<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>STUDIES ON THE RHODIUM-AND IRIDIUM-CATALYZED REACTIONS WITH CARBON MONOXIDE AND HYDROSILANES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Ikeda, Shin-ichi</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Issue Date</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Text Version</strong></td>
<td>ETD</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="https://doi.org/10.11501/3065889">https://doi.org/10.11501/3065889</a></td>
</tr>
<tr>
<td><strong>DOI</strong></td>
<td>10.11501/3065889</td>
</tr>
<tr>
<td><strong>rights</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Note</strong></td>
<td></td>
</tr>
</tbody>
</table>

*Osaka University Knowledge Archive : OUKA*
[https://ir.library.osaka-u.ac.jp/repo/ouka/all/](https://ir.library.osaka-u.ac.jp/repo/ouka/all/)

Osaka University
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

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.

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

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.

Supplementary List of Publications


2. A Convenient Synthesis of 5-Alkyl- and 5-Aryl-1, 2, 3, 4-thiatriazols
Contents

Preface •••• i
List of Publications •••• ii
General Introduction •••• 1

Chapter 1 The Rhodium-Catalyzed Reaction 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 •••• 3
1-1-2 Reaction of Enamines with Carbon Monoxide and a Hydrosilane •••• 4

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

1-2-1 Introduction •••• 9
1-2-2 Reaction of N, N-Acetals with Carbon Monoxide and a Hydrosilane •••• 9
1-2-3 Reaction of N, O-Acetal with Carbon Monoxide and a Hydrosilane •••• 11

1-3 Experimental Section •••• 12
1-4 References and Notes •••• 25

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

2-1 Introduction •••• 28
2-2 The Reaction of 1-Hexene with Carbon Monoxide and a Hydrosilane •••• 29
2-3 The Reaction of Terminal Olefins with Carbon Monoxide and a Hydrosilane  
2-4 The Reaction of Another Olefins with Carbon Monoxide and a Hydrosilane  
2-5 Mechanism  
2-6 Experimental Section  
2-7 References and Notes  

Conclusion
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. On the other hand, it is well known that the reactions of hydrosilane (i.e. HSiR₃) with transition metal complexes parallel those of molecular hydrogen. For example, hydrosilylation, the catalyzed addition of HSiR₃ to an olefin, is formally analogous to catalytic hydrogenation. 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 [Co₂(CO)₈] with carbon monoxide and hydrosilane.

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 Co₂(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 having the silicon-carbon bond into the terminal carbon atom of the olefins.

References


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\textsubscript{3}/CO/Co\textsubscript{2}(CO)\textsubscript{8}, we have reported that the reaction of terminal olefins with a hydrosilane and carbon monoxide in the presence of Co\textsubscript{2}(CO)\textsubscript{8} can bring about catalytic incorporation of CO into olefins to produce a regioisomeric mixture of enol silyl ethers (eq 1).\textsuperscript{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)\textsubscript{2}]\textsubscript{2} to give Rh complexes containing bidentate ligand.\textsuperscript{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.\textsuperscript{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.

\[ \text{C}_4\text{H}_9 \rightarrow \text{C}_6\text{H}_6, 140^\circ\text{C} \rightarrow \text{C}_4\text{H}_9 \rightarrow \text{C}_4\text{H}_9 \rightarrow \text{C}_4\text{H}_9 \rightarrow \text{OSiEt}_2\text{Me} + \text{C}_4\text{H}_9 \rightarrow \text{OSiEt}_2\text{Me} \]

\[ \text{C}_6\text{H}_6, 50 \text{ atm}, 20 \text{ h} \rightarrow 58\% (E/Z = 31/69) \]

\[ 16\% (E/Z = 50/50) \]
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 HSiEt2Me (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).

Interestingly, the Rh-catalyzed reaction of enamines 2 as the another amine-containing olefins with HSiEt2Me 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 HSiEt2Me (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%). 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, Co2(CO)8,1 Ru3(CO)12,1d and RhCl(PPh3)31d were not effective, some rhodium complexes (Me5C5RhCl)2 (65% yield) and Rh6(CO)16 (75% yield) showed catalytic
activity. Since $[\text{RhCl(CO)}_2]_2$ gave higher yields it was chosen as the best catalyst and morpholine enamines were used as substrates.

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 $\alpha$-(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$_2$Me 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 $\alpha$-(siloxymethylene) amines 3c - h with water under acidic condition (H$_2$O/TsOH, 70 °C, 1 d) gave $\alpha$-siloxyketones 4 - 9 in quantitative yields (eq 4).
Table I. \([\text{RhCl(CO)}_2]_2\)-Catalyzed Reaction of Enamines with HSiEt$_2$Me and CO$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>enamine</th>
<th>time, h</th>
<th>(\alpha)-(siloxymethylene) amine</th>
<th>yield, %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2c</td>
<td>20</td>
<td>MeEt$_2$SiO(\rightleftharpoons)N'(\rightleftharpoons)MeEt$_2$SiO</td>
<td>62 (75), (E/Z = 84/16)</td>
</tr>
<tr>
<td>2</td>
<td>Ph(\rightleftharpoons)N'(\rightleftharpoons)Ph</td>
<td>72</td>
<td>MeEt$_2$SiO(\rightleftharpoons)Ph(\rightleftharpoons)MeEt$_2$SiO</td>
<td>74 (91), (E/Z = 81/19)</td>
</tr>
<tr>
<td>3</td>
<td>3e</td>
<td>72</td>
<td>MeEt$_2$SiO(\rightleftharpoons)N'(\rightleftharpoons)MeEt$_2$SiO</td>
<td>72, (E/Z = 81/19)</td>
</tr>
<tr>
<td>4</td>
<td>2f</td>
<td>72</td>
<td>MeEt$_2$SiO(\rightleftharpoons)N'(\rightleftharpoons)MeEt$_2$SiO</td>
<td>65 (72), (E/Z = 52/48)</td>
</tr>
<tr>
<td>5</td>
<td>2g ((E/Z = 63/37))</td>
<td>72</td>
<td>MeEt$_2$SiO(\rightleftharpoons)N'(\rightleftharpoons)MeEt$_2$SiO</td>
<td>57, (E/Z = 61/39)</td>
</tr>
<tr>
<td>6</td>
<td>t-Bu(\rightleftharpoons)N'(\rightleftharpoons)t-Bu</td>
<td>120</td>
<td>MeEt$_2$SiO(\rightleftharpoons)N'(\rightleftharpoons)MeEt$_2$SiO</td>
<td>21, (E/Z = 51/49)</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: enamines (2.5 mmol), HSiEt$_2$Me (7.5 mmol), \([\text{RhCl(CO)}_2]_2\) (0.05 mmol), CO (50 atm), C$_6$H$_6$ (5 mL), 140 °C. $^b$ Isolated yields based on enamines. GC yields are in parentheses. \(E/Z\) ratio is determined by $^1$H NMR.
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. 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.

**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). 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 HSiEt2Me 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 phenyl 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 HSiR3/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 HSiEt2Me (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 Co2(CO)8 or RhCl(PPh3)3 instead of [RhCl(CO)2]2, no reaction occurred.

\[
\begin{array}{c}
\text{Me}_2N \quad \text{NMe}_2 \\
\text{Ph}
\end{array} \xrightarrow{\text{cat. } [\text{RhCl(CO)}_2]_2 \text{ HSiEt}_2\text{Me, CO}} \begin{array}{c}
\text{Me}_2N \quad \text{OSiEt}_2\text{Me} \\
\text{Ph}
\end{array} + \begin{array}{c}
\text{Me}_2N \\
\text{Ph}
\end{array} \\
14 \quad 15 \quad 67\% \\
\quad 27\%
\]

Interestingly, the reaction of methylenediamine 16 with HSiEt2Me 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 MeEt2SiNMe2 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%).

\[
\begin{array}{c}
\text{Me}_2N \quad \text{NMe}_2 \\
\text{Ph}
\end{array} \xrightarrow{\text{cat. } [\text{RhCl(CO)}_2]_2 \text{ HSiEt}_2\text{Me, CO}} \begin{array}{c}
\text{Me}_2N \quad \text{OSiEt}_2\text{Me} \\
\text{Ph}
\end{array} \\
16 \quad 17 \\
\quad 51\% \\
\quad 75\%
\]

The reaction of triaminomethane 18 with HSiEt2Me and CO also gave 17 in 65% yield (eq 7). The first stage of the reaction would be reduction of 18 with HSiEt2Me to give 16 and a silylamine,
MeEt₂SiNMe₂. The subsequent reaction of 16 with HSiEt₂Me and CO might have given 17.

\[
\begin{array}{c}
\text{Me₂N–NMe}₂ & \xrightarrow{\text{cat. } [\text{RhCl(CO)}]₂} & \text{Me₂N–NMe}₂\text{OSiEt}₂\text{Me} \\
\text{18} & \text{C₆H₆, 140 °C,} & \text{17 65%}
\end{array}
\]

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.

\[
\begin{array}{c}
\text{MeN–NMe} & \xrightarrow{\text{cat. } [\text{RhCl(CO)}]₂} & \text{MeN–NMe} \\
\text{19} & \text{C₆H₆, 140 °C, 50 atm, 100 h} & \text{20 R = Ph 51%}
\end{array}
\]

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 HSiEt₂Me (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
The interaction of a key catalyst 23 having a silicon-rhodium bond with \( N, N_2 \)- or \( N, O \)-acetals would be responsible for the formation of \( \alpha \)-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 \( N, N_2 \)-acetals.\(^{10}\)

\[
\begin{align*}
\text{MeN} \quad & R''_3Si-Rh \\
\text{X} = NMeR', OR' \\
\rightarrow & \text{MeN} \quad X^+ \text{SiR''} \\
\rightarrow & \text{MeN} \quad \text{Rh} \\
\text{MeN} \quad & \text{Rh} \\
\text{R} \\
\end{align*}
\]

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 (\( \delta \)), 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), HSiEt2Me (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-C12H26) 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 (CDCl3): δ [0.11 (s, E), 0.12 (s, Z), 3 H, SiCH3], 0.57 - 0.67 (m, 4 H, SiCH2), 0.86 (t, J = 7.0 Hz, 3 H, CH3), 0.97 (t, J = 8.1 Hz, 6 H, SiCCH3), 1.24 - 1.51 (m, 6 H, CH2), [1.82 - 1.88 (t, J = 6.9 Hz, Z), 2.14 - 2.20 (t, J = 6.9 Hz, E), 2 H, =CCH2], [2.64 - 2.67 (m, E), 2.95 - 3.02 (m, Z), 4 H, NCH2], 3.66 - 3.72 (m, 4 H, OCH2), [5.62 (s, Z), 5.80 (s, E), 1 H, =CH].
\(^{13}\text{C} \text{NMR (CDCl}_3\):} \delta -4.98 (\text{SiCH}_3), 6.21 (\text{SiCH}_2), 6.61 (\text{SiCCH}_3), 14.08 (\text{CH}_3), 22.50 (\text{CH}_2), 25.39 (\text{CH}_2), 27.45 (\text{CH}_2), 31.83 (\text{CH}_2), 50.28 (\text{NCH}_2), 67.14 (\text{OCH}_2), 123.82 (=\text{CN}), 137.65 (=\text{CH}).

\text{IR (neat):} 2880s, 2856s, 2816s, 2783m, 1658w, 1461w, 1415w, 1378m, 1360w, 1324m, 1298m, 1263s, 1233m, 1196m, 1172m, 1150s, 1121s, 1099m, 1042m, 1006m, 972m, 926m, 864m, 834m, 800s, 768m, 689m cm\(^{-1}\).

\text{MS (70 eV):} m/z (relative intensity, \%) 299 (85, \text{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 \text{C}_{16}\text{H}_{33}\text{NO}_2\text{Si} (\text{M}^+), \text{calcd} 299.2273, \text{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

\(^1\text{H NMR (CDCl}_3\):} \delta [0.11 (s, E), 0.13 (s, Z), 3 \text{ H, SiCH}_3], 0.56 - 0.63 (m, 4 \text{ H, SiCH}_2), 0.95 (t, J = 7.6 Hz, 6 \text{ H, SiCCH}_3), [2.14 - 2.21 (t, J = 6.8 Hz, Z), 2.43 - 2.46 (t, J = 6.8 Hz, E), 2 \text{ H, =CCH}_2], [2.63 - 2.65 (m, E), 3.03 - 3.07 (m, Z), 4 \text{ H, NCH}_2], 2.72 - 2.75 (m, 2 \text{ H, CH}_2), 3.71 - 3.75 (m, 4 \text{ H, OCH}_2), [5.67 (s, Z), 5.85 (s, E), 1 \text{ H, =CH}], 7.17 - 7.27 (m, 5 \text{ H, Ar}).

\(^{13}\text{C NMR (CDCl}_3\):} \delta -5.91 (\text{SiCH}_3), 6.21 (\text{SiCH}_2), 6.60 (\text{SiCCH}_3), 27.64 (\text{CH}_2), 34.04 (\text{CH}_2), [49.84, 50.36 (\text{NCH}_2)], [67.15, 67.82 (\text{OCH}_2)], 124.71 (=\text{CN}), 125.62, 128.26, 128.40, 142.68 (Ar), 136.55 (=\text{CH}).

\text{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\(^{-1}\).

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

Exact mass for \text{C}_{19}\text{H}_{31}\text{NO}_2\text{Si} (\text{M}^+), \text{calcd} 333.2091, \text{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$_3$): $\delta$ [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$_3$): $\delta$ -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$_3$): $\delta$ [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$_3$): $\delta$ -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
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

$^1$H NMR (CDCl$_3$): $\delta$ [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 - 3.68 (m, 4 H, OCH$_2$), [5.87 (s, Z), 5.94 (s, E), 1 H, =CH].

$^{13}$C NMR (CDCl$_3$): $\delta$ [-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$_2$H$_5$), 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$_2$Si (M$^+$), calcd 299.2269, found 299.2270.
4-[1-(Diethylmethylsiloxy)-4-[4-(1,1-dimethylethyl)phenyl]-3-methyl-1-buten-2-yl] morpholine (3b) (E/Z = 64/36 mixture): a pale yellow oil; bp 170 °C (oven)/0.2 Torr

$^1$H NMR (CDCl$_3$): $\delta$ [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 tBu), 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$_3$): $\delta$ [-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 tBu), [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$_2$Si (M$^+$), calcd 403.2923, found 403.2925.

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

$^1$H NMR (CDCl$_3$): $\delta$ 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$_2$Si: C, 62.55; H, 11.37. Found: C, 62.60; H, 11.44.

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

$^1$H 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$_2$H$_5$), 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$_2$Si: C, 68.13; H, 9.15. Found: C, 68.28; H, 9.33.

1-(Diethylmethylsiloxy)-4,8-dimethyl-7-nonene-2-one (6): a colorless oil

$^1$H 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 =CCH₂), 2.26 (dd, J = 15.9, 8.1 Hz, 1H, COCH₂), 2.44 (dd, J = 15.9, 8.1 Hz, 1 H, O=CCH₂), 4.14 (s, 2 H, OCH₂), 5.08 (m, 1 H, =CH).

¹³C NMR (CDCl₃): δ -5.08 (SiCH₃), 6.12 (SiCH₂), 6.64 (SiCCH₃), 17.61 (CH₃), 19.73 (CH₂), 25.45 (CH₃), 25.68 (CH₃), 28.62 (CH), 37.06(CH₂), 45.54 (CH₂), 69.27 (OCH₂), 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).


1-Cyclohexyl-2-(diethylmethylsiloxy)-1-ethanone (7): a colorless oil

¹H NMR (CDCl₃): δ 0.08 (s, 3 H, SiCH₃), 0.63 (q, J = 7.7 Hz, 4 H, SiCH₂), 0.96 (t, J = 7.7 Hz, 6 H, SiCCH₃), 1.10 -1.91 (m, 10 H, CH₂), 2.47 - 2.63 (m, 1 H, CH), 4.25 (s, 2 H, OCH₂).

¹³C NMR (CDCl₃): δ -5.08 (SiCH₃), 6.15 (SiCH₂), 6.65 (SiCCH₃), 25.63 (CH₂), 25.78 (CH₂), 28.29 (CH₂), 46.24 (CH), 67.59 (OCH₂), 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⁺ - CH₃), 214 (17), 213 (100, M⁺ - C₂H₅), 169 (10), 131 (70), 107 (10), 103 (93).

Anal. Calcd for C₁₃H₂₆O₂Si: C, 64.41; H, 10.81. Found: C, 64.20; H, 10.90.
1-(Diethylmethylsiloxy)-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$_2$H$_5$), 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$_2$Si (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 tBu), 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 tBu), 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$^{-1}$.  

20
MS (70 eV): m/z (relative intensity, %) 334 (0, M+), 305 (8, M+ - C2H5),
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 C19H31O2Si (M+ - CH3), calcd 319.2111, found 319.2109.

N, N-Diethyl-1-(diethylmethylsiloxy)-2-heptanamine: a colorless oil; bp 140 °C (oven)/5 Torr

1H NMR (CDCl3): δ 0.04 (s, 3 H, SiCH3), 0.56 (q, J = 7.8 Hz, 4 H, SiCH2),
0.88 (t, J = 7.0 Hz, 3 H, CH3), 0.94 (t, J = 7.8 Hz, 6 H, SiCCH3), 1.01 (t,
J = 7.0 Hz, 6 H, CH3), 1.19 - 1.48 (m, 8 H, CH2), 2.38 - 2.72 (c, 5 H, NCH2
and NCH), 3.46 (dd, J = 10.3, 6.2 Hz, 1 H, OCH2), 3.68 (dd, J = 10.3, 6.2
Hz, 1H, OCH2).

13C NMR (CDCl3): δ -5.04 (SiCH3), 6.21 (SiCH2), 6.77 (SiCCH3), 14.11
(CH3), 14.75 (CH3), 22.67 (CH2), 26.28 (CH2), 29.01 (CH2), 32.20 (CH2),
44.10 (NCH2), 60.91 (NCH), 63.16 (OCH2).

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+ - CH3),
258 (1, M+ - C2H5), 156 (100).

Exact mass for C16H37NOSi (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 (CDCl3): δ 0.07 (s, 3 H, SiCH3), 0.59 (q, J = 7.8 Hz, 4 H, SiCH2),
0.90 (t, J = 6.9 Hz, 3 H, CH3), 0.97 (t, J = 7.8 Hz, 6 H, SiCCH3), 1.23 - 1.44
(m, 8 H, CH2), 2.24 (s, 3 H, NCH3), 2.61 - 2.65 (m, 1 H, NCH), 3.27 (dd,
J = 10.3, 5.7 Hz, 1 H, OCH2), 3.58 (dd, J = 10.3, 5.7 Hz, 1 H, OCH2), 3.62 -
3.78 (m, 2 H, NCH2), 7.21 - 7.39 (m, 5 H, Ar).
$^{13}$C NMR (CDCl$_3$): $\delta$ -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

$^1$H NMR (CDCl$_3$): $\delta$ 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$_3$): $\delta$ -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$_2$H$_5$), 170 (100).

Anal. Calcd for C$_{16}$H$_{35}$NO$_2$Si: 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$_3$): $\delta$ -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$_3$): $\delta$ -5.22 (SiCH$_3$), 6.07, 6.62 (SiCH$_2$CH$_3$), 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, 2828s, 2776m, 1601w, 1496m, 1460s, 1382w, 1348w, 1314w, 1252s, 1120s, 1008s, 962m, 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$_3$): $\delta$ 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$_3$): $\delta$ -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).

1, 4-Dimethyl-5-phenyl-2, 3-tetrahydropyrazine (20): a pale yellow oil; bp 100 °C (oven)/1.5 Torr

$^1$H NMR (CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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

$^1$H NMR (CDCl$_3$): $\delta$ 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$_3$): $\delta$ -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, 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$_2$Si$_2$: C, 63.24; H, 12.30; N, 3.35. Found: C, 62.97; H, 12.60; N, 3.60.

1-4 References and Notes


(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.


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

2-1 Introduction

In Chapter 1, it has been mentioned that the reaction of amine-containing olefins such as enamines with a hydrosilane (HSiR₃) and carbon monoxide (CO) in the presence of [RhCl(CO)₂]₂ can promote catalytic introduction of siloxymethylidene unit (=CHOSiR₃), which derived from a molecule of CO and HSiR₃, respectively, to give enol silyl ethers. It is the same result as the catalytic reaction system of Co₂(CO)₈/HSiR₃/CO that the introduced silyl unit always attaches to an oxygen atom of CO. The formal analogy to hydroformylation of olefins with HSiR₃ instead of H₂ 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 HSiR₃ and CO has been pointed out.¹ Recently, catalytic reactions of acetylenes with HSiR₃ 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.

\[
\text{catalyst} \quad \text{HSiR}_3, \text{CO} \quad \begin{array}{c}\longrightarrow\end{array} \quad \begin{array}{c} \text{R} \quad \text{H} \quad \text{O} \quad \text{SiR}_3^+ \quad \text{or} \quad \text{R} \quad \text{SiR}_3^+ \quad \text{O} \quad \text{H} \end{array} \quad \text{(1)}
\]
2-2 The Reaction of 1-Hexene with Carbon Monoxide and Hydrosilanes

1-Hexene (3) was found to react with HSiR3 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(SiR3)OSiR3) 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 (HSiEt2Me) 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 HSiEt2Me 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 HSiEt2Me) (run 7). The reaction slowly take place with the use of the excess amount of HSiEt2Me or below 80 °C (runs 1 and 6, respectively). An increase in the rate of 3/HSiEt2Me and reaction time resulted in an increase in the yield of 4a. The use of CH2Cl2 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)(PPh3)2 (run 9) and IrH(CO)(PPh3)3 (run 10) was not effective, Ir4(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 dimethylphenylsilane (HSiRhMe2) and triethylsilane (HSiEt3) can also be used in place of HSiEt2Me 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 HSiEt₂Me and CO

![Chemical structure and reaction equation]

<table>
<thead>
<tr>
<th>run</th>
<th>HSiEt₂Me [mmol]</th>
<th>catalyst</th>
<th>temp., °C</th>
<th>time, h</th>
<th>yield, %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>24</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>48</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>48</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>24</td>
<td>44</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>80</td>
<td>48</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>[IrCl(CO)₃]ₙ</td>
<td>140</td>
<td>48</td>
<td>82 (74)</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>Ir₄(CO)₁₂ eradicate</td>
<td>140</td>
<td>48</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>IrCl(CO)(PPh₃)₂</td>
<td>140</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>IrH(CO)(PPh₃)₃</td>
<td>140</td>
<td>48</td>
<td>0</td>
</tr>
</tbody>
</table>

a Reaction conditions: catalyst (0.02 mmol), CO (50 atm), C₆H₆ (2 mL).
b GC yield based on HSiEt₂Me. Isolated yield is in parenthesis.

Table II. [IrCl(CO)₃]ₙ-Catalyzed Reaction of 1-Hexene with some hydrosilanes and CO

![Chemical structure and reaction equation]

<table>
<thead>
<tr>
<th>run</th>
<th>HSiR₃ yield, %b</th>
<th>E/Z ratio c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HSiEt₂Me 4a: 74</td>
<td>79/21</td>
</tr>
<tr>
<td>2</td>
<td>HSiEt₃ 4b: 50d</td>
<td>66/34</td>
</tr>
<tr>
<td>3</td>
<td>HSiPhMe₂ 4c: 65</td>
<td>87/13</td>
</tr>
<tr>
<td>4</td>
<td>HSi'BuMe₂ trace</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>HSi(OEt)₃ 0</td>
<td>-</td>
</tr>
</tbody>
</table>

a Reaction conditions: [IrCl(CO)₃]ₙ (0.02 mmol), 1-hexene (10 mmol), HSiR₃ (1 mmol), CO (50 atm), C₆H₆ (2 mL), 140 °C, 48 h. b Isolated yield based on HSiR₃. c Determined by ¹H NMR. d Reaction time: 100 h.
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\(_2\)Me and CO was also achieved the incorporation of CO to give the corresponding product in good yield.

\[
\text{AcO} \quad \text{cat. } [\text{IrCl(CO)}_3]_n \quad \text{HSiEt}_2\text{Me, CO} \quad \text{AcO} \quad \text{OSiEt}_2\text{Me} \\
\text{5} \quad \text{1 mmol} \quad \text{C}_6\text{H}_6, 50 \text{ atm} \quad \text{6} \quad \text{31\%} \quad (E/Z = 86/14)
\]

For the reaction of another olefins with HSiEt\(_2\)Me 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>
<thead>
<tr>
<th>olefin</th>
<th>product</th>
<th>yield, %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>E/Z ratio&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4a</td>
<td>74 (82)</td>
<td>79/21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>66 (82)</td>
<td>86/14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>60</td>
<td>69/31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>(50)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>71/28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>67</td>
<td>57/43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>73</td>
<td>73/27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>75</td>
<td>68/32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>53</td>
<td>79/21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OSiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>67</td>
<td>67/33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table III (Continued)

<table>
<thead>
<tr>
<th>olefin</th>
<th>product</th>
<th>yield, %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>E/Z ratio&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO&lt;sup&gt;e&lt;/sup&gt;</td>
<td>EtO&lt;sup&gt;e&lt;/sup&gt;-OEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>58</td>
<td>73/27</td>
</tr>
<tr>
<td>NC&lt;sup&gt;e&lt;/sup&gt;</td>
<td>NC&lt;sup&gt;e&lt;/sup&gt;-OEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>45</td>
<td>73/27</td>
</tr>
<tr>
<td>O&lt;sup&gt;g&lt;/sup&gt;</td>
<td>O&lt;sup&gt;g&lt;/sup&gt;-SiEt&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>56</td>
<td>65/35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67</td>
<td>66/34</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: olefin (10 mmol), HSiEt<sub>2</sub>Me (1 mmol), [IrCl(CO)<sub>3</sub>]<sub>n</sub> (0.02 mmol), CO (50 atm), C<sub>6</sub>H<sub>6</sub> (2 mL), 140 °C, 48 h.  <sup>b</sup> Isolated yields based on HSiEt<sub>2</sub>Me. GC yield is in parentheses.  <sup>c</sup> Determined by <sup>1</sup>H NMR.  <sup>d</sup> Dimerization and polymerization of styrene also took place.  <sup>g</sup> An olefin (5 mmol) was used.  <sup>g</sup> Ethylene (10 atm, initial pressure at 25 °C) was used.

![Chemical reactions (4 and 5)](image-url)

33
For the reaction of dienes with HSiEt₂Me 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).
The products obtained can be easily hydrolyzed to acylsilanes.\textsuperscript{6} For example, treatment of \textit{4a} with acid (acetone/HCl (0.2 M) = 4/1) at 25 °C for 4 h gave an acylsilane \textit{14} in quantitative yield (Scheme I).
The present iridium-catalyzed reaction represents the first example of formation of acylsilane derivatives from the HSiR3/CO combination. The multifunctionality of the products is synthetically attractive and will find application in the future.

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 HSiEt2Me (1 mmol) and CO gave ethylcyclohexane (64% yield based on HSiEt2Me) 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).

\[
\text{cat. } [\text{IrCl(CO)}_3]_n, \text{HSiEt}_2\text{Me, CO } 1 \text{ mmol } \text{C}_6\text{H}_6, 50 \text{ atm } 140^\circ \text{C}, 48 \text{ h } 0.41 \text{ mmol } 0.32 \text{ mmol } 4.1 \text{ mmol } 5.2 \text{ mmol } 15 \text{ 0.41 mmol } 0.32 \text{ mmol }
\]

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 HSiEt2Me 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 HSiEt2Me 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 HSiEt₂Me) (eq 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 iridium-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). 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, 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 (\(\delta\)), 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\(_2\)Me (102 mg, 1 mmol), \([\text{IrCl(CO)}_3]_n\) (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\textsubscript{12}H\textsubscript{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 \textsuperscript{1}H NMR spectra of isolated products.

Diethyl[1-[(diethylmethylsilyl)oxy]-1-hepteny]methylsilane (4a) (E/Z = 79/21 mixture): a colorless oil; bp 150 °C (oven)/3 Torr

\textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta \) [0.03 (s), 0.11 (s), 0.12 (s), 6 H, SiCH\textsubscript{3}], 0.53 - 0.70 (m, 8 H, SiCH\textsubscript{2}), 0.86 - 1.01 (c, 15 H, SiCCH\textsubscript{3} and CH\textsubscript{3}), 1.25 - 1.40 (m, 6 H, CH\textsubscript{2}), [1.98 (dt, \( J = 7.9, 7.1 \) Hz, Z), 2.08 (dt, \( J = 6.8, 7.1 \) Hz, E), 2 H, =CCH\textsubscript{2}], [4.92 (t, \( J = 6.8 \) Hz, E), 5.46 (t, \( J = 7.9 \) Hz, Z), 1 H, =CH].

\textsuperscript{13}C NMR (CDCl\textsubscript{3}): \( \delta \) [6.26 (E), -5.21 (Z), -3.68 (Z), -3.55 (E), SiCH\textsubscript{3}], [4.74, 5.70, 6.84, 6.94, 7.25, 7.34, 7.52, 7.97, SiCH\textsubscript{2}CH\textsubscript{3}], 14.06 (CH\textsubscript{3}), [22.56, 25.71, 27.31, 29.28, 30.73, 31.56, 31.74, CH\textsubscript{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, 796m, 750m, 686m cm\textsuperscript{-1}.

MS (70 eV): m/z (relative intensity, %) 314 (1, M\textsuperscript{+}), 285 (2, M\textsuperscript{+} - C\textsubscript{2}H\textsubscript{5}), 213 (38), 189 (33), 162 (17), 161 (100), 133 (45), 105 (31), 101 (37), 73 (72), 59 (13).

Anal. Calcd for C\textsubscript{17}H\textsubscript{38}O\textsubscript{2}Si\textsubscript{2}: C, 64.89; H, 12.17. Found: C, 64.55; H, 12.28.

Dimethyl[1-[(dimethylphenylsilyl)oxy]-1-hepteny]phenylsilane (4b) (E/Z = 87/13 mixture): a colorless oil; bp 160 °C (oven)/2 Torr

\textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta \) [0.20 (s, E), 0.22 (s, E), 0.30 (s, Z), 0.32 (s, Z) 12 H, SiCH\textsubscript{3}], [0.72 (t, \( J = 7.0 \) Hz, Z), 0.79 (t, \( J = 6.7 \) Hz, E), 3 H, CH\textsubscript{3}], 1.04 - 1.18 (m, 6 H, CH\textsubscript{2}), [1.71 (dt, \( J = 8.1, 7.1 \) Hz, Z), 1.94 (dt, \( J = 6.8, 7.1 \) Hz, E), 2 H,
=CCH₂], [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 (CDCl₃): δ [-3.05 (E), -1.97 (Z), -0.74 (E), -0.64 (Z), SiCH₃], 14.05 (CH₃), [22.45, 26.07, 27.49, 29.08, 30.14, 31.28, 31.70, CH₂], [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⁺ - CH₃), 247 (19), 210 (14), 209 (66), 195 (35), 193 (25), 136 (14), 135 (100).


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

\(^{1}\)H NMR (CDCl₃): δ 0.53 - 0.72 (m, 12 H, SiCH₂), 0.86 - 1.01 (c, 21 H, SiCCH₃ and CH₃), 1.25 - 1.39 (m, 6 H, CH₂), [1.96 (dt, J = 7.8, 7.1 Hz, Z), 2.08 (dt, J = 6.8, 7.1 Hz, E), 2 H, =CH₂], [4.86 (t, J = 6.8 Hz, E), 5.43 (t, J = 7.9 Hz, Z), 1 H, =CH].

\(^{13}\)C NMR (CDCl₃): δ [2.82, 3.81, 5.55, 5.92, 6.88, 6.99, 7.34, 7.52, SiCCH₃ and CH₃], 14.06 (CH₃), [22.54, 22.59, 25.68, 27.23, 29.31, 30.82, 31.57, 31.70, CH₂], [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⁺ - C₂H₅), 227 (28), 217 (28), 190 (19), 189 (100), 161 (53), 133 (22), 115 (25), 105 (19), 87 (45), 59 (42).

Anal. Calcd for C₁₉H₄₂OSi₂: 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

¹H NMR (CDCl₃): δ [0.04 (s), 0.10 (s), 0.12 (s), 6 H, SiCH₃], 0.53 - 0.70 (m, 8 H, SiCH₂), 0.88 - 1.01 (m, 12 H, SiCCH₃), 1.16 - 1.74 (c, 11 H, CH₂ and CH), [1.88 (dd, J = 7.9, 6.7 Hz, Z), 1.98 (dd, J = 7.0, 6.9 Hz, E), 2 H, CH₂], [4.96 (t, J = 6.9 Hz, E), 5.48 (t, J = 7.9 Hz, Z), 1 H, =CH].

¹³C NMR (CDCl₃): δ [-6.23 (E), -5.08 (Z), -3.65 (Z), -3.48 (E), SiCH₃], [4.77, 5.75, 6.84, 6.96, 7.28, 7.35, 7.51, 7.58, SiCH₂CH₃], [26.42, 26.47, 26.65, 33.22, 33.32, 33.38, 34.86, 38.20, 39.38, CH₂, 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).


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

¹H NMR (CDCl₃): δ 0.04 (s), 0.10 (s), 0.11 (s), 6 H, SiCH₃], 0.54 - 0.70 (m, 8 H, SiCH₂), 0.87 (s, 9 H, CH₃), 0.87 - 1.01 (m, 12 H, SiCCH₃), [1.90 (d, J =
7.8 Hz, 2), 1.98 (d, J = 7.1 Hz, E), 2 H, CH2), [5.03 (t, J = 7.1 Hz, E), 5.51 (t, J= 7.8 Hz, 2), 1 H, =CH].

$^{13}$C NMR (CDCl3): δ [-6.18 (E), -4.90 (Z), -3.62 (Z), -3.42 (E), SiCH3], [4.80, 5.80, 6.84, 6.96, 7.29, 7.35, 7.50, 7.61, SiCH2CH3], 29.31 (CH3), 30.93 (C), [39.43 (E), 40.91 (Z), CH2], [121.51 (Z), 122.53 (E), =CH], [155.77 (E), 158.86 (Z), =C].

IR (neat): 2964s, 2884m, 1618w, 1394m, 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-propenylmethylsilane (E/Z = 72/28 mixture): a pale yellow oil; bp 150 °C (oven)/2 Torr

$^1$H NMR (CDCl3): δ [0.11 (s), 0.17 (s), 0.21 (s), 6 H, SiCH3], 0.57 - 0.84 (m, 8 H, SiCH2), 0.89 - 1.09 (m, 12 H, SiCCH3), [3.43 (d, J = 7.8 Hz, Z), 3.52 (d, J = 6.8 Hz, E), 2 H, CH2], [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 (CDCl3): δ [-6.26 (E), -5.11 (Z), -3.63 (Z), -3.40 (E), SiCH3], [4.71, 5.75, 6.80, 6.94, 7.20, 7.35, 7.54, 7.58 SiCH2CH3], [31.85 (E), 33.32 (Z), CH2], [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$^{-1}$. 

43
[3-Butoxy-1-[(diethylmethylsilyl)oxy]-1-propenyl]diethylmethylsilane
(E/Z = 57/43 mixture): a colorless oil; bp 160 °C (oven)/3 Torr

1H NMR (CDCl₃): δ [0.05 (s), 0.12 (s), 0.13 (s), 6 H, SiCH₃], 0.55 - 0.69 (m, 8 H, SiCH₂), 0.89 - 1.00 (c, 15 H, SiCCH₃ and CH₃), 1.41 (sextet, J = 7.1 Hz, 2 H, CH₂), 1.56 (tt, J = 7.1, 6.4 Hz, 2 H, CH₂), [3.38 (t, J = 6.4 Hz, E), 3.40 (t, J = 6.4 Hz, Z), 2 H, OCH₂], [3.91 (d, J = 7.8 Hz, Z), 4.05 (d, J = 6.4 Hz, E), 2 H, OCH₂], [5.15 (t, J = 6.4 Hz, E), 5.56 (t, J = 7.8 Hz, Z), 1 H, =CH].

13C NMR (CDCl₃): δ [-6.44 (E), -5.21 (Z), -3.77 (Z), -3.66 (E), SiCH₃], [4.54, 5.64, 6.70, 6.80, 7.08, 7.26, 7.35, 7.61, SiCH₂CH₃], 13.86 (CH₃), [19.36, 19.41, 31.88, 31.92, CH₂], [65.10, 66.69, 69.38, 70.06, OCH₂], [119.78 (E), 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.

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 (CDCl₃): δ [-0.01 (s), 0.01 (s), 0.10 (s), 0.11 (s), 15 H, SiCH₃], 0.51 - 0.76 (m, 8 H, SiCH₂), 0.92 - 1.01 (m, 12 H, SiCCH₃), [1.38 (d, J = 8.5
Hz, $\beta$, 1.50 (d, $J = 8.5$ Hz, $\beta$), 2 H, CH$_2$], [5.00 (t, $J = 8.5$ Hz, $\beta$), 5.48 (t, $J = 8.5$ Hz, $\beta$), 1 H, -=CH].  

$^{13}$C NMR (CDCl$_3$): $\delta$ [-6.09 ($\beta$), -5.02 ($\beta$), -3.65 ($\beta$), -3.39 ($\beta$), -1.80 ($\beta$), -1.69 ($\beta$), SiCH$_3$], [4.88, 5.70, 6.85, 6.97, 7.28, 7.39, 7.55, 7.65, SiCH$_2$CH$_3$], [16.61 ($\beta$), 16.77 ($\beta$), CH$_2$], [120.44 ($\beta$), 121.33 ($\beta$), -=CH], [152.97 ($\beta$), 153.46 ($\beta$), -=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).  


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

$^1$H NMR (CDCl$_3$): $\delta$ [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, $\beta$), 2.67 (dt, $J = 6.5$, 6.8 Hz, $\beta$), 2 H, CH$_2$], [3.35 (t, $J = 7.9$ Hz, $\beta$), 3.39 (t, $J = 6.8$ Hz, $\beta$), 2 H, OCH$_2$], [3.40 (t, $J = 6.5$ Hz, $\beta$), 3.41 (t, $J = 6.5$ Hz, $\beta$), 2 H, OCH$_2$], [4.97 (t, $J = 6.5$ Hz, $\beta$), 5.44 (t, $J = 7.8$ Hz, $\beta$), 1 H, -=CH].  

$^{13}$C NMR (CDCl$_3$): $\delta$ [-6.29 ($\beta$), -5.67 ($\beta$), -3.75 ($\beta$), -3.66 ($\beta$), SiCH$_3$], [4.68, 5.61, 6.79, 6.90, 7.17, 7.31, 7.45, 7.48, SiCH$_2$CH$_3$], 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 ($\beta$), 121.45 ($\beta$), -=CH], [156.33 ($\beta$), 157.01 ($\beta$), -=C].  

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

45
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 C₁₆H₃₅O₂Si₂ (M+ - C₂H₅), 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 (CDCl₃): δ [-0.02 (s), 0.03 (s), 0.10 (s), 0.12 (s), 15 H, SiCH₃], 0.53 - 0.70 (m, 10 H, SiCH₂), 0.91 - 1.01 (m, 12 H, SiCCH₃), [1.93 - 2.02 (m, 2, 2.06 - 2.15 (m, E), 2 H, CH₂], [4.93 (t, J = 6.7 Hz, E), 5.50 (t, J = 7.9 Hz, Z), 1 H, =CH].

\(^1\)C NMR (CDCl₃): δ [-6.28 (E), -5.19 (Z), -3.65 (Z), -3.54 (E), -1.66 (Z), -1.57 (E), SiCH₃], [4.73, 5.75, 6.87, 6.96, 7.25, 7.37, 7.51, 7.63, SiCH₂CH₃], [16.80 (E), 18.59 (Z), 20.08 (E), 21.78 (Z), CH₂], [128.07 (Z), 129.10 (E), =CH], [153.29 (E), 153.74 (Z), =C].

IR (neat): 2960s, 2920s, 2884s, 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).


[1-[(Diethylmethylsilyl)oxy]-4-(trimethylsilyloxy)-1-butenyl]diethylmethylsilane (E/Z = 67/33 mixture): a colorless oil; bp 160 °C (oven)/3 Torr

\(^1\)H NMR (CDCl₃): δ [0.03 (s), 0.10 (s), 0.11 (s), 0.12 (s), 15 H, SiCH₃], 0.53 - 0.70 (m, 8 H, SiCH₂), 0.90 - 1.00 (m ,12 H, CH₃), [2.23 (dt, J = 7.9, 7.1
Hz, Z), 2.34 (dt, J = 6.8, 7.1 Hz, E), 2 H, CH2], [3.51 (t, J = 7.1 Hz, Z), 3.56 (t, J = 7.1 Hz, E), 2 H, OCH2], [4.96 (t, J = 6.8 Hz, E), 5.41 (t, J = 7.9 Hz, Z), 1 H, =CH].

13C NMR (CDCl3): δ [-6.29 (E), -5.24 (Z), -3.71 (Z), -3.53 (E), -0.53 (Z), -0.45 (E), SiCH3], [4.68, 5.63, 6.19, 6.80, 6.91, 7.16, 7.32, 7.49, SiCH2CH3], [29.30 (E), 30.89 (Z), CH2], [62.22 (E), 63.25 (Z), OCH2], [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⁺ - C₂H₅), 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).


[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 (CDCl₃): δ [0.02 (s), 0.10 (s), [0.11 (s), 0.12 (s), 6 H, SiCH₃], 0.52 - 0.69 (m, 8 H, SiCH₂), 0.89 - 0.98 (m, 12 H, CH₃), [1.18 (t, J = 7.1 Hz, E), 1.19 (t, J = 7.1 Hz, Z), 6 H, CH₃], [2.30 (dd, J = 5.9, 7.9 Hz, Z), 2.42 (dd, J = 6.0, 6.8 Hz, E), 2 H, CH₂], [3.47 (q, J = 7.1 Hz, Z), 3.50 (q, J = 7.1 Hz, E), 2 H, CH₂], [3.63 (q, J = 7.1 Hz, Z), 3.64 (q, J = 7.1 Hz, E), 2 H, CH₂], [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].

13C NMR (CDCl₃): δ [-6.32 (E), -5.82 (Z), -3.80 (Z), -3.54 (E), SiCH₃], [4.65, 5.52, 6.76, 6.87, 7.13, 7.26, 7.35, 7.45, SiCH₂CH₃], [15.16, 15.30, CH₃], [30.40 (E), 31.96 (Z), CH₂], [60.88 (E), 60.99 (Z), OCH₂], [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).


[4-Cyano-1-[(diethylmethyldisilyl)oxy]-1-butenyl]diethylmethyldisilane (E/Z = 73/27 mixture): a colorless oil; bp 170 \(^\circ\)C (oven)/2 Torr

\(^1\)H NMR (CDCl\(_3\)): \(\delta\) [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, \(J = 6.6 \text{ Hz}, \ E\)], 5.40 (t, \(J = 7.8 \text{ Hz}, \ Z\)], 1 H, =CH].

\(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) [-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), 21.6 (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 $170 \degree$ C (oven)/2 Torr
$^1$H NMR (CDCl$_3$): $\delta$ [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$_2$C=], 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$_3$): $\delta$ [-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$_2$CH$_3$], [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$_2$H$_5$), 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$_2$Si$_2$: 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 $120 \degree$ C (oven)/10 Torr
$^1$H NMR (CDCl$_3$): $\delta$ [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, CH₃), [5.04 (q, J = 6.6 Hz, E), 5.51 (q, J= 7.3 Hz, Z), 1 H, -CH].

¹³C NMR (CDCl₃): δ [-6.32 (E), -5.37 (Z), -3.69 (Z), -3.54 (E), SiCH₃], [4.70, 5.60, 6.82, 6.91, 7.23, 7.34, 7.46, 7.52, SiCH₂CH₃], [11.36 (E), 12.53 (Z, CH₃), [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, 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 C₁₃H₃₀OSi₂: C, 60.39; H, 11.70. Found: C, 60.24; H, 11.76.

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

¹H NMR (CDCl₃): δ [0.04 (s, E), 0.10 (s, Z), 3 H, SiCH₃), [0.12 (s, Z), 0.13 (s, E), 3 H, SiCH₃], 0.53 - 0.73 (m, 8 H, SiCH₂), 0.84 - 1.02 (m, 12 H, SiCCH₃), 2.04 (s, 3 H, CH₃), [2.34 (dt, J = 7.9, 8.0 Hz, Z), 2.43 (dt, J = 6.8, 6.8 Hz, E), 2 H, CH₂], [4.01 (t, J = 8.0 Hz, Z), 4.05 (t, J = 6.8 Hz, E), 2 H, OCH₂], [4.91 (t, J = 6.8 Hz, E), 5.44 (t, J = 7.9 Hz, Z), 1 H, -CH].

¹³C NMR (CDCl₃): δ [-6.35, -5.30, -3.82, -3.57 (SiCH₃)], [4.60, 5.52, 6.73, 6.84 (SiCH₂)], [7.11, 7.23, 7.39, 7.45 (SiCCH₃)], [20.85, 20.89 (CH₃), [25.23, 26.87 (CH₂)], [63.80, 64.65 (OCH₂)], [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+ - C2H5), 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 C16H34O3Si2: Calcd, C, 58.13; H, 10.37. Found: C, 58.08; H, 10.46.

[Bicyclo[2.2.1]hept-2-ylidene](diethyldimethylsilyloxy)methyl]diethylmethylsilane (E/Z = 36/64 mixture): a colorless oil; 150 °C (oven)/3 Torr

1H NMR (CDCl3): δ [0.06 (s), 0.10 (s), 0.13 (s) 6 H, SiCH3], 0.56 - 0.69 (m, 8 H, SiCH2), 0.89 - 1.00 (m, 12 H, CH3), 1.22 - 1.64 (m, 6 H, CH2), [1.85 (dd, J = 14.6, 2.7 Hz, E), 1.94 (dd, J = 15.6, 2.3 Hz, Z), 1 H, CH2endo], [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, CH2exo]. 2.31 - 2.39 (m, 1 H, CH), [2.81 - 2.87 (m, Z), 3.15 - 3.19 (m, E), 1 H, CH].

13C NMR (CDCl3): δ [-5.57, -5.13, -3.46, -3.39, SiCH3], [5.28, 5.31, 5.84, 5.87, 7.05, 7.52, 7.61, 7.71, SiCH2CH3], [28.53, 29.01, 30.03, 35.84, 35.88, 36.07, 36.74, 37.36, 38.57, 39.93, 40.53, 40.62, CH2, 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 C18H36OSi2 (M+), Calcd, 324.2277; Found, 324.2291.
[Bicyclo[2. 2. 1]hept-2-en-5-ylidene(diethymethylsilyl)oxy)methyl]-diethylmethyldilane (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$_{34}$O$Si_2$ (M$^+$), Calcd, 322.2148; Found, 322.2166.

[Diethyl[[1-(diethylmethyarsilyl)-1, 6-heptadienyl]oxy)methyl-silane (8) and diethyl[[1-(diethylmethyarsilyl)-1, 5-heptadienyl]oxy)methylsilane (9 and 10) and (8E: 8Z: 9E: 9Z: 10E: 10Z = 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, CH₂), [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, =CH₂), 5.74 - 5.89 (m, 1 H, =CH); 9 and 10, δ 0.02 - 0.14 (c, 6 H, SiCH₃), 0.52 - 0.69 (m, 8 H, SiCH₂), 0.90 - 1.00 (m, 12 H, SiCCH₃), 1.60 (d, J = 6.8 Hz, 10), 1.64 (d, J = 8.5 Hz, 9), 3 H, CH₃, 2.01 - 2.18 (m, 4 H, CH₂), [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).

¹³C NMR (CDCl₃): δ [-6.28, -5.22, -3.74, -3.54 (SiCH₃)], [4.71, 5.69, 6.84, 6.94 (SiCH₂)], [7.19, 7.22, 7.34, 7.49 (SiCCH₃)], [12.79, 17.91 (CH₃)], [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 (CH₂)], [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 (=CH₂, =CH, and =C)].

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

MS (70 eV): m/z (relative intensity, %) 312 (2, M+), 283 (1, M+ - C₂H₅), 257 (20), 211 (20), 189 (14), 162 (13), 161 (72), 147 (11), 133 (44), 105 (35), 101 (54), 73 (100), 59 (15).


¹H NMR (CDCl₃): δ [0.04 (s, E), 0.11 (s, Z), 3 H, SiCH₃], 0.12 (s, 3 H, SiCH₃), 0.51 - 0.72 (m, 8 H, SiCH₂), 0.91 - 1.00 (m, 12 H, SiCCH₃), 1.22 - 2.09 (c, 11 H, CH₂ 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$_3$): $\delta$ [-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$_2$H$_5$), 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).


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

$^1$H NMR (CDCl$_3$): $\delta$ 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$_3$): $\delta$ [-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$^{-1}$. 

54
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).


Diethyl[1-[(diethylmethylsilyl)oxy]-1-nonenyilmethylsilane (E/Z = 71/29 mixture): a colorless oil; bp 170 °C (oven)/2 Torr

¹H NMR (CDCl₃): δ [0.03 (s), 0.11 (s), 0.12 (s), 6 H, SiCH₃], 0.51 - 0.70 (m, 8 H, SiCH₂), 0.86 - 1.01 (c, 15 H, SiCCH₃ and CH₃), 1.20 - 1.38 (m, 6 H, CH₂), [1.93 - 2.03 (m, Z), 2.04 - 2.13 (m, E), 2 H, =CCH₂], [4.92 (t, J = 6.8 Hz, E), 5.46 (t, J = 7.8 Hz, Z), 1 H, =CH].

¹³C NMR (CDCl₃): δ [-6.28 (E), -5.22 (Z), -3.69 (Z), -3.56 (E), SiCH₃], [4.74, 5.70, 6.84, 6.93, 7.25, 7.32, 7.48, 7.52, SiCH₂CH₃], 14.06 (CH₃), [22.67, 25.74, 27.33, 29.19, 29.24, 29.27, 29.43, 29.59, 31.05, 31.86, CH₂], [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⁺ - C₂H₅), 242 (11), 241 (52), 189 (49), 162 (16), 161 (100), 133 (43), 105 (31), 101 (42), 73 (82), 61 (11), 59 (12).


Diethyl(heptanoyl)methylsilane (14): a colorless oil; bp 130 °C (oven)/7 Torr

¹H NMR (CDCl₃): δ 0.15 (s, 3 H, SiCH₃), 0.65 - 0.73 (m, 4 H, SiCH₂), 0.87 (t, J = 6.8 Hz, 3 H, CH₃), 0.89 - 0.98 (m, 6 H, SiCCH₃), 1.19 - 1.33 (m, 6 H, CH₂), 1.42 - 1.56 (m, 2 H, CH₂), 2.55 (t, J = 7.1 Hz, 2 H, CH₂).
$^{13}$C NMR (CDCl$_3$): $\delta$ -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, 754m, 688m cm$^{-1}$.

MS (70 eV): m/z (relative intensity, %) 214 (0, M$^+$), 185 (11, M$^+$ - C$_2$H$_5$), 102 (11), 101 (100), 89 (29), 73 (99).

Anal. Calcd for C$_{12}$H$_{26}$O$^+$Si: C, 67.22; H, 12.22. Found: C, 67.42; H, 12.45.

2-7 References and Notes


Conclusion

The objective of this research was to develop new catalytic reactions using the effective transition metal complexes other than Co₂(CO)₈ with carbon monoxide (CO) and hydrosilanes (HSiR₃). 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 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 introduction of a siloxy(silyl)methylene unit having 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.