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STUDIES ON THE RHODIUM- AND IRIDIUM-CATALYZED REACTIONS WITH CARBON MONOXIDE AND HYDROSILANES

SHIN-ICHI IKEDA

OSAKA UNIVERSITY

1993

STUDIES ON THE RHODIUM- AND IRIDIUM-CATALYZED REACTIONS WITH CARBON MONOXIDE AND HYDROSILANES

（一酸化炭素・ヒドロシランを用いたロジウム
およびイリジウム触媒反応に関する研究）

SHIN-ICHI IKEDA

OSAKA UNIVERSITY

1993

Preface

The studies presented in this thesis have been carried out under the direction of Professor Shinji Murai at the Department of Applied Chemistry, Faculty of Engineering, Osaka University. The thesis is concerned with the rhodium- and iridium-catalyzed reactions with carbon monoxide and hydrosilanes.

I would like to express my deepest gratitude to Professor Shinji Murai for his guidance, insight, encouragement, and inspiration throughout my career as a graduate student.

I would like to acknowledge Associate Professor Naoto Chatani for his helpful suggestions and stimulating discussions.

I would like to thank Dr. Kouichi Ohe for his useful advice and continuing encouragement.

I would like to thank Mr. Yasuteru Kajikawa for his contribution to this work.

The lab atmosphere was greatly enhanced by the friendships with Mr. Yoshiya Fukumoto, Mr. Masa-aki Shinohara and many others.

I would like to thank Professor Shinzi Kato and Associate Professor Toshiaki Murai at Department of Chemistry, Faculty of Engineering, Gifu University, for their continuing encouragement.

Finally, I would like to express my thanks to my parents for their perpetual support.

Suita, Osaka
January 1993

Shin-ichi Ikeda

List of Publications

The contents of this thesis are composed of the following papers.

1. Regioselective Incorporation of CO into Enamines by Rhodium-Catalyzed Reaction with a Hydrosilane and CO
   Ikeda, S.; Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S.
   J. Org. Chem. **1992**, *57*, 2.

2. Rhodium-Catalyzed Reaction of *N, N*- and *N, O*-Acetals with a Hydrosilane and Carbon Monoxide
   Ikeda, S.; Chatani, N.; Murai, S.
   Organometallics **1992**, *11*, 3494.

3. Conversion of Alkenes to Enol Silyl Ethers of Acylsilanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide
   Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S.
   J. Am. Chem. Soc. **1992**, *114*, 9710.

Supplementary List of Publications

1. New Thioacylating Reagents: 1-Methyl-2-thioacylthiopyridinium Salts
   Kato, S.; Masumoto, H.; Ikeda, S.; Ito, M.; Murai, T.; Ishihara, H.
   Z. Chem. **1990**, *30*, 67.

2. A Convenient Synthesis of 5-Alkyl- and 5-Aryl-1, 2, 3, 4-thiatriazols
   Ikeda, S.; Murai, T.; Ishihara, H.; Kato, S.
   Synthesis **1990**, 415.

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Chapter 2 The Iridium-Catalyzed Reaction of Olefins with Carbon Monoxide and a Hydrosilane

General Introduction

Carbon monoxide (CO) is one of the most versatile reagents used in several synthetic and industrial processes. Transition metal-catalyzed carbonylation reactions utilizing CO have been the subject of numerous studies. Particularly, hydrofomylation (i.e. the oxo reaction), which produces aldehydes from the reaction of olefins with carbon monoxide and molecular hydrogen, have been utilized in both organic synthesis and industry.[1] On the other hand, it is well known that the reactions of hydrosilane (i.e. $HSiR_3$) with transition metal complexes parallel those of molecular hydrogen. For example, hydrosilylation, the catalyzed addition of $HSiR_3$ to an olefin, is formally analogous to catalytic hydrogenation.[2] Based on similar reactivity of molecular hydrogen and hydrosilanes with transition metal complexes, it is responsible to expect that new catalytic reactions could be developed utilizing hydrosilanes, than molecular hydrogen, in hydro-formylations. In fact, Murai and co-workers, have recently discovered new catalytic reactions utilizing a cobalt carbonyl [$Co_2(CO)_8$] with carbon monoxide and hydrosilane.[3]

The prime objective of this research was to develop new catalytic reactions using the other transition metal complexes (i.e. Rh and Ir) with carbon monoxide and hydrosilanes. This thesis consists of two chapters.

Chapter 1 deals with rhodium-catalyzed reactions of nitrogen-containing compounds with carbon monoxide and a hydrosilane. Interestingly, these nitrogen-containing substrates do not react with $Co_2(CO)_8$ catalytic system. The presence of an amino group in the substrates is important in the catalytic CO-incorporation. Also, the reaction of enamines as a substrate results in a regioselective incorporation of carbon monoxide. Further, the use of *N*, *N*- and *N*, *O*-

acetals provides a new route to CO-incorporation in the catalytic reaction system.

Chapter 2 deals with a novel iridium-catalyzed conversion of olefins to enol silyl ethers of acylsilanes in the presence of carbon monoxide and hydrosilane. The unprecedented reaction resulted in regioselective introduction of a siloxy(silyl)methylene unit haveing the silicon-carbon bond into the terminal carbon atom of the olefins.

References

(1) (a) Falbe, J. *New Synthesis with Carbon Monoxide*; Springer-Varlag: New York, 1980. (b) Sneeden, R. P. A.; Villeurbanne, N. R. S. In *Comprehensive Organometallic Chemistry:* Wilkinson, G., Ed.; Pergamon Press: Oxford, U. K., 1982, Vol. 8. (c) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*: *Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1989; pp 564-568.

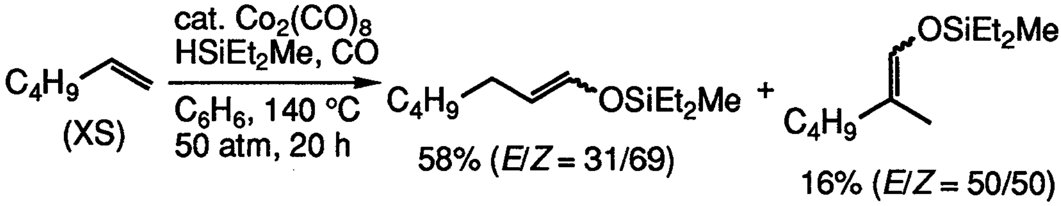
(3) For recent papers of this series, see: Seki, Y.; Kawamoto, K.; Chatani, N.; Hidaka, A.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Organomet. Chem.* **1991**, *403*, 73 and references cited therein.

Chapter 1 The Rhodium-Catalyzed Reactions of Nitrogen-Containing Compounds with Carbon Monoxide and a Hydrosilane

1-1 The Rhodium-Catalyzed Reaction of Enamines with Carbon Monoxide and a Hydrosilane

1-1-1 Introduction

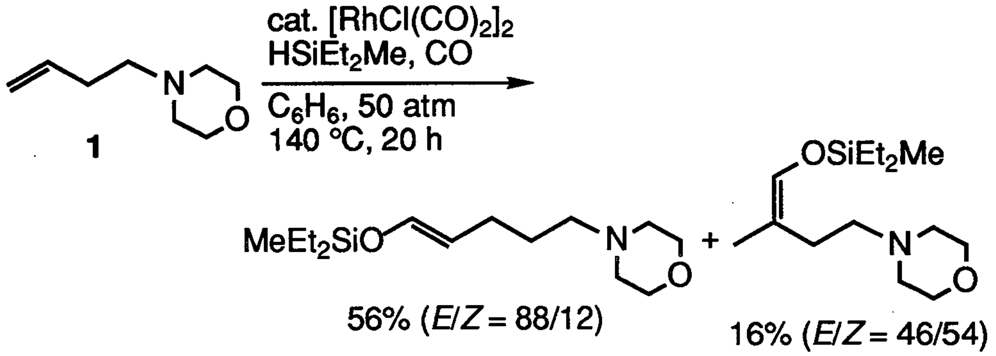
In a series of studies on new catalytic reactions of $HSiR_3/CO/Co_2(CO)_8$, we have reported that the reaction of terminal olefins with a hydrosilane and carbon monoxide in the presence of $Co_2(CO)_8$ can bring about catalytic incorporation of CO into olefins to produce a regioisomeric mixture of enol silyl ethers (eq 1).[1] Although interesting, the reaction is not attractive as a synthetic method since (1) the reaction lacks regiochemical control for incorporation of CO and (2) high ratio of olefins to hydrosilane is required for the reaction to proceed. Recently, amine-containing olefins reacted with rhodium (I) complexes such as $[RhCl(CO)_2]_2$ to give Rh complexes containing bidentate ligand.[2] Krafft et. al. reported that the Rh complex underwent the regioselective hydrocarboxylation to the coordinated olefins and that the amino ligand, tethered to the olefin, might be used to direct the regiochemical outcome.[3] This result has prompted us to search for catalytic reaction of the amine-containing olefins with a hydrosilane and carbon monoxide in the presence of Rh complex.



(1)

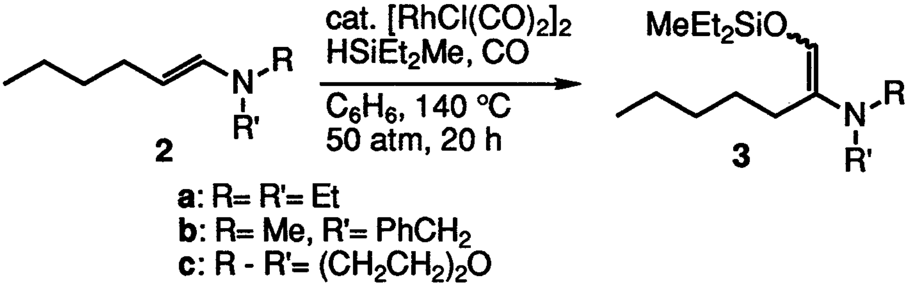
1-1-2 The Reaction of Enamines with Carbon Monoxide and a Hydrosilane

Actually, it was found that the reaction of **1**, did not react in Co-catalyzed reaction system, with $HSiEt_2Me$ (3 equiv) and CO (50 atm) in the presence of $[RhCl(CO)_2]_2$ as a catalyst resulted in the incorporation of CO into **1** to produce a regioisomeric mixture of enol silyl ethers (eq 2).



(2)

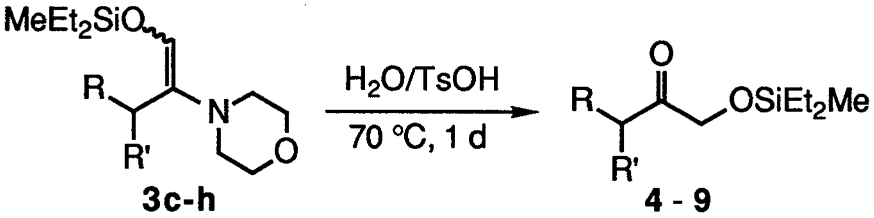
Interestingly, the Rh-catalyzed reaction of enamines **2** as the another amine-containing olefins with $HSiEt_2Me$ and CO underwent the regioselective incorporation of CO into the α-carbon atom of **2**. The results are depicted in eq 3. The reaction was carried out with $HSiEt_2Me$ (3 equiv) in benzene at 140 °C under 50 atm (initial pressure at 25 °C) of CO in the presence of $[RhCl(CO)_2]_2$ (2 mol%) as a catalyst. Incorporation of CO into **2** derived from hexanal took place regioselectively to afford α-(siloxymethylene) amines **3**. Morpholine enamine **2c** gave higher yield of the product (**3c**, 75%) compared with **2a** (**3a**, 32%) and **2b** (**3b**, 25%).[4] With regard to catalysts, a wide range of transition-metal complexes were examined for their catalytic activity for the reaction of **2c**. While $Fe(CO)_5$, $Co_2(CO)_8$,[1] $Ru_3(CO)_{12}$,[1d] and $RhCl(PPh_3)_3$[1d] were not effective, some rhodium complexes $(Me_5C_5RhCl)_2$ (65% yield) and $Rh_6(CO)_{16}$ (75% yield) showed catalytic activity. Since $[RhCl(CO)_2]_2$ gave higher yields it was chosen as the best catalyst and morpholine enamines were used as substrates.



(3)

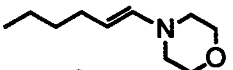
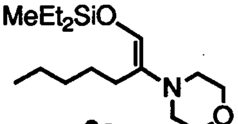
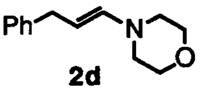
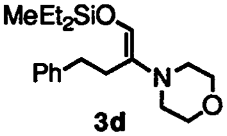
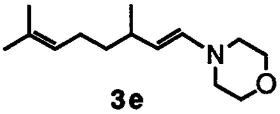
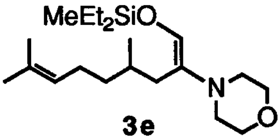
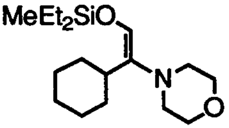
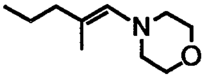
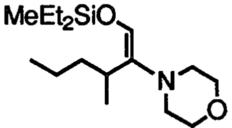
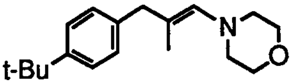
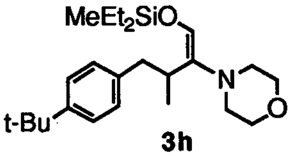
The results of the reaction of morpholine enamines derived from various aldehydes are summarized in Table II. While a product **3d** was obtained in only 14% yield using the reaction time of 20 h, the prolonged reaction time (72 h) led to an increase in the yield of **3d**. The carbon-carbon double bond in **2e** remained intact under the reaction conditions. The reaction of tri-substituted enamines **2f** - **h** also gave α-(siloxymethylene) amines **3f** - **h**, respectively, but in somewhat lower yields. Attempted improvement of the yield of **3h** was not successful even at prolonged reaction times (120 h). In contrast to enamines, the reaction of enamides and enimides with $HSiEt_2Me$ and CO did not result in incorporation of CO, with only the substrates being recovered.[5]

Importantly, the enamine function in the products can be easily hydrolyzed to a carbonyl group. The treatment of α-(siloxymethylene) amines **3c** - **h** with water under acidic condition (H_2O/TsOH, 70 °C, 1 d) gave α-siloxyketones **4** - **9** in quantitative yields (eq 4).

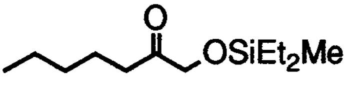


(4)

Table I. $[RhCl(CO)_2]_2$-**Catalyzed Reaction of Enamines with** $HSiEt_2Me$ **and CO**[a]

entry	enamine	time, h	α-(siloxymethylene) amine	yield, %[b]
1	 **2c**	20	 **3c**	62 (75), *E/Z* = 84/16
2	 **2d**	72	 **3d**	74 (91), *E/Z* = 81/19
3	 **3e**	72	 **3e**	72, *E/Z* = 81/19
4	 **2f**	72	 **3f**	65 (72), *E/Z* = 52/48
5	 **2g** (*E/Z* = 63/37)	72	 **3g**	57, *E/Z* = 61/39
6	 **2h** (*E/Z* = 65/35)	120	 **3h**	21, *E/Z* = 51/49

[a] Reaction conditions: enamines (2.5 mmol), $HSiEt_2Me$ (7.5 mmol), $[RhCl(CO)_2]_2$ (0.05 mmol), CO (50 atm), C_6H_6 (5 mL), 140 °C. [b] Isolated yields based on enamines. GC yields are in parentheses. *E/Z* ratio is determined by ^1H NMR.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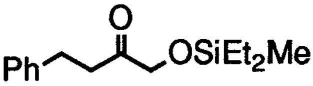
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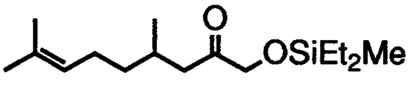
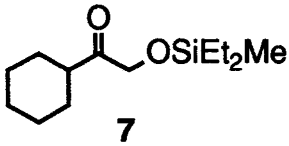
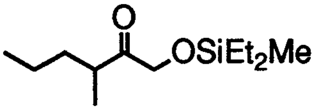

6


7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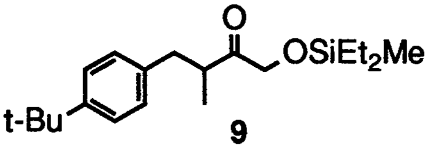
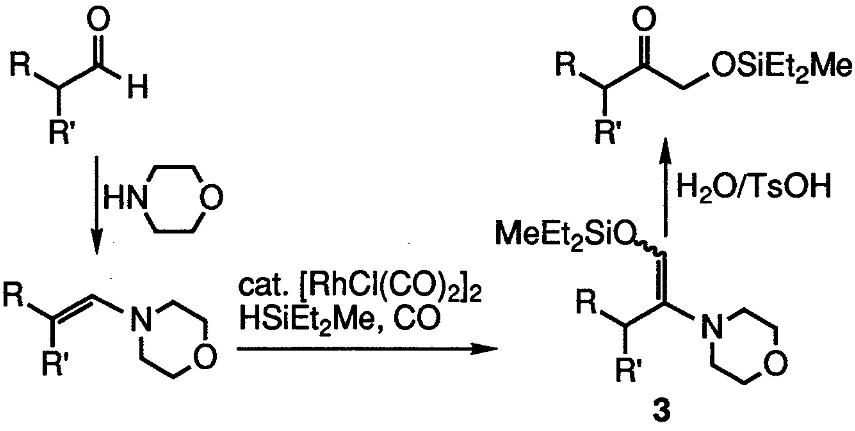

9

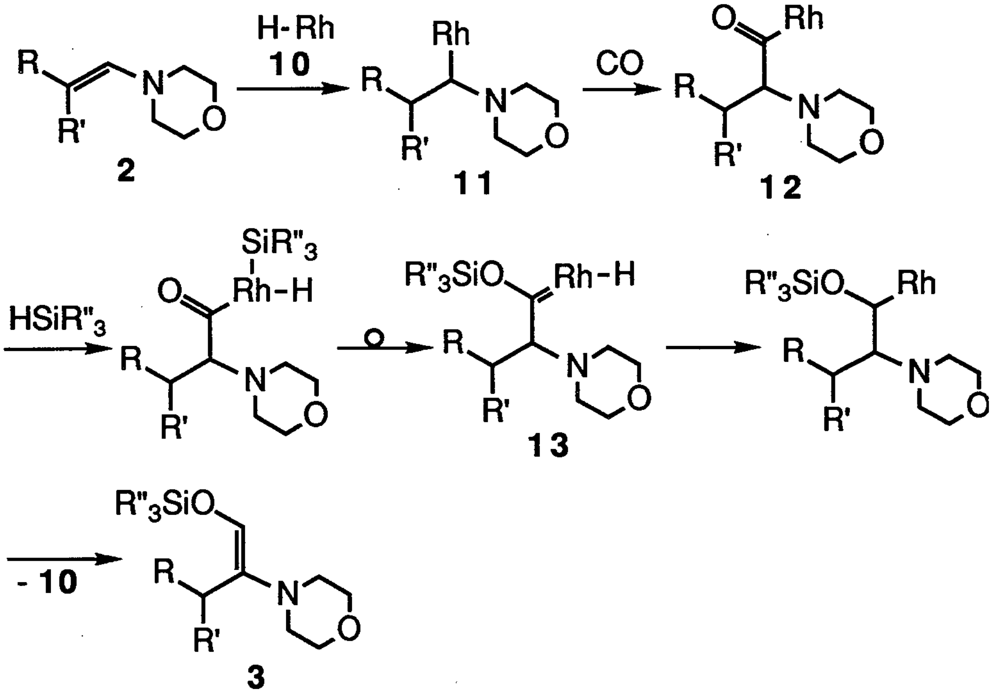
To the best of our knowledge, the rhodium-catalyzed reaction of enamines with a hydrosilane and CO represents a first example of incorporation of CO into enamines. Regioselective incorporation of CO into the α-carbon atom of enamines gives α-(siloxymethylene) amines, which are amenable to further synthetic elaboration because of their multi-functionality.[6] Moreover, the overall process outlined in Scheme I provides a simple route for the conversion of an aldehyde to an α-siloxyketone, which often requires multistep sequences.[7]

Scheme I



Although a mechanism of the catalytic reaction is not known at detail, the plausible one of the reaction is shown in Scheme II. For simplicity, the ligands on the rhodium complex have been omitted. It seems reasonable to postulate, as a key catalyst, a rhodium hydride species **10** which has been formed by reaction of a hydrosilane and the starting rhodium complex. Insertion of **2** into rhodium-hydrogen bond in **10** would give α-aminoalkyl rhodium intermediate **11** in which rhodium is regioselectively substituted at the position α to the amino group of **2**. After CO insertion (alkyl migration to the coordinated CO) to form an acyl rhodium complex **12** and oxidative addition of HSiR"3, the complex **13** would be produced by 1, 3-migration for the silyl group on the rhodium to the acylic oxygen atom (1, 3-silatoropic shift).[8] And the product **3** would be given by α-insertion and then β-elimination of hydrogen.

Scheme II



1-2 The Rhodium-Catalyzed Reaction of *N, N*- and *N, O*-Acetals with Carbon Monoxide and a Hydrosilane

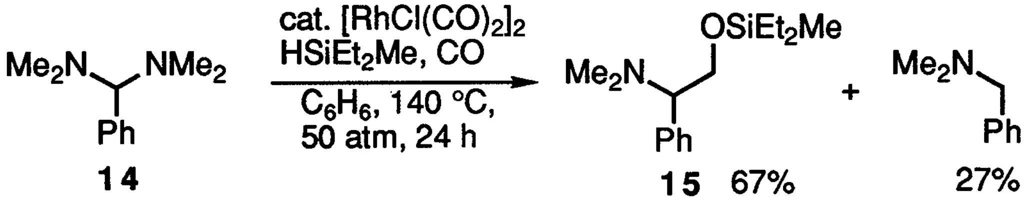
1-2-1 Introduction

The above mentioned reaction of enamines **2** with $HSiEt_2Me$ and CO in the presence of $[RhCl(CO)_2]_2$ resulted in regioselective incorporation of CO into the olefinic carbon atom possessing an amino group to give α-(siloxymethylene) amines **3**. The reaction seemed to be applicable only to amine-containing olefins since other olefins such as 1-hexene, styrene, butyl vinyl ether, and pheny vinyl sulfide did not undergo CO-incorporation under the same reaction conditions using $[RhCl(CO)_2]_2$ as a catalyst. It would be important that α-aminoalkyl rhodium complex **11** in which rhodium was substituted at the position α to the nitrogen atom was involved as common intermediate in the catalytic reaction of CO-incorporation into the substrates. The intermediate of the type **11** might also be formed by Rh-catalyzed reaction of a variety of nitrogen-containing compounds with a hydrosilane and carbon monoxide. As the result, the new CO-incorporation reaction in the catalytic reaction system of $HSiR_3/CO/[RhCl(CO)_2]_2$ is achieved by the use of *N, N*- and *N, O*-acetals as the substrates.

1-2-2 The Reaction of *N, N*-Acetals with Carbon Monoxide and a Hydrosilane

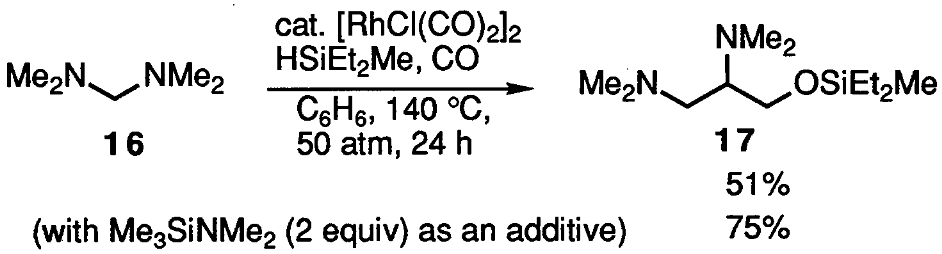
The reaction of *N, N, N', N'*-tetramethylbenzylidenediamine (**14**) (1 equiv) as a *N, N*-acetal with $HSiEt_2Me$ (3 equiv) and CO (50 atm, initial pressure at 25 °C) in the presence of $[RhCl(CO)_2]_2$ (2 mol%) in benzene at 140 °C for 24 h resulted in the incorporation of CO with a cleavage of a carbon-nitrogen bond in **14** to give diethyl[[2-(*N, N*-dimethylamino)-2-

phenylethyl]oxy]methylsilane (**15**) in 67% yield (eq 5). Thus, one of dimethylamino groups in **14** was replaced by (diethylmethylsiloxy)-methyl group. In addition to **15**, benzyldimethylamine was obtained in 27% yield as a byproduct. In the presence of $Co_2(CO)_8$ or $RhCl(PPh_3)_3$ instead of $[RhCl(CO)_2]_2$, no reaction occurred.



(5)

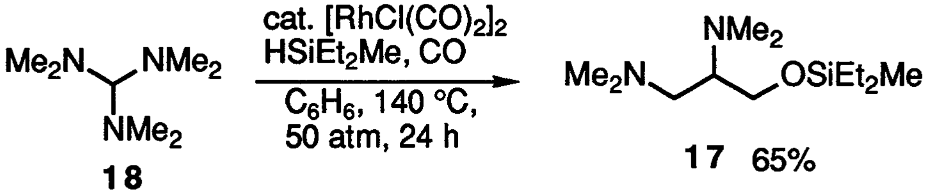
Interestingly, the reaction of methylenediamine **16** with $HSiEt_2Me$ and CO gave an unexpected product **17** in 51% yield without forming a siloxymethylation product similar to **15** (eq 6). The product **17** was obtained by incorporation of two molecules of CO and, curiously, the transposition of one of amino groups to an adjacent carbon atom arising from the first CO. Although the formation **17** from **16** could not be adequately rationalized at this time, a presumed byproduct $MeEt_2SiNMe_2$ seemed to have played an important role. Therefore, the same reaction was run in the presence of trimethylsilyldimethylamine (2 equiv) and the yield of **17** was improved (75%).



(6)

The reaction of triaminomethane **18** with $HSiEt_2Me$ and CO also gave **17** in 65% yield (eq 7). The first stage of the reaction would be reduction of **18** with $HSiEt_2Me$ to give **16** and a silylamine,

$MeEt_2SiNMe_2$. The subsequent reaction of **16** with $HSiEt_2Me$ and CO might have given **17**.

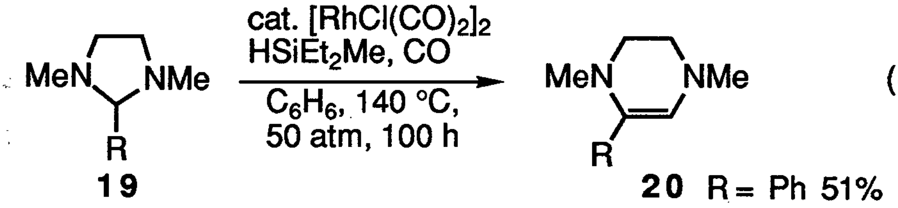


18

17 65%

(7)

The peculiar transposition of an amino group with concomitant the incorporation of CO has applied to the reaction of five-membered cyclic *N*, *N*-acetals **19**. The catalytic reaction of **19** (R = Ph) resulted in the ring expansion with the incorporation of CO to give a cyclic enediamine **20** in 51% yield (eq 8). In contrast, the reaction of alkyl-substituted cyclic *N*, *N*-acetals (**19**, R = heptyl or *t*-butyl) did not take place and the substrates were recovered.



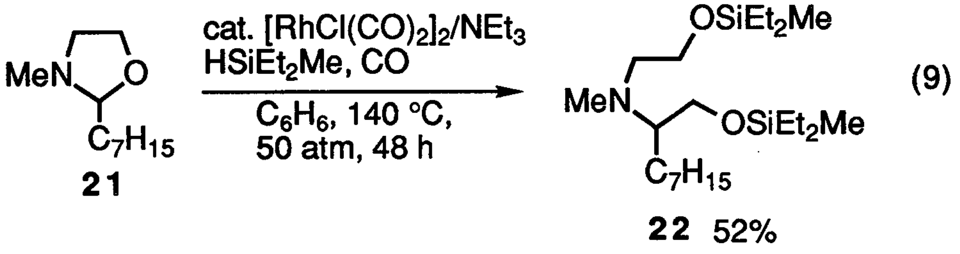
19

20 R= Ph 51%

(8)

1-2-3 The Reaction of *N*, *O*-Acetal with Carbon Monoxide and a Hydrosilane

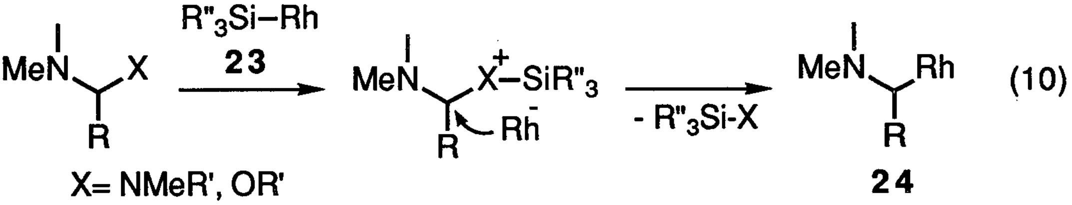
Interestingly, however, a corresponding *N*, *O*-acetals **21** underwent incorporation of CO and gave yet another type of product. The $[RhCl(CO)_2]_2$ (2 mol%)-catalyzed reaction of **21** (1 equiv) with $HSiEt_2Me$ (3 equiv) and CO (50 atm) in the presence of triethylamine (1 equiv) gave a product **22** as the results of ring opening with cleavage of a carbon-oxygen bond in **21** and siloxymethylation (eq 9). On the other hand, *O*, *O*-acetal similar to **21** did not react at all.[9]



21

22 52%

The interaction of a key catalyst **23** having a silicon-rhodium bond with *N*, *N*,- or *N*, *O*-acetals would be responsible for the formation of α-aminoalkyl rhodium intermediate **24**, while that of **10** having a rhodium-hydrogen bond with olefinic moiety to form the similar intermediate **11** might be important for the incorporation of CO into enamines (eq 10). Although the type of products varied significantly according to the substitution patterns of the substrates, the present catalytic reaction stands for a rare example of the incorporation of carbon monoxide with cleavage of carbon-nitrogen bond in *N*, *N*-acetals.[10]



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1-3 Experimental Section

General Methods

Bulb-to-bulb distillations were done on a Shibata glass tube oven GTO-250R; boiling points (bp) refer to air bath temperature and are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JMN-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, q = quartet, m = multiplet, and c =

complex), 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 Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. Elemental analyses were performed by Elemental Analyses Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector. Preparative GC was carried out on Hitachi Model 164 gas chromatograph using 2 m x 10 mm stainless steel column packed with 3% Silicone OV-1 supported on 60/80 mesh.

Typical Procedures

In a 50 mL stainless steel autoclave were placed 4-(1-hexenyl) morpholine (**2c**) (423 mg, 2.5 mmol), $HSiEt_2Me$ (766 mg, 7.5 mmol), $[RhCl(CO)_2]_2$ (19 mg, 0.05 mmol), and 5 mL of benzene. The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring in a silicon-oil bath at 140 °C for 20 h. GC analysis showed that 4-[1-(diethylmethylsiloxy)-1-hepten-2-yl]-morpholine (**3c**) was formed in 75% yield. The pure sample was obtained by Kugelrohr distillation, bp 140 °C (5 Torr), in 62% yield as a pale yellow oil. For GC yields, appropriate hydrocarbons (n-$C_{12}H_{26}$) calibrated against purified products were added before the reaction.

4-[1-(Diethylmethylsiloxy)-1-hepten-2-yl] morpholine (**3c**) (E/Z = 84/16 mixture): a pale yellow oil; bp 140 °C (oven)/5 Torr
^1H NMR ($CDCl_3$): δ [0.11 (s, E), 0.12 (s, Z), 3 H, $SiCH_3$], 0.57 - 0.67 (m, 4 H, $SiCH_2$), 0.86 (t, J = 7.0 Hz, 3 H, CH_3), 0.97 (t, J = 8.1 Hz, 6 H, $SiCCH_3$), 1.24 - 1.51 (m, 6 H, CH_2), [1.82 - 1.88 (t, J = 6.9 Hz, Z), 2.14 - 2.20 (t, J = 6.9 Hz, E), 2 H, $=CCH_2$], [2.64 - 2.67 (m, E), 2.95 - 3.02 (m, Z), 4 H, NCH_2], 3.66 - 3.72 (m, 4 H, OCH_2), [5.62 (s, Z), 5.80 (s, E), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ -4.98 ($SiCH_3$), 6.21 ($SiCH_2$), 6.61 ($SiCCH_3$), 14.08 (CH_3), 22.50 (CH_2), 25.39 (CH_2), 27.45 (CH_2), 31.83 (CH_2), 50.28 (NCH_2), 67.14 (OCH_2), 123.82 (=CN), 137.65 (=CH).

IR (neat): 2880s, 2856s, 2816s, 2783m, 1658w, 1461w, 1415w, 1378m, 1360w, 1324m, 1298m, 1263s, 1233m, 1196m, 1172m, 1150s, 1121s, 1009m, 1042m, 1006m, 972m, 926m, 864m, 834m, 800s, 768m, 689m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 299 (85, M^+), 256 (15), 243 (40), 170 (41), 168 (98), 140), 47), 112 (17), 101 (41), 89 (19), 86 (15), 73 (100), 71 (19), 61 (21), 55 (21).

Exact mass for $C_{16}H_{33}NO_2Si$ (M^+), calcd 299.2273, found 299.2272.

4-[1-(Diethylmethylsiloxy)-4-phenyl-1-buten-2-yl] morpholine (**3d**) (*E*/*Z* = 81/19 mixture): a pale yellow oil; bp 140 °C (oven)/0.2 Torr

^1H NMR ($CDCl_3$): δ [0.11 (s, E), 0.13 (s, Z), 3 H, $SiCH_3$], 0.56 - 0.63 (m, 4 H, $SiCH_2$), 0.95 (t, *J* = 7.6 Hz, 6 H, $SiCCH_3$), [2.14 - 2.21 (t, *J* = 6.8 Hz, Z), 2.43 - 2.46 (t, *J* = 6.8 Hz, E), 2 H, $=CCH_2$], [2.63 - 2.65 (m, E), 3.03 - 3.07 (m, Z), 4 H, NCH_2], 2.72 - 2.75 (m, 2 H, CH_2), 3.71 - 3.75 (m, 4 H, OCH_2), [5.67 (s, Z), 5.85 (s, E), 1 H, =CH], 7.17 - 7.27 (m, 5 H, Ar).

^{13}C NMR ($CDCl_3$): δ -5.91 ($SiCH_3$), 6.21 ($SiCH_2$), 6.60 ($SiCCH_3$), 27.64 (CH_2), 34.04 (CH_2), [49.84, 50.36 (NCH_2)], [67.15, 67.82 (OCH_2)], 124.71 (=CN), 125.62, 128.26, 128.40, 142.68 (Ar), 136.55 (=CH).

IR (neat): 3068w, 3032w, 2960s, 2888s, 2820s, 1662w, 1606w, 1500w, 1458m, 1418w, 1380w, 1326w, 1298w, 1256s, 1190s, 1150s, 1120s, 1050w, 1008m, 970m, 860m, 800s, 766s, 698m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 334 (25, $M^+ + 1$), 333 (85, M^+), 242 (35), 124 (33), 101 (45), 91 (45), 84 (20), 73 (100), 72 (13), 61 (12).

Exact mass for $C_{19}H_{31}NO_2Si$ (M^+), calcd 333.2091, found 333.2094.

4-[1-(Diethylmethylsiloxy)-4,8-dimethyl-1,7-nonadien-2-yl] morpholine (**3e**) (*E*/*Z* = 81/19 mixture): a pale yellow oil; bp 150 °C (oven)/0.05 Torr

^{1}H NMR (CDCl$_3$): δ [0.10 (s, E), 0.11 (s, Z), 3 H, SiCH$_3$], 0.57 - 0.66 (m, 4 H, SiCH$_2$), [0.84 (d, *J* = 7.2 Hz, E), 0.87 (d, *J* = 7.2 Hz, Z), 3 H, CH$_3$), 0.97 (t, *J* = 7.1 Hz, 6 H, SiCCH$_3$), 1.12 - 1.48 (c, 3 H, CH and CH$_2$), 1.60 (s, 3 H, =CCH$_3$), 1.68 (s, 3 H, =CCH$_3$), 1.82 - 2.21 (c, 4 H, =CCH$_2$), [2.52 - 2.59 (m, E), 2.95 - 3.05 (m, Z), 4 H, NCH$_2$], 3.65 - 3.69 (m, 4 H, OCH$_2$), [5.10 (m, E), 5.36 (m, Z), 1 H, =CH], [5.58 (s, Z), 5.88 (s, E), 1 H, =CH].

^{13}C NMR (CDCl$_3$): δ -4.92 (SiCH$_3$), 6.25 (SiCH$_2$), 6.62 (SiCCH$_3$), 17.64 (CH$_3$), 19.49 (CH$_2$), 25.66 (CH$_3$), 25.69 (CH$_3$), 30.64 (CH), 31.92 (CH$_2$), 36.94 (CH$_2$), [49.70, 50.40 (NCH$_2$)], [67.27, 67.82 (OCH$_2$)], 124.93 (=CN), 125.21 (=CH), 130.83 (=C), 136.13 (=CH).

IR (neat): 2962s, 2918s, 2882s, 2856m, 2810m, 1657w, 1460m, 1361w, 1324w, 1298w, 1262m, 1253m, 1183m, 1149s, 1122s, 1069w, 1040m, 1006m, 971m, 864m, 841m, 801m, 770m, 689w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 353 (17, M$^+$), 224 (29), 222 (100), 140 (18), 101 (24), 73 (64), 69 (17), 55 (13).

Exact mass for C$_{20}$H$_{39}$NO$_2$Si (M$^+$), calcd 353.2773, found 353.2776.

4-[1-Cyclohexyl-2-(diethylmethylsiloxy)ethen-1-yl] morpholine (**3f**) (*E*/*Z* = 52/48 mixture): a pale yellow oil; bp 120 °C (oven)/3 Torr

^{1}H NMR (CDCl$_3$): δ [0.11 (s, E), 0.12 (s, Z), 3 H, SiCH$_3$], 0.59 - 0.68 (m, 4 H, SiCH$_2$), 0.92 - 1.01 (m, 6 H, SiCCH$_3$), 1.14 - 1.85 (m, 10 H, CH$_2$), 2.02 - 2.20 (m, 1 H, CH), [2.62 - 2.65 (m, E), 2.93 - 2.96 (m, Z), 4 H, NCH$_2$], 3.65 - 3.70 (m, 4 H, OCH$_2$), [5.86 (s, Z), 5.92 (s, E), 1 H, =CH].

^{13}C NMR (CDCl$_3$): δ -5.02 (SiCH$_3$), [6.14, 6.21 (SiCH$_2$)], [6.62, 6.74 (SiCCH$_3$)], [26.29, 26.35, 26.76, 27.10, 30.24, 32.49 (CH$_2$)], [39.86, 40.79

(CH)], [50.69, 52.69 (NCH_2)], [67.44, 68.05 (OCH_2)], [129.03, 130.27 (=CN)], [136.99, 141.47 (=CH)].

IR (neat): 2960s, 2932s, 2882s, 2854s, 2816m, 1656m, 1453m, 1416w, 1370w, 1358w, 1323w, 1296w, 1257m, 1239m, 1117s, 1064w, 1040w, 1003m, 964m, 890m, 880m, 862m, 852m, 837m, 768s, 766m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 311 (70, M^+), 256 (11), 182 (28), 180 (54), 103 (93), 101 (46), 100 (36), 89 (27), 73 (100), 61 (32), 55 (27).

Exact mass for $C_{17}H_{33}NO_2Si$ (M^+), calcd 311.2294, found 311.2293.

4-[1-(Diethylmethylsiloxy)-3-methyl-1-hexen-2-yl] morpholine (**3g**) (*E*/*Z* = 61/39 mixture): a pale yellow oil; bp 130 °C (oven)/1 Torr

^1H NMR ($CDCl_3$): δ [0.11 (s, E), 0.12 (s, Z), 3 H, $SiCH_3$], 0.57 - 0.68 (m, 4 H, $SiCH_2$), 0.84 - 1.08 (c, 9 H, $SiCCH_3$ and CH_3), 1.15 - 1.44 (c, 3 H, CH_2), 1.50 - 1.66 (m, 1 H, CH_2), [1.93 - 2.01 (m, Z), 2.36 - 2.48 (m, E), 1 H, CH], [2.63 - 2.66 (m, E), 2.93 - 2.96 (m, Z), 4 H, NCH_2], 3.65 - 3.69 (m, 4 H, OCH_2), [5.87 (s, Z), 5.94 (s, E), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-5.01, -4.96 ($SiCH_3$)], [6.21, 6.50 ($SiCH_2$)], [6.76, 6.84 ($SiCCH_3$), [14.20, 14.31, 18.71, 19.90 (CH_3)], [20.68, 21.31, 33.71, 35.82 (CH_2)], [37.03, 37.56 (CH)], [50.90, 52.69 (NCH_2)], [67.92, 68.08 (OCH_2)], [129.63, 131.34 (=CN)], [135.68, 140.93 (=CH)].

IR (neat): 2964s, 2884s, 2820m, 1658m, 1462m 1418m,1378m, 1328w, 1294w, 1256s, 1178s, 1118s, 1010m, 964m, 908w, 852m, 802s, 766m, 688w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 299 (70, M^+), 270 (13, $M^+ - C_2H_5$), 257 (44), 168 (32), 154 (17), 140 (12), 138 (18), 126 (24), 101 (39), 89 (20), 86 (18), 73 (100), 71 (20), 61 (21).

Exact mass for $C_{16}H_{33}NO_2Si$ (M^+), calcd 299.2269, found 299.2270.

4-[1-(Diethylmethylsiloxy)-4-[4-(1,1-dimethylethyl)phenyl]-3-methyl-1-buten-2-yl] morpholine (**3h**) (*E*/*Z* = 64/36 mixture): a pale yellow oil; bp 170 °C (oven)/0.2 Torr

^{1}H NMR (CDCl$_3$): δ [0.07 (s, Z), 0.14 (s, E), 3 H, SiCH$_3$], 0.58 - 0.71 (m, 4 H, SiCH$_2$), 0.92 - 1.00 (m, 6 H, SiCCH$_3$), [1.02 (d, *J* = 7.0 Hz, E), 1.11 (d, *J* = 6.8 Hz), 3 H, CH$_3$], 1.31 (s, 9 H, CH$_3$ of ^{t}Bu), 2.27 - 2.92 (c, 3 H, CH and CH$_2$), 2.49 - 2.58 (m, E), 2.94 - 3.01 (m, Z), 4 H, NCH$_2$), [3.61 - 3.66 (m, E), 3.67 - 3.71 (m, Z), 4 H, OCH$_2$], [5.83 (s, Z), 5.97 (s, E), 1 H, =CH], 7.05 - 7.29 (m, 4 H, Ar).

^{13}C NMR (CDCl$_3$): δ [-5.04, -4.93 (SiCH$_3$)], [6.13, 6.29 (SiCH$_2$)], [6.59, 6.65 (SiCCH$_3$)], [18.11, 19.20 (CH$_3$)], 31.42 (CH$_3$ of ^{t}Bu), [34.29, 36.51 (CH$_2$)], [37.87, 40.13 (CH)], 41.66 (C), [50.87, 52.38 (NCH$_2$)], [67.44, 68.11 (OCH$_2$)], [124.75, 124.87, 125.32, 128.69, 128.81, 129.61, 131.69, 135.00, 138.41, 139.05, 140.11, 148.28 (Ar, =CN, and =CH)].

IR (neat): 2962s, 2890m, 1659w, 1518m, 1464m, 1416w, 1411w, 1368m, 1326w, 1293w, 1257m, 1170s, 1119s, 1068w, 1011m, 963w, 924w, 852m, 804s, 768m, 687w, 570w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 404 (28, M$^+$ + 1), 403 (87, M$^+$), 257 (11), 256 (49), 147 (12), 138 (58), 117 (13), 101 (26), 73 (100), 72 (29), 57 (17).

Exact mass for $C_{24}H_{41}NO_2Si$ (M$^+$), calcd 403.2923, found 403.2925.

1-(Diethylmethylsiloxy)-2-heptanone (**4**): a colorless oil

^{1}H NMR (CDCl$_3$): δ 0.09 (s, 3 H, SiCH$_3$), 0.61 (q, *J* = 7.6 Hz, 4 H, SiCH$_2$), 0.88 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 0.96 (t, *J* = 7.6 Hz, 6 H, SiCCH$_3$), 1.23 - 1.36 (m, 4 H, CH$_2$), 1.58 (m, *J* = 7.2 Hz, 2 H, CH$_2$), 2.46 (t, *J* = 7.2 Hz, 2 H, CH$_2$), 4.16 (s, 2 H, OCH$_2$).

^{13}C NMR ($CDCl_3$): δ -5.11 ($SiCH_3$), 6.10 ($SiCH_2$), 6.61 ($SiCCH_3$), 13.88 (CH_3), 22.41 (CH_2), 23.06 (CH_2), 31.44 (CH_2), 38.44 (CH_2), 68.84 (OCH_2), 210.87 (CO).

IR (neat): 2960s, 2884s, 1726s, 1694m, 1466s, 1416m, 1380w, 1352w, 1256m, 1164s, 1116s, 1052m, 1010m, 970m, 804s, 766s, 688w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 230 (0, M^+), 215 (6, M^+ - CH_3), 131 (100), 115 (12), 103 (92), 101 (49), 91 (12), 89 (39), 75 (11), 73 (52), 61 (29).

Anal. Calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37. Found: C, 62.60; H, 11.44.

1-(Diethylmethylsiloxy)-4-phenyl-2-butanone (**5**): a colorless oil

^1H NMR ($CDCl_3$): δ 0.07 (s, 3 H, $SiCH_3$), 0.60 (q, J = 7.6 Hz, 4 H, $SiCH_2$), 0.95 (t, J = 7.6 Hz, 6 H, $SiCCH_3$), 2.81 - 2.92 (m, 4 H, CH_2), 4.14 (s, 2 H, OCH_2), 7.18 - 7.29 (m, 5 H, Ar).

^{13}C NMR ($CDCl_3$): δ -5.13 ($SiCH_3$), 6.04 ($SiCH_2$), 6.60 ($SiCCH_3$), 29.33 (CH_2), 39.87 (CH_2), 68.99 (OCH_2), 126.09, 128.31, 128.46, 141.01 (Ar), 209.86 (CO).

IR (neat): 3036w, 2960s, 2888m, 1724s, 1606w, 1500m, 1458m, 1416m, 1354m, 1254s, 1156s, 1104s, 1008m, 968m, 804m, 764s, 698w, 498w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 264 (0, M^+), 249 (1, M^+ - CH_3), 235 (23, M^+ - C_2H_5), 129 (11), 103 (25), 101 (20), 91 (100), 89 (23), 86 (14), 84 (21), 73 (22), 61 (11).

Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 68.28; H, 9.33.

1-(Diethylmethylsiolxy)-4,8-dimethyl-7-nonen-2-one (**6**): a colorless oil

^1H NMR ($CDCl_3$): δ 0.09 (s, 3 H, $SiCH_3$), 0.62 (q, J = 7.6 Hz, 4 H, $SiCH_2$), 0.89 (d, J = 6.2 Hz, 3 H, CH_3), 0.96 (t, J = 7.6 Hz, 6 H, $SiCCH_3$), 1.16 -1.38 (m, 2 H, CH_2), 1.59 (s, 3 H, CH_3), 1.67 (d, J = 0.8 Hz, 3 H, CH_3), 1.81 - 2.09

(c, 3 H, CH and =CCH_2), 2.26 (dd, *J* = 15.9, 8.1 Hz, 1H, $COCH_2$), 2.44 (dd, *J* = 15.9, 8.1 Hz, 1 H, O=CCH_2), 4.14 (s, 2 H, OCH_2), 5.08 (m, 1 H, =CH).
^{13}C NMR ($CDCl_3$): δ -5.08 ($SiCH_3$), 6.12 ($SiCH_2$), 6.64 ($SiCCH_3$), 17.61 (CH_3), 19.73 (CH_2), 25.45 (CH_3), 25.68 (CH_3), 28.62 (CH), 37.06(CH_2), 45.54 (CH_2), 69.27 (OCH_2), 124.29 (=CH), 131.47 (=C), 210.29 (CO).
IR (neat): 2964s, 2888s, 1724m, 1464m, 1416m, 1380m, 1254m, 1104m, 1040w, 1010m, 972m, 688w cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 284 (6, M^+), 171 (10), 149 (22), 148 (10), 131 (11), 123 (17), 109 (31), 107 (18), 101 (49), 93 (22), 91 (19), 89 (29), 81 (19), 73 (42), 67 (12), 62 (100), 61 (18), 55 (26).
Anal. Calcd for $C_{16}H_{32}O_2Si$: C, 67.55; H, 11.34. Found: C, 67.29; H, 11.43.

1-Cyclohexyl-2-(diethylmethylsiloxy)-1-ethanone (**7**): a colorless oil
^{1}H NMR ($CDCl_3$): δ 0.08 (s, 3 H, $SiCH_3$), 0.63 (q, *J* = 7.7 Hz, 4 H, $SiCH_2$), 0.96 (t, *J* = 7.7 Hz, 6 H, $SiCCH_3$), 1.10 -1.91 (m, 10 H, CH_2), 2.47 - 2.63 (m, 1 H, CH), 4.25 (s, 2 H, OCH_2).
^{13}C NMR ($CDCl_3$): δ -5.08 ($SiCH_3$), 6.15 ($SiCH_2$), 6.65 ($SiCCH_3$), 25.63 (CH_2), 25.78 (CH_2), 28.29 (CH_2), 46.24 (CH), 67.59 (OCH_2), 212.70 (CO).
IR (neat): 2940s, 2884m, 2860m, 1732m, 1716m, 1454m, 1416m, 1378w, 1321w, 1254m, 1164m, 1142m, 1104m, 1062m, 1000m, 970m, 802m, 764m, 688w cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 242 (0, M^+), 227 (5, M^+ - CH_3), 214 (17), 213 (100, M^+ - C_2H_5), 169 (10), 131 (70), 107 (10), 103 (93).
Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.20; H, 10.90.

1-(Diethylmethylsiolxy)-3-methyl-2-hexanone (**8**): a colorless oil

^{1}H NMR ($CDCl_3$): δ 0.08 (s, 3 H, $SiCH_3$), 0.61 (q, *J* = 7.6 Hz, 4 H, $SiCH_2$), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.96 (t, *J* = 7.6 Hz, 6 H, $SiCCH_3$), 1.05 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.23 - 1.32 (c, 3 H, CH_2), 1.56 - 1.70 (m, 1 H, CH_2), 2.78 (qt, *J* = 7.0, 7.0 Hz, 1 H, CH), 4.23 (d, *J* = 1.8 Hz, 2 H, OCH_2).

^{13}C NMR ($CDCl_3$): δ -5.11 ($SiCH_3$), 6.12 ($SiCH_2$), 6.61 ($SiCCH_3$), 14.02 (CH_3), 16.14 (CH_3), 20.45 (CH_2), 34.90 (CH_2), 41.09 (CH), 68.09 (OCH_2), 213.57 (CO).

IR (neat): 2964s, 2888s, 1738m, 1466m, 1418m, 1380w, 1254m, 1158m, 1100s, 1010s, 968w, 837s, 802s, 764s, 688w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 230 (0, M^+), 215 (6, M^+ - CH_3), 201 (100, M^+ - C_2H_5), 154 (22), 131 (17), 129 (34), 103 (91), 101 (62), 89 (42), 73 (55), 71 (39), 61 (34).

Exact mass for $C_{11}H_{23}O_2Si$ (M^+ - CH_3), calcd 215.1492, found 215.1495.

1-(Diethylmethylsiloxy)-4-[4-(1,1-dimethylethyl)phenyl]-3-methyl-2-butanone (**9**): a colorless oil

^{1}H NMR ($CDCl_3$): δ 0.01 (s, 3 H, $SiCH_3$), 0.55 (m, 4 H, $SiCH_2$), 0.92 (m, 6 H, $SiCCH_3$), 1.09 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.30 (s, 9 H, CH_3 of ^{t}Bu), 2.49 - 3.12 (c, 3 H, CH_2 and CH), 3.98 (d, *J* = 17.8 Hz, 1 H, OCH_2), 4.19 (d, *J* = 17.8 Hz, 1 H, OCH_2), 7.06 - 7.31 (m, 4 H, Ar).

^{13}C NMR ($CDCl_3$): δ -5.15 ($SiCH_3$), 6.06 ($SiCH_2$), 6.62 ($SiCCH_3$), 16.46 (CH_3), 31.34 (CH_3 of ^{t}Bu), 34,35 (CH_2), 38.59 (C), 43.34 (CH), 68.63 (OCH_2), 125.32, 128.59, 136.52, 149.06 (Ar), 212.96 (CO).

IR (neat): 2964s, 2884m, 2734m, 1518w, 1464m, 1416w, 1366w, 1254m, 1156m, 1110m, 1016m, 970w, 834m, 800m, 764m, 568w, 460w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 334 (0, M^+), 305 (8, M^+ - C_2H_5), 249 (14), 148 (12), 147 (100), 143 (18), 131 (13), 117 (17), 103 (23), 101 (18), 91 (15), 73 (21), 57 (50).
Exact mass for $C_{19}H_{31}O_2Si$ (M^+ - CH_3), calcd 319.2111, found 319.2109.

N, *N*-Diethyl-1-(diethylmethylsiloxy)-2-heptanamine: a colorless oil; bp 140 °C (oven)/5 Torr
^1H NMR ($CDCl_3$): δ 0.04 (s, 3 H, $SiCH_3$), 0.56 (q, *J* = 7.8 Hz, 4 H, $SiCH_2$), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.94 (t, *J* = 7.8 Hz, 6 H, $SiCCH_3$), 1.01 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.19 - 1.48 (m, 8 H, CH_2), 2.38 - 2.72 (c, 5 H, NCH_2 and NCH), 3.46 (dd, *J* = 10.3, 6.2 Hz, 1 H, OCH_2), 3.68 (dd, *J* = 10.3, 6.2 Hz, 1H, OCH_2).
^{13}C NMR ($CDCl_3$): δ -5.04 ($SiCH_3$), 6.21 ($SiCH_2$), 6.77 ($SiCCH_3$), 14.11 (CH_3), 14.75 (CH_3), 22.67 (CH_2), 26.28 (CH_2), 29.01 (CH_2), 32.20 (CH_2), 44.10 (NCH_2), 60.91 (NCH), 63.16 (OCH_2).
IR (neat): 2960s, 2934s, 2882m, 2818w, 1462m, 1417w, 1380w, 1253m, 1206w, 1078m, 1011w, 826m, 763m cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 287 (0, M^+), 272 (1, M^+ - CH_3), 258 (1, M^+ - C_2H_5), 156 (100).
Exact mass for $C_{16}H_{37}NOSi$ (M^+), calcd 287.2662, found 287.2660.

N-Methyl-*N*-(phenymethyl)-1-(diethylmethylsiloxy)-2-heptanamine: a colorless oil; bp 140 °C (oven)/5 Torr
^1H NMR ($CDCl_3$): δ 0.07 (s, 3 H, $SiCH_3$), 0.59 (q, *J* = 7.8 Hz, 4 H, $SiCH_2$), 0.90 (t, *J* = 6.9 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.8 Hz, 6 H, $SiCCH_3$), 1.23 - 1.44 (m, 8 H, CH_2), 2.24 (s, 3 H, NCH_3), 2.61 - 2.65 (m, 1 H, NCH), 3.27 (dd, *J* = 10.3, 5.7 Hz, 1 H, OCH_2), 3.58 (dd, *J* = 10.3, 5.7 Hz, 1 H, OCH_2), 3.62 - 3.78 (m, 2 H, NCH_2), 7.21 - 7.39 (m, 5 H, Ar).

^{13}C NMR ($CDCl_3$): δ -5.01 ($SiCH_3$), 6.22 ($SiCH_2$), 6.84 ($SiCCH_3$), 14.11 (CH_3), 22.68 (CH_2), 26.70 (CH_2), 28.52 (CH_2), 32.06 (CH_2), 37.15 (NCH_3), 58.88 (NCH_2), 62.71 (NCH), 63.95 (OCH_2), 126.58, 128.08, 128.65 (Ar).

IR (neat): 3036w, 2940s, 2884s, 2796s, 1950w, 1606w, 1498m, 1420w, 1382m, 1254m, 1100m, 1012m, 968w, 826m, 800m, 764m, 734m, 698m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 335 (0, M^+), 204 (100), 91 (74).

Exact mass for $C_{20}H_{37}NOSi$ (M^+), calcd 335.2600, found 335.2604.

4-[1-(Diethylmethylsiloxy)-2-heptyl] morpholine: a colorless oil; bp 140 °C (oven)/5 Torr

^1H NMR ($CDCl_3$): δ 0.05 (s, 3 H, $SiCH_3$), 0.57 (q, *J* = 7.8 Hz, 4 H, $SiCH_2$), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3), 0.95 (t, *J* = 7.8 Hz, 6 H, $SiCCH_3$), 1.23 - 1.46 (m, 8 H, CH_2), 2.44 (m, 1 H, NCH), 2.54 -2.74 (m, 4 H, NCH_2), 3.56 (dd, *J* = 10.4, 5.7 Hz,1 H, OCH_2), 3.64 - 3.68 (m, 4 H, OCH_2), 3.70 (dd, *J* = 10.4, 5.7 Hz, 1 H, CH_2).

^{13}C NMR ($CDCl_3$): δ -5.07 ($SiCH_3$), 6.16 ($SiCH_2$), 6.77 ($SiCCH_3$), 14.05 (CH_3), 22.60 (CH_2), 26.56 (CH_2), 27.92 (CH_2), 32.03 (CH_2), 46.19 (NCH_2), 62.32 (NCH), 65.63 ($SiOCH_2$), 67.73 (OCH_2).

IR (neat): 2960s, 1464m, 1418w, 1382w, 1356w, 1290w, 1254m, 1206w, 1154m, 1120s, 1010m, 970w, 922w, 824m, 800m, 764m, 688w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 301 (0, M^+), 272 (2, M^+ - C_2H_5), 170 (100).

Anal. Calcd for $C_{16}H_{35}NO_2Si$: C, 63.73; H, 11.70; N, 4.65. Found: C, 63.67; H, 11.86; N, 4.90.

Diethyl[[2-(N, N-dimethylamino)-2-phenylethyl]oxy]methylsilane (**15**): a colorless oil; bp 100 °C (oven)/2 Torr

^{1}H NMR ($CDCl_3$): δ -0.09 (s, 3 H, $SiCH_3$), 0.47 (q, J = 7.6 Hz, 4 H, $SiCH_2$), 0.82 (t, J = 7.6 Hz, 6 H, $SiCCH_3$), 2.22 (s, 6 H, NCH_3), 3.19 (t, J = 5.6 Hz, 1 H, NCH), 3.78 (dd, J = 5.6, 10.5 Hz, 1 H, OCH_2), 3.94 (dd, J = 5.6, 10.5 Hz, 1 H, OCH_2), 7.23 - 7.28 (m, 5 H, Ar).

^{13}C NMR ($CDCl_3$): δ -5.22 ($SiCH_3$), 6.07, 6.62 ($SiCH_2CH_3$), 43.89 (NCH_3), 65.27 (OCH_2), 72.80 (NCH), 127.07, 128.00, 128.51, 140.50 (Ar).

IR (neat): 3068w, 3036w, 2960s, 2884m, 2828m, 2776m, 1601w, 1496m, 1460s, 1416w, 1382w, 1348w, 1314w, 1252s, 1120s, 1008s, 962m, 914w, 878m, 798s, 762s, 702m, 556w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 265 (0, M^+), 135 (29), 134 (100), 91 (10), 73 (12).

Exact mass for $C_{14}H_{24}NOSi$ (M^+ - CH_3), calcd 250.1627, found 250.1602.

Diethylmethyl[[2, 3-(N, N, N', N'-tetramethyldiamino)propyl]oxy]silane (**17**): a colorless oil; bp 80 °C (oven)/2 Torr

^{1}H NMR ($CDCl_3$): δ 0.05 (s, 3 H, $SiCH_3$), 0.56 (q, J = 7.9 Hz, 4 H, $SiCH_2$), 0.94 (t, J = 7.9 Hz, 6 H, $SiCCH_3$), 2.21 (s, 6 H, NCH_3), 2.23 (dd, J = 7.7, 16.1 Hz, 1 H, NCH_2), 2.35 (dd, J = 7.7, 16.1 Hz, 1 H, NCH_2), 2.36 (s, 6 H, NCH_3), 2.62 (tt, J = 5.4, 7.7 Hz, 1 H, NCH), 3.60 (dd, J = 5.4, 11.9 Hz, 1 H, OCH_2), 3.71 (dd, J = 5.4, 11.9 Hz, 1 H, OCH_2).

^{13}C NMR ($CDCl_3$): δ -5.08 ($SiCH_3$), 6.15 ($SiCH_2$), 6.76 ($SiCCH_3$), 41.63, 46.04 (NCH_3), 58.59, 60.91, 62.88 (NCH_2, NCH, OCH_2).

IR (neat): 2960s, 2884m, 2828m, 2772m, 1462m, 1418w, 1252m, 1154w, 1100s, 1044s, 1006m, 968m, 798s, 764m, 686w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 246 (0, M^+), 189 (29), 188 (100), 101 (17), 73 (28), 71 (10), 58 (55).

Anal. Calcd for $C_{12}H_{30}N_2OSi$: C, 58.48; H, 12.27; N, 11.37. Found: C, 58.19; H, 12.44; N, 11.14.

1, 4-Dimethyl-5-phenyl-2, 3-tetrahydropyrazine (**20**): a pale yellow oil; bp 100 °C (oven)/1.5 Torr
^1H NMR ($CDCl_3$): δ 2.42 (s, 3 H, NCH_3), 2.71 (s, 3 H, NCH_3), 2.92-3.02 (m, 4 H, NCH_2), 5.89 (s, 1 H, =CH), 7.11 - 7.42 (m, 5 H, Ar).
^{13}C NMR ($CDCl_3$): δ 42.57, 42.87, 44.19, 49.36 (NCH_3, NCH_2), 122.52, 124.70, 125.18, 126.69, 128.19, 138.85 (Ar, =CH, and =C).
IR (neat): 3060w, 2944m, 2852m, 2804m, 1630s, 1598s, 1494m, 1468m, 1448m, 1426m, 1370m, 1344m, 1314m, 1284m, 1230w, 1212w, 1162s, 1122m, 1080m, 1034m, 1020m, 998w, 934w, 910w, 860w, 814w, 780w, 758s, 698s, 664m, 638w cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 189 (16, $M^+ + 1$), 188 (100, M^+), 173 (59, $M^+ - CH_3$), 144 (16), 132 (10), 131 (12), 130 (12), 118 (43), 117 (12), 103 (19), 94 (13), 93 (19), 91 (11), 77 (25), 51 (11).
Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.36; H, 8.57; N, 14.80.

Diethylmethyl[[2-[N-(diethylmethylsiloxyethyl)-N-methylamino] nonyl]oxy]silane (**22**): a pale yellow oil; bp 140 °C (oven)/2 Torr
^1H NMR ($CDCl_3$): δ 0.04 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$), 0.52 - 0.63 (m, 8 H, $SiCH_2$), 0.88 - 0.98 (c, 15 H, $SiCCH_3$ and CH_3), 1.26 - 1.58 (m, 12 H, CH_2), 2.34 (s, 3 H, NCH_3), 2.44 - 2.76 (c, 3 H, NCH and NCH_2), 3.48 (dd, J = 5.6, 10.3 Hz, 1 H, OCH_2), 3.61 (t, J = 7.6 Hz, 2 H, OCH_2), 3.67 (dd, J = 5.6, 10.3 Hz, 1 H, OCH_2).
^{13}C NMR ($CDCl_3$): δ -5.07, -4.99 ($SiCH_3$), 6.21 ($SiCH_2$), 6.73, 6.77 ($SiCCH_3$), 14.08 (CH_3), 22.67. 27.14, 28.78, 29.30, 29.88, 31.89 (CH_2), 39.03 (NCH_3), 56.31 (NCH_2), 62.00, 62.70, 65.11 (NCH, OCH_2).

IR (neat): 2960s, 2884s, 1464m, 1418w, 1380w, 1252m, 1104s, 1012w, 968w, 800s, 762m, 684w cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 417 (0, M$^+$), 388 (3, M$^+$ - CH$_3$), 288 (23), 287 (17), 286 (100), 101 (12), 73 (24).
Anal. Calcd for $C_{22}H_{51}NO_2Si_2$: C, 63.24; H, 12.30; N, 3.35. Found: C, 62.97: H, 12.60; N, 3.60.

1-4 References and Notes

(1) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 881. (c) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361. (d) Seki, Y.; Kawamoto, K.; Chatani, N.; Hidaka, A.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Organomet. Chem.* **1991**, *403*, 73.

(2) (a) Aresta, M.; Quaranta, E.; Treglia, S.; Ibers, J. A. *Organometallics* **1988**, *7*, 577. (b) Krafft, M. E.; Wilson, L. J.; Onan, K. D. *Organometallics* **1988**, *7*, 2528.

(3) (a) Krafft, M. E.; Wilson, L. J.; Onan, K. D. *Tetrahedron Lett.* **1988**, 29, 6421. (b) Krafft, M. E. *Tetrahedron Lett.* **1989**, 30, 539. (c) Kraft, M. E.; Yu, X. Y.; Stephen, E.; Milczanowski, E.; Donnelly, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 9215.

(4) α-(Siloxymethylene) amines **3a** - **c** were moisture sensitive, so that some of them were converted into α-(siloxymethyl) amines by hydrogenation (1 atm of H$_2$, Pd/C, benzene, 25 °C, 1 day) for characterization.

(5) Hydroformylation of enamides or enimides are known. See: (a) Sato, S. *Nippon Kagaku Zasshi* **1969**, *90*, 404; *Chem. Abstr.* **1969**, *71*, 21828. (b) Becker, Y.; Eisenstadt, A.; Stille, J. K. *J. Org. Chem.* **1980**, *45*, 2145. (c)

Cavinato, G.; Toniolo, L.; Botteghi, C.; Gladiali, S. *J. Organomet. Chem.* **1982**, *229*, 93. (d) Delogu, G.; Faedda, G.; Gladiali, S. *J. Organomet. Chem.* **1984**, *268*, 167. Attempted hydroformylation of **1c** ($[RhCl(CO)_2]_2$, H_2/CO (1 : 1) 50 atm, in benzene, 140 °C) resulted in hydrogenation and not carbonylation.

(6) α-(Siloxymethylene) amines obtained here have both enol silyl ether and enamine moieties. For reviews on the synthetic application of enol silyl ethers, see: (a) Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, Part 13, pp 584 - 592. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 198 - 287. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 206 - 254. For reviews on the synthetic application of enamines, see: (d) Cook, A. G. *Enamines: Synthesis, Structure, and Reactions;* Marcel Dekker: New York, 1969. (e) Tietze, L. F.; Eicher, T. *Reaktionen und Synthesen*; Thieme Verlag: Stuttgart, 1981.

(7) For other synthetic methods of α-hydroxyketone derivatives, see: (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319. (b) Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3247. (c) Wissner, A. *Tetrahedron Lett.* **1978**, 2748. (d) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599. (e) McCormic, J. P.; Tomasik, W.; Johnson, M. W. *Tetrahedron Lett.* **1981**, *22*, 607. (f) Lee, T. V.; Toczek, J. *Tetrahedron Lett.* **1982**, *23*, 2917. (g) Davis, F. A.; Sheppard, A. C. *J. Org. Chem.* **1987**, *52*, 954. (h) Moriatry, R. M.; Duncan, M. P.; Prakash, O. *J. Chem. Soc., Parkin Trans. I* **1987**, 1781. (i) Tanaka, T.; Yamada, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, 281.

(8) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W. K.; Gladysz, J. A. *Organometallics*, **1984**, *3*, 1325.

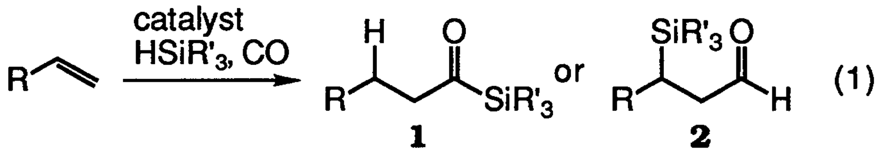
(9) Chatani, N.; Murai, T.; Ikeda, T.; Sano, T.; Kajikawa, Y.; Ohe, K.; Murai, S. *Tetrahedron* **1992**, *48*, 2013.

(10) For the examples of the transition-metal catalyzed carbonylation with the cleavage of a carbon-nitrogen bond in strained molecules, see: (a) Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289. (b) Alper, H.; Mahatantila, C. P. *Organometallics* **1982**, *1*, 70. (c) Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737. (d) Roberto, D.; Alper, H. *Organometallics* **1984**, *3*, 1767. (e) Alper, H.; Hamel, N. *Tetrahedron Lett.* **1987**, *28*, 3237. (f) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931. (g) Roberto, D.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 7539. (h) Alper, H.; Delledonne, D.; Kameyama, M.; Roberto, D. *Organometallics* **1990**, *9*, 762. (i) Spears, G. W.; Nakanishi, K.; Ohfune, Y. *Synlett.* **1991**, 91. For the examples of the insertion of CO into a carbon-nitrogen bond of substrates other than strained heterocycles, see: (j) Merger, F.; Kummer, R.; Hutmacher, H. M. German Patent 3401503, 1985; *Chem. Abstr.* **1986**, *104*, 129650g. (k) Murahashi, S. - I.; Imada, Y.; Nishimura, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1578.

Chapter 2 The Iridium-Catalyzed Reaction of Olefins with Carbon Monoxide and a Hydrosilane

2-1 Introduction

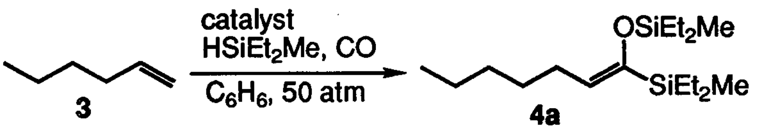
In Chapter 1, it has be mentioned that the reaction of amine-containing olefins such as enamines with a hydrosilane ($HSiR_3$) and carbon monoxide (CO) in the presence of $[RhCl(CO)_2]_2$ can promote catalytic introduction of siloxymethylidene unit (=$CHOSiR_3$), which derived from a molecule of CO and $HSiR_3$, respectively, to give enol silyl ethers. It is the same result as the catalytic reaction system of $Co_2(CO)_8/HSiR_3/CO$ that the introduced silyl unit always attaches to an oxygen atom of CO. The formal analogy to hydroformylation of olefins with $HSiR_3$ instead of H_2 and CO would suggest that acylsilane **1** and β-silyl aldehyde **2** could be products (eq 1). The possibility that **1**, **2**, and their derivatives can be a product of a catalytic reaction using $HSiR_3$ and CO has been pointed out.[1] Recently, catalytic reactions of acetylenes with $HSiR_3$ and CO to give products relating to **2** have been reported.[2] However, the CO-incorporation into olefins accompanying the formation of silicon-carbon bond to give **1** or **2** has not been achieved at all. In this Chapter, it is found that iridium complexes catalyze the reaction of olefins with a hydrosilane and carbon monoxide to yield enol silyl ethers of **1** as a new type product.



2-2 The Reaction of 1-Hexene with Carbon Monoxide and Hydrosilanes

1-Hexene (**3**) was found to react with $HSiR_3$ and CO in the presence of a catalytic amount of $[IrCl(CO)_3]_n$ to give the 1-silyl enol silyl ether **4a** (eq 2). The reaction results in regioselective introduction of a siloxy(silyl)methylene unit (=$C(SiR_3)OSiR_3$) having the silicon-carbon bond into the terminal carbon atom of **3**. No regioisomer was detected. Selected results obtained for the catalytic reaction of **3** using diethylmethylsilane ($HSiEt_2Me$) as a hydrosilane are shown in Table I. The best result with respect to the yield of **4a** was obtained for the reaction carried out with the use of 10 mmol of **3** and 1 mmol of $HSiEt_2Me$ in benzene at 140 °C under 50 atm (initial pressure at 25 °C) of carbon monoxide for 48 h in the presence of $[IrCl(CO)_3]_n$ as the catalyst (or the catalytic precursor) (2 mol%) to give **4a** (82% based on $HSiEt_2Me$) (run 7). The reaction slowly take place with the use of the excess amount of $HSiEt_2Me$ or below 80 °C (runs 1 and 6, respectively). An increase in the rate of **3**/$HSiEt_2Me$ and reaction time resulted in an increase in the yield of **4a**. The use of CH_2Cl_2 or THF in place of benzene gave **4a** as a main product along with many unidentified products. With regards to catalyst, some iridium complexes were examined for their catalytic activity for the reaction of **3**. While $IrCl(CO)(PPh_3)_2$ (run 9) and $IrH(CO)(PPh_3)_3$ (run 10) was not effective, $Ir_4(CO)_{12}$ (run 8) showed catalytic activity (65%) but less efficient than $[IrCl(CO)_3]_n$. Under the conditions equivalent to those of run 7, other hydrosilanes such as dimethtylphenylsilane ($HSiRhMe_2$) and triethylsilane ($HSiEt_3$) can also be used in place of $HSiEt_2Me$ and gave comparable products **4b** and **4c**, respectively, although the formation of **4c** had to prolong reaction times (100 h) (Table II).

Table I. Iridium-Catalyzed Reaction of 1-Hexene with $HSiEt_2Me$ and CO[a]

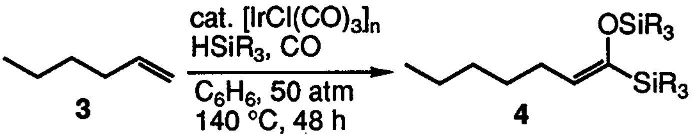


3 → 4a (2)

run	3 [mmol]	$HSiEt_2Me$ [mmol]	catalyst	temp., °C	time, h	yield, %[b]
1	1	3	$[IrCl(CO)_3]_n$	140	24	2
2	3	1	$[IrCl(CO)_3]_n$	140	24	20
3	3	1	$[IrCl(CO)_3]_n$	140	48	34
4	5	1	$[IrCl(CO)_3]_n$	140	48	41
5	10	1	$[IrCl(CO)_3]_n$	140	24	44
6	10	1	$[IrCl(CO)_3]_n$	80	48	44
7	10	1	$[IrCl(CO)_3]_n$	140	48	82 (74)
8	10	1	$Ir_4(CO)_{12}$[c]	140	48	65
9	10	1	$IrCl(CO)(PPh_3)_2$	140	48	0
10	10	1	$IrH(CO)(PPh_3)_3$	140	48	0

[a] Reaction conditions: catalyst (0.02 mmol), CO (50 atm), C_6H_6 (2 mL).
[b] GC yield based on $HSiEt_2Me$. Isolated yield is in parenthesis.
[c] The catalyst (0.005 mmol) is used.

Table II. $[IrCl(CO)_3]_n$-Catalyzed Reaction of 1-Hexene with some hydrosilanes and CO[a]



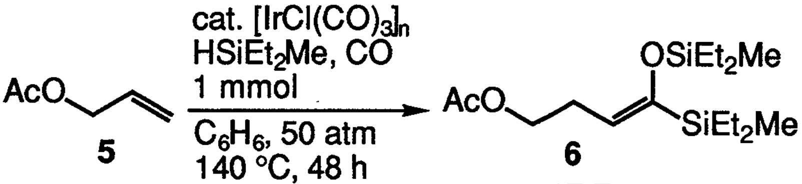
3 → 4

run	$HSiR_3$	yield, %[b]	*E*/*Z* ratio[c]
1	$HSiEt_2Me$	**4a**: 74	79/21
2	$HSiEt_3$	**4b**: 50[d]	66/34
3	$HSiPhMe_2$	**4c**: 65	87/13
4	HSi^tBuMe_2	trace	-
5	$HSi(OEt)_3$	0	-

[a] Reaction conditions: $[IrCl(CO)_3]_n$ (0.02 mmol), 1-hexene (10 mmol), $HSiR_3$ (1 mmol), CO (50 atm), C_6H_6 (2 mL), 140 °C, 48 h. [b] Isolated yield based on $HSiR_3$. [c] Determined by ^1H NMR. [d] Reaction time: 100 h.

2-3 The Reaction of Terminal Olefins with Carbon Monoxide and a Hydrosilane

The new catalytic reaction can be applied to a wide variety of terminal olefins to yield 1-silyl enol silyl ethers (Table III). The reaction of styrene gave a product in somewhat lower yield because of the dimerization or polymerization of the substrate under the present reaction conditions. Noteworthy is that a variety of functional groups, such as acetal,[3] cyano,[4] and epoxide,[5] known to react in transition metal catalyzed reactions with $HSiR_3$ or with $HSiR_3$/CO remain intact and that the olefinic part reacts chemoselectively in the present reaction. However, the reaction of allyl acetate **5** (5 mmol) as a substrate gave **6** in lower yield because an acetoxy group in **5** eliminated to form silyl acetate in the catalytic system (eq 3). The reaction of ethylene (10 atm) with $HSiEt_2Me$ and CO was also achieved the incorporation of CO to give the corresponding product in good yield.



5

6

31% (*E*/*Z* = 86/14)

(3)

2-4 The Reaction of Another Olefins with Carbon Monoxide and a Hydrosilane

For the reaction of another olefins with $HSiEt_2Me$ and CO, 2-methyl-1-butene gave a trace of **7** (eq 4). The reaction of 2-hexene as an internal olefin gave the same product **4a** as the reaction of 1-hexene in 11% yield (eq 5). Although cyclopentene did not react in the catalytic system, norbornene and norbornadiene were reactive (eqs 6 and 7).

Table III. Iridium-Catalyzed Reaction of Terminal Olefins with $HSiEt_2Me$ and CO^a

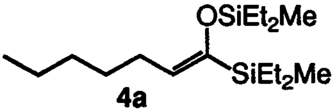
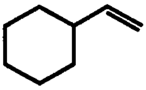
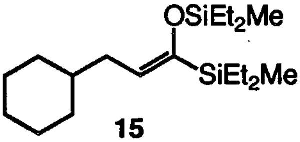
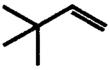
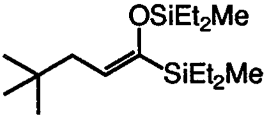
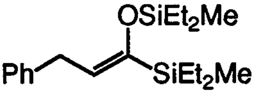
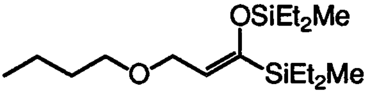
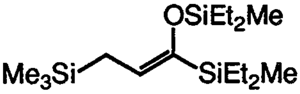
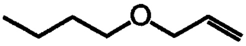
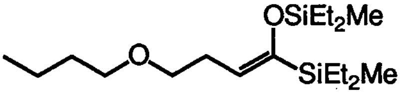
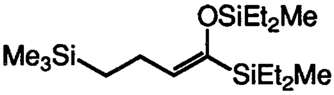
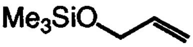
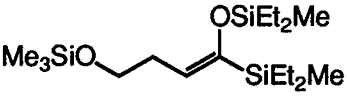
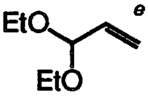
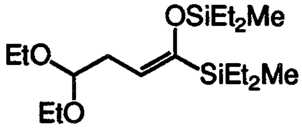
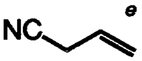
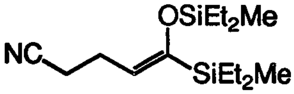
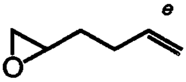
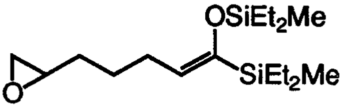
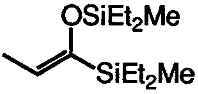
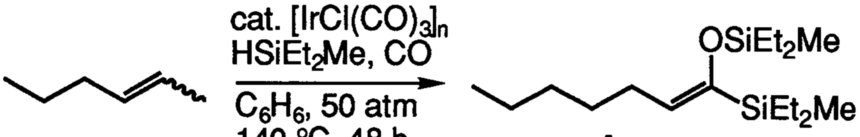
olefin	product	yield, %^{b}	E/Z ratio^c
 **3**	 **4a**	74 (82)	79/21
	 **15**	66 (82)	86/14
		60	69/31
		(50)^d	71/28
		67	57/43
		73	73/27
		75	68/32
		53	79/21
		67	67/33

Table III (Continued)

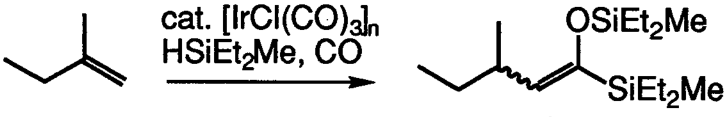
olefin	product	yield, %[b]	E/Z ratio[c]
 [e]		58	73/27
 [e]		45	73/27
 [e]		56	65/35
 [g]		67	66/34

[a] Reaction conditions: olefin (10 mmol), $HSiEt_2Me$ (1 mmol), $[IrCl(CO)_3]_n$ (0.02 mmol), CO (50 atm), C_6H_6 (2 mL), 140 °C, 48 h. [b] Isolated yields based on $HSiEt_2Me$. GC yield is in parentheses. [c] Determined by ^1H NMR. [d] Dimerization and polymerization of styrene also took place. [e] An olefin (5 mmol) was used. [g] Ethylene (10 atm, initial pressure at 25 °C) was used.



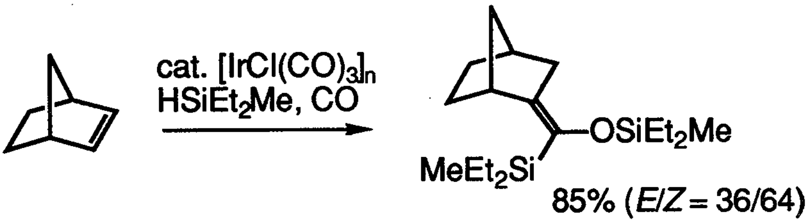
4a

(4)

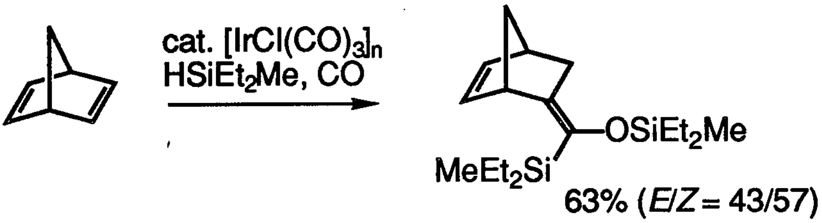


7 trace

(5)

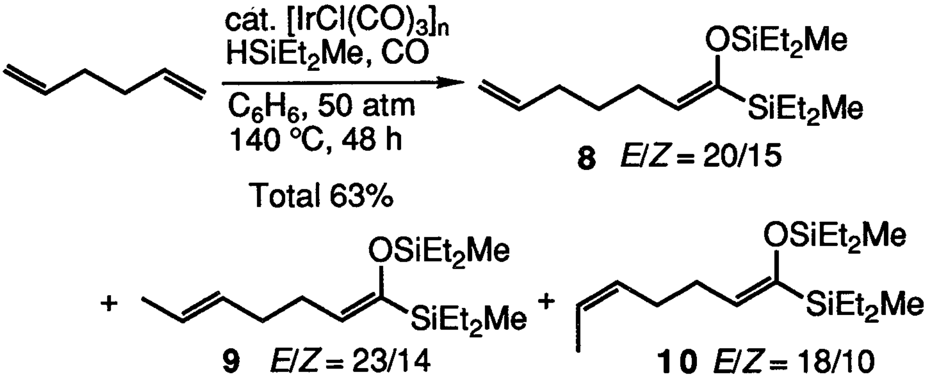


(6)

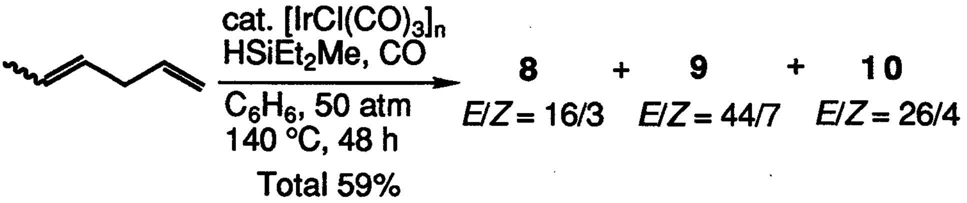


(7)

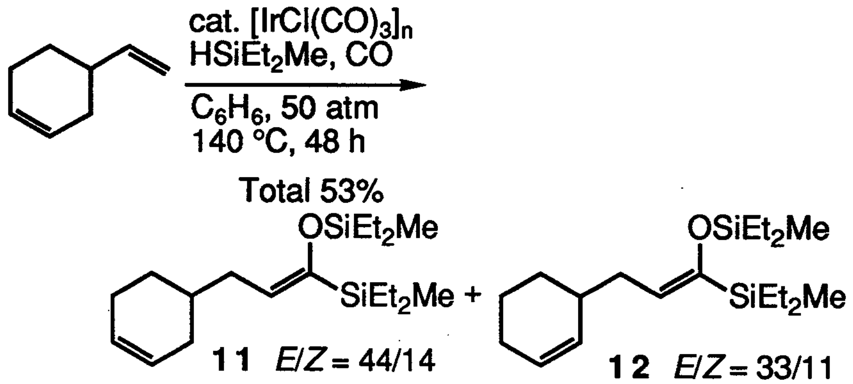
For the reaction of dienes with $HSiEt_2Me$ and CO, 1, 5-hexadiene gave the products **8** and **9** along with the expected product **10** in 63% total yield (eq 8). The reaction of 1, 4-hexadiene also gave the products **8**, **9**, and **10**, respectively, in the same reaction conditions (eq 9). Further, the reaction of 4-vinylcyclohexene gave the regioisomeric products **11** and **12** (eq 10). On the other hand, 2-methyl-1, 4-pentadiene reacted to give **13** and the regioisomer was not detectable (eq 11).



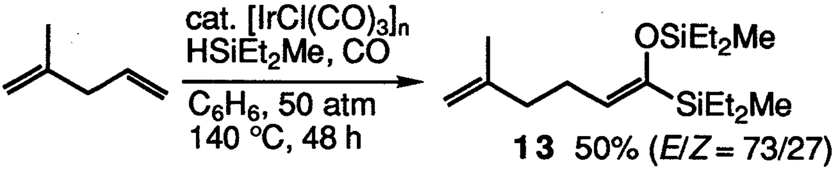
(8)



(9)



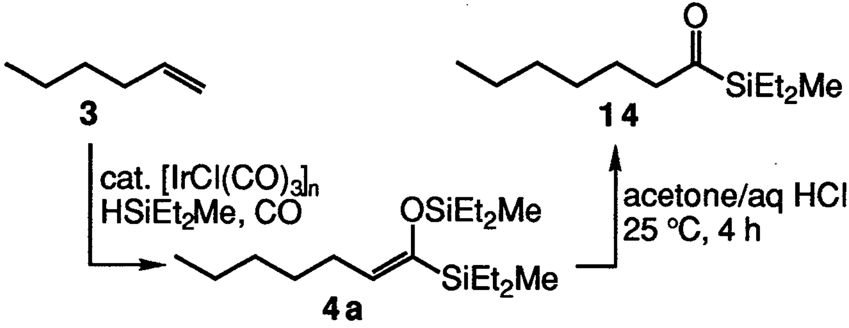
(10)



(11)

The products obtained can be easily hydrolyzed to acylsilanes.[6] For example, treatment of **4a** with acid (acetone/HCl (0.2 M) = 4/1) at 25 °C for 4 h gave an acylsilane **14** in quantitative yield (Scheme I).

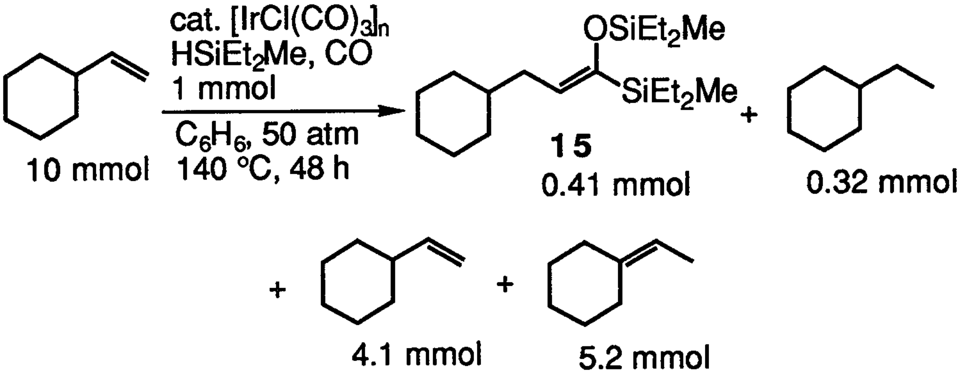
Scheme I



The present iridium-catalyzed reaction represents the first example of formation of acylsilane derivatives from the $HSiR_3$/CO combination.[7] The multifunctionality of the products is synthetically attractive and will find application in the future.[8]

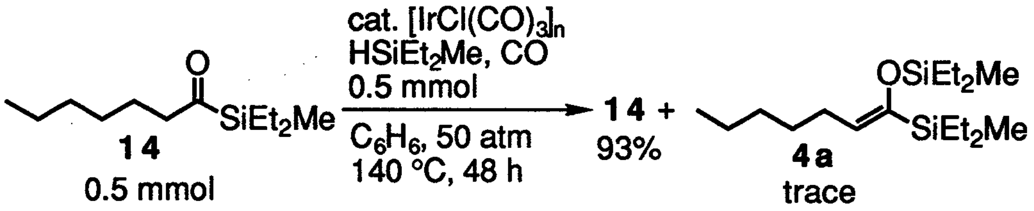
2-5 Mechanism

The material balance of the catalytic reaction indicates that two hydrogen atoms in reactants are not incorporated in the product. These are incorporated into another molecule of the starting olefin. Thus reaction of vinylcyclohexene (10 mmol) with $HSiEt_2Me$ (1 mmol) and CO gave ethylcyclohexane (64% yield based on $HSiEt_2Me$) in addition to **15** (82%). In this reaction, ethylidenecyclohexane was also obtained in 52% yield (based on vinylcyclohexane) as the result of isomerization of vinylcyclohexane, and 41% of vinylcyclohexane was recovered (eq 12).

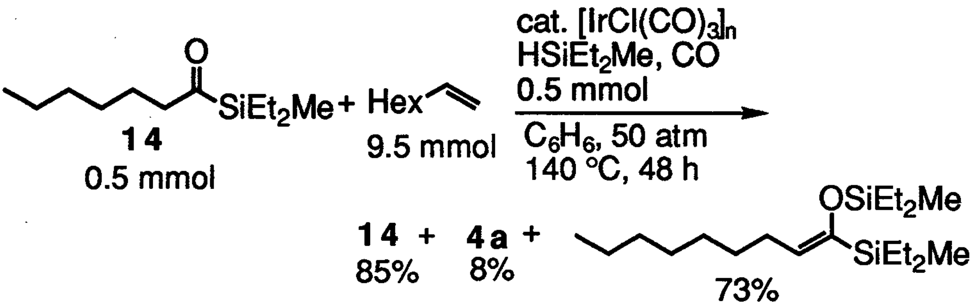


(12)

The mechanism of the catalytic reaction is not known at present. The possibility that an acylsilane intermediate gives the observed product by dehydrogenative silylation was eliminated. Thus reaction of **14** with 1 equiv of $HSiEt_2Me$ in the presence of $[IrCl(CO)_3]_n$ resulted in a trace of **4a** and 93% recovery of **14** (eq 13). And the reaction of **14** with $HSiEt_2Me$ and CO even in the presence of an excess amount of 1-octene under the same reaction conditions also resulted in the recovery of **14** in 85% along with the CO incorporation product derived from 1-octene (73% yield based on $HSiEt_2Me$) (eq 14).



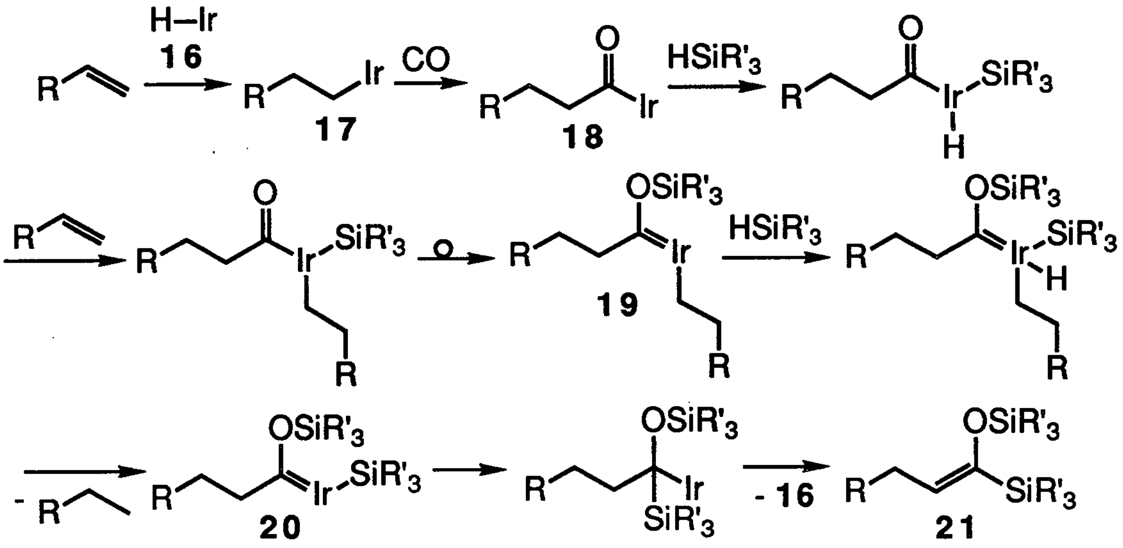
(13)



(14)

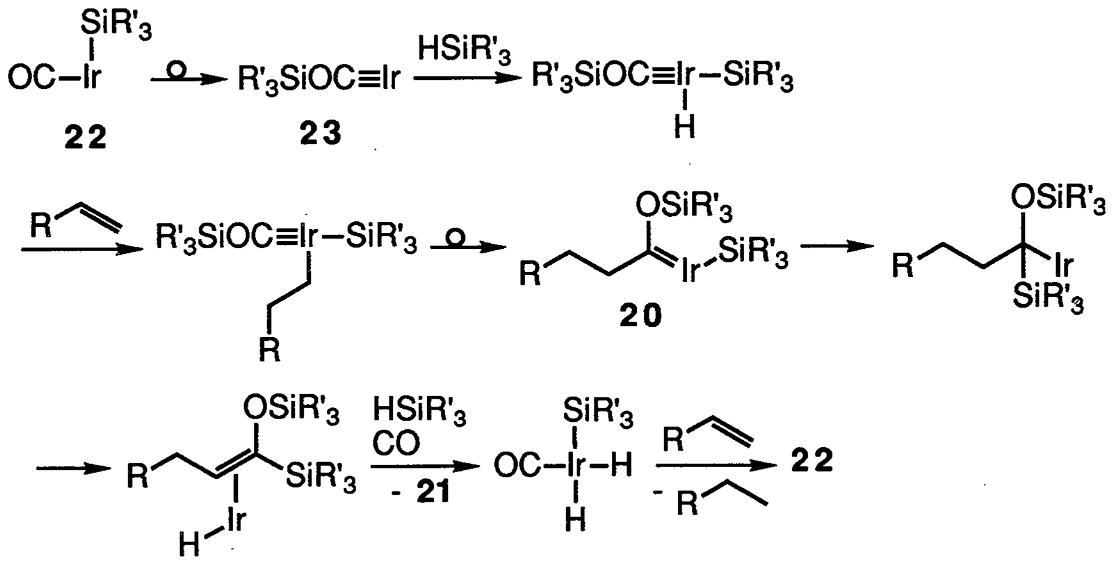
Although a mechanism of the catalytic reaction is not known at detail, the plausible one of the reaction is shown in Scheme II. It seems reasonable to postulate, as a key catalyst, a iridium hydride species **16**. Insertion of an olefin into iridium-hydrogen bond in **16** would give alkyl iridium intermediate **17** in which iridium is regioselectively substituted at the terminal position of olefin. After CO insertion (alkyl migration to the coordinated CO) to form an acyl iridium complex **18**, oxidative addition of $HSiR'_3$, and insertion of olefin into the iridiun-hydrogen bond, the complex **19** would be produced by 1, 3-migration for the silyl group on the iridium to the acylic oxygen atom (1, 3-silatoropic shift).[9] Oxidative addition of $HSiR'_3$ to **19** and reductive elimination would give alkane and **20**. And the product **21** would be given by α-insertion of carbene species in **20** and then β-elimination of hydrogen.

Scheme II



On the other hand, a siloxy carbyne complex **23**, which would be formed by the migration of silyl group to the coordinated CO in **22**,[10] might intervene as an intermediate to yield **21** and alkane (Scheme III).

Scheme III



2-6 Experimental Section

General Methods

Bulb-to-bulb distillations were done on a Shibata glass tube oven GTO-250R; boiling points (bp) refer to air bath temperature and are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JMN-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, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Shimadzu IR-400 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were obtained on a Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. Elemental analyses and high resolution mass spectra were performed by Elemental Analyses Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Preparative GC was carried out on Hitachi Model 164 gas chromatography using 2 m x 10 mm stainless steel column packed with 3% Silicone OV-1 supported on 60/80 mesh.

General Procedures

In a 50-mL stainless steel autoclave were placed $HSiEt_2Me$ (102 mg, 1 mmol), $[IrCl(CO)_3]_n$ (6 mg, 0.02 mmol), 10 mmol of olefin, and 2 mL of benzene. The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring in a silicon-oil bath at 140 °C for 48 h. Solvent was evaporated in vacuo and Kugelrohr distillation gave a pure sample of product. No effort was made for the complete separation of the each isomer, but when necessary partial separation by preparative GC was carried out. For GC yields, appropriate hydrocarbons (n-$C_{12}H_{26}$) calibrated against purified products were added before the catalytic reaction. The ratio of the stereoisomeric products were determined by GC and integration of vinyl proton resonances for ^{1}H NMR spectra of isolated products.

Diethyl[1-[(diethylmethylsilyl)oxy]-1-heptenyl]methylsilane (**4a**) (*E*/*Z* = 79/21 mixture): a colorless oil; bp 150 °C (oven)/3 Torr
^{1}H NMR ($CDCl_3$): δ [0.03 (s), 0.11 (s), 0.12 (s), 6 H, $SiCH_3$], 0.53 - 0.70 (m, 8 H, $SiCH_2$), 0.86 - 1.01 (c, 15 H, $SiCCH_3$ and CH_3), 1.25 - 1.40 (m, 6 H, CH_2), [1.98 (dt, *J* = 7.9, 7.1 Hz, *Z*), 2.08 (dt, *J* = 6.8, 7.1 Hz, *E*), 2 H, $=CCH_2$], [4.92 (t, *J* = 6.8 Hz, *E*), 5.46 (t, *J*= 7.9 Hz, *Z*), 1 H, =CH].
^{13}C NMR ($CDCl_3$): δ [-6.26 (*E*), -5.21 (*Z*), -3.68 (*Z*), -3.55 (*E*), $SiCH_3$], [4.74, 5.70, 6.84, 6.94, 7.25, 7.34, 7.52, 7.97, $SiCH_2CH_3$], 14.06 (CH_3), [22.56, 25.71, 27.31, 29.28, 30.73, 31.56, 31.74, CH_2], [125.06 (*Z*), 126.08 (*E*), =CH], [154.52 (*E*), 154.96 (*Z*), =C].
IR (neat): 2964s, 2884s, 1618m, 1464m, 1418m, 1380w, 1334w, 1302w, 1252m, 1200w, 1146m, 1094m, 1006m, 966m, 886m, 796s, 750m, 686m cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 314 (1, M^+), 285 (2, M^+ - C_2H_5), 213 (38), 189 (33), 162 (17), 161 (100), 133 (45), 105 (31), 101 (37), 73 (72), 59 (13).
Anal. Calcd for $C_{17}H_{38}OSi_2$: C, 64.89; H, 12.17. Found: C, 64.55; H, 12.28.

Dimethyl[1-[(dimethylphenylsilyl)oxy]-1-heptenyl]phenylsilane (**4b**) (*E*/*Z* = 87/13 mixture): a colorless oil; bp 160 °C (oven)/2 Torr
^{1}H NMR ($CDCl_3$): δ [0.20 (s, *E*), 0.22 (s, *E*), 0.30 (s, *Z*), 0.32 (s, *Z*) 12 H, $SiCH_3$], [0.72 (t, *J* = 7.0 Hz, *Z*), 0.79 (t, *J* = 6.7 Hz, *E*), 3 H, CH_3], 1.04 - 1.18 (m, 6 H, CH_2), [1.71 (dt, *J* = 8.1, 7.1 Hz, *Z*), 1.94 (dt, *J* = 6.8, 7.1 Hz, *E*), 2 H,

$=CCH_2$], [5.01 (t, *J* = 6.8 Hz, *E*), 5.46 (t, *J*= 8.1 Hz, *Z*), 1 H, =CH], 7.15 - 7.49 (m, 10 H, Ar).

^{13}C NMR ($CDCl_3$): δ [-3.05 (*E*), -1.97 (*Z*), -0.74 (*E*), -0.64 (*Z*), $SiCH_3$], 14.05 (CH_3), [22.45, 26.07, 27.49, 29.08, 30.14, 31.28, 31.70, CH_2], [127.58, 127.62, 127.67, 128.91, 129.01, 129.24, 129.33, 129.43, 132.99, 133.37, 133.57, 133.95, 134.24, 137.63, 138.35, 138.59, Ar, =CH], [154.07 (*Z*), 154.58 (*E*), =C].

IR (neat): 3076m, 3056m, 3020m, 2964s, 2932s, 2864m, 1654w, 1618m, 1594w, 1492w, 1462m, 1432m, 1380w, 1336w, 1302m, 1252s, 1192m, 1146m, 1116s, 1092s, 1000m, 894s, 730s, 700s, 648m, 620w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 382 (0, M^+), 367 (1, M^+ - CH_3), 247 (19), 210 (14), 209 (66), 195 (35), 193 (25), 136 (14), 135 (100).

Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.96. Found: C, 72.49; H, 8.96.

Triethyl[1-[(triethylsilyl)oxy]-1-heptenyl]silane (**4c**) (*E*/*Z* = 66/34 mixture): a colorless oil; bp 150 °C (oven)/2 Torr

^1H NMR ($CDCl_3$): δ 0.53 - 0.72 (m, 12 H, $SiCH_2$), 0.86 - 1.01 (c, 21 H, $SiCCH_3$ and CH_3), 1.25 - 1.39 (m, 6 H, CH_2), [1.96 (dt, *J* = 7.8, 7.1 Hz, *Z*), 2.08 (dt, *J* = 6.8, 7.1 Hz, *E*), 2 H, $=CCH_2$], [4.86 (t, *J* = 6.8 Hz, *E*), 5.43 (t, *J* = 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [2.82, 3.81, 5.55, 5.92, 6.88, 6.99, 7.34, 7.52, $SiCH_2CH_3$], 14.06 (CH_3), [22.54, 22.59, 25.68, 27.23, 29.31, 30.82, 31.57, 31.70, CH_2], [123.85 (*Z*), 125.97 (*E*), =CH], [153.64 (*E*), 154.38 (*Z*), =C].

IR (neat): 2964s, 2884s, 1660w, 1616m, 1464m, 1418m, 1380m, 1336w, 1302w, 1238m, 1152m, 1096m, 1006m, 974m, 882m, 800m, 738s, 692m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 342 (1, M+), 313 (3, M+ - C_2H_5), 227 (28), 217 (28), 190 (19), 189 (100), 161 (53), 133 (22), 115 (25), 105 (19), 87 (45), 59 (42).

Anal. Calcd for $C_{19}H_{42}OSi_2$: C, 66.59; H, 12.35. Found: C, 66.54; H, 12.47.

[3-Cyclohexyl-1-[(diethylmethylsilyl)oxy]-1-propenyl]diethylmethylsilane (**15**) (*E*/*Z* = 86/14 mixture): a colorless oil; bp 140 °C (oven)/3 Torr

^{1}H NMR ($CDCl_3$): δ [0.04 (s), 0.10 (s), 0.12 (s), 6 H, $SiCH_3$], 0.53 - 0.70 (m, 8 H, $SiCH_2$), 0.88 - 1.01 (m, 12 H, $SiCCH_3$), 1.16 - 1.74 (c, 11 H, CH_2 and CH), [1.88 (dd, *J* = 7.9, 6.7 Hz, *Z*), 1.98 (dd, *J* = 7.0, 6.9 Hz, *E*), 2 H, CH_2], [4.96 (t, *J* = 6.9 Hz, *E*), 5.48 (t, *J* = 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.23 (*E*), -5.08 (*Z*), -3.65 (*Z*), -3.48 (*E*), $SiCH_3$], [4.77, 5.75, 6.84, 6.96, 7.28, 7.35, 7.51, 7.58, $SiCH_2CH_3$], [26.42, 26.47, 26.65, 33.22, 33.32, 33.38, 34.86, 38.20, 39.38, CH_2, CH], [123.37 (*Z*), 124.31 (*E*), =CH], [155.13 (*E*), 155.39 (*Z*), =C].

IR (neat): 2960s, 2932s, 2888s, 2860m, 1616w, 1464m, 1454m, 1418m, 1380w, 1350w, 1330w, 1300m, 1252s, 1202w, 1154m, 1114s, 1078m, 1006m, 970m, 950m, 878m, 796s, 750s, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 340 (2, M+), 257 (26), 239 (25), 190 (10), 189 (57), 162 (15), 161 (89), 133 (38), 105 (31), 101 (44), 73 (100), 59 (14), 57 (24).

Anal. Calcd for $C_{19}H_{40}OSi_2$: C, 66.98; H, 11.83. Found: C, 66.71; H, 12.08.

Diethyl[1-[(diethylmethylsilyl)oxy]-4, 4-dimethyl-1-pentenyl]methylsilane (*E*/*Z* = 69/31 mixture): a colorless oil; bp 130 °C (oven)/3 Torr

^{1}H NMR ($CDCl_3$): δ 0.04 (s), 0.10 (s), 0.11 (s), 6 H, $SiCH_3$], 0.54 - 0.70 (m, 8 H, $SiCH_2$), 0.87 (s, 9 H, CH_3), 0.87 - 1.01 (m, 12 H, $SiCCH_3$), [1.90 (d, *J* =

7.8 Hz, *Z*), 1.98 (d, *J* = 7.1 Hz, *E*), 2 H, CH_2], [5.03 (t, *J* = 7.1 Hz, *E*), 5.51 (t, *J*= 7.8 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.18 (*E*), -4.90 (*Z*), -3.62 (*Z*), -3.42 (*E*), $SiCH_3$], [4.80, 5.80, 6.84, 6.96, 7.29, 7.35, 7.50, 7.61, $SiCH_2CH_3$], 29.31 (CH_3), 30.93 (C), [39.43 (*E*), 40.91 (*Z*), CH_2], [121.51 (*Z*), 122.53 (*E*), =CH], [155.77 (*E*), 158.86 (*Z*), =C].

IR (neat): 2964s, 2884m, 1618w, 1394m, 1380w, 1366w, 1332w, 1278w, 1254s, 1198w, 1178m, 1120s, 1060m, 1010m, 970m, 928w, 898w, 856m, 798s, 748s, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 314 (5, M^+), 258 (23), 257 (96), 189 (20), 175 (12), 162 (15), 161 (90), 147 (17), 133 (49), 105 (36), 103 (10), 101 (46), 73 (100), 59 (17), 57 (15).

Anal. Calcd for $C_{17}H_{38}OSi_2$: C, 64.89; H, 12.17. Found: C, 64.99; H, 12.47.

Diethyl[1-[(diethylmethylsilyl)oxy]-3-phenyl-1-propenyl]methylsilane (*E*/*Z* = 72/28 mixture): a pale yellow oil; bp 150 °C (oven)/2 Torr

^1H NMR ($CDCl_3$): δ [0.11 (s), 0.17 (s), 0.21 (s), 6 H, $SiCH_3$], 0.57 - 0.84 (m, 8 H, $SiCH_2$), 0.89 - 1.09 (m, 12 H, $SiCCH_3$), [3.43 (d, *J* = 7.8 Hz, *Z*), 3.52 (d, *J* = 6.8 Hz, *E*), 2 H, CH_2], [5.19 (t, *J* = 6.8 Hz, *E*), 5.63 (t, *J*= 7.8 Hz, *Z*), 1 H, =CH], 7.20 - 7.39 (m, 5 H, Ar).

^{13}C NMR ($CDCl_3$): δ [-6.26 (*E*), -5.11 (*Z*), -3.63 (*Z*), -3.40 (*E*), $SiCH_3$], [4.71, 5.75, 6.80, 6.94, 7.20, 7.35, 7.54, 7.58 $SiCH_2CH_3$], [31.85 (*E*), 33.32 (*Z*), CH_2], [122.18, 123.96, 125.45, 125.71, 125.85, 125.91, 128.31, 128.39, 141.48, 141.60, Ar, =CH], [155.74 (*E*), 156.76 (*Z*), =C].

IR (neat): 3068w, 3036w, 2964s, 2920m, 2884s, 1650m, 1614m, 1498m, 1460m, 1418m, 1380w, 1308w, 1254s, 1126s, 1074m, 1006m, 966m, 900w, 798s, 748s, 698m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 334 (5, M^+), 305 (1, $M^+ - C_2H_5$), 233 (35), 189 (42), 162 (14), 161 (82), 133 (43), 105 (38), 103 (11), 102 (10), 101 (85), 91 (21), 73 (100), 59 (15).
Exact mass for $C_{19}H_{34}OSi_2$ (M^+), Calcd, 334.2149; Found, 334.2178.

[3-Butoxy-1-[(diethylmethylsilyl)oxy]-1-propenyl]diethylmethylsilane (*E*/*Z* = 57/43 mixture): a colorless oil; bp 160 °C (oven)/3 Torr
^1H NMR ($CDCl_3$): δ [0.05 (s), 0.12 (s), 0.13 (s), 6 H, $SiCH_3$], 0.55 - 0.69 (m, 8 H, $SiCH_2$), 0.89 - 1.00 (c, 15 H, $SiCCH_3$ and CH_3), 1.41 (sextet, *J* = 7.1 Hz, 2 H, CH_2), 1.56 (tt, *J* = 7.1, 6.4 Hz, 2 H, CH_2), [3.38 (t, *J* = 6.4 Hz, *E*), 3.40 (t, *J* = 6.4 Hz, *Z*), 2 H, OCH_2], [3.91 (d, *J* = 7.8 Hz, *Z*), 4.05 (d, *J* = 6.4 Hz, *E*), 2 H, OCH_2], [5.15 (t, *J* = 6.4 Hz, *E*), 5.56 (t, *J* = 7.8 Hz, *Z*), 1 H, =CH].
^{13}C NMR ($CDCl_3$): δ [-6.44 (*E*), -5.21 (*Z*), -3.77 (*Z*), -3.66 (*E*), $SiCH_3$], [4.54, 5.64, 6.70, 6.80, 7.08, 7.26, 7.35, 7.61, $SiCH_2CH_3$], 13.86 (CH_3), [19.36, 19.41, 31.88, 31.92, CH_2], [65.10, 66.69, 69.38, 70.06, OCH_2], [119.78 (*Z*), 122.23 (*E*), =CH], [158.06 (*Z*), 160.78 (*E*), =C].
IR (neat): 2962s, 2940s, 2882s, 1612m, 1524w, 1510w, 1461m, 1418m, 1380w, 1354w, 1253m, 1156m, 1123m, 1091m, 1006m, 965m, 815s, 798s, 752m, 687m cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 330 (0, M^+), 301 (4, $M^+ - C_2H_5$), 273 (35), 189 (16), 161 (27), 145 (12), 133 (20), 105 (18), 103 (12), 102 (11), 101 (100), 99 (14), 89 (15), 73 (98), 59 (11), 57 (30).
Exact mass for $C_{17}H_{38}O_2Si_2$ (M^+), Calcd, 330.2410; Found, 330.2433.

Diethyl[1-[(diethylmethylsilyl)oxy]-3-(trimethylsilyl)-1-propenyl]-methylsilane (*E*/*Z* = 73/27 mixture): a colorless oil; bp 120 °C (oven)/3 Torr
^1H NMR ($CDCl_3$): δ [-0.01 (s), 0.01 (s), 0.10 (s), 0.11 (s), 15 H, $SiCH_3$], 0.51 - 0.76 (m, 8 H, $SiCH_2$), 0.92 - 1.01 (m, 12 H, $SiCCH_3$), [1.38 (d, *J* = 8.5

Hz, *Z*), 1.50 (d, *J* = 8.5 Hz, *E*), 2 H, CH_2], [5.00 (t, *J* = 8.5 Hz, *E*), 5.48 (t, *J* = 8.5 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.09 (*E*), -5.02 (*Z*), -3.65 (*Z*), -3.39 (*E*), -1.80 (*E*), -1.69 (*Z*), $SiCH_3$], [4.88, 5.70, 6.85, 6.97, 7.28, 7.39, 7.55, 7.65, $SiCH_2CH_3$], [16.61 (*E*), 16.77 (*Z*), CH_2], [120.44 (*Z*), 121.33 (*E*), =CH], [152.97 (*E*), 153.46 (*Z*), =C].

IR (neat): 2964s, 2888m, 1610w, 1464w, 1418w, 1302w, 1250s, 1172m, 1144m, 1102s, 1012m, 968m, 906s, 860s, 798s, 750s, 694m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 330 (15, M$^+$), 189 (11), 175 (19), 161 (38), 157 (10), 147 (19), 133 (23), 105 (15), 101 (40), 73 (100), 59 (11).

Anal. Calcd for $C_{16}H_{38}OSi_3$: C, 58.11; H, 11.58. Found: C, 58.14; H, 11.81.

[4-Butoxy-1-[(diethylmethylsilyl)oxy]-1-butenyl]diethylmethylsilane (*E*/*Z* = 68/32 mixture): a colorless oil; bp 130 °C (oven)/3 Torr

^1H NMR ($CDCl_3$): δ [0.03 (s), 0.11 (s), 0.12 (s), 6 H, $SiCH_3$], 0.53 - 0.69 (m, 8 H, $SiCH_2$), 0.89 - 1.00 (c, 15 H, $SiCCH_3$ and CH_3), 1.38 (sextet, *J* = 7.1 Hz, 2 H, CH_2), 1.55 (tt, *J* = 7.1, 6.5 Hz, 2 H, CH_2), [2.27 (dt, *J* = 7.8, 7.9 Hz, *Z*), 2.37 (dt, *J* = 6.5, 6.8 Hz, *E*), 2 H, CH_2], [3.35 (t, *J* = 7.9 Hz, *Z*), 3.39 (t, *J* = 6.8 Hz, *E*), 2 H, OCH_2], [3.40 (t, *J* = 6.5 Hz, *Z*), 3.41 (t, *J* = 6.5 Hz, *E*), 2 H, OCH_2], [4.97 (t, *J* = 6.5 Hz, *E*), 5.44 (t, *J* = 7.8 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.29 (*E*), -5.67 (*Z*), -3.75 (*Z*), -3.66 (*E*), $SiCH_3$], [4.68, 5.61, 6.79, 6.90, 7.17, 7.31, 7.45, 7.48, $SiCH_2CH_3$], 13.88 (CH_3), [19.35, 26.42, 28.03, 31.80, 31.83, CH_2], [70.22, 70.52, 70.72, 71.53, OCH_2], [120.14 (*Z*), 121.45 (*E*), =CH], [156.33 (*E*), 157.01 (*Z*), =C].

IR (neat): 2964s, 2884s, 2800w, 1618w, 1464n, 1418w, 1380w, 1228w, 1296w, 1252m, 1112m, 1076m, 1008m, 966m, 882m, 798s, 750m, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 344 (0, M+), 257 (21), 243 (12), 189 (18), 171 (14), 162 (12), 161 (71), 147 (14), 143 (36), 133 (37), 105 (26), 101 (55), 89 (15), 73 (100), 61 (14), 59 (16), 57 (30).
Exact mass for $C_{16}H_{35}O_2Si_2$ (M^+ - C_2H_5), Calcd, 315.2175; Found, 315.2173.

Diethyl[1-[(diethylmethylsilyl)oxy]-4-(trimethylsilyl)-1-butenyl]-methylsilane (*E*/*Z* = 79/21 mixture): a colorless oil; bp 140 °C (oven)/2 Torr
^{1}H NMR ($CDCl_3$): δ [-0.02 (s), 0.03 (s), 0.10 (s), 0.12 (s), 15 H, $SiCH_3$], 0.53 - 0.70 (m, 10 H, $SiCH_2$), 0.91 - 1.01 (m, 12 H, $SiCCH_3$), [1.93 - 2.02 (m, *Z*), 2.06 - 2.15 (m, *E*), 2 H, CH_2], [4.93 (t, *J* = 6.7 Hz, *E*), 5.50 (t, *J* = 7.9 Hz, *Z*), 1 H, =CH].
^{13}C NMR ($CDCl_3$): δ [-6.28 (*E*), -5.19 (*Z*), -3.65 (*Z*), -3.54 (*E*), -1.66 (*Z*), -1.57 (*E*), $SiCH_3$], [4.73, 5.75, 6.87, 6.96, 7.25, 7.37, 7.51, 7.63, $SiCH_2CH_3$], [16.80 (*E*), 18.59 (*Z*), 20.08 (*E*), 21.78 (*Z*), CH_2], [128.07 (*Z*), 129.10 (*E*), =CH], [153.29 (*E*), 153.74 (*Z*), =C].
IR (neat): 2960s, 2920s, 2884s, 1616w, 1464m, 1380w, 1326w, 1284m, 1250s, 1180m, 1160m, 1104s, 1006s, 966m, 920w, 862s, 838s, 796s, 752s, 690m cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 344 (2, M+), 243 (23), 189 (12), 161 (31), 133 (20), 105 (15), 101 (50), 73 (100), 59 (11).
Anal. Calcd for $C_{17}H_{40}OSi_3$: C, 59.23; H, 11.69. Found: C, 59.50; H, 11.96.

[1-[(Diethylmethylsilyl)oxy]-4-(trimethylsilyloxy)-1-butenyl]diethyl-methylsilane (*E*/*Z* = 67/33 mixture): a colorless oil; bp 160 °C (oven)/3 Torr
^{1}H NMR ($CDCl_3$): δ [0.03 (s), 0.10 (s), 0.11 (s), 0.12 (s), 15 H, $SiCH_3$], 0.53 - 0.70 (m, 8 H, $SiCH_2$), 0.90 - 1.00 (m ,12 H, CH_3), [2.23 (dt, *J* = 7.9, 7.1

Hz, *Z*), 2.34 (dt, *J* = 6.8, 7.1 Hz, *E*), 2 H, CH_2], [3.51 (t, *J* = 7.1 Hz, *Z*), 3.56 (t, *J* = 7.1 Hz, *E*), 2 H, OCH_2], [4.96 (t, *J* = 6.8 Hz, *E*), 5.41 (t, *J*= 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.29 (*E*), -5.24 (*Z*), -3.71 (*Z*), -3.53 (*E*), -0.53 (*Z*), -0.45 (*E*), $SiCH_3$], [4.68, 5.63, 6.19, 6.80, 6.91, 7.16, 7.32, 7.49, $SiCH_2CH_3$], [29.30 (*E*), 30.89 (*Z*), CH_2], [62.22 (*E*), 63.25 (*Z*), OCH_2], [119.94 (*Z*), 121.42 (*E*), =CH], [156.32 (*E*), 157.08 (*Z*), =C].

IR (neat): 2964s, 2916s, 2884s, 1618m, 1464m, 1418m, 1384m, 1338w, 1296m, 1252s, 1148s, 1100s, 1006s, 964m, 880s, 842s, 794s, 750s, 686m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 360 (0, M$^+$), 331 (6, M$^+$ - C_2H_5), 257 (25), 189 (39), 161 (39), 133 (32), 119 (10), 105 (20), 103 (10), 101 (31), 89 (17), 83 (17), 75 (30), 73 (100), 61 (29), 59 (20), 58 (12).

Anal. Calcd for $C_{17}H_{40}O_2Si_3$: C, 56.60; H, 11.18. Found: C, 56.39; H, 11.33.

[4, 4-Diethoxy-1-[(diethylmethylsilyl)oxy]-1-butenyl]diethylmethylsilane (*E*/*Z* = 73/27 mixture): a colorless oil; bp 160 °C (oven)/2 Torr

^1H NMR ($CDCl_3$): δ [0.02 (s), 0.10 (s), [0.11 (s), 0.12 (s), 6 H, $SiCH_3$], 0.52 - 0.69 (m, 8 H, $SiCH_2$), 0.89 - 0.98 (m, 12 H, CH_3), [1.18 (t, *J* = 7.1 Hz, *E*), 1.19 (t, *J* = 7.1 Hz, *Z*), 6 H, CH_3], [2.30 (dd, *J* = 5.9, 7.9 Hz, *Z*), 2.42 (dd, *J* = 6.0, 6.8 Hz, *E*), 2 H, CH_2], [3.47 (q, *J* = 7.1 Hz, *Z*), 3.50 (q, *J* = 7.1 Hz, *E*), 2 H, CH_2], [3.63 (q, *J* = 7.1 Hz, *Z*), 3.64 (q, *J* = 7.1 Hz, *E*), 2 H, CH_2], [4.37 (t, *J* = 5.9 Hz, *Z*), 4.46 (t, *J*= 6.0 Hz, *E*), 1 H, CH], [4.98 (t, *J* = 6.8 Hz, *E*), 5.42 (t, *J*= 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.32 (*E*), -5.82 (*Z*), -3.80 (*Z*), -3.54 (*E*), $SiCH_3$], [4.65, 5.52, 6.76, 6.87, 7.13, 7.26, 7.35, 7.45, $SiCH_2CH_3$], [15.16, 15.30, CH_3], [30.40 (*E*), 31.96 (*Z*), CH_2], [60.88 (*E*), 60.99 (*Z*), OCH_2], [102.30 (*E*), 103.59 (*Z*), CHO], [118.65 (*Z*), 119.80 (*E*), =CH], [156.73 (*E*), 157.33 (*Z*), =C].

IR (neat): 2964s, 2884s, 2744w, 1738w, 1684w, 1620m, 1464m, 1418m, 1372m, 1344m, 1316m, 1252s, 1116s, 1066s, 1008s, 960m, 880m, 798s, 752m, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 360 (0, M$^+$), 315 (12), 314 (45), 161 (43), 133 (28), 105 (22), 101 (54), 73 (100), 61 (10), 59 (12).

Anal. Calcd for $C_{18}H_{40}O_3Si_2$: C, 59.94; H, 11.18. Found: C, 59.89; H, 11.17.

[4-Cyano-1-[(diethylmethylsilyl)oxy]-1-butenyl]diethylmethylsilane (*E*/*Z* = 73/27 mixture): a colorless oil; bp 170 °C (oven)/2 Torr

^{1}H NMR (CDCl$_3$): δ [0.05 (s), 0.12 (s), 0.13 (s), 6 H, SiCH$_3$], 0.54 - 0.73 (m, 8 H, SiCH$_2$), 0.90 - 1.00 (m ,12 H, CH$_3$), 2.31 - 2.48 (m, 4 H, CH$_2$), [4.96 (t, *J* = 6.6 Hz, *E*), 5.40 (t, *J*= 7.8 Hz, *Z*), 1 H, =CH].

^{13}C NMR (CDCl$_3$): δ [-6.38 (*E*), -5.24 (*Z*), -3.80 (*Z*), -3.51 (*E*), SiCH$_3$], [4.54, 5.51, 6.71, 6.80, 7.08, 7.22, 7.37, 7.46, SiCH$_2$CH$_3$], [17.18 (*E*), 18.80 (*Z*), 21.61 (*E*), 23.60 (*Z*), CH$_2$], 119.02, 119.43, 120.61 (=CH, CN), [158.53 (*E*), 159.24 (*Z*), =C].

IR (neat): 2964s, 2920s, 2884s, 2816w, 2252w, 1616m, 1464m, 1420m, 1382w, 1340w, 1294m, 1254s, 1194m, 1132s, 1058s, 1006s, 966m, 874s, 798s, 754s, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 297 (6, M$^+$), 269 (18), 268 (56, M$^+$ - C$_2$H$_5$), 207 (14), 189 (33), 163 (14), 162 (18), 161 (96), 133 (55), 113 (10), 105 (42), 103 (14), 101 (49), 92 (13), 91 (10), 89 (10), 74 (13), 73 (100), 72 (12), 71 (10), 61 (18), 59 (26), 58 (18), 52 (12).

Anal. Calcd for $C_{15}H_{31}NOSi_2$: C, 60.54; H, 10.50; N, 4.71. Found: C, 60.76; H, 10.61; N, 4.88.

Diethyl[1-[(diethylmethylsilyl)oxy]-6-oxiranyl-1-pentenyl]methylsilane (*E*/*Z* = 65/35 mixture): a colorless oil; bp 170 °C (oven)/2 Torr

^{1}H NMR ($CDCl_3$): δ [0.01 (s), 0.09 (s), 0.10 (s), 6 H, $SiCH_3$], 0.52 - 0.67 (m, 8 H, $SiCH_2$), 0.89 - 0.98 (m ,12 H, CH_3), 1.49 - 1.68 (m, 4 H, CH_2), [2.03 (dt, *J* = 7.9, 7.5 Hz, *Z*), 2.13 (dt, *J* = 6.8, 7.1 Hz, *E*), 2 H, $CH_2C=$], 2.44 (dd, *J* = 2.7, 5.1 Hz, 1 H, CH), [2.72 (dd, *J* = 3.5, 5.1 Hz, *E*), 2.73 (dd, *J* = 3.5, 5.1 Hz, *Z*), 1 H, CH], 2.84 - 2.91 (m, 1 H, CH), [4.89 (t, *J* = 6.8 Hz, *E*), 5.42 (t, *J* = 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.32 (*E*), -5.25 (*Z*), -3.72 (*Z*), -3.57 (*E*), $SiCH_3$], [4.64, 5.61, 6.69, 6.88, 7.00, 7.17, 7.31, 7.45, $SiCH_2CH_3$], [25.29, 25.75, 27.05, 27.31, 32.06, 32.14, CH_2], [47.02, 47.13, OCH_2], 52.1 (CH), [123.91 (*E*), 125.06 (*Z*), =CH], [155.31 (*E*), 155.68 (*Z*), =C].

IR (neat): 2964s, 2920s, 2884s, 1730w, 1698w, 1616m, 1464m, 1416m, 1380m, 1252s, 1132s, 1094s, 1006s, 966m, 882m, 798s, 750s, 686m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 328 (4, M^+), 299 (17, $M^+ - C_2H_5$), 273 (26), 231 (13), 189 (36), 177 (33), 161 (54), 149 (12), 139 (28), 138 (16), 133 (26), 131 (12), 123 (13), 121 (16), 119 (18), 107 (11), 105 (45), 103 (16), 101 (15), 91 (11), 89 (29), 87 (12), 84 (11), 81 (46), 79 (15), 77 (12), 75 (11), 73 (33), 67 (28), 61 (37), 59 (27), 58 (41), 57 (100), 55 (25), 53 (11), 52 (11).

Anal. Calcd for $C_{17}H_{36}O_2Si_2$: C, 62.13; H, 11.04. Found: C, 61.97; H, 11.03.

Diethyl[1-[(diethylmethylsilyl)oxy]-1-propenyl]methylsilane (*E*/*Z* = 66/34 mixture): a colorless oil; bp 120 °C (oven)/10 Torr

^{1}H NMR ($CDCl_3$): δ [0.03 (s), 0.10 (s), 0.11 (s), 0.13 (s) 6 H, $SiCH_3$], 0.53 - 0.71 (m, 8 H, $SiCH_2$), 0.82 - 1.07 (m ,12 H, CH_3), [1.60 (d, *J* = 7.3 Hz, *Z*), 1.61 (d, *J* = 6.6 Hz, *E*), 3 H, CH_3], [5.04 (q, *J* = 6.6 Hz, *E*), 5.51 (q, *J*= 7.3 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.32 (*E*), -5.37 (*Z*), -3.69 (*Z*), -3.54 (*E*), $SiCH_3$], [4.70, 5.60, 6.82, 6.91, 7.23, 7.34, 7.46, 7.52, $SiCH_2CH_3$], [11.36 (*E*), 12.53 (*Z*), CH_3], [118.36 (*Z*), 119.54 (*E*), =CH], [155.84 (*Z*), 156.17 (*E*), =C].

IR (neat): 2964s, 2920s, 2884s, 1688w, 1624m, 1464m, 1415m, 1380m, 1296m, 1252s, 1146s, 1098m, 1070s, 1006s, 972m, 856s, 796s, 766s, 750s, 688m, 672m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 258 (3, M^+), 189 (24), 162 (17), 161 (100), 133 (58), 105 (29), 101 (14), 73 (45), 72 (18), 66 (15), 59 (20), 52 (14).

Anal. Calcd for $C_{13}H_{30}OSi_2$: C, 60.39; H, 11.70. Found: C, 60.24; H, 11.76.

[4-Acetoxy-1-(diethylmethylsilyl)-1-butenyl]oxy]diethylmethylsilane (**6**) (*E*/*Z* = 86/14 mixture): a colorless oil; bp 160 °C (oven)/2 Torr

^1H NMR ($CDCl_3$): δ [0.04 (s, *E*), 0.10 (s, *Z*), 3 H, $SiCH_3$), [0.12 (s, *Z*), 0.13 (s, *E*), 3 H, $SiCH_3$], 0.53 - 0.73 (m, 8 H, $SiCH_2$), 0.84 - 1.02 (m, 12 H, $SiCCH_3$), 2.04 (s, 3 H, CH_3), [2.34 (dt, *J* = 7.9, 8.0 Hz, *Z*), 2.43 (dt, *J* = 6.8, 6.8 Hz, *E*), 2 H, CH_2], [4.01 (t, *J* = 8.0 Hz, *Z*), 4.05 (t, *J* = 6.8 Hz, *E*), 2 H, OCH_2], [4.91 (t, *J* = 6.8 Hz, *E*), 5.44 (t, *J* = 7.9 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.35, -5.30, -3.82, -3.57 ($SiCH_3$)], [4.60, 5.52, 6.73, 6.84 ($SiCH_2$)], [7.11, 7.23, 7.39, 7.45 ($SiCCH_3$)], [20.85, 20.89 (CH_3)], [25.23, 26.87 (CH_2)], [63.80, 64.65 (OCH_2)], [118.64, 120.00 (=CH)], [157.52, 158.11 (=C)], [170.99, 171.06 (CO)].

IR (neat): 2964s, 2920s, 2888s, 1748s, 1648w, 1618w, 1464m, 1420m, 1386m, 1366m, 1342m, 1234s, 1148s, 1108m, 1078s, 1036s, 1010s, 970m, 840m, 798s, 752s, 689m, 602w, 496w, 428w, 372w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 330 (0, M$^+$), 301 (2, M$^+$ - C_2H_5), 271 (11), 270 (41), 189 (27), 162 (16), 161 (91), 145 (10), 133 (43), 119 (10), 105 (33), 103 (12), 101 (52), 89 (22), 75 (10), 73 (100), 61 (21), 59 (16).

Anal. Calcd for $C_{16}H_{34}O_3Si_2$: Calcd, C, 58.13; H, 10.37. Found: C, 58.08; H, 10.46.

[Bicyclo[2. 2. 1]hept-2-ylidene[(diethymethylsilyl)oxy]methyl]diethylmethylsilane (*E*/*Z* = 36/64 mixture): a colorless oil; 150 °C (oven)/3 Torr

^{1}H NMR ($CDCl_3$): δ [0.06 (s), 0.10 (s), 0.13 (s) 6 H, $SiCH_3$], 0.56 - 0.69 (m, 8 H, $SiCH_2$), 0.89 - 1.00 (m ,12 H, CH_3), 1.22 - 1.64 (m, 6 H, CH_2), [1.85 (dd, *J* = 14.6, 2.7 Hz, *E*), 1.94 (dd, *J* = 15.6, 2.3 Hz, *Z*), 1 H, CH_2*endo*], [2.16 (ddd, *J* = 14.6, 5.1, 2.2 Hz, *E*), 2.23 (ddd, *J* = 16.6, 4.6, 2.4 Hz, *Z*), 1 H, CH_2*exo*], 2.31 - 2.39 (m, 1 H, CH), [2.81 - 2.87 (m, *Z*), 3.15 - 3.19 (m, *E*), 1 H, CH].

^{13}C NMR ($CDCl_3$): δ [-5.57, -5.13, -3.46, -3.39, $SiCH_3$], [5.28, 5.31, 5.84, 5.87, 7.05, 7.52, 7.61, 7.71, $SiCH_2CH_3$], [28.53, 29.01, 30.03, 35.84, 35.88, 36.07, 36.74, 37.36, 38.57, 39.93, 40.53, 40.62, CH_2, CH], [142.84, 143.71, 144.14, =C].

IR (neat): 2964s, 2880s, 1632w, 1462m, 1420m, 1380w, 1306w, 1284w, 1250s, 1188m, 1162m, 1134s, 1120s, 1106s, 1082s, 1006s, 966m, 930w, 906w, 890m, 880m, 854m, 818s, 796s, 745s, 686m, 610w, 592w, 470w, 416w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 324 (28, M$^+$), 295 (12), 162 (17), 161 (100), 147 (19), 134 (11), 133 (71), 121 (10), 119 (12), 105 (39), 101 (26), 91 (10), 73 (84), 59 (15).

Exact mass for $C_{18}H_{36}OSi_2$ (M$^+$), Calcd, 324.2277; Found, 324.2291.

[Bicyclo[2. 2. 1]hept-2-en-5-ylidene[(diethymethylsilyl)oxy]methyl]-diethylmethylsilane (*E*/*Z* = 43/57 mixture): a colorless oil; bp 170 °C (oven)/2 Torr

^{1}H NMR ($CDCl_3$): δ [0.06 (s, *E*), 0.09 (s, *Z*), 3 H, $SiCH_3$), [0.13 (s, *Z*), 0.14 (s, *E*), 3 H, $SiCH_3$], 0.58 - 0.72 (m, 8 H, $SiCH_2$), 0.88 - 1.01 (m, 12 H, $SiCCH_3$), [1.28 (d, *J* = 8.1 Hz, *E*), 1.33 (d, *J* = 8.1 Hz, *Z*), 1 H, CH_2], 1.48 - 1.56 (m, 1 H, CH_2), [1.70 (dd, *J* = 15.1, 2.4 Hz, *E*), 1.84 (d, *J* = 15.1, 2.4 Hz, *Z*), 1 H, CH_2 *endo*], [2.27 (dd, *J* = 15.1, 2.4 Hz, *E*), 2.29 (d, *J* = 15.1, 2.4 Hz, *Z*), 1 H, CH_2 *exo*], [2.92 - 2.97 (m, *Z*), 2.95 - 3.01 (m, *E*), 1 H, CH], [3.31 - 3.36 (m, *Z*), 3.72 - 3.76 (m, *E*), 1 H, CH], 5.95 - 6.12 (m, 2 H, =CH).

^{13}C NMR ($CDCl_3$): δ [-5.63, -5.02, -4.95, -3.36 ($SiCH_3$)], [5.26, 5.34, 6.01 ($SiCH_2$)], [7.02, 7.35, 7.63, 8.00 ($SiCCH_3$)], 31.27, 33.25, 41.05, 42.05, 45.80, 45.97. 49.39, 50.44, 133.75, 133.92, 136.24, 136.44, 138.56, 139.08, 144.12, 145.94.

IR (neat): 3068w, 2964s, 2920s, 2884s, 1680w, 1630w, 1572w, 1464m, 1420m, 1380w, 1326m, 1276m, 1252s, 1200m, 1166m, 1140s, 1108s, 1086m, 1034m, 1004s, 996m, 904w, 886m, 834s, 760s, 716s, 686m, 598m, 496w, 412w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 322 (18, M$^+$), 221 (42), 161 (39), 133 (28), 105 (22), 103 (11), 101 (57), 78 (11), 73 (100), 61 (12), 59 (13), 58 (14).

Exact mass for $C_{18}H_{34}OSi_2$ (M$^+$), Calcd, 322.2148; Found, 322.2166.

[Diethyl[[1-(diethylmethylsilyl)-1, 6-heptadienyl]oxy]methyl-silane (**8**) and diethyl[[1-(diethylmethylsilyl)-1, 5-heptadienyl]oxy]methylsilane (**9** and **10**) and (**8***E* : **8***Z* : **9***E* : **9***Z* : **10***E* : **10***Z* = 20 : 15 : 23 : 14 : 18 : 10 mixture): a color-less oil; bp 120 °C (oven)/2 Torr

^{1}H NMR ($CDCl_3$): **8**, δ 0.02 - 0.14 (c, 6 H, $SiCH_3$), 0.52 - 0.69 (m, 8 H, $SiCH_2$), 0.90 - 1.00 (m, 12 H, $SiCCH_3$), 1.40 - 1.48 (m, 2 H, CH_2), 2.01 -

2.18 (m, 4 H, CH_2), [4.89 - 4.96 (m, *E*), 5.40 - 5.45 (m, *Z*), 1 H, Si(SiO)C=CH], 4.89 - 5.04 (m, 2 H, =CH_2), 5.74 - 5.89 (m, 1 H, =CH); **9** and **10**, δ 0.02 - 0.14 (c, 6 H, $SiCH_3$), 0.52 - 0.69 (m, 8 H, $SiCH_2$), 0.90 - 1.00 (m, 12 H, $SiCCH_3$), [1.60 (d, *J* = 6.8 Hz, **10**), 1.64 (d, *J* = 8.5 Hz, **9**), 3 H, CH_3], 2.01 - 2.18 (m, 4 H, CH_2), [4.89 - 4.96 (m, *E*), 5.40 - 5.45 (m, *Z*), 1 H, Si(SiO)C=CH], 5.39 - 5.48 (m, 1 H, =CH).

^{13}C NMR ($CDCl_3$): δ [-6.28, -5.22, -3.74, -3.54 ($SiCH_3$)], [4.71, 5.69, 6.84, 6.94 ($SiCH_2$)], [7.19, 7.22, 7.34, 7.49 ($SiCCH_3$)], [12.79, 17.91 (CH_3)], [22.44, 25.22, 25.63, 26.84, 27.31, 27.42, 28.75, 28.88, 30.32, 32.52, 33.44, 33.62, 33.97, 35.06 (CH_2)], [114.42, 123.80, 124.05, 124.12, 124.23, 124.99, 125.24, 125.33, 125.51, 127.39, 130.17, 130.77, 130.95, 138.78, 138.84, 154.76, 154.79, 154.93, 155.27 (=CH_2, =CH, and =C)].

IR (neat): 2964s, 2920m, 2884m, 1686w, 1644w, 1618w, 1464m, 1420w, 1380w, 1294w, 1252m, 1190w, 1132m, 1100m, 1054w, 1006m, 966m, 876m, 798s, 750m, 686m, 596w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 312 (2, M^+), 283 (1, $M^+ - C_2H_5$), 257 (20), 211 (20), 189 (14), 162 (13), 161 (72), 147 (11), 133 (44), 105 (35), 101 (54), 73 (100), 59 (15).

Anal. Calcd for $C_{17}H_{36}OSi_2$: C, 65.31; H, 11.61. Found: C, 65.33; H, 11.56.

[[3-(4-Cyclohexenyl)-1-(diethylmethylsilyl)-1-propenyl]oxy]diethylmethylsilane (**11**) and [[3-(3-Cyclohexenyl)-1-(diethylmethylsilyl)-1-propenyl]oxy]diethylmethylsilane (**12**) (**11***E* : **11***Z* : **12***E* : **12***Z* = 42 : 14 : 33 : 11 mixture): a colorless oil; bp 160 °C (oven)/5 Torr

^{1}H NMR ($CDCl_3$): δ [0.04 (s, *E*), 0.11 (s, *Z*), 3 H, $SiCH_3$], 0.12 (s, 3 H, $SiCH_3$), 0.51 - 0.72 (m, 8 H, $SiCH_2$), 0.91 - 1.00 (m, 12 H, $SiCCH_3$), 1.22 - 2.09 (c, 11 H, CH_2 and CH), [4.98 (t, *J* = 6.9 Hz, *E*), 5.49 (t, *J* = 7.9 Hz, *Z*), 1 H, Si(SiO)C=CH], 5.57 - 5.73 (m, 2 H, =CH).

^{13}C NMR ($CDCl_3$): δ [-6.25, -5.10, -3.66, -3.48 ($SiCH_3$)], [4.76, 5.72, 6.82, 6.94 ($SiCH_2$)], [7.26, 7.35, 7.49, 7.57 ($SiCCH_3$)], [25.20, 25.25, 28.61, 28.70, 31.54, 31.68, 32.41, 33.90, 33.96, 35.09 (CH_2 and CH)], [122.87, 123.83, 126.24, 126.61, 126.95, 127.00 (=CH)], [155.57, 155.81 (=C)].

IR (neat): 3028m, 2964s, 2920s, 2884s, 2844m, 1654w, 1616w, 1462m, 1440w, 1418w, 1380w, 1328w, 1298w, 1252s, 1190w, 1126m, 1088m, 1064m, 1006m, 968m, 898w, 852m, 798s, 750s, 686m, 654m, 594w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 338 (0, M^+), 309 (1, $M^+ - C_2H_5$), 238 (21), 237 (100), 236 (12), 161 (37), 133 (29), 119 (17), 105 (33), 101 (56), 93 (25), 91 (21), 79 (12), 73 (98), 59 (12).

Anal. Calcd for $C_{19}H_{38}OSi_2$: C, 67.38; H, 11.31. Found: C, 67.54; H, 11.61.

Diethyl[[1-(diethylmethylsilyl)-5-methyl-1, 5-hexadienyl]oxy]methylsilane (**13**) (*E*/*Z* = 73/27 mixture): a colorless oil; bp 130 °C (oven)/3 Torr

^1H NMR ($CDCl_3$): δ 0.03 (s, 3 H, $SiCH_3$), [0.11 (s, *Z*), 0.13 (s, *E*), 3 H, $SiCH_3$], 0.53 - 0.71 (m, 8 H, $SiCH_2$), 0.91 - 1.01 (m, 12 H, $SiCCH_3$), 1.73 (s, 3 H, CH_3), 2.02 - 2.28 (m, 4 H, CH_2), 4.69 (d, *J* = 1.0 Hz, 1 H, =CH), 4.71 (d, *J* = 1.0 Hz, 1 H, =CH), [4.93 (t, *J* = 6.7 Hz, *E*), 5.46 (t, *J*= 7.8 Hz, *Z*), 1 H, =CH].

^{13}C NMR ($CDCl_3$): δ [-6.29, -5.27, -3.72, -3.54 ($SiCH_3$)], [4.71, 5.66, 6.82, 6.91 ($SiCH_2$)], [7.20, 7.31, 7.48, 7.51 ($SiCCH_3$)], [22.34, 22.41, 23.93, 25.74, 37.52, 39.20 (CH_3 and CH_2)], [109.88, 110.17 (=CH_2)], [123.91, 125.16 (=CH)], [145.34, 145.58, 154.91, 155.42 (=C)].

IR (neat): 3080w, 2964s, 2920s, 2880s, 1652w, 1616w, 1464m, 1420m, 1378w, 1340w, 1308w, 1252s, 1184m, 1124s, 1064m, 1006s, 966m, 886s, 796s, 752s, 688m, 596w, 542w, 428w cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 312 (5, M$^+$), 257 (22), 211 (14), 189 (14), 175 (10), 162 (13), 161 (80), 147 (14), 133 (49), 105 (34), 101 (55), 73 (100), 59 (16).
Anal. Calcd for $C_{17}H_{36}OSi_2$: C, 65.31; H, 11.61. Found: C, 65.53; H, 11.91.

Diethyl[1-[(diethylmethylsilyl)oxy]-1-nonenyl]methylsilane (*E*/*Z* = 71/29 mixture): a colorless oil; bp 170 °C (oven)/2 Torr
^{1}H NMR ($CDCl_3$): δ [0.03 (s), 0.11 (s), 0.12 (s), 6 H, $SiCH_3$], 0.51 - 0.70 (m, 8 H, $SiCH_2$), 0.86 - 1.01 (c, 15 H, $SiCCH_3$ and CH_3), 1.20 - 1.38 (m, 6 H, CH_2), [1.93 - 2.03 (m, *Z*), 2.04 - 2.13 (m, *E*), 2 H, $=CCH_2$], [4.92 (t, *J* = 6.8 Hz, *E*), 5.46 (t, *J*= 7.8 Hz, *Z*), 1 H, =CH].
^{13}C NMR ($CDCl_3$): δ [-6.28 (*E*), -5.22 (*Z*), -3.69 (*Z*), -3.56 (*E*), $SiCH_3$], [4.74, 5.70, 6.84, 6.93, 7.25, 7.32, 7.48, 7.52, $Si\mathit{C}H_2\mathit{C}H_3$], 14.06 ($CH_3$), [22.67, 25.74, 27.33, 29.19, 29.24, 29.27, 29.43, 29.59, 31.05, 31.86, CH_2], [125.03 (*Z*), 126.08 (*E*), =CH], [154.50 (*E*), 159.94 (*Z*), =C].
IR (neat): 2964s, 2928s, 2884s, 2864m, 1616w, 1464m, 1418m, 1380w, 1334w, 1302w, 1252s, 1142m, 1098s, 1048w, 1008m, 966m, 876m, 798s, 750m, 688m cm^{-1}.
MS (70 eV): m/z (relative intensity, %) 342 (1, M$^+$), 313 (3, M$^+$ - C_2H_5), 242 (11), 241 (52), 189 (49), 162 (16), 161 (100), 133 (43), 105 (31), 101 (42), 73 (82), 61 (11), 59 (12).
Anal. Calcd for $C_{19}H_{42}OSi_2$: C, 66.59; H, 12.35. Found: C, 66.70; H, 12.62.

Diethyl(heptanoyl)methylsilane (**14**): a colorless oil; bp 130 °C (oven)/7 Torr
^{1}H NMR ($CDCl_3$): δ 0.15 (s, 3 H, $SiCH_3$), 0.65 - 0.73 (m, 4 H, $SiCH_2$), 0.87 (t, *J* = 6.8 Hz, 3 H, CH_3), 0.89 - 0.98 (m, 6 H, $SiCCH_3$), 1.19 - 1.33 (m, 6 H, CH_2), 1.42 - 1.56 (m, 2 H, CH_2), 2.55 (t, *J* = 7.1 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ -7.54 ($SiCH_3$), 3.84 ($SiCH_2$), 7.19 ($SiCCH_3$), 14.02 (CH_3), 21.93, 22.50, 29.03, 31.68, 49.61 (CH_2), 248.58 (CO).

IR (neat): 2964s, 2940s, 2884s, 1692w, 1644s, 1466m, 1418m, 1382m, 1356w, 1252m, 1122w, 1014m, 966m, 798s, 754m, 688m cm^{-1}.

MS (70 eV): m/z (relative intensity, %) 214 (0, M^+), 185 (11, M^+ - C_2H_5), 102 (11), 101 (100), 89 (29), 73 (99).

Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.42; H, 12.45.

2-7 References and Notes

(1) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. (c) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431. (d) Ojima, I. Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics*, **1991**, *10*, 38. (e) Ojima, I.; Donovan, R. J.; Shag, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580. (f) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, *33*, 5799.

(3) Chatani, N.; Murai, T.; Ikeda, T.; Sano, T.; Kajikawa, Y.; Ohe, K.; Murai, S. *Tetrahedron* **1992**, *48*, 2013.

(4) Murai, T.; Sakane, T.; Kato, S. *J. Org. Chem.* **1990**, *55*, 449.

(5) Kang, K.-T.; Weber, W. P. *Tetrahedron Lett.* **1985**, *26*, 5415. Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1253. 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.

(6) Kuwajima, I.; Arai, M.; Sato, T. *J. Am. Chem. Soc.* **1977**, *99*, 4181.

(7) The product has functionalities of vinylsilane, enol silyl ether, and masked acylsilane. All these functional groups are quite useful in organic synthesis. For reviews, see: Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Magnes, P. D.; Sarkar, T.; Djurie, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 48. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983.

(8) For recent reviews on acylsilanes, see: Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. Bulman Page, P. C.; Klarir, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. For recent papers on the synthetic application of acylsilanes, see: (a) Ricci, A.; Degl'Innocenti, A., Capperucci, A.; Reginato, G. *J. Org. Chem.* **1989**, *54*, 19. (b) Schinzer, D. *Synthesis* **1989**, 179. (c) Nowick, J. S.; Danheiser, R. L. *J. Org. Chem.* **1989**, *54*, 2798. (d) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198. (e) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441. (f) Larson, G. L.; Soderquist, J. A.; Rivera, Claudio, M. R. *Synth. Commun.* **1990**, *20*, 1095. (g) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609. (h) Cirillo, P. F.; Panek, J. S. *J. Org. Chem.* **1990**, *55*, 6071. (i) Yoshida, J.-i.; Matsunaga, S.-i.; Ishichi, Y.; Maekawa, T.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307. (j) Cirillo, P. F.; Panek, J. S. *Tetrahedron Lett.* **1991**, *32*, 457.

(9) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W. K.; Gladysz, J. A. *Organometallics*, **1984**, *3*, 1325.

(10) Ingle, W. M.; Preti, G.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1973**, 497.

Conclusion

The objective of this research was to develop new catalytic reactions using the effective transition metal complexes other than $Co_2(CO)_8$ with carbon monoxide (CO) and hydrosilanes ($HSiR_3$). The results mentioned in each chapter of this thesis are summarized as follows.

In Chapter 1, it has found that rhodium complexes have catalyzed the reaction of nitrogen-containing compounds, which did not react in Co-catalyzed reaction system, with carbon monoxide and a hydrosilane. Particularly, the reaction of enamines resulted in regioselective incorporation of CO into the α-carbon atom of the substrates to give enol silyl ethers. It would be important that α-aminoalkyl rhodium complex was involved as a common intermediate in the catalytic reaction of CO-incorporation into the substrate. For an another route leading to the intermediate, The reaction of *N*, *N*- and *N*, *O*- acetals as the another substrates with carbon monoxide and a hydrosilane resulted in the incorporation of CO with concomitant a cleavage of a carbon-nitrogen or carbon-oxygen bond in the substrate.

In Chapter 2, it has found that iridium complexes catalyzed the reaction of olefins with carbon monoxide and a hydrosilane to yield enol silyl ethers of acylsilanes. The unprecedented reaction resulted in regioselective introdoction of a siloxy(silyl)methylene unit haveing the silicon-carbon bond into the terminal carbon atom of the olefins.

These new catalytic reactions with carbon monoxide and hydrosilanes would contribute to the development of a part of homogeneous catalyzed reactions.