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Thermally-Induced 1,2-Shifts To Convert Olefins to Carbenes: Does Silicon Do It? If So, Why Not Carbon?

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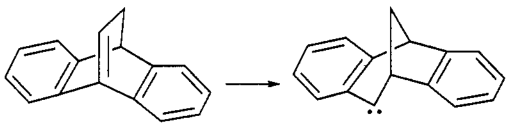
Abstract: Thermal isomerization of olefins to carbenes via a 1,2-silyl shift was examined by both experiment and theory. No evidence of this rearrangement was found for acyclic vinylsilanes, nor could electronic assistance by silicon be identified in cis, trans isomerizations. Serendipitous synthesis of a 2,4-dimethylene-1,3-disilacyclobutane allowed a kinetic examination of its gas-phase, thermal ring expansion to a 2-methylene-1,3-disilacyclopentene. The Arrhenius parameters (log $A = 12.48$, $E_{\mathrm{act}} = 54.09$ kcal/mol) are the first to be reported for an olefin-to-carbene rearrangement. The analogous all-carbon system failed to ring expand. *Ab initio* calculations revealed that this was opposite to any predictions which would be made from ring strain considerations. Calculations showed that for silyl migration the transition state was late and was actually the carbene, while for carbon migration the TS was early and considerably higher in energy than the resulting carbene. The 2-methylene-1-silacyclobutane rearrangement (ref 5) was reexamined to find that reversible ring opening to a 1,4-diradical occurred at temperatures below those required to ring expand via a carbene TS.

Introduction

Thermal isomerization of olefins to produce carbenes is a reaction that students of organic chemistry would love, if they knew about it. It does not happen, so they do not have to memorize it. At least it very, very rarely happens and thus has been the object of considerable attention by practitioners of theory. The activation energy for the thermal isomerization of ethylene to methylmethylene has been variously calculated to be between 74.2 and 84.1 kcal/mol.[1] Thus it is hardly surprising that thermal isomerization of olefins to carbenes has only been reported for four systems (**1**−**4**) and that three of these (**1**−**3**) possess significantly twisted double bonds for which the energetic requirements for isomerization should be considerably reduced.



(ref 2)

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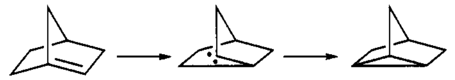

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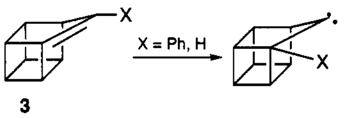

(ref 4)

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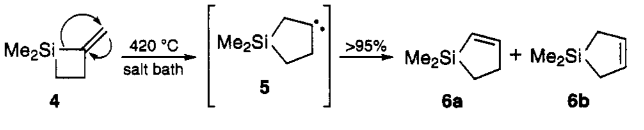

To our knowledge the sole example of the thermal isomerization of an untwisted olefin to a carbene is the 1985 report by Conlin[5,6] that α-methylenesilacyclobutane **4** cleanly isomerized to a mixture of 2- and 3-silacyclopentenes, **6a** and **6b**. Conlin did indeed daringly propose that this ring expansion occurred via the intermediacy of carbene **5** formed by a 1,2-silyl shift, although no mechanistic studies were attempted. While this seems a rational, if not the only, explanation we have for some time been puzzled as to the following: (1) Is it solely relief of ring strain that allows this unique reaction? (2) Is it unique migratory properties of silicon which allow or promote this isomerization? (3) Are there any other examples in the literature which could or should be interpreted in this fashion? (4) Why does carbon not migrate in analogous systems? We will attempt to answer each of these questions through a combination of experiment and theory.

Results and Discussion

A review of the literature of the thermochemistry of vinylsilanes revealed two rearrangements for which olefin-to-carbene isomerization should be considered. Ishikawa[7] has reported the facile isomerization of methylenedisilacyclopropane **7** to disi-

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

[1] Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389. Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. V. R. *Chem. Phys. Lett.* **1982**, *85*, 145. Nobes, R. H.; Radom, L.; Rodwell, W. R. *Chem. Phys. Lett.* **1980**, *74*, 269. The barrier for the reverse reaction from methylmethylene to ethylene has been most recently calculated to be 0.8 kcal/mol: Jensen, J. H.; Morokuma, K.; Gordon, M. S. *J. Chem. Phys.* **1994**, *100*, 1981.

[2] Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936.

[3] Barton, T. J.; Yeh, M. H. *Tetrahedron Lett.* **1987**, *28*, 6421.

[4] (a) Eaton, P. E.; Hoffmann, K. *J. Am. Chem. Soc.* **1987**, *109*, 5285. (b) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067. (c) Eaton, P. E.; White, A. J. *J. Org. Chem.* **1990**, *55*, 1321. (d) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305.

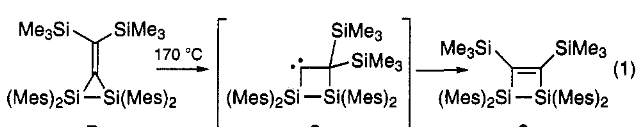
[5] Conlin, R. H.; Huffaker, H. B.; Kawk, Y. *J. Am. Chem. Soc.* **1985**, *107*, 731.

[6] Olefin-to-carbene rearrangement has also been suggested by Scott as a possible mechanism for carbon scrambling in the pyrolysis of aromatic hydrocarbons such as benzene, naphthalene, and benz[*a*]anthracene. However, the authors favored a reversible valence isomerization to a benzvalene-type intermediate and viewed ring contraction to a cyclopentadienyl methylene as plausible but "less attractive on energetic grounds": Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661. Scott, L. T.; Roelofs, N. H.; Tsang *J. Am. Chem. Soc.* **1987**, *109*, 5456. Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461.

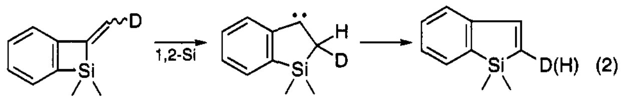
[7] Ishikawa, M.; Matsuzawa, S. *J. Chem. Soc., Chem. Commun.* **1985**, 588.

0002-7863/95/1517-11695$09.00/0

lacyclobutene **9**, and although no mechanism was suggested, it is possible that this occurs via a 1,2-silyl shift to afford the intermediate carbene **8**. Also in 1985 one of us reported[8] the indirect observation that methylenebenzosilacyclobutene **10** thermally isomerized to silaindene **12** and this too can be (although it was not) interpreted as proceeding through rearrangement to an intermediate carbene, **11**.

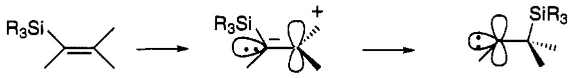


7 **8** **9** (1)



10 **11** **12** (2)

Is it possible that silicon can play a unique role in stabilizing the energy surface of olefin isomerization? Since silicon is well-known to stabilize both β-carbocations and α-carbanions,[9] twisting of a vinylsilane so as to heterolytically break the π-bond should be facilitated by the stabilization of both ends of the resulting zwitterion **13** (eq 3). Of course complete formation of **13** would not occur, as silyl migration in a concerted but nonsynchronous fashion should intervene. Silyl migration to β-carbocations is also well-established, and in the case of hypothetical intermediate **13** this would lead to the formation of a singlet β-silyl carbene, **14**, which should be stabilized by the same hyperconjugative interaction of the Si−C bond and the vacant p-orbital as in the stabilization of β-carbocations. While we are aware of no experimental evidence of this latter suggestion, recent theoretical calculations reveal that replacing a hydrogen of methylene by a silylmethylene unit (i.e., HCH vs $HCCH_2SiH_3$) results in an overall change in the singlet−triplet energy gap of 9.9 kcal/mol so that the singlet actually becomes the more stable state by 1.2 kcal/mol.[10]



13 **14** (3)

"dual-stabilized zwitterion" hyperconjugatively stabilized singlet carbene

In selecting an acyclic vinylsilane with which to search for this isomerization, one does not want to totally forego the energetic advantage of ring strain relief enjoyed by **4**, **7**, and **10**. Since 1,1-disubstituted ethylenes are more sterically strained than their (*E*)-1,2-isomers, the strain energy of 1,1-di-*tert*-butylethylene being about 12.5 kcal/mol,[11] 1,1-bis(trimethylsilyl)ethylene (**15**) was chosen as a likely candidate. However, in flash vacuum pyrolysis (FVP) studies (Scheme 1) **15** proved remarkably stable, with only partial decomposition occurring at 700−800 °C. The major products (among many) were methane, trimethylsilane, and vinyltrimethylsilane for which the most likely origins are homolytic processes. Most notable was the total absence of 1,2-bis(trimethylsilyl)ethylene (**17**), which can be taken as prima facie evidence that carbene **16** is not involved. Independent pyrolysis of **17** revealed that while it decomposed to the same products as did **15**, a significant amount remained and would have been easily detected if present in the pyrolysis of **15**.

Scheme 1

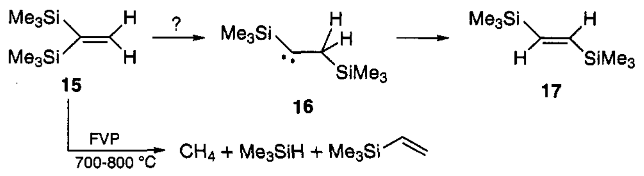
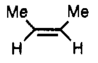
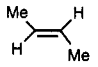
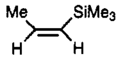
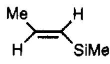
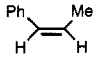
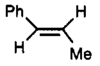
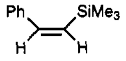
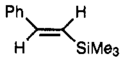
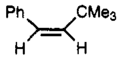
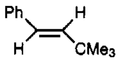
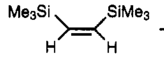
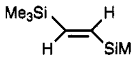
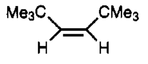
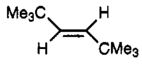


Table 1. Arrhenius Parameters for Gas-Phase, Thermal Cis−Trans Isomerizations

			E_{act}, kcal/mol (log A)
	→		62.3 ± 0.8 (13.5)
	→		56.0 ± 0.3 (13.0)
	→		60.2 ± 0.7 (15.1)
	→		53.0 ± 0.3 (14.3)
	→		54.9 ± 0.2 (14.8)
	→		52.7 ± 0.4 (13.9)
	→		54.4 (ref 13)

The effect of silyl substitution on the facility of π-bond cleavage is potentially detectable by examining the energies required for cis−trans isomerization of variously substituted olefins. Thus gas phase kinetic studies of the geometric isomerization of the olefins presented in Table 1 were undertaken in a previously described[12] stirred flow reactor (SFR) system.

The activation energy for cis-to-trans isomerization of (*Z*)-1-(trimethylsilyl)-1-propene is about 6 kcal/mol lower than that for (*Z*)-2-butene, and a similar reduction in barrier is observed between β-methyl- and β-(trimethylsilyl)styrene, but this cannot be solely, if at all, attributed to electronic stabilization of the transition state by silicon since relief of steric strain must be a factor. Indeed comparison of the data for the β-substituted styrenes reveals a difference of only 2 kcal/mol between the more sterically comparable trimethylsilyl- and *tert*-butyl-substituted systems, and a similar small difference is observed in the isomerization barriers for 1,2-bis(trimethylsilyl)- and 1,2-di-*tert*-butylethylenes. Thus it appears that silyl substitution alone is insufficient to account for the π-bond cleavage involved in olefin-to-carbene isomerization and must be accompanied by an additional promoter such as ring strain.

However, it seems that ring strain alone is also insufficient to demand a pathway of olefin-to-carbene rearrangement. Thus in an attempt to generate a methylenesilacyclopropane (**19a** or **b**) by the copyrolysis of the silylene generator, dimethoxytetramethyldisilane (**18**), and 1,1-dimethylallene (Scheme 2), the major product was 2-dimethylsilylisoprene (**21**) rather than the expected (or at least not unanticipated) 1-dimethylsilylisoprene (**22**), which could have arisen from rearrangement of **19** to

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(7) Barton, T. J.; Groh, B. L. *Organometallics* **1985**, *4*, 575.

(8) Bassindale, A. L.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: New York, 1989; Part 2, Chapter 14 and references therein.

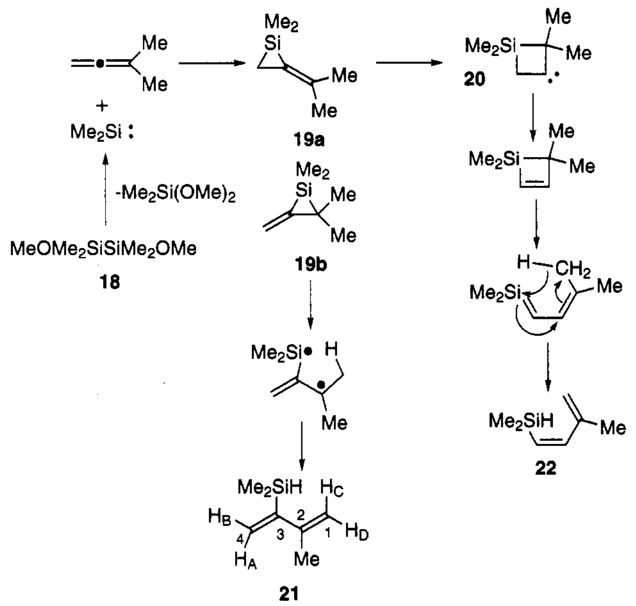
(9) Shimizu, H.; Gordon, M. S. *Organometallics* **1994**, *13*, 186.

(10) Ermer, O.; Lifson, S. *Tetrahedron* **1974**, *30*, 2425.

(11) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.

(12) W. R. Roth quoted in: Gano, J. E.; Lenoir, D.; Park, B. S.; Roesner, R. R. *J. Org. Chem.* **1987**, *52*, 5636.

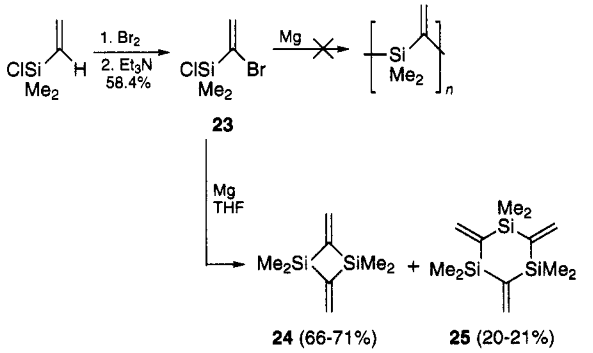
Scheme 2



carbene **20** followed sequentially by C—H insertion, ring opening, and precedented[14] 1,5-hydrogen migration. Formation of **21** is rationalized from either **19a** or **19b** by homolysis of the weaker bond in the silacycle to produce the same 1,3-diradical followed by intramolecular hydrogen abstraction.[15]

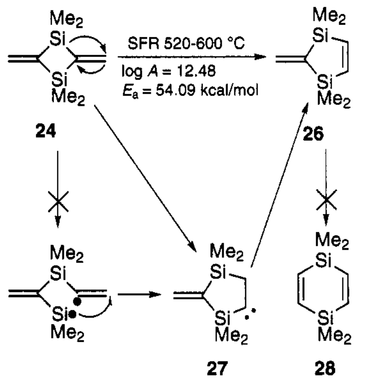
Prior to undertaking the necessary kinetic study of **4**, an analog which could allow at least the determination of generality of this rearrangement in α-methylenesilacyclobutanes serendipitously became available. In an ill-fated attempt to synthesize α,α-silylenevinylene polymers[16] by the reaction of (α-bromovinyl)dimethylchlorosilane (**23**), it was discovered (Scheme 3) that instead cyclization dominated with the major products being the dimer (**24**) and trimer (**25**) along with very minor amounts of the cyclic tetramer and pentamer.

Scheme 3



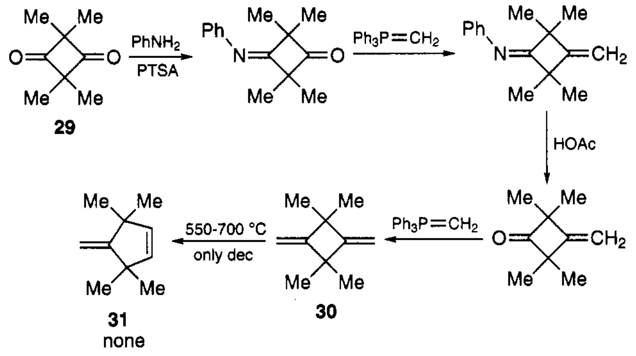
Pyrolysis of **24** in a vertical nitrogen-flow system at 600 °C cleanly produced a mixture of **24** and methylenedisilacyclopentene **26** (25%) (Scheme 4). Increasing the temperature increased the conversion to **26** but did not afford any of the isomeric disilacyclohexadiene **28**. The isomerization of **24** to **26** is most economically rationalized by concerted rearrangement to carbene **27**, but a pathway to **27** via Si—C homolysis and endocyclic closure required kinetics to rule out. Thus a kinetic study of this reaction was conducted over the temperature range of 520—600 °C in the SFR. Based on 23 rate determinations in this temperature range, the Arrhenius parameters for the first-order formation of **26** were log A (s^{-1}) = 12.48 ± 0.33 and E_a (kcal/mol) = 54.09 ± 1.26. Both of these values are consistent with a concerted formation of **26**. Certainly there are no 54 kcal bonds in **24** with the exception of the π-bond, the breaking of which is essentially what is being measured.

Scheme 4



To answer the question as to whether this isomerization requires the presence of silicon, the all-carbon analog of **24**, 1,3-dimethylenecyclobutane **30**, was synthesized from tetramethyl-1,3-cyclobutanedione (**29**) by the sequence of literature procedures[17-19] shown in Scheme 5.[20] In the pyrolysis of **30** decomposition began at 550 °C but no isomerization to cyclopentene **31** was observed up to 700 °C.

Scheme 5



So why does silicon do it and carbon not? The simplest answer would be that the energetic difference between **30** and the corresponding carbene is significantly greater than the difference between **24** and carbene **27**. To probe that question these energy differences were calculated using the program GAMESS[21] for the unsubstituted systems, with geometries optimized at the Hartree—Fock (HF) level with 6-31G(d) basis sets[22] and energies calculated at the second-order perturbation

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[14] Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *209*, C25.

[15] Similarly the photochemical generation of dimesitylsilylene in the presence of 1,1-dimethyl-3-*tert*-butyl-1,2-butadiene or tetramethylallene is reported to produce 2-(hydridosilyl)-1,3-butadiene products: Ando, W.; Saso, H. *Tetrahedron Lett.* **1986**, *27*, 5625.

[16] Lin, J.; Maghsoodi, S. I.; Barton, T. J. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1995**, *36(1)*, 501.

[17] Hamon, D. P. G. *J. Am. Chem. Soc.* **1968**, *90*, 4513.

[18] Lee-Ruff, E. *Can. J. Chem.* **1972**, *50*, 952.

[19] Morton, D. R.; Turro, N. *J. Am. Chem. Soc.* **1973**, *95*, 3947.

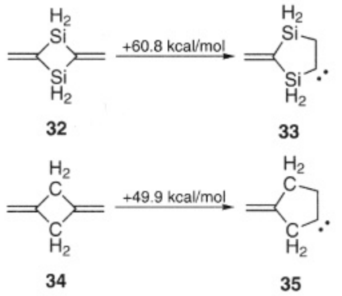
[20] Attempted one-step synthesis of **30** by a Wittig reaction on **29** yields only ring-opened products: LaLancette, E. A. *J. Org. Chem.* **1964**, *29*, 2957.

[21] GAMESS (General Atomic and Molecular Electronic Structure System): Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

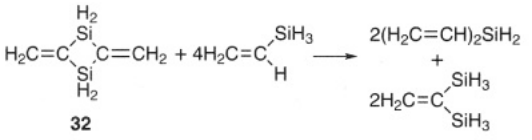
[22] (a) H: Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) C, O: Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Si: Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (d) Standard polarization were used. H (p = 1.1), C (d = 0.8), O (d = 0.8), Si (d = 0.395).

(MP2)[23] level with HF zero-point vibrational energy (ZPE) corrections scaled by 0.89.[24] As shown in Scheme 6, the energy difference is a surprising 10.9 kcal/mol greater for the silacyclic systems than for the carbocyclic rings. Thus on this basis alone one would have predicted that **30** would be much more likely to isomerize to a carbene than would **24**—a prediction that is opposite to the experimental findings.

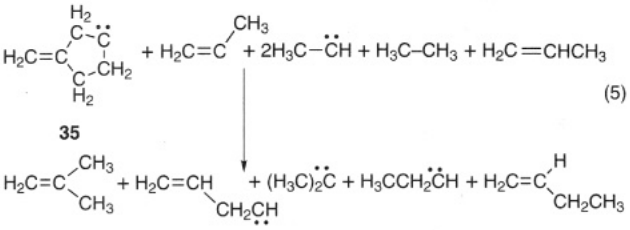
Scheme 6. Energetic Differences in the Dimethylenecyclobutanes and Their Respective Carbenes



To determine the specific role of ring strain in this dichotomous situation we utilized homodesmic reactions,[25] in which the number of each group and type of bond is conserved, two examples of which (**32** and **35**) are shown in eqs 4 and 5.



$$\mathrm{H_2C{=}C(SiH_2)_2C{=}CH_2} + 4\,\mathrm{H_2C{=}C(SiH_3)H} \longrightarrow 2(\mathrm{H_2C{=}CH})_2\mathrm{SiH_2} + 2\,\mathrm{H_2C{=}C(SiH_3)_2} \quad (4)$$



$$\mathbf{35} + \mathrm{H_2C{=}C(CH_3)} + 2\,\mathrm{H_3C{-}\ddot{C}H} + \mathrm{H_3C{-}CH_3} + \mathrm{H_2C{=}CHCH_3} \longrightarrow \mathrm{H_2C{=}C(CH_3)_2} + \mathrm{H_2C{=}CH(CH_2\ddot{C}H)} + (\mathrm{H_3C})_2\ddot{C} + \mathrm{H_3CCH_2\ddot{C}H} + \mathrm{H_2C{=}C(H)CH_2CH_3} \quad (5)$$

Geometries for **32**−**39** and all of the components of the homodesmic reactions were optimized at the HF/6-31G(d) level, followed by MP2/6-31G(d) energies with HF ZPE scaled by 0.89. The calculated ring strains (under the rings) and the relief in ring strain (over the arrows) are shown in Scheme 7. The relief in ring strain energy from **32** to the ultimate product **36** is 20.4 kcal/mol, while 25.4 kcal/mol is relieved for the analogous all-carbon system **34** → **38**. In neither case does ring strain provide a large driving force expansion to the six-membered ring (**37** and **39**). Most dramatic is the result that only 13.8 kcal/mol of ring strain is lost in going from the silacycle **32** to carbene **33**, while 28.5 kcal/mol relief is experienced by the carbocycle **34** in isomerizing to carbene **35**. Thus, once again the calculations would lead one to predict exactly the opposite of the actual experimental results.

The considerable difference in ring-strain energy between carbenes **33** and **35** becomes understandable after examining the optimized geometries shown in Figure 1. The large Si−C−C−Si dihedral angle of **33** must be ascribed to the ring's willingless to accept considerable ring strain in order to maximize the hyperconjugative interaction of the C−Si bond and the vacant p-orbital of the singlet carbene.[10]

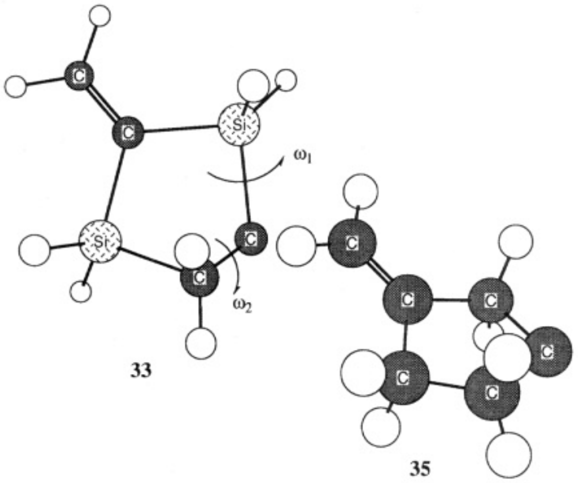
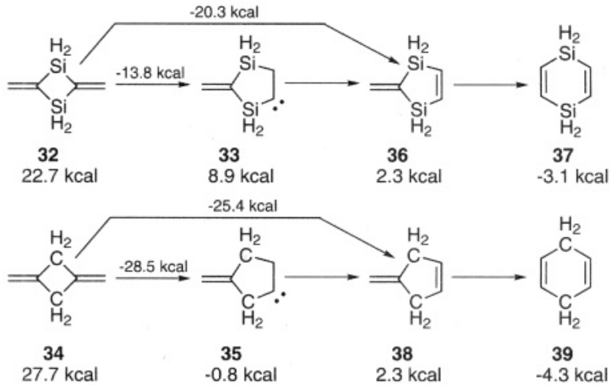


Figure 1. Structures for carbene intermediates using HF/6-31G(d). For structure **33** dihedral $\omega_1 = -58.0°$ and $\omega_2 = 64.4°$. For structure **35** these dihedral angles are 9.4° and 9.8°, respectively.

Scheme 7. Calculated Ring Strains in the Rearrangements of **32** and **34**



The final order of business for these two systems, calculation of the transition states leading to the two carbenes, turned out to be the most revealing. Optimized geometries for the two transition states are shown in Figure 2 and reveal a very late transition state (**40**) for the silacyclic rearrangement, and a very early transition state (**41**) for the carbocyclic system. At the HF/(6-31G(d) level **40** is, barely, an energy maximum 53.5 kcal/mol above **32**, yielding a miniscule 0.4 kcal/mol barrier for carbene **33** to return to **32**. However, introduction of electron correlation to the MP2/6-31G(d) level reverses the relative energies so that **40** is no longer a transition state but simply a point 55.5 kcal/mol above **32** on the path leading to the actual transition state, carbene **33**. For the all-carbon system **34** the HF barrier to carbene **36** is 80 kcal/mol and the reverse barrier is 42.3 kcal/mol. While the addition of correlation by MP2 lowers the forward barrier to 74.3 kcal/mol, the reverse barrier remains a very substantial 24.9 kcal/mol. Thus the strikingly different thermochemical behavior of these two systems is attributed to the fact that carbon migration in **34** has an early and high transition state while for **32** the carbene **33** is the sole barrier to overcome in isomerization to silacyclopentene **36**.

Although ring strain relief clearly plays a role in the two reactions studied, the overall picture does not change for

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[25] George, P.; Trachtman, M.; Bock, C. W.; Brett, Q. M. *Tetrahedron* **1976**, *32*, 317.

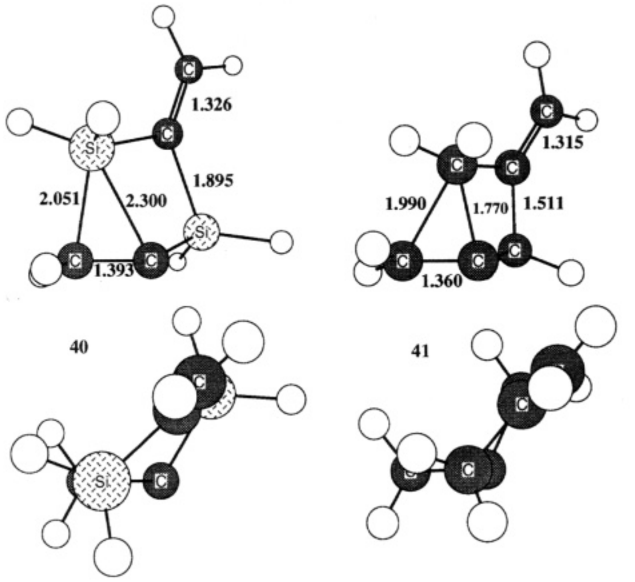
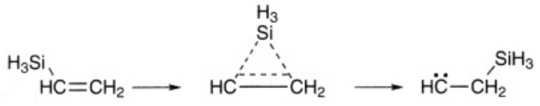
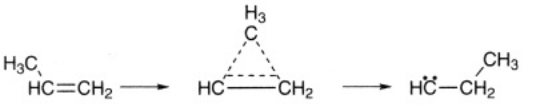


Figure 2. Front view (upper) and top view (lower) of HF/6-31G(d) structures for ring expansion (to carbene) transition states. Selected bond lengths are given in Å.

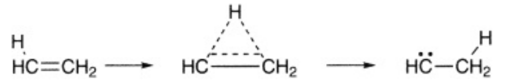
analogous acyclic systems. Thus in the theoretical results tabulated in eqs 6–10 we find that when silyl is the migrating group (eq 6) the transition state disappears with the introduction of increasing electron correlation [MP2/6-31G(d) and MP4[26]/6-311G(d,p)[27]], as is also the case for hydrogen migration (eq 8). However, for carbon migration (eq 7) even at the MP4 level of theory a substantial barrier for return of the carbene to propene remains. For comparison, isomerization of vinylsilane via H-migration is shown in eq 9 where the resulting carbene is 8.8 kcal/mol higher in energy than the carbene formed by silyl migration in eq 6. This difference is due to a combination of β-stabilization and α-destabilization of the singlet carbene by silyl substitution. Likewise, one finds from the results in eqs 6 and 10 that H-migration in propene requires 12.1 kcal/mol less than methyl migration, and produces a carbene (dimethylmethylene) which is more stable by 11.1 kcal/mol.


(6)

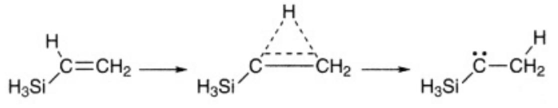
HF/6/31G(d) (kcal/mol)	74.1	68.5
MP2/6-31G(d)	68.5	71.1
MP4/6-311G(d,p)	63.4	68.1


(7)

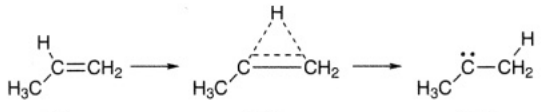
HF	91.3	70.7
MP2	88.6	84.8
MP4	84.9	78.8


(8)

HF	79.0	66.2
MP2	79.6	80.3
MP4	75.0	74.9


(9)

HF	84.5	74.0
MP2	77.8	81.8
MP4	74.9	76.9


(10)

HF	78.8	60.4
MP2	77.8	72.8
MP4	72.8	67.7

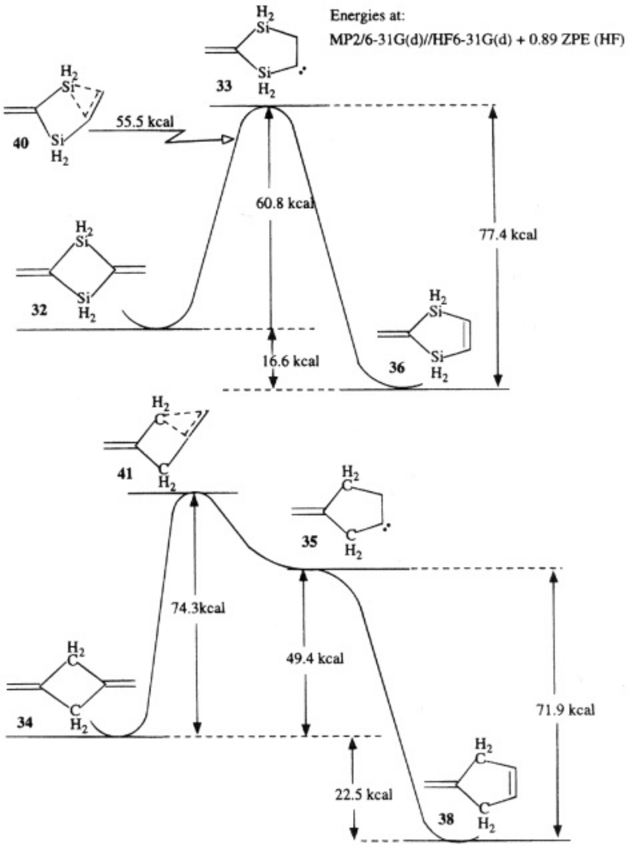
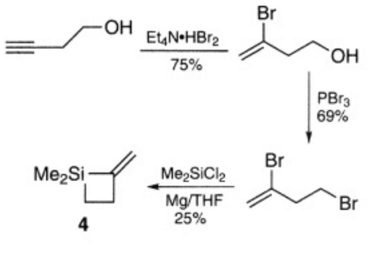


Figure 3. Energy surfaces for the isomerization of **32** and the hypothetical isomerization of **34**.

Thus we return to the question of the mechanism of the thermal isomerization of methylene silacyclobutane **4** to silacyclopentenes **6** with greater confidence that this may indeed be a concerted rearrangement. We were unable to synthesize **4** by the reported[5] route of copyrolysis of dimethylsilacyclobutane (**42**) and allene for in our hands this reaction produced **4** in yields of less than 1%. Thus it was necessary to synthesize **4** by the more tedious stepwise route shown in Scheme 8. Coupling of a 1:1 mixture of dichlorodimethylsilane and 2,4-dibromo-1-butene with magnesium produced **4** contaminated with **6a** (**4**:**6a** ca.8:1) which required final purification of **4** by preparative gas chromatography.

Scheme 8



4

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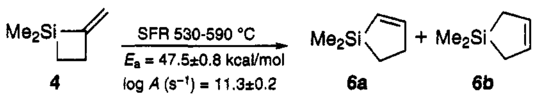
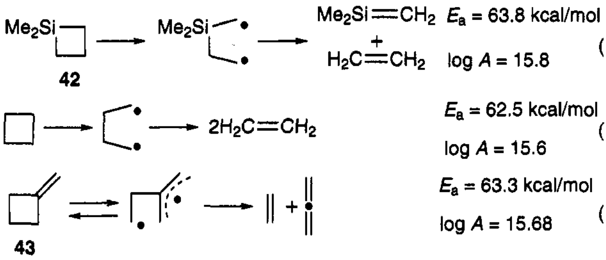
Kinetic investigation of the thermal isomerization of **4** to **6** (eq 11) was carried out in the SFR over a temperature range of 530−590 °C. On the basis of 13 rate determinations in this temperature range, the Arrhenius plot gave the first-order rate constant for the formation of **6** (**a** + **b**). The Arrhenius parameters, $E_a = 47.5 \pm 0.8$ kcal/mol and $\log A = 11.3 \pm 0.2$, are in accord with a concerted process although the energy of activation is close to what one might expect for the strength of a C−C bond in **4**. Certainly the negative value of the activation entropy, $\Delta S^{\ddagger} = -10.7$ eu at 559 °C, demands a constrained transition state as opposed to a homolytic dissociation.



(11)

The rearrangement of **4** is surprising since it has long been known that silacyclobutanes (e.g., **42**, eq 12),[28] in analogy to cyclobutane[29] (eq 13), thermally decomposes to silenes and ethylene via homolytic cleavage of a carbon−carbon bond.[30] It was thus not obvious as to why **4** did not choose to undergo thermal decomposition by an analogous route. Indeed the all-carbon analog of **4**, methylenecyclobutane **43** (eq 14), decomposes to ethylene and allene with almost identical Arrhenius parameters as for cyclobutane.[31] This has been interpreted as assistance to ring opening by the double bond, but cleavage from the diradical requires bond rotation and concomitant loss of allylic resonance.[32]

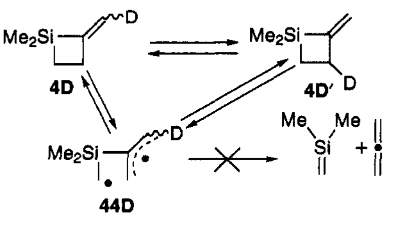


(12)

(13)

(14)

In order to determine whether a nonproductive homolysis of **4** occurs in the thermolysis, deuterium-labeled **4D** (ca. 1:1, *E*:*Z*) was synthesized by the same route as in Scheme 8 using Et_4N^{+}-DBr_2 in the first step. If diradical **44D** were formed, but did not proceed to dimethylsilene and allene, its equilibrium existence would be revealed by scrambling of deuterium between the allylic methylene and the terminal vinyl positions (eq 14). ^{2}H-NMR (Figure 4) of the pyrolysate from FVP of **4D** at a temperature just below that required for significant isomerization to **6** revealed clean scrambling of the deuterium into the allylic methylene by the absorption at δ 2.74. Thus ring opening to the 1,4-diradical is taking place at temperatures below those required for the rearrangement to the carbene.



(15)

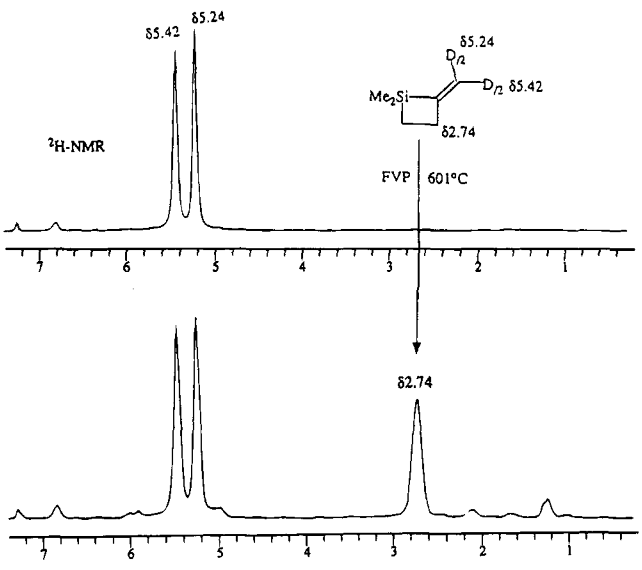
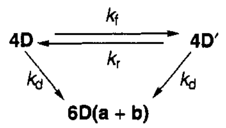


Figure 4. ^{2}H-NMR of monodeuterated **4** before and after FVP at 601 °C.

As seen in Figure 4, the conversion of **4D** to **4D′** was sufficiently clean to attempt kinetic studies. This was accomplished using the SFR system over a temperature range of 460−530 °C with the products being condensed in liquid N_2-cooled NMR tubes and analyzed by ^{2}H-NMR. A rate expression was derived by adopting Davidson's model[33] (Scheme 9). On the basis of 13 determined rate constants of the formation of **4D′** over the temperature range, the Arrhenius plot gave a straight line and yielded Arrhenius parameters of $\log A = 13.56$ and $E_a = 50.85$ kcal/mol, in perfect agreement with a homolytic ring opening. The Arrhenius parameters are also quite similar to those reported by Doering and Gilbert[32] for the interconversion of 2,2-dideuterio- and α,α-dideuteriomethylenecyclobutane ($\log (k_f + k_r) = 14.77 - 49500/2.3RT$), via a diradical intermediate.

Scheme 9. Kinetic Scheme for Thermal Rearrangements of **4D**



Thus an almost complete picture of the energetics of the thermolysis of methylenesilacyclobutane **4** is available and is shown in Figure 5. Of note is the fact that although the energy of activation for homolytic ring opening is greater than that for carbene formation, the former reaction occurs at lower temperatures due to the more favorable entropic factor. Unknown and likely to remain unknown for the foreseeable future is the barrier for closure of 1,4-diradical **44** to return to **4**. Also unknown is the barrier for cleavage of **44** to dimethylsilene and allene since this reaction is not observed and the reverse reaction is not suited for kinetic study. Indeed it is this barrier, to some degree due to the weakness of the silicon−carbon π-bond, to which this first example of a thermal "untwisted" olefin-to-carbene rearrangement owes its existence.

Experimental Section

General Methods. Low resolution mass spectra (GCMS) and infrared spectra (GC-FTIR) were obtained on a Hewlett Packard 5970

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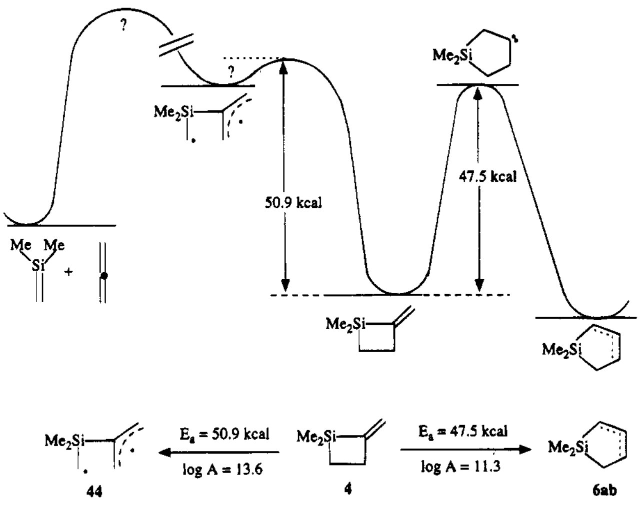

Figure 5. Energetic profile of the thermal isomerizations of **4**.

GC-MS-IR spectrometer and high resolution mass spectra were obtained on a Kratos MS 50 spectrometer. NMR spectra were acquired on a Varian VXR-300 spectrometer with $CDCl_3$ as the solvent unless otherwise specified. To assure quantitation of the ^{13}C- (75.429 MHz) and ^{29}Si-NMR (59.591 MHz) spectra, chromium(III) acetylacetonate was used in $CDCl_3$ with a relaxation delay of 5 s. TMS was used as an external standard for ^{29}Si-NMR. ^2H-NMR spectra were obtained at 46 MHz using a 63° pulse with 4032 data points and 1000 Hz spectral width. Field stability was obtained using a ^1H lock. Preparative gas chromatographic (GC) separations were performed on either a Varian Model 920 (small scale) or a Varex PSGC model (large scale). Flash vacuum pyrolyses (FVP) were carried out by slow distillation of compounds through a heated, seasoned, horizontal quartz pyrolysis tube (16 mm i.d., 200 mm long) packed with quartz chips and the product was collected in a trap cooled with liquid N_2. Pressures measured by ion gauge behind the liquid N_2 trap were typically $10^{-4}-10^{-5}$ Torr. The stirred flow reactor (SFR) system is described in refs 12 and 33 and used a 60 mL/min He flow to sweep the material through the reactor zone immediately into a Varian 6000 GC (FID) with the option of diverting the separated products into a VG SX-300 quadrupole mass spectrometer. Unimolecular, wall-less reaction was maximized by using very low concentrations of the sample (ca. 0.004%) in He. All compounds studied by SFR were purified by preparative GC and had purities >99%. The kinetic equations that are used in this type of reactor are described in ref 33. Commercially available compounds were purchased from Aldrich Chemical Co. unless otherwise specified.

SFR Kinetic Studies of Cis–Trans Olefin Isomerization. The olefins studied are given in Table 1. Cis–trans isomerizations of 2-butene, 1-phenyl-1-propene, and 1-(trimethylsilyl)-1-propene are reversible under the conditions of study. For (*Z*)-2-butene $K_{eq} = 1.31$ obtained by Rabinovitch[34] was utilized to calculate k_f and the Arrhenius parameters from 15 rate determinations over the temperature range of 617–677 °C were a close match with the literature values[28] of $E_a = 62.8$ kcal/mol and $\log A = 13.78$. The K_{eq}'s for β-methylstyrene and 1-(trimethylsilyl)propene were not found in the literature and thus their reaction rates were calculated from equations found in ref 33.

(a) (*Z*)-2-Butene: SFR isomer separation on a 21 ft 20% $AgNO_3$ saturated ethylene glycol on Chromasorb W column; 15 rate determinations over the temperature range of 617–677 °C; $E_a = 62.34 \pm 0.78$ kcal/mol; $\log A = 13.48 \pm 0.19$; $\Delta H^* = 60.50 \pm 0.78$ kcal/mol; $\Delta S^* = 1.09 \pm 0.85$ eu; at $T_{ave} = 651.0$ °C for reaction order 1.000.

(b) (*Z*)-1-(Trimethylsilyl)propene:[35] GC purified on a 25 ft 20% SE30 on Chrom W column, SFR isomer separation on a 15 ft 15% dimethylsulfolane on 60–80 mesh Firebrick, 27 °C; 13 rate determinations over the range of 550–610 °C; $E_a = 56.00 \pm 0.55$ kcal/mol; $\log A = 13.00 \pm 0.14$; $\Delta H^* = 54.30 \pm 0.55$ kcal/mol; $\Delta S^* = -3.10 \pm 0.64$ eu; at $T_{ave} = 582.4$ °C for reaction order 1.000.

(c) β-Methylstyrene: Cis–trans isomer separation by GC with a 5 ft 10% CW-20-M column; 14 rate determinations over a range of 540–590 °C; $E_a = 60.18 \pm 0.68$ kcal/mol; $\log A = 15.05 \pm 0.18$; $\Delta H^* = 58.51 \pm 0.68$ kcal/mol; $\Delta S^* = 6.30 \pm 0.81$ eu; at $T_{ave} = 565.8$ °C for reaction order 1.000.

(d) (*Z*)-β-(Trimethylsilyl)styrene:[36] To a solution of 10 mL of *i*-Bu_2-AlH (10 mmol, 1 M in THF) and 10 mL of heptane was added 0.85 g (10 mmol) of 1-methylpyrrolidine at room temperature. After the mixture was stirred for 2 min, 1.74 g (10 mmol) of 1-phenyl-2-(trimethylsilyl)acetylene was added. The mixture was stirred at 60 °C for 15 h and at 100 °C for 4 h and then cooled to room temperature and quenched with water. The separation organic layer was washed with water and then with brine after which the solvents were removed by distillation to provide (*Z*)-β-(trimethylsilyl)styrene[36] in 91% yield (1.6 g). Preparative GC purification was accomplished on a 25 ft 20% SE30 on Chrom W column. SFR isomer separation was on a 5 ft 10% CW-20-M column; 16 rate determinations over the range of 470–527 °C; $E_a = 53.0 \pm 0.29$ kcal/mol; $\log A = 14.29 \pm 0.08$; $\Delta H^* = 51.47 \pm 0.29$ kcal/mol; $\Delta S^* = 2.984 \pm 0.38$ eu; at $T_{ave} = 497.4$ °C for reaction order 1.000.

(e) (*Z*)-β-*tert*-Butylstyrene:[37] To a suspension of 5.83 g (15 mmol) of benzyltriphenylphosphonium chloride in THF at −78 °C under a N_2 atmosphere was added 6.2 mL (15 mmol, 2.45 M in heptane) of *n*-BuLi via cannula. After the mixture was slowly warmed to room temperature (ca. 1 h), the suspension had disappeared and the resulting solution was red. Trimethylacetaldehyde (1.29 g, 15 mmol) was slowly dropped into the mixture at room temperature and refluxed overnight. After the mixture had cooled, 100 mL of ether was added and the resulting white solid was removed by filtration. The ether was carefully removed by rotary evaporation until a white solid appeared. An additional 20 mL of ether was added with stirring and the solid was removed by filtration. The filtrate was evaporated until the total volume was ca. 10 mL and then percolated through a silica gel column with ether as the eluant. Removal of the ether afforded 0.81 g (34%) of a 3:1 mixture of cis and trans isomers[37] which were separated by preparative GC on a 12 ft 15% SE-30-CW column. SFR isomer separation was accomplished on a 5 ft 10% CW-20-M column; 14 rate determinations over the range of 470–527 °C; $E_a = 54.90 \pm 0.56$ kcal/mol; $\log A = 14.79 \pm 0.07$; $\Delta H^* = 55.37 \pm 0.26$ kcal/mol; $\Delta S^* = 5.279 \pm 0.34$ eu; at $T_{ave} = 498.3$ °C for reaction order 1.000.

(f) (*Z*)-1,2-Bis(trimethylsilyl)ethylene:[38] GC purification on a 25 ft 15% SE-30-CW column, SFR isomer separation on a 5 ft 15% SE-30-CW column; 15 rate determinations over the range of 476–526 °C; $E_a = 52.68 \pm 0.37$ kcal/mol; $\log A = 13.94 \pm 0.11$; $\Delta H^* = 51.14 \pm 0.37$ kcal/mol; $\Delta S^* = 1.37 \pm 0.48$ eu; at $T_{ave} = 500.5$ °C for reaction order 1.000.

Copyrolysis of 18 and 1,1-Dimethylallene. Copyrolysis (475 °C) of 373 mg of 1,2-dimethoxytetramethyldisilane[39] (**18**) and 1.254 g of isoprene was conducted by dropwise addition of a mixture of the two through a vertical quartz tube (ca. 1.6 × 30 cm heated zone) packed with quartz chips with a constant N_2 stream of 40 mL/min. Analysis and separation of the condensed pyrolysate by GC revealed 39% dimethyldimethoxysilane and 31% 2-(dimethylsilyl)-3-methyl-1,3-butadiene (**21**): ^1H-NMR ($CDCl_3$) δ 5.79 ppm (H_A, d of d, $J_{ASiH} = 0.5$ Hz, $J_{AB} = 2.5$ Hz, COSY shows very weak coupling with H_C and/or H_D, 1 H), 5.5 (H_B, overlapped and broadened d of d, $J_{AB} = 2.5$ Hz, $J_{BMe} = 0.9$ Hz, COSY shows weak coupling at δ 5.01/5.03 and stronger coupling at δ 1.88, 1 H), 5.03 (H_D, broadened s, COSY does not resolve H_C and H_D, and shows coupling with δ 5.79, 5.5, and 1.88, 1 H), 5.01 (H_C, q, $J_{CMe} = 1.5$ Hz, 1 H), 4.24 (SiH, d of heptet, $J_{ASiH} = 0.9$ Hz, $J_{MeSiH} = 3.9$ Hz, 1 H), 1.88 (Me, d of d, $J_{CMe} = 1.5$ Hz, J_{BMe} = ca. 0.9 Hz, 3H), 0.22 ($SiMe_2$, d, $J_{MeSiH} = 3.9$ Hz, 6 H); ^{13}C-NMR ($DCCl_3$) δ −3.67 (SiMe), 21.07 (Me), 114.80 (C1), 125.77 (C4), 145.4 (C3), 149.50 (C2), ATP analysis shows only C1 and C4 bonded to H and both are CH_2, HETCOR analysis shows only direct CH coupling between C1 and H_C and/or H_D and between C4 and H_A and H_B, long range HETCOR (HMBC) shows C2 coupled at δ 5.01/5.03 and C3

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coupled at δ 5.5 and 5.79; mass spectrum *m/z* (% relative abundance) 126 (M^+, 15), 112 (11), 111 (100, M − Me), 109 (22), 85 (28), 83 (38), 73 (12), 71 (14), 69 (14), 67 (19), 59 (89), 58 (25), 55 (17), 53 (21), 45 (21), 44 (15), 43 (85); calcd for $C_7H_{14}Si$ 126.08648, measured 126.08699; GCIR 3094, 2970, 2129 (s), 1258, 895 (vs). Anal. Calcd for $C_7H_{14}Si$: C, 66.64; H, 11.18. Found: C, 66.44; H, 11.37.

(α-Bromovinyl)dimethylchlorosilane (23). A 250-mL 3-necked round-bottom flask equipped with a mechanical stirrer, additional funnel, and septum was charged with vinyldimethylchlorosilane (Petrarch Chemical Co.) (13.4 mL, 100 mmol) under slow argon flow. After cooling the flask to −78 °C and initiating magnetic stirring, Br_2 (5.6 mL) was added dropwise to the solution. After completion of the addition the reaction mixture was warmed to room temperature for 15 min. After the reaction mixture was cooled to 0 °C with an ice bath, triethylamine (93 mL, 600 mmol) was added cautiously. After the reaction mixture was stirred at room temperature for 2 h, the precipitated salts were removed by filtration under Ar and washed twice with dry Et_2O. Distillation of the combined filtrates afforded 11.65 g of **23** (58.4%, bp 64−65 °C/35 Torr). GCMS *m/z* (% rel intensity) 202 (9, M + 4), 200 (32, M + 2), 198 (23, M^+), 185 (35), 183 (25), 159 (100), 157 (73); GC-FTIR ν (cm^{-1}) 2979 (w), 1594 (w), 1400 (m), 1264 (s), 922 (s), 827 (vs); ^1H-NMR ($CDCl_3$) δ 0.56 (s, 6 H), 6.38 (d, J = 1.8 Hz, 1 H), 6.47 (d, J = 2.1 Hz, 1 H); ^{13}C-NMR δ 0.43 (2 C), 131.8 (1 C), 131.9 (1 C).

2,4-Dimethylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane (24) and 2,4,6-Trimethylene-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (25). To an oven-dried, argon-filled 50-mL 3-necked round-bottom flask equipped with a magnetic stirrer, condenser, and septum and charged with magnesium (0.292 g, 12 mmol) and 10 mL of dry THF was added 0.1 mL of dibromoethane to activate the magnesium. Chlorosilane **23** (2.06 g, 10.3 mmol) was added dropwise at a rate sufficient to maintain reflux, after which the reaction mixture was refluxed for an additional 3 h. The reaction mixture was poured into a cooled mixture of 20 mL of hexanes and 20 mL of 2.0 M HCl, and the separated organic layer was washed with dilute HCl and then twice with H_2O and dried over sodium sulfate. Solvents were removed by distillation. Analysis by analytical GC of several identical runs gave 66−71% **24**, 20−21% **25**, 1−1.5% trimer, and 0−1.5% tetramer, all of which were separated by preparative GC on a 9 ft, $^1/_8$ in. i.d. column packed with 20% SE-30-CW. **24**: GCMS *m/z* (% rel intensity) 168 (100, M^+), 153 (95, M − Me), 127 (23), 73 (25); HRMS calcd for $C_8H_{16}Si_2$ *m/z* 168.07908, measured *m/z* 168.0789; GC-FTIR ν (cm^{-1}) 3000 (w), 1601 (w), 1426 (w), 1250 (m), 840 (vs), 791 (s); ^1H-NMR δ 0.24 (s, 12 H), 6.37 (s, 4 H); ^{13}C-NMR (75.429 MHz) δ −1.12 (4 C), 137.95 (2 C, with 2 H attached), 161.69 (2 C, with no H attached); ^{29}Si-NMR δ −6.85; UV (nm, hexanes) $\lambda_{max}(\epsilon)$ 212 (2.85×10^4), 298 (330).[40] **25**: GCMS *m/z* (% rel intensity) 252 (7, M^+), 237 (100, M − Me), 73 (13); HRMS calcd for $C_{12}H_{24}Si_3$ *m/z* 252.1189, measured *m/z* 252.1186; GC-FTIR ν (cm^{-1}) 3009 (w), 2963 (w), 2932 (w), 1572 (vw), 1416 (w), 1255 (m), 847 (s); ^1H-NMR ($CDCl_3$) δ 0.16 (s, 18 H), 6.33 (s, 6 H); ^{13}C-NMR δ −2.34 (6 C), 138.94 (3 C), 153.32 (3 C); ^{29}Si-NMR δ −9.04; UV (nm, hexanes) $\lambda_{max}(\epsilon)$ 197 (1.69×10^4), 250 (1070). Cyclic tetramer: mp 159−160 °C; GCMS *m/z* 337 (22, M + 1), 336 (64, M^+), 321 (95, M − Me), 247 (72), 233 (52), 73 (100); HRMS calcd for $C_{16}H_{32}Si_4$ *m/z* 336.15812, measured *m/z* 336.15835; GC-FTIR ν (cm^{-1}) 3001 (w), 2933 (w), 1612 (w), 1256 (m), 961 (w), 926 (w), 841 (vs); ^1H-NMR δ 0.12 (s, 24 H), 6.30 (s, 8 H); ^{13}C-NMR δ −2.10 (8 C), 140.54 (4 C), 152.00 (4 C); ^{29}Si-NMR δ −7.61; UV (nm, hexanes) λ_{max} (ϵ) 197 (1.99×10^4), 245 (856). Cyclic pentamer: GCMS *m/z* 421 (13, M + 1), 420 (30, M^+), 405 (10, M − Me), 347 (44), 197 (82), 73 (100); GC-FTIR ν (cm^{-1}) 2958 (m), 2932 (m), 1612 (w), 1431 (w), 1255 (m), 985 (m), 837 (s), 787 (s).

Flow Pyrolysis of 24. Pyrolysis of **24** was conducted in a vertical N_2-flow system at 600 °C and the pyrolysate collected at −78 °C. GC analysis of the pyrolysate showed only **24** (75%) and **26** (25%). **26**: GCMS *m/z* 169 (6, M + 1), 168 (35, M^+), 153 (100, M − Me), 127 (20), 73 (16), 59 (17); GC-FTIR ν (cm^{-1}) 2996 (w), 2960 (m), 1598 (w), 1441 (w), 1308 (w), 1255 (m), 845 (vs), 794 (s). NMR spectra were obtained from subtraction of the spectra of **24** from the spectra of the pyrolysate. ^1H-NMR δ 0.15 (s, 12 H), 6.43 (s, 2 H), 7.14 (s, 2 H); ^{13}C-NMR δ −1.88 (4 C), 137.98 (1 C), 152.12 (1 C), 154.36 (2 C); ^{29}Si-NMR δ −4.03.

1,3-Dimethylene-2,2,4,4-tetramethylcyclobutane (30).[42] The procedures used in the stepwise synthesis of **30** are adaptations of three literature procedures.[17−19] An oven-dried 100-mL round-bottom flask equipped with a magnetic stirrer and Dean-Stark trap and containing **29** (14.0 g, 100 mmol) and aniline (9.18 mL, 100 mmol) was charged with *p*-toluenesulfonic acid monohydrate (0.125 g) in 50 mL of benzene. The mixture was stirred under reflux for 6 h while the water was removed by azeotropic distillation. After removal of benzene at atmospheric pressure, the products were separated by vacuum distillation. **2,2,4,4-Tetramethyl-3-(phenylimino)cyclobutan-1-one**: 60% yield; bp 100 °C/Torr; GCMS *m/z* 215 (12, M^+), 145 (100), 130 (31), 77 (30); GC-FTIR ν (cm^{-1}) 3075 (w), 2975 (s), 2935 (m), 2876 (w), 1808 (m), 1308 (w), 1697 (vs), 1595 (m), 1462 (m), 1049 (m). A 500-mL 2-necked flask equipped with a magnetic stirrer, addition funnel, and argon flow system was charged with potassium *tert*-butoxide (8.96 g, 80 mmol), *tert*-butyl alcohol (50 mL), and dry ether (200 mL). After the KO-*t*-Bu dissolved, methyltriphenylphosphonium bromide (28.56 g, 80 mmol) was added in one portion and the mixture was stirred at room temperature for 1 h before 2,2,4,4-tetramethyl-3-(phenylimino)cyclobutan-1-one (8.56 g, 40 mmol) after which the yellow mixture was stirred overnight. After filtration the solution was diluted with water and the water layer extracted with ether (40 mL × 2). The ether was removed by rotary evaporation to yield crude 2,2,4,4-tetramethyl-3-(phenylimino)-1-methylenecyclobutane [GCMS *m/z* 213 (33, M^+), 198 (33, M − Me), 145 (55), 117 (100), 95 (60), 77 (67); GC-FTIR ν (cm^{-1}) 3072 (m), 2971 (vs), 2873 (m), 1781 (w), 1724 (s), 1657 (s), 1594 (m), 1485 (m), 1222 (m), 1028 (m), 888 (m)] which was used without further purification. The crude imine was stirred and refluxed in 100 mL of 50% HOAc. The reaction mixture was cooled, quenched with $NaHCO_3$, and extracted three times with ether. The combined ether layers were washed sequentially with dilute HCl, aqueous $NaHCO_3$, and saturated aqueous NaCl before being dried over Na_2SO_4. Evaporation of the ether yielded 3.31 g (60%) of 2,2,4,4-tetramethyl-3-methylenecyclobutan-1-one: GCMS *m/z* 138 (1.5, M^+), 110 (76, M − CO), 95 (100), 70 (26), 67 (85), 55 (29), 53 (28); GC-FTIR ν (cm^{-1}) 3071 (w), 2972 (s), 2876 (m), 1805 (vs), 1673 (m), 1457 (m), 999 (m), 892 (m). A 100-mL 2-necked flask equipped with a magnetic stirrer addition funnel and argon flow system was charged with potassium *tert*-butoxide (2.24 g, 20 mmol), *tert*-butyl alcohol (12 mL), and dry ether (50 mL). Immediately after dissolution of the KO-*t*-Bu methyltriphenylphosphonium bromide (7.14 g, 20 mmol) was added and the mixture was then stirred at room temperature for 1 h before addition of the 3-methylenecyclobutanone (1.27 g, 9.2 mmol) to the yellow mixture, followed by stirring for an additional 6 h. After filtration the solution was diluted with water and the water layer was extracted with pentane (15 mL × 3). The combined pentane extracts were washed by dilute HCl and H_2O and dried over sodium sulfate. Removal of pentane by evaporation yielded crude **30** (1.0 g, 80%) which was purified to >99.5% purity by preparative GC on a 9 ft column ($^1/_8$ in. i.d.) packed with 20%-30-CW. **30**: mp 68−69 °C (lit.[19] mp 66−68 °C); GCMS *m/z* 136 (9, M^+), 121 (100, M − Me), 105 (35), 93 (44), 91 (45), 79 (49), 77 (31), 67 (24), 53 (23); GCMS *m/z* 136 (9, M^+), 121 (100, M − Me), 105 (35), 93 (44), 91 (45), 79 (49), 77 (31), 67 (24), 53 (23); HRMS calcd for $C_{10}H_{16}$ *m/z* 136.12520, measured *m/z* 136.12610; HRMS calcd for C_9H_{13} (M − CH_3) *m/z* 121.10173, measured 121.10187; GC-FTIR ν (cm^{-1}) 3039 (s), 2933 (s), 1492 (m); ^1H-NMR δ 1.23 (s, 12 H), 4.84 (s, 4 H); ^{13}C-NMR δ 27.56 (4 C), 47.90 (2 C), 100.39 (2 C), 168.05 (2 C); UV (nm, hexanes) λ_{max} (ϵ) 195 (1.6×10^3).

2,4-Dibromo-1-butene. HBr was produced by adding PBr_3 (10.46 mL, 110 mmol) dropwise to water (5.94 mL, 330 mmol). The HBr thus produced was bubbled through tetraethylammonium bromide (63.0 g, 300 mmol) in 300 mL of methylene chloride at 0 °C after which the

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[40] We ascribe this band to a $\pi \rightarrow \sigma^*$ transition as discussed in ref 41. This weak band is observable for all bis(silyl)ethylenes and the red shift for **4** is consistent with a strained ring.

[41] Robin, M. B.; Hart, R. R.; Kuebler, N. A. *J. Chem. Phys.* **1966**, *44*, 1803.

[42] Slobodin (Slobodin, Y. M. *Zh. Org. Chem.* **1988**, *24*, 1556) reported the synthesis of **24** by photodimerization of 3-methyl-1,2-butadiene. Their reported ^{13}C NMR spectrum (δ 24.16, 111.74, 144.36) is considerably different than found by us.

Cl_2CH_2 solution was weighed to find that 20.25 g of HBr (250 mmol) was absorbed by the Et_4NBr solution. After injection of 3-butyn-1-ol (18.9 mL, 120 mmol), the reaction mixture was heated at 40 °C for 5 h and cooled to 0 °C and 600 mL of ether was added. After filtration 28.39 g (75%) of 3-bromo-3-buten-1-ol[43] was obtained by vacuum distillation (bp 69−70 °C/11 Torr). GCMS *m/z* 152 (21, M + 2), 150 (21, M^+), 122 (100), 53 (17); GC-FTIR ν (cm^{-1}) 3662 (m), 2948 (s), 1626 (s), 1387 (m), 1125 (s), 1048 (vs), 891 (s); ^1H-NMR δ 2.27 (s, 1 H), 2.64 (d of t, $J = 6$ and 0.9 Hz, 2 H), 3.78 (t, $J = 6$ Hz, 2 H), 5.51 (d, $J = 1.8$ Hz, 1 H), 5.68 (m, 1 H). Without further purification this alcohol was placed in a 100-mL round-bottom flask equipped with an addition funnel and magnetic stirrer and cooled to −10 °C by an ice/salt bath. After dropwise addition of PBr_3 (5.70 mL) the reaction mixture was allowed to warm to room temperature and then stirred overnight. The product was distilled (72−73 °C/18 Torr) into a receiver containing 10 mL of H_2O, washed twice with cold concentrated H_2SO_4, and dried over K_2CO_3. Vacuum distillation gave 26.42 g (69%) of 2,4-dibromo-1-butene: GCMS *m/z* 216 (9, M + 4), 214 (17, M + 2), 212 (9, M^+), 135 (52), 133 (55), 53 (100); GC-FTIR ν (cm^{-1}) 3110 (w), 2980 (m), 1627 (s), 1432 (m), 1315 (m), 1277 (m), 1177 (vs), 1102 (m), 895 (vs), 819 (w); ^1H-NMR δ 2.94 (t, $J = 6$, 9 Hz, 2 H), 3.55 (t, $J = 6.9$ Hz, 2 H), 5.56 (d, $J = 1.8$ Hz, 1 H), 5.71 (d, $J = 1.8$ Hz, 1 H); ^{13}C-NMR δ 29.50 (1 C), 43.87 (1 C), 119.35 (1 C), 129.73 (1 C).

2-Methylene-1,1-dimethyl-1-silacyclobutane (4). A 250-mL 2-neck round-bottom flask equipped with addition funnel, condenser, and magnetic stirrer was charged with magnesium (1.02 g, 42 mmol), 80 mL of dry THF, and 0.2 mL of 1,2-dibromoethane. A solution of 2,4-dibromo-1-butene (2.23 g, 10.4 mmol) and dimethyldichlorosilane (1.26 mL, 10.4 mmol) in 10 mL of THF was added dropwise at a rate sufficient to maintain mild reflux after which the reaction mixture was refluxed for an additional hour. After cooling to room temperature the reaction mixture was poured into a cold mixture of 300 mL of pentane and 50 mL of 2.0 M HCl. THF was removed by repetitive washing with very dilute aqueous acid. After the mixture was dried over sodium sulfate, most of the pentane was removed by distillation through a 30 cm fractionating column. At this point **4** is contaminated by **6a** (ca. 12%) presumably because (*Z*)-1,4-dibromo-1-butene is a minor product in the synthesis of 2,4-dibromo-1-butene. Final purification of **4** was accomplished by preparative GC on a Varex PSGC Model 10-40 with a 6 ft column ($^3/_8$ in. i.d.) packed with 20% SE-30-CW. **4**: GCMS *m/z* 113 (1.2, M + 1), 112 (12, M^+), 97 (57, M − Me), 85 (12), 84 (100), 83 (12), 72 (23), 71 (14), 69 (14), 59 (17), 58 (69), 53 (12); GC-FTIR ν (cm^{-1}) 3045 (m), 2963 (s), 2914 (s), 1832 (w), 1415 (m), 1256 (s), 913 (s), 862 (vs), 814 (s); ^1H-NMR δ 0.32 (s, 6 H), 0.99 (t, $J = 8.7$ Hz, 2 H), 5.24 (d of t, $J = 6.0$, 2.1 Hz, 1 H), 5.42 (q, $J = 2.4$ Hz, 1 H); ^{13}C-NMR δ −0.81 (2 C), 10.19 (1 C), 31.95 (1 C), 118.24 (1 C), 158.50 (1 C). (The NMR resonances are shifted somewhat from those reported by Conlin[5] presumably because ours were obtained in $DCCl_3$ solution while Conlin's were obtained on a neat sample.)

Synthesis of **4D** was by the same procedure except that at the beginning 3-butyn-1-ol (20.0 mL, 263 mmol) and D_2O (23.75 mL, 1.315 mol) were placed in a 100-mL flask equipped with magnetic stirrer and septum. The mixture was stirred at room temperature for 5 h. Methylene chloride (50 mL) was added to extract the product, and the separated aqueous layer was extracted by two portions of H_2CCl_2 (25 mL). The combined methylene chloride layers was dried over Na_2SO_4 and used directly in the next step in which D_2O was used to react with PBr_3 to afford DBr with which to combine with Et_4NBr. The procedure from this point is identical as for **4**. From both the ^1H-NMR and ^2H-NMR spectra the deuterium in **4D** is present only in the syn and anti positions of the methylene unit in ca. a 1:1 ratio.

1,1-Dimethyl-1-silacyclopent-2-ene (6a).[44] GCMS *m/z* 113 (1.7, M + 1), 112 (14, M^+), 98 (10), 97 (100, M − Me), 95 (28), 71 (8), 69 (9), 58 (8), 53 (6); GC-FTIR ν (cm^{-1}) 2957 (s), 2911 (s), 1566 (m), 1445 (w), 1322 (w), 1258 (s), 1139 (w), 979 (w), 848 (vs), 794 (s). The NMR spectral data were obtained by subtracting that of **4** from the product mixture. ^1H-NMR δ 0.15 (s, 6 H), 0.70 (t, $J = 6.9$ Hz, 2 H), 2.48 (m, 2 H), 5.93 (d of t, $J = 2.1$ and 9.9 Hz, 1 H), 6.79 (d of t, $J = 10.2$ and 2.7 Hz, 1 H); ^{13}C-NMR δ −1.29 (2 C), 8.29 (1 C), 31.64 (1 C), 129.90 (1 C), 152.71 (1 C).

1,1-Dimethyl-1-silacyclopent-3-ene (6b).[45] GCMS *m/z* 113 (3.5, M + 1), 112 (31, M^+), 98 (10), 97 (100, M − Me), 95 (26), 71 (11), 59 (11), 58 (24); GC-FTIR ν (cm^{-1}) 3028 (s), 2916 (m), 2904 (s), 1605 (w), 1405 (w), 1260 (m), 1100 (s), 944 (w), 846 (vs); ^1H-NMR δ 0.17 (s, 6 H), 1.27 (d, $J = 1.2$ Hz, 4 H), 5.85 (t, $J = 1.2$ Hz, 2 H).

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