Notes

Thermal Isomerization of an Acyl(ethenyl)disilane via 2-Siladiene Intermediates

Joji Ohshita,* Hidetoshi Takayama, Mamiko Tamai, Toshiyuki Iida, and Atsutaka Kunai*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

*Summary: Heating (Z)-1-adamantoyl-1-(1,2-diphenyl-2-trimethylsilylethenyl)tetramethyldisilane (**Z-1**) at 150 °C for 24 h afforded the E-isomer (**E-1**) almost quantitatively. Similar reactions of **Z-1** and **E-1** in the presence of an excess of methanol gave products arising from isomerization of the substrates leading to 2-siladiene intermediates, followed by quenching the resulting siladienes with methanol. Theoretical and kinetic studies also were carried out to understand the isomerization.*

Introduction

Silenes are important organosilicon species as the analogues of olefins.[1] Since the first class of stable silenes were prepared by the photochemical isomerization of acylpolysilanes by Brook et al.,[2,3] many papers have appeared concerning the photochemical silene formation from acylpolysilanes and the chemical behavior of the resulting silenes.[1−4] Thermally induced similar isomerization of acylpolysilanes has been also extensively studied.[5] In contrast to the photolysis that affords the silenes irreversibly, the thermolysis of acylpolysilanes gives rise to an equilibrium mixture of the acylpolysilane and the silene. Thus, the starting acylpolysilanes are recovered when the acylpolysilanes are substituted with a large protecting group, such as adamantyl and *tert*-butyl, on the carbonyl carbon and the reactions are carried out in the absence of a trapping agent.[5a,b] With a less hindered substituent, they afford the silene dimers.[5b] In the presence of a trapping agent, such as alcohols and unsaturated organic compounds, the thermolysis of acylpolysilanes produces the silene adducts in good yield.[2,5]

Scheme 1

Acylpolysilanes that have been studied, however, are limited to rather simple ones, and little is known of the chemical behaviors of acylpolysilanes having a functional group. Recently, we prepared a series of acyl(ethenyl)disilanes from the reactions of lithium silenolates with phenyl-substituted acetylenes, followed by quenching the resulting anionic species with electrophiles, as the first example of acylpolysilanes having an ethenyl group on the center silicon atom (Scheme 1).[6,7] Here we report the thermal isomerization of an acyl(ethenyl)disilane, which afforded products arising from 2-siladiene intermediates formed from a 1,3-silyl shift from the center silicon to the carbonyl oxygen of the starting acyl(ethenyl)disilane.

Results and Discussion

First we examined the photochemical reactions of (*Z*)-1-adamantoyl-1-(1,2-diphenyl-2-trimethylsilylethenyl)-tetramethyldisilane (**Z-1**). Thus, when a hexane solution of **Z-1** was irradiated with a low-pressure mercury lamp bearing a Vycor filter (254 nm), clean isomerization to the *E*-isomer (**E-1**) was observed at the early stage of the reaction to reach the ratio of **E-1**/**Z-1** = 54:46 (Scheme 2). Further photolysis, however, did not change the ratio but resulted in a slight decrease of the yield of the mixture **E-1**/**Z-1**, accompanied with the formation of many unidentified byproducts in low yield. The isolated yield of the mixture **E-1**/**Z-1** was 67% after 11 h of irradiation. Similar photolysis of **Z-1** in the presence of an excess of methanol again gave a mixture of **E-1**/**Z-1**. No products arising from the reactions with methanol were detected in the reaction mixture, indicating

(1) (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1997; Part 2, Chapter 16.
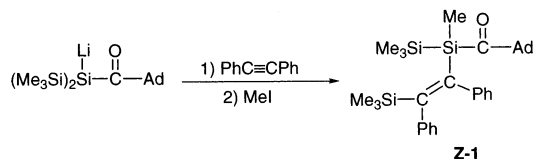(2) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.
(3) Brook, A. G.; Nyburg, S. C.; Abdesekan, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.
(4) Brook, A. G.; Yu, Z. *Organometallics* **2000**, *19*, 1859, and references therein.
(5) (a) Ohshita, J.; Hasebe, H.; Masaoka, Y.; Ishikawa, M. *Organometallics* **1994**, *13*, 1064. (b) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Main Group Chem.* **1996**, *1*, 219. (c) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Organometallics* **1996**, *15*, 3836. (d) Naka, A.; Ishikawa, M.; Matsui, S.; Ohshita, J.; Kunai, A. *Organometallics* **1996**, *15*, 5759. (e) Ohshita, J.; Yoshimoto, K.; Iida, T.; Kunai, A. *J. Am. Chem. Soc.* **2001**, *123*, 8400.

(6) Synthesis and reactions of acylpolysilanes bearing an ethenyl group on the carbonyl carbon have been reported. See: Brook, A. G.; Ionkin, A.; Lough, A. J. *Organometallics* **1996**, *15*, 1275.
(7) Ohshita, J.; Tamai, M.; Sakurai, H.; Kunai, A. *Organometallics* **2001**, *20*, 1065.
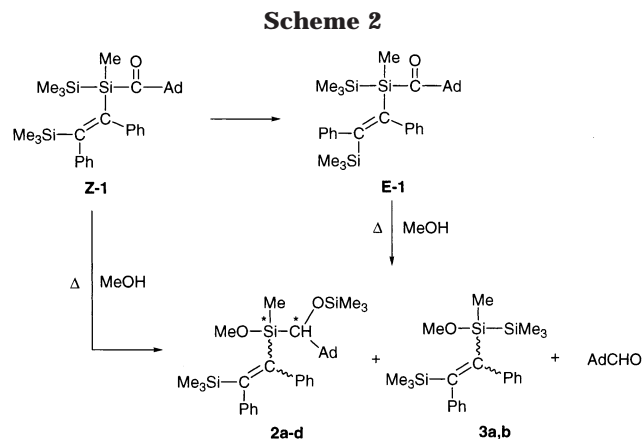
Scheme 2

Table 1. Thermal Reactions of Z-1 and E-1 in the Presence of Methanol for 24 h

| compd | temp/ °C | MeOH/ equiv | yield/%[a] | | |
			2 (a/b/c/d)	**3** (a/b)	**1** (Z/E)
Z-1	125	26	55 (37/38/10/5)	15 (85/15)	16 (100/0)
	125	4	20 (45/35/10/10)	4 (79/21)	72 (72/28)
	125	2	10 (37/28/21/14)	1 (85/15)	86 (72/28)
	150	26	26 (50/46/8/6)	53 (64/35)	0
E-1	125	26	21 (0/0/50/50)	16 (0/100)	62 (0/100)
	150	26	3 (0/0/59/41)	65 (0/100)	0

[a] Yields were determined by the ^{1}H NMR spectra of the reaction mixtures, on the basis of the starting **1** taken.

that the photolysis gave a simple photoequilibrium mixture of **E-1**/**Z-1**, arising from the direct isomerization of the ethenyl unit.

Next, we studied the thermal reactions of **Z-1**. Heating **Z-1** at 150 °C for 20 h afforded **E-1** in 96% isolated yield. In this reaction, the starting **Z-1** was completely consumed, in marked contrast to the photolysis. Furthermore, the presence of methanol significantly affected the reaction mode, producing methanol adducts **2a**−**d** and **3a,b** as shown in Scheme 2 and Table 1. Products **2a**−**d** and **3a,b** were obtained as the isomeric mixtures, respectively, and analyzed as obtained. Although we have no data to determine their stereochemistry, it seems to be reasonable to identify the **2a,b** and **3a** that were obtained as the major isomers from **Z-1** as the *Z*-isomers. Interestingly, compound **E-1** underwent a similar reaction with methanol to give the adducts **2c,d** and **3b**, although the reaction proceeded less rapidly when compared with that of **Z-1**. In this reaction, compounds **2a,b** and **3a** were not obtained. When an isomeric mixture of **2a**−**d** was heated at 180 °C, **3a,b** and adamantanecarboxaldehyde were formed quantitatively, indicating that **2a**−**d**, and **3a,b** and adamantanecarboxaldehyde were initial and secondary products, respectively. Similar treatment of **2a**−**d** (**a/b/c/d** = 46:41:9:4) at 125 °C in benzene with 30 equiv of CCl₄ again afforded **3a,b** (**a/b** = 30:70) in 84% yield, together with adamantanecarboxaldehyde in 69% yield. This seems to suggest that any radical processes were not involved as the major route in this reaction. Presumably, the reaction proceeded in a concerted fashion and the steric repulsion between the bulky substituents in **2a**−**d** would be a driving force for the loss of adamantanecarboxaldehyde from **2a**−**d**. GC−MS analysis of the reaction mixture in the presence of CCl₄ also showed the formation of some chlorinated adamantanecarboxaldehyde in less than 5% yield each. The higher

Scheme 3
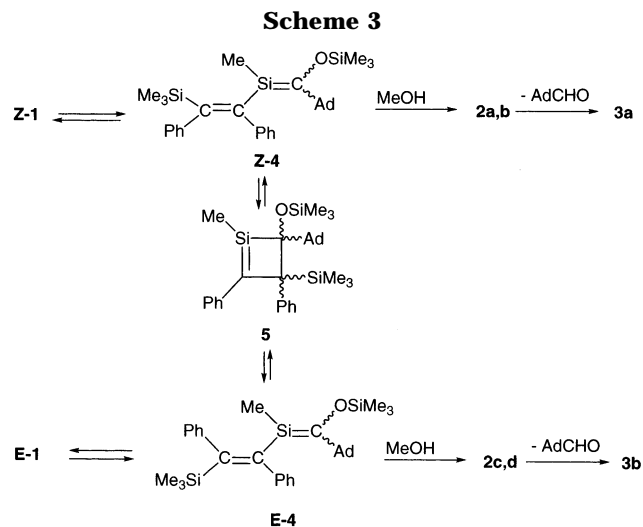
ratio of **3b** relative to **3a** than that expected from the starting ratio of **2a**−**d** in this reaction may be due to *E*/*Z*-interconversion in **3a,b**. In fact, heating a mixture of **3a/b** = 96:4 for 90 h under the same conditions resulted in a decrease of the ratio to **3a/b** = 42:58.

Scheme 3 represents a possible mechanistic interpretation of the reaction course, involving the formation of 2-siladiene intermediates (**Z-4** and **E-4**) at equilibrium with the starting **Z-1** and **E**−**1**, respectively, by a 1,3-silyl shift from the center silicon to carbonyl oxygen. Addition of methanol to siladienes **Z-4** and **E-4** produces the respective adducts **2a,b** and **2c,d**. The interconversion of the isomers of the 2-siladiene (**Z**- and **E-4**) may be best understood by assuming electrocyclic ring closure and the subsequent ring opening of the resulting silacyclobutene intermediates **5**, although we have not yet obtained any direct evidence for the formation of **5**. Similar electrocyclic ring closure of 2-siladienes[8] and *E*/*Z*-isomerization of butadienes via a cyclobutene intermediate[9] have been reported previously. It might be possible to consider the direct transformation of **Z-1** to **E-1** that then isomerizes to give silene **E-4**. However, this seems to be unlikely, since the reactions with lower concentration of methanol gave higher yields of **2c,d** relative to those of **2a,b** (Table 1).

To know more about the isomerization, we carried out molecular orbital (MO) calculations at the HF/6-31G* level on model compounds shown in Figure 1.[10] As can be seen in Figure 1, the siladienes (**4′**) were predicted to be less stable by about 18−20 kcal/mol than the acylethenylsilanes (**1′**). The cyclic adducts (**5′**) were calculated to be even less stable than **4′** by approximately 10 kcal/mol. By taking into account this thermodynamic instability and the existence of bulky substituents in **5** that would cover the silacyclobutene fragment efficiently to prevent methanol from approaching from both sides of the ring, the absence of methanol adducts of **5** in the trapping experiments does not seem to be unexpected. The *E*-isomer of **1′** was found to be more stable only by 2.4 kcal/mol relative to the *Z*-isomer. In the actual system, however, reducing the

(8) Bertrand, G.; Manuel, G.; Mazerolles, P.; Trinquier, G. *Tetrahedron* **1981**, *37*, 2875

(9) Stephenson, L. M.; Brauman, J. I. *Acc. Chem. Res.* **1974**, *7*, 65. (b) Frey, H. M.; Lamont, A. M.; Walsh, R. *J. Chem. Soc. (A)* **1971**, 2642.

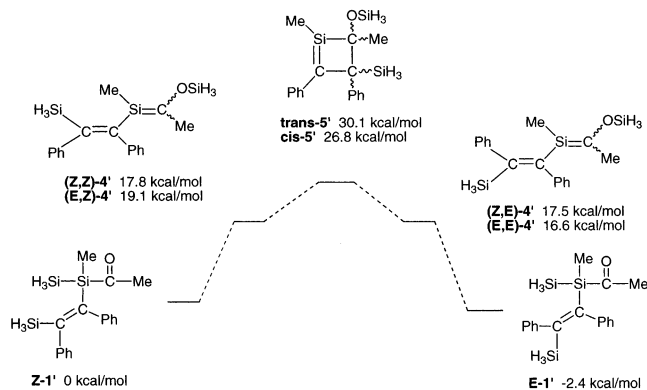(10) *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

Figure 1. Energy diagram for the isomerization of model compound **1′**. The heats of formation were obtained by MO calculations at the HF/6-31G* level.
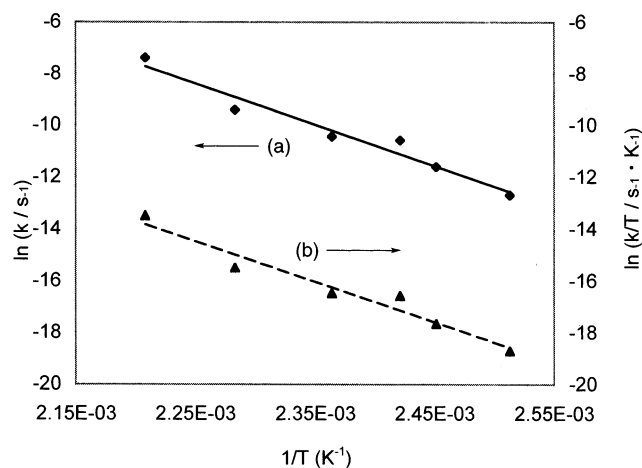

Figure 2. (a) Arrhenius and (b) Eyring plots for the isomerization of **Z-1** to **E-1**.

steric repulsion between the large acylsilyl unit and the trimethylsilyl group in **Z-1** would provide considerable driving force for the isomerization to **E-1**. For the siladienes, no conformers with a planar C=Si–C=C backbone were found as the stable isomers with energy minimum, probably due to the steric repulsion between the substituents. This is indicative of the lack of conjugation in the present 2-siladiene unit. Attempted calculations to find the transition states at each of the steps were unsuccessful.

The thermal isomerization of **Z-1** to **E-1** was monitored by ^{1}H NMR spectra at several temperatures to note the kinetic parameters. The first-order kinetic plots exhibited a linear relationship agreeing with the unimolecular process, and the Arrhenius plots provided the parameters E_a = 32 kcal·mol^{-1} and A = 9.1 × 10^{11} s^{-1} (Figure 2a). The Eyring plots were also examined as presented in Figure 2b, and the kinetic parameters $\Delta H^{\ddagger}$ = 31 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = −6.3 cal·mol^{-1} K^{-1} (at 428 K) were obtained. The $\Delta S^{\ddagger}$ value is negatively much larger than that for the isomerization of *cis*-stilbene in the gas phase ($\Delta S^{\ddagger}$ = −2.8 cal·mol^{-1} K^{-1}).[11] This seems to suggest again that no direct isomerization of **Z-1** to **E-1** was involved in the present system, although there

(11) The $\Delta S^{\ddagger}$ value was obtained by the equation of $\Delta S^{\ddagger}$ = $R[\ln(hA/k_B T) - 1]$ (h = Planck constant, k_B = Boltzmann constant, T = 428 K) using the Arrhenius parameters reported previously (E_a = 42.8 kcal·mol^{-1} and A = 6 × 10^{12} s^{-1}, see: Kistiakowsky, G. B.; Smith, W. R. *J. Am. Chem. Soc.* **1934**, *56*, 638).

may be some other factors that affect the $\Delta S^{\ddagger}$ values, such as solvent and substitution effects.

In conclusion, we have studied the thermal isomerization of an acyl(ethenyl)disilane and found that it undergoes novel thermal isomerization via 2-siladiene intermediates. Linear siladienes are important organosilicon species as the simplest conjugated silenes, but it is true that less is known about linear 2-siladienes and about the 3-sila analogue[7,8,12,13] when compared with the 1-sila analogues.[6,13,14]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. Mass spectra were measured on a Hitachi M-80B spectrometer. NMR spectra were recorded on JEOL EX-270 and Lambda-400 spectrometers using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer.

Materials. Benzene and methanol were dried over sodium–potassium alloy and magnesium methoxide, respectively, and distilled just before use. Compound **Z-1** was prepared as reported in the literature.[7]

Isomerization of Z-1. A solution of 50 mg (0.09 mmol) of **Z-1** in 1 mL of benzene was placed in a degassed sealed glass tube, and the tube was heated at 150 °C for 24 h. After evaporation of the solvent, the residue was subjected to preparative GPC to give 49 mg (98%) of **E-1**: MS m/z 530 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) −0.18 (s, 9H), 0.03 (s, 9H), 0.03 (s, 3H), 1.62 (br s, 6H, Ad), 1.73−1.81 (m, 6H, Ad), 1.93 (s, 3H, Ad), 7.05−7.42 (m, 10H, Ph); ^{13}C NMR (δ in C$_6$D$_6$) −0.6 (Me), −0.5(Me$_3$Si), 0.6 (Me$_3$Si), 28.5, 37.0, 37.9, 51.9 (Ad), 126.3, 126.5, 127.9, 128.1, 128.6, 129.5, 146.0, 146.5 (Ph), 155.0, 161.5 (C=C), 247.3 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −31.2 (center Si), −16.5, −6.0 (Me$_3$Si); IR $\nu_{C=O}$ 1617 cm^{-1}. Anal. Calcd for C$_{32}$H$_{46}$-OSi$_3$: C, 72.39; H, 8.73. Found: C, 72.21; H, 8.73.

Reactions of Z-1 and E-1 in the Presence of Methanol. A mixture of 50 mg (0.094 mmol) of **Z-1** or **E-1**, 0.1 mL of methanol, and 1 mL of benzene was placed in a degassed sealed glass tube, and the tube was heated at 125 or 150 °C for 24 h. After evaporation of the solvent, the residue was directly analyzed by the ^{1}H NMR spectrum to determine the product yields as presented in Table 1. The residue was then subjected to preparative GPC to give analytically pure **2a**−**d** and **3a,b**. Data for the mixture **2a**−**d**: MS m/z 562 (M$^+$); IR ν_{Si-O} 1244 cm^{-1}. Anal. Calcd for C$_{33}$H$_{50}$O$_2$Si$_3$: C, 70.40; H, 8.95. Found: C, 70.06; H, 9.16. Data for **2a**: ^{1}H NMR (δ in C$_6$D$_6$) 0.13 (s, 9H, Me$_3$Si), 0.44 (s, 9H, Me$_3$Si), 0.57 (s, 3H, SiMe), 1.78−2.09 (m, 15H, Ad), 3.54 (s, 3H, OMe), 4.37 (s, 1H, CH), 6.79−7.00 (m, 10H, Ph), Ad and Ph proton signals overlap with those of **2b**; ^{13}C NMR (δ in C$_6$D$_6$) 0.5 (Me$_3$Si), 1.3 (Me$_3$Si), 2.4 (SiMe), 28.7, 37.7, 37.8, 39.3 (Ad), 56.8 (OMe), 108.9 (CH), 124.8, 125.2, 127.4, 128.5, 145.4, 146.2, (Ph), 157.8, 160.4 (C=C); ^{29}Si NMR (δ in C$_6$D$_6$) −20.0 (center Si), −6.0, (Me$_3$Si), 1.0 (OSiMe$_3$). Data for **2b**: ^{1}H NMR (δ in C$_6$D$_6$) 0.07 (s, 3H, SiMe), 0.43 (s, 9H, Me$_3$Si), 0.45 (s, 9H, Me$_3$Si), 1.78−2.09 (m, 15H, Ad), 3.56 (s, 3H, OMe), 4.11 (s, 1H, CH), 6.79−7.00 (m, 10H, Ph); ^{13}C NMR (δ in C$_6$D$_6$) 0.2 (SiMe), 0.5 (Me$_3$Si), 0.7 (Me$_3$-Si), 28.7, 37.3, 37.7, 39.1 (Ad), 57.1 (OMe), 107.6 (CH), 124.9, 125.0, 145.6, 146.3, (Ph), 157.0, 160.9 (C=C); ^{29}Si NMR (δ in

(12) Grobe, J.; Ziemer, H. *Z. Naturforsch, B: Chem. Sci.* **1993**, *48B*, 1193.
(13) Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 6313.
(14) (a) Conlin, R. T.; Namavari, M. *J. Am. Chem. Soc.* **1988**, *110*, 3689. (b) Steinmetz, M. G.; Udayakumar, B. S.; Gordon, M. S. *Organometallics* **1989**, *8*, 530. (c) Conlin, R. T.; Zhang, S.; Namavari, M.; Bobbitt, K. L. *Organometallics* **1989**, *8*, 571. (d) Conlin, R. T.; Namavari, M. *J. Organomet. Chem.* **1989**, *376*, 259 (e) Kerst, C.; Byloos, M.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 975.

C_6D_6) −19.6 (center Si), −5.9, (Me$_3$Si), 0.9 (OSiMe$_3$). Data for **2c**: ^{1}H NMR (δ in C_6D_6) −0.13 (s, 9H, Me$_3$Si), −0.11 (s, 3H, SiMe), 0.20 (s, 9H, Me$_3$Si), 3.25 (s, 3H, OMe), 3.78 (s, 1H, CH), 1.60−2.01 (m, 15H, Ad), 7.13−7.25 (m, 10H, Ph), Ad and Ph proton signals overlap with those of **2d**; ^{13}C NMR (δ in C_6D_6) −0.7 (Me$_3$Si), 0.8 (Me$_3$Si), 0.9 (SiMe), 28.7, 37.3, 37.7, 39.4 (Ad), 57.7 (OMe), 108.0 (CH), 126.2, 126.4, 145.3, 145.8 (Ph), 158.4, 159.9 (C=C). Data for **2d**: ^{1}H NMR (δ in C_6D_6) −0.13 (s, 9H, Me$_3$Si), −0.11 (s, 3H, SiMe), 0.08 (s, 9H, Me$_3$Si), 1.60−2.01 (m, 15H, Ad), 3.50 (s, 3H, OMe), 3.92 (s, 1H, CH), 7.13−7.25 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −0.7 (Me$_3$Si), 0.6 (SiMe), 0.7 (SiMe$_3$), 28.7, 37.5, 37.7, 39.2 (Ad), 57.2 (OMe), 106.9 (CH), 126.4, 126.5, 145.4, 145.8 (Ph), 158.8, 160.0 (C=C). Data for the mixture **3a,b**: MS m/z 398 (M$^+$); IR ν_{Si-O} 1236 cm^{-1}. Anal. Calcd for C$_{22}$H$_{34}$OSi$_3$: C, 66.26; H, 8.59. Found: C, 66.26; H, 8.85. Data for **3a**: ^{1}H NMR (δ in C_6D_6) 0.12 (s, 9H, Me$_3$Si), 0.33 (s, 3H, SiMe), 0.36 (s, 9H, Me$_3$Si), 3.38 (s, 3H, OMe), 6.77−7.00 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −1.9 (SiMe), −0.8 (Me$_3$Si), 1.7 (Me$_3$Si), 50.9 (OMe) 124.8, 125.4, 127.5, 127.7, 128.9, 129.1, 144.3, 146.6, (Ph), 156.3, 160.7 (C=C). Data for **3b**: ^{1}H NMR (δ in C_6D_6) −0.15 (s, 9H, Me$_3$Si), −0.02 (s, 3H, SiMe), 0.07 (s, 9H, Me$_3$Si), 3.05 (s, 3H, OMe), 7.08−7.29 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −1.1 (Me$_3$Si), −1.0 (SiMe), 0.6 (Me$_3$Si), 51.3 (OMe) 126.1, 126.4, 128.0, 128.1, 128.3, 129.2, 145.5, 145.6, (Ph), 158.6, 160.5 (C=C); ^{29}Si NMR (δ in C_6D_6) −20.5

(center Si), −6.4, (Me$_3$Si), 3.6 (Me$_3$Si). Data for adamantane-carboxaldehyde:[15] MS m/z 164 (M$^+$); ^{1}H NMR (δ in C_6D_6) 1.44−1.57 (m, 15H, Ad), 9.16 (s, 1H, CHO); ^{13}C NMR (δ in C_6D_6) 27.7, 35.9, 36.7, 51.3 (Ad), 204.0 (C=O).

Reaction of 2a−d in CCl$_4$. A mixture of 19 mg (0.03 mmol) of **2** (a/b/c/d = 46:41:9:4), 0.1 mL (30 equiv) of CCl$_4$, and 0.8 mL of benzene was placed in a degassed sealed glass tube, and the tube was heated at 120 °C for 90 h. After evaporation of the solvent, the residue was directly analyzed by the ^{1}H NMR spectrum in C_6D_6 as being **3** (84% yield, a/b = 30:70) and adamantanecarboxaldehyde (69% yield). GC−MS analysis of the mixture also showed the formation of some chlorinated adamantanecarboxaldehyde (m/z 198) in addition to **3** and adamantanecarboxaldehyde. The residue was then subjected to preparative GPC to give 8.7 mg of **3** (67% isolated yield).

(15) Alaimo, P. J.; Arndtsen, B. A.; Berbman, R. G. *Organometallics* **2000**, *19*, 2130.