Silenes and Silenoids. 7. Electron-Impact-Induced Decomposition of (Trimethylsilyl)methyl-Substituted Chlorosilanes[1]

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The fragmentation characteristics of cation radicals of the series of ((trimethylsilyl)methyl)chlorosilanes, $(Me_3SiCH_2)_nSiCl_{4-n}$, $n = 1$–3, have been investigated by using both unimolecular and collision-activated mass-analyzed ion kinetic energy (MIKE) and metastable measurements on high-resolution mass spectra. For $n = 2$ and 3 the primary decomposition of the P − Me ion is loss of trimethylchlorosilane. The lower energy unimolecular fragmentations are dominated by the production of neutral or charged species, formulated as multiply-bonded silicon intermediates, and the loss of ethylene from cations containing a dimethylsilyl group. In the higher energy processes occurring with collisional activation the loss of saturated fragments such as methane, ethane, and, for $n = 3$, tetramethylsilane becomes significant.

Introduction

The preparation and reactivity of silenes have been an area of concentrated activity for nearly a decade.[2] In several cases, evidence has been presented for the formation of both neutral and charged silenes produced by electron impact.[3] Of special interest in these studies is the correlation of the mass spectral fragmentation patterns with other high-energy methods of silene generation. Fragmentation patterns have also provided evidence for the formation of neutral species incorporating double bonds between silicon and the calcogens[4] and for charged species with double bonds between silicon and oxygen.[5]

The generation of silenes by the electron-impact method can be an excellent method for studying these highly reactive species if the genetic relationships between the observed fragments can be determined unambiguously. While the observation of metastable peaks in a mass spectrum can support a particular parent–daughter relationship, the unique assignment of the parent and daughter ions is not possible.[6] The use of mass-analyzed ion kinetic energy (MIKE) and collision-activated MIKE spectrometry (CAM) provides a method for unambiguous determination of the fragmentation pathways of particular selected ions.[7] We have recently reported the application of these techniques to the trimethyl-substituted group 4 cations.[8] This paper deals with the analysis of the fragmentation patterns of the ions produced by electron impact on the series of ((trimethylsilyl)methyl)chlorosilanes, $(Me_3SiCH_2)_nSiCl_{4-n}$, $n = 1$–3.

Results and Discussion

The compounds ((trimethylsilyl)methyl)trichlorosilane, **1**, bis((trimethylsilyl)methyl)dichlorosilane, **2**, and tris((trimethylsilyl)methyl)chlorosilane, **3**, were prepared by methods similar to those of Sommer and co-workers.[9] In the process of characterizing these compounds, it became clear that their mass spectral fragmentation patterns showed significant similarities to other silene generation processes to which these compounds might be subjected. We therefore undertook a detailed analysis of these fragmentation patterns and report herein the results of those analyses.

Table I. Mass Spectrum of ((Trimethylsilyl)methyl)chlorosilane (1)

m/z[a]	% of base peak[b]	formula[c]	m/z[a]	% of base peak[b]	formula[c]
211	6.4		79	14.5	CH_4SiCl^+
210	6.4		78	8.5	CH_3SiCl^+
209	36.2		73	78.7	$C_3H_9Si^+$
208	14.2		72	18.2	$C_3H_8Si^+$
207	100		71	9.2	
206	14.9		67	6.0	
205	92.2	$C_3H_9Si_2Cl_3^+$	65	36.2	H_2SiCl^+
171	9.7		64	5.7	
169	10.8	$C_3H_7Si_2Cl_2^+$	63	64.5	$SiCl^+$
145	10.6		59	12.1	
135	8.5		58	7.8	$C_2H_6Si^+$
133	8.5	Cl_3Si^+	57	11.3	$C_2H_5Si^+$
115	7.1		55	20.9	
113	7.4		53	7.8	
95	14.9		46	5.7	
93	29.1	$C_2H_6SiCl^+$	45	40.4	CH_5Si^+
92	8.5		44	31.2	
91	7.1		43	74.5	CH_3Si^+
81	7.8		42	14.2	

[a] Masses less than m/z 42 are not reported. [b] Intensities less than 5% are not reported. [c] Isotopic ratios are consistent with these formulas.

$Me_3SiCH_2SiCl_3$, 1. The medium-resolution mass spectrum for compound **1** is reported in Table I. Metastable peaks were observed at M* (parent → daughter): 27.7 (73 → 49), 42.2 (205 → 93), 45.1 (72 → 57), 46.7 (72 → 58), 65.4 (93 → 78), 86.3 (205 → 133), and 139.3 (205 → 169). As is common with organosilicon compounds, the parent molecular ion is not observed, but loss of methyl accounts for the base peak at m/z 205. The general details of the fragmentation pattern are illustrated in Scheme I. The high stability of the m/z 205 ion is indicated by its intensity. This along with its fragmentation patterns leads us to formulate the ion as the bridged species indicated in Scheme I. The fragmentations of methoxydisilanes have

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[1] Preceding paper in this series: Conlin, R. T.; Bessellieu, M. P.; Jones, P. R.; Pierce, R. A. *Organometallics* **1982**, *1*, 396–7.

[2] For a recent review see: Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981** *4*, 297–367.

[3] Auner, N.; Grobe, J. *J. Organomet. Chem.* **1981**, *222*, 33–54 and references therein.

[4] Drake, J. E.; Glavincevski, B. M.; Wong, C. *J. Inorg. Nucl. Chem.* **1980**, *42*, 175.

[5] Larsen, G. L.; Oliva, A.; Tsai, R. S.-C *Org. Mass Spectrom.* **1979**, *14*, 364.

[6] Bowen, R. D.; Howe, I.; Williams, D. H. "Mass Spectrometry", 2nd ed.; McGraw-Hill: New York, 1981; p 54 ff.

[7] Schlunegger, U. P. "Advanced Mass Spectrometry"; Pergamon Press: New York, 1980. Beynon, J. H.; Cooks, R. G. *Res./Dev.* **1971**, *22*, 26.

[8] Groenewold, G. S.; Gross, M. L.; Bursey, M. M.; Jones, P. R. *J. Organomet. Chem.* **1982**, *235*, 165–75.

[9] Sommer, L. H.; Murch, R. M.; Mitch, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1619–21.

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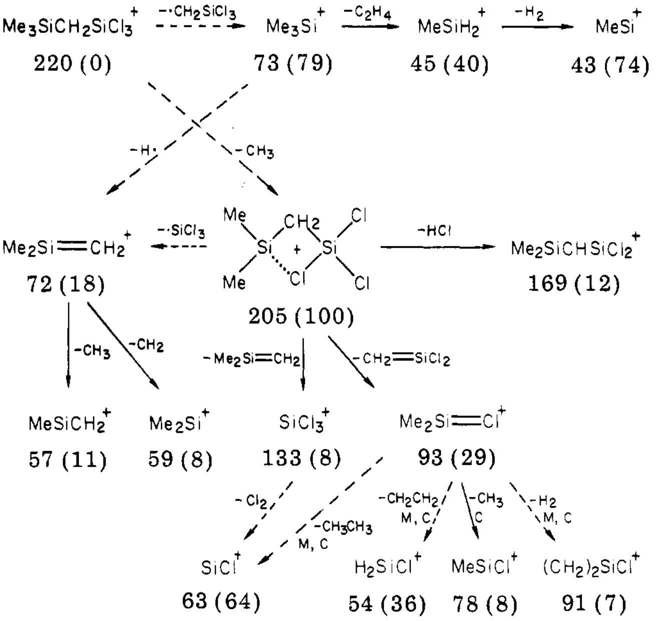
Scheme I. Mass Spectral Fragmentation Pattern for ((Trimethylsilyl)methyl)trichlorosilane (1)[a]



[a] Solid arrows represent processes supported by metastable peaks. Processes labeled M or C have been confirmed by MIKE or CAM spectra. Values are given in m/z. Numbers in parentheses give the intensity of the fragment as a percent of the base peak in the spectrum.

similar features that have been explained in terms of bridged structures involving electronegative oxygen atoms.[10]

The significant fragmentations of the m/z 205 ion are losses of dimethylsilene, dichlorosilene, or HCl. A study of the relative energetics of the former two fragmentations that can provide a measure of the relative stability of dimethylsilene compared to dichlorosilene has been initiated. We have shown previously that the dimethylsilenenium ion at m/z 72 arises by loss of a hydrogen atom from the trimethylsilyl cation.[8] The m/z 72 ion is much more intense in the spectrum of 1 leading us to suggest that it is also produced by the loss of a trichlorosilyl radical from the bridged cation, m/z 205, in this system.

The formation of the $Me_2Si{=}Cl^+$ ion (m/z 93) was investigated with the MIKE and CAM techniques using 2 as the source of the ion, and the results are given in Table III. Its decomposition is quite similar to that for Me_3Si^+,[8] the most significant lower energy pathway being the loss of ethylene to give H_2SiCl^+, with losses of H_2 or CH_3CH_3 to give the ions shown in Scheme I becoming more important at higher energies in the CAM spectra.

$(Me_3SiCH_2)_2SiCl_2$, 2. The mass spectrum of compound 2 is summarized in Table II. Again the parent ion is not observed and the base peak in the spectrum is that arising from loss of methyl at m/z 257. Metastables occurred at 58 (149 → 93), 86.4 (257 → 149), 45.4 (93 → 65), 98.3 (149 → 121), and 59.7 (121 → 85). The unimolecular decomposition MIKE and the collision-activated MIKES (CAM) spectra of the major ions were determined and are reported in Table III. The results of the dominant pathways are summarized in Scheme II. The major decomposition of the bridged ion at m/z 257 involves the loss of trimethylchlorosilane, giving rise to the silenenium ion m/z 149. This process is formally analogous to the β elimination of Me_3SiOMe from appropriate precursors, a demonstrated thermal method for generating silenes.[11]

Table II. Mass Spectrum of Bis((trimethylsilyl)methyl)dichlorosilane (2)

m/z[a]	% of base peak[b]	formula[c]	m/z[a]	% of base peak[b]	formula[c]
262	5.3		121	18.3	$C_2H_6Si_2Cl^+$
261	20.1		95	12.4	
260	18.9		93	28.4	$C_2H_6SiCl^+$
259	76.9		85	8.9	$C_2H_5Si_2^+$
258	24.3		79	5.3	CH_4SiCl^+
257	100.0	$C_7H_{19}Si_3Cl_2^+$	75	10.7	
243	6.5		74	24.9	
152	5.6		73	59.5	$C_3H_9Si^+$
151	36.7		72	5.6	
150	16.0		71	8.9	
149	91.7	$C_4H_{10}Si_2Cl^+$	65	5.3	H_2SiCl^+
135	7.1		59	21.9	
133	7.1	$C_3H_6Si_2Cl^+$	55	6.2	
129	19.8		45	20.1	
127	7.1		44	6.5	
123	5.3		43	14.2	CH_3Si^+
122	14.8				

[a] Masses less than m/z 43 are not reported. [b] Intensities less than 5% are not reported. [c] Peak intensity ratios are consistent with these formulas.

The other major pathways of the m/z 257 ion involve the loss of a fragment which can be formulated as a 1,3-disilacyclobutane to give Me_3Si^+ and a loss of methane to give the m/z 241 ion, both of which are clearly higher energy processes as is indicated by the CAM results.

It is striking that the remainder of the fragmentation scheme is dominated by the formation of unsaturated neutral species or ions containing multiply-bonded silicon. The majority of the dimethylchlorosilenium ion, 93, m/z arises from loss of 2-silaallene from m/z 149. However m/z 93 also appears in the CAM, but not the MIKE spectra of m/z 257. Thus in Scheme II an alternate pathway involving loss of a 1,3-disila-1,3-butadiene from m/z 241 is indicated. The low intensities of the m/z 241, 113, and 85 ions precluded probing their structures by additional collisional activation studies. Comparison of the MIKE and CAM results given in Table III for the m/z 149 ion indicates that the loss of these multiply-bonded fragments are relatively low-energy pathways. Especially intriguing is the prevalence of species with a 1,3-disila-1,3-butadiene skeleton, suggesting that such a system should be a fruitful, and to our knowledge, unstudied research area. The loss of ethylene from cations containing a dimethylsilyl group, m/z 149, 113, 93, and 73, as mentioned above for Me_3Si^+ and Me_2SiCl^+ again is an important lower energy process. At higher energies losses of methane and ethane become significant. The decomposition pathways indicated for the Me_2SiCl^+ ion in Scheme I are supported by the MIKE and CAM results given for this ion in Table III.

$(Me_3SiCH_2)_3SiCl$, 3. The mass spectrum of 3 has been reported previously, although it was not analyzed in detail.[12] Our results for the high-resolution spectrum are given in Table IV, and the MIKE and CAM results for the m/z 309 and 201 ions are given in Table V. Scheme III illustrates the major fragmentation pathways. Metastable peaks were observed at 26.5 (201 → 73), 71.8 (293 → 145), 95.1 (221 → 145) 158.1 (309 → 221), 277.8 (309 → 293), 147.3 (129 → 113), and 83.0 (201 → 129).

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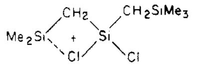
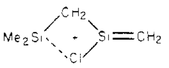
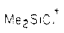
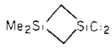
(10) Nakadaira, Y.; Kobayashi, T.; Kira, M.; Sakurai, H.; Yamada, Y.; Shida, Y. *J. Organomet. Chem.* **1976**, *113*, 249–56.

(11) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, 7. Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5. Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788.

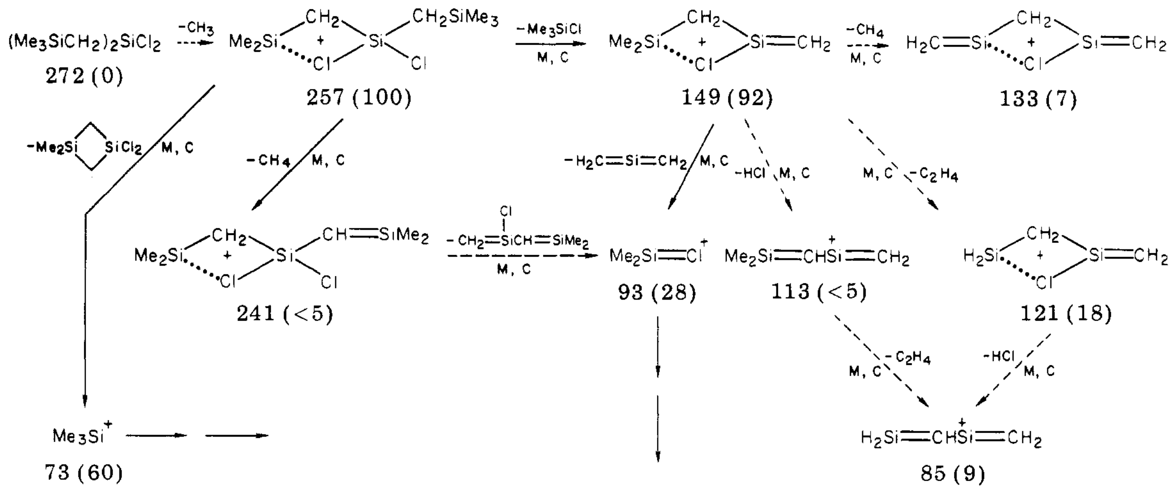
(12) Homer, G. D.; Sommer, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 7700.

Table III. MIKE and CAM Results for the Ions *m/z* 257, 149, and 93 Formed in the Mass Spectrum of Bis((trimethylsilyl)methyl)dichlorosilane (2)[a]

	 *m/z* 257			 *m/z* 149			 *m/z* 93		
		rel int, %			rel int, %			rel int, %	
m/z	loss of	MIKE	CAM	loss of	MIKE	CAM	loss of	MIKE	CAM
241	CH_4	10.5	31.4						
227	C_2H_6	3.5	6.0						
225			1.8						
205			2.9						
184			2.3						
164			2.1						
149	Me_3SiCl	70.2	25.0						
148				H	16.1	6.4			
147				H_2	3.8	4.4			
135			1.6						
134				CH_3		5.5			
133			1.8	CH_4	9.7	16.4			
129	Me_2SiCl_2	0.1	4.1						
123						1.2			
121				CH_2CH_2	12.4	7.6			
120				C_2H_5		5.4			
119				C_2H_6		9.0			
113			2.8	HCl	50.0	13.6			
105					0.1	4.7			
99						1.6			
93	$CH_2{=}\overset{Cl}{Si}CH{=}SiMe_2$	0.1	3.6	$H_2C{=}Si{=}CH_2$	0.1	2.5			
92							H		11.0
92							H_2	11.1	
85				CH_3CH_2Cl	8.1	5.6			
79						2.6			
78							CH_3		10.7
77							CH_4		5.4
73		15.8	14.5						
71						1.3			
68						1.5			
65							CH_2CH_2	83.2	27.9
63							CH_3CH_3	5.6	32.1
59						1.6			
55						2.0			
43						3.3			7.0
42									3.8
41									1.9

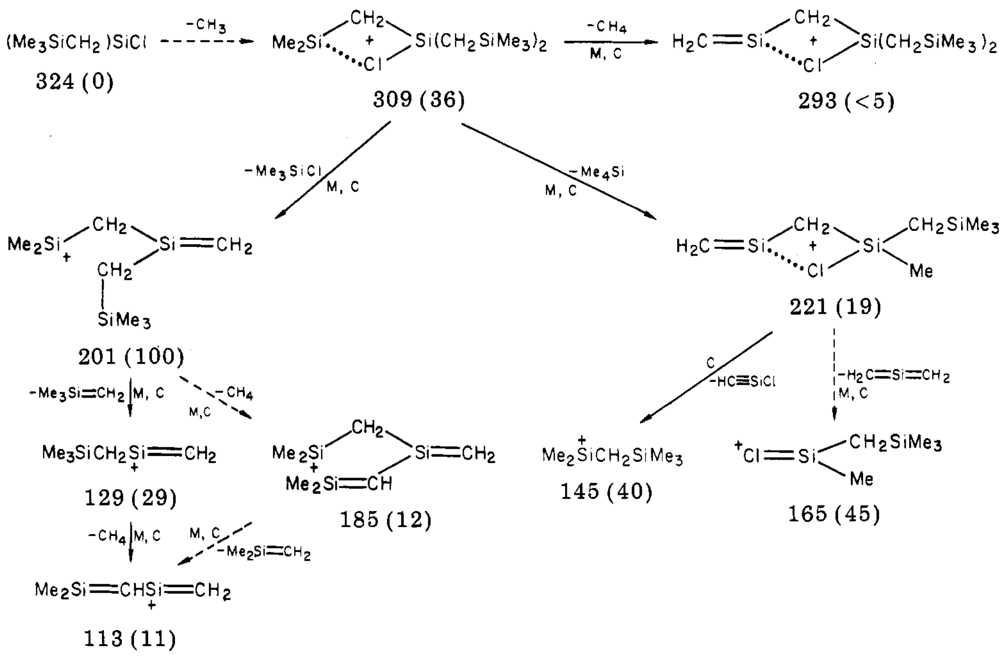
[a] Intensities of the MIKE and CAM peaks are reported as percent of the total ion current.

Scheme II. Mass Spectral Fragmentation Patternf ro Bis((trimethylsilyl)methyl)dichlorosilane (2)[a]



[a] Solid arrows represent processes supported by metastable peaks. Processes labeled M or C have been confirmed by MIKE and CAM spectra. Values are given in *m/z*. Numbers in parentheses give the intensity of the fragment as a percent of of the base peak in the spectrum.

Scheme III. Mass Spectral Fragmentation Pattern for Tris((trimethylsilyl)methyl)chlorosilane (3)[a]



[a] Solid arrows represent processes supported by metastable peaks. Processes labeled M or C have been confirmed by MIKE or CAM spectra. Values are given in m/z. Numbers in parentheses give the intensity of the fragment as a percent of the base peak in the spectra.

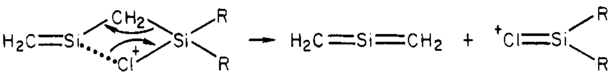
Table IV. Mass Spectrum of Tris((trimethylsilyl)methyl)chlorosilane (3)

m/z[a]	% of base peak[b]	formula[c]	m/z[a]	% of base peak[b]	formula[c]
312	5.6		165	45.1	$C_5H_{14}Si_2Cl^+$
311	17.3		147	4.9	
310	11.1		146	6.8	
309	35.2	$C_{11}H_{30}Si_4Cl^+$	145	39.5	$C_6H_{17}Si_2^+$
223	10.5		131	6.2	
222	4.9		130	4.9	
221	19.1	$C_7H_{18}Si_3Cl^+$	129	29.0	$C_5H_{13}Si_2^+$
203	18.5		115	5.6	
202	25.3		113	11.1	$C_4H_9Si_2^+$
201	100.0	$C_8H_{21}Si_3^+$	84	5.6	
187	4.9		73	33.3	
185	12.3		59	18.5	
167	19.8		42	10.5	
166	8.0				

[a] Masses less than m/z 42 are not reported. [b] Intensities less than 5% are not reported. [c] Peak intensity ratios are consistent with these formulas.

As with compound **2** the loss of trimethylchlorosilane from the P − Me ion (m/z 309) is the most important fragmentation and gives rise to the silenenium ion at 201, the base peak in the spectrum. The loss of tetramethylsilane from m/z 309 to give rise to the m/z 221 ion which was not a significant decomposition pathway for compounds **1** and **2** begins to compete with the loss of Me_3SiCl for compound **3** and, as the CAM results for 309 indicate, is favored by higher energies.

The remainder of the fragmentation scheme is again dominated by the loss of neutral dimethylsilene and 2-silaallene species. It is interesting to note that on the basis of the high-resolution mass spectrum of **3** alone one might be tempted to assign the ion at m/z 145 as a daughter formed by the loss of 2-silaallene from m/z 201. The MIKES unimolecular decomposition spectrum of m/z 201 clearly shows that this is not the case and that m/z 145 is a daughter of the ion at m/z 221. Like the single chlorine-bridged silenenium ion, m/z 149 arising from compound **2**, the m/z 221 ion derived from **3** looses 2-silaallene, in this case producing the chlorosilylenium ion at m/z 165. In both cases the stability afforded to the trivalent silylenium ion by the chlorine substituent may well be the driving force for the elimination. The CAM results for m/z 149, Table III, and m/z 221, Table V, show that this process is favored by higher energies. Evidence for silylenium ions in solution stabilized by sulfur substituents have recently been reported.[13]



One previous report suggests a loss of allene from a structurally analgous ion.[5]

Previous studies have demonstrated the facile generation of silenes under conditions of electron impact from mono- and disilacyclobutanes, in ring cleavage reactions which are similar to those used for the thermal generation of silenes.[2] Our results indicate that electron-impact-induced unimolecular decomposition processes for ((trimethylsilyl)methyl)chlorosilanes involve the initial formation of P − Me ions presumably stabilized by bridging chlorines. When possible, the loss of trimethylchlorosilane giving rise to silenenium ions is the major decomposition pathway. The resulting ions give complicated fragmentations which are dominated by the loss of neutral unsaturated species including ethylene, dimethylsilene, dichlorosilene, 2-silaallene, and 1,3-disila-1,3-butadiene. At higher energies fragmentations producing 2-silaallene, methane, ethane, and tetramethylsilane are favored over those yielding the other unsaturated species. It is not to be expected that the thermal decompositions of these compounds will exactly parallel the strictly unimolecular pathways observed in the electron-impact-induced decompositions because of the lower internal energies and collisional phenomena involved in thermal decompositions. Nevertheless, these

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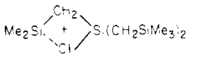
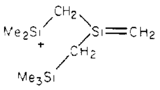
[13] Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671–72.

Table V. MIKE and CAM Results for the Ions m/z 309 and 201 Formed in the Mass Spectrum of Tris((trimethylsilyl)methyl)chlorosilane (3)[a]

m/z						
	loss of	MIKE	CAM	loss of	MIKE	CAM
309						
293	CH_4	2.4	14.1			
279	C_2H_6		3.0			
221	Me_4Si	8.2	12.5			
201	Me_3SiCl	84.0	37.0			
199				H_2	3.0	
185			5.3	CH_4	37.9	39.3
173				C_2H_4	29.3	4.7
171				C_2H_6	7.1	10.7
165	221 − $H_2C{=}Si{=}CH_2$	5.3	13.2			
157					2.1	3.3
145	221 − $HC{\equiv}SiCl$		6.2			
141					3.2	3.6
129			3.0	$Me_2Si{=}CH_2$	5.4	11.4
127					3.2	4.0
113			1.1	129 − CH_4 or 195 − $Me_2Si{=}CH_2$	3.2	6.7
100					0.1	2.2
99					0.1	2.7
84						2.7
73		0.1	4.6		3.2	5.6
58					2.4	3.1

[a] Intensities of the MIKE and CAM peaks are reported as percent of the total ion current.

results do point the way toward possible precursors of some very interesting unsaturated organosilicon species. They also indicate that the study of the thermal decomposition of carbosilanes containing the –Si–C–Si–Cl structural unit should be a fruitful area of endeavor for silene chemists.

Experimental Section

Medium-resolution mass spectra were obtained by using an Hitachi Perkin-Elmer RMU-6E Mass spectrometer with a 90° magnetic sector. The ionization energy was 60 eV, and the source temperature was 100 °C. MIKE and CAM spectra were obtained by using a KRATOS MS-50 triple analyzer at the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, NE. The ionization energy was 70 eV, and the source temperature was 250 °C. The accelerating potential was 8 kV. Collisional activation was achieved by bleeding helium gas into the third field-free region of the spectrometer until the intensity of the main beam was decreased by 50%.

Nuclear magnetic resonance spectra were obtained on an Hitachi Perkin-Elmer R-24B 60 MHz spectrometer or a JEOL FX-90Q with D_2O as an external lock with carbon tetrachloride as the solvent and chloroform or deuteriochloroform as an internal standard. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Analytical samples were obtained by preparative GLC using a 20 ft × $^3/_8$ in. stainless-steel column packed with 10% SE-30 on 60-80 mesh Chromosorb W programmed from 230 to 280 °C at 10 °C/min.

For the syntheses all glassware was assembled and flame-dried with a rapid purge of argon. All reactions and distillations were carried out under argon. Hexanes were distilled from sodium/potassium alloy under a nitrogen atmosphere prior to use. Tetrahydrofuran or diethyl ether were distilled from lithium aluminum hydride under nitrogen.

((Trimethylsilyl)methyl)trichlorosilane, 1, was prepared in 28% yield by the method of Sommer and co-workers:[9] bp 47 °C (1.5 torr) (lit.[9] 167 °C (738 torr)); ^1H NMR δ 0.82 (br s).

((Trimethylsilyl)methyl)lithium. A 1-L Morton flask was charged with 500 mL of paraffin oil, which had been dried over 4A molecular sieves, and about 5 g of lithium wire. The flask was heated to 200 °C with occasional stirring until the lithium was completely melted, at which time four drops of oleic acid was added. The flask was shaken vigorously for several minutes as it cooled, resulting in lithium shot ranging from 0.5 to 2 mm in diameter. After the mixture was cooled to room temperature, the metal was filtered and washed with two 50-mL portions of dry hexanes. A 500-mL Morton flask equipped with a mechanical stirrer, addition funnel, reflux condenser, and argon inlet was charged with the lithium shot and 200 mL of dry hexanes. A small amount of sodium metal and several pieces of broken glass were added, and the mixture was stirred vigorously overnight to clean the metal surface. Three drops of methyl iodide were added to the mixture, and a solution of 5.0 g (41 mmol) of (chloromethyl)trimethylsilane (Petrarch) was added to the stirring mixture dropwise over a period of 10 h. After being refluxed overnight the resulting milky lavender mixture, when analyzed by using the diphenylacetic acid procedure of Kofron,[14] was found to contain a 71% yield of ((trimethylsilyl)methyl)lithium, based on starting silane.

Bis((trimethylsilyl)methyl)dichlorosilane, 2, and Tris((trimethylsilyl)methyl)chlorosilane, 3. Freshly prepared ((trimethylsilyl)methyl)lithium was transferred to a 1-L addition funnel and was added dropwise to a refluxing solution of 16.6 mL (145 mmol) of silicon tetrachloride (Petrarch) in dry tetrahydrofuran. The reaction mixture was filtered and fractionally distilled under reduced pressure. The fraction boiling between 80 and 90 °C at 0.375 torr gave 31.9% **3** and 5.24% **2**, based on (chlormethyl)trimethylsilane.

2: lit.[9] bp 92 °C (9 torr); ^1H NMR 0.19 ppm (br s); ^{13}C NMR 12.55 (methylene), 1.04 ppm (methyl).

3: lit.[9] bp 112 °C (4 torr); ^1H NMR 0.30 ppm (br s); ^{13}C NMR 9.88 (methylene), 1.49 ppm (methyl).

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Registry No. 1, 16538-62-8; 2, 18420-19-4; 3, 18077-32-2; ((trimethylsilyl)methyl)lithium, 1822-00-0; (chloromethyl)trimethylsilane, 2344-80-1; silicon tetrachloride, 10026-04-7.

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(14) Kofron, W. *J. Org. Chem.* **1976**, *41*, 1869.