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Silylative Coupling of Vinyl Alkyl Ethers with Vinylsilanes Catalyzed by Ruthenium Complexes

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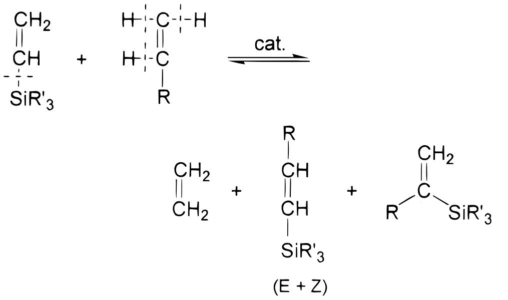
Ruthenium complexes such as $RuHCl(CO)(PPh_3)_3$ (**I**), $RuCl(SiMe_3)(CO)(PPh_3)_2$ (**II**), $RuCl_2(PPh_3)_3$ (**III**), and $Ru(CO)_3(PPh_3)_2$ (**IV**) appear to be very effective catalysts of cross-disproportionation of vinyl-trisubstituted silanes $CH_2{=}CHSiR_3$ (where $R_3 = Me_3$, $PhMe_2$, $(OEt)_3$) with vinyl alkyl ethers $CH_2{=}CHOR'$ (where R′ = ethyl, *n*-propyl, *n*-butyl, *tert*-butyl, *tert*-pentyl, 2-ethylhexyl, cyclohexyl, trimethylsilyl) to yield a mixture ($E+Z$) of 1-silyl-2-alkoxyethenes. Stoichiometric insertion of vinyl *n*-propyl ether into Ru−Si bonds of **II** and MS study of the products of the deuterated vinyltrimethylsilane with vinyl ethyl ether indicate that the mechanism of cross-disproportionation involves a migratory insertion of the vinyl ether into the Ru−Si bond (and vinylsilane into the Ru−H bond) followed by β-H (and β-Si) transfer to eliminate 1-triorganosilyl-2-alkoxyethenes (and ethene).

Introduction

Recent reports on disproportionation of vinyl-substituted silicon compounds and their co-disproportionation (*trans*-silylation) with olefins[1] catalyzed by ruthenium and rhodium complexes containing (or generating) M−H and M−Si bonds have shown that the new reactions occur through the cleavage of the =C−Si bond of the vinylsilane and the C−H bond of the olefin (also vinylsilane in the self-disproportionation) according to the following equation:



(1)

The mechanism of this new type of the silyl olefin conversion was evidenced by an insertion of ethylene,[1b] vinylsilane,[1e] or styrene[1f] into Ru−Si bonds in the stoichiometric reactions.[2]

Cross-disproportionation of vinyl *n*-butyl ether with vinyltrimethylsilane and vinyldimethylethoxysilane was reported as an example of co-disproportionation catalyzed by $RuHCl(CO)(PPh_3)_3$.[1b] The products were identified (similarly to others in that paper) as a mixture of $E+Z$ isomers. In the case of homo-disproportionation of vinylsilanes the products originally assigned as the Z-isomer subsequently were identified as a 1,1-bis(silyl)ethene[1e,i] suggesting the *trans*-silylation mechanism.

1-Silyl-2-alkoxyethenes are organosilicon reagents commonly used in organic synthesis.[3] It is possible to prepare them (mainly trimethylsilyl derivatives were synthesized) using traditional methods, e.g., via hydroboration of 1-trimethylsilyl-2-alkoxyethyne followed by alcoholysis of the B−C bond, giving mainly the Z-isomer in 50−90% yield,[4a] via silylation of vinyl alkyl ethers with trimethyliodosilane in the presence of a tertiary amine (70−85% of $E+Z$ products)[4b] and via functional organomagnesium compounds (up to 85% yield).[4c]

The aim of this work was to develop a synthetic method for 1-silyl-2-alkoxyethenes using cross-disproportionation of vinyl-substituted silanes with vinyl alkyl ethers in the presence of a ruthenium complex and to provide evidence for the mechanism of this new reaction.

Results and Discussion

The reaction of vinyl-trisubstituted silanes with vinyl alkyl ethers proceeds in the presence of many ruthe-

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[1] (a) Marciniec, B.; Guliński, J. *J. Organomet. Chem.* **1984**, *266*, C19. (b) Wakatsuki, Y.; Yamazaki, Y.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (c) Marciniec, B.; Pietraszuk, C.; Foltynowicz, Z. *J. Organomet. Chem.* **1994**, *474*, 83. (d) Marciniec, B.; Foltynowicz, Z.; Pietraszuk, C.; Guliński, J.; Maciejewski, H. *J. Mol. Catal.* **1994**, *90*, 213. (e) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (f) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320. (g) Marciniec, B.; Lewandowski, M. *Tetrahedron Lett.* **1997**, 3777. (h) Marciniec, B.; Walczuk-Gusciora, E.; Pietraszuk, C. *Catalysis Lett.* **1998**, *55*, 125. (i) Mise, T.; Takaguchi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. *Chem. Commun.* **1998**, 699. (j) Marciniec, B.; Pietraszuk, C.; Kujawa, M. *J. Mol. Catal.* **1998**, *133*, 41. (k) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Organometallics* **1999**, *18*, 2033.

[2] For recent reviews on the silylative coupling of olefins with vinylsilanes see: (a) Marciniec, B. *New J. Chem.* **1997**, *21*, 815. (b) Marciniec, B. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Chapter 2.6. (c) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 203−208.

[3] Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; Chapter 3.

[4] (a) Ponomarev, C. V.; Erikova, M. V.; Nikolaeva, S. N.; Zel, R.; Kostyuk, A. C. *Zh. Obshch. Khim.* **1987**, *57*, 1741. (b) Efimova, I. V.; Kazankova, M. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1985**, *55*, 1646. (c) Barbot, F.; Miginiac, P. *Bull. Chem. Soc. Fr.* **1983**, *1−2*, II−41.

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Table 1. Effect of Alkyl Substituent at Vinyl Alkyl Ether in the Reaction with Vinyltrimethylsilane Catalyzed by Complexes I−IV on the Yield and Selectivity of the Products[a]

$$\underset{\mathbf{a}}{H_2C{=}CHSiMe_3} + \underset{\mathbf{1-8}}{(RO)HC{=}CH_2} \xrightleftharpoons{[Ru]} \underset{\mathbf{1a-8a}}{(RO)HC{=}CHSiMe_3} + H_2C{=}CH_2$$

catalyst	(RO)HC═CH₂ R	products		
			yield (*E*+*Z*) [%]	*E*/*Z*
I	ethyl	**1a**	99	4
II			97	4
III			56	4
IV			78	3
I	*n*-propyl	**2a**	88	4
			74[b]	4
II			97	4
			43[c]	4
I	*n*-butyl	**3a**	96	4
II			94	4
I	*tert*-butyl	**4a**	75	2
II			91	2
I	*tert*-pentyl	**5a**	84	1
II			73	3
I	(2-ethyl)hexyl	**6a**	96	4
II			98	4
I	cyclohexyl	**7a**	91	2
II			90	2
I	Me_3Si	**8a**	76	2
II			77	2

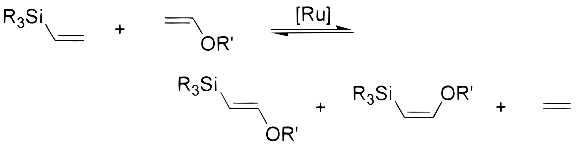
[a] Reaction conditions: $[H_2C{=}CHSiMe_3]$:[ether]:[catalyst] = 1:5:1 × 10^{-2}, 80 °C, 24 h, air. [b] 80 °C, 24 h (argon). [c] $[H_2C{=}CHSiMe_3]$:[ether]:[catalyst] = 1:5:5 × 10^{-3}.

Table 2. Cross-disproportionation of Vinyltriethoxysilane (b) and Vinyldimethylphenylsilane (c) with Selected Vinyl Alkyl Ether Catalyzed by Ruthenium Complexes[a]

	$H_2C{=}CHSi(OEt)_3$ (**b**)		$H_2C{=}CHSiMe_2Ph$ (**c**)	
catalyst	yield (*E* + *Z*) [%]	*E*/*Z*	yield (*E* + *Z*) [%]	*E*/*Z*
	Vinyl Ethyl Ether			
I	60	3	97	5
II	66	2	98	5
III	50	2	63	3
IV			77	3
	Vinyl Cyclohexyl Ether			
I	94	2	89	2
II	95	2	93[a]	2

[a] Reaction conditions: $[H_2C{=}CHSi/]$:[ether]:[catalyst] = 1:5:1 × 10^{-2}, 80 °C, 24 h, air.

nium(II) complexes in a wide temperature range (80−130 °C) according to eq 2,



(2)

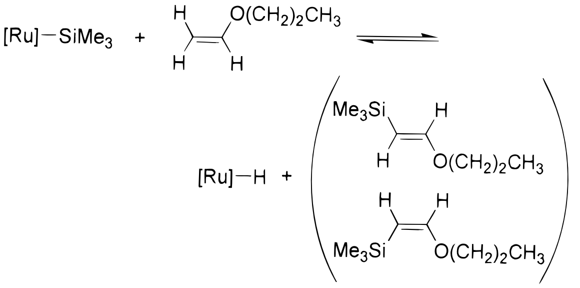
where $SiR_3 = SiMe_3$ (**1**), $SiMe_2Ph$ (**2**), and $Si(OEt)_3$ (**3**), giving the two isomeric products *E*- and *Z*-1-silyl-2-alkoxyethenes and ethylene. The results of reactions of vinyltrimethylsilane (**1**) with various vinyl alkyl ethers carried out in the presence of ruthenium catalysts ($RuHCl(CO)(PPh_3)_3$ (**I**), $RuCl(SiMe_3)(CO)(PPh_3)_2$ (**II**), $RuCl_2(PPh_3)_3$ (**III**), and $Ru(CO)_3(PPh_3)_2$ (**IV**)) are compiled in Table 1.

The yield of the products (two isomers *E*+*Z*) is essentially equal to the percent conversion of the vinylsilane used. Vinyl ethyl ether and vinyl cyclohexyl ether were selected for catalytic reactions with two other vinyl-trisubstituted silanes, i.e., vinyltriethoxysilane (**3**) and vinyldimethylphenylsilane (**2**).

All catalytic results provided the basis for a synthesis of eight silyl derivatives of ethers (see Experimental Section). All products were isolated (as a mixture of *E*+*Z* isomers) and characterized by ^1H NMR and ^{13}C NMR spectroscopy (DEPT analyses were used to exclude the formation of 1-silyl-1-alkoxyethenes). The hydride (**I**) and silyl (**II**) complexes of ruthenium are the most effective catalysts. The stereoselectivity of the catalytic reactions (always *E*-product was favored) is the same for all catalysts used, suggesting that the same mechanism of catalysis is obtained for all. The catalytic effect of dioxygen was confirmed by comparing the product yield of the reaction catalyzed by $RuHCl(CO)(PPh_3)_3$ (**I**) conducted in air and in argon (Table 1). It might be due either to oxygenation of one phosphine ligand releasing a more active five-coordinate complex (**I**, **III**, **IV**)[1c] or, as observed in $RuCl_2(PPh_3)_3$-catalyzed ROMP of norbornene,[5] to facile generation of ruthenium−carbene species, if a metal−carbene mechanism is operative.

The study of the effect of catalyst (**I**−**IV**) concentration on the efficiency of the cross-disproportionation indicates the optimum ratio $[H_2C{=}CHSiR_3]:[Ru] = 100:1$. Exemplary catalyst **II** is less efficient when $[H_2C{=}CHSiR_3]:[Ru] = 200:1$, giving under such conditions a product yield of only 43%.

The reaction of equimolar amounts of complex (**II**) (which contains a Ru−Si bond) with vinyl *n*-propyl ether was carried out to yield 1-silyl-2-propoxyethene (60% yield, *E*/*Z* = 4) (eq 3).



(3)

As in the reaction with styrene reported previously,[1f] ^1H NMR examination did not confirm the formation of a complex containing a Ru−H bond even in the presence of an excess of ether. This presumably is due to the high activity of Ru−H with ethers and vinylsilanes. Additional experiments on the stoichiometric reaction of $RuHCl(CO)(PPh_3)_3$ with 1-silyl-2-propoxyethene gave no product either under air or argon.

The reaction of a vinyl alkyl ether with $HDC{=}C\text{-}DSiMe_3$ instead of $H_2C{=}CHSiMe_3$ was examined using **I** and **II** as catalysts in order to distinguish between two possible mechanisms. If the reaction proceeded according to eq 4, the product, 1-silyl-2-alkoxyethene, would contain no deuterium atom.

However, if the reaction occurred according to the metallacarbene mechanism (cross-metathesis), the process shown in eq 5 would take place, leading to 1-silyl-2-alkoxyethene-d_1).

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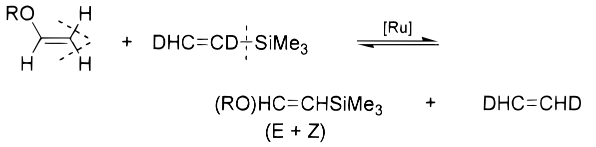
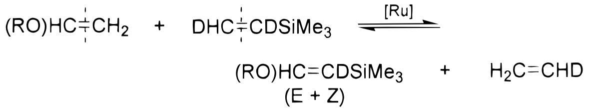
(5) Ivin, K. J.; Reddy, B. S. R.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1062.



(4)

A GC–MS study of the reaction of the deuterated vinylsilane with vinyl ethyl ether showed the exclusive formation of a product containing no deuterium for the catalysts **I**–**III** used.

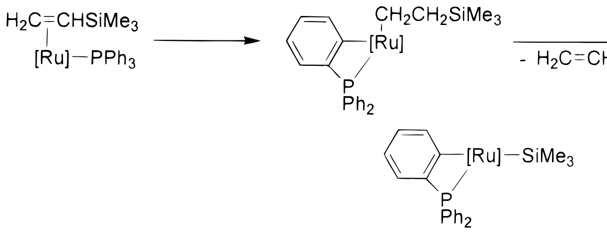


(5)

The results of the catalytic studies, the stoichiometric reactions of vinyl *n*-propyl ether with Ru–Si bonds of the complex **II**, and the deuterium labeling reactions using **II** provide convincing evidence for the reverse migratory insertion of vinyl alkyl ethers into the Ru–Si bond, yielding (*E*+*Z*) 1-silyl-2-alkoxyethenes. Additionally, the irreversibility of the Ru–H (**I**) complex with the products, confirmed by stoichiometric studies, and the earlier results of Wakatsuki[1b] as well as our experiments on the insertion of styrene[1f] and vinylsilane[1e] into the Ru–Si bond led us to propose a reasonable mechanism for the reaction of vinylsilanes with vinyl alkyl ethers (Scheme 1).

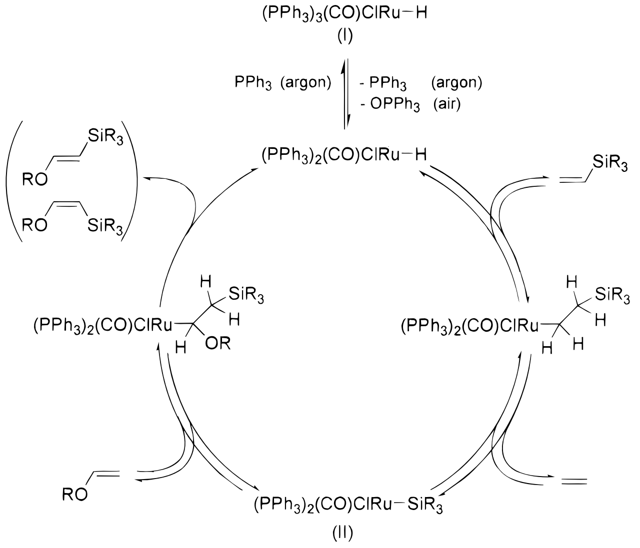
The formation of the initial pentacordinate Ru–H intermediate proceeds via the elimination of triphenylphosphine. It can be realized either by its oxygenation (promotion by oxygenation in air) or by its dissociation (in argon). The catalytic cycle involves insertion of vinylsilane into the Ru–H bond[1f] followed by the insertion of the vinyl alkyl ether into the Ru–Si bond. The latter step occurs via formation of a β-silyl-α-alkoxyethylruthenium intermediate, which, after hydrogen transfer, eliminates two isomers of 1-silyl-2-alkoxyethenes while regenerating Ru–H complex.

However, the efficiency of ruthenium complexes **III** and **IV** containing initially no Ru–H and Ru–Si bonds requires further discussion. The deuterium test also in the case of **III** confirms the course of the reaction occurring via Ru–H/Ru–Si intermediates. In our previous work on the self-disproportionation of vinyltrimethylsilane in the presence of **III** (as well as other complexes containing triphenylphosphine ligands) we proposed a mechanism occurring via orthometalation of ruthenium triphenylphosphine complexes, which is a well-known reversible process taking place in particular in a coordinatively deficient complex.[1c,d] In the reaction of a vinyl alkyl ether with vinyltrimethylsilane the initial Ru–Si bond formation starting from **III** or **IV** can proceed as follows:



(6)

Scheme 1



The inactivity of $Ru_3(CO)_{12}$ in contrast to $Ru(CO)_3(PPh_3)_2$ (**IV**) also can be cited as evidence for catalysis by the orthometalated intermediates discussed above.

Conclusions

1. A new, very efficient method for preparation of (*E*+*Z*) 1-silyl-2-alkoxyethenes (with predominance of the *trans*-product) based on the silylative coupling of vinyl alkyl ethers with vinylsilanes catalyzed by ruthenium complexes was elaborated.

2. The reactions carried out in the presence of catalysts **I**–**IV**, the stoichiometric study of reactions of **II** with vinyl *n*-propyl ether, and the deuterium labeling experiments provide convincing evidence for the mechanism of this new process, which involves intermediates containing the Ru–H and Ru–Si complexes, i.e., the insertion of the vinyl ether into the Ru–Si bond (and vinylsilane into the Ru–H bond) followed by β-H (and β-silyl) transfer to 1-silyl-2-alkoxyethenes (and ethene).

Experimental Section

General Methods and Chemicals. All syntheses and catalytic tests were carried out in the air or under argon.

^1H and ^{13}C NMR spectra of isolated products were recorded in C_6D_6 on a Varian Gemini 300 VT spectrometer (300 and 75 MHz, respectively). When necessary for a correct signal assignment, DEPT (1H, 1H) or (1H, 13C) correlation spectra were recorded. 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.

The chemicals were obtained from the following sources: vinyl alkyl ethers from Aldrich, benzene from Lachema (Czech Rep.), toluene from R&D Center of Petrochemie Płock (Poland), benzene-d_6 from Dr. Glaser A.G. $RuHCl(CO)(PPh_3)_3$ (**I**) was purchased from Aldrich, $RuCl_2(PPh_3)_3$ (**III**) was prepared by standard procedure, and $Ru(CO)_3(PPh_3)_2$ and $RuCl(SiMe_3)(CO)(PPh_3)_2$ (**II**) were prepared according to procedures described in refs 1f and 5, respectively. $Ru(CO)_3(PPh_3)_2$ was synthesized by the method reported.[6] Lindlar catalyst was

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[6] Ahmad, N.; Levinson, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

purchased from Strem Chemicals. Prior to use, all solvents were dried over CaH_2.

Syntheses. The syntheses were performed in dry air using $RuHCl(CO)(PPh_3)_3$ as the catalyst and dry, but not deoxygenated, reagents and solvents. In all cases the mixture of isomers *E*+*Z* were isolated. The details are presented below.

(*Z*,*E*)-1-Trimethylsilyl-2-ethoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl ethyl ether (1.24 g, 17.2 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-ethoxyethene (bp 120−126 °C, 0.46 g, 92%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.12 (s, 9H) ($SiMe_3$)(*E*), 0.30 (s, 9H) ($SiMe_3$)(*Z*), 4.52 (d, 1H) (J = 15.3 Hz) (CHSi)(*E*), 4.31 (d, 1H) (CHSi) (J = 8.4 Hz)(*Z*), 6.52 (d, 1H) (CHO) (J = 15.3 Hz)(*E*), 6.36 (d, 1H) (CHO) (J = 8.4 Hz)(*Z*), 3.47 (q, 2H) (CH_2)(*E*), 3.35 (q, 2H) (CH_2)(*Z*), 1.06 (t, 3H) (CH_3)(*E*), 0.72 (t, 3H) (CH_3)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.21 ($SiMe_3$)(*E*), 0.62 ($SiMe_3$)(*Z*), 95.56 (CHSi)(*E*), 100.85 (CHSi)(*Z*), 156.87 (CHO)(*E*), 158.97 (CHO)(*Z*), 63.49 (CH_2)(*E*), 67.88 (CH_2)(*Z*), 15.07 (CH_3)(*E*), 15.74 (CH_3)(*Z*); MS [*m*/*z* (rel int)] 144 (M, 14)(*E*), 144 (M, 13)(*Z*), 129 (25)(*E*), 129 (21)(*Z*), 103 (100)(*E*), 103 (100)(*Z*), 75 (47)(*E*), 75 (44)(*Z*), 73 (13)(*E*), 73 (10)(*Z*), 59 (13)(*E*), 59 (12)(*Z*). Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18. Found: C, 58.07; H, 11.09

(*Z*,*E*)-1-Trimethylsilyl-2-propoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl *n*-propyl ether (1.48 g, 17.2 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-propoxyethene (bp 139−145 °C, 0.44 g, 80%). Selected analytical data: ^{1}H NMR (C_6D_6), (δ, ppm) 0.12 (s, 9H) ($SiMe_3$)(*E*), 0.29 (s, 9H) ($SiMe_3$)(*Z*), 4.52 (d, 1H) (J = 15.0 Hz) (CHSi)(*E*), 4.29 (d, 1H) (J = 15.0 Hz) (CHSi)(*Z*), 6.53 (d, 1H) (CHO) (J = 15.0 Hz)(*E*), 6.38 (d, 1H) (CHO) (J = 15.0 Hz)(*Z*), 3.42 (t, 2H) (OCH_2)(*E*), 3.31 (t, 2H) (OCH_2)(*Z*), 1.51 (m, 2H) (CH_2)(*E*), 1.34 (m, 2H) (CH_2)(*Z*), 0.83 (t, 3H) (CH_3)(*E*), 0.77 (t, 3H) (CH_3)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.24 ($SiMe_3$)(*E*), 0.63 ($SiMe_3$)(*Z*), 95.44 (CHSi)(*E*), 100.36 (CHSi)(*Z*), 157.04 (CHO)(*E*), 159.32 (CHO)(*Z*), 69.56 (OCH_2)(*E*), 74.11 (OCH_2)(*Z*), 23.17 (CH_2)(*E*), 23.89 (CH_2)(*Z*), 11.16 (CH_3)(*E*), 10.94 (CH_3)(*Z*); MS [*m*/*z* (rel int)] 158 (M, 11)(*E*), 158 (M, 8)(*Z*), 143 (23)(*E*), 143 (21)(*Z*), 118 (17)(*E*), 118 (14)(*Z*), 117 (100)(*E*), 117 (100)(*Z*), 75 (18)(*E*), 75 (14)(*Z*). Anal. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46. Found: C, 60.08; H, 11.52.

(*Z*,*E*)-1-Trimethylsilyl-2-butoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl *n*-butyl ether (1.78 g, 17.8 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-butoxyethene (bp 160−166 °C, 0.51 g, 87%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.12 (s, 9H) ($SiMe_3$)(*E*), 0.30 (s, 9H) ($SiMe_3$)(*Z*), 4.54 (d, 1H) (J = 15.3 Hz) (CHSi)(*E*), 4.29 (d, 1H) (J = 15.3 Hz) (CHSi)(*Z*), 6.54 (d, 1H) (CHO) (J = 15.3 Hz)(*E*), 6.40 (d, 1H) (CHO) (J = 15.3 Hz)(*Z*), 3.49 (t, 2H) (CH_2)(*E*), 3.37 (t, 2H) (CH_2)(*Z*), 1.19−1.54 (m, 4H) (CH_2CH_2)(*E*), 1.19−1.54 (m, 4H) (CH_2CH_2)(*Z*), 0.81 (t, 3H) (CH_3)(*E*), 0.81 (t, 3H) (CH_3)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.24 ($SiMe_3$)(*E*), 0.63 ($SiMe_3$)(*Z*), 95.41 (CHSi)(*E*), 100.34 (CHSi)(*Z*), 157.07 (CHO)(*E*), 159.36 (CHO)(*Z*), 67.76 (OCH_2)(*E*), 72.30 (OCH_2)(*Z*), 31.94 (CH_2)(*E*), 32.65 (CH_2)(*Z*), 20.05 (CH_2)(*E*), 19.80 (CH_2) (*Z*), 14.44 (CH_3)(*E*), 14.34 (CH_3)(*Z*); MS [m/*Z* (rel int)] 172 (M, 4)(*E*), 172 (M, 6)(*Z*), 157 (21)(*E*), 157 (16)(*Z*), 131 (100)(*E*), 131 (100)(*E*), 89 (11)(*E*), 89 (10)(*Z*), 75 (72)(*E*), 75 (57)(*Z*), 73 (15)(*E*), 73 (10)(*Z*). Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70. Found: C, 62.26; H, 11.80.

(*Z*,*E*)-1-Trimethylsilyl-2-*tert*-butoxyethene. $RuH(CO)Cl(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl *tert*-butyl ether (1.75 g, 17.5 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-*tert*-butoxyethene (bp 152−157 °C, 0.36 g, 61%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.15 (s, 9H) ($SiMe_3$)(*E*), 0.31 (s, 9H) ($SiMe_3$)(*Z*), 5.02 (d, 1H) (J = 14.7 Hz) (CHSi)(*E*), 4.38 (d, 1H) (J = 14.7 Hz) (CHSi)(*Z*), 6.56 (d, 1H) (CHO) (J = 14.7 Hz)(*E*), 6.72 (d, 1H) (CHO) (J = 14.7 Hz)(*Z*), 1.10 (s, 9H) (CH_3)(*E*), 1.04 (s, 9H) (CH_3)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.26 ($SiMe_3$)(*E*), 0.72 ($SiMe_3$)(*Z*), 100.12 (CHSi)(*E*), 100.24 (CHSi)(*Z*), 151.37 (CHO)(*E*), 153.36 (CHO)(*Z*), 76.14 (C)(*E*), 75.96 (C)(*Z*), 28.62 (CH_3)(*E*), 28.41 (CH_3)(*Z*); MS [*m*/*z* (rel int)] 172 (M, 10)(*E*), 172 (M, 6)(*Z*), 157(16)(*E*), 157(17)(*Z*), 129 (50)(*E*), 129 (38)(*Z*), 127 (48)(*E*), 127 (30)(*E*), 117 (100)(*E*), 117 (100)(*Z*), 101 (33)(*E*), 101 (28)(*Z*), 57 (54)(*E*), 57 (45)(*Z*).

(*Z*,*E*)-1-Trimethylsilyl-2-*tert*-pentoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl *tert*-pentyl ether (1.17 g, 10.3 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-*tert*-pentoxyethene (bp 70−75 °C/15 mmHg, 0.41 g, 64%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.15 (s, 9H) ($SiMe_3$)(*E*), 0.31 (s, 9H) ($SiMe_3$)(*Z*), 5.03 (d, 1H) (J = 14.4 Hz) (CHSi)(*E*), 4.37 (d, 1H) (J = 14.4 Hz) (CHSi)(Z), 6.55 (d, 1H) (CHO) (J = 14.4 Hz)(*E*), 6.70 (d, 1H) (CHO) (J = 14.4 Hz)(*Z*), 1.42 (q, 2H) (CH_2)(*E*), 1.34 (q, 2H) (CH_2)(*Z*), 1.07 (s, 3H) (CCH_3)(*E*), 1.34 (s, 3H) (CCH_3)(*Z*), 0.82 (t, 3H) (CH_3)(*E*), 0.80 (t, 3H) (CH_3)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.30 ($SiMe_3$)(*E*), 0.72 ($SiMe_3$)(*Z*), 100.09 (CHSi)(*E*), 100.74 (CHSi)(*Z*), 151.27 (CHO)(*E*), 153.25 (CHO)(*Z*), 78.34 (C)(*E*), 78.19 (C)(*Z*), 34.56 (CH_2)(*E*), 34.42 (CH_2)(*Z*), 26.16 (CCH_3)(*E*), 25.98 (CCH_3)(*Z*), 8.79 (CH_3)(*E*), 8.79 (CH_3)(*Z*); MS [*m*/*z* (rel int)] 186 (M, 13)(*E*), 186 (M, 7)(*Z*), 171 (20)(*E*), 171 (23)(*Z*), 127 (23)(*E*), 127 (20)(*Z*), 117 (100)(*E*), 117 (100)(*Z*), 101 (30)(*E*), 101 (27)(*Z*), 73 (18)(*E*), 73 (11)(*Z*).

(*Z*,*E*)-1-Trimethylsilyl-2-(2-ethyl)hexoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl 2-(ethyl)hexyl ether (1.63 g, 10.4 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-(2-ethyl)hexoxyethene (bp 95−102 °C/1 mmHg, 0.57 g, 72%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.12 (s, 9H) ($SiMe_3$)(*E*), 0.28 (s, 9H) ($SiMe_3$)(*Z*), 4.56 (d, 1H) (J = 15.0 Hz) (CHSi)(*E*), 4.27 (d, 1H) (J = 15.0 Hz) (CHSi)(*Z*), 6.56 (d, 1H) (CHO) (J = 15.0 Hz)(*E*), 6.44 (d, 1H) (CHO) (J = 15.0 Hz)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.27 ($SiMe_3$)(*E*), 0.66 ($SiMe_3$)(*Z*), 95.25 (CHSi)(*E*), 100.03 (CHSi)(*Z*), 157.24 (CHO)(*E*), 159.61 (CHO)(*Z*); MS [*m*/*z* (rel int)] 228 (M, 8)(*E*), 228 (M, 4)(*Z*), 213 (56)(*E*), 213 (31)(*Z*), 127 (100)(*E*), 127 (100)(*E*), 101 (21)(*E*), 101 (21)(*Z*), 73 (17)(*E*), 73 (13)(*Z*).

(*Z*,*E*)-1-Trimethylsilyl-2-cyclohexoxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene 0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyl cyclohexyl ether (1.3 g, 10.3 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-cyclohexoxyethene (bp 105−111 °C/15 mmHg, 0.51 g, 74%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 0.13 (s, 9H) ($SiMe_3$)(*E*), 0.32 (s, 9H) ($SiMe_3$)(*Z*), 4.80 (d, 1H) (J = 15.0 Hz) (CHSi)(*E*), 4.32 (d, 1H) (J = 15.0 Hz) (CHSi)(*Z*), 6.40 (d, 1H) (CHO) (J = 15.0 Hz)(*E*), 6.47 (d, 1H) (CHO) (J = 15.0 Hz)(*Z*); ^{13}C NMR (C_6D_6) (δ, ppm) 0.28 ($SiMe_3$)(*E*), 0.72 ($SiMe_3$)(*Z*), 97.13 (CHSi)(*E*), 100.14 (CHSi)(*Z*), 155.86 (CHO)(*E*), 157.96 (CHO)(*Z*); MS [*m*/*z* (rel int)] 198 (M, 4)(*E*), 198 (M, 2)(*Z*), 183 (12)(*E*), 183 (11)(*Z*), 157 (17)(*E*), 157 (12)(*Z*), 117 (21)(*E*), 117 (17)(*Z*), 101 (49)(*E*), 101 (50)(*Z*), 75 (100)(*E*), 75 (100)(*Z*), 73 (24)(*E*), 73 (20)(*Z*), 55 (61)(*E*), 55 (49)(*Z*).

(*Z*,*E*)-1-Trimethylsilyl-2-trimethylsiloxyethene. $RuHCl(CO)(PPh_3)_3$ (33 mg, 0.035 mmol), benzene (0.5 mL), vinyltrimethylsilane (0.35 g, 3.45 mmol), and vinyloxytrimethylsilane (1.2 g, 10.3 mmol) were placed in a 20 mL glass ampule. The ampule was sealed and heated at 80 °C for 24 h. The reaction mixture was distilled to yield (*Z*,*E*)-1-trimethylsilyl-2-trimethylsiloxyethene (bp 137−142 °C, 0.54 g, 82%). Selected analytical data: ^{1}H NMR (C_6D_6) (δ, ppm) 5.05 (d, 1H) (CHSi) (J = 14.1 Hz)(*E*), 4.53 (d, 1H) (CHSi) (J = 14.1 Hz)(*Z*), 6.76 (d, 1H) (CHO) (J = 14.1 Hz)(*E*), 6.55 (d, 1H) (CHO) (J = 14.1 Hz)(*Z*); MS [m/z (rel int)] 188 (M, 4)(*E*), 188 (M, 5)(*Z*), 173 (11)(*E*), 173 (10)(*Z*), 148 (16)(*E*), 148 (16)(*Z*), 147 (100)(*E*), 147 (100)(*Z*), 73 (14)(*E*), 73 (12)(*Z*).

HDC═CDSiMe$_3$. Decane (20 mL), trimethylsilylacetylene (0.69 g), quinoline (15 drops), and Lindlar catalyst (0.04 g) were introduced into a standard hydrogenation reactor. Reaction with gaseous deuterium was carried out under atmospheric pressure at room temperature. After 90 min (in few cases shorter reaction time was observed), the theoretical value of deuterium (158 mL) was consumed. Although the consumption did not cease, the reaction was stopped. The catalyst was filtered. The product was isolated by distillation. The fraction boiling in the range 53−54 °C was collected. A total of 0.68 g of the product (mixture of isomers *E*/*Z* = 5:1) was obtained (yield 91%).

(*E*)-HDC═CDSiMe$_3$: ^{1}H NMR (C_6D_6) (δ, ppm) 5.63(t) (CHD) ($^3J_{HD}$ = 3.0 Hz); ^{2}H NMR (C_6H_6) (δ, ppm) 6.17 (d) (CDH) ($^3J_{DH}$ = 3.0 Hz), 5.91(s) (CDSi).

Catalytic Examinations. In a typical catalytic test, a benzene solution of the ruthenium catalyst was placed in a glass ampule in the air or under argon. Then the reagents (usually used in the ratio [H_2C═$CHSiR_3$]:[ether]:[Ru]=1:5:0.01) and toluene as internal standard were added. The sealed ampule was heated at the specified conditions. The composition of the reaction mixture was analyzed by GC. The yield was calculated by GC using the internal standard method.

Labeling Experiments. Reaction of HDC═CDSiMe$_3$ with H$_2$C═CHOEt Catalyzed by RuCl(SiMe$_3$)(CO)(PPh$_3$)$_2$ (II) and RuCl$_2$(PPh$_3$)$_3$ (III) Catalysts. RuCl($SiMe_3$)(CO)(PPh_3)$_2$ (0.001 g, 1.3110^{-6} mol) or $RuCl_2(PPh_3)_3$ (0.002 g, 2.08×10^{-6} mol), benzene (0.3 mL), HDC═CDSiMe$_3$ (0.013 g, 1.31×10^{-4} mol), and H_2C═CHOEt (0.047 g, 6.56×10^{-4} mol) were introduced into a 2 mL glass ampule. The ampule was heated at 100 °C for 24 h. The reaction mixture was analyzed by GC−MS. Two isomers (*E*+*Z*) of (EtO)HC═CHSiMe$_3$ were identified. The mass spectrum did not show the presence of deuterium-containing 1-trimethylsilyl-2-ethoxyethenes.

Stoichiometric Reactions. RuCl($SiMe_3$)(CO)(PPh_3)$_2$ (0.036 g, 4.72×10^{-5} mol) was placed in an NMR ampule containing 0.7 mL of benzene-d_6 in air, then vinyl *n*-propyl ether (16 μL, 1.9×10^{-4} mol) was added and the sealed glass ampule was heated at 80 °C for 24 h. The analyses of the reaction mixture by ^{1}H NMR spectroscopy and GC−MS indicated the selective formation of 1-trimethylsilyl-2-propoxyethenes (mixture of *E* and *Z* isomers). The number of conversions and yields were calculated on the basis of GC analyses using the internal standard method (conversion 60%, yield 60%, *E*/*Z* = 4).

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