Organometallics 1986, 5, 698–707

parameters for rhodium, phosphorus, chlorine and oxygen and isotropic thermal parameters for all remaining atoms. Hydrogen atoms were not located. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[28] An absorption correction (XABS) was applied.[29] The atoms of the three dichloromethane molecules were assigned isotropic U values of 0.05 and were allowed to refine with variable occupancy. The final occupancies were 0.824 (6) for Cl(3)C(97)Cl(4), 0.774 (6) for Cl(5)C(98)Cl(6), and 0.859 (6) for Cl(7)C(99)Cl(8). Two low-angle reflections suffering from extinction were removed from the data set for the final cycles of refinement. A conventional R factor of 0.073 was obtained. The final difference map showed some residual electron density in the vicinity of the dichloromethane molecules, but otherwise no significant features were present.

Acknowledgment. We thank the National Science Foundation (CHE8217954) for financial support.

Registry No. 1·BPh4, 84774-75-4; **2a**, 100082-53-9; **2b**, 100082-55-1; **2b**·3CH$_2$Cl$_2$, 100164-67-8; **3**, 100082-57-3; **4**, 100082-59-5; **5a**, 100082-63-1; **5b**, 100102-33-8; **6**, 100082-65-3; [Rh$_3$(dpma)$_2$(CO)$_3$Cl$_2$]BPh$_4$, 100082-61-9; dimethyl acetylenedicarboxylate, 762-42-5; diethyl acetylenedicarboxylate, 762-21-0; rhodium, 7440-16-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positions, and structure factor amplitudes (53 pages). Ordering information is given on any current masthead page.

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[28] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[29] The method obtains an empirical absorption tensor from an expression relating F_o and F_c: Hope, H.; Moezzi, B., Department of Chemistry, University of California, Davis, CA.

[30] In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Transposition—A New Rearrangement of α-Silylsilylenes Involving Disilene Intermediates

Bong Hyun Boo and Peter P. Gaspar*

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received August 28, 1985

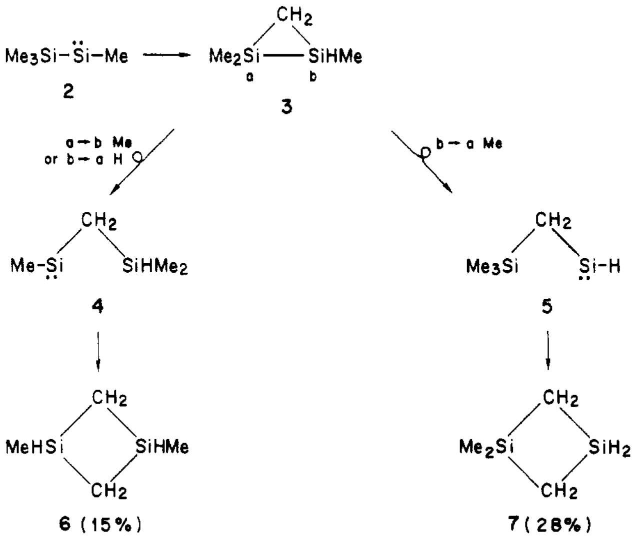
Evidence has been found for the rearrangement of $\mathrm{Me_3Si{-}\ddot{S}i{-}H}$ to $\mathrm{Me_2HSi{-}\ddot{S}i{-}Me}$ and for the formation of a $\mathrm{Me_2Si{=}SiHMe}$ intermediate. $\mathrm{Me_3Si{-}\ddot{S}i{-}H}$ also rearranges to two isomeric β-silylsilylenes $\mathrm{Me_2HSiCH_2{-}\ddot{S}i{-}H}$ and $\mathrm{Me{-}\ddot{S}i{-}CH_2SiH_2Me}$, the latter having been previously overlooked. The question whether methyl shifts occur in the ring opening of disiliranes $\overline{\mathrm{Me_2Si{-}SiHR{-}CH_2}}$ (R = H, Me) is discussed in light of these findings. An experimental value of 29 kcal/mol is derived for the activation energy for intramolecular C–H insertion by a divalent silicon center to form 1-methyl-1,3-disilacyclobutane.

Introduction

Reinvestigation of the gas-phase chemistry of (trimethylsilyl)silylene was prompted by the belated recognition that our previous observations on the rearrangements of $\mathrm{Me_3Si{-}\ddot{S}i{-}H}$ (**1**) underscored a nagging mechanistic question concerning the isomerization of alkylated α-silyl- to β-silylsilylenes.[2,3]

In 1978 Wulff, Goure and Barton both enlivened and revolutionized the study of divalent silicon species by a daring suggestion: that intramolecular C–H insertion by the divalent silicon center of methyl(trimethylsilyl)silylene (**2**) forms a disilirane, **3**, whose ring opening by competing hydrogen and methyl shifts completes the conversion of an α-silylsilylene **2** to a pair of isomeric β-silylsilylenes, **4** and **5**.[4] Further intramolecular C–H insertions by **4** and **5** can explain the formation of the stable 1,1- and 1,3-dimethyl-1,3-disilacyclobutanes **6** and **7**, obtained as end products of Scheme I.

Scheme I



While α-eliminations of acyclic disilanes forming silylenes and monosilanes by migration of hydrogen, halogen, and alkoxy groups are well-known,[5] Davidson and co-

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[1] Mo, S.-H.; Holten, J. D., III; Konieczny, S.; Ma, E. C.-l; Gaspar, P. P. *J. Am. Chem. Soc.* **1982**, *104*, 1424.

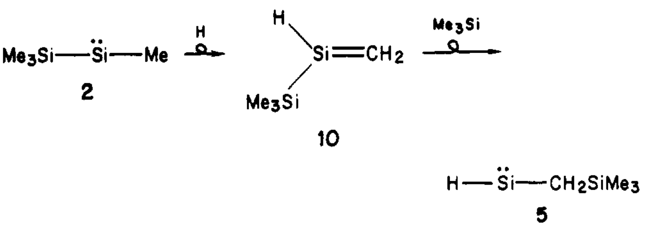
[2] Boo, B. H.; Gaspar, P. P.; Ghosh, A. K.; Holten, J. D.; Kirmaier, C. R.; Konieczny, S. "Transposition-A New Silylene Rearrangement, and the Laser Photolysis of Polysilanes", 17th Organosilicon Symposium, North Dakota State University, Fargo, ND, June 1983, abstracts, p 12.

[3] Boo, B. H.; Gaspar, P. P. 187th National Meeting of American Chemical Society, St. Louis, MO, 1984; American Chemical Society: Washington, D.C., 1984; ORGN 227.

[4] Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

0276-7333/86/2305-0698$01.50/0

Scheme II

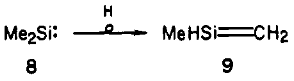


workers have found that migration of a methyl group in such a reaction requires a higher activation energy.[6,7]

	log *A*	E_a kcal/mol	
$Me_3SiSiMe_3 \xrightarrow{\Delta} Me_2Si{:} + Me_4Si$	13.7 ± 0.7	67.4 ± 2.9	(ref 6)
$Me_3SiSiHMe_2 \xrightarrow{\Delta} Me_2Si{:} + Me_3SiH$	12.93 ± 0.31	47.35 ± 0.93	(ref 7)

Why then should the yield of product 7, whose formation, according to Scheme I, *requires* the migration of a methyl group, be greater than that of product 6, for which hydrogen migration is expected to be largely responsible? Barton and co-workers suggested that the explanation may be the *reversibility* of hydrogen migration, permitting an equilibrium between 3 and 4.[4] A reaction entirely different from the pathway shown in Scheme I may however be responsible for the conversion of $Me_3Si{-}\ddot{Si}{-}Me$ (2) to $Me_3SiCH_2{-}\ddot{Si}{-}H$ (5).

In 1976 it was suggested that dimethylsilylene (8) might undergo isomerization to methylsilene (9) via a hydrogen shift.[8]



$$\underset{8}{Me_2Si{:}} \xrightarrow{H} \underset{9}{MeHSi{=}CH_2}$$

The evidence presented for the reverse reaction, rearrangement of 9 to 8,[9,10] has caused considerable controversy,[11,12] but both theoretical and experimental results seem to be reconciled by the view that a reversible hydrogen shift with a ca. 40 kcal/mol energy barrier can interconvert a hydridosilylene and a silene.[13-15]

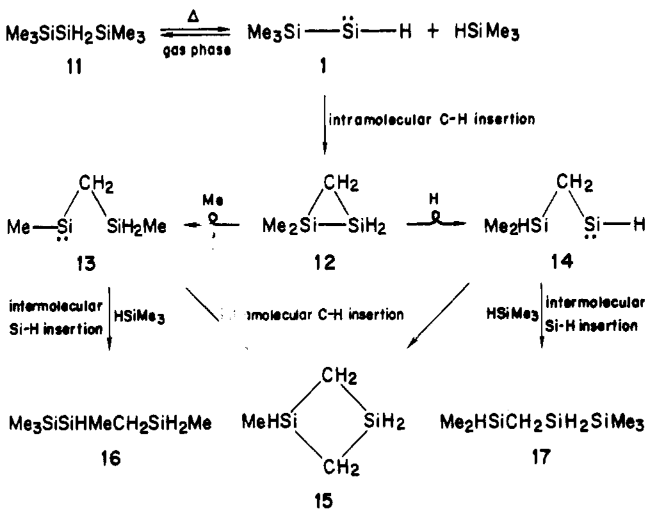
A similar isomerization, with a shift of a trimethylsilyl group serving to convert a silene 10 in Scheme II to silylene 5 can serve for the isomerization of 2 to 5.[2,16]

Since this pathway is not accessible to a silylene without a directly attached alkyl group, such as $Me_3Si{-}\ddot{Si}{-}H$ (1), study of its rearrangements clearly merits closer scrutiny than it has previously received.[1]

We previously invoked only hydrogen-migration in the ring-cleavage of the disilirane intermediate 12 suggested for the rearrangement of (trimethylsilyl)silylene 1, Scheme III, because only one product, 17, seemed to arise from intermolecular trapping of a β-silylsilylene 14 by insertion into the Si–H bond of trimethylsilane.[1]

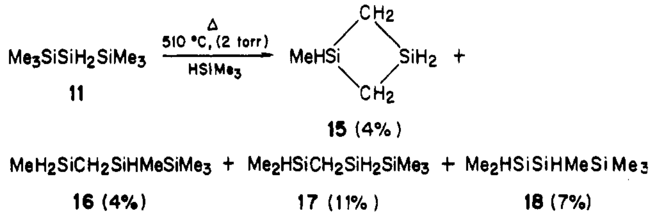
Scheme III differs from Scheme I in that methyl and hydrogen migration in the ring opening of the disilirane intermediate 12 in Scheme III lead to structurally *distinct* β-silylsilylenes 13 and 14. Since both 13 and 14 give rise to the same 1,3-disilacyclobutane 15 upon intramolecular C–H insertion,[1] intermolecular trapping is necessary to distinguish them. The absence of product 16 from those previously observed from the pyrolysis of 1,1,1,3,3,3-hexamethyltrisilane (11) in the presence of excess trimethylsilane has in retrospect attained considerable interest as an indication that methyl migration leading to its precursor 13 might indeed be slow.

Scheme III



Results and Discussion

We therefore decided to reinvestigate the intermolecular reactions of $Me_3Si{-}\ddot{Si}{-}H$ (1) and its rearrangement products. When 1,1,1,3,3,3-hexamethyltrisilane (11) was subjected to gas-phase flow pyrolysis at 510 °C, residence time of ca. 0.01 s in the presence of a 39-fold excess of trimethylsilane, four products were isolated, in a combined yield of 26%. These included an unexpected compound in addition to the three predicted in Scheme III.



The product of an entirely intramolecular reaction sequence, 1-methyl-1,3-disilacyclobutane (15), is still observed, but in a yield far lower than the 37–45% found for 15 as the sole product formed from 11 in the absence of added substrate.[1] Both β-silylsilylene intermediates 13 and 14 shown in Scheme III have now been detected via their intermolecular trapping products, $MeH_2SiCH_2SiHMeSiMe_3$ (16) and $Me_2HSiCH_2SiH_2SiMe_3$ (17), respectively, the former having been previously unresolved chromatographically or spectroscopically from the latter.

The trapping of $Me{-}\ddot{Si}{-}CH_2SiH_2Me$ (13) would have seemed to be conclusive evidence for the occurrence of the methyl shift in the ring opening of disilirane 12 shown in Scheme III, had a new and unexpected product $Me_2HSiSiHMeSiMe_3$ (18) not been found. This compound, like the other two $C_6H_{20}Si_3$ products 16 and 17, is an isomer of the starting material, but a change in the trapping agent established beyond doubt that all three arise from intermolecular reactions of silylenes.

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(5) Gaspar, P. P. *React. Intermed. (Wiley)* 1978, *1*, 229; 1981, *2*, 335; 1985, *3*, 333.

(6) Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* 1975, *71*, 69.

(7) Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1*, 1976, *72*, 1403.

(8) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* 1976, *98*, 878.

(9) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* 1981, *103*, 1843.

(10) Conlin, R. T.; Kwak, Y.-W. *Organometallics* 1984, *3*, 918.

(11) Barton, T. J.; Burns, G. T. *Organometallics* 1982, *1*, 210.

(12) Schaefer, H. F., III *Acc. Chem. Res.* 1982, *15*, 283.

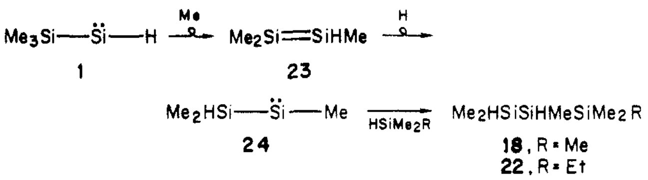
(13) Walsh, R. *J. Chem. Soc., Chem. Commun.* 1982, 1415.

(14) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* 1984, 141.

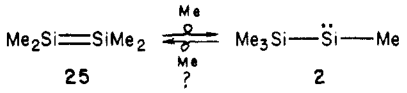
(15) Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Barton, T. J.; Tillman, N. *J. Chem. Soc., Chem. Commun.* 1984, 478.

(16) Davidson, I. M. T.; Scampton, R. J. *J. Organomet. Chem.* 1984, *271*, 249.

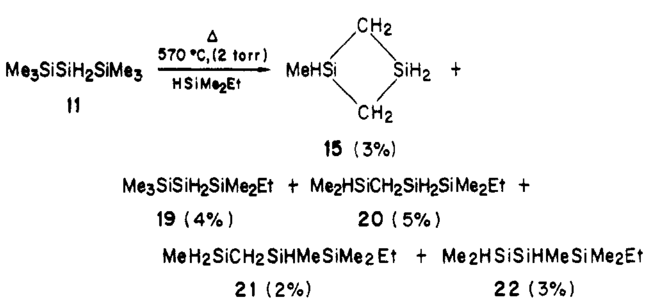
Scheme IV



Scheme V



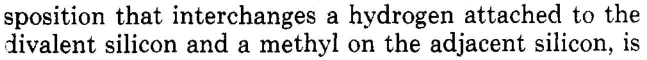
Pyrolysis of $Me_3SiSiH_2SiMe_3$ (11) in the presence of excess $EtMe_2SiH$ led to the formation of products analogous to those found with Me_3SiH trapping agent. In addition, the product of insertion of unrearranged silylene Me_3Si-$\ddot{\mathrm{Si}}$-H (1) into the Si-H bond of $EtMe_2SiH$ was found.

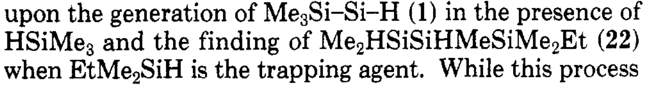


We believe that a new silylene rearrangement, a transposition that interchanges a hydrogen attached to the divalent silicon and a methyl on the adjacent silicon, is responsible for the formation of $Me_2HSiSiHMe_2SiMe_3$ (18) upon the generation of Me_3Si-$\ddot{\mathrm{Si}}$-H (1) in the presence of $HSiMe_3$ and the finding of $Me_2HSiSiHMeSiMe_2Et$ (22) when $EtMe_2SiH$ is the trapping agent. While this process could in principle be a diotropic rearrangement of the type formulated by Reetz,[17] a stepwise reaction with a disilene intermediate seems more likely as shown in Scheme IV. Si-H insertion by the transposed silylene 24 gives rise to products 18 and 22.

The first step in Scheme IV closely resembles the inverse of a process found by Wulff, Goure, and Barton, the conversion of tetramethyldisilene (25) to methyl(trimethylsilyl)silylene (2) via a methyl shift (Scheme V).[4]

While Barton and co-workers found little evidence for the reverse step in Scheme V, calculations indicating that $H_2Si{=}SiH_2$ and $H_3Si{-}\ddot{\mathrm{Si}}{-}H$ are of nearly equal energy[18,19] suggest that disilene-to-α-silylsilylene isomerizations should occur at comparable rates in both directions. Isomerization of an α-silylsilylene to a disilene had been suggested previously[20] and has been placed on a firm footing by the work of Sakurai.[21]





Evidence for the intermediacy of $Me_2Si{=}SiHMe$ (23) in the transposition of $Me_3Si{-}\ddot{\mathrm{Si}}H$ (1) has been obtained in another trapping experiment, employing butadiene. The results, and a suggested mechanism, are shown in Scheme VI.

While there are a large number of products, they all speak for a mechanism in which three nonconverging processes consume the initially generated silylene 1. Scheme VI has been divided into three blocks to show these three channels as clearly as possible. From left to right the three primary processes are methyl migration converting $Me_3Si{-}\ddot{\mathrm{Si}}{-}H$ (1) to $Me_2Si{=}SiHMe$ (23), intramolecular C—H insertion forming disilirane 12, and addition to butadiene.

The 2 + 4 cycloaddition of disilenes to 1,3-butadienes is a well-attested process,[21] and thus the formation of 1,1,2-trimethyl-1,2-disilacyclohex-4-ene (26) may be taken to indicate that trimethyldisilene 23 was formed. The silacyclopentene 27 that is expected from addition of transposed silylene 24 to butadiene has *not* been found, but silacyclopentene 28 may arise from 27 by loss of dimethylsilylene which is trapped by butadiene to form 29. The relative yields of 26, 28, and 29 are in accord with, but do not demand, the intermediacy of disilene 23 in the α-silylsilylene transposition, the rearrangement of 1 to 24. The methyl migration channel accounts for about a sixth of the total yield of isolated products from the rearrangement of (trimethylsilyl)silylene (1), as gauged by the sum of the yields of products 26 and 28 or 29.

Intramolecular C–H insertion by the initially generated silylene 1 followed by ring opening of the resulting disilirane 12 by competing hydrogen and methyl migration can form the isomeric β-silylsilylenes 14 and 13, respectively. These can both yield disilacyclobutane 15 by intramolecular C–H insertion and add to butadiene to give silacyclopentenes 30 and 31. This intramolecular insertion channel, as judged from the yields of products 15, 30, and 31, gives rise to about a third of the ca. 45% total yield of products isolated from 1 in the presence of butadiene. An alternative route to β-silylsilylene 13 will be discussed below.

Silylenes have long been known to undergo efficient addition to butadienes,[5] and this is a stepwise process for substituted butadienes.[22] About half of the isolated products in Scheme VI are formed via direct addition of unrearranged silylene 1 to butadiene. The primary addition product of initially generated silylene 1 is vinylsilirane 32 whose rearrangement via a silicon–carbon bond cleavage gives the expected silacyclopentene 33. Since 33 is a hydridodisilane, it can undergo α-elimination under the reaction conditions, and the resulting cyclic silylene 34 can add to butadiene to yield the spiro compound 35.[23] 34 also rearranges to a species believed to be silole 36 whose dimer 37 is isolated.[24]

Vinylsilirane 32 apparently can also rearrange via migration of the trimethylsilyl group, generating isomeric γ-silylsilylenes 38 and 39, a process with precedent in the work of Barton (Scheme VII).[25]

Silacyclopentene products 42 and 43 can be explained by intramolecular insertions into activated C–H bonds by

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[17] Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129, 130.

[18] Lischka, H.; Köhler, H. J. *Chem. Phys. Lett.* **1982**, *85*, 467.

[19] Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 5884.

[20] Chen, Y.-S.; Cohen, B. H.; Gaspar, P. P. *J. Organomet. Chem.*, **1980**, *195*, C1.

[21] Sakurai, H.; Sakaba, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6156.

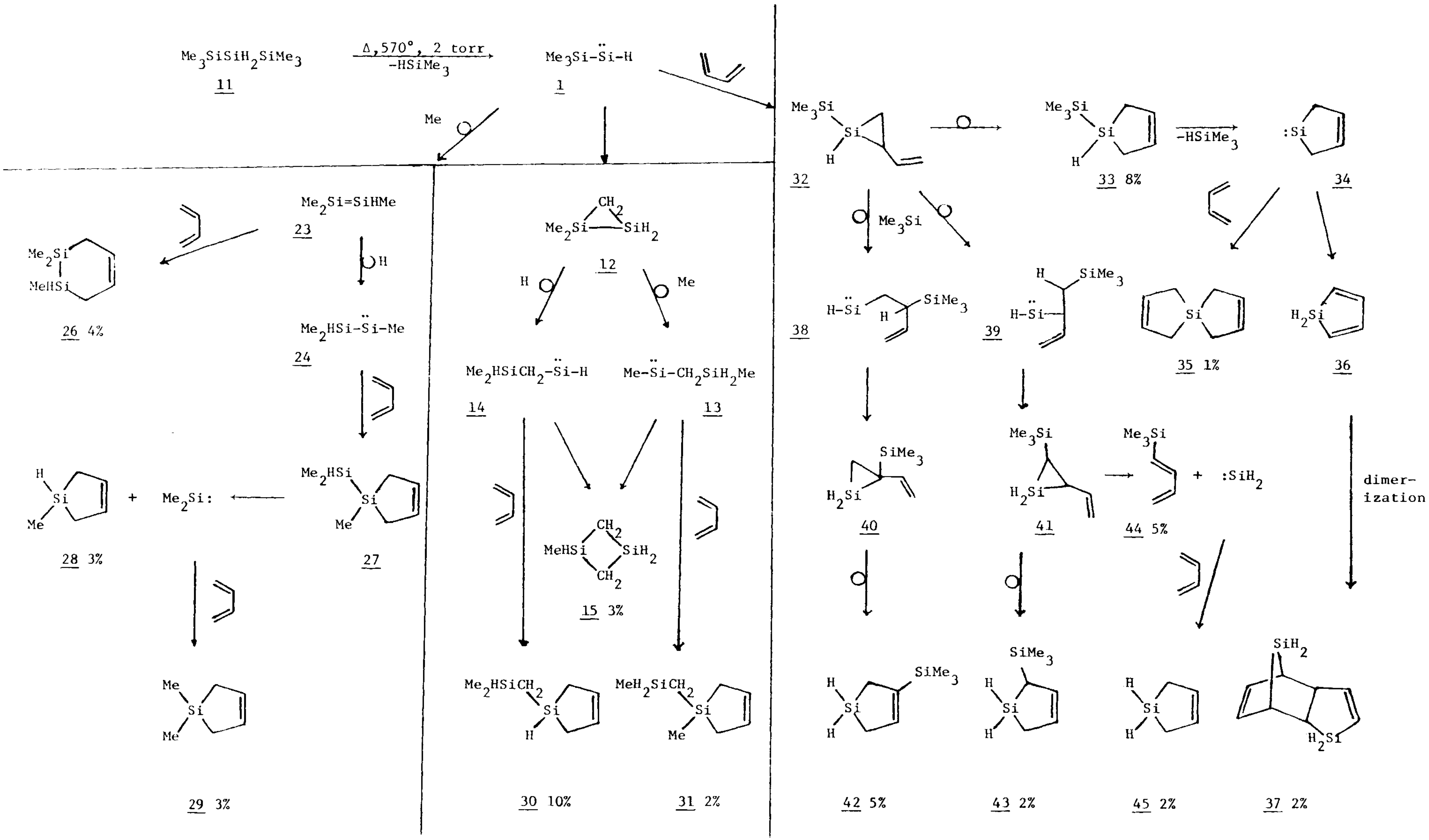
[22] Lei, D.; Hwang, R.-J.; Gaspar, P. P. *J. Organomet. Chem.*, **1984**, *271*, 1.

[23] Gaspar, P. P.; Chen, Y.-S.; Helfer, A. P.; Konieczny, S.; Ma, E. C.-L.; Mo, S.-H. *J. Am. Chem. Soc.* **1981**, *103*, 7344.

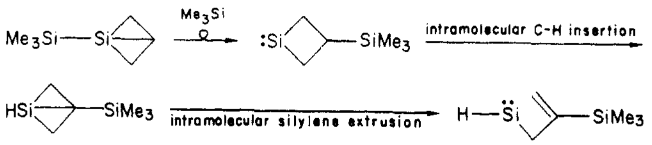
[24] Chen, Y.-S.; Chari, S.; Boo, B. H.; Svoboda, D.; Frueh, J.; Gaspar, P. P., to be submitted for publication.

[25] Burns, S. A.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6140.

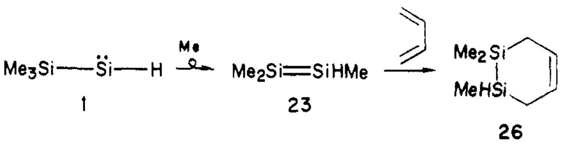
Scheme VI. Gas-Phase Reactions of $Me_3Si\text{-}\ddot{S}i\text{-}H$ (1) upon Pyrolysis of $Me_3SiSiH_2SiMe_3$ (11) in the Presence of Excess Butadiene



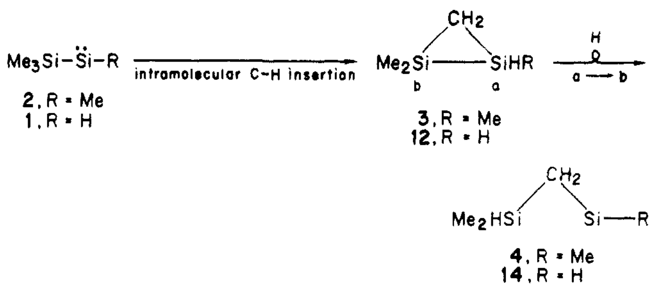
Scheme VII



Scheme VIII



Scheme IX



silylenes **38** and **39** forming new vinylsiliranes **40** and **41**. These latter molecules, lacking a migrating group on the silicon more labile than hydrogen, can rearrange to the observed products **42** and **43**.

The formation of 1-(trimethylsilyl)-1,3-butadiene can be rationalized by extrusion of SiH_2 from silirane **41**. The butadiene adduct of SiH_2 was found as 1-silacyclopent-3-ene (**45**).

The isolation of 1,1,2-trimethyl-1,2-disilacyclohex-4-ene (**26**) following the generation of $Me_3Si—\ddot{S}i—H$ (**1**) in the presence of butadiene is strong evidence for the formation of $Me_2Si=SiHMe$ (**23**), since **26** is the expected Diels-Alder adduct of **23** and butadiene (Scheme VIII).

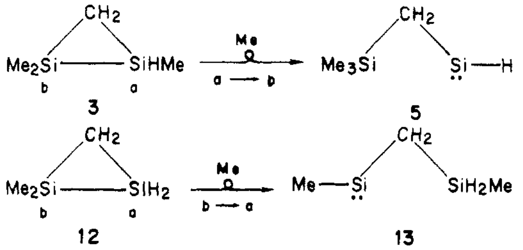
One can ask, however, whether these experiments have established that disilene **23** is an intermediate in the transposition of $Me_3Si\text{-}\ddot{S}i\text{-}H$ (**1**) to $Me_2HSi\text{-}\ddot{S}i\text{-}Me$ (**24**), as suggested in Scheme IV. Here the evidence is not unequivocal. The butadiene adduct **27** of transposed silylene **24** was not detected, but products **28** and **29** may have arisen from decomposition of **27** under the reaction conditions. Other sources may account for the formation of **28** and **29**, however, and the α-silylsilacyclopentene **33**, which should be no more stable than **27**, was the product isolated in second highest yield. The observed results of the butadiene trapping experiment are thus in accord with the view but do not establish beyond doubt that the transposition does proceed via a disilene intermediate.

It must be admitted, however, that the newly discovered transposition of α-silylsilylenes muddies an otherwise clear picture of disilirane ring opening.

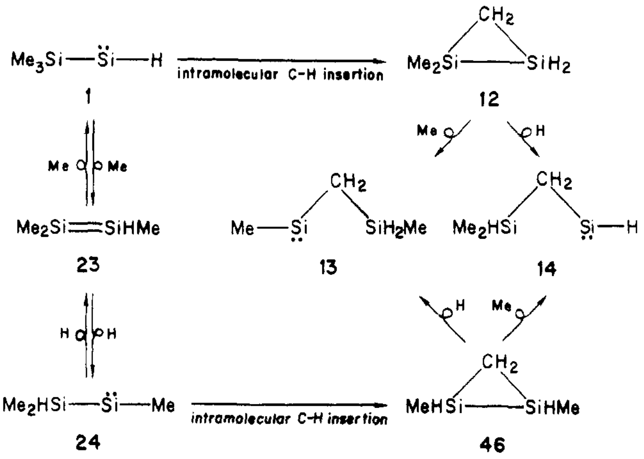
Both $Me_3Si\text{-}\ddot{S}i\text{-}Me$ (**2**)[4] and $Me_3Si\text{-}\ddot{S}i\text{-}H$ (**1**) rearrange to β-silylsilylenes, for whose formation the most reasonable pathway, shown in Scheme IX, consists of disilirane formation followed by hydrogen migration.[26]

Davidson and Scampton have recently estimated the activation energies for the conversion of **2** to **3** and **3** to **4** to be 39.4 and ≤27.5 kcal/mol, respectively.[16] Since these are lower barriers than that for the formation of **2** from its precursors, it is quite reasonable that these reactions

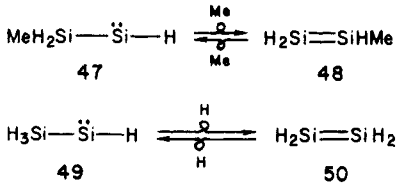
Scheme X



Scheme XI



Scheme XII



should be rapid under low-pressure flow pyrolysis conditions.

Both $Me_3Si\text{-}\ddot{S}i\text{-}Me$ (**2**) and $Me_3Si\text{-}\ddot{S}i\text{-}H$ (**1**) have also been found to rearrange to β-silylsilylenes than can be formulated as resulting from methyl shifts during the disilirane ring opening as shown in Scheme X.

Davidson and Scampton estimated an energy of activation for the rearrangement of **3** to **5** of ≤47.5 kcal/mol, indicating that a methyl shift in disilirane ring opening has a ca. 20 kcal/mol higher barrier than a hydrogen shift. For this reason Davidson favored the mechanism of Scheme II for the conversion of $Me_3Si\text{-}\ddot{S}i\text{-}Me$ (**2**) to $Me_3SiCH_2—\ddot{S}i—H$ (**5**). Energy barriers for the two steps in Scheme II were estimated to be 40.6 (**2** → **10**) and 28.7 (**10** → **5**) kcal/mol, respectively.[16]

The alternative mechanism of Scheme II is *not* available for the conversion of $Me_3Si\text{-}\ddot{S}i\text{-}H$ (**1**) to $MeSiH_2CH_2—\ddot{S}i—Me$ (**13**), since **1** lacks a methyl on the divalent silicon. The newly discovered transposition, however, provides another possible pathway (Scheme XI) for the rearrangement of **1** to **13**, a pathway unavailable to $Me_3Si\text{-}\ddot{S}i\text{-}Me$ (**2**) because its transposition is degenerate.[27]

Nagase and Kudo have calculated that there is a 27.8 kcal/mol barrier for the methyl shift that converts silylsilylene **47** in Scheme XII to disilene **48**.[28] The reverse reaction was predicted to have an activation energy of 34.7

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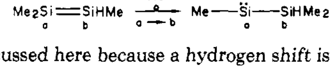
[26] For R = Me, the same β-silylsilylene could also arise from migration of a methyl from silicon b to silicon a during the disilirane ring opening.

[27] Completion of the transposition by a second methyl shift:



has not been discussed here because a hydrogen shift is likely to be much more rapid.

[28] Nagase, S.; Kudo, T. *Organometallics* 1984, *3*, 1320.

Scheme XIII

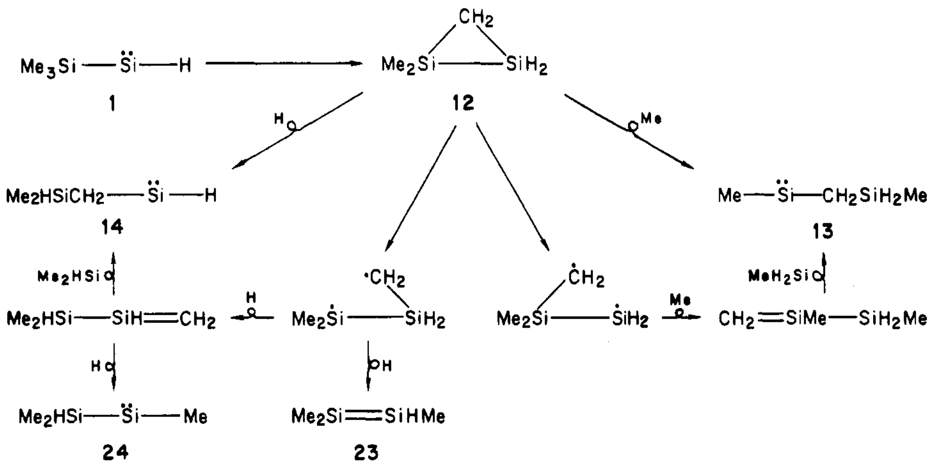
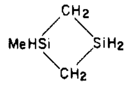


Table I. Dependence on Temperature of the Product Yields[a] from the Flow Pyrolysis of $Me_3SiSiH_2SiMe_3$ (11) in Excess Me_3SiH[b]

	temp, °C					
	480	500	510	540	570	600
% decomp of 11	67	78	80	92	92	98
 15	0.4	1.5	4.4	6.0	10	11
$MeH_2SiCH_2SiHMeSiMe_3$ (16) + $Me_2HSiCH_2SiH_2SiMe_3$ (17)	4.3	5.6	14	9.9	9.9	5.6
$Me_2HSiSiHMeSiMe_3$ (18)	3.0	3.1	7.4	7.4	5.0	1.0

[a] Product yields are expressed as % absolute, based on unrecovered starting material. [b] Me_3SiH:11 = 40; pressure = 2 torr; residence time = 0.01 s.

kcal/mol, the disilene having been calculated to be 6.9 kcal/mol more stable than the silylsilylene. Krogh-Jerspersen has calculated a barrier of 12.3 kcal/mol for the rearrangement of unsubstituted silylsilylene **44** to disilene **50**, with a 17.3 kcal/mol barrier in the reverse direction, **50** thus being predicted to be 5 kcal/mol more stable than **49**.[29]

If the estimates of the activation barriers for the related systems mentioned above are correct, then the four-step sequence of Scheme XI **1** → **23**, **23** → **24**, **24** → **46**, and **46** → **13** that converts $Me_3Si–\ddot{S}i–H$ (**1**) to $Me–\ddot{S}i–CH_2SiH_2Me$ (**13**) via the newly discovered transposition is energetically favorable by ca. 10 kcal/mol when compared with the shorter two-step sequence **1** → **12** and **12** → **13** that includes a methyl shift in a disilirane ring opening.

Does the transposition contribute to the conversion of **1** to **13**? The evidence available in the present work does not settle the issue but suggests that it does. In the presence of a substrate that traps $Me_2Si{=}SiHMe$ (**23**) a probable intermediate in the transposition route for the conversion of **1** to **13**, the extent to which **13** is formed decreases relative to that of its isomer $Me_2HSiCH_2–\ddot{S}i–H$ (**14**), as gauged by the yields of their respective butadiene adducts **31** and **30**. The butadiene adduct yields from **13** and **14**, 2 and 10%, respectively, should be compared with yields of 4 and 11%, respectively, from insertion of **13** and **14** into $HSiMe_3$ and yields of 2 and 5%, from insertion of **13** and **14**, respectively, into $HSiMe_2Et$. Neither $HSiMe_3$ nor $HSiMe_2Et$ is capable of directly trapping a disilene, and thus the reduction of ca. 50% of the ratio of **13** to **14** in the presence of butadiene may speak for a contribution from the transposition route of Scheme XI for the formation of **13** from **1**. Since the reduction of the *absolute* yield of **13** in the presence of butadiene is only ca. 2%, the significance of this observation should perhaps not be overstressed, particularly as the placement of disilene **23** along the reaction coordinate between **1** and **13** is not altogether certain.

At present, then, one can say only that if $MeH_2SiCH_2–\ddot{S}i–Me$ (**13**) and $Me_3SiCH_2–\ddot{S}i–H$ (**5**) both arise *via the same mechanism* from the rearrangements of $Me_3Si–\ddot{S}i–H$ (**1**) and $Me_3Si–\ddot{S}i–Me$ (**2**), respectively, then methyl shifts are likely to occur in the ring opening of the disiliranes $Me_2Si–SiH_2–CH_2$ (**12**) and $Me_2Si–SiHMe–CH_2$ (**3**). For such methyl shifts to be unimportant, quite different mechanisms would need to operate in the rearrangements of **1** and **2**. Scheme II for the conversion of **2** to **5** and the transposition route of Scheme XI for the rearrangement of **1** to **13** represent such different mechanisms, and no doubt many more could be written, such as the following, Scheme XIII, a diradical pathway in which disilene **23** is formed *in parallel* with the transposition.

The rearrangement of $Me_3Si–\ddot{S}i–H$ (**1**), by whatever mechanisms, to $Me_2HSiCH_2–\ddot{S}i–H$ (**14**) and $MeH_2SiCH_2–\ddot{S}i–Me$ (**13**), silylenes that react by the competing intramolecular C–H insertion and intermolecular Si–H insertion pathways shown in Scheme III provided an opportunity for an experimental determination of the activation energy for a silylene C–H insertion. We have studied the temperature dependence of the product yields in the pyrolysis of $Me_3SiSiH_2SiMe_3$ (**11**) in the presence of a 40:1 ratio of Me_3SiH. The results are given in Table I, and in Figure 1 is displayed an Arrhenius plot for the ratio of Si–H to C–H insertion products from rearranged silylenes **13** and **14**.

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(29) Krogh-Jespersen, K. *Chem. Phys. Lett.* **1982**, *93*, 327.

Table II. NMR and Mass Spectral Data for Reaction Products from Flow Pyrolyses of 1,1,1,3,3,3-Hexamethyltrisilane with Various Substrates

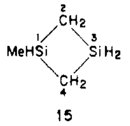
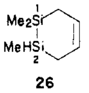
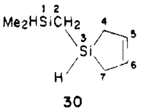
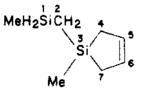
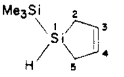
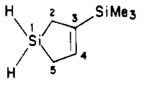
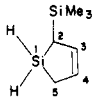
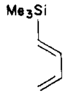
 15	^{1}H NMR^a (C_6D_6) δ −0.01 (dq, 2 H, $J_{\rm gem}$ = 16.5, J = 4.2 Hz, C_2-H, C_4-H), 0.11 (d, 3 H, J = 3.6 Hz, Si-CH_3), 0.30 (dq, 2 H, $J_{\rm gem}$ = 16.5, J = 4.2 Hz, C_2-H′, C_4-H′), 4.62 (quintet, 1 H, J = 4.2 Hz, Si_3-H), 4.63 (quintet, 1 H, J = 4.2 Hz, Si_3H′), 4.80 (broad octet, 1 H, J_{12} = 4.2, $J_{1,\rm Me}$ = 3.6 Hz, Si_1-H) mass spectrum, *m/e* (relative intensity) 102 (parent, 81), 101 (28), 100 (26), 85 (22), 74 (63), 73 (38), 59 (base, 100), 45 (76), 43 (39)
$\mathrm{MeH_2SiCH_2SiHMeSiMe_3}$ 16	^{1}H NMR^b (C_6D_6) δ −0.31 (m, 2 H, CH_2), 0.01-0.14 (m, 15 H, Si-CH_3), 4.01 (m, 3 H, Si-H) ^{13}C NMR (C_6D_6) δ −10.24, −6.85, −6.32, −2.05 mass spectrum, *m/e* (relative intensity) 176 (parent, 11), 161 (45), 159 (21), 115 (17), 103 (45), 102 (base, 100), 101 (41), 73 (96), 59 (40)
$\mathrm{Me_2H\overset{1}{Si}\overset{2}{C}H_2\overset{3}{Si}H_2\overset{4}{Si}Me_3}$ 17	^{1}H NMR^b (C_6D_6) δ −0.28 (dt, 2 H, J_{12} = 3.5, J_{32} = 5.5 Hz, CH_2), 0.12 (d, 6 H, J = 3.5 Hz, Si_1-CH_3), 0.14 (s, 9 H, Si_4-CH_3), 3.70 (t, 2 H, J_{23} = 5.5 Hz, SiH_2), 4.23 (nonet, 1 H, J_{21} = 3.5, $J_{CH_3,1}$ = 3.5 Hz, Si_1-H) ^{13}C NMR (C_6D_6) δ −11.41, −2.29, 0.77 mass spectrum, *m/e* (relative intensity) 176 (parent, 7.7), 161 (29), 159 (15), 104 (11), 103 (29), 102 (base, 100), 101 (24), 73 (98), 59 (26), 45 (21), 73 (18)
$\mathrm{Me_2H\overset{1}{Si}\overset{2}{Si}HMe\overset{3}{Si}Me_3}$ 18	^{1}H NMR^a (C_6D_6) δ 0.15 (d, 3 H, J_{2,CH_3} = 5.3 Hz, Si_2-CH_3), 0.16 (s, 9 H, Si_3-CH_3), 0.19 (d, 3 H, J_{1,CH_3} = 4.4 Hz, Si_1-CH_3), 0.20 (d, 3 H, $J_{1,CH_3'}$ = 4.4 Hz, Si_1-CH_3′), 3.42 (dq, 1 H, J_{12} = 2.9, $J_{CH_3,2}$ = 5.3 Hz, Si_2-H), 4.10 (doublet of septets, 1 H, J_{21} = 2.9 $J_{CH_3,1}$ = 4.4 Hz, Si_1-H) ^{13}C NMR (C_6D_6) δ −13.17, −5.50, −5.33, −1.12 mass spectrum, *m/e* (relative intensity) 176 (parent, 2.6), 161 (10), 117 (8.8), 116 (15), 115 (7.4), 103 (17), 102 (90), 101 (35), 74 (12), 73 (base, 100), 59 (15)
$\mathrm{Me_3\overset{1}{Si}\overset{2}{Si}H_2\overset{3}{Si}Me_2Et}$ 19	^{1}H NMR^c (C_6D_6) δ 0.17 (s, 6 H, Si_3-CH_3), 0.20 (s, 9 H, Si_1-CH_3), 0.57-1.22 (m, 5 H, Si_3-Et), 2.95 (s, 2 H, Si_2-H) mass spectrum, *m/e* (relative intensity) 190 (parent, 8.0), 159 (18), 147 (18), 102 (15), 101 (15), 88 (38), 87 (92), 86 (14), 85 (14), 73 (83), 59 (base, 100)
$\mathrm{Me_2H\overset{1}{Si}\overset{2}{C}H_2\overset{3}{Si}H_2\overset{4}{Si}Me_2Et}$ 20	^{1}H NMR^b (C_6D_6) δ −0.28 (dt, 2 H, J_{12} = 3.6, J_{32} = 5.5 Hz, CH_2), 0.12 (s, 6 H, Si_4-CH_3), 0.12 (d, 6 H, J = 3.6 Hz, Si_1-CH_3), 0.65 (m, 2 H, Si_4-CH_2), 0.98 (m, 3 H, Et-CH_3), 3.71 (t, 2 H, J_{23} = 5.5 Hz, SiH_2), 4.24 (nonet, 1 H, J_{21} = 3.6, $J_{CH_3,1}$ = 3.6 Hz, Si_1-H) mass spectrum, *m/e* (relative intensity) 190 (parent, 10), 161 (84), 159 (19), 147 (41), 103 (43), 102 (base, 100), 101 (32), 87 (88), 85 (18), 73 (35), 59 (93)
$\mathrm{MeH_2\overset{1}{Si}\overset{2}{C}H_2\overset{3}{Si}HMe\overset{4}{Si}Me_2Et}$ 21	^{1}H NMR^a (C_6D_6) δ −0.23 (m, 2 H, Δδ = 0.11, $J_{\rm gem}$ = 14, J_{12},J_{32} = 5 Hz, C_2-H,H′), 0.087 (s, 3 H, Si_4-CH_3), 0.090 (s, 3 H, Si_4-CH_3′), 0.11 (t, 3 H, J = 4.5 Hz, Si_1-CH_3), 0.20 (d, 3 H, J = 4.8 Hz, Si_3-CH_3), 0.60 (q, 2 H, J = 8.2 Hz, Si_4-CH_2), 0.96 (t, 3 H, J = 8.2 Hz, Et-CH_3), 4.01 (sextet, 1 H, J_{23} = 4.8, $J_{CH_3,3}$ = 4.8 Hz, Si_3-H), 4.09 (sextet, 2 H, J_{21} = 4.5, $J_{CH_3,1}$ = 4.5 Hz, SiH_2) mass spectrum, *m/e* (relative intensity) 190 (parent, 9.1), 161 (40), 147 (21), 104 (19), 103 (65), 102 (99), 101 (44), 87 (base, 100), 85 (24), 73 (78), 59 (97)
$\mathrm{Me_2H\overset{1}{Si}\overset{2}{Si}HMe\overset{3}{Si}Me_2Et}$ 22	^{1}H NMR^a (C_6D_6) δ 0.115 (s, 3 H, Si_3-CH_3), 0.120 (s, 3 H, Si_3-CH_3′), 0.15 (d, 3 H, J = 6 Hz, Si_2-CH_3), 0.185 (d, 3 H, J = 5 Hz, Si_1-CH_3), 0.195 (d, 3 H, J = 5 Hz, Si_1-CH_3′), 0.62 (q, 2 H, J = 9 Hz, Si_3-CH_2), 0.98 (t, 3 H, J = 9 Hz, Et-CH_3), 3.39 (dq, 1 H, J_{12} = 3, $J_{CH_3,2}$ = 6 Hz, Si_2-H), 4.05 (doublet of septets, 1 H, J_{21} =3 Hz, $J_{CH_3,1}$ = 5 Hz, Si_1-H) ^{13}C NMR (C_6D_6) δ −12.93, −5.51, −5.27, −3.46, −3.34, 7.78, 7.89 mass spectrum, *m/e* (relative intensity) 190 (parent, 2.2), 104 (7.7), 103 (20), 102 (93), 88 (9.3), 87 (39), 86 (6.1), 85 (9.7), 73 (46), 60 (7.3), 59 (base, 100)
 26	^{1}H NMR^b (C_6D_6) δ 0.05 (s, 3 H, Si_1-CH_3), 0.08 (d, 3 H, J = 4 Hz, Si_2-CH_3), 0.14 (s, 3 H, Si_1-CH_3′), 1.25-1.59 (m, 4 H, CH_2, CH_2′), 3.82 (sextet, 1 H, $J_{CH_3,2}$ = 4, $J_{CH_2,2}$ = 4 Hz, Si_2-H), 5.68 (m, 2 H, -CH=CH-) ^{13}C NMR (C_6D_6) δ −7.88, −3.72, −2.55, 12.89, 17.10, 125.63, 126.51 mass spectrum, *m/e* (relative intensity) 156 (parent, 27), 141 (61), 102 (base, 100), 97 (39), 96 (22), 95 (21), 85 (20), 73 (94), 69 (21), 59 (64)
 30	^{1}H NMR^b (C_6D_6) δ −0.21 (t, 2 H, J_{12},J_{32} = 4.0 Hz, C_2-H), 0.05 (d, 6 H, J = 3.5 Hz, Si_1-CH_3), 1.41 (m, 4 H, Δδ = 0.21, $J_{\rm gem}$ = 14, J_{34},J_{37} = 4.0, J_{54},J_{67} = 2, J_{64},J_{57} ≈ 0.5 Hz, CH_2, CH_2′), 4.08 (septet, 1 H, J_{23},J_{43},J_{73} = 4.0 Hz, Si_3-H), 4.33 (triplet of septets, 1 H, $J_{CH_3,1}$ = 3.5, J_{21} = 4.0, Si_1-H), 5.85 (m, 2 H, C_5-H, C_6-H) ^{13}C NMR (C_6D_6) δ −3.97, −2.51, 15.52, 130.63 mass spectrum, *m/e* (relative intensity) 156 (parent, 15), 141 (52), 128 (78), 115 (base, 100), 113 (79), 102 (64), 85 (31), 73 (90), 69 (31), 59 (71), 55 (30)
 31	^{1}H NMR^b (C_6D_6) δ −0.25 (t, 2 H, J_{12} = 4.2 Hz, C_2-H), 0.04 (t, 3 H, J = 4.2 Hz, Si_1-CH_3), 0.12 (s, 3 H, Si_3-CH_3), 1.29 (m, 4 H, CH_2, CH_2′), 3.98 (sextet, 2 H, $J_{CH_3,1}$,J_{21} = 4.2 Hz, Si_1-H), 5.92 (m, 2 H, C_5-H, C_6-H) mass spectrum, *m/e* (relative intensity) 156 (parent, 18), 141 (55), 128 (85), 115 (base, 100), 113 (73), 102 (70), 101 (25), 85 (30), 73 (87), 69 (31), 59 (56)
 33	^{1}H NMR^b (C_6D_6) δ 0.09 (s, 9 H, Si-CH_3), 1.56 (m, 4 H, Δδ = 0.23, $J_{\rm gem}$ = 16, J_{12},J_{15} = 4.6, J_{32},J_{45} ≈ 2, J_{42}, J_{35} ≈ 1 Hz, CH_2, CH_2′), 4.09 (quintet, 1 H, J_{21}, J_{51} = 4.6 Hz, Si_1-H), 5.95 (m, 2 H, C_3-H, C_4-H) mass spectrum, *m/e* (relative intensity) 156 (parent, 14), 141 (57), 113 (18), 102 (41), 97 (30), 96 (16), 95 (22), 82 (19), 73 (base, 100), 59 (38), 55 (16)

Table II (*Continued*)

 **42**	^{1}H NMR^b (C_6D_6) δ 0.07 (s, 9 H, Si-CH_3), 1.42–1.55 (m, 2 H, C_5-H), 1.48 (t, 2 H, J_{12} = 3.9 Hz, C_2-H), 4.08 (quintet, 2 H, J_{21}, J_{51} = 3.9 Hz, SiH_2), 6.14 (t, 1 H, J_{54} = 2.0 Hz, C_4-H) mass spectrum, *m/e* (relative intensity) 156 (parent, 15), 142 (16), 141 (base, 100), 115 (22), 113 (52), 95 (14), 85 (11), 73 (54), 59 (27), 55 (12)
 **43**	^{1}H NMR^b (C_6D_6) δ 0.007 (s, 9 H, Si-CH_3), 1.07 (dt, 1 H, J_{12} = 0.8, J_{32} = 1.6 Hz, C_2-H), 1.41 (m, 2 H, C_5-H), 4.19 (q, 2 H, J_{21}, J_{51} = 3.8 Hz, SiH_2), 5.81 (m, 2 H, C_3-H, C_4-H) mass spectrum, *m/e* (relative intensity) 156 (parent, 3.2), 96 (6.5), 78 (31), 77 (8.4), 77 (8.4), 74 (10), 73 (base, 100), 59 (13), 55 (6.4), 52 (6.9), 51 (7.9), 50 (6.8)
 **44**	^{1}H NMR^c (acetone-d_6) δ 0.13 (s, 9 H, Si-CH_3), 4.90–6.90 (m, 5 H, olefinic H) ^{13}C NMR (acetone-d_6) δ −1.292, 118.06, 134.93, 140.78, 145.75 mass spectrum, *m/e* (relative intensity) 126 (parent, 13), 112 (12), 111 (base, 100), 109 (22), 95 (18), 85 (33), 84 (14), 83 (48), 74 (13), 73 (14), 59 (49)

^{a} 360 MHz. ^{b} 100 MHz. ^{c} 60 MHz.

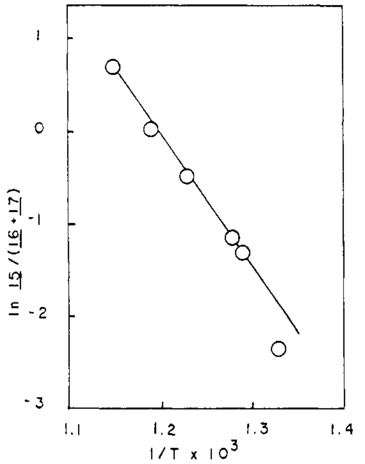
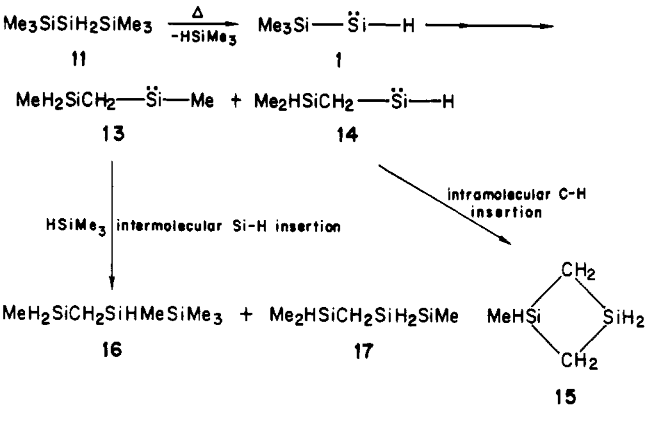


Figure 1. Arrhenius plot: ln ratio of yields of **15** to sum of yields of **16** and **17** vs. 1/*T*. Data taken from Table I.

Scheme XIV



The ratio decreases with temperature as expected for the C–H insertion as the process with the higher activation energy. From the Arrhenius plot a difference in activation energies of 29 kcal/mol is calculated. This value is in good agreement with the barrier of 27.5 kcal/mol calculated by Gordon for the insertion of SiH_2 into a C–H bond of methane.[30] Davidson and Scampton have pointed out, however, that ca. 13 kcal/mol of ring strain must be overcome in reaching the transition state for ring closure of a β-silylilylene to a 1,3-disilacyclobutane by intramolecular C–H insertion.[16] Correction for this ring strain would lower the barrier for C–H insertion to 16 kcal/mol, in good agreement with the estimate by Davidson and Scampton of a barrier of ca. 20 kcal/mol for insertion of simple silylenes into C–H bonds.

Experimental Section[31]

General Data. ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz, a JEOL JNM-FX-100 FT, and a Bruker WH-360 FT spectrometer. ^{13}C NMR spectra were recorded at 23.0 MHz on the JEOL instrument. Gas chromatograph–mass spectra (GC–MS) were recorded on a Finnegan 3200 mass spectrometer operating at an ionization voltage of 70 eV. Exact mass measurements were obtained on an AEI MS-902 mass spectrometer. Flame ionization detector (FID) and thermal conductivity detector (TCD) instruments were employed for analytic gas chromatography. The FID instrument was Gow-Mac Model 39-750. The TCD chromatograph was constructed in this laboratory, employing dual rhenium tungsten filaments (Code 13-002, Gow-Mac Instrument Co.). The TCD instrument was also used routinely for separation of product mixtures and absolute yield determinations. Yields were based on the amount of unrecovered silylene precursors and were determined with the use of external standards. Chromatographic response factors were determined for isolated products or for isomers of closely similar structure. Most of the products were separated by using a 10 ft × 1/4 in. o.d. glass column with a stationary phase of tricresyl phosphate 20% on ABS Anakrom 60/80 mesh diatomaceous earth, a 30 ft × 1/4 in. o.d. stainless-steel column with 20% DC-702 silicone oil on ABS Anakrom 60/80, a 20 ft × 1/4 in. o.d. aluminum column containing 20% SF-96 silicone oil on ABS Anakrom 60/80, or a 3 ft × 1/4 in. o.d. aluminum column containing 20% DC-200 silicone oil on ABS Anakrom 60/80.

Materials. Tetrakis(trimethylsilyl)silane: synthesized by the method of Gilman and Smith.[32]

Tris(trimethylsilyl)silane: synthesized by the method of Gilman, Holmes, and Smith;[33] bp 78–79 °C (7 torr) (lit.[34] 78–85 °C (7–9 torr)).

Chlorotris(trimethylsilyl)silane: synthesized by the method of Gilman and Harrell.[35]

2,2-Dichlorohexamethyltrisilane. A solution of 44.1 g (0.157 mol) of chlorotris(trimethylsilyl)silane in 300 mL of dry pentane through which N_2 was bubbled was cooled to −23 °C, and Cl_2, ca. 2 bubbles/s, replaced the nitrogen. The reaction mixture was monitored hourly by gas chromatography, and the maximum yield of 2,2-dichlorohexamethyltrisilane was reached at ca. 14 h. At that point N_2 replaced Cl_2 and after 20 min solvent was removed by distillation under N_2. The product was isolated by fractional

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[30] Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421.

[31] Fuller details can be found in: Boo, B. H. "The Chemistry of Silylsilylenes: Generation and Reactions of Trimethylsilylsilylene and Silylsilylene", Doctoral dissertation, Washington University, St. Louis, Dec 1984.

[32] Gilman, H.; Smith, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 1454.

[33] Gilman, H.; Holmes, H. M.; Smith, C. L. *Chem. Ind.* (*London*) **1965**, 848.

[34] Ishikawa, M.; Nakagawa, K. I.; Kumada, M. *J. Organomet. Chem.* **1977**, *131*, C15.

[35] Gilman, H.; Harrell, R. *J. Organomet. Chem.* **1966**, *5*, 199.

distillation under reduced pressure, affording 37.3 g (94%); bp 76 °C (9 torr) (lit.[35] 76–77 °C (10 torr)).[35]

1,1,1,3,3,3-Hexamethyltrisilane (11). To a stirred solution of 10 g (0.041 mol) of 2,2-dichlorohexamethyltrisilane in 100 mL of dry diethyl ether under nitrogen was added over a 3-h period 2.5 g (0.066 mol) of lithium aluminum hydride (LAH) from a bent addition tube. After an additional 20 h of stirring excess LAH was destroyed by addition of 10 mL of H_2O to the reaction mixture, which was now cooled in an ice bath. The reaction mixture was filtered to remove salts and fractionally distilled to yield 5.0 g (70%) of 1,1,1,3,3,3-hexamethyltrisilane: bp 50 °C (23 torr) (lit.[35] 65 °C (45 torr));[35] ^1H NMR (60 MHz, C_6H_6) δ 0.03 (s, 18 H, Si–CH_3), 2.98 (s, 2 H, SiH_2); MS (70 eV), *m/e* (relative intensity) 176 (M^+, 5), 161 (8), 159 (4), 102 (4), 101 (8), 88 (24), 86 (5), 74 (8), 73 (100), 59 (11). A less than 1% impurity of 1,1,1,2,3,3,3-heptamethyltrisilane was detected by mass spectrometry (70 eV): *m/e* (relative intensity) 190 (M^+, 8) 175 (9), 117 (8), 116 (26), 115 (6), 103 (6), 102 (29), 101 (19), 73 (100), 59 (9).

1,1,2-Trichlorotrimethyldisilane: synthesized by the method of Hennge, Pletka, and Hofler.[36] A mixture was obtained of 1,1,2-trichlorotrimethylsilane (42% yield) and 1,2-dimethyltetrachlorodisilane (23% yield). These were separated by gas chromatography: ^1H NMR (60 MHz, C_6D_6): $Cl_2MeSiSiMe_2Cl$, δ 0.10 (s, 6 H, $Si(CH_3)_2$), 0.38 (s, 3 H, $SiCH_3$); $Cl_2MeSiSiMeCl_2$ δ 0.11 (s, 6 H, $Si(CH_3)_2$).

1-Chloro-1,2,2-trimethyl-1,2-disilacyclohex-4-ene. Synthesized by the method of Birkofer and Weniger described for the preparation of 1,1,2,2-tetramethyl-1,2-disilacyclohex-4-ene.[37] To a vigorously stirred suspension of 11 g (0.45 mol) of magnesium shavings in 120 mL of dry THF under N_2 was added dropwise a solution of 13.6 g (0.064 mol) of *cis*-1,4-dibromo-2-butene, and 21 g of a mixture consisting of 0.045 mol of 1,1,2-trichlorotrimethyldisilane and 0.055 mol of 1,2-dimethyltetrachlorodisilane in 30 mL of dry THF. The rate of addition was controlled to keep the strongly exothermic reaction at 50 °C. After addition was complete, the reaction mixture was stirred an additional hour and then the reaction flask was immersed in a water-ice bath, at which point appreciable while solid separated. The liquid phase was decanted and solvent removed under reduced pressure. The products were separated by gas chromatography yielding 1% 1-chloro-1,2,2-trimethyl-1,2-disilacyclohex-4-ene: ^1H NMR (100 MHz, C_6D_6) δ −0.05 (s, 3 H, Si–CH_3), 0.18 (s, 3 H, Si–CH_3), 0.35 (s, 3 H, Si–CH_3), 1.32 (d, 2 H, *J* = 6.4 Hz, C_3–H), 1.67 (d, 1 H, *J* = 7.1, C_6–H), 1.71 (d, 1 H, *J* = 6.0 Hz, C_6–H′), 5.53 (m, 2 H –CH═CH–), MS (70 eV), *m/e* (relative intensity) 190 (M^+), 138 (base). In addition a 1.2% yield of a mixture of *cis*- and *trans*-1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene was obtained: ^1H NMR (100 MHz, C_6D_6) δ 0.44 (s, 6 H, Si–CH_3), 1.53 (m, 4 H, CH_2), 5.47 (t, 2 H, *J* 5.2 Hz, –CH═CH–); MS (70 eV) *m/e* (relative intensity) 210 (M^+), 73 (base).

1,1,2-Trimethyl-1,2-disilacyclohex-4-ene. To a stirred suspension of 1.0 g (26 mmol) of lithium aluminum hydride in 60 mL of dry ether under nitrogen was added dropwise a solution of 0.25 g of a mixture of 0.55 mmol of 1-chloro-1,2,2-trimethyl-1,2-disilacyclohex-4-ene and 0.64 mmol of 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene in 9 mL of dry THF. Stirring was continued for 12 h, during which white precipitate developed. Unreacted LAH and the precipitate were removed by filtration, and solvent was removed under reduced pressure at −15 °C. The product mixture was separated by gas chromatography giving a 50% yield of 1,1,2-trimethyl-1,2-disilacyclohex-4-ene whose spectroscopic properties were identical with those from a product obtained from generation of $Me_3Si{-}\ddot{Si}{-}H$ (1) in the presence of butadiene (vide infra and Table II). In addition there was obtained a 55% yield of *cis*-1,2-dimethyl-1,2-disilacyclohex-4-ene [^1H NMR (100 MHz, C_6D_6) δ 0.14 (d, 6 H, *J* = 3.9 Hz, Si–CH_3), 1.53 (m, J_{gem} = 16 Hz, C_3–H, C_6–H), 1.71 (m, J_{gem} = 16 Hz, C_3–H′, C_6–H′), 3.82 (m, 2 H, Si–H), 5.65 (t, 2 H, *J* = 4.9 Hz, –CH═CH–); MS (70 eV), *m/e* (relative intensity) 142 (M^+), 127 (base)] and a 33% yield of *trans*-1,2-dimethyl-1,2-disilacyclohex-4-ene [^1H NMR (100 MHz, C_6D_6) δ 0.01 (d, 6 H, *J* = 4.4 Hz, Si–CH_3), 1.42 (m, 4 H, CH_2), 3.92 (m, 2 H, Si–H), 5.64 (t, *J* = 4.6 Hz, –CH═CH–).

Gas-Phase Pyrolyses. The pyrolyses were carried out in a vacuum flow system whose hot zone was a 10 mm i.d. × 18 cm quartz tube wrapped with ca. 22 ft of 26-gauge nichrome heating wire with an inner and outer layer of asbestos ribbon. The temperature of the hot zone was measured with an iron–constantan thermocouple placed between the outer surface of the quartz tube and the inner layer of asbestos. The flow system was throttled downstream from the hot zone with a copper disk with a 0.036 in. diameter orifice. Products were trapped ca. 12 cm from the hot zone in a U-trap immersed in liquid nitrogen. A gaseous mixture of silylene precursor and reaction substrate was delivered from a 1-L reservoir through ball-type flow meters (Fisher and Porter Co., Crest Div.). The pressure was measured just upstream from the hot zone by a calibrated thermocouple gauge. Under the standard operating conditions ca. 18 mg/min of $Me_3SiSiH_2SiMe_3$ (11) was passed through the hot zone. At 510 °C and 2 torr the residence time was ca. 0.01 s. After a pyrolysis (typical duration 4 min) the reaction mixture was subjected to a preliminary fractionation by trap-to-trap distillation in the vacuum line to which the flow system was attached in order to separate the large excess of much more volatile trapping agent from the mixture of remaining silylene precursor and reaction products. Further separation and isolation of products was by gas chromatography.

Pyrolysis of 1,1,1,3,3,3-Hexamethyltrisilane (11) without Trapping Agent. In a typical experiment a sample of 218 mg (1.24 mmol) of **11** was passed through the hot zone at 600 °C (0.3 torr) at a rate of 100 mg/h with a contact time of 0.5 s. In the trap-to-trap distillation of the reaction mixture unreacted 11 (2%) and 1-methyl-1,3-disilacyclobutane (**15**; 37% yield) were retained in a toluene slush bath (−95 °C) while trimethylsilane (107% yield) was collected in liquid N_2. Final purification was by gas chromatography on an SF96 column. Spectral data for **15** are given in Table II. Exact mass determination: calculated for $C_3H_{10}Si_2$ (**15**), 102.032 11; measured 102.032 43.

Pyrolysis of 11 in the Presence of Trimethylsilane. In a typical experiment a mixture of 80 mg of **11** (0.45 mmol) and 1.33 g of trimethylsilane (18 mmol, 39-fold excess) was passed through the hot zone in 4.5 min at 510 °C (2 torr); residence time 0.01 s. The trimethylsilane was separated from the reaction mixture by trap-to-trap distillation from a toluene slush bath to liquid N_2. Final purification was by gas-chromatography on a TCP column. **11** (ca. 20%) was recovered. The products obtained were 1-methyl-1,3-disilacyclobutane (**15**; 4%), 2,2,3-trimethyl-2,3,5-trisilahexane (**16**; 4%), 2,2,5-trimethyl-2,3,5-trisilahexane (**17**; 11%), and 1,1,1,2,3,3-hexamethyltrisilane (**18**; 7%). Spectroscopic data for **15–18** are given in Table II. Exact mass determinations: calculated for $C_6H_{20}Si_3$ (**16–18**), 176.087 29; measured 176.086 97 (**16**), 176.086 97 (**17**), 176.087 53 (**18**).

Pyrolysis of 11 in the Presence of Ethyldimethylsilane. A mixture of 88 mg **11** (0.50 mmol) and 0.88 g of ethyldimethylsilane (10 mmol, 19-fold excess) was passed through the hot zone over a period of 2 min at 570 °C (2 torr); residence time = 6 ms. The pyrolysis was repeated three times to collect a larger amount of product mixture. A total of 350 mg of **11** and 3.5 g of $EtMe_2SiH$ was reacted. The $EtMe_2SiH$ was separated from the reaction mixture by trap-to-trap distillation from a dry ice–2-propanol bath to liquid N_2. Products were separated by gas chromatography on a TCP column. **11** (ca. 17%) was recovered. The products obtained were 1-methyl-1,3-disilacyclobutane (**15**; 3%), 1-ethyl-1,1,3,3,3-pentamethyltrisilane (**19**; 4%), 2,5,5-trimethyl-2,4,5-trisilaheptane (**20**; 5%), 4,5,5-trimethyl-2,4,5-trisilaheptane (**21**; 2%), and 1-ethyl-1,1,2,3,3-pentamethyltrisilane (**22**; 3%). Spectroscopic data for **19–22** are given in Table II. Exact mass determinations: calculated for $C_7H_{22}Si_3$ (**19–22**) 190.102 94, measured 190.103 22 (**19**), 190.102 60 (**20**), 190.102 84 (**21**), 190.102 83 (**22**).

Pyrolysis of 11 in the Presence of 1,3-Butadiene. A mixture of 76 mg of **11** (0.43 mmol) and 1.3 g of butadiene (23 mmol, 53-fold excess) was passed through the hot zone over a period of 3 min at 570 °C (2 torr); residence time = 4 ms. The pyrolysis was repeated for a total of six times under the same conditions, and the reaction mixtures were combined. Butadiene and trimethylsilane were separated by trap-to-trap distillation from a

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toluene slush bath to liquid N_2. Products were isolated by gas chromatography, with peaks separated by a TCP column collected and further fractionated on a DC-702 column. **11** (ca. 16%) was recovered. The products obtained were 1-methyl-1,3-disilacyclobutane (**15**; 3%), 1,1,2-trimethyl-1,2-disilacyclohex-4-ene (**26**; 4%), 1-methyl-1-silacyclopent-3-ene (**28**; 3%), 1,1-dimethyl-1-silacyclopent-3-ene (**29**; 3%), 1-(2-methyl-2-silapropyl)-1-silacyclopent-3-ene (**30**; 10%), 1-methyl-1-(2-silapropyl)-1-silacyclopent-3-ene (**31**; 2%), 1-(trimethylsilyl)-1-silacyclopent-3-ene (**33**; 8%), 5-silaspiro[4.4]nona-2,7-diene (**35**; 1%), disilacyclopentadiene (**37**; 2%), 3-(trimethylsilyl)-1-silacyclopent-3-ene (**42**; 5%), 2-(trimethylsilyl)-1-silacyclopent-3-ene (**43**; 2%), 1-(trimethylsilyl)-1,3-butadiene (**44**; 5%), and 1-silacyclopent-3-ene (**45**; 2%). Spectroscopic data for **26**, **30**, **31**, **33**, **42**, **43**, and **44** are given in Table II. The properties of **26** were identical with those of an authentic sample whose synthesis was described above. **29**,[38] **35**,[39] and **45**[40] are known compounds and were identified by comparison with literature spectra. **28** was identical with an authentic sample prepared in 34% yield by flow pyrolysis of a mixture of 210 mg (1.8 mmol) of 1,1,1,2-tetramethyldisilane and 1.2 g (23 mmol, 12-fold excess) of 1,3-butadiene at 500 °C (2 torr); contact time = 6 ms. The evidence for the structure of the compound believed to be the dimer of silole **37** will be published separately.[24]

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Registry No. **11**, 5089-32-7; **15**, 80540-80-3; **16**, 99811-08-2; **17**, 80540-72-3; **18**, 99811-09-3; **19**, 5089-32-7; **20**, 99811-10-6; **21**, 99811-11-7; **22**, 99829-78-4; **28**, 55544-25-7; **29**, 16054-12-9; **30**, 99811-18-4; **31**, 99811-19-5; **33**, 99811-20-8; **35**, 52856-32-3; **37**, 99811-21-9; **42**, 99811-22-0; **43**, 99811-23-1; **44**, 1798-76-1; **45**, 7049-25-4; 2,2-dichlorohexamethyltrisilane, 5181-42-0; chlorotris(trimethylsilyl)silane, 5565-32-2; 1,1,2-trichlorotrimethyldisilane, 13528-88-6; 1-chloro-1,2,2-trimethyl-1,2-disilacyclohex-4-ene, 99811-12-8; 1,1,2-trimethyl-1,2-disilacyclohex-4-ene, 99811-13-9; *cis*-1,4-dibromo-2-butene, 18866-73-4; 1,2-dimethyltetrachlorodisilane, 4518-98-3; *cis*-1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-14-0; *trans*-1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-15-1; *cis*-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-16-2; *trans*-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-17-3; 1,3-butadiene, 106-99-0.

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Reaction of Acetyl Complexes with HMR_3 (M = Si, Sn). Mechanism of Acetaldehyde Formation

R. W. Wegman

Union Carbide Corporation, South Charleston, West Virginia 25303

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The thermal reaction of the acyl complexes $CH_3C(O)M(CO)_xL$ (M = Co, Mn; L = PPh_3) with $HM'R_3$ (M′ = Si, Sn; R = Bu, Ph) results in the formation of acetaldehyde and $R_3M'M(CO)_xL$. The rate law for the reaction is consistent with a pathway involving initial CO dissociation from $CH_3C(O)M(CO)_xL$, oxidative addition of the H–M′ bond, and reductive elimination of acetaldehyde. With $HSnR_3$ the rate-determining step is CO dissociation from $CH_3C(O)M(CO)_xL$. In the case of $HSiR_3$ the rate-determining step is oxidative addition of the H–Si bond.

Introduction

Metal acyl complexes play a pivotal role in numerous catalytic processes. For example, in the Rh–I catalyzed carbonylation of methanol to acetic acid, reductive elimination of acetyl iodide from $CH_3C(O)Rh(CO)_2I_3^-$ leads to the formation of the intermediate acetyl iodide (eq 1).[1] In

$$CH_3C(O)Rh(CO)_2I_3^- \rightarrow CH_3C(O)I + Rh(CO)_2I_2^- \tag{1}$$

olefin hydroformylation formation of a metal acyl complex is followed by cleavage of the carbon–metal bond to yield an aldehyde.[2] With a Rh–PPh_3 catalyst it is generally accepted that $RC(O)Rh(CO)L_2$ oxidatively adds dihydrogen and then eliminates an aldehyde according to eq 2.

$$RC(O)Rh(CO)L_2 + H_2 \rightarrow RC(O)H + HRh(CO)L_2 \tag{2}$$

Cleavage of cobalt acyl complexes is somewhat less well understood. In chemistry related to olefin hydroformylation, it is thought that cleavage occurs with H_2 or $HCo(CO)_4$ (eq 3 and 4).[4]

$$RC(O)Co(CO)_4 \xrightarrow{H_2} RC(O)H + HCo(CO)_4 \tag{3}$$

$$RC(O)Co(CO)_4 \xrightarrow{HCo(CO)_4} RC(O)H + Co_2(CO)_8 \tag{4}$$

Recently the kinetics of reactions 3 and 4 with $EtOC(O)Co(CO)_4$ were reported.[5] The reactions were carried out in *n*-octane and proceed by the initial dissociation of CO from $EtOC(O)Co(CO)_4$ followed by a slower reaction of the coordinatively unsaturated $EtOC(O)Co(CO)_3$ with H_2 or $HCo(CO)_4$. The reaction of $HCo(CO)_4$ (eq 4) is approximately 12 times faster than H_2 (eq 3).

In contrast, only hydrogenolysis (eq 3) of the carbon–cobalt bond of phosphine-substituted $CH_3C(O)Co(CO)_3L$

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