Silylation of Styrene with Vinylsilanes Catalyzed by RuCl(SiR₃)(CO)(PPh₃)₂ and RuHCl(CO)(PPh₃)₃

Bogdan Marciniec* and Cezary Pietraszuk

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

Received April 28, 1997[®]

The coupling reaction of styrene with vinylsilanes catalyzed by ruthenium complexes was investigated. RuHCl(CO)(PPh₃)₃ (I) and RuCl(SiR₃)(CO)(PPh₃)₂ (where R₃ = Me₃ (II), Me₂-Ph (III), (EtO)₃ (IV)) were found to be efficient and selective catalysts for the formation of *E*-1-phenyl-2-silylethene and evolution of ethene. Stoichiometric reactions of styrene with the Ru–Si bonds of II–IV in argon and silylstyrene with the Ru–H bond in air (I*) as well as a MS study of the product of the deuterated styrene with vinylsilanes are convincing evidence for the mechanism of the process involving the migratory insertion of styrene into the Ru–Si bond (and vinylsilane into Ru–H bond) followed by β -H (and β -Si) elimination to give phenylsilylethene (and ethene). Kinetic tests (TOF) indicate a prior dissociation of the PPh₃ molecule (or by its oxygenation) from I to yield pentacoordinated RuHCl(CO)(PPh₃)₂ which is almost as active as II.

Introduction

While many metallacarbene species catalyze the metathetical conversion (e.g., ADMET, ROMP) of siliconcontaining olefins,¹ even well-defined Mo, W, and Ru complexes are inactive in the metathesis of vinylsubstituted silanes and siloxanes.² Evidence for the insertion of ethylene³ and vinylsilane⁴ into the Ru-Si bond, yielding a vinylsilane and two *E*-1,2- and 1,1-bis-(silyl)ethene) isomers, respectively, has shown that in the reaction catalyzed by ruthenium complexes, referred to as "metathesis" (or disproportionation) of olefins, a new type of olefin conversion-silylation (coupling) of olefins with vinylsilane (Scheme 2) instead of C=C bond splitting (formally characterizing the olefin metathesis) (Scheme 1) occurred. The process occurs through the cleavage of the =C-Si bond of vinylsilane and the =C-H bond of the olefin.⁴ In the disproportionation of vinylsilanes, E-1,2-bis(silyl)ethene is accompanied by 1,1-bis(silyl)ethene (Scheme 2) ($R = SiR'_3$; $R'_3 = (EtO)_3$, Me₂Ph, Me₃, Me₂(OEt), Me(OEt)₂;³⁻⁵ R = C_nH_{2n+1} , n = 1-18, R'₃ = (EtO)₃, Me₃, Me₂Ph, Me(OEt)₂, Me₂(OEt)). The latter isomer was incorrectly identified in Wakat-

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Activation of -C=C- bond

Scheme 2. Silylation (Coupling) of Olefins with Vinylsilanes



Activation of =C—H and =C—Si bond

suki's and our preliminary examinations as a Z-isomer. Silylation ("co-metathesis") of 1-alkenes with vinylsilanes afforded 1-silyl-1-alkene, the *E*-isomer, accompanied by the Z-isomer as well as 2-silyl-1-alkene, which were predominantly byproducts.^{5,6}

The results of the mechanistic study of the disproportionation of vinyltrimethylsilane in the presence of a variety of ruthenium(0) and ruthenium(II) complexes as precursors suggested five pathways initiating two essential mechanisms, through the insertion of vinyl-silane into the Ru–Si (Ru–H) bond and β -H (β -Si) elimination of products (four routes) and by metal carbene species (one route).^{5b} The first striking proof of the insertion of ethylene into the Ru–Si bond was given by Wakatsuki et al. who revealed the reversibility of the stoichiometric reaction shown in Scheme 3),³ where R = Me, OEt. Our examinations of the insertion of vinylsilane into the Ru–Si bond of the same complex

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Scheme 5. Disproportionation (Homocoupling) of Vinyl Trisubstituted Silanes Catalyzed by Ru Complexes



indicate a reversible formation of two isomers⁴ (Scheme 4). The simplified model of the homocoupling of vinylsilanes employs conventional insertion-elimination steps to explain the experiments (Scheme 5).⁴ The aim of this work is to provide evidence for the insertionelimination mechanism of the coupling of styrene with vinyl-trisubstituted silanes catalyzed by RuCl(SiR₃)-(CO)(PPh₃)₂ as well as its Ru-H analogue.

Up to know the selected silylstyrenes, very common organic reagents,⁷ have been prepared mainly by dehydrogenative silylation of vinylsilane by hydrosilane (usually triethylsilane) catalyzed by Ru, Fe, and Rh complexes⁸ or by hydrosilylation of phenylacetylene.⁹ Our preliminary examination of the reaction of styrene with vinyltriethoxysilane in the presence of RuCl₂- $(PPh_3)_3$ indicated a new route for the preparation of silylstyrene.^{6b,c} The silylation of styrene by various vinyl-substituted silanes markedly extends the possibility of preparing numerous styrylsilanes obtained effectively and selectively in a one-step process.

Results and Discussion

Catalytic Examinations. The reaction of styrene with vinyl-substituted silanes occurs in the presence of many ruthenium(0) and ruthenium(II) complexes in a wide temperature range (from room temperature to 150 °C) according to eq (1), where $SiR_3 = SiMe_3$ (**a**), $SiMe_2$ -Ph (**b**), $Si(OEt)_3$ (**c**). *E*-1-Phenyl-2-silylethene, the

$$Ph = + = \overset{SiR_3}{\underbrace{[Ru]}} \overset{[Ru]}{Ph} + = (1)$$

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Table 1. Silylation of Styrene with Vinyltrimethylsilane (1a), Vinyldimethylphenylsilane (1b), and Vinyltriethoxysilane (1c) Catalyzed by Ruthenium Complexes^a

		1				
catalyst	conv. of 1a , %	yield of 2a (3a), %	conv. of 1b , %	yield of 2b (3b), %	conv. of 1c , %	yield of 2c (3c), %
RuCl ₂ (PPh ₃) ₃	10	10 (0)	46	39 (1)	60	52 (5)
Ι	60	58 (2)	70	63 (1)	70	60 (4)
I*	58	56 (2)	67	57 (1)	69	62 (3)
II	90	90 (0)	82	75 (1)	85	75 (5)
III	80	78 (1)	80	73 (1)	81	71 (5)
IV	62	58 (2)	67	56 (1)	68	60 (4)
$Ru_{3}(CO)_{12}$	10	5 (4)	45	22 (20)	52	34 (16)

^{*a*} Reaction conditions: 110 °C, 6 h, argon (asterisk indicates air), $[CH_2=CHSi=]:[styrene]:[catalyst]=1:1:10^{-2}$.

product of a heterocoupling (silylation of styrene), is the main and very often exclusive liquid product of the reaction. E-1,2-Bis(silyl)ethene (**3**) can be a byproduct of the homocoupling of vinylsilane. Exemplary catalytic data on the silylation of styrene with vinyltrimethylsilane (**1a**), vinyldimethylphenylsilane (**1b**), and vinyltriethoxysilane (**1c**) are compiled in Table 1.

Complexes containing initially Ru-Si (RuCl(SiMe₃)-(CO)(PPh₃)₂ (II), RuCl{Si(OEt)₃}(CO)(PPh₃)₂ (III), RuCl-(SiMe₂Ph)(CO)(PPh₃)₂ (IV)) and Ru-H bonds (RuHCl- $(CO)(PPh_3)_3$ (I)) are much more effective than others. The reaction is regio- and stereoselective. Among the byproducts there is a product of a homocoupling, *E*-1,2bis(silyl)ethene (3a-c), and in the case of 1b and 1c, siloxanes. All products were isolated and characterized by ¹H and ¹³C NMR spectroscopy. The catalytic activity of Ru(0) and Ru(II) phosphine complexes, which initially do not have Ru-H and/or Ru-Si bonds, in the silvlation of styrene can be accounted for in a manner similar to that of the disproportionation of vinyltrimethylsilane, i.e., formation of the Ru-H bond via ortho-metalation of the ruthenium triphenylphosphine complex in competition with the pathways involving metal-carbene species.^{5b,c} Ruthenium carbonyl with no phosphine ligands, Ru₃(CO)₁₂, catalyzes the silylation of styrene, which is strongly accompanied by homocoupling of vinylsilanes. Spectroscopic analysis of Ru₃(CO)₁₂ treated with vinylsilane, reported previously,^{5b} showed the presence of a Ru-Si bond whose formation was proposed to occur via hydrovinylation of the Ru(0) complex followed by insertion of vinylsilane into the Ru-H bond and β -Si elimination to give ethene and the Ru–Si complex.

The activity of some catalysts was tested at a lower temperature, i.e., at 80 °C and room temperature as well as in open systems (under atmospheric pressure), enabling ethylene to be removed. Selected data for I^* and II are presented in Table 2. The reaction of CH_2 =CHSiMe₂Ph with styrene occurring at 80 °C is even more efficient (higher yields and selectivities) than at 110 °C.

Kinetic Studies. Preliminary kinetic examinations were performed to measure the uptake of vinyldimethylphenylsilane in its reaction with styrene at a 10-fold excess (without solvent) at 80 °C. The cocatalytic effect of dioxygen can be confirmed by comparing the kinetic measurements of the reaction catalyzed by RuHCl(CO)-(PPh₃)₃ conducted in air (**I***) or in argon (**I**). Selected results of the kinetic examinations are presented in

Table 2. Effect of Temperature and OtherReaction Conditions on the Silylation of Styrenewith Vinyl-Trisubstituted Silanes Catalyzed byRuthenium Complexes (I*) and (II)

catalyst	conv. of 1a , %	yield of 2a , %	conv. of 1b , %	yield of 2b , %	conv. of 1c, %	yield of 2c , %
I *	43 ^a	40 ^{<i>a</i>}	74 ^a	70 ^a	35 ^a	32 ^a
	60 ^b	58^{b}	87 ^c	84 ^c	32^d	30^d
			30	26		
II	90	90	85	80	38	36
	72^{b}	71 ^b	97 ^e	95 ^e	43^d	40^d
			31	27		

^{*a*} Reaction conditions: argon air, 6 h, 80 °C, [CH₂=CHSi=]: [styrene]:[catalyst] = 1:1:10⁻², sealed glass ampoules. ^{*b*} Reaction conditions: argon (asterisk indicates air), 6 h, 50 °C, open system, [CH₂=CHSi=]:[styrene]:[catalyst] = 1:10:5 × 10⁻³. ^{*c*} Reaction conditions: air, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*d*} Reaction conditions: argon (asterisk indicates air), 6 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*d*} Reaction conditions: argon (asterisk indicates air), 6 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*e*} Reaction conditions: argon, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*e*} Reaction conditions: argon, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*e*} Reaction conditions: argon, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*e*} Reaction conditions: argon, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:5 × 10⁻³. ^{*e*} Reaction conditions: argon, 2 h, 80 °C, open system, [CH₂=CHSi=]:[styrene]: [catalyst] = 1:10:2 × 10⁻³.



Figure 1. Conversion of vinyldimethylphenylsilane in its reaction with styrene catalyzed by **I**, **I***, and **II**. Reaction conditions as given in Table 3.

 Table 3. Maximum Rate (TOF) of Styrene

 Silylation with Vinyldimethylphenylsilane^a

catalyst	TOF, h ⁻¹	notes
II I* I	900 450 78	$\begin{array}{l} [H_2C=CHSi\equiv]:[Ru]=500:1\\ [H_2C=CHSi\equiv]:[Ru]=200:1\\ [H_2C=CHSi\equiv]:[Ru]=200:1 \end{array}$

^{*a*} Reaction conditions: 80 °C, $[H_2C=CHSi\equiv]:[H_2C=CHPh] = 1:10$, open system, argon (asterisk indicates air).

Figure 1. The maximum rate (TOF) of the silylation of styrene with vinyldimethylphenylsilane decreases in the order $\mathbf{II} > \mathbf{I}^* > \mathbf{I}$ (Table 3).

Although the yields of the products of the reaction catalyzed by **I** in argon and in air \mathbf{I}^* are similar (see Table 1), the maximum rate of the reaction occurring in air is much higher. Oxygenation of one phosphine ligand in **I** apparently releases a five-coordinate complex leading to an active intermediate, containing the Ru–H bond, according to eq 2. The formation of phosphine

$$RuHCl(CO)(PPh_3)_3 \xrightarrow{O_2} RuHCl(CO)(PPh_3)_2 \qquad (2)$$

oxide was monitored by GC-MS. However, siloxanes as byproducts were detected in this case. In the absence of oxygen, the dissociation of one molecule of PPh_3 from I is the initiating step of the coupling of the silane with styrene. A comprehensive kinetic study of this new reaction will be the subject of a separate publication.

 Table 4. Stoichiometric Reaction of

 RuCl(SiR₃)(CO)(PPh₃)₂ (II–IV) with PhCH=CH₂^a

complex	conversion of styrene, %	yield of 2 (ethylbenzene), %
II	86	70 (15)
III	95	90 (5)
IV	25	24 (traces)
	_	

 a Reaction conditions: 110 °C, 6 h, argon, [Ru–Si]:[PhCH=CH₂] = 1:1.

Table 5. Stoichiometric Reaction of RuHCl(CO)(PPh₃)₃ with Silylstyrene PhCH=CHSiR₃^a

silylstyrene	conversion of silylstyrene, %	yield of styrene (ethylbenzene), %
2a	45	24 (12)
2b	41	29 (10)
2c	78	36 (17)

 a Reaction conditions: 110 °C, 6 h, argon, [Ru–H]: [PhCH=CHSiR_3] = 1:1.

Stoichiometric Reactions of Styrene with Ruthenium Complexes. The reaction of equimolar amounts of complexes containing a Ru–Si bond (II– IV) with styrene was carried out to yield styrylsilanes 2a-c (identified by NMR spectroscopy and GC-MS) according to the proposed equation (eq 3), although spectroscopic examination does not confirm formation of a complex containing a Ru–H bond, even in an excess amount of styrene. Apparently, the Ru–H complex

$$[Ru] - SiR_3 + \frac{Ph}{H}C = C + \frac{110^{\circ}C, 6h}{H} + \frac{Ph}{H}C = C + \frac{Ph}{SiR_3} (3)$$

produced is used subsequently for the hydrogenation of styrene to get ethylbenzene as well as for its transformations to yield clusters. The results are compiled in Table 4.

Additional experiments involving the reaction of $RuHCl(CO)(PPh_3)_3$ with styrylsilane enabled us to show the reversibility of the insertion process described by eq 4 (Table 5). Competitive reaction of Ru-H with

$$[Ru]-H + \frac{Ph}{H}C = C \frac{H}{SiR_3} \xrightarrow{110^{\circ}C, 6h}$$

$$[Ru]-SiR_3 + \frac{Ph}{H}C = C \frac{H}{H}$$
(4)

styrene also yields ethylbenzene.

The above experiments allowed us to provide evidence for the insertion of styrene into the Ru–Si bond (or migration of silyl ligands), occurring similar to the insertion of ethene³ and vinylsilane.⁴ An illustration of the entire insertion scheme is given in Scheme 6. Nevertheless, the present study does not allow a prediction of the real geometry of the Ru–carbonyl intermediate and does not provide direct evidence for a "migration" or an "insertion".

Isotopic Labeling Studies. The effect of the coupling of vinylsilane with $C_6D_5CD=CD_2$ employed in place of $C_6H_5CH=CH_2$ was examined in the reaction catalyzed by **II**. This reaction is a very convenient model since it yields only one *E*-isomer. The aim of the



Figure 2. The mass spectrogram of the product of the reaction of $C_6D_6CD=CD_2$ with $CH_2=CHSiMe_2Ph$ in the presence of **II**.



test was to distinguish between the two above-mentioned mechanisms. If the reaction were to occur according to the metallacarbene mechanism, the process shown in eq 5 would take place, leading to the formation



of the product containing six deuterium atoms, but if the silylation of styrene by vinylsilane proceeded then the process shown in eq 6 would take place, leading to silylstyrene- d_7 , where SiR₃ = SiMe₃, SiMe₂Ph, and Si-(OEt)₃.



A GC-MS study of the deuterated styrene in the preliminary stage of its reaction with vinylsilane showed the exclusive formation of a product $-d_7$ for the three vinyl-trisubstituted silanes tested.

An exemplary mass spectrogram is given in Figure 2. The peaks m/z = 245 (M⁺) and 230 (M⁺ - CH₃) recorded after 0.5 h of the reaction of styrene- d_8 with Me₂PhSiCH=CH₂, catalyzed by RuCl(SiMe₃)CO(PPh₃)₂ (50 °C) where the yield of the product does not exceed 1%, are convincing evidence for the formation of the product containing seven deuterium atoms. No m/z = 244 signal was detected at the beginning step of the reaction. After 5 h, the mass spectrum reveals a



complex sequence of peaks, indicating the formation of d_6 and d_5 isotopomers, presumably due to intramolecular H/D exchange, e.g., in Ru intermediates. Thus, the result of the isotopic test is additional proof for the insertion–elimination mechanism of the reaction of styrene with vinylsilane.

Mechanistic Implications. Stoichiometric reactions of styrene with Ru–Si bonds of complexes **II**–**IV** and the reversible equimolar reactions of styrylsilanes with the Ru–H bond of complex **I** are convincing evidence for the reverse migratory insertion of styrene into the Ru–Si bond selectively yielding *E*-1-phenyl-2silylethene. Additionally, the results of the MS study of the products of the deuterated styrene reaction with vinylsilanes and the earlier results of Wakatsuki³ and our⁴ experiments on the insertion of ethylene and vinylsilane into Ru–Si bonds allow us to propose a reasonable non-metallacarbene mechanism for the reaction of vinylsilanes with styrene (Scheme 7).

The silylation (coupling) of styrene with vinylsilanes catalyzed by pentacoordinate ruthenium complexes (PPh₃)₂(CO)ClRu-H and (PPh₃)₂(CO)ClRu-SiR₃ involves two methods of initiation of the catalytic cycle. Kinetic data also confirm this scheme. The TOF of the process started by both types of catalysts is of the same order. The formation of the initial pentacoordinate Ru-H intermediate proceeds via the elimination of a triphenylphosphine molecule. It can occur either (fast) by its oxygenation with air or (slow) by its dissociation. The catalytic cycle involves insertion of vinylsilane into the Ru–Si bond followed by competitive β -H or β -Si eliminations from the intermediate β -silylethylruthenium and β -silylphenylethylruthenium complexes, respectively. The key point of the mechanism presented is the formation of octahedral ruthenium complexes in

which the *cis* position of the Ru-SiR₃ and Ru-H bonds with respect to π -bonded styrene and vinylsilane, respectively, is necessary for the observed insertion. However, spectroscopic and X-ray determination of the structure of five-coordinate complexes of the formulas $RuCl(SiR_3)(CO)(PPh_3)_2^{10}$ and $RuHCl(CO)(PR_3)_2^{11}$ a,b showed their approximately square-pyramidal geometry with the silyl ligand and the hydride ligand, respectively, at the apical positions and the triphenylphosphine ligands arranged mutually trans. According to these data, the attack of the olefin (styrene and vinylsilane) should readily lead to the olefin binding trans to the hydride (4) or silvl (5) ligands, respectively, so these isomers would not easily lead to the insertion of the C=C bond of the examined olefins into the Ru-Si and Ru-H bond. Therefore, we should consider isomer-



ization of square-pyramidal complexes of ruthenium. Coulton et al. have done an *ab initio* calculation and MO analysis in order to understand the reactivity of $RuHCl(CO)(PH_3)_2$ dependence on the particular ligand position, i.e., as shown below.

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K. G. Inorg. Chem. 1994, 32, 3325.



The *Ab initio* potential energy surface for this complex, $E = f(\alpha, \beta)$ (where α and β are respectively the H–Ru–Cl and H–Ru–CO angles), shows that the transformation of T_H to T_{CO} corresponding to the opening of the Cl–Ru–H (α) angle, maintaining the H–Ru–CO (β) close to 90°, requires only 6.8 kcal/mol while the transformation of T_H to T_{Cl} needs 26.8 kcal/mol. Consequently, the structure of the T_{CO} -type (although not of minimum energy) has a sufficiently low energy to be proposed as the active intermediate. In this isomer, the hydride is at the *cis* position to the empty site, i.e., to the incoming silylolefin in a square pyramid. On the



other hand, according to the considerations of Caulton at al.^{11c} the five-coordinate energy surface implies that attack of an incoming ligand (e.g., vinylsilane) is facile via direction **a** (in the HRu(CO) plane of complex 4). In



both isomers (6 and 6') the migratory insertion of the C=C bond of vinylsilane into the Ru-H bond can readily occur. Per analogy, the isomerization of Ru-Si complexes of the distorted square-pyramid geometry can also be preliminary predicted. However, to find the real structure and reactivity of the Ru-H and Ru-Si intermediates, additional experimental spectroscopic tests at low temperatures are needed and a more comprehensive kinetic study should be undertaken.

Experimental Section

General Methods and Chemicals. All syntheses and manipulations were carried out using standard Schlenk and high-vacuum-line techniques unless otherwised stated. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300 VT spectrometer in C₆D₆ at 300 and 75 MHz, respectively. ³¹P NMR spectra were recorded on Varian Unity 300 spectrometer in C₆D₆ at 121 MHz. ¹H and ¹³C HETCOR spectra were recorded on a Varian Gemini 300 VT spectrometer. Infrared spectra (KBr plates) were recorded using FT-IR, Brucker IFS-113v. The mass spectra of the products and substrates were determined by GC-MS analysis (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 performed on a Hewlett Packard HP 5890 Series II with a 30 m megabore HP-1 column and TCD. Chemicals were obtained from the following sources: vinyltrimethylsilane and vinyldimethylphenylsilane from ABCR, vinyltriethoxysilane and styrene from Fluka, benzene from Lachenie (Czech Republic), toluene from R&D Center of Petrochemie (Plock, Poland), hexane from Merck, and benzene d_6 and styrene- d_8 from Dr. Glaser, AG Basel. RuHCl(CO)-(PPh₃)₃ (I) was purchased from Aldrich and used without further purification and drying. All solvents and vinylsilanes were dried and distilled over CaH₂ under dry argon atmosphere prior to use.

Synthesis of Ruthenium–Silyl Complexes. The silyl complexes of ruthenium(II) were prepared essentially according to the method described earlier,³ based on the reaction of RuHCl(CO)(PPh₃)₃ with the corresponding vinylsilanes.

RuCl(SiMe₃)(CO)(PPh₃)₂ (II). RuHCl(CO)(PPh₃)₃ (306 mg, 0.32 mmol) was refluxed in benzene (10 mL) forming a suspension. Subsequently, CH₂=CHSiMe₃ (0.23 mL, 1.60 mmol) was added to the mixture, and the suspension was refluxed for 24 h to give a yellow-brown solution. Evaporation of the excess solvent under reduced pressure, followed by addition of hexane, gave a yellow precipitate. The latter was filtered, washed with cold hexane, and dried in vacuo (0.18 g, 73% yield). Analytical data:^{3,10} ¹H NMR (C₆D₆, ppm) δ 0.63 (s, 9H, Si–Me₃), 7.03–7.11 (m, 18H, Ph), 7.83–7.91 (m, 12H, Ph); ³¹P NMR (C₆D₆, ppm) δ 32.5 (s); mp 159–161 °C (dec); IR (KBr, cm⁻¹) 1915 (ν (CO)).

RuCl(SiMe₂Ph)CO(PPh₃)₂ (III). Complex **III** was prepared using the same procedure and the following reagents: RuHCl(CO)(PPh₃)₃ (314 mg, 0.33 mmol) and CH₂=CHSiMe₂-Ph (0.3 mL, 1.65 mmol). Finally, a yellow precipitate was obtained (0.188 g, 69% yield). Analytical data: ¹H NMR (C₆D₆, ppm) δ 0.93 (s, 6H, SiMe₂), 6.99–7.16 (m, 21H, PPh (18H) and SiPh (3H), 7.61–7.71 (m, 14H, PPh (12H) and SiPh (2H)); ³¹P NMR (C₆D₆, ppm) δ 30.58 (s); mp 150–152 °C (dec); IR (KBr, cm⁻¹) 1931 (ν (CO)). Anal. Calcd for C₄₅H₄₁ClOP₂SiRu: C, 65.56; H, 5.01. Found: C, 65.87; H, 5.32.

RuCl{Si(OEt)₃}(CO)(PPh₃)₂ (IV). Complex **IV** was prepared using the same procedure and the following substrates: RuHCl(CO)(PPh₃)₃ (273 mg, 0.29 mmol) and CH₂=CHSi(OEt)₃ (0.31 mL, 1.45 mmol). The pale-yellow precipitate was isolated (0.171 g, 70%). Analytical data:¹⁰ ¹H NMR (C₆D₆, ppm) δ 1.11 (t, 9H, SiOCH₂CH₃), 3.80 (q, 6H, SiOCH₂CH₃), 7.02–7.15 (m, 18H, Ph), 7.63–7.75 (m, 12H); ³¹P NMR (C₆D₆) δ 35.6 (s); mp 182–184 °C (dec); IR (KBr, cm⁻¹) 1926 (ν (CO)).

General Procedure for the Catalytic Examinations. The ruthenium complex, benzene, toluene (internal standard), vinyltrisubsituted silane, and styrene were placed in the evacuated and filled with argon glass ampoules in the ratio [Ru]:[CH₂=CHSi=]:[styrene]= 10^{-2} :1:1. The sealed ampoule was heated at the required conditions. The composition of the reaction mixture was analyzed by GC. The yield was calculated by GC using the internal standard method.

Synthesis of 1-Phenyl-2-silylethenes. The syntheses were performed in dry air using $RuHCl(CO)(PPh_3)_3$ as the catalyst and dry but not deoxygenated reagents and solvents. The details are presented below.

1-Phenyl-2-(trimethylsilyl)ethene. RuHCl(CO)(PPh₃)₃ (98.2 mg, 0.103 mmol), benzene (3 mL), vinyltrimethylsilane (2.07g, 20.6 mmol), and styrene (6.44 g, 61.8 mmol) were placed in a 100 mL glass ampoule. The ampoule was sealed and heated at 100 °C for 6 h. The reaction mixture was distilled to yield *E*-1-phenyl-2-(trimethylsilyl)ethene (77–82 °C/3 mmHg, 3.1 g, 85%). Selected analytical data:¹² ¹H NMR (C₆D₆, ppm) δ 0.35 (s, 9H, SiMe₃), 6.67 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Si≡, 7.14 (d, 1H, J_{HH} = 19.1 Hz, =C*H*Ph), 7.23–7.58 (m, 5H, Ph); ¹³C NMR (C₆D₆, ppm) δ –0.60 (SiMe₃), 129.67 (=*C*HSi≡), 144.92 (=*C*HPh), 127.31 (C_o), 128.71 (C_p), 129.22 (C_m), 139.24 (C_d); MS(EI) *m*/*z* (relative intensity) 176 (14, M⁺), 163 (11), 162 (39) 161 (100), 73 (10).

1-Phenyl-2-(dimethylphenylsilyl)ethene. RuHCl(CO)-(PPh₃)₃ (131 mg, 0.138 mmol), CH_2 =CHSiMe₂Ph (4.46 g, 27.5 mmol), and styrene (8.59 g, 82.5 mmol) were heated in a 20

mL glass reactor. The reactor was heated at 100 °C for 6 h. The reaction mixture was subsequently distilled in vacuo giving *E*-1-phenyl-2-(dimethylphenylsilyl)ethene (bp: 137–141 °C/3 mmHg, 5.1 g, 78%). Selected analytical data:¹² ¹H NMR (C₆D₆, ppm) δ 0.58 (s,6H, SiMe₂), 6.78 (d,1H, *J*_{HH} = 19.1 Hz, =*CH*Si=), 7.20 (d,1H, *J*_{HH} =19.1 Hz, =*CH*Ph); ¹³C NMR (C₆H₆, ppm) δ –1.64 (Si–Me₂), 127.65 (=*C*HSi=), 146.45 (=*C*HPh); MS(EI) *m*/*z* (relative intensity) 238 (41, M⁺), 224 (39), 223 (100), 161 (17), 145 (40), 135 (18), 121 (12), 91 (27), 77 (20).

1-Phenyl-2-(triethoxysilyl)ethene. RuHCl(CO)(PPh₃)₃ (114 mg, 0.120 mmol), CH₂=CHSi(OEt)₃ (4.55 g, 23.9 mmol), and styrene (7.47 g, 71.7 mmol) were introduced to a 20 mL glass reactor. The contents were then degassed, and dry air was introduced. The sample was heated at 110 °C for 6 h followed by distillation in vacuo. *E*-1-Phenyl-2-(triethoxysilyl)-ethene was isolated (bp: 108–113 °C/3 mmHg, 4.8 g, 75%). Selected analytical data:¹³ ¹H NMR (C₆D₆, ppm) δ 1.23 (t, 9H, SiOCH₂CH₃, 3.89 (q, 6H, SiOCH₂CH₃, 6.33 (d, 1H, *J*_{HH} = 19.2 Hz, =CHSi=, 7.44 (d, 1H, *J*_{HH} = 19.2 Hz, =CHPh), 7.04–7.33 (m, 5H, Ph); ¹³C NMR (C₆D₆, ppm) δ 19.18 (SiOCH₂CH₃), 59.27 (SiO*C*H₂CH₃), 119.40 (=*C*HSi=), 149.63 (=*C*HPh), 127.57 (C_o), 129.26 (C_m), 129.31 (C_p), 138.65 (C_d); MS(EI) *m*/*z* (relative intensity) 266 (20, M⁺), 251 (100), 223 (55), 163 (32), 147 (68), 131 (54), 103 (58), 77 (30), 91 (10).

Equimolar Reactions of Ruthenium–Silyl Complexes with Styrene. RuCl(SiMe₃)(CO)(PPh₃)₂ (16.6 mg, 0.022 mmol), benzene (0.1 mL), toluene (1 μ L standard), and styrene (2.5 μ L, 0.022 mmol) were placed under argon in degassed and filled with argon glass ampoules. Then each ampoule was sealed, and the sample was heated at 110 °C for 6 h.

The corresponding reactions with RuCl(SiMe₂Ph)(CO)-(PPh₃)₂ (18.00 mg, 0.022 mmol) and RuCl{Si(OEt)₃}(CO)-(PPh₃)₂ (18.6 mg, 0.022 mmol) were performed using the same procedure. The products were identified by GC-MS. The number of conversions and yield were calculated on the basis of GC analyses using the internal standard method.

Equimolar Reactions of RuHCl(CO)(PPh₃)₃ with 1-Phenyl-2-silylethenes. RuHCl(CO)(PPh₃)₃ (20.0 mg, 0.021 mmol), benzene (0.3 mL), toluene (2 μ L standard), and *E*-1phenyl-2-(trimethylsilyl)ethene (3.7 mg, 0.021 mmol) were heated in a sealed ampoule (in dry air) at 110 °C for 6 h. The corresponding reactions of RuHCl(CO)(PPh₃)₃ with *E*-1-phenyl-2-(dimethylphenylsilyl)ethene (5.0 mg) and *E*-1-phenyl-2-(triethoxysilyl)ethene (5.59 mg) were performed using the same procedure as that for *E*-1-phenyl-2-(trimethylsilyl)ethene. The products were identified by GC-MS. The number of conversions and yield were calculated on the basis of GC analyses using the internal standard method.

Reactions of Vinyl-Trisubstituted Silanes with CD₂= CDC₆D₅ Catalyzed by RuCl(SiMe₃)(CO)(PPh₃)₂. RuCl-(SiMe₃)(CO)(PPh₃)₂ (2.1 mg, 2.76 μ mol), C₆D₆ (0.2 mL), CH₂=CHSiMe₃ (138 mg, 1.38 mmol), and CD₂=CDC₆D₅ (155 mg, 1.38 mmol) were introduced to a glass vial (Supelco) equipped with a mininert valve. The vial was heated at 50 °C. Similar experiments were performed using two other vinylsilanes according to the following detailed procedure: RuCl(SiMe₃)(CO)(PPh₃)₂ (1.7 mg, 2.23 μ mol), C₆D₆ (0.2 mL), CH=CHSiMe₂Ph (180 mg, 1.11 mmol), and CD₂=CHC₆D₅ (124 mg, 1.10 mmol) were heated in a Supelco vial at 50 °C; RuCl-(SiMe₃)(CO)(PPh₃)₂ (1.5 mg, 1.97 μ mol), C₆D₆ (0.2 mL), CH₂=CHSi(OEt)₃ (187 mg, 0.98 mmol), and CD₂=CDC₆D₅ (110 mg, 0.98 mmol) were heated in a Supelco vial at 80 °C. The progress of the reactions was monitored by GC-MS.

General Procedure for Kinetic Study on the Silylation of Styrene with Vinylsilanes. The glass reactor (20 mL, equipped a with reflux condenser, thermostated heating mantle, and magnetic stirring bar) was evacuated and purged with argon (or dry air). The ruthenium complex, dodecane (internal standard), and styrene were added to the reactor. At the given temperature, vinylsilane was added. The mixture was stirred under the conditions shown in the figures and tables. The progress of the reaction was monitored by GC. The conversion of vinylsilane was calculated using the internal standard method.

Acknowledgment. This work is supported by a Grant No. 13T09A074 from the State Committee for Scientific Research. We thank Ms. Małgorzata Kujawa for assistance in the kinetic studies.

OM9703550

⁽¹²⁾ For the extensive NMR study of silylstyrenes, see: Liepins, E.; Goldberg, Yu.; Iovel, I.; Lukevics, E. *J. Organomet. Chem.* **1987**, *335*, 301.

⁽¹³⁾ For crystal structure and NMR spectroscopy data, see: Lewis, L. N.; Sy, K. G.; Bryant, G. R., Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.