for $(C_6H_6)Mn(CO)_3^+$ and 450 for $(C_6H_6)Re(CO)_3^+$. Thus, the k_{CO}^* values predict the relative rate order, but not the K_{eq} order, though the differences in both the rate and equilibrium constants may be too small to yield a substantial conclusion. The $(C_6H_6)_2M^{2+}$ complexes (M = Fe, Ru, Os), which all have higher k_{CO}^*'s than the Mn and Re compounds, react rapidly to give quantitative yields of the $P(n\text{-}Bu)_3$ adducts, and neither $(C_6H_6)Mn(CO)_3^+$ nor $(C_6H_6)Re(CO)_3^+$ forms an adduct with PPh_3. Therefore, while k_{CO}^* apparently reflects large qualitative differences in reactivity, it appears not to be sensitive to small differences in closely related compounds.

On the basis of the above studies, one must conclude that it is not clear whether k_{CO}^* is related to kinetic or thermodynamic factors and that k_{CO}^* is useful primarily for predictions when fairly large differences in reactivity are involved.

Conclusions

Results of this paper show that k_{CO}^* is a very useful parameter for predicting the susceptibility of π-ethylene or π-benzene ligands to nucleophilic addition. The k_{CO}^* values of the π-ethylene or π-benzene complexes may be calculated from experimental $\nu(CO)$ values of the analogous metal carbonyl complexes or by Timney's method[9] using known, additive parameters. This latter method is a particularly useful and simple way to obtain k_{CO}^* values. Threshold k_{CO}^* values establish approximate lower limits for reaction of π-ethylene and π-benzene ligands with different nucleophiles; these threshold values should be of particular value in designing syntheses where nucleophilic addition to the π-ligands is involved. The usefulness of k_{CO}^* values for predicting nucleophilic addition to CO^6 and the π-hydrocarbon ligands reported herein suggests that k_{CO}^* may be helpful for predicting reactions of other ligands and correlating properties of complexes which depend upon the electron density on the metal.

Silylene-to-Silanone Thermal Isomerization

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Abstract: Thermal generation of (allyloxy)methylsilylene, C_3H_5OSiMe, by flash vacuum pyrolysis of 1,1-bis(allyloxy)-tetramethyldisilane unexpectedly produced products strongly suggestive of the intermediacy of allylmethylsilanone, $C_3H_5MeSi=O$. Alternative routes were probed through the pyrolysis of model systems, and the silanone was apparently trapped with $Me_2Si(OMe)_2$. It is proposed that this silanone arises from isomerization of the initially formed silylene via a [2,3] sigmatropic allyl migration, although a stepwise process proceeding through the intermediacy of an oxasilabicyclo[2.1.0]pentane ring cannot be ruled out. Thermal generation of (allyloxy)(trimethylsilyl)silylene, $C_3H_5OSiSiMe_3$, initiated an apparent silylene → silanone → silylene rearrangement sequence culminating in the formation of a silacyclobutene. Here consideration of an oxasilabicyclo[2.1.0]pentane intermediate reveals the possibility that the reaction actually involves a silylene-to-silylene rearrangement without silanone intermediacy.

Recently we reported that butenylmethylsilylene (**1**), generated by flash vacuum pyrolysis (FVP), isomerized to silacyclopentene (**3**) and have suggested that this isomerization proceeds through the intermediacy of vinylsilarane (**2**) followed by a 1,3-migration of silicon.[1]
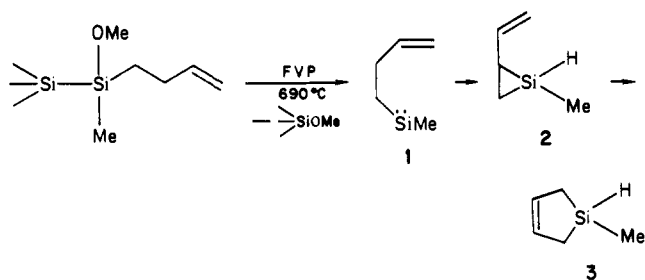

We now report an attempt to extend this reaction to the synthesis of a dihydrosilafuran and the unexpected chemistry to which this approach led.

Results and Discussion

The obvious precursor, at least from a synthetic viewpoint, to the silylene **5** required for the proposed dihydrosilafuran synthesis is 1,1-bis(allyloxy)tetramethyldisilane (**4**). One confidently anticipates[2] that thermolysis of **4** would induce reductive elimination of (allyloxy)trimethylsilane (**7**) to produce silylene **5** for which

cyclization to dihydrosilafuran **6** was a reasonable expectation based on the known chemistry of silylene **1**. Synthesis of **4** was easily accomplished in 53% yield from coupling of the lithium salt of allyl alcohol and 1,1-dichlorotetramethyldisilane.
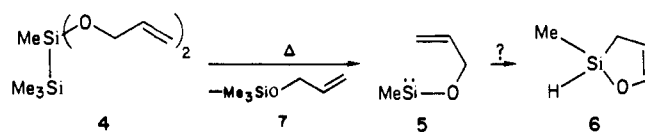

FVP of **4** was performed by slowly distilling neat **4** through a quartz-chip-packed tube at 700 °C ($\sim 10^{-5}$ torr) with an 81% mass recovery. Three major products were isolated by preparative GC: (allyloxy)trimethylsilane (**7**, 74%), 1-allyl-1-allyloxy-1,3,3,3-tetramethyldisiloxane (**8**, 13%), and 2,4,6-trimethyl-2,4,6-tri(2-propenyl)cyclotrisiloxane (**9**, 13%). No evidence for **6** even in trace amounts could be found by GCMS analysis.
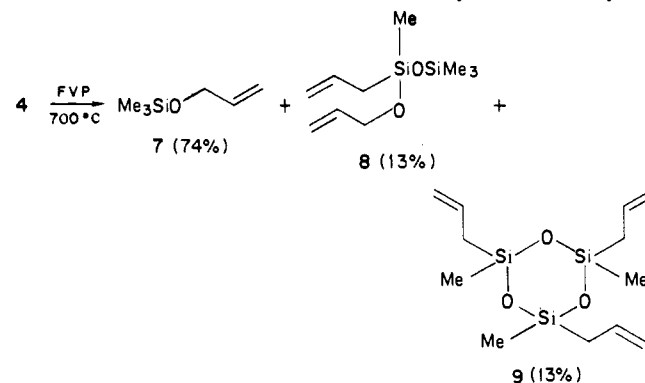

(1) Barton, T. J.; Burns, G. T. *Organometallics* **1983**, *2*, 1.
(2) Weyenberg, D. R.; Atwell, W. H. *Pure Appl. Chem.* **1969**, *19*, 343.

Scheme I

Scheme II
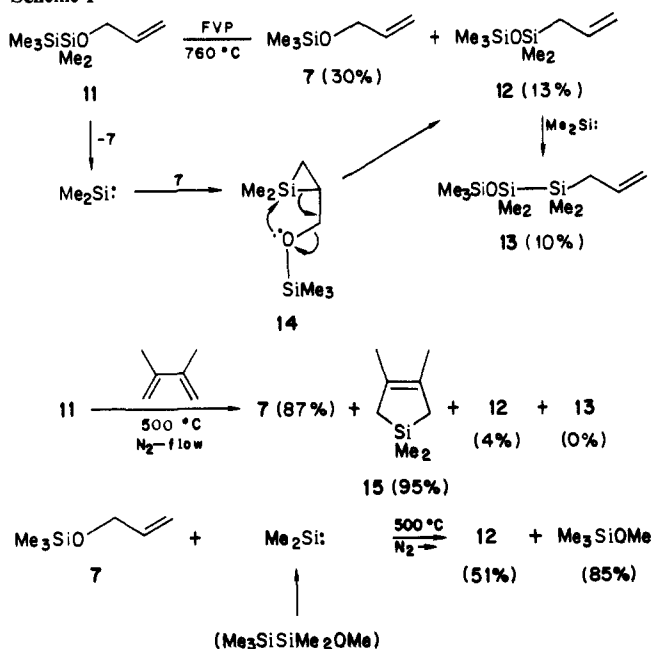
Although formation of disiloxane **8** formally corresponds to insertion of allylmethylsilanone **10** (trimerization of which would afford **9**) into the Si–O bond of **7**, a less complex route to **8** is unimolecular rearrangement of **4** via concomitant Me_3Si- and allyl-migrations.
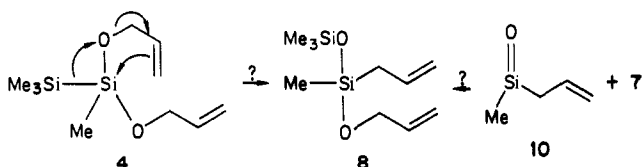
In order to test this latter possibility, the FVP of a simple model system, 1-(allyloxy)pentamethyldisilane (**11**), was conducted at 760 °C with 77% mass recovery. Only three volatile products were obtained (Scheme I): **7** (30%), allylpentamethyldisiloxane (**12**, 13%), and 1-(trimethylsilyl)-2-allyl-1,1,2,2-tetramethyldisilane (**13**, 10%).[3] Rearrangement of the starting material, **11**, would account for disiloxane **12**, but as **11** is by all precedents expected[2] to thermally extrude Me_2Si:, we favored the reaction of this silylene and **7** as the origin of **12**. The reaction of silylenes and allyl ethers to afford allylsiloxanes is also well precedented and is believed to proceed through a silarane intermediate analogous to **14**.[4] That **11** does indeed thermally extrude Me_2Si: was demonstrated by trapping of this silylene in a copyrolysis of **11** and 2,3-dimethyl-1,3-butadiene (500 °C, vertical N_2 flow, 13-fold excess butadiene) to produce the expected silacyclopentene **15** (95%) and reduce the yields of **12** and **13** to 4% and 0%, respectively. Further confirmation that isomer **12** arose from a bimolecular silylene process was obtained by the copyrolysis of allyl trimethylsilyl ether (**7**) and methoxypentamethyldisilane, an efficient generator of Me_2Si:,[2] to produce **12** in 51% yield. Thus, by extrapolation it seems very unlikely that disiloxane **8** arises from a simple rearrangement of **4**.
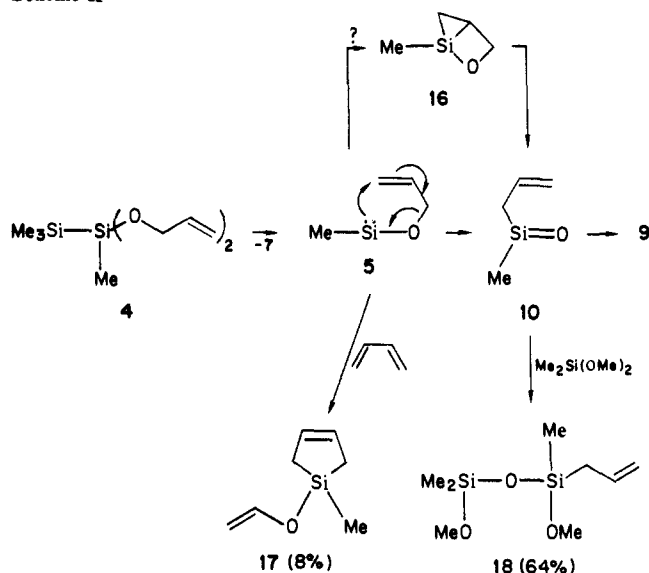
It is the formation of cyclotrisiloxane **9** which most strongly suggests the production of a silanone in the thermolysis of **4** since cyclic oligomerization of silanones is inevitably observed when silanones are produced in either solution or gas phase, and this process has recently been calculated to proceed without barriers.[5]

The most economical pathway to the silanone, **10**, required for the formation of cyclotrisiloxane **9** would simply involve a [2,3] sigmatropic allyl migration in initially formed (allyloxy)-methylsilylene **5** as shown in Scheme II. However, one cannot rule out the possibility that this process is not concerted but proceeds through the intermediacy of oxasilabicyclo[2.1.0]pentane (**16**). Evidence for the intermediacy of silylene **5** was obtained by pyrolysis of **4** at 510 °C in a flow system employing 1,3-butadiene as the carrier gas. Only marginal trapping of **5** to produce silacyclopentene **17** (8%) was achieved even under such extreme conditions of stoichiometric imbalance, which is, of course, consistent with competitive consumption of **5** via rearrangement to silanone **10**. In contrast, the copyrolysis of **4** and $Me_2Si(OMe)_2$, a frequently employed silanone trap, afforded in 64% yield the disiloxane, **18**, expected from insertion of silanone **10** into an Si–O bond. Thus, it appears that the isomerization of **5** to **10** represents the first example of a silylene-to-silanone rearrangement and joins an ever-increasing list of interconversions of organosilicon reactive intermediates.

The rearrangment of silanone, $H_2Si{=}O$, to hydroxysilylene, HSiOH, via 1,2-hydrogen migration has been the subject of a recent theoretical investigation. Kudo and Nagase[6] found that although the reaction was slightly exothermic (2.4 kcal/mol), the barrier was greater than 60 kcal/mol. Thus, it appears that the allyloxy substituent on silylene **5** provides a lower energy pathway for the silylene-to-silanone rearrangement, and it will be of considerable interest to directly generate silanone **10** and search for evidence of equilibration with **5**. Another method of lowering the barrier for the silanone → silylene isomerization which has been recently investigated by us involved making the isomerization more thermodynamically favorable by using a trimethylsilyl group as the migrating moity.[7] Thus, in the transformation **19** → **20**, a relatively weak Si–Si bond is broken and a strong Si–O bond is formed. Although the results of that study were ambiguous, consistent with but not demanding the isomerization of **19** → **20**, we nevertheless decided to attempt to incorporate this rear-

rangement into a sequence initiated by the production of the desired silanone via isomerization of an (allyloxy)silylene. Thus, we hoped to use a single precursor to provide both a silylene-to-

(3) The spectral data for this product do not allow distinction from the equally likely isomer, $Me_3SiSi(Me_2)OSi(Me_2)C_3H_5$, resulting from silylene insertion into the other Si–O bond.

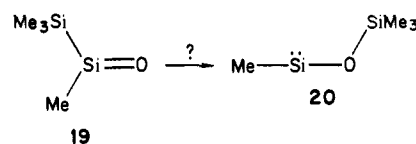(4) Ishikawa, M.; Katayama, S.; Kumada, M. *J. Organomet. Chem.* **1983**, *248*, 251.

(5) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(6) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.

(7) Barton, T. J.; Hussmann, G. P. *J. Am. Chem. Soc.*, in press.

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Scheme III

$(Me_3Si)_2Si\left(O\diagup\diagdown\diagdown\right)_2$ →(FVP, 545 °C, -7 (81%))→ $\diagup\diagdown\diagdown SiMe_3$ + $SiMe_3$

21   26 (23%)   27 (23%)

↓ -7   +

$Me_3Si—Si—O\diagup\diagdown$

22

$H—Si$

$OSiMe_3$

25 (4.1%)

↓ b

$Si=O$ / Me_3Si

23

→ a → $Si—OSiMe_3$

24

Scheme IV

21 →(-7)→ $Me_3Si—Si—O$

22

$Si-O$?

28

/ 1,2-SiMe₃

$Si=O$ + $Me_3Si\diagup\diagdown$ ←(1,2-Si)— $Si—O / H / SiMe_3$ —(1,2-H)→ $Si=O$ + $SiMe_3$

26   29   27

$Me_3Si—Si$ —(1,2-Si, Ref. 9)→ $Si / SiMe_3$

30   31

$Me_3Si, Si-O$

28   ? → $Si—OSiMe_3$

24
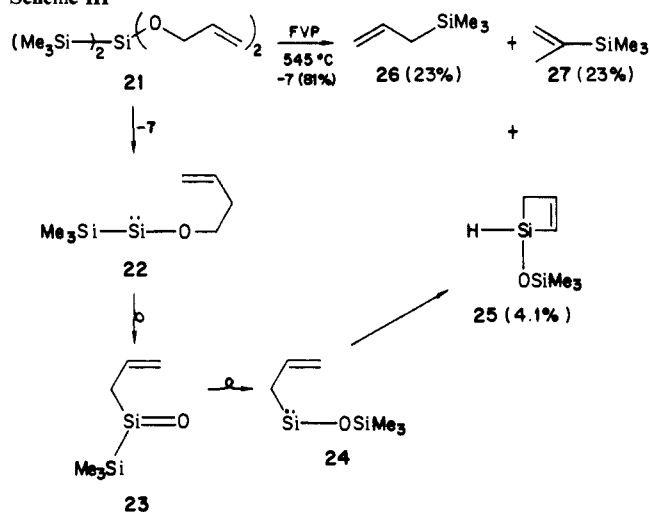
silanone rearrangement and a silanone-to-silylene isomerization. The chosen precursor was 2,2-bis(allyloxy)hexamethyltrisilane (21) for which it was planned that thermolysis would via reductive elimination produce (allyloxy)(trimethylsilyl)silylene (22), which would isomerize to allyl(trimethylsilyl)silanone (23), which in turn would rearrange to allylsilylene 24 (Scheme III). It was anticipated that the sequence would be terminated by cyclization of 24 since we had earlier demonstrated[8] that allylsilylenes afford the silacyclobutene ring. Indeed, FVP (545 °C) of 21 did apparently follow this torturous path to form the desired silacyclobutene 25, albeit in only 4.1% yield. The formation of silacyclobutene 25 in the FVP of 21 can be taken as prima facie evidence for a unique silylene-to-silanone-to-silylene isomerization which has a counterpart in our earlier demonstration[9] of a silylene-to-silene-to-silylene rearrangement sequence and further demonstrates the complexity of high-temperature organosilicon chemistry.

The relatively low yield of silacyclobutene 25 is certainly not surprising in view of the variety of reactive intermediates which must be sequentially formed on the route to 25; what is surprising is the considerable production of allylsilane 26 and isopropenylsilane 27. The most difficult product of this isomeric pair to mechanistically rationalize is 27. We offer here (Scheme IV) a tentative suggestion whose major merit perhaps rests in its economy since it provides a route to both 26 and 27, as well as silanone 23, from a single intermediate, oxasilabicyclo[2.1.0]-pentane 28, which can be formed from intramolecular π-addition of silylene 22. The transannular 1,2-migration of Me₃Si to isomerize 28 to 29 has precedent in the proposal[9] that the analogous 1-(trimethylsilyl)-1-silabicyclo[1.1.0]butane (30) undergoes a similar 1,2-silyl shift to produce silylene 31, which was trapped in good yield. Thermal extrusion of SiO from silylene 29 can occur either with migration of Me₃Si or H to afford 26 or 27, respectively. Unfortunately, consideration of bicyclopentane 28 as an intermediate reveals the possibility of proceeding directly to silylene 24, without involvement of silanone 23, by rearrangement of 28 as shown in Scheme IV. Thus, we are unable to confidently claim the silylene → silanone → silylene orchestrated sequence of rearrangements. Future efforts will include direct generation of silylene 29 and related species in a continuing program designed to further reveal the increasingly complex and fascinating thermochemistry of organosilicon reactive intermediates.

Experimental Section

Routine 60-MHz proton NMR spectra were recorded on either a Varian EM-360 or a Varian EM-360L. High-resolution proton NMR
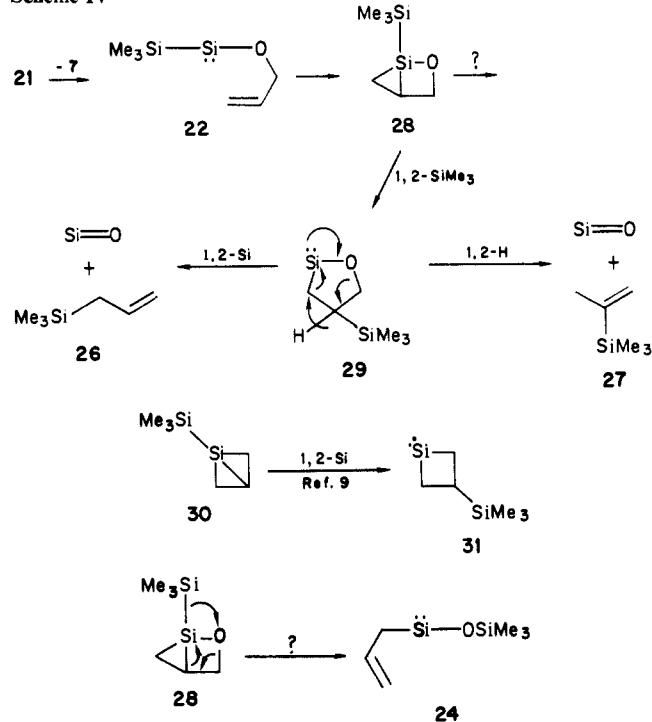
spectra and decoupling results were obtained on a Nicolet Model 1280 300-MHz spectrometer. Either the Nicolet or a JOEL Model FX90Q 90 MHz spectrometer was used for recording ^{13}C NMR spectra. IR spectra were recorded on an IBM IR 90 Series FTIR spectrometer. Preparative GC was done on either a Varian-Aerograph Series 1700 or a Varian-Aerograph Model 920. Gas chromatographic/mass spectra (GCMS) were obtained on a Finnegan Model 4023 mass spectrometer. Mass spectra (MS) are reported as m/e (% relative intensity). FVP pressures are measured behind a liquid N_2 trap and thus do not accurately reflect pressures in the reaction zone. Product yields were performed with internal standards on either a Varian-Aerograph Series 1700 or a Hewlett-Packard Model 5790A Series gas chromatograph. Exact mass measurements were obtained on an AEI MS-902 spectrometer. Combustion analyses were performed by MicAnal, Tucson, AZ.

(Allyloxy)trimethylsilane (7). The method of Ghose[10] was used to synthesize 7 in 85% yield after distillation (90–95 °C).

1,1-Bis(allyloxy)tetramethyldisilane (4). To a stirred solution of allyl alcohol (6.21 g, 0.107 mol) in 250 mL of dry degassed Et_2O at 0 °C was added 46.5 mL of 2.3 M n-BuLi in hexane. After 20 min, 1,1-dichlorotetramethyldisilane[11] (9.78 g, 0.052 mol) was added via syringe over 1 h. The mixture was allowed to warm to room temperature and then stirred for 5 h. Hexane (500 mL) was added and the mixture was cooled to 0 °C. After removal of salts by Celite filtration, the filtrate was concentrated by rotary evaporation. Distillation of the residue at 101.5 °C (.23 torr) yielded 6.45 g (53%) of 1,1-bis(allyloxy)tetramethyldisilane: ^1H NMR (CDCl₃) δ 0.14 (s, 9 H), 0.19 (s, 3 H), 4.24 (d of d of d of d, J_{ab} = 4.8 Hz, $J_{ad} \approx J_{ac}$ = 1.8 Hz, 2 H), 5.09 (d of d of t, J_{bd} = 10.5 Hz, $J_{ad} \approx J_{cd}$ = 1.8 Hz, 1 H), 5.27 (d of d of t, J_{bc} = 17.1 Hz, $J_{cd} \approx J_{ad}$ = 1.8 Hz, 1 H), 5.93 (d of d of t, J_{bc} = 17.1 Hz, J_{bd} = 10.5 Hz, J_{ab} = 4.8 Hz, 1 H); ^{13}C NMR (C_6D_6) δ -1.69, -1.65, 63.91, 114.02, 137.61; MS 215 (0.1), 189 (6), 173 (0.7), 133 (100), 117 (11), 101 (31), 73 (5), 59 (15); calcd for $C_7H_{17}O_2Si_2$, m/e 189.07671, found 189.07721. Anal. Calcd for $C_{10}H_{22}O_2Si_2$: C, 52.11; H, 9.62. Found: C, 52.14; H, 9.88.

Flash Vacuum Pyrolysis (FVP) of 4. Neat 4 was distilled (39 °C, 10^{-5} torr) through a horizontal quartz-chip-packed tube at 700 °C with an 80.8% mass recovery. The three major products were isolated by preparative GC (11 ft, 12% OV-101 Chromosorb W column, temperature programmed from 140 °C at 4°/min). The first product collected was (allyloxy)trimethylsilane (7, 74%). The second compound was identified as 1-allyl-1-(allyloxy)-1,3,3,3-tetramethyldisiloxane (8, 13%); ^1H NMR (CDCl₃) δ 0.09 (s, 3 H), 0.10 (s, 9 H), 1.58 (apparent d, 2 H, J = 6.91 Hz), 4.89 (apparent d of t, 2 H, J = 4.87, 1.68 Hz), 4.95–4.86 (m, 2 H), 5.09 (apparent d of q, 1 H, J = 10.31, 1.58), 5.26 (apparent d of q, 1 H, J = 17.18 Hz), 5.98–5.71 (2 overlapping m, 2 H); ^{13}C NMR (CDCl₃) δ -2.84, 1.87, 23.92, 63.46, 114.17, 114.60, 133.62, 137.09; MS 230 (M⁺, 0.2), 215 (1), 189 (36), 173 (2), 133 (100), 119 (11), 73 (15), 59 (9); calcd for $C_{10}H_{22}O_2Si_2$, m/e 230.11584, found 230.11517. Anal. Calcd

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(10) Ghose, B. N. *J. Organomet. Chem.* **1979**, *169*, 11.

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Silylene-to-Silanone Thermal Isomerization

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for $C_{10}H_{22}O_2Si_2$: C, 52.11; H, 9.62. Found: C, 51.11; H, 9.85. The third product was identified as 2,4,6-trimethyl-2,4,6-triallylcyclotrisiloxane (**9**, 13%): ^{1}H NMR (CDCl$_3$) δ 0.17 (s, 3 H), 1.62 (m, 2 H), 4.94 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ −0.96, 25.09, 114.61, 132.72; MS 300 (0.1), 259 (14), 243 (1), 231 (13), 217 (100); calcd for $C_9H_{19}O_3Si_3$ (M − C_3H_5), m/e 259.06431, found 259.06503. Anal. Calcd for $C_{12}H_{24}O_3Si_3$: C, 47.95; H, 8.04. Found: C, 47.87; H, 8.20.

Copyrolysis of 4 with 1,3-Butadiene. A flow pyrolysis using 1,3-butadiene as the carrier gas was conducted with 0.6452 g (0.0028 mol) of **1** through an 18-cm quartz-chip-packed tube with a flow rate of 60 mL/min at 510 °C. In addition to **7**, vinylcyclohexene and high molecular weight products from butadiene, and unreacted **4** (6%), the products were **8** (12%) and the trapping product, 1-methyl-1-(allyloxy)-1-silacyclopent-3-ene (**17**, 8%): ^{1}H NMR (CDCl$_3$) δ 0.33 (s, 3 H), 1.19 (d, 2 H, J = 17.63 Hz), 1.42 (d, 2 H, J = 17.63 Hz), 4.14 (apparent d of t, 2 H, J = 4.91, ∼1.5 Hz), 5.10 (d of apparent q, 1 H, J = 10.4, 5 Hz), 5.21 (d of apparent q, 1 H, J = 17.10 Hz), 5.96–5.86 (m, 3 H); ^{13}C NMR δ −2.41, 16.23, 64.39, 114.86, 130.63, 136.82; MS 154 (6), 139 (5), 126 (8), 113 (24), 99 (100), 85 (77). Anal. Calcd for $C_8H_{14}SiO$: C, 62.28; H, 9.15. Found: C, 62.38; H, 9.36.

Copyrolysis of 4 with Dimethyldimethoxysilane. A flow pyrolysis of 0.3013 g (0.0013 mol) of **4** mixed with 1.2887 g (0.0107 mol) of Me$_2$Si(OMe)$_2$ was conducted at 500 °C (30 mL/min N$_2$ flow) through a vertical quartz-chip-packed tube with an 86% mass recovery. Besides (allyloxy)trimethylsilane (**7**) and unreacted **4** (32%), 1,2,2-trimethyl-1,2-dimethoxy-1-allyldisiloxane (**18**) was obtained in 64% yield: ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.10 (s, 9 H), 1.58 (apparent d, J ∼ 8 Hz), 3.46, 3.47 (together 6 H), 5.10–4.65 (m, 2 H), 6.15–5.42 (apparent sextet, 1 H, J ∼ 10 Hz); ^{13}C NMR (C$_6$D$_6$ δ −3.67, −1.67, 23.35, 49.41, 49.68, 114.26, 133.43; MS 205 (M − Me, 11), 189 (M − MeO, 1), 179 (M − C$_3$H$_5$, 79), 149 (100), 133 (58), 119 (48), 73 (35), 59 (49); calcd for $C_7H_{17}O_3Si_2$ (M$^+$ − CH$_3$), m/e 205.07163, found 205.07099. Anal. Calcd for $C_8H_{20}O_3Si_2$: C, 43.59; H, 9.15. Found: C, 43.75; H, 9.43.

Copyrolysis of (Allyloxy)trimethylsilane (7) with Me$_2$Si(OMe)$_2$. A flow pyrolysis was performed on a mixture of **7** (0.1766 g, 0.0014 mol) and dimethyldimethoxysilane (1.46 g, 0.0122 mol) through an 18-cm quartz-chip-packed vertical tube under a 30 mL/min nitrogen flow at 500 °C with 91% mass recovery. GCMS was used to ascertain that products from the copyrolysis of **4** and Me$_2$Si(OMe)$_2$ were not due to secondary reactions between **7** and Me$_2$Si(OMe)$_2$. No evidence for formation of **4**, isomers of **4**, 2,4,6-trimethyl-2,4,6-tri(2-propenyl)cyclotrisiloxane (**9**), or 1,2,2-trimethyl-1,2-dimethoxy-1-allyldisiloxane (**18**) was found under these conditions. Isolation and characterization of the redistribution products formed was not done due to the abundance of minor products obtained. Of the four major products, only two could be identified with reasonable certainty on the basis of GCMS alone: Me$_3$SiOMe, 104 (6), 89 (100), 73 (10), 59 (84); and Me$_2$Si(OMe)OCH$_2$CH:CH$_2$, 146 (2.4), 131 (100), 117 (38), 101 (70), 89 (48), 75 (21), 59 (21).

1-(Allyloxy)pentamethyldisilane (11). The method of Hosomi[12] was used to synthesize **11**. The lithium alkoxide of allyl alcohol was prepared under N$_2$ by addition of 15 mL (31 mmol) of 2.1 M n-BuLi to a stirred solution of 1.9 g (33 mmol) of allyl alcohol in 100 mL of Et$_2$O at −78 °C. Next 5.0 g (30 mmol) of 1-chloropentamethyldisilane[11] was added dropwise, and the mixture was warmed to 25 °C and distilled (25 °C, 0.05 torr) into a flask cooled to −78 °C. After solvent removal (rotovac), distillation (146–155 °C) afforded 4.3 g (76%) of **11**:[12] ^{1}H NMR (DCCl$_3$) δ 0.07 (s, 9 H), 0.17 (s, 6 H), 4.00–4.18 (m, 2 H), 5.53–6.17 (m, 1 H); ^{13}C NMR (DCCl$_3$) δ −2.03, −0.73, 64.69, 114.33 137.4; IR (neat) 1072 cm^{-1} (SiOC); MS 173 (M − Me, 1), 149 (8), 148 (15), 147 (M − allyl, 100), 133 (23), 131 (13), 117 (11), 115 (13), 85 (17), 73 (60), 59 (27).

FVP of 1-(Allyloxy)pentamethyldisilane (11). Disilane **11** (0.1832 g, 0.974 mmol) was slowly distilled at 25 °C (1 × 10^{-4} mmHg) through a quartz tube packed with quartz chips and heated to 760 °C with 77% mass recovery. By GC analysis, the pyrolysate showed three major products which were isolated by preparative GC on a 15-ft, 20% OV101 Chromosorb W column at 130 °C. They were identified as (allyloxy)-trimethylsilane (**7**, 30%),[10] 1-allylpentamethyldisiloxane (**12**, 13%),[13] and 1-(trimethylsiloxy)-2-allyl-1,1,2,2-tetramethyldisilane (**13**, 10%).[3] All spectral properties and GC retention time for **7** exactly matched that of an authentic sample. **12**: ^{1}H NMR (C$_3$D$_6$O) δ 0.14 (s, 15 H), 1.64 (d, 2 H, J = 8.0 Hz), 4.73–5.12 (m, 2 H), 5.54–6.33 (M, 1 H); ^{13}C NMR (C$_3$D$_6$O) δ 0.00, 2.01, 26.93, 113.61, 135.22; IR (neat) 1099 cm^{-1} (SiO-Si); MS 173 (M − 15, 9), 149 (8), 148 (15), 147 (100), 133 (12), 131 (7), 73 (24), 66 (11), 59 (12). **13**: ^{1}H NMR (C$_3$D$_6$O) 0.10 (s, 15 H),

0.20 (s, 6 H), 1.57 (d, 2 H, J = 8.0 Hz), 4.67–5.17 (m, 2 H), 5.45–6.23 (m, 1 H); ^{13}C NMR (C$_3$D$_6$O) δ −2.27, 0.22, 2.12, 27.04, 113.61, 135.22; IR (neat) 1066 cm^{-1} (SiOSi); MS 246 (1), 205 (12), 174 (14), 173 (82), 157 (7), 147 (23), 133 (38), 131 (13), 117 (15), 85 (7), 74 (8), 73 (100), 59 (26).

Copyrolysis of 11 and 2,3-Dimethylbutadiene. A solution of 0.1295 g (0.687 mmol) of **11** in a tenfold excess of 2,3-dimethylbutadiene was dripped into a vertical quartz tube packed with quartz chips and heated to 500 °C under a flow of N$_2$ (35 mL/min). The pyrolysate (86% mass recovery) was collected in a trap cooled to −78 °C. Analysis by GC revealed three products in addition to unreacted **11** (12%) and excess 2,3-dimethylbutadiene. The compounds were identified as 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (**15**, 95%),[14] **7** (87%), and 1-allyl-pentamethyldisiloxane (**12**, 4%) based on comparison of GCMS data and GC retention time with that of authentic samples of **7** and **15** and of **12** formed in the pyrolysis of **11**.

Copyrolysis of (Allyloxy)trimethylsilane (7) and 1-Methoxypentamethyldisilane. A solution of 0.185 g (1.43 mmol) of **7** and 0.241 g (1.49 mmol) of 1-methoxypentamethyldisilane, prepared in 92% yield by the method of Ghose,[10] was dripped into a quartz tube packed with quartz chips and heated to 500 °C. The tube was swept with N$_2$ at 35 mL/min, and the pyrolysate was collected in a trap cooled to −78 °C. GC analysis of the pyrolysate (82% mass recovery) revealed two new major products along with unreacted **7** (4%) and methoxydisilane (2%). The products were isolated by preparative GC on a 9-ft, 20% OV-101 Chromosorb W column and were identified as 1-allylpentamethyldisiloxane (**12**) (51%)[13] (spectra exactly matched that of **12** obtained from **11**) and trimethyl-methoxysilane (85%, matched with authentic sample).

2,2-Bis(allyloxy)hexamethyltrisilane (21). To a stirred solution containing triethylamine (2.68 g, 0.0265 mol), allyl alcohol (1.54 g, 0.027 mol), and 250 mL of dry Et$_2$O was added 2,2-dichloro-1,1,1,3,3,3-hexamethyltrisilane[15] (3.2471 g, 0.0133 mol) dropwise via syringe. After 24 h, 250 mL of Skellysolve "B" was added, and the resulting mixture was filtered through Celite and concentrated by rotary evaporation. The residue was distilled at 112–114.5 °C (9 torr) to yield 2.80 g (86%) of **21**. Further purification was accomplished by preparative GC (10 ft, 10% SE-30 Chromosorb Q-11 column at 170 °C, isothermal). ^{1}H NMR (CDCl$_3$) δ 0.15 (s, 18 H), 4.26 (apparent t, 4 H, J = 2.15 Hz), 5.09 (apparent d of d, 2 H, J = 10.52, 1.34 Hz), 5.28 (apparent d of d, 2 H, J = 15.45, 1.65 Hz), 5.81–5.87 (m, 2 H) ; ^{13}C NMR (C$_6$D$_6$) δ −0.94, 65.90, 113.92, 137.63; MS 247 (1.5), 191 (80), 133 (60), 117 (25), 73 (100); calcd for $C_9H_{23}O_2Si_3$ (M$^+$ − C$_3$H$_5$), m/e 247.10059, found 247.10122. Anal. Calcd for $C_{12}H_{28}O_2Si_3$: C, 49.94; H, 9.78. Found: C, 49.24; H, 9.73.

FVP of 21. 2,2-Bis(allyloxy)hexamethyltrisilane (**21**) (0.6740 g, 0.00234 mol) was distilled (545 °C, 8 × 10^{-5} torr) through a horizontal quartz-chip-packed tube with a mass recovery of 67%. Previous runs at 450 °C, 2 × 10^{-6} torr (no decomposition), 530 °C, 6 × 10^{-6} torr (60% conversion, uncorrected), and 620 °C, ∼10^{-4} torr (extensive decomposition), indicated this to be an optimum temperature. Along with minor amounts of higher molecular weight products, the four major products were isolated by preparative GC: **7** (81%), an equimolar mixture of allyltrimethylsilane (**26**, 23%), isopropenyltrimethylsilane (**27**, 23%), and 1-(trimethylsiloxy)-1-silacyclobut-2-ene (**25**, 4.1%). The first three compounds were identified by spectral comparison with authentic samples. Silacyclobutene **25** was characterized as follows: ^{1}H NMR (C$_6$D$_6$) δ 0.10 (s, 9 H), 1.72 (d of d of d, 2 H, J$_{AA'}$ = 16.7 Hz, J$_{A'C}$ = 1.54 Hz, J$_{AD}$ = 1.95 Hz, J$_{A'D}$ = 1.77 Hz), 5.49 (d, 1 H, J$_{BD}$ = 5.9 Hz), 6.24 (d of d, 1 H$_C$, J$_{A'C}$ = 1.54, J$_{CD}$ = 7.2 Hz), 7.04 (d of d of d of d, 1 H$_D$, J$_{A'D}$ = 1.77 Hz, J$_{AD}$ = 1.95 Hz, J$_{BD}$ = 5.9 Hz, J$_{CD}$ = 7.2 Hz); ^{13}C NMR (C$_6$D$_6$) δ 1.56, 25.48, 143.09, 151.60; IR (neat) 2141 cm^{-1} (Si–H), 1072 cm^{-1} (SiOSi); MS 158 (0.7), 157 (3), 143 (100), 117 (19), 99 (29), 73 (33), 59 (25); calcd for $C_6H_{13}OSi_2$, m/e 157.0505, found 157.0493.
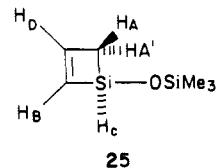
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Copyrolysis of 21 with Me$_2$Si(OMe)$_2$. A mixture of **21** (0.2568 g, 8.917 × 10^{-4} mol) and Me$_2$Si(OMe)$_2$ (1.3488 g, 12-fold molar excess) was pyrolyzed through a vertical quartz-chip-packed tube at 510 °C (N$_2$ flow rate 30 mL/min) with a mass recovery of 84%. Besides **21**, a small amount (<3% uncorrected) of a compound m/e 278 (M$^+$?) correspond-

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ing to trapped silylene (**22, 24**) or silanone (**23**) was found. An even smaller amount of **7** (<2%) was identified by GCMS. When compared with the results of copyrolysis of **7** with excess dimethyldimethoxysilane (vide supra) under the same conditions, many of the numerous unidentified compounds formed can be attributed to redistribution reactions. No attempt was made to isolate the presumed trapping product or to provide positive identification of the redistribution products.

Copyrolysis of 21 with 1,3-Butadiene. Trisilane **21** (0.3448 g, 1.2 × 10⁻³ mol) was pyrolyzed in a vertical flow system with 1,3-butadiene as the carrier gas. At 510 °C (35 mL/min butadiene flow rate), a mass recovery (after evaporation of volatiles) of 46% was obtained. No compound of *m/e* 212 (corresponding to silylene trapping product) was found by GCMS.

Communications to the Editor

EXAFS of *Klebsiella pneumoniae* Nitrogenase MoFe Protein from Wild-Type and *nif V* Mutant Strains

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The enzyme nitrogenase catalyzes the biological reduction of N₂ to NH₃.[1] In *Klebsiella pneumoniae* a cluster of 17 genes in seven transcriptional units has been associated with nitrogen fixation.[2] The nitrogenase enzyme from the *nif V* mutants is relatively ineffective at dinitrogen reduction, is more efficient than the wild-type enzyme at HCN reduction,[3] and has its hydrogen evolution activity inhibited up to 80% by CO.[4,5] This altered substrate specificity has been shown to be associated with the iron–molybdenum cofactor, "FeMo-co", of the enzyme.[6] X-ray absorption spectroscopy has been a valuable tool for probing the molybdenum environment of wild-type nitrogenase,[7-11] and we

report here similar studies on the Nif V⁻ enzyme.[12,13]

The Mo K absorption edge regions for wild-type and Nif V⁻ MoFe proteins are nearly identical. In both cases the first inflection point occurs at 20010.9 (5) eV, and the overall edge shape is the same within experimental error.[14] The extreme similarity in edge position and shape suggests that the Mo exists in the same oxidation state in both cases. On the basis of previous work with Mo,Fe,S cluster model compounds,[20] the edges also indicate that the number of sulfur donor ligands to molybdenum is four or five and most likely the same in both cases.

The EXAFS Fourier transforms of Nif V⁻ and wild-type Kp1 at 4 K are compared in Figure 1. Two strong peaks corresponding to Mo–S and Mo–Fe interactions are observed. These features are stronger and better resolved than in previously reported spectra because of the lower temperature and wide k range. Quantitation of these spectra[7-11] involved curve-fitting analysis,[21,24] the results

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(12) Large-scale cultures of the wild-type *Klebsiella pneumoniae* strain M5al¹⁵ and the *nif V* mutant strain UNF1613⁴ were grown and harvested as previously described. The MoFe proteins from both strains were purified and assayed for activity and Mo content by the methods described for the wild-type Kp1.¹⁵,¹⁶ The EXAFS spectra of three different preparations of each protein were measured. The Kp1 samples had specific activities between 1600 and 1750 units/mg (1 unit of activity – 1 nmol of C₂H₂ reduced/min) and activities/Mo between 255 and 315 units/mol of Mo. The Nif V⁻ Kp1 samples had specific activities between 1180 and 1550 units/mg and activities/Mo between 222 and 283 units/nmol of Mo. The oxidation state of the sample correspond to the EPR-active *S* = ³/₂ state.

(13) The X-ray absorption spectra were recorded on beam line VII-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) during dedicated conditions (3.0 GeV and ∼50 mA) by using Si(220) monochromator crystals. The protein data were measured in the fluorescence detection mode by using an array of sodium iodide scintillation detectors and zirconium filters.¹⁷ Measurements at 4 and 100 K were made by using a continuous He flow Oxford Instruments cryostate (CF 1204) with aluminized Mylar windows. The spectra were calibrated, processed, and fit by using previously described procedures.⁹,¹⁸,¹⁹

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(21) The curve-fitting procedure²² used empirical phase-shift and amplitude functions¹⁸ for all Mo–X interactions except for the Mo–Fe amplitude function. This was better fit by using the theoretical Fe amplitude²³ and a scale factor of 0.345.