

Activation of the Vinylic =C–H Bond of Styrene by a Rhodium–Siloxide Complex: The Key Step in the Silylative Coupling of Styrene with Vinylsilanes

Bogdan Marciniec,* Edyta Walczuk-Guściora, and Cezary Pietraszuk

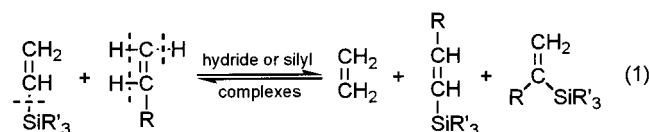
Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received January 29, 2001

A highly stereo- and regioselective silylative coupling of styrene and *p*-substituted styrenes with trisubstituted vinylsilanes, siloxanes, and divinyl-substituted silicon compounds catalyzed by $[\{(\text{cod})\text{Rh}(\mu\text{-OSiMe}_3)_2\}]_2$ (**I**) is reported. The reaction proceeds even at room temperature to give respective *E*-silyl(siloxy)styrenes. Quantitative syntheses of silylstyrenes are mostly observed at 60 °C and siloxystyrenes at 90 °C. A labeling study (GC–MS analysis) with the deuterated styrene indicates the exchange of the vinylic proton and suggests the non-metallacarbene mechanism of the reaction proceeding via generation of active metal-hydride species by oxidative addition of =C–H to siloxy–rhodium complex **Ia**. The kinetic measurements allow us to propose the dissociative mechanism of the silylative coupling, which does not involve migratory insertion of olefin into the Rh–Si bond.

Introduction

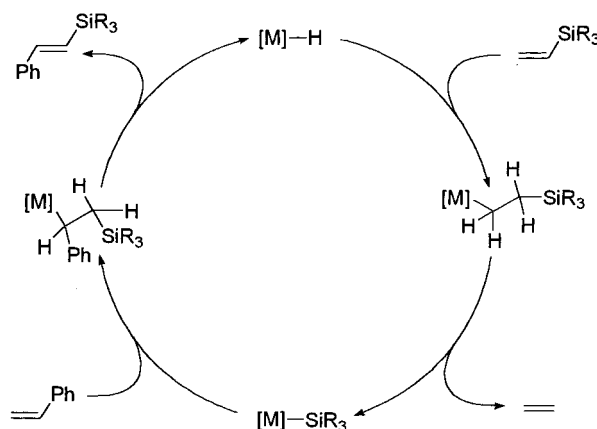
Self-disproportionation (homocoupling) of vinyl-substituted silicon compounds and their cross-disproportionation (trans-silylation, silyl group transfer) with olefins can be effectively catalyzed by ruthenium,¹ rhodium,^{1b,d,2} cobalt,^{3a} and iron^{3b} complexes. The catalytic, synthetic, and mechanistic studies of the process have shown that in the presence of catalysts containing initially M–H or M–Si bonds (or those in which these bonds can be generated in situ) the reaction proceeds through the cleavage of the =C–Si bond of the vinyl–silicon compound and the =C–H bond of the olefin (also the vinyl–silicon compound in the self-disproportionation). The reaction is depicted in eq 1:



* To whom correspondence should be addressed. Tel: (48) 61 8291509. Fax: (48) 61 8291508. E-mail: marcinb@main.amu.edu.pl.

(1) (a) Marciniec, B.; Guliński, J. *J. Organomet. Chem.* **1984**, *266*, C19. (b) Marciniec, B.; Rzejak, L.; Guliński, J.; Foltynowicz, Z.; Urbaniak, W. *J. Mol. Catal.* **1988**, *46*, 329. (c) Marciniec, B.; Maciejewski, H.; Guliński, J.; Rzejak, L. *J. Organomet. Chem.* **1989**, *362*, 273. (d) Foltynowicz, Z.; Marciniec, B. *J. Organomet. Chem.* **1989**, *376*, 15. (e) Foltynowicz, Z.; Marciniec, B. *J. Mol. Catal.* **1991**, *65*, 113. (f) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (g) Marciniec, B.; Pietraszuk, C. *J. Organomet. Chem.* **1991**, *412*, C1. (h) Marciniec, B.; Pietraszuk, C.; Foltynowicz, Z. *J. Organomet. Chem.* **1994**, *474*, 83. (i) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (j) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320. (k) Marciniec, B.; Lewandowski, M. *Tetrahedron Lett.* **1997**, *38*, 3777. (l) Mise, T.; Takaguchi, Y.; Umemijo, T.; Shimizu, S.; Wakatsuki, Y. *J. Chem. Commun.* **1998**, 699. (m) Marciniec, B.; Pietraszuk, C.; Kujawa, M. *J. Mol. Catal.* **1998**, *133*, 4. (n) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Organometallics* **1999**, *18*, 2033. (o) Marciniec, B.; Lewandowski, M.; Bijpost, E.; Małeczka, E.; Kubicki, M.; Walczuk-Guściora, E. *Organometallics* **1999**, *18*, 3968. (p) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677.

Scheme 1



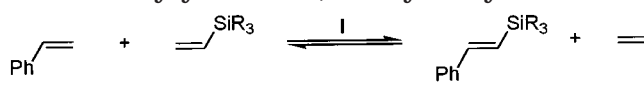
where: M = Ru, Rh, Co; R = alkyl, aryl, alkoxy, siloxy

This type of reaction is conceptually related to the dehydrogenative silylation since it involves the silylation of a substrate such as styrene by vinylsilane instead of the hydrosilane. The catalytic cycle of this new type of silylolefin conversion involves the migratory insertion of olefin (or vinylsilane) into the M–Si bond where M = Ru,^{1f,i,j,p} Rh,² and Co³ (and vinylsilane into the M–H bond), followed by β -H (and β -Si) transfer to the metal atom with elimination of phenyl(silyl)ethene (and ethene)⁴ (Scheme 1).

(2) (a) Marciniec, B.; Walczuk-Guściora, E.; Pietraszuk, C. *Catal. Lett.* **1998**, *55*, 125. (b) Marciniec, B.; Walczuk-Guściora, E.; Błażewska-Chadyniak, P. *J. Mol. Catal.* **2000**, *160*, 165.

(3) (a) Marciniec, B.; Kownacki, I.; Chadyniak, D. *Inorg. Chem. Commun.* **1999**, *2*, 581. (b) Marciniec, B.; Majchrzak, M. *Inorg. Chem. Commun.* **2000**, *3*, 371.

(4) For recent reviews on the silylative coupling of olefins with vinylsilanes see: (a) Marciniec, B. *New J. Chem.* **1997**, *21*, 815. (b) Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527. (c) Reichel, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 203. (d) Marciniec, B. *Mol. Cryst. Liq. Cryst.* **2000**, *354*, 173.

Table 1. Effect of Substituents at Silicon and Temperature on the Yield of Styrylsilane (and Styrylsiloxanes) Catalyzed by I^a


R ₃	yield of styrylsilane (%)	
	60 °C	90 °C
Me ₃	91 (11) ^c	100 (4 h), ^b 42 ^c
Me ₂ Ph	100 (1 h), ^b 60 ^d	100 (0.5 h) ^b
Me(OEt) ₂	98	100 (4 h), ^b 52 ^c
(OCH ₂ CH ₂ OCH ₃) ₃	94	98
Ph ₂ (OEt)	100	100
(OEt) ₃	81	100
(OSiMe ₃) ₃	0	46
Me(OSiMe ₃) ₂	5	100
Me ₂ (OSiMe ₃)	94	100

^a [Rh]:[H₂C=CHSiR₃]:[styrene] = 1 × 10⁻²:1:10, glass ampules, argon, 24 h. ^b Other time. ^c In air. ^d Room temperature.

This general mechanism is proved by the established insertion of ethylene,^{1f} vinylsilane,¹ⁱ and styrene,^{1j,2a} into M–Si (where M = Ru, Rh, Co) bonds in stoichiometric reactions.

Effective disproportionation of trisubstituted vinylsilanes silanes has been also recently reported by us to proceed if [(cod)Rh(*μ*-OSiMe₃)₂]₂ (**I**) and, to less extent, if [(cod)Rh(*μ*-Cl)]₂ is used as a catalyst.^{2b} The reactions yield 1,1-bis(silyl)ethenes, 1,2-bis(silyl)ethenes, and ethylene. The mechanistic implications based on catalytic data and recent evidence reported by Brookhart and co-workers⁵ on hydrovinylation of Rh complexes by vinyltrimethylsilane enabled us to suggest the involvement of Rh–H and Rh–Si intermediates that are responsible for the catalytic disproportionation of vinylsilanes.

The aim of this work was to test catalyst **I** as a precursor of the silylative coupling (silyl group transfer) of styrene and *p*-substituted styrenes with various vinyl-substituted silicon compounds and to find a possible mechanism of catalysis with precursors initially having no Rh–H or Rh–Si bonds.

Results and Discussion

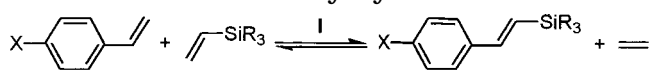
Catalytic Examinations. The reaction of vinyltrisubstituted vinylsilanes with styrene proceeds in the presence of **I** regio- and stereoselectively even at room temperature according to eq 2:



where: R = alkyl, aryl, alkoxy, siloxy

Exemplary catalytic data showing the effect of substituents at silicon and temperature on the yield of silylstyrenes are compiled in Table 1. All products were isolated and characterized by ¹H and ¹³C NMR and GC–MS analyses.

Under the conditions of the reaction examined ([vinylsilane]:[styrene] = 1:10) no products of vinylsilane homocoupling reactions were observed. The efficiency

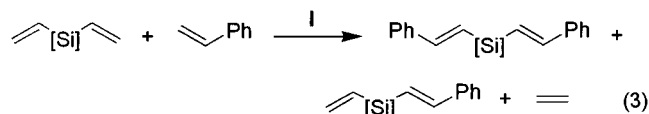
Table 2. Effect of *p*-Substituent in Styrene on the Yield of Silylstyrenes^a


R ₃	yield of styrylsilane [%]		
	ClC ₆ H ₄ CH=CH ₂	MeC ₆ H ₄ CH=CH ₂	(MeO)C ₆ H ₄ CH=CH ₂
	60 °C		
Me ₃	93	11	1.5
Me ₂ Ph	100	97	26
Me(OEt) ₂	100	100	44
(OEt) ₃	67	65	17
	90 °C		
Me ₃	96	100	25
Me ₂ Ph	100	100 ^b	100
Me(OEt) ₂	100	100	53
(OEt) ₃	91	93	17

^a [Rh]:[H₂C=CHSiR₃]:[X–C₆H₄CH=CH₂] = 1 × 10⁻²:1:10, glass ampules, argon, 24 h. ^b 2 h.

of the catalyst **I** was much higher than that of the respective well-defined Ru–H,^{1j} Ru–Si,^{1j} and Rh–H^{2a} complexes. This catalyst can be used for stereoselective synthesis of all styrylsilanes regardless of the substituents at silicon. Only a significant steric hindrance of three siloxyl substituents at silicon in vinyltrisiloxane disturbs the quantitative conversion of the silylative coupling.

High catalytic activity of **I** in silylative coupling of styrene with respective divinyl-substituted silicon compounds occurs according to the following equation (see also Experimental Section).



where: [Si] = –Si(Me)₂–, –Si(Me)₂OSi(Me)₂–, –Si(Me)₂NHSi(Me)₂–, –Si(Me)₂CH₂CH₂Si(Me)₂–

Exclusive synthesis of di(styryl)siloxanes, -silanes, and -silazanes (90 °C, 18–24 h, argon, [H₂C=CHSi]:[styrene]:[Rh] = 1:10:1 × 10⁻²) is observed. In the case where H₂C=CHSi(Me)₂CH₂CH₂Si(Me)₂CH=CH₂ is used, 60% of the distyryl derivative is accompanied by 40% of monostyrylcarbosilane.

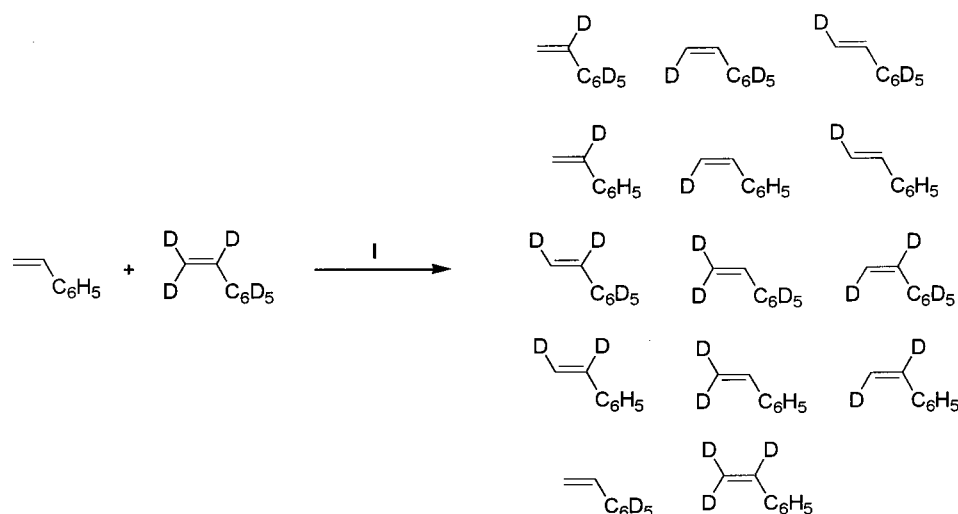
Because of high activity and selectivity of **I** observed in the reaction of many vinyl-substituted silanes and siloxanes with styrene, its use makes it possible to synthesize new silylstyrenes by the silylative coupling route. Silylstyrenes are commonly used as efficient organic reagents.⁶ To find an electronic effect of the substituents at styrene on the yield and selectivity of the reaction examined, *p*-substituted Cl-, Me-, and MeO-styrenes were chosen to study the catalytic activity of **I** with the selected trisubstituted vinylsilanes. The results are compiled in Table 2.

A general effect of electron-withdrawing substituents at the *p*-position of styrenes is considerable, although the effect is also combined with electronic, mesomeric, and steric effects of the substituents at silicon. However, a quantitative transformation of *p*-chlorostyrene in the

(5) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 4385.

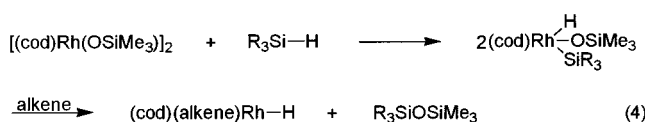
(6) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; Chapter 3. (b) Fleming, I.; Duneques, J.; Smithors, R. H. *Org. React.* **1989**, *37*, 57.

Scheme 2



reaction with all trisubstituted vinylsilanes catalyzed by **I** (at 90 °C) is a key point for mechanistic implications. On the other hand, electron-releasing properties of MeO in *p*-MeO-styrene inhibit (or even stop) the reaction regardless of the substituents (except dimethylphenyl) at silicon used.

Stoichiometric Study. To characterize the rhodium complex during catalysis, a series of pseudostoichiometric reactions between **I** and the substrates (vinylsilane and styrene) was undertaken. A ¹H NMR study showed no dissociation of cod from the rhodium complex and Rh–H detection. On the other hand, a GC–MS study in the same conditions ([Rh]:[PhMe₂SiHC=CH₂]:[styrene] = 1:5:10) revealed no traces of siloxane, PhMe₂-SiOSiMe₃, which would have been the evidence for replacement of the siloxy ligand by reductive elimination from the [Rh]–SiMe₂Ph(–OSiMe₃) intermediate. The latter process was observed in the hydrosilylation of alkene catalyzed by **I**, i.e., when [Rh]–H is formed directly by oxidative addition of trisubstituted silanes, Et₃SiH⁸ and (EtO)₃SiH,⁹ to the rhodium complex according to the following equation:

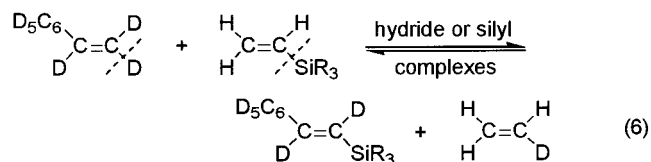
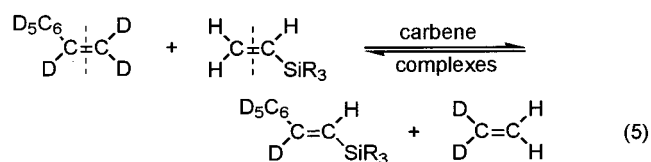


where: SiR₃ = SiEt₃, Si(OEt)₃

However, the silylative coupling reaction examined occurs in the absence of H–SiR₃; therefore, generation of Rh–H by such a pathway can be excluded.

Labeling Studies. To learn more about the mechanism of the reaction, experiments with deuterium-labeled reagents were performed. Thus, the reaction of H₂C=CHSiMe₂Ph with styrene-*d*₈ allows a distinction between the metallacarbene⁷ (eq 5) and non-metalla-

carbene (insertion–elimination) mechanism^{1j} (eq 6):



GC–MS analysis of the reaction mixture in a very early stage shows exclusive formation of silylstyrene-*d*₇ (and ethylene that has not been analyzed). This result strongly confirms the non-metallacarbene mechanism of the reaction. It was therefore decided to study the mechanism of hydride (or silyl) complex generation in the system. To this end, the reaction between styrene-*d*₀ and styrene-*d*₈ in the presence of catalytic amounts of **I** was tested. The obtained results are schematically depicted in Scheme 2.

The presence of a mixture of styrenes (*d*₀, *d*₁, *d*₂, *d*₃, *d*₅, *d*₆, *d*₇, and *d*₈) was confirmed by GC–MS. ¹H NMR spectrum clearly shows that H/D exchange takes place in all positions of the vinyl group of styrenes. A similar experiment with the use of *p*-methylstyrene-*d*₀ and styrene-*d*₈ confirms this result and shows that there is no other H/D exchange in the aromatic ring or the methyl group. To exclude the possibility of the participation of deuterated benzene in the H/D exchange as was reported recently in a similar system,⁵ an analogous experiment was performed in which styrene-*d*₀ was treated with catalytic amounts of **I** in deuterated benzene as the solvent. No H/D exchange was observed in that case.

The H/D exchange in the vinyl group of styrenes observed in the presence of **I** suggests that the generation of active hydride species proceeds by hydrovinylation, i.e., oxidative addition of the =C–H bond to rhodium atom.

Kinetic Measurements. In the kinetic experiments the uptake of vinyl dimethylphenylsilane in its reaction

(7) Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

(8) Marciniak, B.; Krzyżanowski, P. *J. Organomet. Chem.* **1995**, *493*, 261.

(9) Marciniak, B.; Krzyżanowski, P.; Walczuk-Guściora, E.; Duczmal, W. *J. Mol. Catal.* **1999**, *144*, 263.

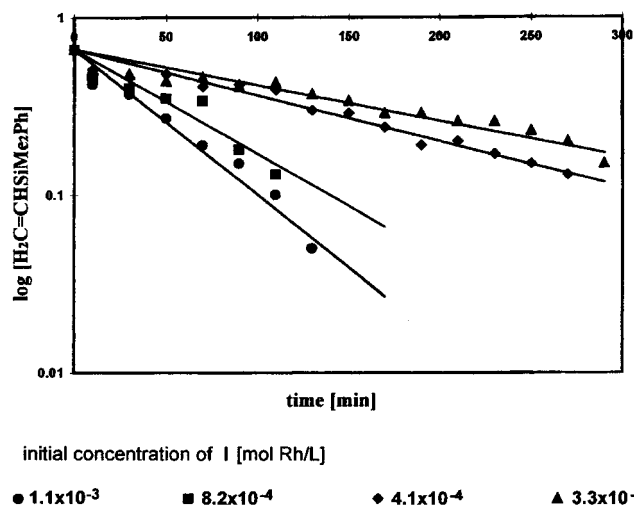


Figure 1. Pseudo-first-order dependence of the silylative coupling of styrene with vinyl dimethylphenylsilane catalyzed by **I**.

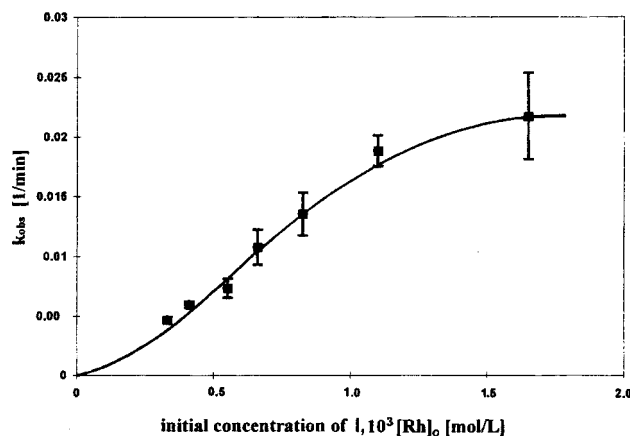


Figure 2. Plot of k_{obs} vs the initial concentration of rhodium **I**.

with styrene at a 10-fold excess and with benzene as a solvent was measured. The essential series of measurements were carried out at 60 °C. *E*-Silylstyrene is the exclusive product of this reaction in the conditions used. The reaction was found to be first-order with respect to vinylsilane. The selected kinetic curves of the silylative coupling course in the presence of **I**, shown in Figure 1, were used to determine k_{obs} . They were calculated by fitting the experimental silane concentration $\ln[\text{vinylsilane}]_x/[\text{vinylsilane}]_0$ vs time to an exponential function using the nonlinear least-squares procedure.

The slope of the dependence illustrated in Figure 1 is equal to the pseudo-first-order rate constants k_{obs} .

The relationship between k_{obs} and the initial concentration of $[\text{Rh}]_0$ is presented in Figure 2. The course of the dependence characterizing autocatalytic reactions indicates that the reaction order with respect to the initial (total) catalyst precursor concentration has been changed. At concentrations higher than 1.5×10^{-3} mol Rh/L, pseudo-zero reaction order with respect to this precursor is observed and the maximum rate constant, $k_{\text{max}} = 0.025 \text{ min}^{-1}$, can be determined. TOF = 680 at 60 °C is of the same order as those for $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, well-defined complexes (but at 80 °C), 450 and 900, respectively.^{1j}

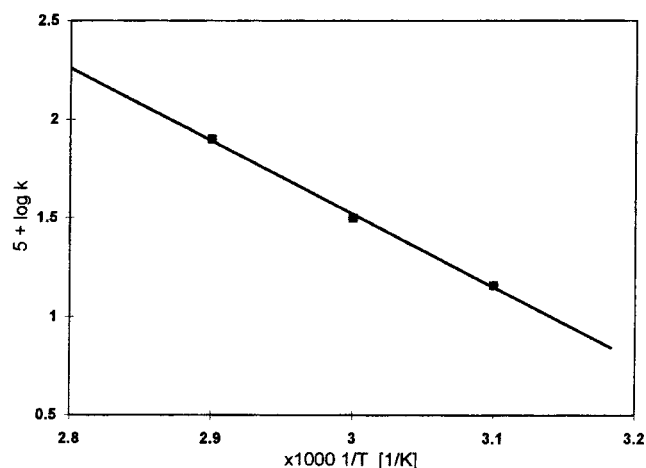
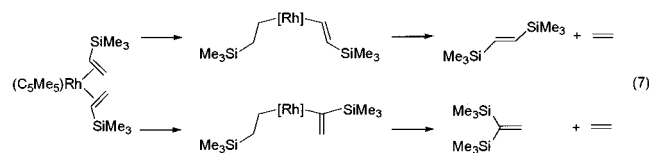


Figure 3. Arrhenius plot of the silylative coupling of styrene with vinyl dimethylphenylsilane catalyzed by **I**.

The Arrhenius plot of the silylative coupling determined in the temperature range 50–70 °C shows good linearity (Figure 3), allowing us to calculate $E_a = 16.9 \pm 0.7 \text{ kcal/mol}$.

Mechanistic Implications. A previous study on the use of **I** as an effective catalyst in self-disproportionation of vinyl-trisubstituted silanes showed the formation of two products, *E*-1,2-bis(silyl)ethene and 1,1-bis(silyl)ethene. A strong preference of *E*-1,2-bis(silyl)ethene was observed.^{2b}

Very stimulating experiments performed by the Brookhart group⁵ under thermolysis conditions (140 °C, cyclohexane- d_{12} , 10-fold excess of $\text{H}_2\text{C}=\text{CHSiMe}_3$) showed the occurrence of the following process (eq 7),



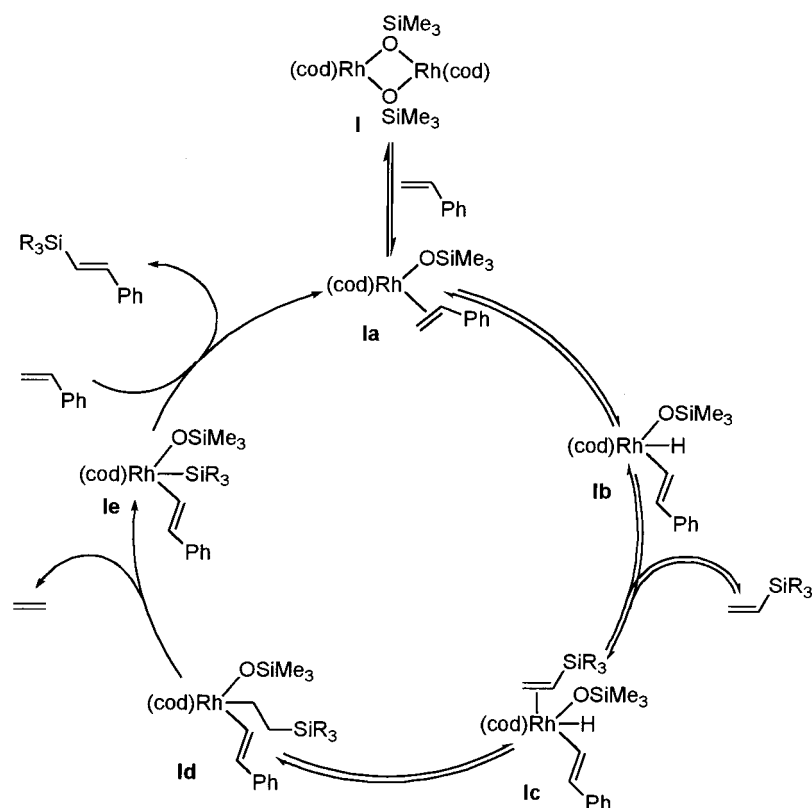
and thus allowed us to propose the mechanism involving Rh–H and Rh–Si intermediates. This pseudostoichiometric experiment provided the evidence for hydrovinylation of one of the coordinated molecules of vinylsilane followed by the insertion of the second molecule into the generated Rh–H bond, subsequent elimination of ethylene, and reductive elimination of two types of bis(silyl)ethenes. On the basis of the Brookhart experiment, a catalytic scheme for disproportionation of vinylsilanes involving prior hydrovinylation was presented.^{2b}

The results of the labeling study permit us to propose a reasonable non-metallacarbene mechanism for the reaction of vinylsilanes and vinylsiloxanes with styrene (Scheme 3).

The H/D exchange processes occurring between styrene- d_0 and styrene- d_8 as well as *p*-methylstyrene- d_0 and styrene- d_8 provide convincing evidence for oxidative addition of the =C–H bond of styrenes to the siloxy–rhodium complex.

The kinetic measurements of the reaction examined confirm the first-order dependence of its rate on the concentration of vinylsilane and the pseudo-zero-order dependence on the initial concentration of rhodium, i.e., on the total concentration of all rhodium complexes in

Scheme 3



where: $R_3 = \text{Me}_3, \text{Me}_2(\text{OEt}), \text{Me}(\text{OEt})_2, \text{Me}_2\text{Ph}, (\text{OEt})_3, (\text{OCH}_2\text{CH}_2\text{OCH}_3)_3, \text{Ph}_2(\text{OEt}), \text{Ph}(\text{OEt})_2, \text{Me}_2(\text{OSiMe}_3), \text{Me}(\text{OSiMe}_3)_2, (\text{OSiMe}_3)_3$

the solution (when $[\text{Rh}]_0 > 1.5 \times 10^{-3}$ mol/L). The value k_{max} , however, may correspond to the maximum concentration of the intermediate **Ib**, generated in the excess of styrene, i.e., that which subsequently reacts in the rate-determining step with vinylsilane. Unfortunately, kinetic measurements do not allow us to determine the real reaction order with respect to **Ib**.

The formation of the Rh–H intermediate **Ib** is stimulated by preequilibrium involving the coordination of styrene to give **Ia** and the subsequent oxidative addition of styrene to **Ia**.

The catalytic and kinetic data suggest that the sequence of these two processes is a key step for generation of the Rh–H complex **Ib**, which is apparently accelerated by an electron-withdrawing group in *p*-substituted styrenes.

The insertion of vinylsilane into the Rh–H bond is followed by elimination of ethylene (β -Si transfer) to give the Rh–Si intermediate **Ie** according to the dissociative mechanism. Then, the reductive elimination of *E*-silylstyrene takes place in an excess of styrene, regenerating **Ia**. Contrary to all previously reported silylative coupling of olefins with vinylsilanes catalyzed by well-defined M–H and M–Si complexes, the catalysis of **I** does not have to involve a migratory insertion of the olefin into the M–Si bond (i.e., the associative mechanism).

The competitive insertion of alkenes into the M–H bond or into the M–Si bond is a subject of two different mechanisms of alkene hydrosilylation. The classic Chalk–Harrod mechanism assumes the insertion of the

olefin into the (silyl)M–H bond followed by elimination of alkylsilane, but the modified Chalk–Harrod scheme involves the insertion of the alkene into the (H)M–Si bond as the rate-determining step.¹⁰ The latter mechanism is proposed for non-platinum (e.g., rhodium¹¹) catalyzed hydrosilylation of olefins to interpret the observation of vinylsilane products yielded via the dehydrogenative silylation step. Recent detailed theoretical studies of platinum-catalyzed hydrosilylation of ethylene have led to a conclusion that this process proceeds through the Chalk and Harrod mechanism. The rate-determining step in this mechanism is the formation of the Pt(silyl)(ethyl) complex as a result of ethylene insertion into the Pt–H bond. The activation barrier of this step is 23 kcal/mol when R is Me and 26 kcal/mol when R is Cl. In the modified Chalk–Harrod mechanism, however, the rate-determining step is the ethylene¹² insertion into the Pt–SiR₃ bond, and its activation barrier is 44 kcal/mol when R is Me and 60 kcal/mol when R is Cl. A similar calculation was made

(10) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.

(11) (a) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (b) Milan, A.; Fernandez, N. J.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, *26*, 89. (c) Milan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (d) Doyle, M. P.; Devore, G. A.; Nefedov, A. O.; High, K. G. *Organometallics* **1992**, *11*, 549. (e) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748. (f) Cornish, A. J.; Lappert, M. F. *J. Organomet. Chem.* **1984**, *271*, 153. (g) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1991**, *408*, 297. (h) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (i) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

(12) (a) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510. (b) Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, X. *Coord. Chem. Rev.* **1999**, *190*, 933.

for the ethylene insertion into the Rh–SiH₃ of Rh(H)–(SiH₃)Cl(PH₃)₂.^{12a} Moreover, contrary to other rhodium complex catalyzed hydrosilylation of alkenes involving the dehydrogenative silylation side reaction,¹¹ the addition of triethoxysilane to alkene (1-hexene) catalyzed by **I** has yielded no unsaturated product of the dehydrogenative silylation even in an excess of the alkene.⁹

The above considerations explain why silylative coupling of styrene in the presence of **I** occurs much easier under milder conditions than in the presence of previously used catalysts whose use always implied the insertion of the olefin into the M–Si bond. Therefore, a catalyst such as **I** generating effective 16e monomeric species of the type **Ia** (with an already coordinated molecule of olefin, i.e., styrene) can be a valuable precursor for catalysis initiated by M–H (Rh–H) complexes.

Conclusions

1. Siloxy–rhodium dimeric complex **I** appears to be a very effective catalyst for stereo- and regioselective silylative coupling of trisubstituted vinylsilanes, siloxanes, and divinylsilanes with styrene and *p*-substituted styrenes. Moreover, the reaction occurs under milder conditions than those with previously reported well-defined Ru, Rh, and Co complexes containing initially M–H and M–Si bonds.

2. The reaction proceeds according to the non-metal-carbene mechanism involving Rh–H 16e intermediate **Ib**, which is generated in situ via oxidative addition of the =C–H bond of a styrene molecule coordinated to the rhodium atom.

3. Contrary to the previously reported silylative coupling of olefins with M–H and M–Si complexes, the proposed catalytic cycle of **I** does not involve migratory insertion of olefin into the Rh–Si bond (the associative mechanism) since the final step of the product formation occurs via reductive elimination of the product (the dissociative mechanism).

Experimental Section

General Methods and Chemicals. All syntheses and manipulations were carried out using standard Schlenk and high-vacuum techniques. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Varian Gemini 300 VT spectrometer in C₆D₆. The mass spectra of the products and substrates were determined by GC–MS (Varian 3300 gas chromatograph equipped with a DB-1, 30 m capillary column, and a ITD 800 Finnigan MAT (ion trap detector)). GC analyses were carried out on a Varian 3300 gas chromatograph with a Megabore column DB-1, 30 m and TCD. The chemicals were obtained from the following sources: vinylsilanes and vinylsiloxanes from ABCR, benzene from OBR PR Plock (Poland), styrene from Fluka, *p*-methylstyrene, *p*-chlorstyrene, and *p*-methoxystyrene from Aldrich, and benzene-*d*₆ and styrene-*d*₈ from Dr. Glaser, AG Basel. All solvents, vinylsilanes, and vinylsiloxanes were dried and distilled under dry argon atmosphere prior to use. [(cod)Rh(μ-OSiMe₃)₂] (**I**) was prepared according to the previously reported procedure.⁸

Catalytic Examinations. In a typical catalytic test, rhodium complex, olefin, toluene (internal standard), and trisubstituted vinylsilane were placed under argon in a glass ampule ([Rh]:[H₂C=CHSiR₃]:[olefin] = 1 × 10⁻²:1:10). The sealed

ampule was heated at the specified conditions. The composition of the reaction mixture was analyzed by GC. The conversion, yield, and selectivity were calculated by the internal standard method.

Kinetic Examinations. A typical kinetic test was carried out under argon in a thermostated vessel of 5 mL capacity. Solutions for kinetic studies were prepared by mixing 0.12 mL (6.6 × 10⁻⁴ mol) of vinyldimethylphenylsilane, 0.75 mL (6.6 × 10⁻⁴ mol) of styrene, 0.09 mL (1.0 × 10⁻³ mol) of benzene, and decane (internal standard). Then the required aliquot of **I** in benzene was added. The consumption of vinylsilane was monitored by GC.

Synthesis of *E,E*-PhCH=CHSi(Me)₂CH=CHPh. [(cod)Rh(μ-OSiMe₃)₂] (0.039 g, 6.5 × 10⁻⁵ mol) was dissolved under argon in 0.75 mL of benzene in a glass ampule under argon. Then divinyldimethylsilane (1 mL, 6.5 × 10⁻³ mol) and styrene (7.4 mL, 6.5 × 10⁻² mol) were added. The ampule was flame sealed and heated at 90 °C for 18 h. To isolate the product, the catalyst was removed by passing the sample through a small silica column with hexane as an eluent, followed by precipitation of polystyrene with methanol. The solvents were then distilled off, and the product was isolated by distillation in vacuo. A 75% yield was obtained on the basis of vinylsilane used. ¹H NMR (C₆D₆, ppm): δ 0.32 (s, 6 H, CH₃); 6.57 (d, *J*_{H,H} = 19.2 Hz, 2 H, CHSi); 7.12 (d, *J*_{H,H} = 19.2 Hz, 2 H, CHPh); 7.10–7.35 (m, 10 H, Ph). ¹³C NMR (C₆D₆, ppm): δ -2.42 (CH₃); 127.32 (CHSi); 146.15 (CHPh); 139.12 (C_{ipso}); 127.41, 127.77, 129.26, (Ph). ²⁹Si NMR (C₆D₆, ppm): δ -12.38. MS: *m/z* 145 (M – Me – PhCHCH)⁺, 161 (M – PhCHCH)⁺, 173 (M – PhCH)⁺, 223 (M – Me – Vi)⁺, 249 (M – Me)⁺, 264 (M)⁺.

Synthesis of *E,E*-PhCH=CHSi(Me)₂NHSi(Me)₂CH=CHPh. The same procedure as above was applied. ¹H NMR (C₆D₆, ppm): δ 0.34 (s, 12 H, CH₃); 6.50 (d, *J*_{H,H} = 19.2 Hz, 2 H, CHSi); 7.06 (d, *J*_{H,H} = 19.2 Hz, 2 H, CHPh); 7.10–7.31 (m, 10 H, Ph). ¹³C NMR (C₆D₆, ppm): δ 1.37 (CH₃); 127.47 (CHSi); 145.69 (CHPh); 138.99 (C_{ipso}); 128.82, 128.96, 129.26, (Ph). ²⁹Si NMR (C₆D₆, ppm): δ -1.80. MS: *m/z* 218 (M – Me – PhCHCH)⁺, 234 (M – PhCHCH)⁺, 247 (M – PhCH)⁺, 322 (M – Me)⁺, 337 (M)⁺.

Experiments with Deuterated Reagents. Reaction between Styrene-*d*₀ and Styrene-*d*₈. [(cod)Rh(μ-OSiMe₃)₂] (0.006 g, 2.0 × 10⁻⁵ mol) was dissolved under argon in 0.4 mL of C₆D₆ in an NMR tube. Then styrene-*d*₀ (0.12 mL, 1.0 × 10⁻³ mol) and styrene-*d*₈ (0.13 mL, 1.0 × 10⁻³ mol) were added. The tube was sealed and heated at 60 °C for 24 h. The mixture was analyzed by GC–MS and ¹H NMR spectroscopy before and after the reaction.

The reaction with the use of *p*-methylstyrene-*d*₀ was conducted according to the analogous procedure.

Reaction between Styrene-*d*₈ and Vinylidimethylphenylsilane. [(cod)Rh(μ-OSiMe₃)₂] (0.0015 g, 5.5 × 10⁻⁶ mol) was dissolved under argon in 0.6 mL of C₆D₆ in a Supelco vial. To the solution were added H₂C=CHSiMe₂Ph (0.1 mL, 5.5 × 10⁻⁴ mol) and styrene-*d*₈ (0.067 mL, 5.5 × 10⁻⁴ mol). The vial was heated in a heating chamber at 60 °C. The run of reaction was controlled by GC–MS.

Reaction between **I, Styrene, and Vinylidimethylphenylsilane.** [(cod)Rh(μ-OSiMe₃)₂] (0.27 g, 9.0 × 10⁻⁵ mol) was dissolved under argon in 0.6 mL of C₆D₆ in a NMR tube. To the solution were added H₂C=CHSiMe₂Ph (0.08 mL, 4.4 × 10⁻⁴ mol) and styrene (0.1 mL, 8.8 × 10⁻⁴ mol). The NMR tube was heated in a heating chamber at 60 °C. The run of reaction was controlled by ¹H NMR and GC–MS.

Acknowledgment. This work was supported by Grant No. K012/T09/2000 from the State Committee for Scientific Research (Poland).

OM0100683