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Naoto Chatani

Naoto Chatani received his Ph.D. in 1984 from Osaka University under the guidance of Professors Noboru Sonoda and Shinji Murai. He subsequently joined the Institute of Scientific and Industrial Research at Osaka University as an Assistant Professor in Professor Terukiyo Hanafusa's laboratory. After postdoctoral studies with Professor Scott E. Denmark at the University of Illinois, Urbana-Champaign (1988-1989), he returned to Osaka University to join Professor Shinji Murai's laboratory as an Assistant Professor and was promoted to the rank of Associate Professor in 1992 and then Full Professor in 2003.

Shinji Murai

Shinji Murai received his Ph.D. in 1966 from Osaka University. He was appointed as an Assistant Professor at Osaka University in 1966, then Full Professor in 1989. He did a postdoc work in 1967 for Professor Robert West at the University of Wisconsin. In 2002, he moved to the Japan Science and Technology Agency (JST) as an executive fellow. In 2005, he was appointed as a Director, a Vice President, and then a Specially Appointed Professor at the Nara Institute of Science and Technology. Since 2013, he has also served as a Director for the Iwatani Cooperation R&D Center and since 2016 as an Outside Director.

Abstract

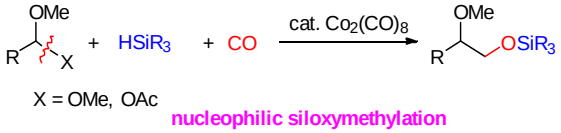
The $Co_2(CO)_8$-catalyzed reaction of acetals with hydrosilanes and CO under mild reaction conditions (an ambient temperature under an ambient CO pressure), leading to the production of vicinal diols is reported. A siloxymethyl group can be introduced via the cleavage of one of two alkoxy groups in the acetal. The effects of the types of hydrosilanes, acetals, solvents, and reaction temperatures on the yield of siloxymethylation products were examined in detail. The reactivity for hydrosilanes is as follows; $HSiMe_3$ > $HSiEtMe_2$ > $HSiEt_2Me$ > $HSiEt_3$. Hemiacetal esters are more reactive than dimethyl acetals. The polarity of the solvent used also has a significant effect on both the course of the reaction as well as the reaction rate. The site-selective siloxymethylation can be achieved in the case of cyclic acetals such as tetrahydrofuran (THF) and tetrahydropyrane (THP) derivatives, depending on the nature of the oxygen substituent attached adjacent to the oxygen atom in the ring. When 2-alkoxy THF or THP derivatives are used as substrates, the siloxymethylation takes place with cleavage of the ring C-O bond. In contrast, the reaction of 2-acetoxy THF or THP derivatives results in siloxymethylation with the cleavage of C-OAc bond. The ring-opening siloxymethylation of lactones was also examined.

Keywords: Carbon monoxide, Oxymethylation, Acetals

1. Introduction

Acetals and ketals are extensively used in organic synthesis, not only as protecting groups for aldehydes and ketones, but also in many organic synthetic transformations because the reactions afford a variety of valuable synthetic building blocks.[1] The reaction of acetals with organosilicon nucleophiles, such as enol silyl ethers, allylsilanes, silyl azide, hydrosilanes, and silyl cyanide has been of particular interest.[2] In these reactions, one of the alkoxide groups in an acetal is replaced by α-ketonyl, allyl, azide, hydride, or cyano groups, respectively. The high affinity of the silicon atom in these reagents toward the oxygen atom in an acetal is the driving force for the reaction to proceed. Although a variety of functional groups can be introduced into the acetal-carbon, the direct introduction of an oxymethyl group into an acetal, a conversion that would be of considerable interest to chemists, does not appear to have been reported. In addition, the use of oxymethylating reagents or their equivalents[3] in nucleophilic oxymethylation reactions do not appear to be applicable to acetals, although the oxymethylation of acetals would be expected to lead to the formation of 1,2-diol derivatives, which are useful compounds in organic synthesis.[4] The commonly employed methods for the synthesis of vicinal diol units include the hydrolytic ring opening of epoxides, the dihydroxylation of olefins, and the reduction of α-hydroxy ketones.[4] These methods all involve the manipulation of a functional group on already existing two carbon units. The oxymethylation of acetals would be expected to provide a new method for preparing vicinal diol derivatives that involves the concomitant formation of C-C bonds starting from acetals. Our methodology for the preparation of vicinal diols by oxymethylation is based on our previously reported findings that siloxymethylation with the cleavage of C-O bonds in oxygenated substrates can be achieved by a $Co_2(CO)_8/HSiR_3/CO$ catalytic system.[5] Although the carbonylation of oxygen-containing compounds is generally carried out under harsh reaction

conditions,[6] we demonstrated that our system is effective for the incorporation of CO into oxygenated compounds, such as tetrahydrofurans,[7] epoxides,[8] oxetanes,[9] glycosides,[10] benzyl acetates,[11] and orthoesters,[12] under mild reaction conditions. In our efforts to expand the scope of the $Co_2(CO)_8$/$HSiR_3$/CO catalytic cleavage of a C-O bond under exceptionally mild reaction conditions, we found a new type of siloxymethylation of acetals using a hydrosilane and CO (Scheme 1). In this paper, our progress in developing a method for introducing a siloxymethyl group with the cleavage of a C-O bond in acetals under mild reaction conditions is described. The present reaction is also applicable to the ring-opening siloxymethylation of lactones. As will be discussed later, the siloxymethylation proceeds in multi-step manner, carbonylation followed by addition of a hydrosilane. The overall process is equivalent to nucleophilic oxymethylation.



Scheme 1 $Co_2(CO)_8$-catalyzed siloxymethylation of acetals

2. Results and Discussion

Reaction of Formaldehyde Acetals. In initial experiments, we examined the $Co_2(CO)_8$-catalyzed reaction of formaldehyde acetals with hydrosilanes and CO and the results are summarized in Table 1. The reaction parameters examined include (i) the acetal structure, (ii) the hydrosilane substitution pattern, (iii) the solvent, (iv) the reaction temperature, and (v) the reaction time. To evaluate these reaction parameters, the reaction of various formaldehyde acetals was examined in detail under varying reaction conditions. The reaction of dimethoxymethane (**1**) reacted with $HSiMe_3$ and CO in C_6H_6 at 25 °C for 2 days gave (2-methoxyethoxy)trimethylsilane (**2a**) in 70% yield (entry 1). The use of $HSiEtMe_2$ and $HSiEt_2Me$ in place of $HSiMe_3$ resulted in the need for longer reaction times, and led to lower yields (entries 2 and 3). Thus, the reactivity of hydrosilane decreases as follows: $HSiMe_3$ > $HSiEtMe_2$ > $HSiEt_2Me$. It was found that hemiacetal ester **3** is much more reactive than **1**. Thus, the reaction of **3** with $HSiMe_3$ and CO in C_6H_6 was complete within 13 h, even at a temperature of 5 °C (entry 4), while the reaction of **1** required for 2 days at 25 °C (entry 1). The effect of the solvent used was also examined for the reaction of **3**. The use of CH_2Cl_2 led to a comparable yield of the product, even in a shorter reaction time than those obtained by the use of C_6H_6 (entries 5 vs 6 and 7 vs 8). A higher reactivity of hemiacetal esters were also shown by the reaction of **3** with $HSiEt_3$, which gave the corresponding product **2d** in 65% yield (entry 9), although $HSiEt_3$ proved to be unreactive in the reaction of **1**. The phenoxymethyl acetate (**4**) also reacted with hydrosilanes and CO to afford the corresponding ethylene glycol derivatives **5** in good yields (entries 10-13). Although the reaction of trioxane gave a mixture of numerous products (results not shown), 1,3-dioxolane (**6**) reacted with $HSiMe_3$ and CO to give the bis[2-(trimethylsiloxy)ethyl]ether (**7**), in which the C(2)-O(1) bond was selectively cleaved, no products from the cleavage of the C(4)-O(3) bond were observed (entry 14). There has been great interest in the synthesis of ethylene glycol from formaldehyde catalyzed by transition metal complexes. However, the reaction requires extremely harsh reaction conditions (high reaction temperatures and high syngas pressures), which limits the development of this process.[13] In contrast, the present reactions provide a new transformation of formaldehyde derivatives to ethylene glycol derivatives under extremely mild reaction conditions, i.e., at ambient temperature and under an ambient CO pressure. This result would have an impact on the development of the carbonylation of formaldehyde.

Table 1. $Co_2(CO)_8$-catalyzed reactions of formaldehyde acetals with hydrosilanes and CO.[a]

Entry	Acetal	Hydrosilane	Solvent	Temp, °C	Time	Product	Yield, %[b]
1	$CH_3OCH_2OCH_3$ (**1**)	$HSiMe_3$	C_6H_6	25	2 d	$CH_3OCH_2CH_2OSiMe_3$ (**2a**)	70
2	**1**	$HSiEtMe_2$	C_6H_6	25	6 d	$CH_3OCH_2CH_2OSiEtMe_2$ (**2b**)	60
3	**1**	$HSiEt_2Me$	C_6H_6	25	7 d	$CH_3OCH_2CH_2OSiEt_2Me$ (**2c**)	10
4	CH_3OCH_2OAc (**3**)	$HSiMe_3$	C_6H_6	5	13 h	**2a**	62
5	**3**	$HSiEtMe_2$	C_6H_6	15	14 h	**2b**	69
6	**3**	$HSiEtMe_2$	CH_2Cl_2	15	6 h	**2b**	61
7	**3**	$HSiEt_2Me$	C_6H_6	15	2 d	**2c**	75
8	**3**	$HSiEt_2Me$	CH_2Cl_2	15	1 d	**2c**	76
9	**3**	$HSiEt_3$	C_6H_6	40	5 d	$CH_3OCH_2CH_2OSiEt_3$ (**2d**)	65
10	$PhOCH_2OAc$ (**4**)	$HSiMe_3$	C_6H_6	15	2 d	$PhOCH_2CH_2OSiMe_3$ (**5a**)	80
11	**4**	$HSiEtMe_2$	C_6H_6	25	17 h	$PhOCH_2CH_2OSiEtMe_2$ (**5b**)	86
12	**4**	$HSiEt_2Me$	C_6H_6	25	3 d	$PhOCH_2CH_2OSiEt_2Me$ (**5c**)	82
13	**4**	$HSiEt_2Me$	CH_2Cl_2	25	1 d	$PhOCH_2CH_2OSiEt_2Me$ (**5c**)	97
14	 (**6**)	$HSiMe_3$	CH_2Cl_2	15	1 d	Me_3SiO O $OSiMe_3$ **7**	85

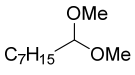
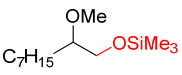
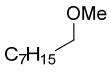
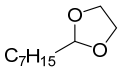
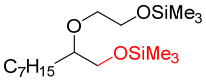
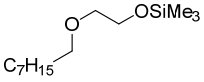
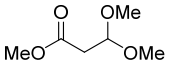
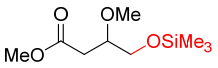
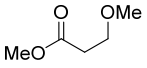
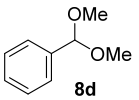
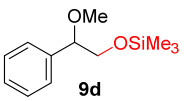
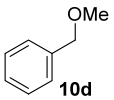
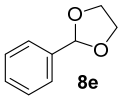
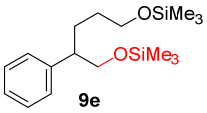
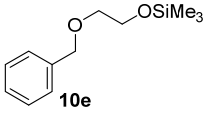
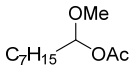
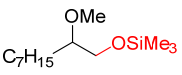
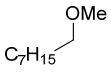
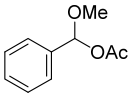
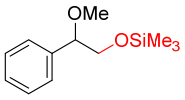
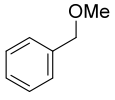
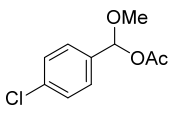
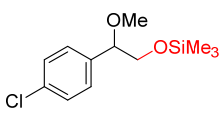
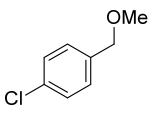
[a] Reaction conditions: acetal (2.5 mmol), $HSiMe_3$ (25 mmol, 2.9 mL) or other hydrosilanes (7.5 mmol), $Co_2(CO)_8$ (0.1 mmol, 34 mg), solvent (5 mL) under CO (1 atm). [b] GC yield.

Reaction of Acetals. To establish the scope and limitations of the present siloxymethylation reaction, we studied the $Co_2(CO)_8$-catalyzed reaction of acetals derived from both aliphatic and aromatic aldehydes and the results are summarized in Table 2. Because of its higher reactivity and the ease of removing it from the products, $HSiMe_3$ was used as the hydrosilane throughout this work. Although the only drawback to the use of $HSiMe_3$ is its high volatility (bp 6.7 °C), we were able to overcome this drawback by designing a unique type of syringe for handling volatile liquids.[8b] Octanal dimethyl acetal (**8a**) was reacted with $HSiMe_3$ and CO (1 atm) in C_6H_6 at 25 °C for 6 days to give ((2-methoxynonyl)oxy)trimethylsilane (**9a**), in

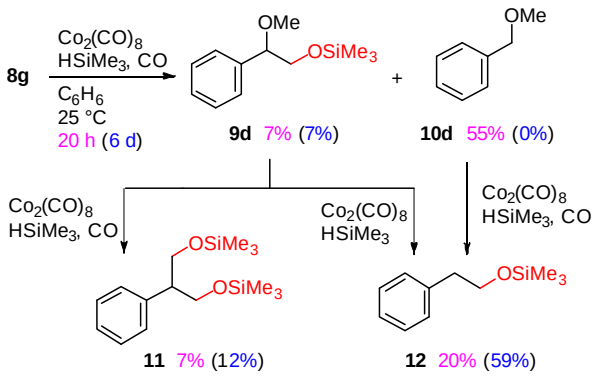
which one of the methoxy groups in **8a** was replaced with a siloxymethyl group, as a main product, in 86% yield. The major byproduct was methyl octyl ether (**10a**), which was produced by the reduction of **8a** by $HSiMe_3$.[14] The reaction of octanal ethylene acetal (**8b**) also afforded the corresponding siloxymethylation product **9b** in 60% yield. Curiously, trimethyl(2-(octyloxy)ethoxy)silane (**10b**) was formed as a sole product in 78% yield, with no **9b** being obtained, when CH_3CN was used as a solvent. This reaction represents a simple method for the transformation of acetals to ethers. The reaction of the ester-substituted acetal **8c** gave the corresponding diol derivative **9c** in good yield. Benzaldehyde acetals **8d** and **8e** also gave the corresponding products **9d** and **9e**, respectively.

The lower reaction temperatures are desirable in that the formation of a byproduct **10** can be avoided, which is formed by the reduction with $HSiMe_3$. The use of a lower temperature, however, requires much longer reaction times. To overcome this problem, the use of hemiacetal esters, which were already found to be much more reactive than the corresponding acetals as shown in Table 1, would be desirable. Thus, we examined the reaction of hemiacetal esters which are easily produced by the reaction of acetals with acid anhydrides.[15] The reaction of the hemiacetal esters, **8f-8h**, with $HSiMe_3$ and CO gave the corresponding siloxymethylation products **9a**, **9d**, and **9h**, respectively, in good yields. When the reaction was carried out with $HSiMe_3$ in C_6H_6 at 15 °C, the hemiacetal ester **8g** reacted much faster ($t_{1/2}$ = 3 h) than the dimethyl acetal **8d** ($t_{1/2}$ = 30 h), as expected. The reaction of the benzaldehyde hemiacetal acetate **8g** was studied under variable reaction conditions, some of the conditions are summarized in Table 2. The reaction of **8g** was also markedly affected by the reaction conditions, especially the reaction temperature, the structure of the hydrosilane, and solvent used. The use of CH_2Cl_2 as a solvent in the reaction of **8g** accelerated the rate of the reaction, however, the undesired reduction product **10d** was produced in higher yield When the reaction was carried out using $HSiEt_2Me$ as a hydrosilane in place of $HSiMe_3$ in C_6H_6 at 15 °C, the yield of the reduction product **10d** decreased markedly but the reaction required a much longer reaction time (data not shown). Generally, a lower reaction temperature gave a higher yield of **9d** and a higher reaction temperature gave more of the undesired product **10d**.

Table 2. $Co_2(CO)_8$-catalyzed reactions of acetals with $HSiMe_3$ and CO.[a]

 **8a**	C_6H_6	25 °C	6 d	 **9a**	86%	 **10a**	4%
	CH_2Cl_2	10 °C	5 d		71%		nd
 **8b**	CH_2Cl_2	10 °C	5 d	 **9b**	60%	 **10b**	nd
	CH_3CN	25 °C	2 d		nd		78%
 **8c**	C_6H_6	25 °C	5 d	 **9c**	48%	 **10c**	nd
 **8d**	CH_2Cl_2	15 °C	6 d	 **9d**	65%	 **10d**	nd
 **8e**	CH_2Cl_2	10 °C	7 d	 **9e**	67%	 **10e**	nd
 **8f**	C_6H_6	25 °C	5 h	 **9a**	56%	 **10a**	30%
	$C_6H_5CH_3$	0 °C	2 d		86%		nd
 **8g**	CH_2Cl_2	15 °C	2 h	 **9d**	32%	 **10d**	54%
	CH_2Cl_2	5 °C	9 h		67%		12%
	C_6H_6	15 °C	8 h		47%		34%
	$C_6H_5CH_3$	0 °C	2 d		75%		9%
	$C_6H_5CH_3$	-10 °C	4 d		84%		2%
 **8h**	C_6H_6	5 °C	1 d	 **9h**	80%	 **10h**	11%

[a] Reaction conditions: acetal (2.5 mmol), $HSiMe_3$ (25 mmol, 2.9 mL), $Co_2(CO)_8$ (0.1 mmol, 34 mg), solvent (5 mL), under CO (1 atm). GC yields based on an acetal. Nd refers to not determined.

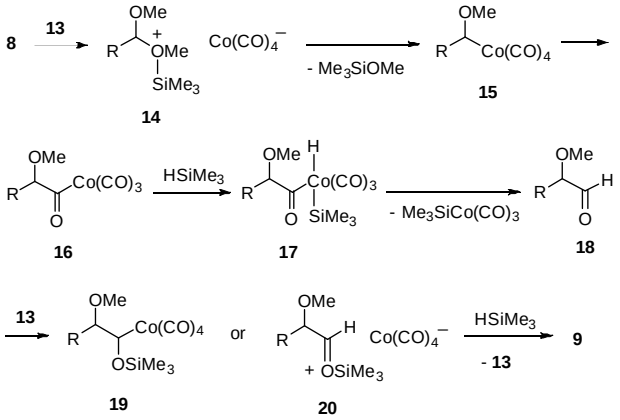


Scheme 2. The time-course study of **8g**.

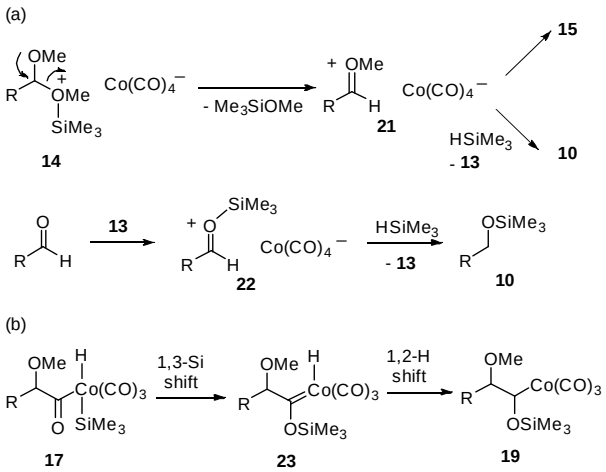
The time-course study of **8g** in C_6H_6 at 25 °C indicated that two other undesirable side-reaction products were formed, namely, **11** and **12** (Scheme 2). Product **12** is produced by further reactions, such as the $Co_2(CO)_8$-catalyzed siloxymethylation of **10d** with $HSiMe_3$ and CO[16] or by the reduction of **9d** with $HSiMe_3$. Product **11** appears to be formed by the siloxymethylation of the initial product **9d** through a path similar to that for the formation of **12** from **10d**. After 20 h, the product yields were as follows; **9d** 7% yield, **10d** 55%, **11** 7%, **12** 20%. When the reaction was run for 6 days, **12** was produced as a main product in 59% yield, along with **9d** (7%) and **11** (12%). In sharp contrast, **9d** was selectively formed in 84% yield when the reaction was carried out in toluene at -10 °C for 4 days (Table 2). Thus, a lower reaction temperature is the key to the successful transformation to siloxymethlation products.

Mechanistic Aspects. The silylcobalt complex $Me_3SiCo(CO)_4$ (**13**), which is known to be formed by the reaction of $Co_2(CO)_8$ with $HSiMe_3$,[17] is postulated as the key catalyst species in the present reaction. A possible reaction mechanism is shown in Scheme 3 on the basis of the knowledge obtained from our previous works,[7-12] Gladsyz's findings regarding the stoichiometric reaction of $Me_3SiMn(CO)_5$,[18] and some other studies on the stoichiometric reaction using $Me_3SiCo(CO)_4$.[19] The interaction of the catalytic active species **13** with the acetal **8** gives an α-alkoxyalkylcobalt complex **15**[20] via a silyloxonium ion intermediate **14**. The complex **15** undergoes a CO migratory insertion to give an acylcobalt complex **16**. The oxidative addition of $HSiMe_3$ to **16** followed by reductive elimination gives the aldehyde intermediate **18**. Under the reaction conditions used in this study, the aldehyde **18** would be susceptible to hydrosilylation to afford the final product **9** via **19** or **20**.

An alternative pathway to the alkylcobalt complex **15** involves the direct loss of methyl trimethysilyl ether from **14** leading to the formation of the oxocarbenium ion **21**, followed by the attack of $Co(CO)_4^-$ (Scheme 4a). We disfavor this pathway on the basis of the following experimental results. The $Co_2(CO)_8$-catalyzed reaction of hexanal with $HSiMe_3$ and CO under reaction conditions that are identical to those in the dimethylacetal of hexanal **8a** gave the predominant formation of a hydrosilylation product along with a small amount of the siloxymethylation product.[21] In the case of acetals, the generation of the alkylcobalt complex **15** would proceed via an S_N2 type reaction, where $Co(CO)_4^-$ attacks at **14** prior to the liberation of methyl silyl ether. In contrast, the reaction of aldehydes involves the initial interaction of **13** with an aldehyde leading to a silyloxonium ion **22**, which is easily reduced by $HSiMe_3$ to give the hydrosilylation product **10**. If the complex **15** were formed via **21**, the reduction product **10** should be the major product, as expected from the results for hexanal. However, this is not the case. A hydrosilane can react with **21** or **22**, but not with **14**. The use of a polar solvent such as CH_2Cl_2 resulted in an increase in the yield of **10**. In a polar solvent, **14** is easily converted to an oxocarbenium ion **21** because **21** is stabilized by a polar solvent.



Scheme 3. A proposed mechanism.

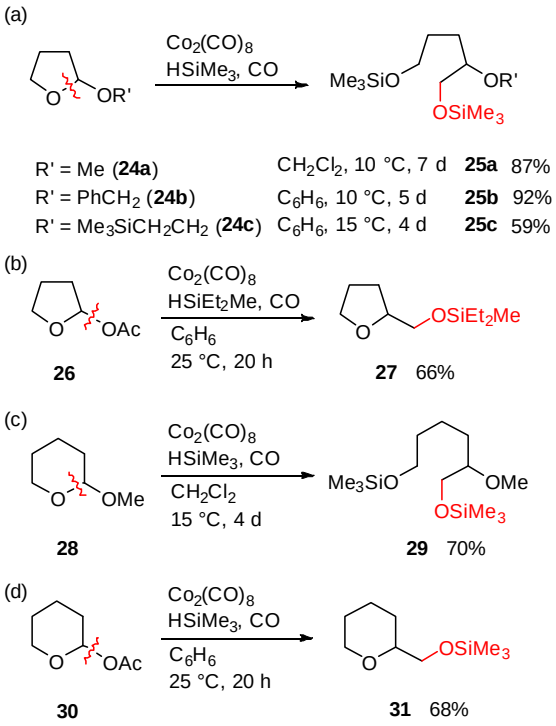


Scheme 4. Alternative reaction pathways.

The next question is whether or not the reaction proceeds via an aldehyde **18** as an intermediate. Wegman reported that the reaction of an acetylcobalt complex, $CH_3COCo(CO)_4(PPh_3)$, with $HSiEt_3$ gave CH_3CHO and $Et_3SiCo(CO)_3(PPh_3)$.[19a] These results support our proposed mechanism. However, in a later study, Markó and coworkers reported that $HSiEt_3$ reacts with $Me_2CHCOCo(CO)_4$ to give, not only the expected Me_2CHCHO and $Et_3SiCo(CO)_4$ but also $Me_2C{=}CHOSiEt_3$ and $Me_2CHCH_2OSiEt_3$ as the organic products, which were not formed from Me_2CHCHO.[19b] On the basis of their results, our reaction mechanism can be reconsidered as shown in Scheme 4b. Thus, a key step is a 1,3-Si shift from **17** leading to the formation of the carbenoid complex **23**, which undergoes 1,2-H shift to give the alkyl Co complex **19**. This reaction pathway is similar to that already proposed by Gradysz for analogous Mn complexes.[18] These alternative paths cannot be excluded at this point.

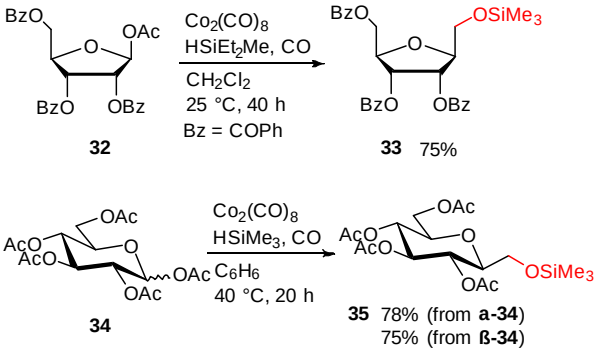
Reaction of Cyclic Acetals. The siloxymethylation reported herein is promising as a synthetic method for

introducing an siloxymethyl group into an organic molecule. It was found that the site-selective siloxymethylation can be achieved by taking advantage of differences in reactivity between a cyclic acetal and a cyclic hemiacetal ester (Scheme 6). In the case of 2-alkoxy tetrahydrofuran derivatives **24**, the siloxymethylation occurred with the site-selective cleavage of a ring C-O bond. Thus, **24** catalytically reacted with $HSiMe_3$ and CO (1 atm) to afford the 1,2,5-triol derivatives **25a**-**25c** (Scheme 6a).[22] In contrast, the reaction of 2-acetoxy tetrahydrofuran **26** gave the diethylmethylsilyl ether of the tetrahydrofurfuryl alcohol **27**, with the ring remaining intact (Scheme 6b). The difference in the reaction site between **24** and **26** is due to the difference between the ability of leaving groups. Thus, an acetoxy group in **26** acts a good leaving group as a silyl acetate. The reaction of tetrahydropyrane derivatives **28** and **30** also resulted in the same site-selective reaction (Scheme 6c and d).



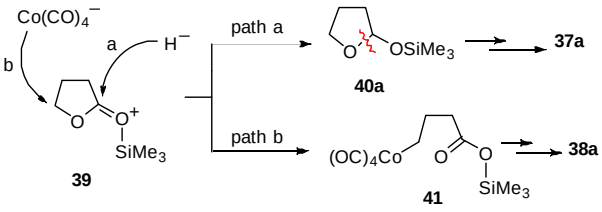
Scheme 6. Site-selective siloxymethylation.

The siloxymethylation reactions of cyclic acetals shown in Scheme 6b and 6d were applicable to the preparation of *C*-nucleocide (Scheme 7).[10] The acetoxy group at the anomeric center of a sugar can be selectively replaced with a siloxymethyl group. The stereoselective substitution of an acetoxy group at the C-1 position of a furanose ring by a siloxymethyl group upon the reaction of **32** with $HSiEt_2Me$ and CO gave **33** in a stereoselective manner indicative of participation by the neighboring 3-benzoyl group. In the reaction of glucosyl acetate **34**, the siloxymethyl group is introduced predominantly from the β-face regardless the stereochemistry of the starting materials. The reaction of the α-isomer of **34** gave β-**35** in 78% yield and the β-isomer also gave β-**35** in 75% yield. The stereochemistry of the formation of glucose derivative **35** is consistent with participation by the neighboring 3-acetoxy group.



Scheme 7. Siloxymethylation of glycosyl acetates.

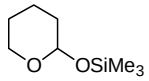
Reaction of Lactones. As described above, the reaction of cyclic acetals or hemiacetal esters with hydrosilanes and CO proceeded smoothly to yield siloxymethylation products in a site-selective manner. In a further extension of the present siloxymethylation, the reaction of lactones with hydrosilanes and CO was examined. As a result, two types of the products, 1,2,ω-triols **37** and ω-siloxy acids **38**, were obtained, the ratio being dependent on the structure of lactones being used. The results are summarized in Table 3. The reaction of the γ-butyrolactone (**36a**) with $HSiMe_3$ and CO in C_6H_6 at 15 °C for 7 days gave **37a** in 60% yield along with 6% of **38a.** The product distribution was influenced by the reaction temperature employed. Higher temperatures favored the formation of **38a**. The reaction at 40 °C gave **38a** in 31% yield as the main product, although the total yield was not high. The course of the reaction is rationalized by the consideration as shown in Scheme 8. The product **37a** is apparently formed via the intermediacy of 2-siloxytetrahydrofuran **40a** which is formed by the hydrosilylation of the carbonyl group in **36a** via path a.[23] Ring-opening siloxymethylation then takes place from **40a** via steps similar to the formation of **25** from **24** (Scheme 6a). The attack of $Co(CO)_4^-$ at the γ-carbon in **39** (path b) gives the alkylcobalt intermediate **41**, which subsequently produces **38a**. At lower temperatures, path a is faster than path b.



Scheme 8. The reaction paths to **37a** and **38a**.

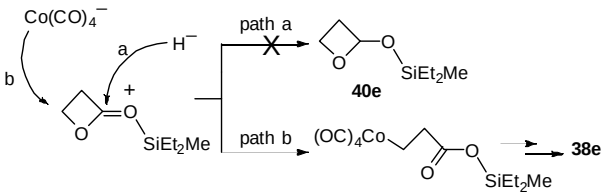
In contrast to the parent γ-butyrolactone **36a**, the reaction of γ-substituted γ-lactones **36b** and **36c** selectively gave 1,2,5-triol derivatives **37b** and **37c**, and no 4-siloxy acids **38b** and **38c** were obtained. This can be attributed to the steric hindrance of the γ-carbon of the lactones, which inhibits path b. The reaction of the δ-valerolactone (**36d**) with $HSiMe_3$ and CO gave the corresponding 1,2,6-triol **37d** in 60% yield. It should be noted that 2-(trimethylsiloxy)tetrahydropyrane (**40d**) was formed as the main product in 66% yield when hexane was used as the solvent at 25 °C. This result provides strong evidence that supports our mechanistic proposal that **40a** and **40d** are intermediates in the production of **37a** and **37d**. In contrast to the reaction of a δ-lactone, a 2-siloxytetrahydrofuran, such as **40a**, could not be detected in the reaction of γ-lactones, indicating that

the ring-opening of the five-membered ether **40a** is much easier than that for the six-membered ether **40d**.



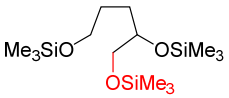
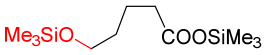
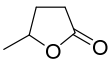
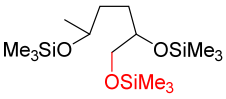
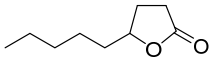
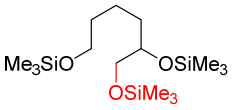
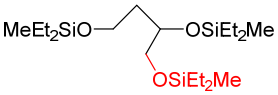
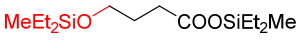
40d

Curiously, in the reaction of β-lactones **36e**, 4-siloxybutyric acid derivative **38e** was obtained as a single product, with no evidence for the formation of **37e**. The difference in the product distribution between γ-lactones and β-lactones is due to their ring strain (Scheme 9). The hydrosilylation of a carbonyl group leading to 2-siloxyoxetane **40e** (path a), which still has ring strain, cannot compete with path b where the ring strain is released.



Scheme 9. The reaction paths in β-lactone **36e**.

Table 3. $Co_2(CO)_8$-catalyzed reactions of lactones with hydrosilanes and CO.[a]

Lactone	Hydrosilane	Temp (°C)	Time	Products [b]			
 **36a**	$HSiEt_2Me$	25	20 h	 **37a**	NR	 **38a**	NR
	$HSiMe_3$	15	7 d		60		6
	$HSiMe_3$	25	20 h		23		26
	$HSiMe_3$	40	20 h		10		31
 **36b**	$HSiMe_3$	15	7 d	 **37b**	75		
 **36c**	$HSiMe_3$	15	7 d	 **37c**	61		
 **36d**	$HSiMe_3$	15	7 d	 **37d**	60		
 **36e**	$HSiEt_2Me$	25	20 h	 **37e**	0	 **38e**	70

[a] Reaction conditions: lactone (2.5 mmol), $HSiMe_3$ (25 mmol, 2.9 mL) or $HSiEt_2Me$ (12.5 mmol), $Co_2(CO)_8$ (0.1 mmol, 34 mg), C_6H_6 (5 mL), under CO (1 atm). GC yields based on a lactone. NR refers to no reaction.

4. Conclusion

The incorporation of one molecule of CO into acetals and lactones proceeds under exceptionally mild reaction conditions (ambient CO pressure and ambient temperature) with the site-selective cleavage of the C-O bonds in acetals and lactones. In the view of organic synthesis, the present reaction provides a new and convenient method for nucleophilic introduction of a siloxymethyl group at an acetal-carbon and for the preparation of vicinal diol derivatives. The introduced siloxymethyl group can easily be converted into useful functional groups, such as hydroxymethyl,[24] acetoxymethyl,[25] halomethyl,[26] aldehyde,[27] and ester groups.[28]

4. Experimental

General Procedures. Bulb-to-bulb distillations were performed on a Sibata glass tube oven GTO-250R; boiling points (bp) refer to air bath temperature and are uncorrected. ^1H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer in CCl_4 or a JEOL GSX-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, c = complex, and br = broad), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Shimadzu IR-400 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a Hitachi Model RMU-6E spectrometer with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimadzu GC-3BF gas chromatograph, equipped with a flame ionization detector, using a 6-m x 3-mm stainless steel column packed with 5% Silicone

OV-1 on 60-80-mesh Chromosorb W. Benzene and toluene were distilled from sodium-lead alloy. CH_2Cl_2 and CH_3CN were distilled from CaH_2. $Co_2(CO)_8$ was obtained from Strem Chemicals, Inc., and purified by low-temperature recrystallization from hexane. The acetals **8a**, **8c**, and **8d** were prepared by the acetalization of the corresponding aldehydes with trimethyl orthoformate.[18b] The acetals **8b** and **8e** was prepared from the corresponding aldehydes and ethylene glycol.[29] The hemiacetal esters **3** and **8f-8h** were prepared by the treatment of corresponding dimethyl acetals with Ac_2O in the presence of *p*-TsOH.[15] Compound **4** was prepared according to a literature method.[30] Tetrahydrofuran derivatives **24b** and **24c** were prepared according to a literature method.[31] Compounds **26** and **30** were according to a literature method.[32] Compounds **1**, **6**, **24a**, **28**, and **36a-36e** were commercially available. $HSiMe_3$ was prepared from Me_3SiCl and $LiAlH_4$ following a literature procedure.[33] We designed a special apparatus shown in Figure 1 for handling $HSiMe_3$, which has low boiling point (bp 6.7 °C). This apparatus may be conveniently used for any other low boiling compounds that have a vapor pressure below 20 atm at room temperature. It is composed of a stainless steel reservoir A in sizes from 50 to 200 mL, a needle valve B, a thick-walled calibrated glass barrel of 10 mm x 150 mm C, a needle bulb having a needle locking tip (Luer-Lok) D, and a Luer-Lok syringe needle E. The $HSiMe_3$ is transferred into A through B and an appropriate connector by trap-to-trap distillation. (container A should not be more than 80% filled for trap-to-trap distillation for safety issues.). C, D, and E are then connected to A, but B is closed. Positioning the apparatus with E in an upward direction, the needle valves D and B are opened in this order and remain open until the glass tube C is filled with $HSiMe_3$ vapor. After D is closed, the entire assembly is held upside down to allow the $HSiMe_3$ to be transferred into C as a liquid. Slightly cooling C can be helpful. When the desired amount of $HSiMe_3$ is collected in C, valve B is closed. The needle E is then inserted through the septum of the reaction vessel, and the liquid $HSiMe_3$ can be injected by opening the bulb D similar to the operation when a normal syringe technique is used. The entire apparatus (A-E) can be conveniently disassembled for use in a subsequent procedure.

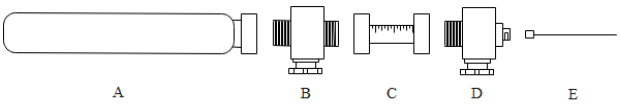


Fig. 1. An apparatus for handling $HSiMe_3$.

General Procedure for the $Co_2(CO)_8$-Catalyzed Reaction of Acetals with Hydrosilane and Carbon Monoxide. In a 10-mL reaction flask with an efficient condensed (dry-ice-CH_3OH) was placed $Co_2(CO)_8$ (0.1 mmol, 34 mg), after the flask was flashed with CO (1 atm from a stock balloon), $HSiMe_3$ (25 mmol, 2.9 mL) was added using a pressure syringe at 25 °C.[34] After 5 min, benzene (5 mL) and octanal dimethylacetal (**8a**) (2.5 mmol, 435 mg) were added and the mixture was stirred at 25 °C (bath temperature, under reflux of $HSiMe_3$) for 6 days under CO (1 atm). GC analysis showed that [(2-methoxynonyl)oxy]trimethylsilane (**9a**) was formed in 86% yield. Kugel rohr distillation (110-120 °C/10 Torr) gave essentially pure **9a** (410 mg, 67% yield). An analytical sample was obtained by preparative GC purification (Silicone OV-1).

2,2,10,10-Tetramethyl-3,6,9-trioxa-2,10-disilaundecane (7). Bp 100-110 °C (11 Torr); ^{1}H NMR δ 0.12 (s, 18 H), 3.44 (dd, *J* = 4, 6 Hz, 4 H), 3.68 (dd, *J* = 4, 6 Hz, 4 H); IR (neat) 2950, 2850, 1460, 1250, 1140, 1100, 940, 840, 750, 680; MS, *m*/*z* (relative intensity) 250 (M^+, 0), 235 (4), 191 (5), 147 (14), 117 (52), 103 (14), 73 (100); Anal. Calcd for $C_{10}H_{26}O_3Si_2$: C, 47.95; H, 10.46. Found: C, 47.60; H, 10.59.

((2-Methoxynonyl)oxy)trimethylsilane (9a). Bp 110-120 °C (10 Torr); ^{1}H NMR δ 0.08 (s, 9 H), 0.86 (t, *J* = 6 Hz, 3 H), 1.09-1.45 (m, 12 H), 2.87-3.17 (m, 1 H), 3.29 (s, 3 H), 3.35-3.55 (m, 2 H); IR (neat) 2920, 2850, 1470, 1460, 1250, 1110, 1080, 870, 840, 750; MS, *m*/*z* (relative intensity) 246 (M^+, 0), 231 (9), 143 (100), 111 (37), 89 (29), 73 (37), 69 (57); Anal. Calcd for $C_{13}H_{30}O_2Si$: C, 63.35; H, 12.27. Found: C, 63.21; H, 12.44.

5-Heptyl-2,2,10,10-tetramethyl-3,6,9-trioxa-2,10-disilaundecane (9b). Bp 140-150 °C (2 Torr); ^{1}H NMR δ 0.10 (s, 18 H), 0.90 (t, *J* = 6 Hz, 3 H), 1.14-1.64 (m, 12 H), 3.04-3.70 (m, 7 H, CH); IR (neat) 2930, 2870, 1470, 1260, 1110, 950, 850, 760, 690; MS, *m*/*z* (rel intensity) 348 (M^+, 0), 245 (49), 201 (34), 117 (100), 103 (10), 73 (7); Anal. Calcd for $C_{17}H_{40}O_3Si_2$: C, 58.56; H, 11.56. Found: C, 58.62; H, 11.72.

Trimethyl(undecyloxy)silane (10b). Bp 120-130 °C (10 Torr); ^{1}H NMR δ 0.08 (s, 9 H), 0.88 (t, *J* = 6 Hz, 3 H), 1.12-1.58 (m, 12 H), 3.33 (t, *J* = 6 Hz, 4 H), 3.60 (t, *J* = 6 Hz, 2 H); IR (neat) 2920, 2850, 1460, 1250, 1100, 940, 840, 750; MS, *m*/*z* (rel intensity) 246 (M^+, 0), 231 (30), 119 (100), 103 (49), 75 (61), 73 (62), 57 (48); Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 63.35; H, 12.27. Found: C, 63.26; H, 12.42.

Methyl 3-methoxy-4-((trimethylsilyl)oxy)butanoate (9c). Bp 100-120 °C (20 Torr); ^{1}H NMR δ 0.11 (s, 9 H), 2.50-2.60 (m, 2 H), 3.41 (s, 3 H), 3.69 (s, 3 H), 3.56-3.71 (m, 3 H); IR (neat) 2960, 2836, 1744, 1442, 1374, 1202, 1254, 1200, 1166, 1116, 1032, 1004, 956, 876, 844, 752, 690; MS, *m*/*z* 205 (M^+-15); Anal. Calcd for $C_9H_{20}O_4Si$: C, 49.06; H, 9.15. Found: C, 48.78; H, 9.22.

(2-Methoxy-2-phenylethoxy)trimethylsilane (9d). Bp 100-120 °C (10 Torr); ^{1}H NMR δ 0.07 (s, 9 H), 3.29 (s, 3 H), 3.64 (dd, *J* = 10.5, 4 Hz, 2 H), 3.75 (dd, *J* = 10.5, 7.5 Hz, 2 H), 4.25 (dd, *J* = 7.5, 4 Hz, 1 H), 7.29-7.35 (m, 5 H, Ph); IR (neat) 3060, 3030, 2950, 2870, 2825, 1500, 1460, 1360, 1250, 1210, 1180, 1100, 1060, 1040, 840, 760, 700; MS, *m*/*z* (rel intensity) 224 (M^+, 1), 209 (1), 121 (100), 89 (14), 73 (13). Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.22; H, 9.10.

2,2,10,10-Tetramethyl-5-phenyl-3,9-dioxa-2,10-disilaundecane (9e). Bp 100-120 °C (2 Torr); ^{1}H NMR δ 0.02 (s, 9 H, Me_3Si), 0.08 (s, 9 H), 3.26-3.80 (m, 6 H), 4.18-4.36 (m, 1 H); IR (neat) 3070, 3030, 2950, 2860, 1495, 1455, 1250, 1100, 840, 750, 700; MS, *m*/*z* (rel intensity) 326 (M^+, 0), 223 (61), 189 (30), 147 (25), 117 (54), 73 (100); Anal. Calcd for $C_{16}H_{30}O_3Si$: C, 58.84; H, 9.26. Found: C, 59.04; H, 9.09.

(2-(4-Chlorophenyl)-2-methoxyethoxy)trimethylsilane (9h). Bp 100-120 °C (2 Torr); ^{1}H NMR δ 0.04 (s, 9 H), 3.24 (s, 3 H), 3.44 (dd, *J* = 11, 6 Hz, 2 H), 3.64 (dd, *J* = 11, 7 Hz, 2 H), 4.10 (dd, *J* = 7, 6 Hz, 1 H), 7.29-7.35 (m, 4 H, Ph); IR (neat) 2950, 1600, 1490, 1410, 1255, 1210, 1100, 850; MS, *m*/*z* (rel intensity) 258 (M^+), 155 (100), 103(10), 89 (28), 73 (30).

5-Methoxy-2,2,10,10-tetramethyl-3,9-dioxa-2,10-disilaundecane (25a). Bp 100-120 °C (10 Torr); ^{1}H NMR δ 0.08 (s, 18 H), 1.28-1.64 (m, 4 H), 2.96-3.20 (m, 1 H), 3.32 (s, 3 H), 3.36-3.64 (m, 4 H): IR (neat) 2950, 2900, 2870, 2830, 1450, 1390, 1250, 1090, 940, 840, 750, 690; MS, *m*/*z* (rel intensity) 278 (M^+, 0), 175 (20), 85 (100), 73 (35), 71 (91); Anal. Calcd for $C_{12}H_{30}O_3Si_2$: C, 51.75; H, 10.86. Found: C, 51.70; H, 10.83.

5-(Benzyloxy)-2,2,10,10-tetramethyl-3,9-dioxa-2,10-disilaundecane (25b). Bp 140-150 °C (1 Torr); ^{1}H NMR δ 0.08 (s, 18 H), 1.28-1.68 (m, 4 H), 3.24-3.70 (m, 5 H), 4.52 (m, 2 H), 7.19 (s, 5 H); IR (neat) 3070, 3040, 2950, 2860, 1945, 1870, 1810, 1500, 1460, 1390, 1355, 1250, 1210, 1100, 840, 750; MS, *m*/*z* (rel intensity) 354 (M^+, 0), 251 (4), 158 (13), 143 (10), 103 (10), 91 (100), 73 (21); Anal. Calcd for $C_{18}H_{34}O_3Si_2$: C, 60.96;

H, 9.6. Found: C, 60.82; H, 9.78.

2,2,11,11-Tetramethyl-7-(((trimethylsilyl)oxy)methyl)-3,8-dioxa-2,11-disiladodecane (25c). Bp 130-140 °C (2 Torr); ^{1}H NMR δ 0.01 (s, 9 H), 0.09 (s, 9 H), 0.82 (t, *J* = 7 Hz, 2 H), 1.29-1.65 (m, 4 H), 3.01-3.67 (m, 7 H); IR (neat) 2960, 2900, 2870, 1250, 1000, 940, 850, 750, 690; MS, *m*/*z* (rel intensity) 364 (M^+, 0), 233 (12), 143 (94), 101 (13), 73 (100); Anal. Calcd for $C_{16}H_{40}O_3Si_3$: C, 52.69; H, 11.05. Found: C, 52.76; H, 11.24.

5-Methoxy-2,2,11,11-tetramethyl-3,10-dioxa-2,11-disiladodecane (29). Bp 110-120 °C (10 Torr); ^{1}H NMR δ 0.06 (s, 18 H), 1.20-1.56 (m, 6 H), 2.88-3.12 (m, 1 H), 3.26 (s, 3 H), 3.32-3.60 (m, 4 H); IR (neat) 2950, 2900, 2850, 2820, 1470, 1440, 1390, 1250, 1100, 840, 750, 660; MS, *m*/*z* (rel intensity) 293 (M^+, 0), 189 (13), 103 (14), 99 (14), 85 (100), 73 (54); Anal. Calcd for $C_{13}H_{32}O_3Si_2$: C, 53.37; H, 11.02. Found: C, 53.60; H, 11.18.

Trimethyl((tetrahydro-2H-pyran-2-yl)methoxy)silane (31). ^{1}H NMR δ 0.10 (s, 3 H), 0.61 (q, *J* = 7.8 Hz, 4 H), 0.96 (t, *J* = 7.8 Hz, 6 H), 1.48-1.92 (m, 6 H), 3.43-3.51 (m, 1 H), 2.92-3.97 (m, 1 H), 4.88 (dd, *J* = 6, 3 Hz, 1 H); IR (neat) 2956, 2884, 1462, 1446, 1418, 1397, 1352, 1324, 1273, 1254, 1202, 1166, 1134, 1118, 1089, 1030, 1024, 992, 934, 910, 874, 846, 828, 802, 770, 690; MS, *m*/*z* (rel intensity) 202 (M^+, 0), 174 (30), 117 (10), 99 (100); Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.55; H, 11.14.

2,2,10,10-tetramethyl-5-((trimethylsilyl)oxy)-3,9-dioxa-2,10-disilaundecane (37a). Bp 90-100 °C (3 Torr); ^{1}H NMR δ 0.08 (s, 27 H), 1.16-1.76 (m, 4 H), 3.34 (d, *J* = 6 Hz, 2 H), 3.42-3.76 (m, 3 H); IR (neat) 2950, 2890, 2850, 1440, 1390, 1250, 1100, 840, 750, 680; MS, *m*/*z* (rel intensity) 336 (M^+, 0), 233 (17), 147 (17), 143 (100), 85 (13), 73 (63); Anal. Calcd for $C_{19}H_{36}O_3Si_3$: C, 49.94; H, 10.78. Found: C, 49.96; H, 10.87.

2,2,4,10,10-Pentamethyl-7-((trimethylsilyl)oxy)-3,9-dioxa-2,10-disilaundecane (37b). Bp 90-100 °C (2 Torr); ^{1}H NMR δ 0.00 (s, 27 H), 1.00 (d, *J* = 6 Hz, 3H), 1.16-1.44 (m, 4 H), 3.25 (d, *J* = 5 Hz, 2 H), 3.36-3.72 (m, 2 H); IR (neat) 2950, 2900, 2860, 1450, 1380, 1250, 1080, 840, 750, 680; MS, *m*/*z* (rel intensity) 348 (M^+, 0), 247 (15), 157 (100), 147 (14), 117 (15), 73 (49); Anal. Calcd for $C_{20}H_{38}O_3Si_3$: C, 51.37; H, 10.92. Found: C, 51.41; H, 11.20.

2,2,10,10-Tetramethyl-4-pentyl-7-((trimethylsilyl)oxy)-3,9-dioxa-2,10-disilaundecane (37c). Bp 100-120 °C (1 Torr); ^{1}H NMR δ 0.08 (s, 27 H), 0.87 (t, *J* = 5 Hz, 3 H), 1.12-1.56 (m, 12 H), 3.30 (d, *J* = 5 Hz, 2 H), 3.38-3.68 (m, 2 H); IR (neat) 2950, 2860, 1450, 1380, 1250, 1080, 840, 750, 680; MS, *m*/*z* (rel intensity) 406 (M^+, 0), 303 (23), 213 (100), 173 (25), 129 (44), 73 (47); Anal. Calcd for $C_{19}H_{46}O_3Si_3$: C, 56.09; H, 11.40. Found: C, 56.27; H, 11.61.

2,2,11,11-Tetramethyl-5-((trimethylsilyl)oxy)-3,10-dioxa-2,11-disiladodecane (37d). Bp 100-110 °C (10 Torr); ^{1}H NMR δ 0.06 (s, 27 H), 1.16-1.56 (m, 6 H), 3.22-3.34 (m, 2 H), 3.34-3.58 (m, 3 H); IR (neat) 2950, 2870, 1460, 1440, 1390, 1250, 1100, 860, 750, 690; MS, *m*/*z* (rel intensity) 350 (M^+, 0), 247 (15), 157 (16), 147 (31), 129 (21), 85 (100), 73 (72); Anal. Calcd for $C_{20}H_{38}O_3Si_3$: C, 51.37, H, 10.92. Found: C, 51.60; H, 11.19.

Diethyl(methyl)silyl 4-((diethyl(methyl)silyl)oxy)butanoate (38e). Bp 110-120 °C (2.2 Torr); ^{1}H NMR δ 0.02 (s, 3 H, Me_3Si), 0.19 (s, 3 H), 0.37-1.19 (m, 20 H), 1.69 (quit, *J* = 7 Hz, 2 H), 2.27 (t, *J* = 7 Hz, 2 H), 3.54 (t, *J* = 7 Hz, 2 H); IR (neat) 2950, 2870, 1720, 1465, 1420, 1260, 1190, 1100, 1010, 800, 760; MS, *m*/*z* (rel intensity) 304 (M^+, 0), 289 (6), 275 (100), 189 (71), 161 (71), 101 (29), 73 (43); Anal. Calcd for $C_{14}H_{32}O_3Si_2$: C, 55.21; H, 10.59. Found: C, 55.25; H, 10.65.

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