Selective Cleavage of C–O and/or Si–O Bonds in Trimethylsilyl Ethers Promoted by Cobalt(I), Rhodium(I), and Ruthenium(II) Hydride Complexes

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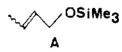
$CoH(N_2)(PPh_3)_3$ selectively promotes C–O bond cleavage in allylic and vinylic trimethylsilyl ethers to give $Co(OSiMe_3)(PPh_3)_3$, releasing the corresponding olefins at room temperature. On the other hand, $RhH(PPh_3)_4$ is active mainly for the Si–O bond cleavage at 80 °C, while $RuH_2(PPh_3)_4$ promotes both C–O and Si–O bond cleavage reactions of alkenyl trimethylsilyl ethers at 80 °C. Addition of triphenylphosphine selectively inhibits the C–O bond cleavage. The mechanism of C–O bond cleavage is envisioned in terms of insertion of the olefinic double bond into the M–H bond followed by β-elimination of the trimethylsiloxy group from the transition-metal complex. The Si–O bond cleavage is compatible with nucleophilic attack of the metal hydrides on the silyl ethers.

Cleavage of carbon–halogen bonds in aryl halides and carbon–oxygen bonds in allylic esters and carbonates promoted by transition-metal complexes has been extensively utilized in organic syntheses.[1,9,10,16] Exploration of other cleavage reactions induced by transition-metal complexes is expected to provide new synthetic methods. As an extension of our attempts to cleave C–O bonds in alkenyl and aryl esters by group 8–10 transition-metal complexes,[2] we have examined the reactivity of alkenyl and alkyl trimethylsilyl ethers with cobalt, rhodium, and ruthenium hydride complexes that contain triphenylphosphine ligands. Trimethylsilyl ethers have found extensive application in organic synthesis,[3] but their utility in combination with transition-metal complexes has not been exploited. A recent report on nickel-catalyzed cross-coupling reactions of allyl trimethylsilyl ethers or silyl enol ethers with Grignard reagents represents an ingenious application of C–O bond cleavage in silyl ethers promoted by transition-metal complexes.[4] We now report that cleavage of the trimethylsilyl alkenyl ethers proceeds under mild conditions on treatment with group 8 and 9 transition-metal hydrides. Marked variations in the site of cleavage of the silyl ethers, depending on the metal hydride, have been observed. It has been further demonstrated that the site for the bond cleavage can be altered by addition of a suitable ligand to the system.

Results

The following group 8 and 9 transition-metal hydrides 1–3 and trimethylsilyl ethers A–D have been used for examining reactivities of the metal hydrides and the site of bond cleavage. These hydrides undergo ligand dissociation in solution and readily afford coordinatively unsaturated species.[5] The silyl ethers A–E have been chosen with the object of examining reactivities of allylic and vinylic ethers and of comparing their reactivities with that of a saturated ether.

$CoH(N_2)(PPh_3)_3$ $RhH(PPh_3)_4$ $RuH_2(PPh_3)_4$
1 2 3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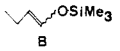
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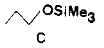
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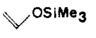
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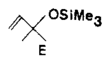
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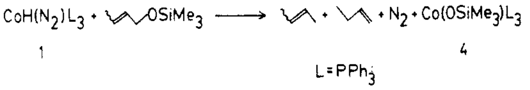
Reactions of Alkenyl Trimethylsilyl Ethers with $CoH(N_2)(PPh_3)_3$ (1). Table I summarizes products of the reactions of various trimethylsilyl ethers with 1. Reactions of the allylic and vinylic trimethylsilyl ethers A and B proceed smoothly at room temperature, liberating mainly nitrogen, 2-butenes, and a minor amount of 1-butene from both ethers. The allylic trimethylsilyl ether A used in the reaction was completely isomerized to B during the reaction. The resulting cobalt complex was characterized as $Co(OSiMe_3)(PPh_3)_3$, 4, on the basis of its elemental analysis and IR spectrum, as well as by chemical reactions. The IR spectrum of 4 shows characteristic band at 990 cm^{-1} due to Si–O stretching vibration.[6] Hydrolysis of 4 with HCl liberated 0.5 equiv of hexamethyldisiloxane/mol of 4.



Similar C–O bond cleavage also was observed in the reaction of 1 with vinyl trimethylsilyl ether D, affording ethylene, nitrogen, and complex 4. On the other hand, the

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(1) Davies, S. G. "Organotransition Metal Chemistry-Application to Organic Synthesis"; Pergamon Press: Oxford, 1982. Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springler Verlag: Berlin, 1975. Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. Scheffold, R. "Modern Synthetic Methods"; Otto Salle Verlag: Frankfurt, 1983; Vol. 3.

(2) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1975**, *87*, 333. Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758. Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Ibid.* **1981**, *103*, 6863. Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808. Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. Kushi, Y.; Kuramoto, M.; Hayashi, Y.; Yamamoto, T.; Yamamoto, A.; Komiya, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1033. Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 977.

(3) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

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(5) Komiya, S.; Yamamoto, A. *J. Mol. Catal.* **1979**, *5*, 279.

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Table I. Reactions of $CoH(N_2)(PPh_3)_3$ with Trimethylsilyl Ethers[a]

run	$CoH(N_2)$-$(PPh_3)_3$, mmol	ether (mmol)[e]	temp, °C	time, h	reaction products, mmol				
					C_3H_6	C_3H_8	1-C_4H_8	2-C_4H_8	others
1	0.434	A (1.12)	rt	24	...	...	0.005	0.208	$Co(OSiMe_3)(PPh_3)_3$ 0.312, N_2 0.44
2	0.310	B (1.68)	rt	24	...	...	0.003	0.196	$Co(OSiMe_3)(PPh_3)_3$,[b] N_2 0.31
3	0.284	C (1.66)	rt	24	...	...	...	...	$CoH(N_2)(PPh_3)_3$
4	0.208[f]	A (0.694)	rt	24	0.002	...	0.006	0.003	
							C_5H_{10}[c]	C_5H_{10}[d]	
5	0.528	E (1.26)	rt	10			0.420	0.090	$Co(OSiMe_3)(PPh_3)_3$ 0.450, N_2 0.52
							C_2H_4	C_2H_6	
6	0.166	D (0.539)	rt	6			0.113	...	$Co(OSiMe_3)(PPh_3)_3$,[b] N_2 0.134

[a] In benzene. [b] Not measured. [c] 2-Methyl-2-butene. [d] 3-Methyl-1-butene. [e] A–E: see text. [f] Plus 4.18 mmol of PPh_3.

Table II. Reactions of $RhH(PPh_3)_4$ with Trimethylsilyl Ether A[a]

run	$RhH(PPh_3)_4$, mmol	ether (mmol)	temp, °C	time, h	reaction products, mmol				
					C_3H_6	C_3H_8	1-C_4H_8	2-C_4H_8	others
7	0.382	A (3.37)	80	48	0.106	0.076	...	0.015	
8	0.300	A (3.37)	100	6	0.098	...	0.029	0.103	$(Me_3Si)_2O$ 0.012
9	0.368[b]	A (3.37)	100	18	0.173	...	...	...	

[a] In benzene. [b] Plus 4.29 mmol of PPh_3.

Table III. Reactions of $RuH_2(PPh_3)_4$ with Trimethylsilyl Ethers[a]

run	RuH_2-$(PPh_3)_4$, mmol	ether (mmol)	temp, °C	time, h	reaction products, mmol				
					C_3H_6	C_3H_8	1-C_4H_8	2-C_4H_8	others
10	0.191	A (1.12)	80	24	0.034	0.065	0.003	0.096	$RuH_2(CO)(PPh_3)_3$ 0.145, $Ru(CO)_3(PPh_3)_2$,[b] $(Me_3Si)_2O$ 0.043
11	0.245	B (1.68)	80	24	0.082	0.099	0.006	0.159	$RuH_2(CO)(PPh_3)_3$ 0.120, $RuH_2(PPh_3)_4$[b]
12	0.243	C (1.66)	80	168	...	0.021	...	...	
13	0.360[f]	A (0.337)	80	72	0.090	0.100	0.020	0.003	$RuH_2(CO)(PPh_3)_3$[b]
14	0.0184	A (0.112)	60	1	0.008	0.003	0.001	0.000	$RuH_2(CO)(PPh_3)_3$[b]
15	0.0184	B (0.112)	60	1	0.001	0.001	...	...	$RuH_2(CO)(PPh_3)_3$[b]
							C_5H_{10}[c]	C_5H_{10}[d]	
16	0.333	E (0.379)	80	24			0.026	0.036	no carbonyl complex
						CH_4	C_2H_4	C_2H_6	
17	0.064	D (0.360)	80	3		0.027	0.036	0.004	$RuH_2(CO)(PPh_3)_3$,[b] $Ru(CO)_3(PPh_3)_2$[b]

[a] In benzene. [b] Not measured. [c] 2-Methyl-2-butene. [d] 3-Methyl-1-butene. [e] A–E: see text. [f] Plus 4.54 mmol of PPh_3.

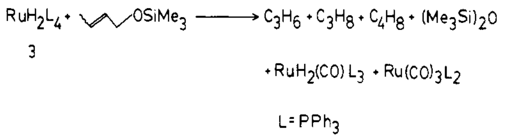
saturated alkyl trimethylsilyl ether C showed no reactivity at all toward 1 at room temperature. Increase in the reaction temperature caused only thermal decomposition of 1.

It was observed that removal of atmospheric nitrogen from the reaction system accelerated the reaction, indicating that the prior liberation of nitrogen from 1 is an important factor for the cleavage reaction to proceed.[7] In the presence of PPh_3, the reaction was strongly hindered and 2-butene formation was severely suppressed.

Reactions of Silyl Ethers with $RhH(PPh_3)_4$ (2). Results of the reactions of 2 with the trimethylsilyl ether A are shown in Table II. In contrast to the high reactivity of 1, which selectively cleaves the C–O bonds in alkenyl ethers at room temperature, the rhodium hydride 2 does not react at all with any trimethylsilyl ether at room temperature. However, reaction with A took place at 80 °C to liberate propylene and propane as major gaseous products (run 7). The formation of C_3 gases may be taken as an indication of the Si–O bond cleavage of trimethylsilyl ethers (vide infra). When the reaction temperature was further raised to 100 °C, formation of butenes together with the C_3 gases also was observed, indicating the occurrence of C–O bond cleavage as in the case of reactions with the cobalt hydride 1. Formation of hexamethyldisiloxane also was observed. The resulting complexes appear to be a mixture of $RhH(CO)(PPh_3)_n$ and other carbonyl complexes of rhodium as judged on the basis of the IR spectra of the recovered solid (see Experimental Section).

Addition of free PPh_3 to the reaction system severely suppressed the formation of butenes, but the evolution of propylene still was observed under these conditions.

Reactions of Trimethylsilyl Ethers with $RuH_2(PPh_3)_4$ (3). Reaction products of $RuH_2(PPh_3)_4$, 3, with the trimethylsilyl ethers under various conditions are summarized in Table III. The reaction of 3 with the allylic trimethylsilyl ether A proceeds smoothly at 80 °C to liberate propylene, propane, 1-butene, 2-butenes, and hexamethyldisiloxane (run 10 in Table III). The resulting



ruthenium complexes were a mixture of $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$, as confirmed by IR and ^1H NMR spectroscopy. The allylic trimethylsilyl ether A used also was completely isomerized to B during the reaction. Examination of the time course of the reaction (Figure 1) reveals that butenes are liberated only in the initial stage

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[7] Similar effect of dinitrogen on the rate of the reaction of 1 with substituted olefins has been reported: Kubo, Y.; Yamamoto, A. *J. Organomet. Chem.* **1973**, *60*, 165.

[8] Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, *16*, 1415.

[9] Flemming, I. "Comprehensive Organic Chemistry", Part 13; Pergamon Press: Oxford, 1979; p 576.

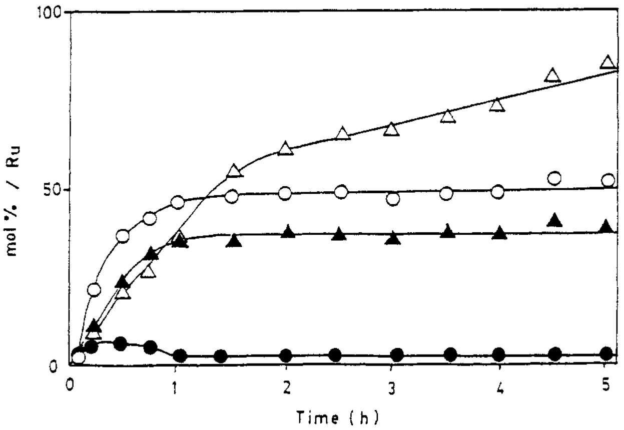


Figure 1. Time courses of the reaction of **3** with A in CH_2Ph_2 at 80 °C: ●, 1-butene; ○, 2-butenes; △, propane; ▲, propylene.

of the reaction, and no further evolution of butenes was observed after 1 h. The ratio of 1-butene to 2-butene evolved decreased with time and a thermodynamic equilibrium mixture of butenes was obtained after 1 h. Propane was liberated continuously even after 1 h, whereas evolution of propylene stopped then. In contrast, the reaction of **3** with *n*-butyl trimethylsilyl ether did not proceed at 80 °C and only a small amount of propane was detected when the reaction was carried out for a prolonged period (run 12). Both reactions of the allylic and butenyl trimethylsilyl ethers A and B afforded C_3 and C_4 hydrocarbons of similar composition (runs 10 and 11). Complete isomerization of the allylic trimethylsilyl ether A to B took place during the reaction. However, the reaction of **3** with 3-methyl-3-(trimethylsiloxy)-1-butene, E, which carries two methyl groups at the allylic position and is incapable of isomerizing to a vinylic ether, liberates 2-methyl-2-butene and 3-methyl-1-butene (run 16). On the other hand, the C–O bond in the simple vinyl trimethylsilyl ether also was smoothly cleaved by **3** to give ethylene accompanied by the evolution of ethane and methane (run 17).

Discussion

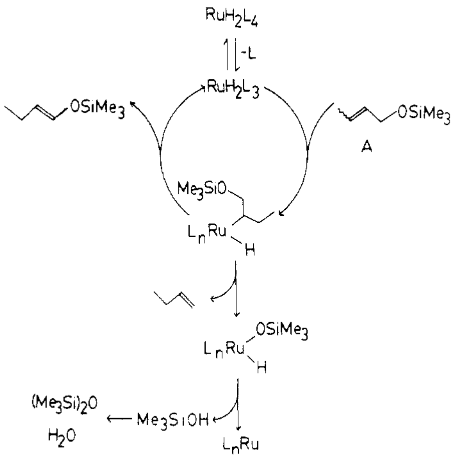
In the reactions of the trimethylsilyl butenyl ethers with group 8 and 9 transition-metal hydrides, both C–O and Si–O bonds in silyl ethers are cleaved. Thus, the formation of C_4 olefins such as butenes indicates that the C–O bonds in A and B are cleaved on interaction with hydrides, whereas the formation of C_3 hydrocarbon can be taken as an indication of the Si–O bond cleavage followed by decarbonylation as will be discussed later.

Interestingly, the cobalt hydride complex **1** primarily cleaves the C–O bond at room temperature, whereas the rhodium hydride complex **2** mainly cleaves the Si–O bond at 80 °C, although at 100 °C C–O bond cleavage by **2** also occurs. The ruthenium hydride complex **3** cleaves both C–O and Si–O bonds in the alkenyl trimethylsilyl ethers, but this C–O bond cleavage is hindered by addition of PPh_3.

C–O Bond Cleavage. For the allylic and vinylic O bond cleavage to occur, two possiblilities are conceivable. One is a process involving a direct oxidative addition reaction, and the other is a mechanism involving the participation of the hydride ligand in causing the C–O bond fission.

Treatment of 2-butenyl and 1-butenyl ethers A and B, respectively, with **3** produced equilibrated mixtures of butenes after 1 day at room temperature. However, the time course of the reaction of the 2-butenyl ether A with **3** (Figure 1) and run 14 in Table III (carried out at a lower temperature in order to observe the distribution of gaseous products in the initial period of the reaction) indicate that 1-butene is formed first and subsequently isomerized to 2-butenes. The formation of 1-butene as the primary kinetic product is incompatible with the oxidative addition mechanism involving the allylic O bond cleavage of the 2-butenyl trimethylsilyl ether (A) which would produce 2-butene as the primary kinetic product. One could argue that the allylic O bond cleavage of A would produce a π-crotyl complex which is attacked by the hydride ligand in **3** at the C-3 position to give 1-butene. In this mechanism, however, the attack of the hydride ligand at the C-3 position would compete with the attack at the less substituted C-1 position and the predominant formation of 1-butene is not to be expected.[10]

Scheme I



Since the ruthenium hydride complex **3** is known to cause isomerization of allylic trimethylsilyl ethers to vinylic ethers[8] and other transition-metal hydrides also are expected to catalyze the isomerization, a reaction route involving first a double-bond migration in A to give B, followed by vinyl–O bond cleavage via oxidative addition process, also is a possibility in the reactions of A with **1** and **3**. In fact, C–O bond of vinyl trimethylsilyl ether (D) is smoothly cleaved by these hydride complexes **1–3** under the same conditions. The similar product distributions of olefins in the reactions of A and B with **1** and **3** are compatible with possible involvement of the vinyl–O bond cleavage. However, this route is excluded, since the allylic ether E, inert to isomerization, also is readily cleaved by **1** and **3**. Consequently, whether the substrate is an allylic ether or a vinylic ether is not important.

Thus we favor the alternative mechanism as shown in Scheme I.

Scheme I contains a predissociation step of **3** liberating a triphenylphosphine ligand, since the C–O bond cleavage of A is hindered by addition of PPh_3 to the reaction system (run 13). The mechanism involves the insertion of C=C double bond in the alkenyl ether into the Ru-H bond forming an alkylruthenium(II) species followed by elimination of the trimethylsiloxy group at the β-position.[11] The insertion mechanism is compatible with the fact that none of the C–O bond of saturated ethers is cleaved in the reactions. β-Hydrogen elimination from the alkylruthenium intermediate gives the isomerized ether and/or

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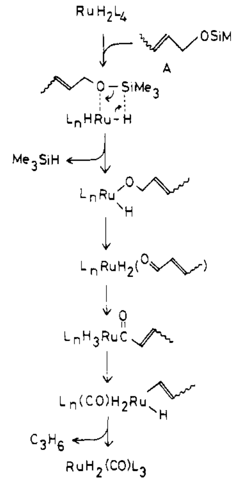
[10] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 673.

[11] Abstraction of alkoxo group by transition metal has been proposed: Maruyama, K.; Ito, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 849. Komiya, S.; Shindo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1672.

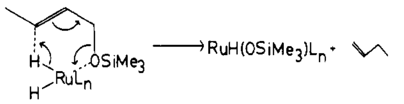
Scheme II. Mechanism of the Si-O Bond Cleavage in A Promoted by the Ruthenium Hydride Complex 3



the starting ether. The trimethylsilanol liberated in the subsequent reductive elimination of the trimethylsiloxy group and the hydride ligand may be converted into hexamethyldisiloxane and water. The ruthenium(0) species formed in the reaction is considered to be still active to interact with the ether as will be discussed later.

The reactions of alkenyl trimethylsilyl ethers with the cobalt hydride complex 1 also are accommodated by a mechanism similar to Scheme I. However, the absence of a hydride ligand in the resulting cobalt complex leads to the isolation of (trimethylsiloxy)cobalt(I) complex 4.

On the other hand, the following S_N2'-type process involving a double bond shift, reminiscent of a sigmatropic reaction such as Claisen and Cope rearrangements, also is compatible with the selective C-O bond cleavage reaction of the allylic trimethylsilyl ethers by the hydride complex.



However, the mechanism is less probable, since both allylic and vinylic C-O bonds are easily cleaved and a facile reversible insertion of alkenyl ether and ester into transition-metal hydride is observed prior to the C-O bond cleavage reaction. Thus the formation of transition-metal alkyls having the trimethylsiloxy group at the β-position is considered to be a key step for the C-O bond cleavage to be promoted by transition-metal hydrides.

Si-O Bond Cleavage. In the reaction of the allylic and vinylic trimethylsilyl ethers A and B with 3 at 80 °C, evolution of propylene and propane and formation of carbonyl complexes $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ also were observed in addition to the reaction products accountable via the C-O bond cleavage. The rhodium hydride 2 also selectively liberates C_3 hydrocarbons on interaction with A at 80 °C. The results can be accounted for by assuming concomitant occurrence of the Si-O bond cleavage of the trimethylsilyl ethers as shown in Scheme II. In the first step, nucleophilic attack of the metal hydride on Si induces Si-O bond cleavage giving trimethylsilane and a (butenyloxy)metal complex. Similar nucleophilic reactions of lithium aluminum hydride,[12] alkyllithiums,[13] and Grignard reagents[14] with trimethylsilyl ethers are known. An alternative path for the formation of the (butenyloxy)metal intermediate involves the oxidative addition of silyl ether, followed by reductive elimination of trimethylsilane. However the latter process is less probable, since an oxidative addition process generally requires coordinative unsaturation in the metal complex prior to the reaction, whereas addition of PPh_3 to systems containing 2 or 3 does not inhibit the Si-O bond cleavage (vide supra).

A hydrido(butenyloxy)ruthenium(II) complex formed by Si-O bond cleavage then undergoes a β-hydrogen elimination reaction to afford 2-butenal and a dihydridoruthenium(II) complex. Since it is known that reactions of aldehydes, RCHO, with 3 result in a decarbonylation reaction yielding RH and $RuH_2(CO)(PPh_3)_3$,[15] it is reasonable to assume the formation of propylene and $RuH_2(CO)(PPh_3)_3$ by the reaction of 2-butenal with dihydridoruthenium(II) complex. Involvement of this route also is supported by decarbonylation of crotonaldehyde by 3 to give propylene and $Ru(CO)_3(PPh_3)_2$. That the β-hydrogen elimination from the C-1 position of the allylic trimethylsilyl ether is a necessary step in inducing the subsequent decarbonylation reaction is supported by the absence of any ruthenium carbonyl complex formed in the reaction of 3 with α,α'-dimethyl-substituted allyl ether E (run 15).

In reactions of ethers A and B with 3, formation of propylene is accompanied by production of propane. The propane formation may be caused by partial hydrogenation of propylene which may be formed as shown in Scheme II.

If a mechanism involving the Si-O bond cleavage as shown in Scheme II is operative, formation of trimethylsilane is expected but attempts to detect it failed. It is probable that the trimethylsilane formed was consumed in the hydrosilylation of alkenyl trimethylsilyl ethers since hydrosilanes are known to be reactive for hydrosilylation of olefins.[12]

In the reaction of vinyl trimethylsilyl ether (D) with 3, formation of some methane was observed in addition to ethylene produced by the C-O bond cleavage of D. This is compatible with concomitant Si-O bond cleavage yielding a (vinyloxy)ruthenium hydride intermediate. Reductive elimination of vinyl alcohol which is transformed to acetaldehyde and its subsequent decarbonylation account for the formation of methane as well as $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)$. It should be pointed out that besides the starting ruthenium dihydride 3 other Ru species formed in the C-O bond cleavage reaction as shown in Scheme I can also cause the Si-O bond cleavage of the alkenyl silyl ethers. In fact, $Ru(C_2H_4)(PPh_3)_3$[18] reacted with the allylic and vinylic trimethylsilyl ethers A and B to yield predominantly $Ru(CO)_3(PPh_3)_2$ with liberation of ethylene, ethane, propylene, and propane. Ortho metalation of the PPh_3 ligand to give a ruthenium(II) hydride complex may be involved in the process. Formation of $Ru(CO)_3(PPh_3)_2$ is accounted for by successive decarbo-

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(12) Brook, A. G.; Pascoe, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 6224. Biernbaum, M. S.; Mosher, H. S. *Ibid.* **1971**, *93*, 6221. Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem.* **1980**, *92*, 974.

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nylation processes with $RuH_2(CO)(PPh_3)_3$ which was in fact shown to afford $Ru(CO)_3(PPh_3)_2$ on treatment with the allylic ether A.

Formation of C_3 hydrocarbons on heating the 2-butenyl trimethylsilyl ether (A) with the rhodium hydride **2** can be also accounted for by a mechanism similar to Scheme II. An interesting feature is the effect of temperature and the addition of triphenylphosphine to the reaction system. The rhodium hydride complex favors Si–O bond cleavage at lower temperature like the ruthenium complex **3** and unlike the cobalt complex **1**. Raising the temperature promotes C–O bond cleavage, probably by favoring the ligand dissociation process, creating coordinative unsaturation. When an excess of triphenylphosphine is added to the system, the C–O bond cleavage route is completely blocked. Interestingly, propane formation also was suppressed. The result is consistent with the requirement of a coordination site in olefin hydrogenation by **2** and **3**.

Comparison of the three hydrides **1–3** in the reactions with the alkenyl trimethylsilyl ethers reveals considerable variation in reactivities of the three group 8 and 9 transition-metal hydrides. The present results suggest the possibility of promoting a particular type of bond cleavage reaction by selecting an appropriate metal hydride. Alteration of the reaction course in the bond cleavage reactions by adding an extra ligand has been further indicated in the present study.

Experimental Section

All manipulations were carried out under a nitrogen or argon atmosphere or in vacuo. Solvents were dried, distilled in the usual manner, and stored under nitrogen before use. Infrared spectra were measured on a Hitachi-295 spectrometer. ^1H NMR spectra were recorded on a JEOL PS-100 or PMX-60 spectrometer. Microanalyses were performed with a Yanagimoto CHN Autocorder Type MT-2. The analyses of the gaseous and liquid products were carried out by using Shimadzu GC-3BT and GC-6A gas chromatographs. GC–MS spectra were recorded on a Hitachi M-80 spectrometer. Magnetic susceptibility was measured by Shimadzu Magnetic Balance Type MB-100.

Complexes $RuH_2(PPh_3)_4$,[18] $RuH_2(CO)(PPh_3)_3$,[19] $Ru(C_2H_4)(PPh_3)_3$,[17] $CoH(N_2)(PPh_3)_3$,[20] and $RhH(PPh_3)_4$[19,20] were prepared by methods reported in the literature. Crotyl trimethylsilyl ether, butyl trimethylsilyl ether, and 3-methyl-3-(trimethylsiloxy)butene were prepared by reactions of the corresponding alcohols with trimethylsilyl chloride.[22] Vinylic trimethylsilyl ethers B and D were synthesized by the literature methods.[8,23]

Reaction of Various Trimethylsilyl Ethers with Ru, Co, and Rh Hydride Complexes. Typical experimental procedures are described below. Details of reaction conditions and results are summarized in Table I–III. Allylic trimethylsilyl ether A used was completely isomerized into B after the reactions with 1, 2, and 3.

Reaction of 1 with Allylic Trimethylsilyl Ether A. To a Schlenk type flask containing 1 (0.434 mmol) and benzene (2.5 mL) was added allylic trimethylsilyl ether A (1.12 mmol) by trap to trap distillation. After the mixture was stirred for 1 day at room temperature, N_2 (0.44 mmol), 1-butene (0,005 mmol), 2-butenes (0.208 mmol), and traces of propylene and propane were generated. After volatile substances were removed, a yellow solid, $Co(OSiMe_3)(PPh_3)_3$, **4**, was recrystallized from toluene: IR ν(C–O) 1240, ν(Si–O) 990 cm^{-1}, (diamagnetic). Anal. Found (Calcd for $C_{57}H_{54}OP_3SiCo$): C, 73.75 (73.22); H, 5.59 (5.82); Co, 6.17 (6.30). Molecular weight by the cryoscopic method in benzene increases on increasing the concentration of complex, indicating extensive dissociation of ligand in dilute solutions: m/e 501 (1.224×10^{-2} g/g benzene), 597 (3.070×10^{-2}), 823 (4.987×10^{-2}); calcd for $Co(OSiMe_3)(PPh_3)_3$ 934.

Acidolysis of 4 (0.0929 mmol) with an excess of dry HCl in benzene (1.0 mL) liberated hexamethyldisiloxane (0.0427 mmol) after hydrolysis.

Reaction of 2 with Allylic Trimethylsilyl Ether A. A mixture of 2 (0.383 mmol) and A (0.60 mL) in benzene (5.0 mL) was degassed. After the mixture was stirred at 80 °C for 4 h, propylene (0.106 mmol), propane (0.076 mmol), and 2-butene (0.015 mmol) were detected. Evaporation of volatile components in vacuo afforded a yellowish solid whose IR spectrum shows ν(C≡O) bands at 1800 (m), 1965 (s), and 2000 (sh) cm^{-1} due to a mixture of $RhH(CO)(PPh_3)_3$ and other rhodium carbonyl complexes.[24]

Reaction of 3 with Allylic Trimethylsilyl Ether A. Allylic trimethylsilyl ether A (1.12 mmol) was added to a Schlenk tube containing 3 (0.191 mmol) in benzene (2.5 mL). The reaction mixture was stirred at 80 °C under vacuum. After 1 day, propylene (0.034 mmol), propane (0.065 mmol), 1-butene (0.003 mmol), and *cis*- and *trans*-2-butenes (0.096 mmol) were detected by GLC. Examination of the liquid phase by GLC and GC–MS revealed the formation of hexamethyldisiloxane (0.043 mmol) after separation of the volatile materials by trap-to-trap distillation, a white solid was obtained. The IR and ^1H NMR of the recrystallized product were identical with those of $RuH_2(CO)(PPh_3)_3$:[19] IR ν(C≡O) 1940 cm^{-1}; ^1H NMR ($CDCl_3$) −6.67 (J(P–H) = 28, 16 Hz, J(H–H) = 6 Hz), −8.67 (J(P–H) = 74, 28 Hz, J(H–H) = 6 Hz) ppm for hydride ligands trans and cis to the CO ligand. The IR spectrum of the crude product showed ν(C≡O) bands at 1900 cm^{-1} in addition to a band at 1940 cm^{-1}. When recovered $RuH_2(CO)(PPh_3)_3$ was further heated with allylic trimethylsilyl ether A at 80 °C for 1 day, a yellow solid was obtained on evaporating the volatile materials. The IR spectrum of the solid was identical with that of an authentic sample of $Ru(CO)_3(PPh_3)_2$ (ν(C≡O) 1900 cm^{-1}).[15]

Reaction of 1 with Crotonaldehyde. The reaction of 1 (0.282 mmol) with crotonaldehyde (12.17 mmol) at room temperature for 5 h afforded propylene (0.044 mmol), crotyl alcohol (0.20 mmol), butyraldehyde 0.18 mmol), traces of butenes, and $Ru(CO)_3(PPh_3)_2$.

Reaction of $Ru(C_2H_4)(PPh_3)_3$ with Allylic Trimethylsilyl Ether A. The reaction was performed analogously to that of 1. Treatment of $Ru(C_2H_4)(PPh_3)_3$ (0.562 mmol) with allylic trimethylsilyl ether A (2.78 mmol) in benzene (5.0 mL) at room temperature for 2 days gave ethylene (0.323 mmol), ethane (0.010 mmol), propylene (0.128 mmol), propane (0.065 mmol), and $Ru(CO)_3(PPh_3)_2$.

Reaction of PPh_3 with Allylic Trimethylsilyl Ether A. No reaction of PPh_3 (0.448 mmol) with A (0.337 mmol) in toluene (5.0 cm^3) was observed 80 °C after 1 day.

Registry No. 1, 16920-54-0; 2, 18284-36-1; 3, 19529-00-1; 4, 97073-73-9; A, 18269-32-4; B, 6651-33-8; C, 1825-63-4; D, 6213-94-1; E, 19916-99-5; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; 1-C_4H_8, 106-98-9; 2-C_4H_8, 107-01-7; C_3H_6, 115-07-1; C_2H_4, 74-85-1; C_2H_6, 74-84-0; C_3H_8, 74-98-6; $(Me_3Si)_2O$, 107-46-0; CH_4, 74-82-8; 2-methyl-2-butene, 513-35-9; 3-methyl-1-butene, 563-45-1; crotonaldehyde, 4170-30-3; crotyl alcohol, 6117-91-5; butyraldehyde, 123-72-8.

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