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Kinetic Studies on the Thermal Decomposition of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane and the Mechanism of Silylene Generation

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trans-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) has been prepared in 98% yield by the treatment of $(^t\mathrm{Bu}_3\mathrm{Si})(^i\mathrm{Pr}_3\mathrm{Si})\mathrm{SiBr}_2$ with activated magnesium in the presence of *trans*-2-butene. Trapping studies suggested that silylene $(^t\mathrm{Bu}_3\mathrm{Si})(^i\mathrm{Pr}_3\mathrm{Si})\mathrm{Si}$: (**2**) was extruded by thermolysis of **1**. Without added trapping agents self-trapping of silylene **2** formed a stable product, 1,1-di-*tert*-butyl-4,4-dimethyl-2-triisopropylsilyl-1,2-disiletane (**5**), by intramolecular C−H insertion. Thermolysis of **1** presented an ideal reaction for a kinetic study of the thermal decomposition of a silirane. It was found that thermal decomposition of **1** is stereospecific and first-order in benzene solution. From the rates of reaction at various temperatures activation parameters were obtained. The results were consistent with a non-least motion pathway for silylene retroaddition and hence addition.

The thermally induced extrusion of silylenes from siliranes was discovered by Seyferth in 1975[1] and has often been used for thermal generation of silylenes ever since.[2] Both a concerted mechanism for silylene extrusion, the reverse of single-step singlet state silylene addition to a C═C bond, and a stepwise process proceeding via a diradical formed by Si−C homolysis were initially considered for the pyrolysis of siliranes.[1,3] Seyferth et al. found, in 1982, that transfer of $\mathrm{Me_2Si}$ from hexamethylsilirane to olefins generating new siliranes was stereospecific.[4] Boudjouk et al. found stereospecific extrusion of di-*tert*-butylsilylene from diastereomeric siliranes.[5] In 1991, experimental results from the Gaspar group showed that the decomposition of *cis*- and *trans*-2,3-dimethyl-1,1-diadamantylsilirane to the corresponding 2-butene was stereospecific, as was the transfer to diastereomeric olefins of the diadamantylsilylene unit $\mathrm{Ad_2Si}$.[6] Stereospecific transfer of silylene units upon photolysis of their non-silirane precursors had been established by Jones et al.[7,8] and by Kumada, Ishikawa et al.[9] for $\mathrm{Me_2Si}$,[7,8] $\mathrm{Ph_2Si}$,[8] and PhMeSi.[9]

The stereospecificity of silylene transfer from siliranes and to olefins was interpreted in terms of a concerted mechanism: single-step thermal extrusion of free silylenes as the inverse of single-step addition of free silylenes to olefins.

Despite initial doubts regarding the formation of free silylenes upon the pyrolysis of siliranes and photolysis of oligosilanes,[10] clear evidence for the intermediacy of free silylenes has accumulated over the years.[2] This can be summarized as being comprised of the clear indication of a common reactive intermediate from quite different plausible precursors of the same silylene and the direct detection of several silylenes by electronic spectroscopy upon the photolysis of a variety of oligosilanes.[2,8]

The case for concerted addition and retroaddition reactions of silylenes is more tenuous. Scheme 1 compares concerted and stepwise silylene addition and retroaddition mechanisms.

The general acceptance of the concerted addition (k_{add})−retroaddition (k_{ex}) pathway rests largely on the observed stereospecificity of the addition and retroaddition reactions. This lends support to a concerted process when interpreted via the “Skell rule” of carbene chemistry.[11] An important part of this notion is that singlet carbenes, and by extension their heavier analogues, are expected to add to olefins in a single step and therefore preserve *cis*−*trans* stereochemistry. Since triplet carbenes (and their analogues) cannot give a singlet ground state cyclopropane in a single fast step, two-step addition must occur, and rotation about single bonds in the diradical intermediate should be rapid compared to intersystem crossing followed by ring closure. Hence non-stereospecific addition by triplet carbenes (and their analogues) was to be expected.

As early as 1964 it was pointed out that singlet carbenes might undergo stepwise addition to olefins, which might or might not be stereospecific, depending on the relative rates of rotation and ring closure.[12]

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[1] Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 7162.

[2] (a) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, pp 335−385. (b) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, pp 333−427. (c) Gaspar, P. P.; West, R. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp 2463−2568.

[3] Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *117*, C51.

[4] Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

[5] Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

[6] Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

[7] Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1425.

[8] Tortorelli, V. J.; Jones, M., Jr.; Wu, S.-H.; Li, Z.-H. *Organometallics* **1983**, *2*, 759.

[9] Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* **1979**, *178*, 105.

[10] Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, pp 229−277.

[11] Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.

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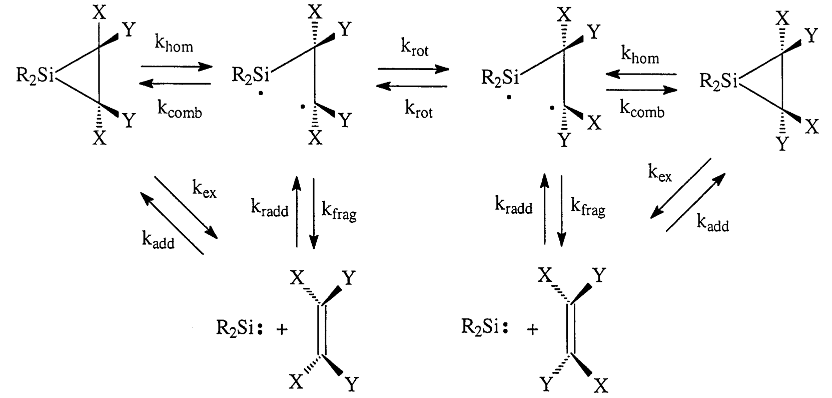
Publication on Web 04/22/2003

Scheme 1. Concerted and Stepwise Silylene Addition and Retroaddition Mechanisms



Indeed, DeMore and Benson argued in the same year that all addition reactions of CH_2 proceeded via diradical intermediates, and the stereochemical outcome depended on the relative rates of ring closure and rotation.[13] In 1964 it appeared that rotation in a biradical intermediate (k_{rot}) in Scheme 1 could not be slow enough to allow stereospecific cyclopropane formation, and thus stereospecific addition appeared to demand a concerted process.[12a] But it was subsequently suggested that the presence of a silyl substituent β to a radical center in a β-silylethyl radical causes an increase of ca. 1 kcal/mol in the barrier height for rotation around the $C_\alpha-C_\beta$ bond.[14] Both hyperconjugation and p−d homoconjugation were believed to contribute to the increase in barrier height. Thus a reduction in the rate of interconversion of diastereomeric intermediates in stepwise additions could lead to a breakdown of the Skell rule for carbene analogues below the first row of the periodic table.[15] It is worth noting in this context that the only published failure of the Skell rule involves a heavy atom: both ^1D and ^3P sulfur atoms add sterospecifically to *cis*-2-butene.[16]

Even for the concerted addition−retroaddition pathway, questions have been raised about the structure of the transition state. In 1963 Moore suggested that concerted addition to an olefin by a singlet carbene implied a maximization of what we now call frontier orbital interactions, half of which are shown for a silylene in Scheme 2.[17] By 1968 it was recognized that a least motion pathway for singlet carbene addition is forbidden by symmetry, and a non-least motion pathway was predicted by Hoffmann in 1968 on the basis of extended Hückel calculations.[18] Hoffmann's calculations predicted a significant barrier for least motion addition but none for the non-least motion pathway.

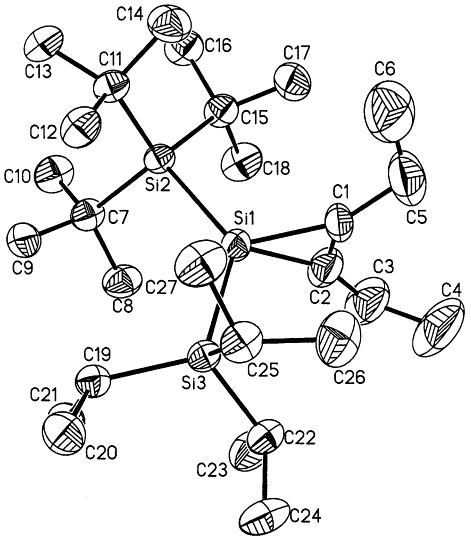


Figure 1. X-ray diffraction structure (ORTEP) for 2,3-diethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirene (**3**).

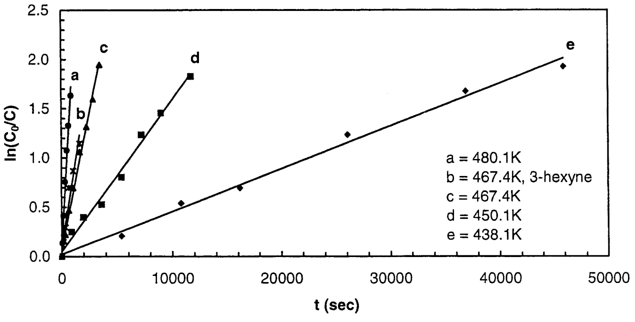


Figure 2. First-order kinetic plots for the thermolysis of **1**.

In the language of frontier molecular orbital theory, which has had widespread success in rationalizing and predicting reaction pathways,[19] the optimum transition state structure maximizes bonding in the transition state by maximizing HOMO−LUMO interactions.

Addition of a singlet silylene to an olefin is predicted by frontier orbital theory to follow a non-least motion pathway as shown in Scheme 2.

Maximization of bonding in a transition state is an enthalpic effect, but transition states are defined by free

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[12] (a) Gaspar, P. P.; Hammond, G. S. In *Carbene Chemistry*, 1st ed.; Kirmse, W., Ed.; Academic Press: New York, 1964; pp 235−274. (b) Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, pp 207−362.

[13] DeMore, W. B.; Benson, S. W. *Adv. Photochem.* **1964**, *2*, 219.

[14] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. Kawamura, T.; Meakin, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 8065.

[15] Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Winchester, W. R.; Braddock-Wilking, J.; Rath, N. P.; Klooster, W. T.; Koetzle, T. F.; Mason, S. A.; Albinati, A. *Organometallics* **1999**, *18*, 3921.

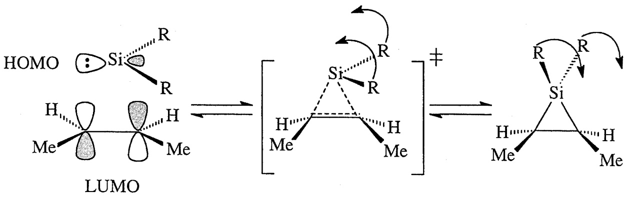
[16] Gunning, H. E.; Strausz, O. P. *Adv. Photochem.* **1966**, *4*, 143. Strausz, O. P. In *Organosulfur Chemistry*; Janssen, M. J., Ed.; Wiley: New York, 1967; p 11.

[17] Moore, W. R.; Moser, W. R.; Laprade, J. E. *J. Org. Chem.* **1963**, *28*, 2200. See also: Jersosch Herold, B.; Gaspar, P. P. *Fortschr. Chem. Forsch.* **1965**, *5*, 89.

[18] Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

[19] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

Scheme 2. Frontier Orbital Interactions for Silylene Addition and Retroaddition Reactions

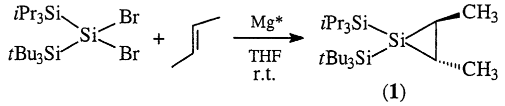


energy barriers, and the activation barriers for highly reactive species such as carbenes and silylenes are very small, and indeed are often observed to be *negative*.[20] Very little bonding has occurred when the transition state for an addition reaction is reached. Houk has proposed entropic control of the free energy barrier for carbene addition reactions.[21] Entropic rather than enthalpic control of addition rates might lead to the failure of the maximization of bonding as a predictive model for transition state structure.[22]

The non-least motion transition states predicted by the FO model and supported by calculations of minimum energy pathways for addition reactions of the "carbene family",[23] should lead to a lower entropy of activation than a least-motion transition state for both the forward and reverse reactions. This is the expected result of the "extra" steric interactions between substituents on the olefin and those on the electron-deficient species that are not present in the adduct or in the free reagents. Qualitative data support a non-least motion pathway: increasing the steric congestion on the silirane ring of 1,1-diadamantylsiliranes was found to decrease the rate of silirane thermolysis, as expected for a non-least motion mechanism.[6]

It was hoped that a kinetic study of the thermal decomposition of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) would shed light on the structure of the transition state and thus indirectly on the question whether frontier orbital theory predictions of the pathways of reactions with very low energy barriers are to be relied upon.

Synthesis of the starting silirane was straightforward, as depicted in eq 1. By the use of activated magnesium, *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) was prepared in 98% yield. A silylenoid pathway was probably involved. Silirane **1** was fairly stable to air and moisture at room temperature; there was no decomposition observed when it was open to air for several weeks.[24]



(**1**)

(1)

The results shown in Scheme 3 indicate that silylene (^{t}Bu$_3$Si)(^{i}Pr$_3$Si)Si: (**2**) is generated upon the thermal decomposition of silirane **1**. When 0.1 M **1** in dry benzene-d_6 was thermolyzed at 220 °C in the presence of excess 3-hexyne, silirene **3** was formed in 87% yield. An X-ray diffraction structure for **3** is shown in Figure 1, and selected bond lengths and bond angles are given in Table 1. When 2,3-dimethyl-1,3-butadiene was used as the trapping agent, **4** was formed in 43% yield. In the absence of added trapping agent, pyrolysis of the precursor **1** in benzene solution (0.1 M) gave rise to the intramolecular C−H insertion product **5** as the major product: 194 °C/1 h, 62% yield; 207 °C/20 min, 73% yield. The formation of *trans*-butene as the coproduct (39%, 194 °C/1 h; 49%, 207 °C/20 min) pointed to the stereospecificity of the decomposition reaction.

Table 1. Selected Geometric Parameters for 2,3-Diethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirene (3)

r(Si1−Si2)	2.4088(8) Å	∠Si2−Si1−Si3	131.30(3)°
r(Si1−Si3)	2.3941(9) Å	∠C1−Si1−C2	39.9(2)°
r(Si1−C1)	1.848(4) Å	∠C1−C2−Si1	68.3(3)°
r(Si1−C2)	1.888(4) Å	∠C2−C1−Si1	71.7(3)°
r(C1−C2)	1.276(8) Å		

Table 2. First-Order Rate Constants for the Pyrolysis of Silirane (1) in Benzene-d_6

temperature	$k_1 \times 10^5$ (s^{-1})
438.1 K (165.0 °C)	4.33 ± 0.16
450.1 K (177.0 °C)	15.4 ± 0.6
467.4 K (194.3 °C)	54.8 ± 1.4
467.4 K (194.3 °C) with 3-hexyne	67.9 ± 0.8
480.1 K (207.0 °C)	185 ± 8

The thermal decomposition of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilyl silirane (**1**) to silylene (^{i}Pr$_3$Si)(^{t}Bu$_3$Si)Si: (**2**) offers an excellent reaction for kinetic study. No added trapping agents need be employed, because silylene (^{i}Pr$_3$Si)(^{t}Bu$_3$Si)Si: (**2**), upon generation from silirane **1**, can be self-trapped by intramolecular insertion into a C−H bond of a *tert*-butyl group to form thermally stable product **5** in high yield. Complications from induced decomposition of the silirane were expected to be minimized by the steric shielding afforded to the silirane by the bulky trialkylsilyl groups. Nevertheless a control reaction (vide infra) was carried out to demonstrate that silirane **1** was not being lost via attack by silylene **2**. Silirane **1** is fairly stable to air and moisture and thus easy to handle compared with less sterically encumbered siliranes. Also the ^{1}H NMR signal for one of the ring methyl groups of silirane **1** is sufficiently isolated for accurate integration in kinetic experiments.

Kinetic experiments were performed in sealed tubes (3 mm o.d., 1.5 mm i.d.) thermostated in vapor baths employing pure solvents. Concentrations were determined from integral ratios in ^{1}H NMR spectra. The kinetic samples were immersed in a standard solution of the reference compound contained in a standard NMR sample tube. Rate constants were taken from the slopes of first-order kinetic plots (Figure 2). The standard deviations of the slopes are reported as the probable error for each rate constant in Table 2.

An absence of induced decomposition is indicated by the small change in the first-order rate constant at 194.4

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[20] Jasinnski, J. M.; Bacerra, R.; Walsh, R. *Chem. Rev.* **1995**, *95*, 1203.

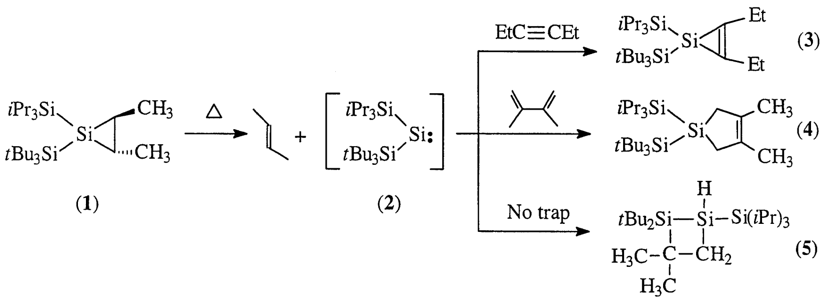
[21] Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

[22] Gaspar, P. P.; Qian, H.; Beatty, A. M.; d'Avignon, D. A.; Kao, J. L.-F.; Watt, J. C.; Rath, N. P. *Tetrahedron* **2000**, *56*, 105.

[23] For carbenes see: Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10805, and earlier references contained therein. For SiH$_2$ see: Anwari, F.; Gordon, M. S. *Isr. J. Chem.* **1983**, *23*, 129.

[24] Use of *cis*-2-butene in the reaction shown in eq 1 yields a mixture of *E,E*- and *Z,Z*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane that could not be separated.

Scheme 3. Silylene Generation from Thermal Decomposition of Silirane 1



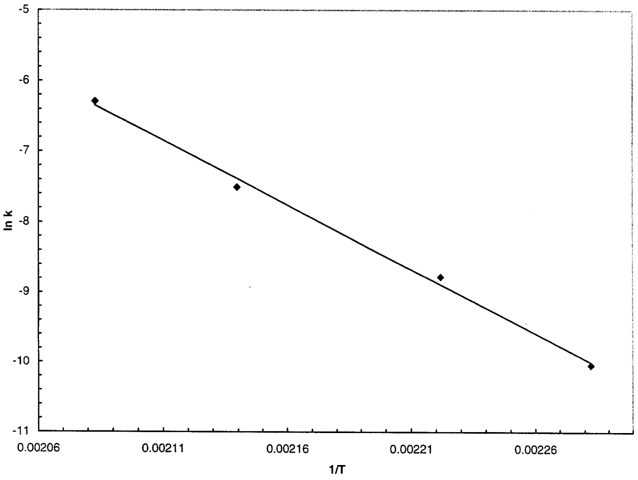


Figure 3. Arrhenius plot for the thermolysis of **1**.

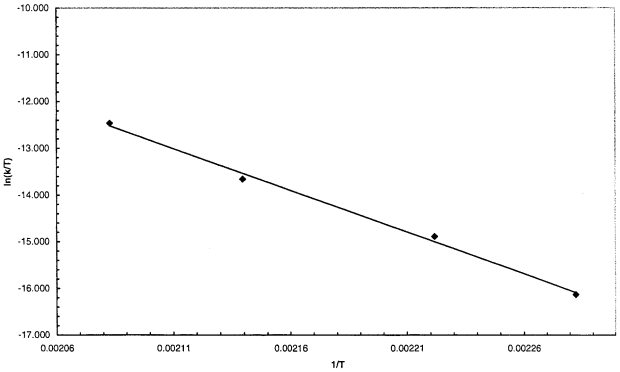


Figure 4. Eyring plot for the thermolysis of **1**.

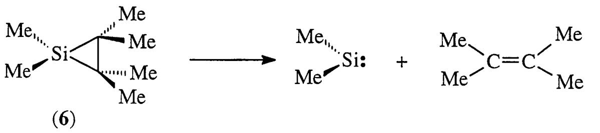
Table 3. Comparison of Activation Parameters Obtained for Pyrolysis of Siliranes 1 and 6

silirane	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	E_a (kcal/mol)	log A/s
1	35.5 ± 1.4	1.8 ± 3.0	36.4 ± 1.6	13.8 ± 0.8
6	31.6 ± 2.7	11.2 ± 0.6	31.3 ± 1.2	15.2 ± 0.7

°C in the presence of a 20-fold excess of 3-hexyne, which leads to the formation of the hexyne adduct (**3**) in ca. 90% yield. If the silylene intermediate attacked the silirane starting material (**1**), the presence of 3-hexyne trapping agent would have led to a *decrease* in the rate constant for disappearance of **1**. Instead, a small increase was observed, (6.79 ± 0.08) × 10^{-4} s^{-1} vs (5.48 ± 0.14) × 10^{-4} s^{-1}.

Activation parameters for the pyrolysis of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) were calculated from the Arrhenius equation (Figure 3) and the Eyring equation (Figure 4).

To date, the only kinetic study of a silylene retroaddition has been carried out by the Berry group on the pyrolysis of hexamethylsilirane (**6**) (eq 2).[25] Activation parameters from the present experiments are compared with those obtained by Berry in Table 3.



(2)

While E_a and $\Delta H^\ddagger$ for the decomposition of siliranes **1** and **6** are similiar, $\Delta S^\ddagger$ and log A are quite different. Let us consider the implications of the FMO theory prediction of a non-least motion pathway for silylene addition to an olefin and the retroaddition: the extrusion of a silylene from a silirane (Scheme 2). For the transformation from silirane to free silylene, the transition state structure should resemble the product (the free silylene and olefin) more than the silirane according to the Hammond postulate; that is, there should be considerable bond breaking. This follows from the endothermicity of the retroaddition (ca. 36 kcal/mol). There should be a positive contribution to the entropy of activation due to bond loosening and a negative contribution due to an increase in congestion accompanying the tilting of the R groups toward the ring carbon atoms, as shown in Scheme 2.

For the case studied by Berry, with R = Me in silirane **6**, it is plausible that the positive contribution is dominant, leading to a net positive $\Delta S^\ddagger$. Given that complete bond breaking upon pyrolysis of a silirane leads to an entropy increase of ca. 40 eu, the observed modestly positive value of $\Delta S^\ddagger$ for pyrolysis of **6**, 11.2 ± 0.6 eu, may represent the effect of some crowding in the transition state due to a non-least motion mechanism. The bulkiness of the substituents, R = ^{t}Bu$_3$Si and ^{i}Pr$_3$Si, in silirane **1** would be expected to lead to even more congestion in a non-least motion transition state, and this may be responsible for the reduced $\Delta S^\ddagger$ for **1**, 1.8 ± 3.0 eu.

In his analysis of the kinetics of addition of H_2Si and Me_2Si to olefins, Walsh modeled the retroadditions and concluded that log A/s for extrusion of Me_2Si from 1,1-dimethylsilirane, ca. 15, is significantly lower than that for extrusion of H_2Si from unsubstituted silirane, ca. 17.[26,27] Walsh viewed this implied difference in

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(25) Popoff, C. M.; Berry, D. H. Kinetics and Mechanism of Dimethylsilylene Extrusion from Hexamethylsilirane. Approximation of ΔH_f and the Ring Strain Enthalpy of a Silirane. Private communication from Professor Berry, July 28, 1993, with permission to quote.

(26) Al-Rubaiey, N.; Walsh, R. *J. Phys. Chem.* **1994**, *98*, 5303.

transition state structure as support for a non-least motion mechanism.[27] The further decrease in log *A*/s to ca. 14 for extrusion of bulky silylene **2** speaks for a yet tighter transition state.

While the low values for the $\Delta S^{\ddagger}$ and log *A*/s activation parameters observed for the pyrolysis of silirane **1** could also be explained by an earlier transition state, greater crowding due to a non-least motion pathway is more likely, in the view of the present authors, to be the source of a tighter transition state for the pyrolysis of **1** relative to **6** than a less product-like transition state that might have been expected to manifest itself by a lower activation energy or enthalpy.

Finally, does this study of the pyrolysis of silirane **1** shed any light on the electronic state of silylene **2**? The formation of disiletane **5** in 21.5% yield by formal C−H insertion of the silylene center upon photochemical generation of **2** at room temperature suggested that **2** was reacting from a triplet electronic state.[28] The argument supporting that suggestion was that singlet silylenes only yield intramolecular insertion products at high temperatures because the predicted activation barrier is ca. 20 kcal/mol. Very recently, however, this interpretation of the chemical evidence has been questioned by Yoshida and Tamoki, whose DFT calculations have predicted nearly isoenergetic lowest singlet and triplet states for **2**.[29]

In the present report formation of **5** is reported in higher yield (44−74%) upon thermal generation of **2** by stereospecific extrusion from **1** at 165−207 °C. Does this information shed any light on the electronic state of silylene **2** upon its formation or as it reacts? The evidentiary value of the stereospecificity of thermal silylene extrusion can be dismissed. It was pointed out at the beginning of this paper that, for heavier analogues of carbenes, addition and hence retroaddition reactions such as the extrusion of **2** from **1** may be stereospecific, even if they are the stepwise processes required for triplet species. And whatever the ground state of **2** is, a concerted extrusion consistent with the activation parameters reported here would be expected to yield singlet **2** initially, and this singlet could subsequently relax to or equilibrate with a nearby triplet state. If extrusion is concerted, microscopic reversibility demands that addition of silylene **2** to *trans*-2-butene occur via a singlet state, whether ground state or not.

It is suggested, however, that the increased yield of **5** upon thermal generation of **2** is in accord with reaction from a triplet state. Activation energies for the formation of oligomers of **2** observed as the major product formed in competition with **5** are likely to be nearly zero. Therefore a crude approximation of the activation energy for the formation of **5** can be deduced from the increase in yield of **5** with increasing temperature, if it is assumed that product formation is irreversible under the reaction conditions. The increase in yield of **5** from 21% in the room-temperature photochemical experiments (i.e., a yield ratio of **5**:oligomer ca. 0.26) to ca. 59% in the thermolysis at 165 °C (yield ratio **5**:oligomer ca. 1.4) corresponds to a difference of 3 kcal/mol between the activation energy for the formation of **5** and that for the formation of silylene oligomers. Even if the activation energy for silylene oligomerization is ca. 5 kcal/mol, an activation energy below 10 kcal/mol for the formation of **5** is indicated, and this is much more likely for a triplet state than for a singlet state of the silylene.

In conclusion, *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) undergoes stereospecific thermal decomposition to form free silylene (iPr$_3$Si)(tBu$_3$Si)Si: (**2**) and *trans*-butene. Silylene (iPr$_3$Si)(tBu$_3$Si)Si: (**2**) can be captured by added trapping agents or self-trapped through intramolecular insertion into a C−H bond of a *tert*-butyl group, forming stable disiletane **5**. Kinetic studies found that the thermal decomposition of silirane was first-order in benzene solution. Activation parameters were obtained that are consistent with a non-least motion pathway for silylene addition and retroaddition.

Experimental Section

General Procedures. Proton NMR spectra were recorded on a Varian Unity-300 (300 MHz) or a Varian Unity-500 (500 MHz) NMR spectrometer. Carbon-13 NMR spectra were recorded on a Varian Unity-300 (75.4 MHz) or a Varian Unity-500 (125 MHz) NMR spectrometer. Unless otherwise indicated, they are proton decoupled. Silicon-29 NMR spectra were recorded on a Varian Unity-300 (59.6 MHz) NMR spectrometer employing TMS as the external standard. All spectra were recorded at room temperature. High-resolution mass spectral data were recorded on a VG ZAB-SE mass spectrometer in the Washington University MS Facility; GC−MS data were recorded on a Hewlett-Packard Model 5890 Series II instrument employing a 25 m 5%-OVS capillary column. All experiments were carried out under an atmosphere of dry nitrogen. Schlenk line procedures were generally used. The yields were calculated as moles of products divided by moles of starting materials converted. Unless otherwise indicated, all chemicals were of reagent grade quality. Benzene and tetrahydrofuran were distilled from a blue solution of the benzophenone sodium ketyl under nitrogen and used immediately.

X-ray Crystallography for 3. A single crystal with dimensions 0.36 × 0.33 × 0.24 mm^3 was mounted on glass fibers in a random orientation. Preliminary examination and data collection were performed using a Bruker SMART charge coupled device (CCD) detector system single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) equipped with a sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ϖ scans). A typical data set consists of 4028 frames of intensity data collected with a frame width of 0.3° in ϖ and counting time of 15 s/frame at a crystal-to-detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages[30] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *xyz* centriods of 8192 reflections. Collected data were corrected for systematic errors using SADABS based upon the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are available in Table 1 in the Supporting Information. Structure solution and refinement was carried out using the SHELXTL-

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(27) Al-Rubaiey, N.; Carpenter, I. W.; Walsh; R.; Bacerra, R.; Gordon, M. S. *J. Phys. Chem.* **1998**, *102*, 8564.

(28) Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622.

(29) Yoshida, M.; Tamaoki, N. *Organometallics* **2002**, *21*, 2587.

(30) Sheldrick, G. M. *SMART* and *SAINT*; Bruker Analytical X-ray: Madison, WI, 1999.

PLUS software package.[31] The structure was solved by direct methods and refined successfully in the space group $P2_1/n$. Full-matrix least-squares refinements were carried out on F^2. The non-hydrogen atoms were refined anisotropically to convergence.

The final residual values are $R(F) = 4.7\%$ ($I > 2\sigma I$) and $R_w(F^2)$ for 5959 reflections and 289 parameters. Relevant structure refinement parameters, atomic coordinates, geometrical parameters, and anisotropic thermal parameters are provided in the Supporting Information. Projection view of the molecules with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling is presented in Figure 1.

Synthesis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1). Freshly prepared activated magnesium[32] (from 150 mg of anhydrous $MgCl_2$ reduced with 2 equiv of lithium naphthalenide) in 10 mL THF contained in a 50 mL Schlenk tube with a magnetic stirring bar was cooled to 77 K; then 1.5 mL of *trans*-butene stored in a calibrated tube with a stopcock was transferred on vacuum into the mixture by condensation. The reaction flask was cooled to ≤0 °C (bp of *trans*-butene: 1 °C), and 2,2-dibromo-1,1,1-tri-*tert*-butyl-3,3,3-triisopropyltrisilane[33] (272 mg, 0.5 mmol) was added to it. The reaction mixture was stirred at 0 °C for 1 h, then at room temperature for 8 h. After filtration and concentration of the residue, *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) (215 mg, 98%) was obtained as a colorless oil. This compound is fairly stable to air and moisture. ^{1}H NMR (C_6D_6, ppm): 0.82 (m, 1H, $CH_3{-}C\mathit{H}{-}CH{-}CH_3$), 1.01 (m, 1H, $CH_3{-}CH{-}C\mathit{H}{-}CH_3$), 1.26 (m, 45H, $(\mathit{Me}_3C)_3Si$, $(\mathit{Me}_2CH)_3Si$), 1.36 (m, 3H, $(Me_2C\mathit{H})_3Si$), 1.59 (d, $^3J_{H-H} = 6.6$ Hz, 3H, $\mathit{CH_3}{-}CH{-}CH{-}CH_3$), 1.72 (d, $^3J_{H-H} = 6.9$ Hz, 3H, $CH_3{-}CH{-}CH{-}\mathit{CH_3}$). ^{13}C NMR ($C_6D_6$, ppm): 15.4 ($(Me_2\mathit{C}H)_3Si$), 18.8 ($\mathit{C}H_3{-}CH{-}CH{-}CH_3$), 19.3 ($CH_3{-}CH{-}CH{-}\mathit{C}H_3$), 20.4, 21.0 ($(\mathit{Me}_2CH)_3Si$), 20.8 ($CH_3{-}\mathit{C}H{-}CH{-}CH_3$), 21.4 ($CH_3{-}CH{-}\mathit{C}H{-}CH_3$), 24.3 ($(Me_3\mathit{C})_3Si$), 32.7 ($(\mathit{Me}_3C)_3Si$). ^{29}Si NMR ($C_6D_6$, ppm): 28.1 ($^t\mathrm{Bu}_3\mathit{Si}$), 13.3 ($^i\mathrm{Pr}_3\mathit{Si}$), −140.7 (ring *Si*). HRMS: calcd $(M - 56)^+$ $C_{21}H_{48}Si_3$ 328.2438, found 328.2442.

Thermolysis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1) in the Presence of 3-Hexyne. Into a pyrolysis tube attached to a Teflon stopcock was placed a mixture of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) (44 mg, 0.1 mmol) and 3-hexyne (164 mg, 2.0 mmol) dissolved in freshly dried benzene-d_6 (1 mL). After being degassed on a vacuum line to 0.02 Torr by three freeze−pump−thaw cycles, the tube was sealed with a torch and then heated to 220 °C for 2 h. After cooling, the ampule was opened and the pyrolysate was transferred into a 10 mL round-bottom flask. GC−MS indicated that 2,3-diethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirene (**3**) was formed in 87% yield. ^{1}H NMR (C_6D_6, ppm): 1.24−1.30 (m, 54H), 2.60−2.75 (m, 4H). ^{13}C NMR (C_6D_6, ppm): 14.1 ($\mathit{C}H_2CH_3$), 14.2 ($Si(\mathit{C}HMe_2)_3$), 20.5 ($Si(CH\mathit{Me}_2)_3$), 24.0 ($-CH_2\mathit{C}H_3$), 24.4 ($Si(\mathit{C}Me_3)_3$), 32.2 ($Si(C\mathit{Me}_3)_3$), 140.7 ($\mathit{C}{=}\mathit{C}$). ^{29}Si NMR (C_6D_6, ppm): −152.3 (ring *Si*), 6.8 ($^i\mathrm{Pr}_3\mathit{Si}$), and 16.0 ($^t\mathrm{Bu}_3\mathit{Si}$). HRMS: calcd for $C_{24}H_{51}Si_3$ $(M^+ - {}^i\mathrm{Pr})$ 423.3298, found 423.3313; calcd for $(M^+ - {}^t\mathrm{Bu})$ $C_{23}H_{49}Si_3$ 409.3142, found 409.3144.[34]

Thermolysis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1) in the Presence of 2,3-Dimethyl-1,3-butadiene. Into a pyrolysis tube attached to a Teflon stopcock was placed a mixture of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) (44 mg, 0.1 mmol) and 2,3-dimethyl-1,3-butadiene (246 mg, 3.0 mmol) dissolved in freshly dried benzene-d_6 (1 mL). After being degassed on a vacuum line to 0.02 Torr and three freeze−pump−thaw cycles, the tube was sealed with a torch and then heated to 220 °C for 2 h. After cooling, the ampule was opened, and the pyrolysate was transferred into a 10 mL round-bottom flask. GC−MS indicated that 3,4-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilyl-1-silacyclopent-3-ene (**4**) was formed in 43% yield. ^{1}H NMR (C_6D_6, ppm): 1.22 (d, 18H, $Si(CH\mathit{Me_2})_3$), 1.25 (s, 27H, $Si\mathit{t}Bu_3$), 1.47 (m, 3H, $Si(C\mathit{H}Me_2)_3$), 1.74 (s, 6H, $C{=}C\mathit{CH_3}$), 2.06−2.22 (m, 4H, $C\mathit{H_2}{-}Si{-}C\mathit{H_2}$). ^{13}C NMR ($C_6D_6$, ppm): 14.7 ($Si(\mathit{C}HMe_2)_3$), 19.5 ($Si\mathit{C}H_2$), 20.9 ($Si(CH\mathit{Me_2})_3$), 24.6 ($Si(\mathit{C}Me_3)_3$), 28.2 ($=C\mathit{C}H_3$), 32.3 ($Si(C\mathit{Me_3})_3$), 132.9 ($C{=}C$). ^{29}Si NMR ($C_6D_6$, ppm): − 41.0 (ring *Si*), 0.3 ($^i\mathrm{Pr}_3\mathit{Si}$), 17.9 ($^t\mathrm{Bu}_3\mathit{Si}$). HRMS: calcd for $C_{27}H_{58}Si_3$ 466.3846, found 466.3815.

Thermolysis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1) in the Absence of Added Trapping Agents. Into a pyrolysis tube attached to a Teflon stopcock was placed *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**) (66 mg, 0.15 mmol) dissolved in freshly dried benzene-d_6 (1 mL). After being degassed on a vacuum line to 0.02 Torr by three freeze−pump−thaw cycles, the tube was sealed with a torch and then heated to 220 °C for 2 h. After cooling, the ampule was opened, and the pyrolysate was transferred into a 10 mL round-bottom flask and volatiles were evaporated in vacuo. The residue was dissolved in benzene-d_6 and NMR was recorded. ^{1}H NMR indicated that starting material **1** was completely gone and 1,1-di-*tert*-butyl-4,4-dimethyl-2-triisopropylsilyl-1,2-disiletane (**5**) was formed (81% yield). ^{1}H NMR (C_6D_6, ppm): 1.15 (d, $^3J_{H-H} = 7.5$ Hz, 18H, $Si(CH\mathit{Me}_2)_3$), 1.20−1.25 (m, 4H, $Si(C\mathit{H}Me_2)_3$, $Si(C\mathit{H}HCMe_2)$), 1.23 (s, 9H, $Si(C\mathit{Me}_3)(CMe_3)$), 1.27 (s, 9H, $Si(CMe_3)(C\mathit{Me_3})$), 1.36 (s, 3H, $SiCH_2C\mathit{Me}Me$), 1.36 (m, 1H, $SiCH\mathit{H}CMe_2$), 1.48 (s, 3H, $SiCH_2CMe\mathit{Me}$), 4.13 (dd, $^3J_{H-H} = 5.5$, 9 Hz, 1H, SiH). ^{13}C NMR (C_6D_6, ppm): 13.5 ($Si(\mathit{C}HMe_2)_3$), 20.0 ($Si(CH\mathit{Me}Me)_3$), 20.1 ($Si(CHMe\mathit{Me})_3$), 22.7 ($Si(\mathit{C}Me_3)(CMe_3$), 23.4 ($Si(CMe_3)(\mathit{C}Me_3)$), 27.7 ($Si\mathit{C}H_2CMe_2$), 31.1 ($Si(C\mathit{Me}_3)(CMe_3)$), 31.2 ($Si(CMe_3)(C\mathit{Me}_3)$), 31.6 ($Si\mathit{Me}MeCH_2$), 31.7 ($SiMe\mathit{Me}CH_2$), 37.6 ($Si\mathit{C}Me_2CH_2$). ^{29}Si NMR ($C_6D_6$, ppm): −70.2 (SiH), 6.0 ($^i\mathrm{Pr}_3Si$), 34.9 ($^t\mathrm{Bu}_2Si$). HRMS (EI) for $C_{17}H_{40}Si_3$ $(M - 56)^+$: calcd 328.2438, found 328.2442. The H's of the CH_2 group were located in a COSY experiment; connection between H's and C's were confirmed in an HMQC experiment; C's were indentified in an APT experiment.

General Procedure for the Kinetic Studies on the Thermolysis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1). A regular NMR tube containing a chloroform-d_1 solution of $MeP(O)(OMe)_2$ was used as the standard. Into a capillary tube was added about 0.1 mL of a solution of 0.1 M *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (**1**). The sample was degassed by three freeze−pump−thaw cycles to 10^{-4} Torr on a high-vacuum line, and then the tube was sealed immediately. This capillary tube was placed into the regular NMR tube containing standard chloroform-*d* solution, and ^{1}H NMR was recorded with $d_1 = 10$ s. Then the capillary tube with sample was lifted from the standard tube and placed in the vapor space of a long-neck 1 L flask containing a refluxing solvent: tetralin (207.0 °C); diethylene glycol methyl ether (194.3 °C); *p*-cymene (177.6 °C); mesitylene (165.0 °C). The temperature was constant within ±0.1 °C and measured by a digital thermometer (Fluke 52). The temperature reported is the average difference between the temperature of the vapor bath and that of an ice−water bath. At various time intervals the capillary tube was removed, cooled, and placed into the standard NMR tube, and the ^{1}H NMR spectrum was recorded. The concentration of the remaining material was determined on the basis of the ^{1}H NMR integrations of the starting material and the standard: δ 1.70

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[32] Riecke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.

[33] Details of the synthesis and characterization of 2,2-dibromo-1,1,1-tri-*tert*-butyl-3,3,3-triisopropyltrisilane are described in the Supporting Information for Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622. This material is available free on the Internet at http://pubs.acs.org.

[34] These spectroscopic data matched those of an authentic sample, the details of whose synthesis by a silylenoid route and characterization are included in the Supporting Information to which footnote 33 refers. X-ray crystallography was carried out on a sample prepared by the silylenoid route.

ppm (d, one of the ring methyl groups in **1**) and δ 3.78 ppm (d, MeP(O)(O*Me*)$_2$ of the standard).

Thermolysis of *trans*-2,3-Dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane (1): At 438.1 ± 0.1 K (165.0 ± 0.1 °C). In glovebox, 0.1 mL of a 0.1 M solution of **1** in C_6D_6 was added to a 3 mm o.d. (1.5 mm i.d.) Pyrex tube. Then the sample was degassed carefully on a high-vacuum line at 10^{-4} Hg. After the tube was sealed it was placed in a vapor bath of refluxing mesitylene. Thermolysis was interrupted and the sample tube cooled to room temperature at various times to record ^{1}H NMR spectra from which the concentration of **1** and the yield of **5** (44−59%) were determined. The slope of the first-order kinetic plot (Figure 2) yielded a rate constant of $(4.33 \pm 0.16) \times 10^{-5}$ s^{-1}.

At 450.1 ± 0.1 K (177.0 °C). The same procedure was followed employing a vapor bath of refluxing *p*-cymene. Yields of **5** between 57 and 76% were observed. The slope of the first-order kinetic plot (Figure 2) yielded a rate constant of $(1.54 \pm 0.06) \times 10^{-4}$ s^{-1}.

At 467.4 ± 0.1 K (194.3 °C). The same procedure was followed employing a vapor bath of refluxing diethylene glycol methyl ether. Yields of **5** between 64 and 71% were observed. The slope of the first-order kinetic plot (Figure 2) yielded a rate constant of $(5.48 \pm 0.14) \times 10^{-4}$ s^{-1}.

At 480.1 ± 0.1 K (207.0 °C). The same procedure was followed employing a vapor bath of refluxing tetralin. Yields of **5** between 58 and 70% were observed. The slope of the first-order kinetic plot (Figure 2) yielded a rate constant of $(1.85 \pm 0.08) \times 10^{-3}$ s^{-1}.

Thermolysis of 1 at 467.4 ± 0.1 K (194.3 °C) in the Presence of 3-Hexyne. The same procedure was followed with a 20-fold excess of 3-hexyne and a vapor bath of refluxing diethylene glycol methyl ether. The slope of the first-order kinetic plot (Figure 2) yielded a rate constant of $(6.79 \pm 0.08) \times 10^{-4}$ s^{-1}.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for 2,3-diethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirene (**3**). Tables of concentrations and conversions of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilyl-silirane (**1**) and product yields at various times in the pyrolysis of **1** at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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