acetylide complexes refer to ref 22. In this study no indication for such an interaction has been found. The Mulliken population of the π^* orbitals on the ligand fragments is calculated as 0.05 e or less in all cases by HFS.

Since UP data in combination with reliable MO calculations is the most direct method to study the electronic structure of compounds, these data shed some doubt upon the existence of π back-bonding in this type of complex, at least with cyanide and alkyl or unsubstituted acetylides.

In some cases X-ray data on palladium and platinum acetylide complexes has shown unusually short M–C distances.[43-45] Although ligands and/or coligands in these cases were much different from those used in this study, we still feel an alternative explanation from π back-bonding may be offered on the basis of the present data.

It has been shown that the highest π orbitals in all complexes were orbitals with M–C antibonding character. If π withdrawing substituents are added to the acetylide part, then charge will be withdrawn from this type of orbital and the M–C bond order will thus be increased. Replacement of one acetylide ligand by another ligand with similar fragment orbitals might have the same effect.

Conclusions

By using empirical criteria and the results from HFS calculations on model compounds, the UP spectra of a series of square-planar Pd(II) and Pt(II) complexes of acetylide and cyanide ligands can be assigned.

It is shown that there exists strong interaction between metal d orbitals and the coordination environment, leading to delocalized orbitals of π symmetry with respect to the M–C bond in one case and a very high-lying d_{z^2} type orbital in another.

It is shown that, despite π interaction between occupied orbitals on metal and ligand fragments, π back-bonding plays only a very minor role in the complexes studied.

Energy levels are very similar for corresponding palladium and platinum complexes, in agreement with results from the calculations. One important exception is the IE of the ionization due to the $\sigma_{M-C}{}^u$ orbital in the bis(acetylide) and dicyanide complexes. Since no metal d orbitals are involved in this orbital, apparently the role of Pd and Pt p orbitals in bonding is not insignificant.

Acknowledgment. This work was supported in part by financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). R.L.D. also acknowledges the grant support of the Netherlands America Commission for Educational Exchange and Calvin College for a Calvin Research Fellowship.

Registry No. $[(PEt_3)_2Pd(C{\equiv}C{-}H)_2]$, 34230-57-4; $[(PEt_3)_2Pt(C{\equiv}C{-}H)_2]$, 34230-58-5; $[(PEt_3)_2Pd(C{\equiv}C{-}CH_3)_2]$, 34230-60-9; $[(PEt_3)_2Pt(C{\equiv}C{-}CH_3)_2]$, 34230-61-0; $[(PEt_3)_2Pd(C{\equiv}N)_2]$, 15638-57-0; $[PEt_3)_2Pt(C{\equiv}N)_2]$, 15712-02-4; $[(PEt_3)_2PdCl(C{\equiv}N)]$, 89579-33-9; $[(PEt_3)_2PtCl(C{\equiv}N)]$, 68225-04-7; $[(Ph_3)_2Pd(C{\equiv}C{-}H)_2]$, 89579-34-0; $[(Ph_3)_2Pd(C{\equiv}C{-}CH_3)_2]$, 89579-35-1; $[(Ph_3)_2Pt(C{\equiv}C{-}H)_2]$, 89579-36-2; $[(Ph_3)_2Pd(C{\equiv}N)_2]$, 89579-37-3; $[(Ph_3)_2PdCl(C{\equiv}N)]$, 89579-38-4; $[(Ph_3)_2PtCl(C{\equiv}N)]$, 89596-63-4.

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(43) Behrends, U.; Hoffmann, K.; Kopf, J.; Moritz, J. *J. Organomet. Chem.* **1976**, *117*, 91.

(44) Behrends, U.; Hoffmann, K. *J. Organomet. Chem.* **1977**, *129*, 273.

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The Isomerization of Methylsilene to Dimethylsilylene. Further Evidence

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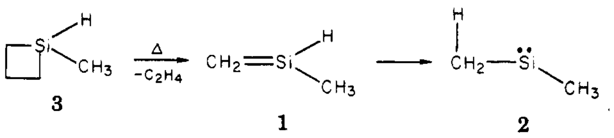
Methylsilene, generated thermally from three different precursors 1-methylsilacyclobutane, 2,3-bis(trifluoromethyl)-7-methyl-7-sialabicyclo[2.2.2]octa-2,5-diene, and 1-methoxy-1-methyl-1-[(trimethylsilyl)methyl]silane, isomerizes to dimethylsilylene. Trapping studies with butadiene and trimethylsilane lead to products expected from dimethylsilylene.

Introduction

Following our preliminary report that generation of 1-hydrido(1-methyl)silene from low-pressure pyrolysis of 1-methylsilacyclobutane (**3**) leads to products characteristic of the isomeric dimethylsilylene,[1] the proposed hydridosilene to methylsilylene isomerization has become a controversial reaction mechanism. Matrix isolation studies of Drahnak, Michl, and West[2] on photogenerated[3] methylsilene (**1**) and dimethylsilylene (**2**) were interpreted as evidence for rapid thermal conversion of **1** to **2** at 100 K. These gas-phase and condensed-phase experiments appeared to complement the earlier theoretical studies from the groups of Gordon[4] and Schaefer[5] which indicated methylsilene and dimethylsilylene to be nearly isoenergetic.



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(1) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *193*, 1843. For an example of the isomerization of the parent silene 1,1-dihydridosilene, see: Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 618.

(2) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845. Further work on matrix-isolated dimethylsilylene and methylsilene has been reported recently. Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176. In this communication the authors offer the interesting suggestion that the act of trapping the hydridosilene induces a hydrogen shift from silicon to carbon.

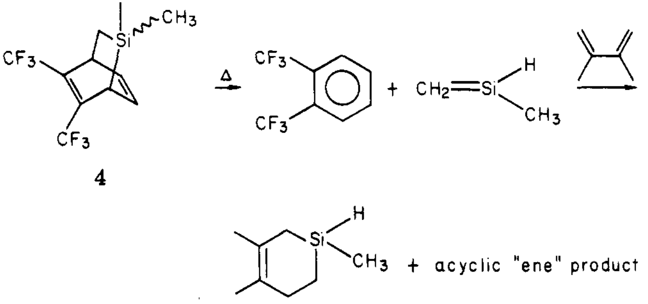
(3) Photochemical conversion of **2** to **1** was also reported in ref 2 and the reversibility of the photoisomerization between hydridosilenes and methylsilylenes has recently been described. Reisehauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 854.

(4) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9.

(5) Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288.

0276-7333/84/2303-0918$01.50/0

Most recent calculations of Schaefer,[6] however, predict a sizeable barrier of ~41 kcal/mol for the proposed isomerization in conflict with a low-temperature isomerization of 1 to 2. Subsequently Barton et al.[7] have shown that methylsilene formed in a retro Diels–Alder thermolysis of the silabicyclooctadiene 4 reacts in a manner typical of species containing a silicon–carbon π bond but without intervention of the silylene isomer in a 450–550 °C temperature range. Consistent with a reluctant silene isomerization are the ion cyclotron double-resonance studies of Hehre and co-workers[8] which suggest that 1-methylsilene is some 28 kcal/mol more stable than dimethylsilylene. Yet, the ICR experiments are in discord with the experiments of Conlin and Wood and those of Drahnak, Michl, and West as well as Schaefer's calculations and the recent theoretical results of Köhler and Lischka.[9] Amid this collection of contradictory interpretations of results is the report of Walsh[10] in which thermochemical and kinetic estimates are used to reconcile the apparent differences between the experiments of Barton and of Conlin with Schaefer's calculated barrier for the isomerization of a hydridosilene to a methylsilylene.

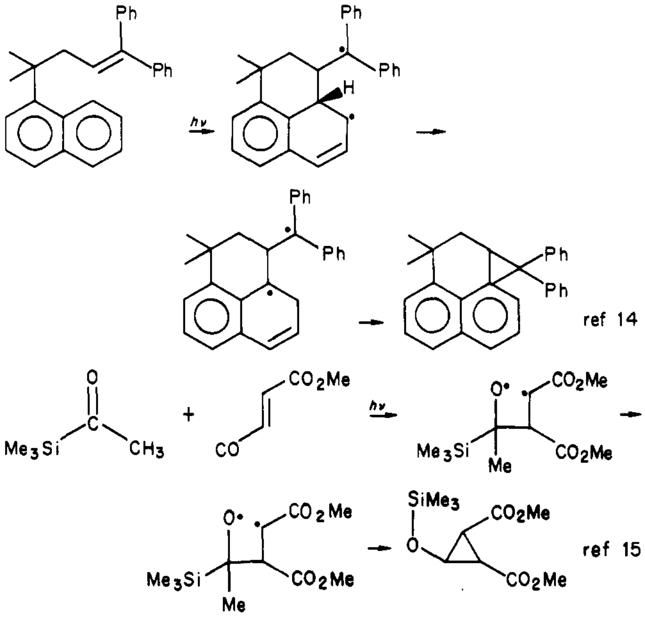


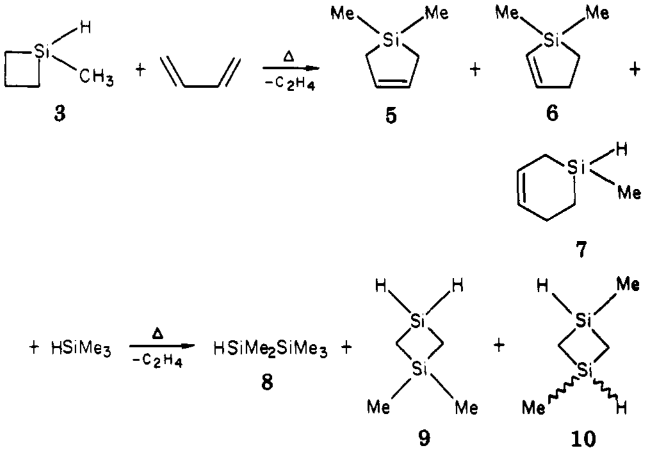
To settle the primary issue: does a silene bearing a hydrogen on the trivalent silicon isomerize to methylsilylene, we have reinvestigated our original work with hydridomethylsilacyclobutane 3, the proposed 1-methylsilene precursor. Since there are questions concerning the formation of 1-methylsilene from the four-membered ring 3 as well as the isomerization, we have subjected two additional methylsilene generators to the same experimental conditions in which the silene to silylene rearrangement was originally observed.

Results and Discussion

Pyrolysis of 1-methylsilacyclobutane (3) in a tenfold excess of butadiene at 600 °C yields three major products: 1,1-dimethylsilacyclopentenes 5 and 6 (30% and 9%, respectively) and 1-methylsilacyclohex-3-ene (7; 16%). At 650 °C pyrolyses in a eightfold excess of butadiene, 7 was formed in considerably lower yield (4%) and was not characterized in our initial report.[1] Formation of dimethylsilylene from the thermal decomposition of methylsilacyclobutane at 650 °C was established when trimethylsilane was the coreactant. Pentamethyldisilane 8, produced by insertion of dimethylsilylene into the silicon–hydrogen bond of trimethylsilane, was isolated in 14% yield along with the disilacyclobutanes 9 (25%) and 10 (36%) previously attributed to the dimer of dimethylsilylene.[11] A reasonable explanation of dimethylsilylene formation is that fragmentation of 1-methylsilacyclobutane afforded ethylene and 1-methylsilene which isomerized to dimethylsilylene.

Scheme I





9 10

The observation of predominantly silylene adducts, even at the lowest temperatures required for silene generation in our low-pressure pyrolyses, deserves comment. While butadiene is an efficient trapping agent for both reactive intermediates (estimates of activation energies are 5–10 kcal/mol[12] for silene cycloaddition to dienes and 1–3 kcal/mol[13] for silylene addition), the comparatively higher barrier for the bimolecular cycloaddition of the silene permits isomerization to the more reactive silylene under our experimental conditions.

Barton pointed out that dimethylsilylene might be formed not by isomerization of the hydridosilene fragment from methylsilacyclobutane but through another sequence in which a 1,4 biradical isomerizes to a 1,3 biradical which jettisons the dimethylsilylene. We know of only two cases[14,15] for which isomerization of the 1,4 biradical to 1,3 biradical has been necessarily invoked to rationalize product formation. In both cases conversion of the 1,4 biradical to a 1,3 biradical was initiated by a photochemical

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(6) (a) Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1981**, *103*, 7366; (b) Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F., III, *Ibid.* **1980**, *102*, 7644.

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

(8) Pau, C. F.; Pieto, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 16.

(9) Kohler, J. K.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884.

(10) Walsh, R. *J. Chem. Sox., Chem. Commun.* **1982**, 1415.

(11) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 868.

(12) Frey, H. M.; Kashoulis, A.; Lee, M.-L.; Lodge, S. P.; Pidgeon, I. M.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1981**, 915.

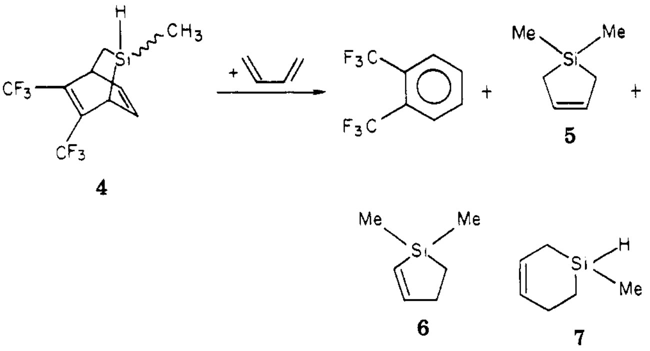
(13) Dzarnoski, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217.

(14) Hixson, S. S.; Tausta, J. C. *J. Org. Chem.* **1977**, *42*, 2191.

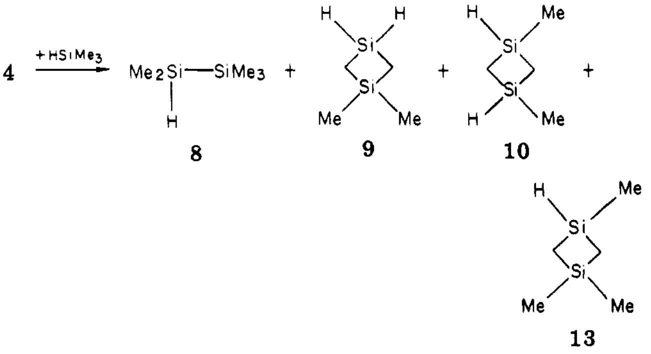
(15) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Chem.* **1981**, *103*, 699.

reaction between π-electron systems at ambient temperature. Although each example remains speculative, neither possibility has been eliminated and such a mechanism remains possible in the thermal decomposition of hydridosilacyclobutanes (Scheme I).

To avoid this uncertainity, we have made use of the hydridomethylsilabicyclooctadiene 4, from previous work[7] a known precursor to 1-methylsilene. Under our experimental conditions vacuum pyrolysis of 4 in a stream of 1–3 torr of butadiene at 650 °C afforded *o*-bis(trifluoromethyl)benzene in 85% yield, the expected silene dimer **10** (14%), 1-methylsilacyclohex-3-ene (**7**; 7%), and significantly, the silylene adducts **5** and **6** (3% and 4%, respectively). The temperature dependence of the ratios of the dimethylsilacyclopentenes to methylsilacyclohexene in our vacuum flow pyrolyses varied erratically due to the difficulty in vaporizing **4** at a constant rate. Nevertheless, it would seem that the hydridosilene is the penultimate source of the dimethylsilylene adducts **5** and **6**. Conclusive evidence for the role of dimethylsilylene in the fragmentation of **4** was obtained from the copyrolysis of **4** with trimethylsilane at 650 °C. Of the four silicon-containing products pentamethyldisilane **8** (3%), 1,1-dimethyldisilacyclobutane **9** (6%), 1,3-dimethyldisilacyclobutane **10** (14%), and 1,1,3-trimethyldisilacyclobutane **13** (4%), both **8** and **9** are known products of the respective dimethylsilylene[16] insertion and tetramethyldisilene isomerization.[17] At this stage it would seem that formation of dimethylsilylene adducts from the expected 1-methylsilene precursors offers secure evidence for silene to silylene isomerization. However, an alternate explanation is possible. The mechanism of the thermal decomposition of the silabicyclooctadiene **4** could also proceed in a stepwise manner. If so, such a mechanism again introduces occasion for an intramolecular H shift in a possible intermediate biradical prior to the fragmentation step leading to the silene.

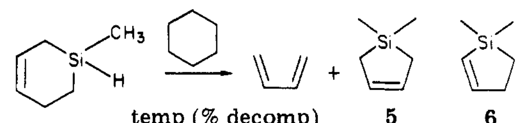


4 5 6 7



8 9 10 13

Scheme II

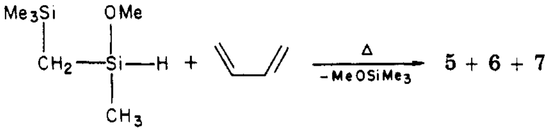


7

temp (% decomp)	5	6
600 °C (0)	no reaction	
650 °C (36%)[a]	8%	4%
750 °C (82%)[a]	36%	24%

[a] Relative yields of butadiene were variable since no special precautions were taken to prevent loss of the C_4H_6 vapors.

These mechanistic ambiguities involving possible biradicals can be circumvented if an acyclic precursor to the hydridosilene is induced to undergo a 1,2 elimination (β elimination). Recently, generation of a variety of silenes from a 1,2 elimination of methoxytrimethylsilane has been described,[18] and such eliminations most likely proceed through a "loose" four-center transition state.[19] Accordingly, pyrolysis of 1-methoxy-1-methyl-1-[(trimethylsilyl)methyl]silane (**11**) at 600 °C in stream of 1–3 torr of butadiene yielded four products: methoxytrimethylsilane (**12**, 78%), dimethylsilacyclopentenes **5** (33%) and **6** (22%), and **7** (24%). Yields were based on 6% decomposition of **11** at 600 °C. At 700 °C, but with otherwise identical reaction conditions, **11** underwent 49% decomposition.



11 12

The same products were observed, but the ratio of dimethylsilylene adducts **5** and **6** to methylsilene adduct **7** increased from 2.3 to 17.2. The observed change in product ratios is consistent with the increasing importance of isomerization of the hydridosilene to methylsilylene at higher temperature.

A potential difficulty in drawing quantitive mechanistic conclusions from the ratio of silacyclopentenes **5** and **6** to silacyclohexene **7** at the higher temperature range (>650 °C) is that the six-membered ring may undergo a retro Diels–Alder reaction to yield the hydridosilene and butadiene. Indeed, pyrolysis of **7** with an equal volume of cyclohexane at 650 °C did produce butadiene and **5** and **6** which most likely originate from isomerization of silene to silylene followed by cycloaddition to butadiene. Product distributions at three different temperatures, 750, 650, and 600 °C, are shown in Scheme II.

In the unlikely event that some **7** might isomerize to **5** and **6** by a unimolecular process, formation of silacyclopentenes from decomposition of **3**, **4**, and **11** in butadiene would *not* provide unequivocal evidence for the presence of dimethylsilylene. However, isolation of a disilane from insertion into the Si–H bond of trimethylsilane is uniquely consistent with formation of dimethylsilylene. Since we have previously demonstrated a silylene pathway with the hypothetical methylsilene precursors methylsilacyclobutane **3** and silabicyclooctadiene **4**, it remained to carry out a similar copyrolysis with trimethylsilane and the less ambiguous methylsilene source **11**. Thermal decomposition of **11** at 650 °C in a 12-fold excess of trimethylsilane led to pentamethyldisilane **8** in 31% yield, trimethyldisilacyclobutane **13** (27%), methoxydimethyl-

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[16] For a comprehensive and critical review of silylene chemistry, see: Gaspar, P. P. In "Reactive Intermediates"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, pp 335–387.

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

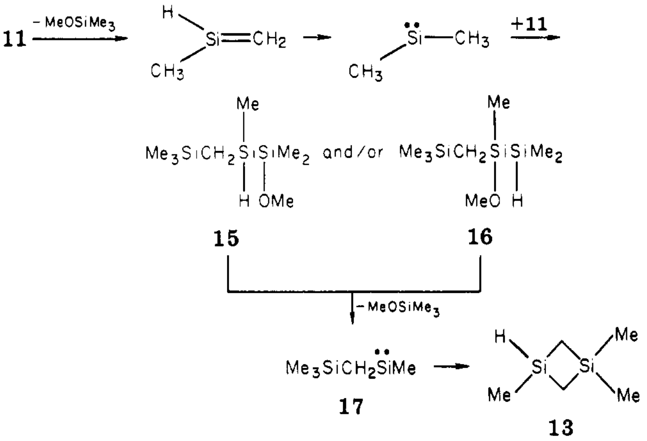
[18] Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, 216, C5 and references therein.

[19] Maccoll, A. *Chem. Rev.* **1969**, *69*, 33.

silane (14; 22%), and methoxytrimethylsilane (12; 65%). Formation of silylene products, disilanes, from three different precursors of a hydridosilene, provides convincing evidence for the prototypal silene to silylene isomerization.

$$11 \xrightarrow[+\mathrm{HSiMe_3}]{\Delta} 8 + 13 + 14 + 12$$

The frequent appearance of 1,1,3-trimethyldisilacyclobutane 13 and methoxydimethylsilane (14) in thermal reactions of 11 illustrates the complexity of reactions involving reactive intermediates in organosilicon chemistry. With our experimental conditions (low pressure and high temperature), it is unlikely that the trimethyldisilacyclobutane is produced by dimerization of the necessary silenes. Instead, the formation of 13 is more reasonably attributed to an intramolecular C–H insertion of methyl(trimethylsilylmethyl)silylene (17) as previously shown by Barton.[20] Of the many possible routes to the silylene 17 from 11, we favor one in which dimethylsilylene, produced by isomerization of the hydridosilene, inserts into an Si–H or Si–O bond of the starting material. Although we have not isolated either of the resulting trisilanes 15 or 16, this is not surprising as both 15 and 16 would be especially prone to an α elimination of methoxydimethylsilane 14. Supporting evidence of 15 or 16 is the formation of trimethyldisilacyclobutane 13 whenever 14 is observed.



Experimental Section

General Data. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R24B. 60-MHz spectrometer using methylene chloride as an external standard. Carbon NMR spectra were obtained on a JEOLCO-JEOL FX 90Q spectrometer referenced to external Me_4Si.

Preparative gas chromatography was performed on a Varian 90A gas chromatograph (thermal conductivity detector). Analytical gas chromatography was performed on a HP 5840A gas chromatograph (flame ionization detector). Product yields from pyrolyses were based on the amount of decomposed silene precursor and determined chromatographically with cyclohexane as an internal standard and predetermined response factors for the organosilanes.

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer or a Finnegan 9500 or a Finnegan 1020 gas chromatograph/mass spectrometer. Infrared spectra of thin films on NaCl disks were obtained on a Perkin-Elmer 1330 spectrometer. Exact mass measurements were carried out at the Midwest Center for Mass Spectrometry.

Methylsilacyclobutane was synthesized as described in the literature.[21] Trimethylsilane (PCR) and butadiene (Phillips) were dried and distilled prior to each experiment.

Synthesis of 1-Methoxy-1-methyl-1-[(trimethylsilyl)methyl]silane (11). To a well-stirred mixture of excess Mg turnings in 200 mL of dry ether was added 15 g (0.123 mol) of (chloromethyl)trimethylsilane in 60 mL of ether. After being stirred for 3 h at room temperature, the solution was transferred by syringe to a solution of 14 g (0.12 mol) of dichloromethylsilane in 450 mL of ether. The reaction mixture was stirred for 3 h at room temperature, cooled to 0 °C, and treated with a solution of 6 mL of methanol and 11 mL of pyridine. After being warmed to room temperature and stirred overnight, the mixture was filtered through Celite. Distillation through a 36-cm Vigreaux column afforded 8 g (0.06 mol, 49% yield) of 11 (bp 137 °C at 760 mm). Samples of 11 used for pyrolysis were obtained by preparative GC on a $^1/_2$ in. × 16 ft, 20% OV-17 column on Chromosorb W: ^{1}H NMR (neat) δ –0.41 (2 H, br s, $SiCH_2Si$), –0.30 (9 H, s, $(CH_3)_3Si$), –0.20 (3 H, d, CH_3Si), 3.03 (3 H, s, CH_3O), 4.28 (1 H, m, HSi); ^{13}C NMR (neat) δ –1.56, 0.388, 2.79, 50.50; mass spectrum, *m/e* (relative intensity) 162 (1.4), 161 (9), 147 (100), 131 (25), 118 (94), 74 (62), 59 (88); IR (NaCl plates) 2952 (s), 2898 (m), 2828 (m), 2101 (s), 1244 (s), 1184 (m), 1086 (s), 1040 (s), 872 (s), 835 (s) cm^{-1}. Several attempts to obtain a satisfactory elemental analysis were unsuccessful. Furthermore, a high-resolution mass spectrum could not be obtained for the parent ion as might be expected for a highly substituted hydridosilane. Excellent analytical data could be obtained, however, for the P – 1 and P – 15 ions; calcd for $SiC_6H_{18} - 1$ 161.0818, found 161.0818; calcd for $SiC_6H_{18} - CH_3$ 147.0661, found 147.0659. In the course of our exercise in analysis, we have learned that methoxysilanes bearing a hydrogen on silicon are extremely susceptible to catalytic hydrolysis by trace amounts of water adsorbed on the surface of the container. The product, a siloxane, can also be an efficient silene precursor.

Synthesis of *syn*- and *anti*-2,3-Bis(trifluoromethyl)-7-methyl-7-silabicyclo[2.2.2]octa-2,5-diene (4). A solution of 99 g (1.5 mol) of cyclopentadiene and 68 g (0.3 mol) of 1,1,2,2-tetrachloro-1,2-dimethyl-1,2-disilane was added dropwise to a vertical quartz tube (18 in. × $1^1/_3$ in.) packed with quartz chips and heated to 600 °C. The pyrolysate was swept through the reaction chamber with N_2 (flow rate 10 mL/11 s) into 250-mL flask cooled in an 2-propanol/CO_2 bath. Fractional distillation of the dark tarry solution afforded a 3:1 mixture of the conjugated and unconjugated 1-chloro-1-methylsilacyclohexadienes, 18.6 g (0.13 mol, 43% yield). Reduction of the chlorosilanes (0.13 mol in 40 mL of ether) with lithium aluminum hydride (0.185 mol in 100 mL of ether) produced the corresponding methylsilacyclohexadienes; 11.7 g (82%); ^{1}H NMR of the unconjugated isomer (neat) δ 0.05 (3 H, d, CH_3Si), 2.65 (2 H, m, CH_2), 4.05 (1 H, m, SiH), 5.52 (2 H, m, HC═), 5.32 (2 H, m, HC═); ^{13}C NMR (neat) δ –3.6, 33.2, 112.3, 145.4; ^{1}H NMR of conjugated isomer δ 0.11 (3 H, d, CH_3Si), 1.46 (2 H, m, CH_2), 4.07 (1 H, m, SiH), 5.62 (3 H, m, HC═), 7.43 (1 H, m, HC═); ^{13}C NMR (neat) δ –4.7, 9.9, 122.0, 125.0, 127.0, 142.0. Reaction of the conjugated silacyclohexadiene (4 g, 36 mmol)[22] with excess perfluorobutyne was carried out in a sealed tube held at 80 °C for 96 h. After removal of the volatiles, vacuum distillation of the residue yielded 3.8 g (51%) of 4. Chromatographically pure silabicyclooctadiene used in pyrolyses was obtained from the previously mentioned OV-17 column at 95 °C. Although the syn and anti isomers were resolved by GC and collected separately, spectroscopic data indicated the same chemical shifts for both isomers: ^{1}H NMR (neat) δ –0.18 (3 H, d, CH_3Si), 0.07 (1 H, m, CH_2Si), 0.53 (1 H, m, CH_6Si), 3.43 (1 H, m, C_3CH), 3.44 (1 H, m, SiH), 3.87 (1 H, m, C_3CH), 5.68 (1 H, br t, HC═), 5.94 (1 H, br t, HC═); ^{13}C NMR (neat) δ –6.9, 9.68 32.2, 35.5, 128.7, 129.4, signals were not observed for the trifluoromethyl carbons nor for the adjacent olefinic carbons; mass spectrum, *m/e* (relative intensity) 272 (2%), 203 (27), 195 (100), 177 (30), 176 (31), 145 (72), 127 (24), 81 (32), 77 (33); IR (NaCl plates) 3060 (w), 2968 (w), 2918 (2), 2148 (s), 1706 (m), 1692 (m), 1598 (w), 1362 (m), 1282 (s), 1252 (s), 1180 (s), 1138 (s), 1008 (m), 970 (s) cm^{-1}; calcd for $SiC_{10}H_{10}F_6$ 272.0456, found 272.0448.

General Procedures for Low-Pressure Pyrolysis (LPP). All pyrolyses, unless noted otherwise, were carried out in a sea-

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[20] Barton, T. J.; Jacobi, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 7979.

[21] Seyferth, D.; Damrauer, R.; Andrews, S. B.; Washburn, S. S. *J. Am. Chem. Soc.* **1971**, *93*, 3709.

[22] Reactions were carried out on a mixture of conjugated and unconjugated silacyclohexadienes, and yields were based on the quantity of the conjugated isomer.

soned hot zone consisting of a 10-mm i.d. × 30-cm quartz tube wrapped with nichrome ribbon and covered with asbestos tape. Residence times in the hot zone were on the order of the tenths of seconds, and pressures in the hot zone were on the order of 1–3 torr. Pyrolysis temperatures were the average of two measurements taken 4 cm from the beginning and the end of the hot zone. Residence time, pressure, and collision frequency were controlled by a 0.8-mm aperture placed at the end of the pyrolysis chamber.

Vapors of the methylsilene precursors (**3**, **4**, or **11**) were introduced to the pyrolysis zone from a reservoir placed 2 cm before the hot zone. The quantity of vaporized material was regulated by the bath temperature of the reservoir. For example, vapors of **3** (held at −42 °C), **4** (70 °C), or **11** (20 °C) were mixed before the hot zone with vapors of butadiene or trimethylsilane from a different reservoir in the vacuum system. Vapors of the pyrolysate were condensed on a liquid N_2-cooled surface placed 2 cm from the end of the hot zone.

LPP of 1-Methylsilacyclobutane (3). a. Butadiene Trapping. Vapors from 0.80 g (9.3 mmol) of **3** were introduced at a rate of ~100 mg/15 min with a 10-fold molar excess of butadiene to the pyrolysis chamber at 600 °C. Bulb to bulb distillation of the condensate followed by preparative GC on a $^1/_4$ in. × 20 ft, 15% DC 710 column yielded unreacted **3** (42%) and **5** (30%): ^{1}H NMR (neat) δ 0.14 (6 H, s, $(CH_3)_2Si$), 1.08 (4 H, app d, $(CH_2)_2Si$), 5.50 (2 H, t, $HC{=}CH$); ^{13}C NMR (neat) δ −2.60, 17.49, 130.32; mass spectrum, *m/e* (relative intensity) 112 (12), 97 (100), 95 (33), 58 (16), 43 (13). **6** (9%): ^{1}H NMR (neat) δ 0.15 (6 H, s, $(CH_3)_2Si$), 0.55 (2 H, app t, CH_2Si), 2.25 (2 H, m, CCH_2C), 5.46 (1 H, m, $HC{=}CC$), 6.01 (1 H, m, $(SiCH{=}C)$; ^{13}C NMR (neat) δ −1.56, 8.58, 31.54, 152, m, 129.67; mass spectrum, *m/e* (relative intensity) 112 (11), 97 (100), 95 (42), 58 (26), 43 (22). **7** (16%): ^{1}H NMR (neat) δ 0.15 (3 H, d, CH_3Si), 0.75 (2 H, m, CH_2Si), 1.25 (2 H, d, $={C}\ CH_2Si$), 2.10 (2 H, m, $={C}\ CH_2C$), 5.45 (2 H, br s, $HC{=}CH$); ^{13}C NMR (neat) δ −5.86, 6.96, 9.49, 22.04, 124.86, 129.93; mass spectrum, *m/e* (relative intensity) 112 (46), 111 (12), 97 (43), 95 (14), 85 (12), 84 (100), 71 (23), 69 (17), 58 (43); calcd for SiC_6H_{12} 112.0709, found 112.0701. A fourth product, 1-methylsilacyclopent-3-ene,[1] is formed in minor amounts.

b. Trimethylsilane Trapping. Vapors from 0.94 g (10.9 mmol) of **3** were copyrolyzed with an eightfold excess of trimethylsilane at 650 °C. Bulb to bulb distillation of the pyrolysate, followed by preparative GC on an OV-17 column, afforded four new products: Pentamethyldisilane **8** (14%) identical with an authentic sample[23] [previously unreported ^{13}C NMR (neat) δ −6.96, −2.21], 9 (25%), and **10** (36%). Spectral characteristics of both disilacyclobutanes **9** and **10** were identical with those previously reported.[11] The 1,3-dimethyldisilacyclobutane **10** is presumably a mixture of cis and trans isomers which could not be separated by GC on a variety of columns and displayed overlapping signals in the previously unreported ^{13}C NMR [(neat) δ −1.30, −0.33; for **10**, ^{13}C NMR (neat) δ −2.15, 2.34]. Trace amounts (<2%) of 1,1,3-trimethyldisilacyclobutane **13** were also produced: ^{13}C NMR (neat) δ −0.65, 1.36, 1.88, 2.73.

c. Neat Pyrolysis. Vapors from 0.91 g (10.5 mmol) of **3** were pyrolyzed at 650 °C to afford 9 (13%) and **10** (23%).

LPP of 4. a. Butadiene Trapping. Vapors from 1.4 g (5.1 mmol) of **4** were copyrolyzed with a 10-fold excess of butadiene to produce *o*-bis(trifluoromethyl)benzene (85%), **10** (14%), **5** (3.4%), **6** (3.8%), and **7** (8%).

b. Trimethylsilane Trapping. Pyrolysis of vapors from 1.8 g (6.6 mmol) of **4** with a 12-fold excess of trimethylsilane afforded *o*-bis(trifluoromethyl)benzene (91%), **8** (3%), **9** (6%), **10** (14%), and **13** (8%).

c. Neat. Vapors from 1.8 g (6.6 mmol) of **4** were pyrolyzed at 650 °C to yield *o*-bis(trifluoromethyl)benzene (97%), **9** (3%), **10** (8%), and **13** (3%).

LPP of 11. a. Butadiene Trapping. Vapors from 1.1 g (6.8 mmol) of **11** were copyrolyzed with a 10-fold excess of butadiene at 600 °C to afford **12** (78%), **5** (33%), **6** (22%), and **7** (24%).

b. Trimethylsilane Trapping. Pyrolysis of vapors from 1.1 g (6.8 mmol) of **11** with a 12-fold excess trimethylsilane at 650 °C produced **12** (65%), **14** (22%), **8** (31%), **9** (6%), **10** (14%), and **13** (27%).

c. Neat. Vapors from 0.8 g (4.9 mmol) of **11** were pyrolyzed at 600 °C to afford **12** (56%), **14** (25%), and **13** (32%).

LPP of 7. Pyrolyses of 1-methylsilacyclohex-3-ene (**7**) diluted with an equal volume of cyclohexane carrier were performed in the same apparatus described earlier but modified at the inlet to allow liquid injections. In a typical experiment ~70 µL of the solution of **7** and cyclohexane were injected into the pyrolysis chamber over a period of 1 h. At 600 °C there was no reaction, but at 650 °C, 30% decomposition afforded a mixture of **5** (8%) and **6** (4%). At 700 °C decomposition of **7** was 85% and dimethylsilacyclopentenes **5** and **6** were formed in 36% and 24% respective yields. Without a large volume of volatile trapping agent as in these experiments, the pressure drop across the hot zone is much less than in the previously described trapping experiments. Since contact time in the hot zone is directly related to this pressure differential, it is probable that contact times were significantly longer during these injection pyrolyses.

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