Stoichiometric and Catalytic Activation of Si−H Bonds by a Triruthenium Carbonyl Cluster, (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$: Isolation of the Oxidative Adducts, Catalytic Hydrosilylation of Aldehydes, Ketones, and Acetals, and Catalytic Polymerization of Cyclic Ethers

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Treatment of the ruthenium cluster (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**) with stoichiometric amounts of trialkylsilanes results in liberation of a CO ligand followed by oxidative addition of a Si−H bond. The trinuclear silyl complexes (μ_3,η^2:η^3:η^5-acenaphthylene)-$Ru_3(H)(SiR_3)(CO)_6$ (**2**) were isolated in good yield. They were characterized by NMR spectroscopy and X-ray crystallography. Compound **1** catalyzes the hydrosilylation of olefins, acetylenes, ketones, and aldehydes. In particular, the reactions of aldehydes and ketones proceed at room temperature to form the corresponding silyl ethers in good yield; the catalytic activities are superior to those with $RhCl(PPh_3)_3$. The $RhCl(PPh_3)_3$-catalyzed hydrosilylation of ketones with $Me_2(H)SiCH_2CH_2Si(H)Me_2$ results in selective reaction of only one Si−H terminus, while similar reactions, when catalyzed by **1**, allow utilization of both Si−H groups. Significantly different regio- and stereoselectivities, compared with those obtained in reactions catalyzed by $RhCl(PPh_3)_3$, also were observed in the hydrosilylation of α,β-unsaturated carbonyl compounds and 4-*tert*-butylcyclohexanone, respectively. The reactions with acetals and cyclic ethers also take place under similar conditions. The reaction of trialkylsilanes with an excess of a cyclic ether resulted in ring-opening polymerization. Polymerization of THF was investigated as a representative example. Treatment of trialkylsilanes with an excess of THF ($10-10^2$ equiv with respect to silanes) in the presence of a catalytic amount of **1** resulted in production of polytetrahydrofuran with $M_n = 1000-200\,000$ and $M_w/M_n = 1.3-2.0$. Changing the ratio of THF to $HSiR_3$ can control the molecular weight. NMR studies suggested that the structure of the polymer is $R_3SiO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$. Mechanistic considerations based on differences in the catalytic activities between the catalysts **1** and **2** are discussed.

Introduction

Hydrosilylation of unsaturated molecules is catalyzed by a wide range of transition-metal salts and complexes.[1] Oxidative addition of H−Si bonds of hydrosilanes to transition-metal species is believed to be an important elementary reaction in the catalytic hydrosilylation of unsaturated organic molecules; this has stimulated numerous studies on the preparation and reactions of transition-metal complexes bearing metal−silicon bonds.[2] Catalysis by di- or polynuclear metal carbonyl complexes of hydrosilylation reactions has recently received attention from organometallic chemists.[3−6] In particular, use of $Co_2(CO)_8$,[4] $Rh_4(CO)_{12}$,[4d] and Co−Rh heteronuclear carbonyl clusters[4d] provides novel aspects for the hydrosilylation of alkenes, alkynes, or ketones. Some of these processes are related to

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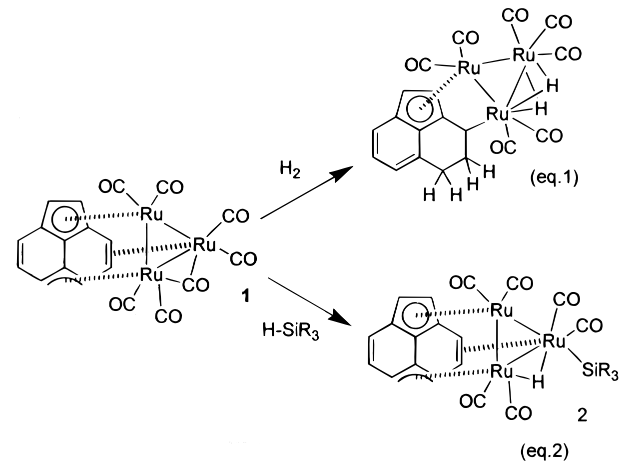
silylformylation of these substrates,[5] and they offer interesting mechanistic insights on the role of cluster species in the catalytic cycles. In some cases, oxidative addition of H−Si bonds to cluster species has been studied in relation to the mechanism;[4a−c,5b,e,f] however, further investigation is required in order to understand the role of cluster species in the catalytic cycle.

Only a few papers have reported hydrosilylations catalyzed by ruthenium carbonyl cluster complexes, compared with the numerous publications on reactions catalyzed by cobalt and rhodium clusters.[7−10] Reactions of organosilanes with olefins catalyzed by $Ru_3(CO)_{12}$ resulted in hydrosilylation and dehydrogenative silylation, providing a mixture of saturated and unsaturated organosilanes.[7] The $Ru_3(CO)_{12}$-catalyzed hydrosilylation of acetophenone by $HSi(OEt)_3$ was briefly mentioned.[7e] Studies on the oxidative addition of H−Si bonds to $Ru_3(CO)_{12}$ were undertaken by several groups,[8] who found that the reaction often was accompanied by fragmentation of the cluster framework, particularly with trialkylsilanes.[8b−d] The cluster fragmentation at the oxidative addition step can be suppressed by introduction of bridging ligands to reinforce the cluster framework. An anionic cluster bearing a bridging hydride ligand, $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$, catalyzed the hydrosilylation and dehydrogenative silylation of olefins.[9] Oxidative addition of two trialkylsilanes to this cluster reportedly proceeded without cluster fragmentation, which may be involved in the catalytic cycle as an intermediate step.[9a,c] A face-capping pyridine ligand (ampy = 2-amino-6-methylpyridine) also was used as the bridging ligand; successful oxidative addition of $H-SiEt_3$ to $Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9$ was reported, but there was no catalytic reaction using $Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9$.[10] Since the catalytic reactions using the above ruthenium clusters generally required temperatures higher than 80 °C, they are less active than the rhodium or cobalt clusters. Although these ruthenium catalysts are interesting in view of their high reactivity for dehydrogenative silylation in the reactions of silicon hydrides with olefins, further studies are required to identify other characteristic features, e.g., regio- or stereoselectivities of the reactions, as a function of the hydrosilylation catalysts used.

Scheme 1



We have been interested in the possibility that conjugated π-ligands such as polyaromatic hydrocarbons may act as an unique face-capping ligand in ruthenium clusters designed to reinforce the cluster framework.[11] Since it is known that facile hapticity changes of certain conjugated π-ligands open a coordination site and facilitate organometallic reactions in many transition-metal complexes,[12] multimetallic complexes bearing conjugated π-ligands may also have the potential to produce reactive organometallic species through a hapticity change of the π-ligand on the cluster. In the course of our studies on the activation of molecular hydrogen by di-, tri-, and tetranuclear ruthenium carbonyl complexes bearing polyaromatic or polyene ligands, we discovered the particularly high reactivity of $(\mu_3,\eta^2:\eta^3:\eta^5\text{-acenaphthylene})Ru_3(CO)_7$ (**1**) or triruthenium clusters bearing azulenes as the face-capping ligand with H_2 as shown in Scheme 1 (eq 1).[11] Since it is known that activation of H_2 by organometallic complexes resembles that of $H-SiR_3$, the facile activation of H_2 by **1** prompted us to examine whether the activation of $H-SiR_3$ might easily be realized by **1**.

In this paper, we summarize our studies on stoichiometric and catalytic activation of $H-SiR_3$ by the triruthenium carbonyl cluster **1**. Oxidative addition of $H-SiR_3$ to **1** took place without cluster fragmentation, as shown in Scheme 1 (eq 2). To our knowledge, this is the first example of a triruthenium−silyl complex in which conjugated π-ligands act as a μ_3 ligand. Success of the oxidative addition implies that **1** may be an active catalyst for hydrosilylation reactions. Indeed, we found that **1** was an efficient catalyst for hydrosilylation of

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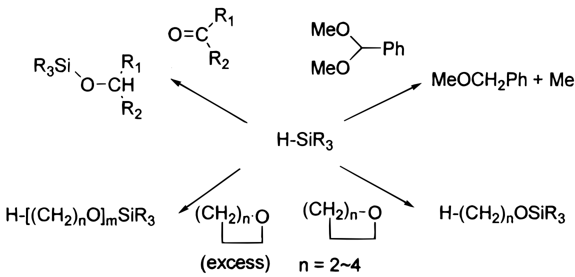
Scheme 2



unsaturated molecules, especially of ketones and aldehydes, for which catalytic activity was superior to that of $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$. Furthermore, the regio- and stereoselectivities were different from those of the well-investigated $RhCl(PPh_3)_3$. Interestingly, **1** also catalyzed the reduction of an acetal and of cyclic ethers by hydrosilanes. The products of the hydrosilylation of cyclic ethers were dependent on the charged ratio of the cyclic ether to the hydrosilane; use of an excess of the ether resulted in its successful ring-opening polymerization. The variety of reactions summarized in Scheme 2 is a characteristic feature of the catalytic activation of hydrosilanes by **1**, which has not been observed in other ruthenium-catalyzed hydrosilylation reactions. Success of the hydrosilylation of these substrates catalyzed by **1** stimulates a profound interest in the catalytic species; this topic is discussed later in the paper.

Results and Discussion

Oxidative Addition of H−Si Bonds to 1. As reported earlier, **1** reacts with molecular hydrogen at room temperature to form $(\mu_2,\eta^1:\eta^5\text{-4,5-dihydroacenaphthylene})Ru_3H_2(CO)_7$.[11a] Two hydrogen atoms contribute to the formation of ruthenium hydrides, whereas the other two hydrogen atoms hydrogenate a carbon−carbon double bond of the coordinated acenaphthylene ligand. A stable oxidative adduct was not obtained when **1** was treated with hydrosilanes at room temperature. However, heating a benzene solution of **1** in the presence of $H{-}SiR_3$ resulted in dissociation of a CO ligand followed by oxidative addition of the H−Si bond to a ruthenium atom, as shown in eq 2 of Scheme 1. For example, a mixture of **1** with 20 molar equiv of $HSiMe_2Ph$ was heated in benzene for 3 h to give **2a** in 61% yield. Similarly, reactions of **1** with Et_3SiH and $(PhCH_2)Me_2SiH$ afforded the corresponding oxidative adducts **2b** and **2c** in 73 and 60% yields, respectively. Attempted reaction of **1** with Ph_2SiH_2 gave a mixture of products.

The ^1H NMR spectrum of **2a** revealed that this product contains the acenaphthylene ligand. A singlet at δ −15.21 ppm is assignable to a hydride bonded to two ruthenium atoms, because this Ru−H signal appears at higher field than that observed in mononuclear metal hydride complexes such as *cis*,*mer*-$(OC)_3(Ph_3P)(H)Ru(SiPh_3)$ (δ −6.24), $(OC)_4(H)Ru(SiCl_3)$ (δ −7.35), and $(OC)_2(H)_2Ru(SiMe_2CH_2CH_2PPh_2)$ (δ −6.29) and is similar to signals due to $(OC)_9(\mu\text{-}H)_3Ru_3(SiCl_3)$ (δ −15.52), $(OC)_{10}(\mu\text{-}H)_2Ru_3(SiMe_2C_5H_4FeC_5H_4SiMe_2)$ (δ −14.78 and −17.04), and $(OC)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})Ru_3\{Si(OMe)_3\}$ (δ −11.41).[2a] Comparison of the integrated intensities of signals due to the $PhMe_2Si$ moiety and the acenaphthylene ligand showed that the molecule contained one silyl group and one acenaphthylene ligand. Signals derived from the methyl groups of the $PhMe_2Si$ moiety appeared as two singlets around 0.6 ppm (Me), suggesting that these two methyl groups are magnetically inequivalent. The CO regions of the ^{13}C NMR spectrum showed six peaks in the typical terminal CO region (δ 190−210 ppm). The ^{29}Si resonance appeared as a singlet at δ 29.46 ppm. Absorptions assigned to terminal CO ligands were observed at 1920−2040 cm^{-1} in the IR spectrum. Similar spectral data were also available for **2b**,**c**, and details are summarized in the Experimental Section.

Table 1. Crystallographic Data for 2c

formula	$C_{27}H_{22}O_6SiRu_3$
fw	773.7
habit	red plate
cryst dimens (mm)	0.15 × 0.20 × 0.30
space group	$P2_1/n$
Z	4
a (Å)	10.865(2)
b (Å)	17.050(4)
c (Å)	14.384(3)
β (deg)	101.36(2)
V (Å^3)	2612.4(9)
D_{calcd} (g/cm^{-1})	1.967
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
transmissn factors[a]	0.97−1.03
μ_{calcd} (cm^{-1})	18.00
scan type	$\omega-2\theta$
scan rate (deg/min)	32
2θ range (deg)	$3.0 < 2\theta < 55.0$
no. of data collected	6557
no. of unique data	6241
no. of used data	5146 ($F_o > 3\sigma(F_o)$)
no. of valuables	422
R	0.029
R_w	0.028 ($w = [\sigma^2(F_o)]^{-1}$)
GOF	2.45
$(\Delta/\sigma)_{max}$	0.64
$\Delta\rho_{max}$ (e Å^{-3})	0.64

[a] Scan method; normalized to an average unity.

Table 2. Representative Bond Distances (Å) and Angles (deg) for 2c

Distances			
Ru(1)−Ru(2)	2.9662(6)	Ru(3)−C(5)	2.287(4)
Ru(1)−Ru(3)	2.9009(8)	Ru(3)−C(6)	2.409(4)
Ru(2)−Ru(3)	2.8742(6)	Ru(1)−C(9)	2.270(4)
Ru(2)−Si(1)	2.429(1)	Ru(1)−C(10)	2.226(4)
Ru(1)−C(1)	2.256(4)	Ru(1)−C(11)	2.222(4)
Ru(1)−C(2)	2.241(4)	Ru(3)−C(12)	2.214(3)
Ru(2)−C(3)	2.392(4)	Ru(2)−H(22)	1.75(3)
Ru(2)−C(4)	2.404(4)	Ru(3)−H(22)	1.67(3)

Angles			
Ru(2)−Ru(1)−Ru(3)	58.65(1)	Ru(1)−Ru(2)−Ru(3)	59.54(1)
Ru(2)−Ru(3)−Ru(3)	61.81(2)	Ru(1)−Ru(2)−Si(1)	164.68(3)
Ru(3)−Ru(2)−Si(1)	106.11(3)	Ru(2)−H(22)−Ru(3)	108(2)

The spectroscopic data for **2a**−**c** are in accord with the structures depicted in Scheme 1 (eq 2). They were supported by the X-ray structure determination of **2c**. Crystal data and representative bond distances and angles are summarized in Tables 1 and 2, respectively. Figure 1 shows an ORTEP drawing of the structure. In the molecular structure of **2c**, the Ru(2)−Si bond distance is 2.429(1) Å, and the existence of a bridging hydrogen ligand between Ru(2) and Ru(3) is suggested by the difference Fourier map. Two terminal carbonyl groups are bonded with each ruthenium atom. The coordination mode of the acenaphthylene ligand to the

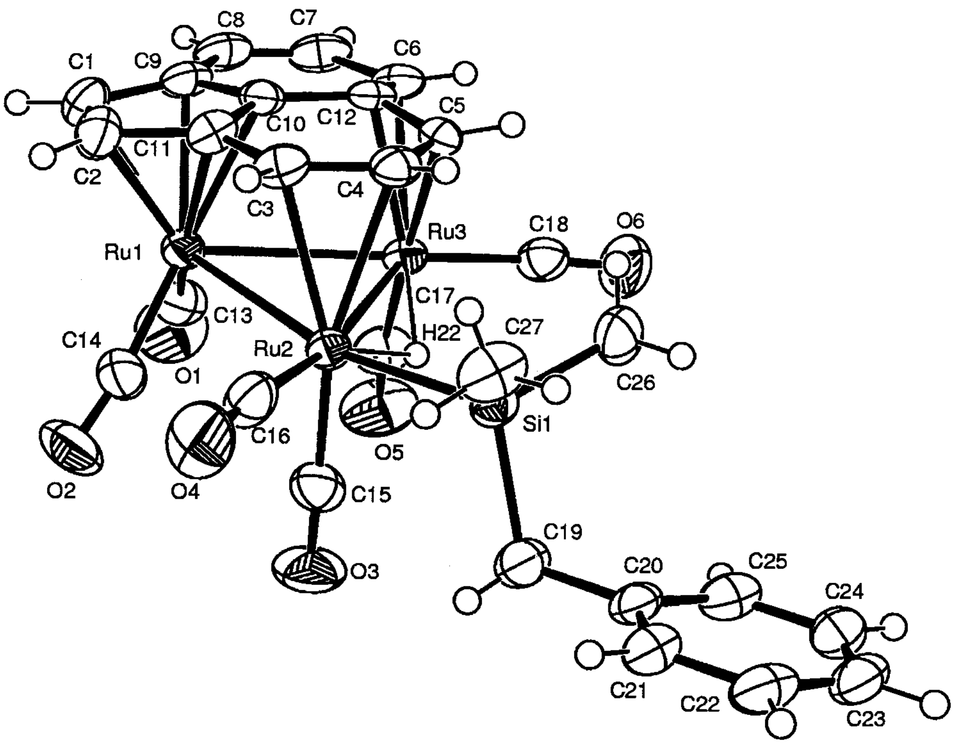
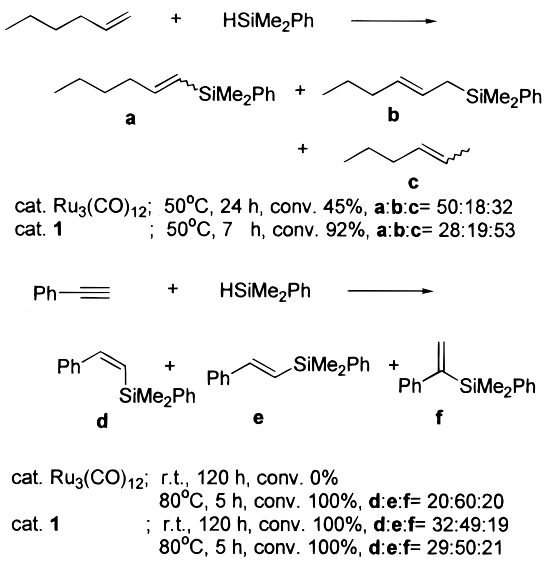


Figure 1. ORTEP drawing of **2c** (50% probability thermal ellipsoids).

Ru_3 moiety, $\mu_3,\eta^2:\eta^3:\eta^5$, is similar to that observed in **1**. As reported earlier, hydrogenation of **1** resulted in formation of ($\mu_3,\eta^1:\eta^5$-4,5-dihydroacenaphthylene)$Ru_3H_2(CO)_7$ as shown in eq 1 of Scheme 1. The reaction of **1** with trialkylsilanes is similar to that of the hydrogenation of **1** in the sense that the reaction proceeded with retention of the triruthenium framework. However, a striking difference is that dissociation of the bridging CO ligand is required for the oxidative addition of H−SiR$_3$. It is also different from the hydrogenation of **1** in that neither transformation of the acenaphthylene ligand, e.g., hydrosilylation of carbon−carbon double bonds, nor change of coordination mode of the acenaphthylene ligand from **1** was observed.

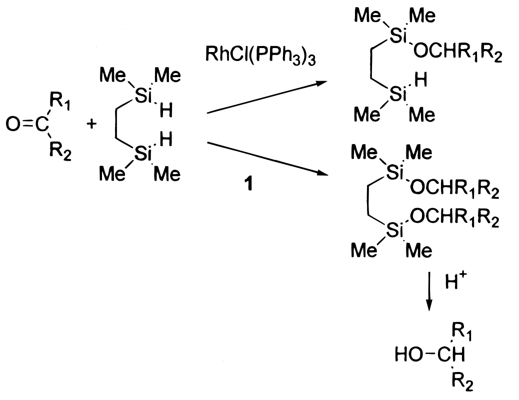
As described in the Introduction, oxidative addition of Si−H bonds to $Ru_3(CO)_{12}$ was investigated in the early 1970s; however, the reactions with trialkylsilanes usually induced the cleavage and recombination of ruthenium−ruthenium bonds to form silyl complexes with lower nuclearity.[8] Introduction of bridging ligands which reinforce the trinuclear framework contribute to promoting successful oxidative addition of trialkylsilanes without inducing cluster fragmentation. An anionic cluster containing a bridging hydride, $[Ru_3(\mu\text{-}H)(CO)_{10}]^-$,[9] and a complex containing the 2-amino-6-methylpyridyl group (ampy), $Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9$,[10] reacted with trialkylsilanes to afford the corresponding trinuclear cluster containing Ru−Si bonds. Successful formation of the trinuclear oxidative adduct **2** by the reaction of **1** with trialkylsilanes can be attributed to the fact that the acenaphthylene ligand in **1** acts as a reinforcer to suppress the cluster fragmentation. To our knowledge, this is the first example that bridging π-ligands effectively reinforce the cluster framework in the oxidative addition of hydrosilanes.

Scheme 3



Catalytic Hydrosilylation of Ketones and Aldehydes. Since the oxidative addition of Si−H bonds to transition-metal species generally is considered to be the initial step of the catalytic cycle, successful oxidative addition of trialkylsilanes to **1** prompted us to examine whether **1** may act as the catalyst for hydrosilylation of unsaturated molecules. Preliminary studies of the catalytic hydrosilylation of 1-hexene showed that dehydrogenative silylation formed a mixture of vinyl and allyl silanes. The reaction is similar to the $Ru_3(CO)_{12}$-catalyzed silylation reported by Seki and Murai.[5a] Hydrosilylation of phenylacetylene also was catalyzed by **1** to give a mixture of vinylsilanes. In these reactions, the catalytic activity of **1** is somewhat higher than that of $Ru_3(CO)_{12}$. However, no significant difference in selectivity of the products was available, as shown in Scheme 3. In sharp contrast, **1** catalyzed hydrosilylation of ketones and aldehydes smoothly; interesting features in regio- and stereoselectivities were observed.

Scheme 4



Catalytic hydrosilylation of ketones and aldehydes has been investigated in detail using $RhCl(PPh_3)_3$ as the catalyst (Scheme 4).[13,14] The rate of the reaction was sensitive to the structure of the silanes. Dihydrosilanes exhibited much higher reactivity than trialkylsilanes.[13] Use of α,ω-bifunctional organosilanes, $R_2HSi(CH_2)_nSiHR_2$ ($n = 2, 3$), accelerates the reaction of one Si–H terminus with the other group intact.[14] For example, $Me_2(H)Si(CH_2)_2Si(H)Me_2$, reacted with ketones ca. 50 times faster than monofunctional trialkylsilanes such as $EtMe_2SiH$. Thus, the rate dependence on the structure of silanes is $R_2SiH_2 >$ one Si–H group of $R_2HSi(CH_2)_nSiHR_2$ ($n = 2, 3$) $\gg R_3SiH$. Selectivities of the hydrosilylation also were investigated in the $RhCl(PPh_3)_3$-catalyzed reactions: (1) the hydrosilylation of 4-*tert*-butylcyclohexanone with trialkylsilanes by **1** generally afforded predominantly the trans isomer; with Ph_2SiH_2 the cis isomer was obtained preferentially;[15] (2) hydrosilylation of α,β-unsaturated carbonyl compounds with trialkylsilanes generally gave the corresponding 1,4-adduct, whereas reaction with Ph_2SiH_2 afforded the 1,2-adduct predominantly. These trends in the reaction rates and selectivities were often used as the standard to evaluate the catalytic hydrosilylation of carbonyl compounds. For example, Cutler and coworkers reported comparison of rates and selectivities of several manganese catalysts with $RhCl(PPh_3)_3$,[14] whereas Ojima et al. compared those of $Rh_4(CO)_{12}$ with $RhCl(PPh_3)_3$.[4d]

Table 3. Comparison of Catalytic Activity in the Hydrosilylation of Acetone or Acetophenone[a]

entry	ketone	catalyst	time (h)	yield (%)
1	acetone	**1**	8	84
2	acetone	$Ru_3(CO)_{12}$	8	0
3	acetone	$RhCl(PPh_3)_3$	20	27
4	acetophenone	**1**	7	100
5	acetophenone	$Ru_3(CO)_{12}$	7	0

[a] All reactions were carried out in C_6D_6 at room temperature. The yields were determined by ^1H NMR.

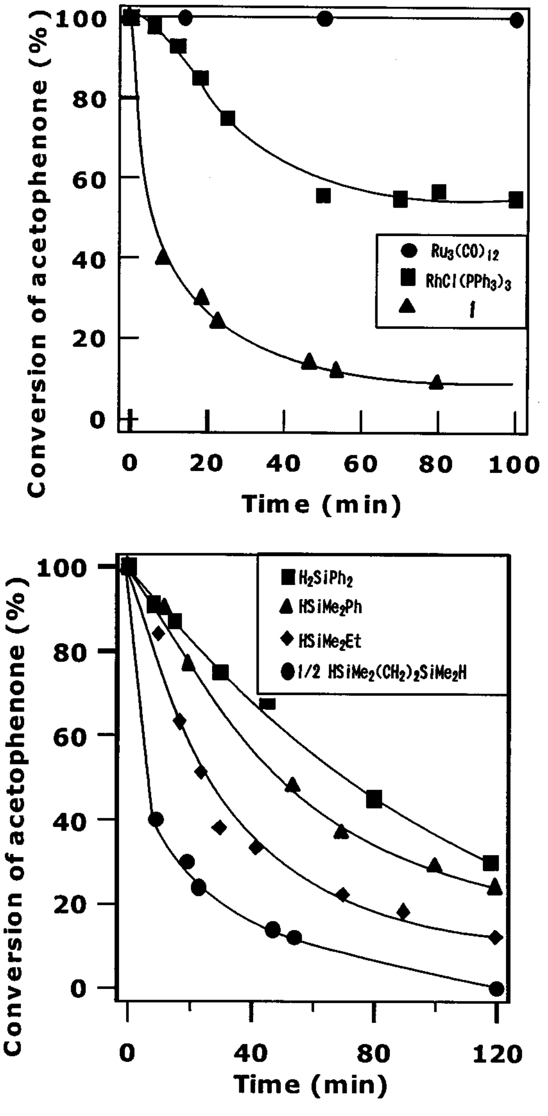


Figure 2. Reaction profiles for hydrosilylation of acetophenone: (a, top) hydrosilylation of acetophenone with $HMe_2Si(CH_2)_2SiMe_2H$ by three catalysts; (b, bottom) hydrosilylation of acetophenone with various hydrosilanes by **1**.

We carried out hydrosilylation of acetone and acetophenone with $HSiMe_2Ph$ in the presence of **1** (1 mol %). A silyl ether, $PhMe_2Si{-}O^iPr$ or $PhMe_2Si{-}OCH(Me)Ph$, respectively, was obtained as the sole product. No silyl enol ether derived from dehydrogenative silylation of ketones,[4d,e,14] often seen as a side reaction in metal-catalyzed hydrosilylation of ketones, was detectable. A reaction using a 1:1 mixture of the ketone and HMe_2SiPh was carried out in C_6D_6 at room temperature, and the conversions monitored by ^1H NMR spectroscopy were compared with those in reactions catalyzed by $Ru_3(CO)_{12}$ or $RhCl(PPh_3)_3$ under the same conditions (Table 3). All of the starting ketone was converted to the corresponding silyl ether after 7–8 h in the reactions catalyzed by **1**, while no reaction took place in that mediated by $Ru_3(CO)_{12}$. The reaction with $RhCl(PPh_3)_3$ apparently was slower than that with **1**. In Figure 2 are shown the reaction profiles for the hydrosilylation of acetophenone with Ph_2SiH_2, the α,ω-bifunctional trialkylsilane $Me_2HSi(CH_2)_2SiHMe_2$, and trialkylsilanes $EtMe_2SiH$ and $PhMe_2SiH$. In contrast to the trends observed for the $RhCl(PPh_3)_3$-catalyzed hydrosilylation,

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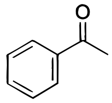
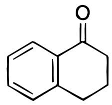
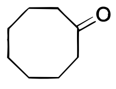
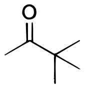
[13] (a) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (b) Semmelhack, M. F.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 2689. (c) Recent examples for the hydrosilylation of ketones catalyzed by Rh–phosphine complexes: Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70 and references therein.

[14] Cavanaugh, M. D.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1996**, *15*, 2764.

[15] (a) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Nakaoka, A.; Sakakibara, J.; Itoh, K. *Organometallics* **1995**, *14*, 2868. (b) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Sakakibara, J.; Itoh, K. *Organometallics* **1989**, *8*, 2495.

Table 4. Hydrosilylation of Ketones by 1[a]

	Isolated yield of the silyl ether	Isolated yield of the alcohol
	85%	72%
	--	80%
	76%	98%
	99%	--

[a] All reactions were carried out in the presence of 1 mol % of **1** in C_6D_6 at room temperature for 5−25 min.

Ph_2SiH_2 reacted more slowly than the trialkylsilanes. Thus, the rate decreases in the order $Me_2HSi(CH_2)_2SiHMe_2$ > trialkylsilanes > Ph_2SiH_2 and **1** > $RhCl(PPh_3)_3 \gg Ru_3(CO)_{12}$. Although the hydrosilylation was accelerated when $Me_2HSi(CH_2)_2SiHMe_2$ was used as the silane, both of the Si−H groups in $Me_2HSi(CH_2)_2SiHMe_2$ concomitantly reacted with acetophenone to give the corresponding silyl ether $Me_2[(Ph(Me)CHO)]Si(CH_2)_2Si[(Ph(Me)CHO)]Me_2$ as the sole product.

Hydrosilylation reactions of other ketones by $Me_2HSi(CH_2)_2SiHMe_2$ are summarized in Table 4. In all cases, the reaction was complete within 30 min and $Me_2(RO)Si(CH_2)_2Si(OR)Me_2$ was obtained as a single product, saponification of which afforded the corresponding alcohols in good yield. The reaction of 4-*tert*-butylcyclohexanone provides interesting data on rates of the reactions and stereochemical outcome of the products in comparison with those catalyzed by $RhCl(PPh_3)_3$ or $RuCl_2(PPh_3)_3$ (Table 5, entries 6−11).[13b] Except for the hydrosilylation with Ph_2SiH_2 (entry 5 and 9), the reactions catalyzed by **1** were faster than the others. The major isomer of 4-*tert*-butylcyclohexanol was cis in the **1**-catalyzed hydrosilylation with trialkylsilanes, whereas trans selectivity was observed in the reactions with other catalysts.

Another problem in the selectivity of hydrosilylation is 1,4- vs 1,2-reduction of α,β-unsaturated carbonyl compounds. It is known that the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of α,β-unsaturated ketones and aldehydes with trialkylsilanes results in 1,4-addition of the silane, whereas that with dihydrosilanes proceeds in the 1,2-addition mode.[13a,c] The $Rh_4(CO)_{12}$-catalyzed reaction of 2-cyclohexenone showed similar differences in the addition mode between $PhMe_2SiH$ and Ph_2SiH_2.[4d] The reactions of 2-cyclohexenone catalyzed by **1** showed similar dependence on the structure of the silane. The ratios of the 1,2-adduct to the 1,4-adduct were 12:88 and 91:9 when $PhMe_2SiH$ and Ph_2SiH_2 were used as the hydrosilanes, respectively. Interestingly, other α,β-unsaturated carbonyl compounds, for which the $RhCl(PPh_3)_3$-catalyzed hydrosilylation with trialkylsilanes showed selective 1,4-addition,[13a,c] reacted with $PhMe_2SiH$ in the presence of **1** to result in 1,2-addition with high selectivity. In particular, hydrosilylation of the acyclic unsaturated carbonyl compounds α-ionone, citral, and mesityl oxide gave the corresponding 1,2-adduct in over 80% selectivity. It was also seen that the rate of the reaction with $PhMe_2SiH$ was generally higher than that with Ph_2SiH_2 in the reactions of 2-cyclohexenone and other substrates listed in Table 6 catalyzed by **1**. As mentioned above, this tendency in the reaction rate was the reverse of the other catalysts; the hydrosilylation of 2-cyclohexenone catalyzed by $RhCl(PPh_3)_3$,[13] $Rh_4(CO)_{12}$,[4d] or $Mn(PPh_3)(CO)_4(COMe)$[14] proceeded more rapidly with Ph_2SiH_2 than $PhMe_2SiH$.

Reduction of Acetals and Cyclic Ethers and Silane-Induced Ring-Opening Polymerization of Cyclic Ethers. Transition-metal-catalyzed hydrosilylation of ketones and aldehydes involves addition of a Si−H bond activated by metal catalysts to a carbon−oxygen double bond. In contrast, reduction of acetals with hydrosilanes was generally promoted by a Lewis acid via an ionic mechanism,[16] not by transition-metal catalysts. Interestingly, **1** catalyzed the reduction of the dimethylacetal of benzaldehyde with $PhMe_2SiH$ or $Me_2HSi(CH_2)_2SiHMe_2$ to afford methyl benzyl ether and the corresponding methoxysilane quantitatively (Scheme 5, eq 1). Cyclic ethers also reacted with hydrosilanes; treatment of styrene oxide, cyclohexene oxide, or THF with hydrosilanes followed by hydrolysis gave β-phenethyl alcohol, cyclohexanol, or *n*-butanol, respectively, in moderate yield (Scheme 5, eqs 2−4). These reactions concomitantly caused formation of considerable amounts of intractable products, the NMR spectra of which suggested that a mixture of oligomers of the cyclic ethers was present.

The reactions of THF with $PhMe_2SiH$ were investigated in detail. As shown in Scheme 5 (eq 4), the NMR spectrum of a 1:1 mixture of $PhMe_2SiH$ and THF in the presence of 1 mol % of **1** showed signals derived from $PhMe_2SiOCH_2CH_2CH_2CH_3$ and those assignable to a mixture of THF oligomers. Formation of the oligomers also was supported by GC-MS analysis of the reaction mixture, which gave evidence of the presence of $PhMe_2SiO[(CH_2)_4]_nOCH_2CH_2CH_2CH_3$ ($n = 1, 2$). The ratio of the silyl butyl ether to the oligomers varied with the reaction temperature; at higher temperatures, the silyl butyl ether was formed in higher yield (butyl silyl ether: oligomer = 69:31 (40 °C), 88:12 (60 °C), >90:10 (80 °C)). This finding led to successful polymerization of THF, when $PhMe_2SiH$ was treated with an excess of THF (10−100 equiv with respect to the silane) in the presence of **1** (0.01 mol % of THF), as shown in Scheme 6.

Addition of C_6D_6 made monitoring of the reaction possible. In a typical example, a 10:1 mixture of THF and $PhMe_2SiH$ was treated with **1** (10^{-2} mol % with respect to THF), sealed in a 5 mm o.d. NMR tube in the presence of C_6D_6, and the mixture was heated at 40 °C (Table 7, entry 4). After a short induction period (~1 h), peaks derived from poly-THF emerged in the ^1H NMR spectrum. The conversion of THF reached 65−70% after 20 h. The ^1H NMR spectrum of this mixture suggested that the structure of the polymer was CH_3-

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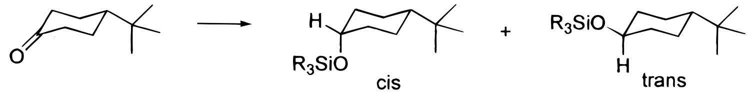
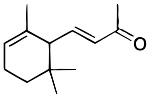
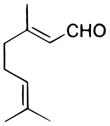
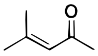
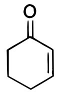
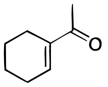
[16] For example: Frainnet, E.; Esclamadon, C. *C. R. Hebd. Seances Acad. Sci.* **1962**, *C254*, 1814. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1979**, 4679.

Table 5. Hydrosilylation of 4-*tert*-Butylcyclohexanone



entry	catalyst	silane	temp (°C)	time (h)	yield (%)	cis/trans	ref
1	**1**	$(HMe_2SiCH_2)_2$	room temp	0.25	81	66/34	
2	**1**	$HSiMe_2Ph$	50	3	100	72/28	
3	**1**	$HSiEt_3$	room temp	4	100	74/26	
4	**1**	$HSiPh_3$	room temp	20	0		
5	**1**	H_2SiPh_2	room temp	17	79	54/46	
6	$RhCl(PPh_3)_3$	$(HMe_2SiCH_2)_2$	room temp	1	77	20/80	13b
7	$RhCl(PPh_3)_3$	$HSiMe_2Ph$	80	12		29/71	13b
8	$RhCl(PPh_3)_3$	$HSiEt_3$	110	1.5		12/88	13b
9	$RhCl(PPh_3)_3$	H_2SiPh_2	25	0.25		54/46	13b
10	$RuCl_2(PPh_3)_3$	$HSiMe_2Ph$	80	10		12/88	13b
11	$RuCl_2(PPh_3)_3$	H_2SiPh_2	80	12		49/51	13b

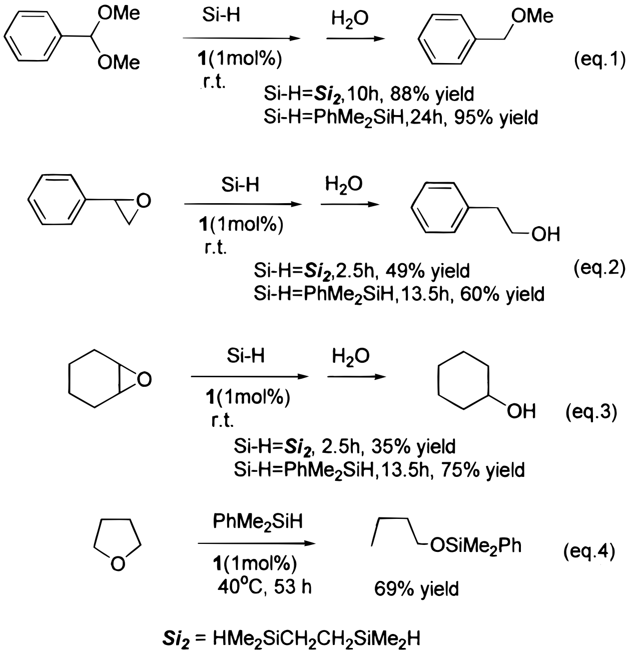
Table 6. Reduction of α,β-Unsaturated Ketones and Aldehydes[a]

Entry	Substrate	Silane	Time (h)	Yield (%)	Ratio 1,2 / 1,4
1		***Si*₂**	0.5	79	92 / 8
2		***Si*₂**	1	94	94 / 6
		Ph_2SiH_2	2.5	74	100 / 0
3		***Si*₂**	0.5	85	80 / 20
4		***Si*₂**	1	80	12 / 88
		Ph_2SiH_2	4	93	91 / 9
5		***Si*₂**	2	81	45 / 55

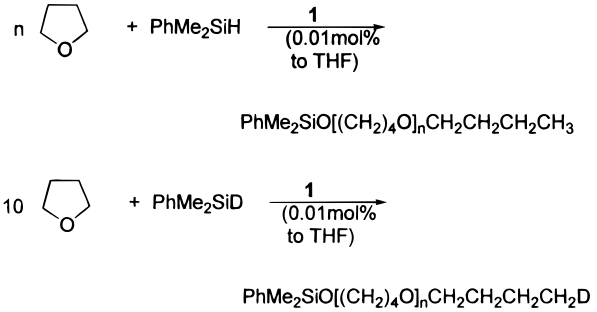
[a] ***Si*₂** = $HMe_2Si(CH_2)_2SiMe_2H$.

$(CH_2)_3-[O(CH_2)_4]_{n-1}-OSiMe_2Ph$, as described later in this paper. The calculated molecular weight based on the integral values of CH_3 at the polymer terminus and CH_2 of the polymer chain was 1900, which was consistent with that based on the conversions of THF and $PhMe_2SiH$ (2100). The molecular weight determined by SEC (calibration: polystyrene standard) was $M_n = 3700$, and $M_w/M_n = 1.7$.[17] Other data for polymerization of THF in C_6D_6 are summarized in Table 7. The molecular weight can be controlled by changing the reaction temperature (entries 1−3 and 6) or the ratio of THF to $PhMe_2SiH$ (entries 4 and 5). At higher temperature, the molecular weight was lower. Use of the trialkylsilanes Et_3SiH, Ph_3SiH, and $^tBuMe_2SiH$ generally gave the corresponding polymer, the yields, average molecular weight, and dispersity of which were similar to those obtained with $PhMe_2SiH$. In contrast, use of the di- or trihydrosilanes Ph_2SiH_2, $PhMeSiH_2$, and $PhSiH_3$ gave only a small amount of polymeric materials. Deuterium labeling using $PhMe_2SiD$ gave the polymer $PhMe_2SiO-[(CH_2)_4O]_nCH_2CH_2CH_2CH_2D$ selectively.[18] This clearly

Scheme 5



Scheme 6



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[17] The molecular weight determined by SEC is roughly in accord with that calculated from either the integral ratio of ^1H resonances or the conversions of THF and $PhMe_2SiH$. It is known that the molecular weights determined by SEC calibrated by polystyrene standards are reportedly half of those calibrated by poly-THF standards. See: Burgess, F. J.; Cunliffe, A. V.; Dawkins, J. V.; Richards, D. H. *Polymer* **1977**, *18*, 733. Slomkowsky, S.; Winnik, M. A.; Furlong, P.; Reynolds, W. F. *Macromolecules* **1989**, *22*, 503.

[18] Using $HSiMe_2PhD$ (99% D), the deuterium content in the methyl terminus of the polymer was >95%. The ^1H NMR spectrum of the polymer showed that the methyl group appeared as triplets of triplets ($J_{CH_2D-CH_2} = 7.3$ Hz, $J_{H-D} = 1.8$ Hz), suggesting the existence of a CH_2D group. Details are given in the Supporting Information.

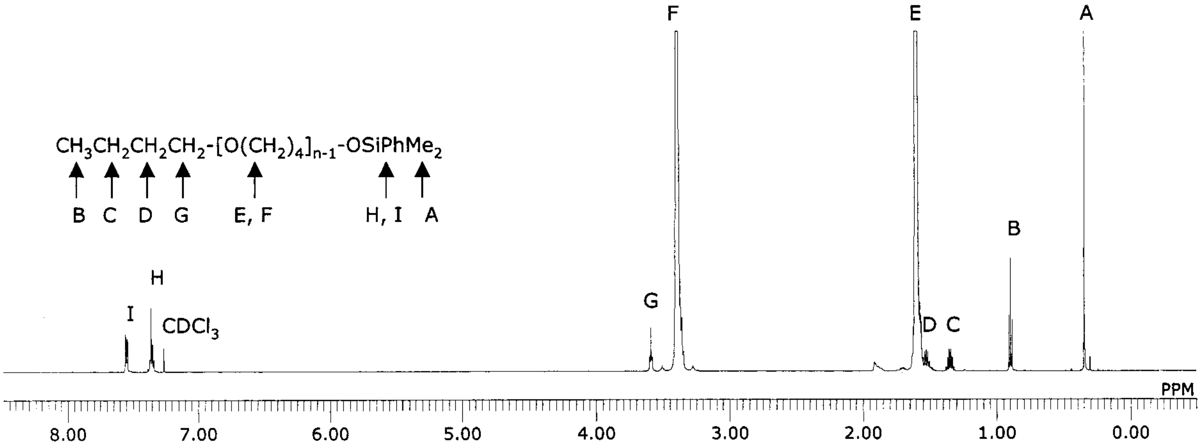

Figure 3. ^{1}H NMR spectrum of the polymer (M_n(SEC) = 3000, M_w/M_n = 1.3).

Table 7. NMR Observation of Silane-Induced Ring-Opening Polymerization of THF[a]

entry	THF/SiH	temp (°C)	time (h)	conversn of THF (%)	M_n NMR[b]	M_n SEC[c]	M_w/M_n SEC[c]
1	100	80	5	8	640	1000[c]	2.6[d]
2	100	60	9	39	3100	11 000	1.7
3	100	40	20	60	4900	19 000	1.6
4	10	40	65	58	1900	3700	1.7
5	100	5	117	50	47 000	97 000	1.7

[a] All reactions were carried out using 0.01 mol % of **1** as the catalyst based on charged THF in the presence of 10 vol % of C_6D_6. [b] Determined by the integral ratio (see text). [c] Calibration of SEC was carried out by polystyrene standards. [d] Not accurate because it was out of range of the SEC column.

Table 8. Bulk Polymerization of THF Using $PhMe_2SiH$[a]

					after precipitation		
entry	THF/SiH	temp (°C)	time (h)	crude yield[c] (%)	yield[c] (%)	M_n[b]	M_w/M_n[b]
1	10	40	20	66	33	3000	1.3
2	20	40	20	65	40	5500	1.4
3	100	40	20	67	44	16 000	1.5
4	100	60	10.5	47	31	13 000	1.5
5	500	40	48.5	25	24	206 000	1.8

[a] All reactions were carried out using 0.01 mol % of **1** as the catalyst based on charged THF. [b] Determined by SEC calibrated by polystyrene standards. [c] The yield was based on the charged THF.

showed that the polymerization described above involves insertion of the $OCH_2CH_2CH_2CH_2$ unit derived from THF into the Si−H bond.

Bulk polymerization was carried out in a similar manner. In a typical example, a mixture of THF, $PhMe_2SiH$, and **1** (1000:10:1) was sealed in a glass ampule, and the mixture was heated at 40 °C for 20 h. The crude polymer ($M_n = 2000$, $M_w/M_n = 1.6$; determined by SEC) was dissolved in diethyl ether and purified by precipitation by adding hexane at −35 °C. The precipitate (48 wt % of the crude polymer) was separated from the liquid phase and subjected to NMR and SEC analysis. The ^{1}H NMR spectrum of the purified polymer is shown in Figure 3. Two broad singlets due to CH_2 groups in the polymer chain were seen at 1.60 and 3.40 ppm (E and F). The presence of the Me_2PhSi group was evidenced by a singlet at 0.35 ppm (A) and signals around 7 ppm (H and I). It is important that the four peaks B−D and G appeared as a triplet, multiplet, multiplet, and triplet, respectively, which are assignable to the terminal butyl group. Correlations among B−D and G were supported by a H−H COSY spectrum. The integrated intensities of A−D and G−I were 6:3:2:2:2:3:2, which indicate that the polymer contains one butyl and one $PhMe_2Si$ group. These data are in accord with the structure of the polymer as $CH_3(CH_2)_3[O(CH_2)_4]_{n-1}$-$OSiMe_2Ph$. ^{13}C NMR, DEPT, H−C COSY, and ^{29}Si NMR spectra were also consistent with this formula. The integral ratio of B and E (or F) gave an average molecular weight of 1500. SEC analysis of the purified polymer showed $M_n = 3000$ and $M_w/M_n = 1.3$. Other data of bulk polymerization experiments are summarized in Table 8. Similar to the results shown in Table 7, the molecular weight of the polymer depended on the reaction temperature or the charged SiH/THF ratio. Molecular weight distributions of the polymers obtained were 1.3−1.6.

Polymerization of THF was briefly mentioned by Chalk in 1970 as occurring in a $Co_2(CO)_8$-catalyzed reaction of Et_3SiH in the presence of an excess of THF; he obtained poly-THF with M_w = 50 000.[19] Hydrosilylation and silylformylation of unsaturated molecules catalyzed by metal carbonyl clusters have recently received considerable attention as unique methods for chemical transformation of organic molecules, and polymerization of THF was sometimes stated to be a side reaction.[5] Nevertheless, there have been few investigations on the features of polymerization or analysis of the polymer produced.[20] We reinvestigated Chalk's silane-induced ring-opening polymerization of THF catalyzed by $Co_2(CO)_8$. With 5 mol % of the catalyst, $Co_2(CO)_8$ showed similar reactivity (Co, 40% conversion of THF after 3.5 h; **1**, 48% conversion under the same conditions) to give the polymer (Co, M_n(SEC) = 82 000, M_w/M_n = 1.9; **1**, M_n(SEC) = 50000, M_w/M_n = 1.8). Since $Co_2(CO)_8$ is not stable in THF, rapid precipitation of paramagnetic metallic species took place. With lower catalyst concentration (1 mol %), the catalyst decomposition predominated over the polymerization and no polymeric materials were formed. Since NMR analysis showed that the polymer obtained with the Co catalyst has a structure similar to that with **1**, we concluded that $Co_2(CO)_8$ and **1** show similar behavior in the silane-induced ring-opening polymerization of THF but that **1**

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(19) Chalk, A. J. *J. Chem. Soc., Chem. Commun.* **1970**, 847.
(20) Crivello, J. V.; Fan, M.-X. *J. Polym. Sci. A* **1991**, *29*, 1853.

was the more active catalyst at the lower catalyst concentration. We also found that facile decomposition of $Co_2(CO)_8$ in THF caused problems in controlling the molecular weight of the polymer.

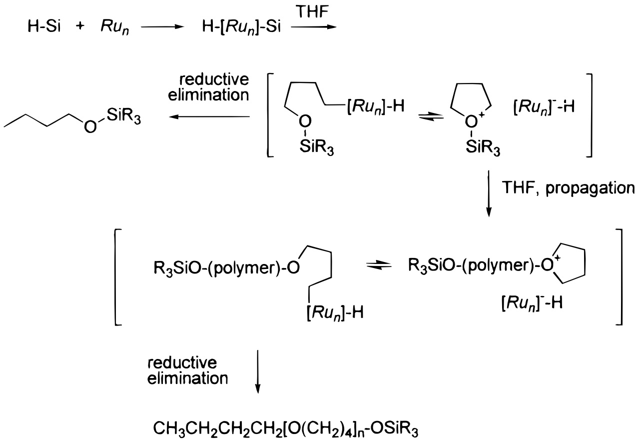
The ruthenium-catalyzed silane-induced ring-opening polymerization protocol could be applied to polymerization of other cyclic ethers such as oxetane and cyclohexene oxide. Under conditions similar to those described in Table 7, entry 3, oxetane and cyclohexene oxide were polymerized to the corresponding polymers (polyoxetane, M_n(SEC) = 22 000, $M_w/M_n = 2.4$; polycyclohexene oxide, M_n(SEC) = 14 000, $M_w/M_n = 1.9$).[21] Attempted polymerization of styrene oxide under similar conditions gave polymers of relatively small molecular weight. As in the case of the well-known cationic polymerization of cyclic ethers, neither 2- nor 3-methyltetrahydrofuran underwent the trialkylsilane-mediated polymerization by catalysis of **1**.[22]

Polymerization of THF generally is initiated by strong acids.[22] Trials to produce poly-THF of narrow molecular weight distribution attained success when the living polymerization was quenched at the initial stage of the reaction, where conversion of THF is low.[23] There are only a few examples of high-molecular-weight poly-THF being produced in good conversion with relatively narrow molecular weight distribution.[24] Although the molecular weight distribution is not very narrow, the present polymerization is unique in the selective production of polymers with $M_n = 10^3-10^5$.

Mechanistic Considerations. There are several questions concerning the reaction mechanism. Existence of the induction period (~1 h) for the catalytic reactions suggests that **1** would be a catalyst precursor. The ruthenium cluster **1** catalyzes the reactions of silanes with a wide variety of substrates such as olefins, acetylenes, ketones, acetals, and cyclic ethers. There are similarities in catalysis by **1** to catalysis by $Co_2(CO)_8$, which promotes the hydrosilylation of olefins and ketones, and the polymerization of cyclic ethers via an intermediate containing the R_3Si-Co species.[4] This may suggest the possible involvement of a species containing the R_3Si-Ru moiety as the net catalytic species. As described above, we found that the reaction of **1** with trialkylsilanes afforded the oxidative adduct **2** in good yield. Since the oxidative addition is generally considered to be an initiation step of the catalytic cycle, the oxidative adduct **2**, or an analogous species, could be involved in this cycle. The oxidative addition of **1** to **2** required application of temperatures over 80 °C to remove a CO ligand from **1**, while the reactions catalyzed by **1** proceeded at room temperature. Thus, **2** itself could not be involved in the catalytic cycle. Attempted catalysis of the hydrosilylation of acetone or acetophenone with $PhMe_2SiH$ by **2a** was very slow; the conversion was below 10% after 7−8 h at room temperature. It was also found that **2c** was much less active in the ring-opening polymerization of THF. Interestingly, attempted hydrosilylation of 1-hexene with $PhMe_2SiH$ in the presence of catalytic amounts of **2a** led only to isomerization of 1-hexene to 2-hexene.

Although **2** is not an intermediate in the catalytic hydrosilylation, NMR spectroscopic evidence was available, suggesting that an oxidative adduct similar to **2** was formed at an initial stage of the catalytic reaction. The ^1H NMR spectrum of a mixture of **1** with an excess of $HSiMe_2Ph$ was measured in C_6D_6 at room temperature. Under conditions similar to the catalytic hydrosilylation (room temperature, under vacuum), a Ru−H signal different from those in **2** appeared in the region of bridging hydride ligands (−18 ppm vs −15.2 ppm for δ(Si−H) in **2a**) as a singlet. The observed significant upfield shift of the acenaphthylene protons (δ 3.19−6.05 ppm), compared with that of uncoordinated acenaphthylene (δ 7−8 ppm), suggested the acenaphthylene molecule was coordinated to the cluster species. The methyl protons due to *Me*Si−Ru groups were seen in the ^1H NMR spectrum at δ 0.315 and 0.375 ppm as singlets. This suggests that *the activation of H−Si bonds by the triruthenium cluster species could be involved in the initial step of the reaction*, followed by insertion of the unsaturated substrate into either a Ru−Si or a Ru−H bond.[25] Reductive elimination of the product then would complete the catalytic cycle. Unfortunately, this Ru−H species is unstable in solution, and its trapping, e.g., by reaction with ketones, has not been possible to date.

Scheme 7



In the **1**-catalyzed reaction of cyclic ethers with R_3SiH, a polar intermediate, $R_3Si^{\delta+}-M^{\delta-} \leftrightarrow R_3Si^{+}\cdots M^{-}$, possibly may be involved. Murai and co-workers proposed that $R_3Si^{\delta+}-Co^{\delta-}$ species induce ring opening of THF to give $R_3SiO-(CH_2)_4-Co$ byproducts in their silyl carbonylation reactions.[26] In contrast, Chalk proposed

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[21] Crivello and Fan reported that $Co_2(CO)_8$ in the presence of $BuSiH_3$ catalyzed polymerization of oxetane and epoxides: Crivello, J. V.; Fan, M.-X. *J. Polym. Sci., A* **1992**, *30*, 31.

[22] Recent general reviews for cationic polymerization of cyclic ethers: Kubisa, P. In *Cationic Polymerization*; Matyjawzewski, K., Ed.; Marcel Dekker: New York, 1996; p 437. Penczek, S.; Kubisa, P. In *Ring-Opening Polymerization: Mechanisms, Catalysis, Structure, Utility*; Brunelle, D. J., Ed.; Hanser: Munich, 1993. Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.

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[24] Olah, G. A.; Farooq, O.; Li, C. X.; Farnia, M. A. M. F.; Akloins, J. J. *J. Appl. Polym. Sci.* **1992**, *45*, 1355. McCarthy, B. J.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 3035 and references therein.

[25] Mechanistic studies on catalytic hydrosilylations have recently been investigated particularlily concerning the Chalk−Harrod or the modified Chalk−Harrod mechanism: Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308. Stein, J.; Lewis, L. N.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693. Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, Y. *Coord. Chem. Rev.* **1999**, *190−192*, 933 and references therein.

generation of R_3Si^+ species from $R_3SiCo(L)_4$ (L = THF, CO) which initiate the cationic ring-opening polymerization of THF, in which oxonium intermediates with anionic cobalt species as the counterion exist at the polymer terminus.[19] In the ruthenium-catalyzed reactions of cyclic ethers, simple ring-opening reduction and polymerization occur when the reaction temperature and the substrate/silane ratios are changed. As shown in Scheme 7, there may exist a neutral Ru species **A** or **C** and an ionic species **B** or **D**, which are mutually interconverted. The former gives butyl silyl ether, whereas the latter results in polymerization.[27]

Conclusion

As described above, **1** is a good catalyst for hydrosilylation of unsaturated molecules, reduction of acetals and cyclic ethers, and silane-induced ring-opening polymerization of cyclic ethers. In comparison with the hydrosilylation reactions of ketones and aldehydes catalyzed by $RhCl(PPh_3)_3$, the **1**-catalyzed reactions with trialkylsilanes are faster, and characteristic differences, e.g., differences in regio- or stereoselectivities, are observed as described in the text. The polymerization of THF is similar to the $Co_2(CO)_8$-catalyzed reaction reported by Chalk; however, **1** is a superior catalyst at lower catalyst concentration. The oxidative addition of trialkylsilanes to **1** results in liberation of CO and oxidative addition of the Si−H bond of trialkylsilanes to form **2**. This evidences the reaction pathway of oxidative addition of Si−H bonds to triruthenium species without cluster fragmentation. Although catalytic reactions using **2** revealed that **2** was not a catalytic species, we obtained NMR evidence that there was a reaction pathway to activate an H−Si bond in keeping the cluster framework under the conditions close to the catalytic reactions. Existence of the oxidative addition pathway of **1** offers a possibility for the involvement of cluster species in the catalytic hydrosilylations, and further investigation to specify net species produced from **1** in the catalytic reactions is underway.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under an argon atmosphere. NMR spectra (270, 400, 600 MHz) were measured in $CDCl_3$ unless otherwise noted; δ value are given in ppm and coupling constants (J) in Hz. Assignments of the NMR signals were made with the aid of DEPT, INEPT, and 2D techniques. THF, C_6H_6, C_6D_6, and Et_2O were distilled from sodium benzophenone ketyl just before use. Size exclusion chromatography (SEC) analysis of the polymer was carried out using a Jasco HPLC system in THF using a standard sample of polystyrene.

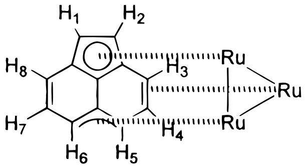

Figure 4.

Oxidative Addition of Hydrosilanes to (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$ (1). In a typical example, $PhMe_2SiH$ (837 mg, 6.1 mmol) was added to a solution of **1** (200 mg, 0.3 mmol) dissolved in C_6H_6 (120 mL), and the mixture was heated under reflux for 3 h. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel, o.d. 3 cm, length 9.5 cm, eluent hexane and CH_2Cl_2) to give **2a** (132 mg, 0.174 mmol; 61%). A small amount of **1** was recovered (15 mg, 0.024 mmol). By a similar procedure, adducts of Et_3SiH and $(PhCH_2)Me_2SiH$ (**2b**,**c**, respectively) were isolated.

2a (see Figure 4 for hydrogen numbering): ^1H NMR δ −15.21 (s, 1H, Ru−H), 0.57 (s, 3H, SiMe), 0.60 (s, 3H, Me), 2.88 (d, J = 6.9, 1H, H5), 4.85 (d, J = 3.0, 1H, H2), 4.97 (d, J = 5.9, 1H, H6), 5.22 (t, J = 6.9, 1H, H4), 5.55 (d, J = 9.4, 1H, H8), 5.62 (d, J = 6.9 Hz, 1H, H3), 5.77 (dd, J = 5.9, 9.4, 1H, H7), 5.87 (d, J = 3.0, 1H, H1), 7.28−7.38 (m, 3H, Ph), 7.39−7.46 (m, 2H, Ph); ^{13}C NMR δ 5.98, 8.38, 40.86, 62.44, 65.12, 72.49, 80.81, 83.89, 87.96, 90.55, 97.46, 113.80, 127.51 (2C), 127.96, 130.24, 131.89 (2C), 132.61, 145.15, 190.25, 191.83, 204.29, 204.55, 206.62, 207.56; ^{29}Si NMR δ 29.46 (s); IR (KBr) 2032 (s), 1999 (s), 1970 (s), 1934 (sh) cm^{-1}; TLC R_f = 0.70 (1:1 hexane/CH_2Cl_2); mp 155−156 °C dec. Anal. Calcd for $Ru_3SiO_6C_{26}H_{20}$: C, 41.10; H, 2.65. Found: C, 41.11; H, 2.77.

2b: ^1H NMR δ −15.41 (s, 1H, Ru−H), 0.60−0.88 (m, 6H, $SiCH_2$), 0.99 (t, J = 7.4, 9H, $SiCH_2$*Me*), 3.07 (d, J = 6.4, 1H, H5), 4.90 (d, J = 2.5, 1H, H2), 5.02 (d, J = 6.4, 1H, H3), 5.58 (t, J = 9.4, 1H, H8), 5.70 (t, J = 6.4, 1H, H4), 5.77 (dd, J = 5.9, 9.4, 1H, H7), 5.83 (d, J = 5.9, 1H, H6), 5.90 (d, J = 2.5 Hz, 1H, H1); ^{13}C NMR δ 8.44 (CH_3), 12.29 (CH_2), 41.17 (CH), 62.54 (CH), 65.75 (CH), 72.67 (CH), 76.48 (CH), 80.48 (CH), 80.97 (CH), 88.39 (C), 90.84 (C), 97.70 (C), 114.05 (CH), 130.31 (C), 190.71 (CO), 192.18 (CO), 204.66 (CO), 204.98 (CO), 207.06 (CO), 208.10 (CO); ^{29}Si NMR δ 51.04 (s); IR (KBr) 2030 (s), 1998 (s), 1968 (s), 1952 (s), 1924 (sh) cm^{-1}; TLC R_f = 0.69 (1:1 hexane/CH_2Cl_2); mp 138−139 °C dec. Anal. Calcd for $Ru_3SiO_6C_{24}H_{24}$: C, 38.97; H, 3.27. Found: C, 38.92; H, 3.31.

2c: ^1H NMR δ −15.25 (s, 1H, Ru−H), 0.16 (s, 3H, Me), 0.28 (s, 3H, Me), 2.26 (d, J = 2.5 Hz, 2H, CH_2), 2.99 (d, J = 5.9, 1H, H5), 4.90 (d, J = 2.5, 1H, H2), 5.01 (d, J = 5.9, 1H, H6), 5.30 (t, J = 5.9, 1H, H4), 5.58 (d, J = 8.9, 1H, H8), 5.71 (d, J = 5.9, 1H, H3), 5.79 (dd, J = 5.9, 8.9, 1H, H7), 5.90 (d, J = 2.5, 1H, H1), 6.98−7.23 (m, 5H, Ph); ^{13}C NMR δ 6.26 (CH_3), 6.74 (CH_3), 34.88 (CH_2), 41.71 (CH), 63.21 (CH), 66.00 (CH), 73.18 (C), 77.19 (CH), 80.72 (CH), 81.81 (CH), 88.53 (C), 91.32 (C), 98.27 (C), 114.54 (CH), 124.16 (CH), 128.18 (CH, two carbons), 128.23 (CH, two carbons), 130.88 (CH), 140.99 (C), 191.22 (CO), 192.24 (CO), 205.30 (CO), 205.43 (CO), 207.94 (CO), 288.92 (CO); IR (KBr) 2033 (s), 1993 (s), 1975 (s), 1960 (s), 1950 (s), 1924 (sh) cm^{-1}; TLC R_f = 0.46 (1:1 hexane/CH_2Cl_2); mp 144−146 °C dec. Anal. Calcd for $Ru_3SiO_6C_{27}H_{22}$: C, 41.91; H, 2.87. Found: C, 41.17; H, 2.89.

Catalytic Hydrosilylation of 1-Hexene and Phenylacetylene. In a 5 mm o.d. NMR tube, 1-hexene or phenyl-

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(26) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938.

(27) The R_3Si^+-initiated cationic polymerization of THF was reported by Gong in 1986 using Me_3SiOTf.[28] The reaction is believed to proceed via silylated onium ion intermediates, but recent mechanistic studies pointed out the possibility that triflic acid formed by hydrolysis of Me_3SiOTf may be a net initiator.[29] Interestingly, recent studies by Olah and co-workers revealed that both Me_3SiOTf and Me_3Si(fluorinated borate) produced silylated onium ions of THF, but only the former initiated the polymerization.[30] The counterion apparently affects the fate of polymerization, presumably in the propagation steps. Triflates sufficiently stabilize the active polymer terminal, whereas fluorinated borates decompose it. In this sense, the counterion in the ruthenium-catalyzed polymerization, i.e. anionic ruthenium hydride species, must sufficiently stabilize the polymer terminal enough to allow propagation steps such as triflates to operate.

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acetylene (0.077 mmol), a trialkylsilane (0.077 mmol), and a catalytic amount of **1** (1 mol %, 0.77 mmol) were dissolved in C_6D_6 (0.6 mL) containing 0.077 mmol of 1,2-dichloroethane. The NMR sample was carefully degassed several times and sealed in vacuo. The products were assigned according to the literature.[7b,31] The yield of the product was determined by ^1H NMR spectrometry on the basis of the integrated intensity of the internal standard (1,2-dichloroethane).

General Procedure for the Catalytic Hydrosilylation of Ketones and Aldehydes. The hydrosilylation of ketones or aldehydes gave the corresponding silyl ethers as the primary product, which were isolated by distillation of the crude product. Representative examples of the isolation of silyl ethers are the following: acetophenone (600 mg, 5 mmol), $HMe_2Si(CH_2)_2SiMe_2H$ (366 mg, 2.5 mmol), and the ruthenium cluster **1** (33 mg, 0.05 mmol, 1 mol %) were dissolved in benzene (10 mL). The mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo, followed by bulb-to-bulb distillation of the residue, to give $[(PhMeCHO)SiMe_2CH_2]_2$ (856 mg, 89%). By a similar procedure, the silyl ethers were obtained from cyclooctanone and pinacolone.

$[(PhMeCHO)SiMe_2CH_2]_2$: ^1H NMR δ 0.01 (s, 12H, SiMe), 0.39 (s, 4H, CH_2Si), 1.39 (d, $J = 6.0$, 6H, CH*Me*), 4.79 (d, $J = 6.0$, 2H, CH), 7.15−7.34 (m, 10H, Ph); ^{13}C NMR δ −2.33 (SiMe), 7.98 ($SiCH_2$), 26.98 (CH*Me*), 70.61 (*C*HMe), 125.26, 126.77, 128.06, 146.51 (Ph); IR (neat) 1090, 1260 cm^{-1}; HRMS calcd for $C_{22}H_{34}O_2Si_2$ 386.2098, found 386.2085.

$[(cyclooctanoxy)SiMe_2CH_2]_2$: ^1H NMR δ 0.07 (s, 12H, SiMe), 0.48 (s, 4H, CH_2Si), 1.30−1.79 (m, 28H, CH_2), 3.72−3.83 (m, 2H, CHO); ^{13}C NMR δ −2.20 (SiMe), 8.22 ($SiCH_2$), 22.86 (CH_2), 25.34 (CH_2), 27.38 (CH_2), 35.36 (CH_2), 72.68 (CH); IR (neat) 1060, 1260 cm^{-1}; HRMS calcd for $C_{22}H_{46}O_2Si_2$ 398.3038, found 398.3064.

$[(^tBuCHMeO)SiMe_2CH_2]_2$: ^1H NMR δ 0.06 (s, 12H, SiMe), 0.47 (s, 4H, CH_2Si), 0.82 (s, 18H, Me_3C), 1.02 (d, $J = 6.3$, 6H, CH*Me*), 3.41 (q, $J = 6.3$, 2H, OC*H*); ^{13}C NMR δ −2.21 (Me), −1.91 (Me), 8.52 (CH_2), 18.51 (CH_3), 25.78 (CH_3), 35.29 (C), 75.89 (CH); IR (neat) 1100, 1260 cm^{-1}; HRMS calcd for $C_{18}H_{42}O_2Si_2$ 346.2725, found 346.2715.

In other experiments described in this text, the formed silyl ethers were subjected to acid-catalyzed hydrolysis to give the corresponding alcohols, the spectral data of which were in accord with those of commercially available authentic samples. In a typical example, α-ionone (192 mg, 1 mmol), $Me_2HSi(CH_2)_2SiHMe_2$ (146 mg, 1 mmol), and **1** (6.5 mg, 0.01 mmol) were dissolved in C_6H_6 (2 mL), and the mixture was stirred at room temperature for 30 min and then treated with 10% H_2SO_4 in methanol. The mixture was poured into cold aqueous $NaHCO_3$ and extracted with diethyl ether. The combined extracts were washed with brine and concentrated. Chromatographic purification (silica gel, eluent hexane and ether) afforded the corresponding alcohol (145 mg, 75%) and dihydroionone (7 mg, 4%).

General Procedures for the Catalytic Silane-Induced Ring-Opening Polymerization of THF. A. NMR Experiment. In a typical example, a mixture of THF (7.6 mmol, 551 mg, 0.62 mL), C_6D_6 (0.05 mL), $PhMe_2SiH$ (0.78 mmol, 107 mg, 0.12 mL), and **1** (7.7×10^{-4} mmol, 0.5 mg, 10^{-2} mol % to THF) was sealed in a 5 mm o.d. NMR tube, and the mixture was heated at 40 °C (Table 7, entry 4). After a short induction period (∼1 h), peaks due to poly-THF emerged in the ^1H NMR spectrum. The conversion of THF reached 65−70% after 20 h. The ^1H NMR spectrum of this mixture suggested that the structure of the polymer was $CH_3(CH_2)_3{-}[O(CH_2)_4]_{n-1}{-}OSiMe_2{-}Ph$, as described earlier in this paper. The calculated molecular weight based on the integrated intensities of the terminal CH_3 signal vs that due to CH_2 of the polymer chain was 1900, which was consistent with that based on the conversions of THF and $PhMe_2SiH$ (2100). The molecular weight determined by SEC (calibration: polystyrene standard) was $M_n = 3700$, and $M_w/M_n = 1.7$.

B. Bulk Polymerization. In a typical example, a solution of THF (39 mmol, 2.67 g, 3.0 mL), $PhMe_2SiH$ (3.8 mmol, 516 mg, 0.58 mL), and **1** (0.004 mmol, 2.4 mg) was sealed in a glass ampule, and the mixture was heated at 40 °C for 20 h. The crude polymer ($M_n = 2000$, $M_w/M_n = 1.6$; determined by SEC) was dissolved in diethyl ether and was purified by precipitation by adding hexane at −35 °C. The precipitate (48 wt % of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. The integral ratio described in the text gave an average molecular weight of 1500. The SEC analysis showed $M_n = 3000$, $M_w/M_n = 1.3$. ^{13}C NMR ($CDCl_3$): δ −1.8, 13.9, 19.3, 26.1, 26.5, 29.2, 31.8, 62.8, 70.5, 127.7, 129.5, 133.4, 137.9. ^{29}Si NMR ($CDCl_3$): δ 6.7. H−H and H−C COSY spectra are shown in the Supporting Information.

Polymerization of THF in the Presence of $PhMe_2SiD$. $PhMe_2SiD$ (99% D) was prepared by reduction of $PhMe_2SiCl$ by $LiAlD_4$. Polymerization was carried out using THF (551 mg, 7.6 mmol), $PhMe_2SiD$ (104 mg, 0.76 mmol), and **1** (0.48 mg, 0.7 μmol) in C_6D_6 at 40 °C for 20 h in a fashion similar to the procedure described above (conversion of THF 57%). The crude silylated poly-THF (306 mg) available by removal of the volatiles was subjected to purification by precipitation (hexane/ether at −35 °C), giving polymer with $M_n(\mathrm{SEC}) = 6400$, $M_w/M_n = 1.4$ (60 wt % of the crude product). The ^1H and ^{13}C NMR spectra of the product showed the presence of a CH_2D group at the polymer terminus (the data are shown in the Supporting Information).

NMR Observation of a Species Showing a Ru−H Signal in the Bridging Hydride Region. A mixture of $PhMe_2SiH$ (1.8 mg, 13 μmol) and **1** (0.9 mg, 1.3 μmol) was dissolved in C_6D_6 (0.6 mL) in a 5 mm o.d. NMR tube, and the sample was sealed in vacuo. The reaction was monitored by ^1H NMR at room temperature. After 30 min, new peaks assignable to a species different from **2** were observed, which gradually diminished and disappeared after a few hours. ^1H NMR (C_6D_6): δ −18.25 (s, 1H, Ru−H), 0.315 and 0.375 (s, 3H each, SiMe), 3.19 (d, $J = 2.7$, 1H, H2), 3.24 (d, $J = 6.4$, 1H, H5), 4.18 (d, $J = 6.4$, 1H, H3), 5.10 (t, $J = 6.4$, 1H, H4), 5.10 (dd, $J = 5.9$, 9.3, 1H, H6), 5.46 (d, $J = 2.7$ Hz, 1H, H1), 6.02 (dd, $J = 5.9$, 9.3, 1H, H7), 6.05 (d, $J = 9.3$, 1H, H8), 7.3−7.8 (m, overlapping with other phenyl signals, SiPh). (cf. **1** in C_6D_6: δ 1.53 (d, $J = 6.4$, 1H, H5), 3.56 (d, $J = 2.4$, 1H, H2), 4.52 (t, $J = 6.4$, 1H, H4), 4.59 (dd, $J = 5.9$, 9.3, 1H, H6), 4.86 (d, $J = 2.4$ Hz, 1H, H1), 4.99 (d, $J = 9.3$, 1H, H8), 5.37 (d, $J = 6.4$, 1H, H3), 5.46 (dd, $J = 5.9$, 9.3, 1H, H7)). Assignment was unequivocally carried out on the basis of the results of H−H COSY experiments. Attempted measurement of ^{13}C and ^{29}Si NMR spectra failed even below −40 °C, because of low solubility and thermal instability of this species.

X-ray Structure Determination. A crystal of **2c** was grown from a mixture of CH_2Cl_2 and hexane and mounted on a glass fiber. X-ray data were collected with a Rigaku AFC 7R diffractometer equipped with a graphite monochromator. Calculations were carried out using the Unics-III program system.[32] Neutral atomic scattering factors and anomalous dispersion effects were taken from ref 33. All of the data were corrected for absorption on the basis of empirical azimuthal scans.[34] The positions of the heavy atoms were determined from the Patterson map and expanded using Fourier tech-

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niques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **2c** were located in successive difference Fourier syntheses, and their atomic coordinates were refined.

Acknowledgment. A part of this study was financially supported by the Japan Society of Promotion of Science (Grant-in-aid for Scientific Research 10450343).

Supporting Information Available: Results of crystallographic studies, including tables of atomic coordinates and all bond distances and angles for **2c**, an SEC chart and ^{1}H, ^{13}C, H−H COSY, and H−C COSY spectra of the silylated poly-THF (M_n = 1500), and ^{1}H and ^{13}C NMR spectra of silylated poly-THF bearing CH_2D terminus. This material is available free of charge via the Internet at http://pubs.acs.org.

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