH)_3SiPh$ (for more information see Electronic Supplementary Data), which proved to show higher catalytic activity than expected on the basis of the higher energy value of the trivinyl silicon ligand interactions with the metal centre.

The kinetic measurements performed in the temperature range of 50–70 °C for dehydrogenative silylation and of 0–10 °C for hydrosilylation, followed by GC, enabled the calculation of the pseudo first-order rate constants k_{obs}^{HD} and k_{obs}^{H}, respectively. The basis of both processes was the consumption of the substrate ($HSiMe_2Ph$) (see Table 2).

The effect of temperature on the k_{obs}^{HD} and k_{obs}^{H} permitted the estimation of activation energy E_a, for dehydrogenative silylation (15.8 [kcal/mol], $[HSiMe_2Ph]$: $[PhCH = CH_2] = 1: 2$) (Fig. 2) and hydrosilylation (15.9 [kcal/mol], $[HSiMe_2Ph]$: $[PhCH = CH_2] = 1: 1$) (Fig. 3).

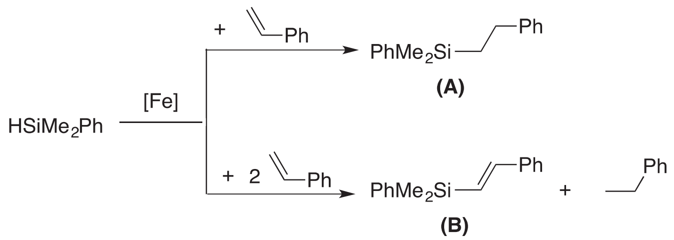
The reactivity of iron complex **1** was also studied in the reaction with $HSiMe_2Ph$ in which the ^{1}H NMR measurements were started at −40 °C. The first signs of $HSiMe_2Ph$ oxidative addition to the initial iron precursor were observed at −20 °C, as at this temperature the resonance at −11.34 ppm appeared. An increase in temperature up to −10 °C caused a significant increase in the height of this signal, but addition of styrene to the reaction mixture at −10 °C, led to total disappearance of the resonance line at −11.34 ppm with the simultaneous appearance of new lines at −9.60 ppm (coming from a new hydride-silyl iron(II) species) as well as −0.36 and −0.46 ppm (derived from alkyl complexes formed after insertion of styrene molecule into the Fe–H bond), as shown in Scheme 5.

Considering the DFT calculations of interaction energies of iron(II) species $[FeH(CO)_3(SiMe_2Ph)]$ with $(H_2C{=}CHSiMe_2)_2O$ (24.8 kcal/mol) and $H_2C{=}CHPh$ (22.8 kcal/mol) (see Electronic Supplementary Data, Table S3) it may be assumed that in the first step of the oxidative addition of $HSiMe_2Ph$ to the initial iron(0) carbonyl complex, the formation of hydride-silyl iron(II) species with η^2-bonded 1,3-divinyltetramethyldisiloxane ligand is preferred, according to Scheme 4 (see Electronic Supplementary Data, Fig. 1). However, in the next step, the addition of styrene to



Reaction conditions: [$HSiR_3$] : [$PhCH{=}CH_2$] : [Fe] = 1 : 2 : 10^{-2}, Temperature = 80 °C, Reaction time = 24h, toluene, under argon; (a) – 1h

Fig. 1. Dehydrogenative silylation of styrene with trisubstituted silanes. Reaction conditions: [$HSiR_3$] : [$PhCH{=}CH_2$] : [Fe] = 1 : 2 : 10^{-2}, Temperature = 80 °C, Reaction time = 24h, toluene, under argon; (a) – 1h.



Scheme 3. General scheme of hydrosilylation *vs.* dehydrogenative silylation of styrene.

the reaction mixture containing of the latter iron(II) species results in the formation of hydride-silyl iron(II) complex with η^2-bonded styrene molecule which formally initiate the formation of silicon styrene derivatives, as shown in Scheme 5.

Analysis of the reaction mixture obtained under these conditions by GC–MS technique confirmed the formation of the product of styrene hydrosilylation ($PhCH_2CH_2SiMe_2Ph$).

The quantitative calculations revealed that in the temperature range from −40 to 0 °C, only 21% of the initial amount of $HSiMe_2Ph$ was consumed. It was only when the reaction mixture had reached a temperature 10 °C, that a rapid conversion of the starting silane at this temperature was observed and it reached a value of 92%. Under these conditions, only 42% of the initial amount of HSi≡ reagent was involved in the formation of styrene hydrosilylation product. The point is that in the system studied, $HSiMe_2Ph$ applied for the reaction had an opportunity to react with two additional moles of unsaturated groups coming from 1,3-divinyltetramethyldisiloxane ligand, besides the vinyl group coming from styrene which was added to the reaction mixture according to the molar ratio [Fe]: [HSi≡]: [$H_2C{=}CHPh$] = 1: 1: 1. The GC–MS analysis of the reaction mixture obtained, unambiguously confirmed the presence of 1,3-divinyltetramethyldisiloxane derivatives, such us hydrosilylation and hydrogenation products, e.g. $H_2C{=}CHSiMe_2OSiMe_2CH_2CH_2Si$ Me_2Ph (Yield = 8%) (MS data (%): 322.3 (M, 5.2); 307.2 (M−15, 12.5); 293.3 (8.5); $CH_3CH_2SiMe_2OSiMe_2CH_2CH_2SiMe_2Ph$ (Yield = 24%) (MS data (%): 309.2 (M−15, 75.0); 295.2 (23.5)).

Table 1
Calculated interaction energies (counterpoise corrected) between the vinylsilicon ligand and $Fe(CO)_3$ moiety.

Complex	Alkene[a]	Interaction energy [kcal/mol]
1	$(H_2C{=}CHSiMe_2)_2O$	−62.8
2	$(H_2C{=}CH)_2SiMe_2$	−68.5
3	$(H_2C{=}CH)_2SiPh_2$	−67.4
4	$(H_2C{=}CH)_3SiMe$	−68.8
5	$(H_2C{=}CH)_3SiPh$	−68.8

[a] Despite much effort we did not obtain the convergence of SCF calculations for systems containing two Fe centres.

Additionally, in order to check for other pathways of transformation of vinylsilicon-stabilized iron(0) precursors, for example the substitution process of divinylsilicon ligands with the styrene, the reaction of complex **1** with the latter at ambient conditions was also performed and followed by NMR technique. Introduction of styrene to the solution of complex **1** resulted in significant changes in the ^{1}H and ^{13}C NMR spectra with respect to those obtained for the solution of the initial complex (see Electronic Supplementary Data, Fig. 2). In the ^{1}H NMR spectrum recorded after addition of styrene to the solution of complex **1** the appearance of new lines at 6.16, 5.91, 5.75, 5.25 as well as 0.17 ppm confirmed the presence of free vinyldimethylsilyl moiety as a part of 1,3-divinyltetramethyldisiloxane ligand bonded to Fe metallic centre. Moreover, new resonances observed in this spectrum and located at 3.26 and 2.80 could be assigned to hydrogen atoms coming from new vinyl groups bonded to the iron metallic centre. In the ^{13}C NMR spectrum, significant changes were also observed; particularly interesting was the appearance of two new singlets at 73.15 and 68.63 ppm, that is in the region of the chemical shifts of carbon atoms, typical of vinyl groups coordinated to the metallic centre, which may indicate the coordination of styrene to the iron atom and the formation of a new iron(0) complex. The formation of a new iron(0) carbonyl complex is also supported by the appearance of a new resonance at 211.82 ppm typical of CO ligands. Additionally, the signals coming from free vinyl group of η^2-bonded 1,3-divinyltetramethyldisiloxane ligand at 139.63 (−SiCH=), 131.84 (=CH_2) and 0.51 (−Me) ppm were also detected. Taking into account the above-described results of spectroscopic studies, it may be assumed that in the initial step of the catalytic cycle, the

Table 2
Hydrosilylation (**A**) *vs.* dehydrogenative silylation (**B**) of styrene with $HSiMe_2Ph$ catalysed by complex **1** at the given temperatures.

$[HSiMe_2Ph]$: [Styrene]	Temp. [°C]	Time [h]	Conversion of $HSiR_3$ [%]	Yield A(B) [%]	k_{obs}
H					
1: 1	−15	48	68	60(8)	–
	0	24	68	68(0)	0.1189
	5	24	67	67(0)	0.1463
	10	24	59	59(0)	0.1870
	20	24	100	12(88)	–
DS					
1: 2	−15	48	68	46(22)	–
	0	24	80	54(26)	–
	10	48	83	56(27)	–
	20	24	100	10(90)	–
	50	24	100	0(100)	0.0944
	60	24	100	0(100)	0.2151
	70	24	100	0(100)	0.4698

Reaction conditions: [Fe] = 10^{-2}, toluene, argon.
H – Hydrosilylation, **DS** – Dehydrogenative Silylation.

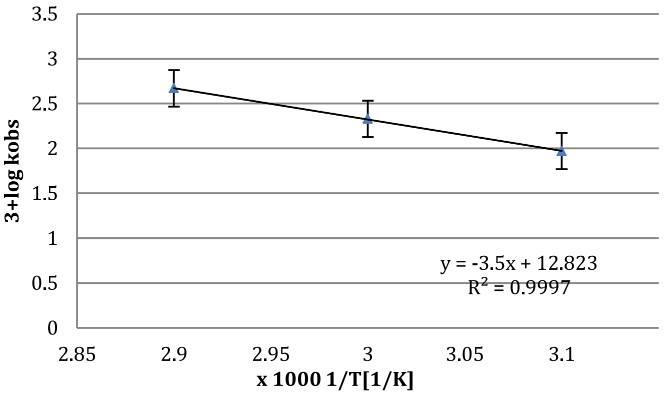


Fig. 2. Arrhenius plot of the dehydrogenative silylation of styrene with dimethylphenylsilane catalysed by complex **1**.

transformation of the starting iron precursors to five-coordinated iron species may also take place, according to Scheme 6.

The DFT calculations performed for the complex $[Fe(CO)_3\{\eta^2\text{-}(H_2C{=}CHSiMe_2)_2O\}(CH_2{=}CHPh)]$ (see Scheme 6), in which the central Fe atom coordinated in square-planar geometry or tetragonal pyramid, during optimization showed a tendency to converge towards trigonal bipyramid structure in which the π electrons of C=C moieties from styrene and one terminus of 1,3-divinyltetramethyldisiloxane coordinated the central Fe atom. In the lowest energy structure, the C=C ligands were in equatorial orientation. (for more information see Electronic Supplementary Data, Table S2).

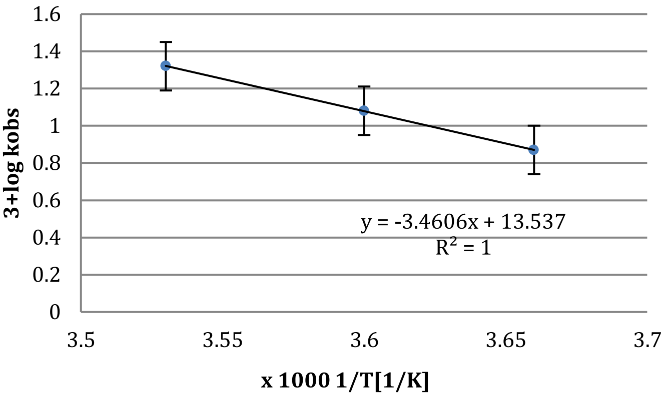


Fig. 3. Arrhenius plot of the hydrosilylation of styrene with dimethylphenylsilane catalysed by complex **1**.

The above Scheme 5 presents the possible routes for the formation of hydrosilylation and dehydrogenative silylation products in the $HSiMe_2Ph$/styrene system, catalysed by iron complex **1**. Results of the stoichiometric study, i.e. the NMR spectroscopic data for the reaction of complex **1** with $HSiMe_2Ph$ and styrene at different temperatures, were supported by theoretical findings.

Relative energies of the transition states as well as intermediates were calculated at DFT level and the energy profile for the catalysis of the reaction of $HSiMe_2Ph$ with styrene in the presence of complex $[Fe(CO)_3\{(H_2C{=}CHSiMe_2)_2O\}]$ (**1**) is documented in Fig. 4. The DFT calculations indicate that when the iron complex (**1**) is used, the energy barriers appear to be the lowest for the reaction of $HSiMe_2Ph$ with styrene according to the Chalk-Harrod mechanism, through the insertion of olefin into the Fe–H bond. However, when the reaction proceeds through the insertion of olefin into the Fe–Si bond, the process of dehydrogenative silylation is preferred as the energy barrier for the formation of dehydrogenative silylation product and complex $[Fe(CO)_3(H)_2]$ as a result of β-transfer of a hydrogen atom, is lower than that for the reductive elimination process and formation of a C–H bond in the hydrosilylation product.

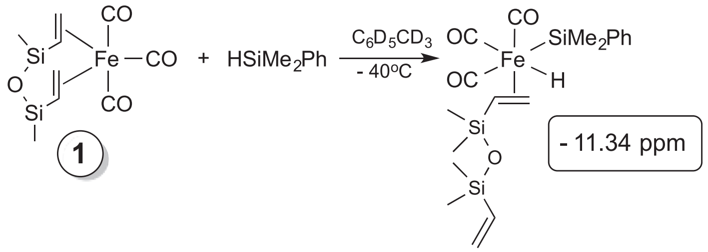
The results concerning the catalytic activity of iron(0) complexes stabilized by vinyl silicon ligands and the reactivity of $[Fe(CO)_3\{(H_2C{=}CHSiMe_2)_2O\}]$ (**1**) precursor in equimolar reactions with selected substrates, confirmed that the core "$[Fe(CO)_3]$" is involved in the transformations occurring in the $HSiR_3/PhCH = CH_2$ system (see Scheme 7).

According to the spectroscopic analysis, during the equimolar reactions, 1,3-divinyltetramethyldisiloxane ligand is removed from the coordination sphere of iron under the influence of substrates in the reaction of $HSiR_3$, leading to the formation of complex $[Fe(CO)_3]$ (**a**) which is the formal catalytic intermediate (see Scheme 5). In the first step, an oxidative addition of hydrosilane (complex (**b**)) followed by olefin coordination, or alternatively the coordination of olefin (complex (**b′**)) (see Scheme 7) followed by the oxidative addition of Si–H lead to formation of the six-coordinated complex (**c**). In the next step, depending on temperature and substituents at silicon, the insertion of olefin either into the Fe–H bond (complex (**d**)) or into the Fe–Si bond (complex (**d′**)) is preferred.

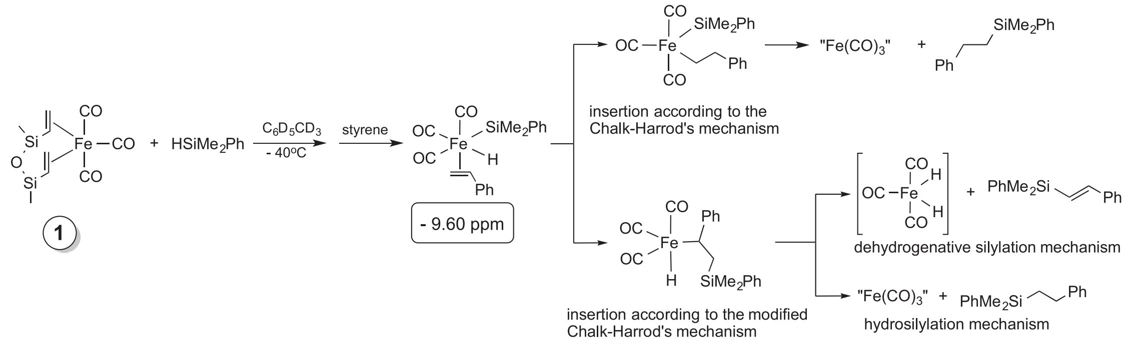
The DFT calculations have shown that interaction energy between iron centre and η^2-bonded 1,3-divinyltetramethyldisiloxane is higher than in the complex with styrene (see Electronic Supplementary Data, Table S3). We have confirmed formation such type of complex by NMR, but in the first catalytic run this ligand is removed from the coordination sphere as a product of dehydrogenative silylation process, as we reported in previous paper [19]. However, even if somewhat of this complex will remain in solution, in the real catalytic system, excess of styrene will shift the equilibrium towards the formation of iron species (**c**) with bonded styrene molecule.

The reaction of styrene with $HSiMe_2Ph$, at low temperatures (−15 – 10 °C), catalysed by complex **1** showed a very high selectivity for silane addition to the vinyl group in the styrene molecule for equimolar ratio of substrates. Evidence of the preference for the hydrosilylation reaction was also obtained from the spectroscopic study of sequential reactions of iron complex **1** with $HSiMe_2Ph$ and styrene in equimolar amounts at low temperatures.

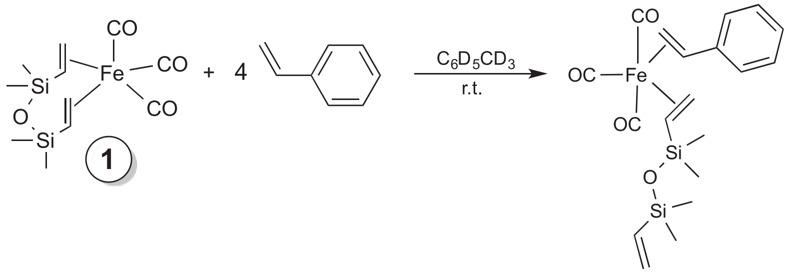
These experimental data show that under such reaction conditions, the process of styrene insertion into the Fe–H bond (**c**) takes place, leading to the formation of complex (**d**), according to the Chalk-Harrod mechanism.



Scheme 4. The reaction of complex **1** with $HSiMe_2Ph$.



Scheme 5. Possible routes for the formation of the hydrosilylation and dehydrogenative silylation products in the $HSiMe_2Ph$/styrene system in the presence of complex **1**.



Scheme 6. The reaction of complex **1** with styrene.

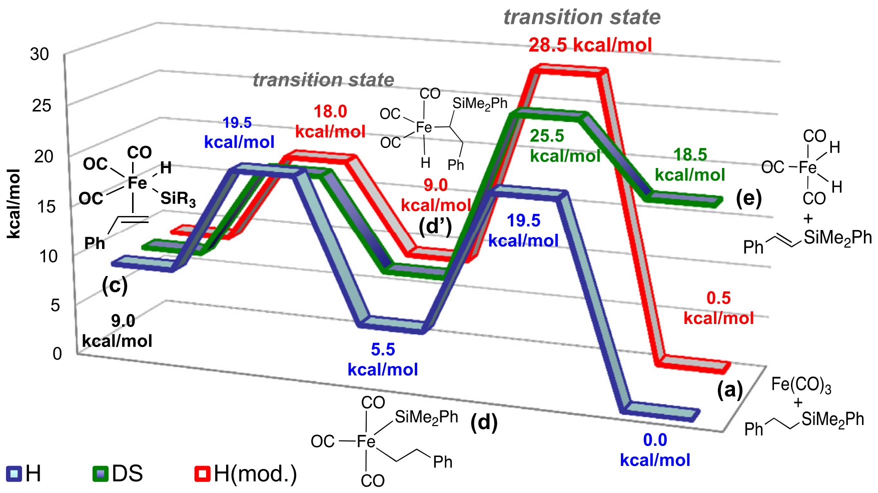
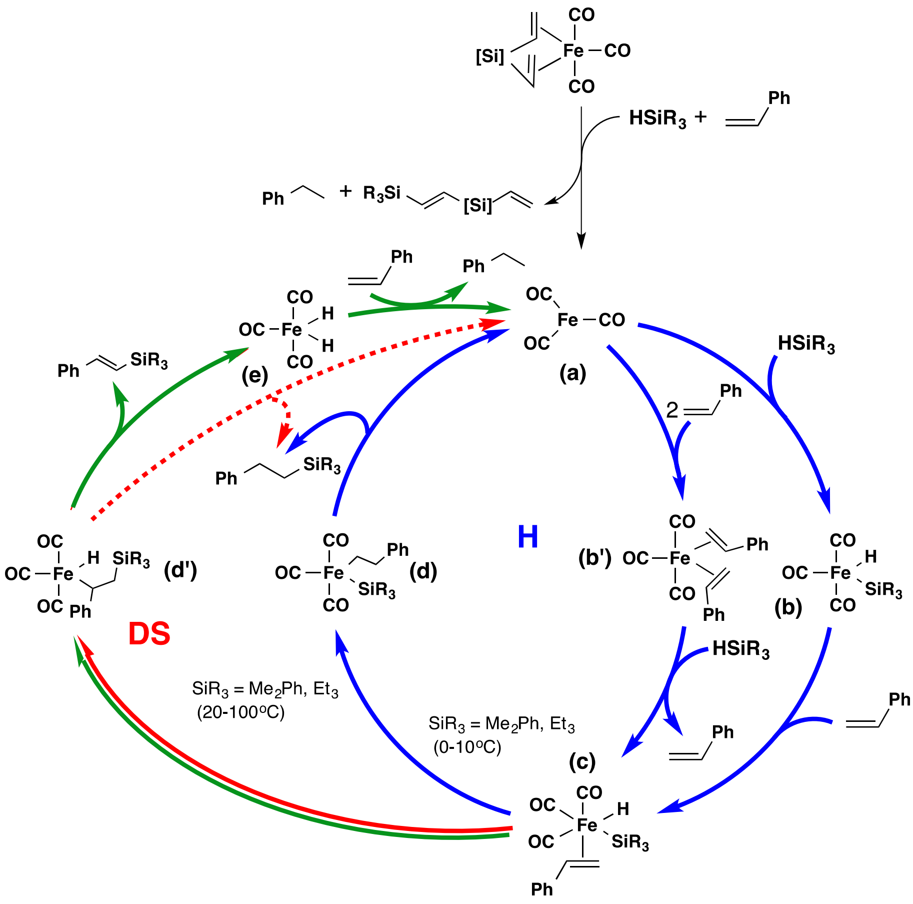


Fig. 4. Energy profile for the two possible reactions of styrene with $HSiMe_2Ph$, i.e. Hydrosilylation (**H**) and Dehydrogenative Silylation (**DS**).



Scheme 7. Mechanism of hydrosilylation (**H**) *vs.* dehydrogenative silylation (**DS**) of styrene at given temperatures.

The results of DFT calculations seem to confirm the thesis for a transformation of this type, in spite of the energy barrier for styrene insertion into the Fe—Si bond (18.0 [kcal/mol]) being slightly lower than that of styrene insertion into the Fe—H bond (19.5 [kcal/mol]), intermediate (**d**) is created, due to the energy release which accompanies this process (3.5 [kcal/mol]). Another important factor that supports the preference of Si—H addition to styrene under these conditions, according to the Chalk-Harrod hydrosilylation mechanism, is a relatively low value of the energy barrier calculated for (**d**)→(**a**) (18.0 [kcal/mol]) transformation (14 kcal/mol) which is the determining step of the hydrosilylation (see $E_a = 15.9$ kcal/mol). At higher temperatures (i.e. above 20 °C and particularly 50–70 °C) at which the insertion of styrene into the Fe—Si bond takes place, the energy barrier (calculated by DFT) accompanying by the elimination of hydrosilylation product (**d**)→(**a**) would require higher energy (19.5 kcal/mol) then the formation of intermediate (**d**)→(**e**) with evolution of silylsubstituted styrene (16.5 kcal/mol). The latter is the rate-determining step for selective dehydrogenative silylation ($E_a = 15.8$ kcal/mol).

The results show that depending on temperature and molar ratio of reagents, the process can run either towards selective formation of hydrosilylation (according to the Chalk-Harrod mechanism) or dehydrogenative silylation (according to the modified Chalk-Harrod mechanism) products.

It was also found that with increasing excess of styrene in relation to $HSiMe_2Ph$, although the temperature was low, the selectivity of the unsaturated product formed through the sequence (**a**)→(**b**)→(**c**)→(**d′**)→(**e**)→(**a**) increased. However, the maximum value of energy barrier for the transformation (**d′**)→(**e**) is compensated by the energy gained at the next stage (**e**)→(**a**), in which hydrogenation of styrene takes place. When the stoichiometric amounts of reagents are taken at a low reaction temperature, the transformation (**a**)→(**b**)→(**c**)→(**d**)→(**a**), i.e. towards the hydrosilylation product is preferred, because of the high-energy barriers of stages (**d′**)→(**a**) and (**d′**)→(**e**).

Conclusions

The new iron(0) carbonyl catalysts $[Fe(CO)_3L]$ or $[\{Fe(CO)_3\}_2L']$ stabilized by multivinylsilicon ligands (where L = silicon dienes, trienes, tetraenes and polyvinylsilicon derivatives), whose syntheses and structures determined by spectroscopic and X-ray methods we reported previously [10], were tested in selected reactions of trisubstituted silanes and hydrosiloxanes with styrene and show good activity compared to those of the other well-known iron carbonyls- $[Fe(CO)_3(cod)]$ and $[Fe(CO)_5]$) in the hydrosilylation or dehydrogenative silylation reactions of styrene.

The results obtained show that depending on temperature and molar ratio of reagents, the process can run either towards the selective formation of hydrosilylation or dehydrogenative silylation product.

Kinetic measurements of selected reactions as well as NMR studies of stoichiometric reactions of $[Fe(CO)_3(DVTMDS)]$ with the substrates, supported by DFT determination of the energy of relative transition states and intermediates, enabled us to suggest a general scheme for the catalysis of hydrosilylation and/or of dehydrogenative silylation by these Fe(0) carbonyl precursors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.051.

References

[1] (a) B. Marciniec, J. Guliński, W. Urbaniak, Z.W. Kornetka, in: B. Marciniec (Ed.), Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford, 1992, p. 754;
(b) B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluć, in: B. Marciniec (Ed.), Hydrosilylation. A Comprehensive Review on Recent Advances, Springer, Berlin, 2009, p. 410.

[2] C. Suzanne, C. Bart, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 126 (2004) 13794.

[3] (a) P.J. Chirik, Science 335 (2012) 567;
(b) P.J. Chirik, et al., Organometallics 31 (2012) 4886;
(c) J. G. P. Delis, P. J. Chirik, A. M. Tondreau, US 2011/0009565 A1;
(d) J. G. P. Delis, S. A. Nye, K. M. Lewis, K. J. Weller, P. J. Chirik, A. M. Tondreau, S. K. Russell, US 2011/0009573 A1;
(e) J. G. P. Delis, S. A. Nye, K. M. Lewis, K. J. Weller, P. J. Chirik, A. M. Tondreau, Patent Application: WO 2011/006044 A2; (f) H. Nakazawa, K. Kouji, A. Suzuki, Y. Nakai, Organometallics 31 (2012) 3825;
(g) K. J. Weller, C. C. H. Atienza, J. Boyer, P. Chirik, J. G. P. Delis, K. Lewis, S. A. Nye, US2013/0158281 A1.

[4] J.Y. Wu, B.N. Stanzl, T. Ritter, J. Am. Chem. Soc. 132 (2010) 13214.

[5] H. Nakazawa, J. Am. Chem. Soc. 134 (2011) 804.

[6] M. Zhang, A. Zhang, Appl. Organometal. Chem. 24 (2010) 751.

[7] C.A. Tsipis, C.E. Kefalidis, J. Organomet. Chem. 692 (2007) 5245.

[8] (a) A.N. Nesmeyanov, R. Kh Friedlina, E.C. Chukovskaya, R.G. Petrova, A.B. Belyavsky, Tetrahedron Lett. 17 (1962) 61;
(b) F. Kakiuchi, Y. Tanaka, N. Chantani, S. Murai, J. Organomet. Chem. 456 (1993) 45.

[9] C. Randolph, M.S. Wringhton, J. Am. Chem. Soc. 108 (1986) 3366.

[10] (a) M.-S. Tzou, R. Taylor, I. Kownacki, B. Nguyen, B. Marciniec, A. Kownacka, A. Surgenor, US Pat App. WO 2013081794; (b) A. Kownacka, I. Kownacki, M. Kubicki, B. Marciniec, R. Taylor, J. Organomet. Chem. 750 (2014) 132.

[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Rob, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Gaussian, Inc., Wallingford, CT, 2003.

[12] http://www.chemaxon.com/products/marvin/.

[13] A. Plutecka, M. Hoffmann, U. Rychlewska, Struct. Chem. 18 (2007) 379.

[14] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[15] (a) T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum, New York, 1976, pp. pp.1–28;
(b) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.

[16] W.J. Hehre, L. Radom, P.V. Schleyer, J. Pople, AB Initio Molecular Orbital Theory, Wiley-Interscience, 1986.

[17] H.P. Hratchian, H.B. Schlegel, in: C.E. Dykstra, G. Frenking, K.S. Kim, G. Scuseria (Eds.), Theory and Applications of Computational Chemistry: the First 40 Years, Elsevier, Amsterdam, 2005, pp. 195–249.

[18] S. Simon, M. Duran, J.J. Dannenberg, J. Chem. Phys. 105 (1996) 11024–11031.

[19] B. Marciniec, A. Kownacka, I. Kownacki, R. Taylor, Appl. Catal. A: General 486 (2014) 230.