The X-ray crystallographic experiments were performed on a Nicolet P3/F diffractometer for 3 and on a Syntex-Nicolet P$\bar{1}$ diffractometer for 4; both were equipped with a graphite-monochromated Mo Kα X-radiation source (λ = 0.71072 Å) and a low-temperature device.

Unit cell parameters were determined by least-squares refinements based on 25 centered reflections. Three standard reflections were measured after every 50 reflections during the data collection. No significant decreases in the intensity of the standard reflections were observed during the data collection of both compounds.

The structures were solved by direct methods with the SHELXTL PLUS program on a Microvax II computer and refined by the full-matrix least-squares refinement method by use of the reflections with $F_o > 4.0\sigma(F)$. In the final refinement cycles the non-hydrogen atoms were assumed to vibrate anisotropically while the hydrogen atoms were included as idealized isotropic fixed contributors; the refinement converged to unweighted and weighted agreement factors of R = 5.67% and R_w = 8.14% for 3 and R = 5.18% and R_w = 6.22% for 4. Crystal data and experimental details for the structure determination of 3 and 4 are provided in Table VI.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. AFOSR-89-0004 and by the National Science Foundation under Grant No. CHE-8704353. We thank Jackson Ma for his help in mounting crystals.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles for 3 and 4 (15 pages); listings of observed and calculated structure factor amplitudes for 3 and 4 (26 pages). Ordering information is given on any current masthead page.

Preparation of Preceramic Polymers via the Metalation of Poly(dimethylsilene)†

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Model compound studies employing $Me_3SiCH_2SiMe_3$, $(Me_3SiCH_2)_2SiMe_2$, $(Me_3Si)_2CHSiMe_2CH_2SiMe_3$, and c-$(Me_2SiCH_2)_3$ showed *n*-BuLi/*t*-BuOK to be the most effective metalation reagent for CH_2 groups in a $SiCH_2Si$ environment. With use of this reagent in 1:1 *n*-BuLi/*t*-BuOK to $SiCH_2$ molar ratio, it was found that about every fourth CH_2 group of poly(dimethylsilene), $(Me_2SiCH_2)_n$, could be metalated. Reactions of the resulting $[(Me_3SiCH_2)_3(Me_2SiCHK)]_n$ species with Me_2HSiCl, $Me_2(CH_2{=}CH)SiCl$, Me_3SiCl, $Me_2(ClCH_2)SiCl$, and Et_3SiCl are described. Reactions of the $\{(Me_2SiCH_2)_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$ polycarbosilane with the $[(MeSiH)_{0.8}(MeSi)_{0.2}]_x$ polysilane (AIBN catalyst) gave a hybrid polymer whose pyrolysis under a stream of argon to 1500 °C gave a ceramic residue that contained about 91% by weight of SiC and 9% free carbon.

Introduction

Since Yajima and his co-workers developed the first polymeric precursor for silicon carbide,[1] there has been much interest in organosilicon polymers whose pyrolysis gives ceramic materials with a high content of silicon carbide.[2] Among the known organosilicon polymers that might be considered as potentially useful SiC precursors, poly(dimethylsilene), $(Me_2SiCH_2)_n$, is of interest. Polysilenes (or polysilmethylenes), $(R_2SiCH_2)_n$, linear polymers based formally on the $R_2Si{=}CH_2$ monomer, are organosilicon polymers that belong to the general class of polycarbosilanes.[3] Their preparation and properties have been discussed in a recent review.[4] Of the known polysilenes, $(Me_2SiCH_2)_n$ is the easiest to prepare and it has received the most study. Polymers of this kind, of relatively low molecular weight, have been prepared by active metal condensation of $ClCH_2SiMe_2Cl$,[5] but material of considerably higher molecular weight is accessible by transition-metal-catalyzed ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.[6] Such linear polymers, however, are not useful SiC precursors, their pyrolysis to 1000 °C under a stream of argon leaving little or no ceramic residue. The requirements for a good preceramic polymer have been discussed in some detail.[7] Notable among these is that the polymer give as high a yield of ceramic residue on pyrolysis as possible, preferably above 70%. With few exceptions, the polymers with which this requirement can be met are ones that either are highly cross-linked to begin with (network polymers) or that contain a reactive (latent) functionality whose reactivity

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† Dedicated to Prof. Dr. Marianne Baudler on the occasion of her 70th birthday.

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(1) Review: Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.

(2) (a) Schilling, C. L., Jr. *Br. Polym. J.* **1986**, *18*, 355. (b) Atwell, W. H. In *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry 224, American Chemical Society: Washington, DC, 1990; Chapter 32, and references cited therein.

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(5) (a) Goodwin, J. T., Jr. U.S. Patent 2,483,972, 1949; *Chem. Abstr.* **1950**, *44*, 2011e. (b) Goodwin, J. T., Jr. U.S. Patent 2,607,791, 1952; *Chem. Abstr.* **1954**, *48*, 13732.

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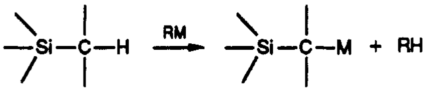
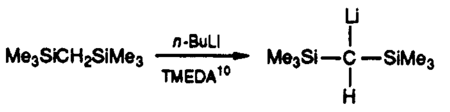
will result in substantial cross-linking during the initial stages of the pyrolysis. Poly(dimethylsilene) is neither cross-linked nor does it contain latent functionality. Accordingly, if its pyrolysis is lead to a high yield of ceramic residue, the $(Me_2SiCH_2)_n$ polymer will have to be modified appropriately.

One approach with this objective in mind was reported by French workers.[8] Utilizing known Si-C bond-cleavage chemistry, they treated a $(Me_2SiCH_2)_n$ polymer fraction of molecular weight 250000 with the $Me_3SiCl/AlCl_3$ reagent. Their goal, the selective cleavage of one of the two methyl groups on silicon to give $[Me(Cl)SiCH_2]_n$, was realized. However, extensive Si–CH_2 cleavage took place as well, and the molecular weight of their product was only 2500. Nevertheless, the $[Me(Cl)SiCH_2]_n$ polymer was reduced with $LiAlH_4$ to $[Me(H)SiCH_2]_n$, which, it was hoped, would, as a result of the reactive Si–H bonds, give SiC in high ceramic yield on pyrolysis. However, thermal cross-linking via the Si-H bonds apparently did not occur, and pyrolysis of $[Me(H)SiCH_2]_n$ gave a ceramic residue yield of only 5%.[8b]

Although at first sight the $(Me_2SiCH_2)_n$ polymer contains no useful functionality for further chemical modification, we have made use of the fact that methylsilyl groups activate adjacent C–H bonds toward deprotonation by strong bases (eq 1).[9] In particular, it has been shown that methylene bridges between two silicon atoms are more readily deprotonated by strong organometallic bases than are methyl groups bonded to a single silicon atom.[10,11] Equations 2 and 3 give two examples of such selective reactivity of the Si–CH_2–Si functionality. In the case of the trisilacyclohexane further metalation did not occur at 20 °C even when an excess of metalation reagent was used.

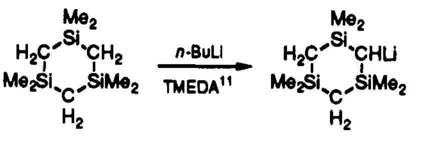


(1)



$$Me_3SiCH_2SiMe_3 \xrightarrow[\text{TMEDA}^{10}]{n\text{-BuLi}} Me_3Si{-}\overset{\overset{\text{Li}}{|}}{\underset{\underset{\text{H}}{|}}{C}}{-}SiMe_3 \quad (2)$$

TMEDA = $Me_2NCH_2CH_2NMe_2$



(3)

If such Si–CH_2–Si metalation could be carried out on poly(dimethylsilene), then we would be able, through further chemical conversions of the metalated polymer, to introduce the functionality required for nonoxidative cross-linking of the polymer.

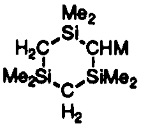
Results and Discussion

Model Compound Studies. In order to assess the potential utility of various possible metalating reagents, we carried out studies of the metalation of $Me_3SiCH_2SiMe_3$, $Me_3SiCH_2SiMe_2CH_2SiMe_3$, and c-$(Me_2SiCH_2)_3$, using several strong organometallic bases. Such studies, with c-$(Me_2SiCH_2)_3$ and 1,3,5,7-tetrasilaadamantane (1) as substrates and the *n*-BuLi/Me_3COK, Me_3SiCH_2Li/Me_3COK, *n*-BuLi/TMEDA (TMEDA = $Me_2NCH_2CH_2NMe_2$), and *t*-BuLi/$(Me_2N)_3PO$ basic reagent systems, had been reported earlier by Fritz and his co-workers.[3,11] In our studies the basic reagents used were *t*-BuLi/TMEDA, *sec*-BuLi/TMEDA, *n*-BuLi/Me_3COK, and *n*-/BuLi/Me_3COK/TMEDA.[12] In these studies, the metalation reaction was followed by subsequent addition of a chlorosilane to react with the reactive organoalkali-metal reagent present and hydrolytic workup, if appropriate, and isolation of the silylated product.

In the case of $Me_3SiCH_2SiMe_3$, use of the *n*-BuLi/Me_3COK reagent in the THF solution resulted in slightly better silylated product yields than when *t*-BuLi/TMEDA was used. Furthermore, the organometallic reagent is formed very rapidly in the case of the former, even at −70 °C, and only very slowly by the latter. Silylated product yields for the system $Me_3SiCH_2SiMe_3$/*n*-BuLi/Me_3COK were in the range 78–91%. Reactions were carried out with Me_2RSiCl (R = H, CH_3, CH=CH_2, Ph) and $ClMe_2SiCH_2CH_2SiMe_2Cl$ as the chlorosilanes.

The carbosilane $Me_3SiCH_2SiMe_2CH_2SiMe_3$ was of particular interest, since it had two $SiCH_2Si$ units. The question of interest, whether both CH_2 groups could be metalated, was answered in the negative in this study. Monometalation of this trisilicon carbosilane occurred readily in high yield when 1 molar equiv of organometallic base was used. Here also, *n*-BuLi/Me_3COK was marginally better than *t*-BuLi/TMEDA in terms of final product yield and substantially better in terms of metalation rate. Monometalation to give $Me_3SiCH_2SiMe_2CHMSiMe_3$ (M = Li, K) was observed as the sole process even when a 5-fold excess of strong base reagent was used. Monometalation of the carbosilane $(Me_3Si)_2CHSiMe_2CH_2SiMe_3$ gave, as expected, $(Me_3Si)_2CMSiMe_2CH_2SiMe_3$, since the indicated carbanion is stabilized by three silyl groups (rather than two, as would be the case if the methylene group had been metalated). Trimethylchlorosilane quenches of the reagents obtained with *t*-BuLi/TMEDA and *n*-BuLi/Me_3COK resulted in formation of $(Me_3Si)_3CSiMe_2CH_2SiMe_3$ in yields of 92% and 94%, respectively.

Only monometalation could be achieved as well for c-$(Me_2SiCH_2)_3$, regardless of the quantity of the reactive organometallic base used, giving 2.



2

These model compound studies brought two important results: (1) use of *n*-BuLi/Me_3COK in THF as the organometallic base is preferred since it reacts most rapidly with carbosilanes and results in the best yields; (2) we cannot expect to metalate every CH_2 group in poly(dimethylsilene).

Metalation of Poly(dimethylsilene). The metalation of poly(dimethylsilene) was studied with the *n*-BuLi/Me_3COK reagent in THF solution. The $(Me_2SiCH_2)_n$ polymer, prepared by $H_2PtCl_6{\cdot}6H_2O$-catalyzed ring-open-

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[8] (a) Bacqué, E.; Pillot, J.-P.; Birot, M.; Dunoguès, J. *Macromolecules* **1988**, *21*, 30. (b) Bacqué, E.; Pillot, J.-P. Birot, M. Dunoguès, J. *Macromolecules* **1988**, *21*, 34.

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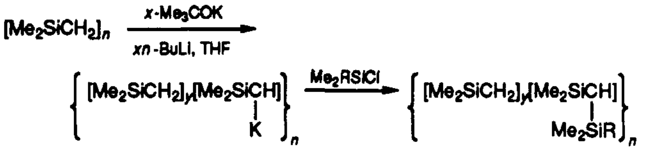
[10] Gröbel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

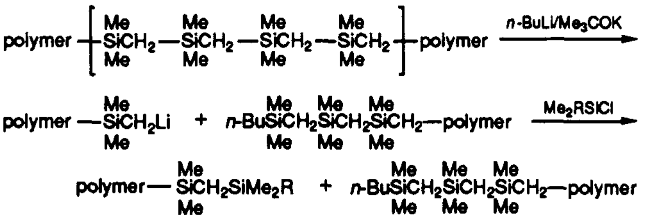
[11] Fritz, G.; Neutzner, J.; Volk, H. *Z. Anorg. Allg. Chem.* **1983**, *497*, 21.

[12] For reliable syntheses of such reagents see: Brandsma, L.; Verkruijsse. *Preparative Polar Organometallic Chemistry 1*; Springer-Verlag: Berlin, 1987; Chapter I.

Scheme I

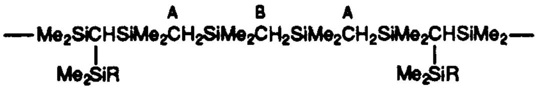


Scheme II



ing polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane,[6b,c,e] was a colorless, rubbery material that began to flow on standing at room temperature. According to gel permeation chromatography (GPC) (in toluene solution, polystyrene standard), it contained three fractions, two in the 1000–3000-Da range and one (very broad GPC peak) in the 50 000–200 000-Da range, with the low-molecular-weight components being the major ones. By cryoscopy in benzene the "molecular weight" was 2018.

The metalation of the $(Me_2SiCH_2)_n$ polymer was effected in THF solution at −78 °C with use of unsolvated potassium *tert*-butoxide (added first) and 1 molar equiv of *n*-butyllithium in pentane. An immediate color change to yellow/yellow-orange (due to the interaction of *n*-BuLi with Me_3COK, according to a control experiment), occurred. To the reaction mixture, now at 0 °C, then was added the chlorosilane (Me_2HSiCl, $Me_2(CH_2{=}CH)SiCl$, etc.; Scheme I). Ratios of base:Me_2SiCH_2 of 1:6, 1:2, 1;1, 2:1, 3:1, and 5:1 were used. There was no correspondence of these ratios with the degree of metalation. When the indicated base:Me_2SiCH_2 ratio was 1:6, y in the formula of the silylated product (Scheme I) was about 15. When it was 1:2, y was about 9. A base:Me_2SiCH_2 ratio of 1 resulted in metalation of about every fourth Me_2SiCH_2 unit in the polymer (y = 3). The observed ^1H NMR spectra of these products of type



$$-Me_2Si\underset{Me_2SiR}{CH}SiMe_2\overset{A}{CH_2}SiMe_2\overset{B}{CH_2}SiMe_2\overset{A}{CH_2}SiMe_2\underset{Me_2SiR}{CH}SiMe_2-$$

were as expected, showing two CH_2 resonances in a 2:1 integrated intensity ratio. These may be assigned to the type A and type B CH_2 groups, respectively, which differ in position with respect to the CH groups bearing the $SiMe_2R$ substituents. Use of larger excesses of *n*-BuLi/Me_3COK reagent, according to cryoscopic molecular weights of the silylated products and complications in the proton NMR spectra of the products, appears to lead to some chain cleavage, most likely via nucleophilic attack by *n*-BuK at silicon (Scheme II). Such a process will lower the average molecular weight (as was observed) and, through introduction of *n*-butyl groups and Me_2RSi groups on terminal sites, will result in more complicated proton NMR spectra in the aliphatic C–H region. Even in the case of 1:1 reactions there was some limited Si–C cleavage, on the basis of these experimental criteria.

All further experiments were carried out with use a *n*-BuLi/Me_3COK base to Me_2SiCH_2 ratio of 1. After reaction of the metalated polycarbosilane with the respective Me_2RSiCl compound, all volatiles were removed under high vacuum and the residue was extracted with benzene/hexane mixtures. The products were isolated by evaporation of the extracts at reduced pressure as viscous oils that were soluble in benzene, toluene, dichloromethane, and chloroform. The yields of these products, based on charged $(Me_2SiCH_2)_n$, were in the 92–98% range.

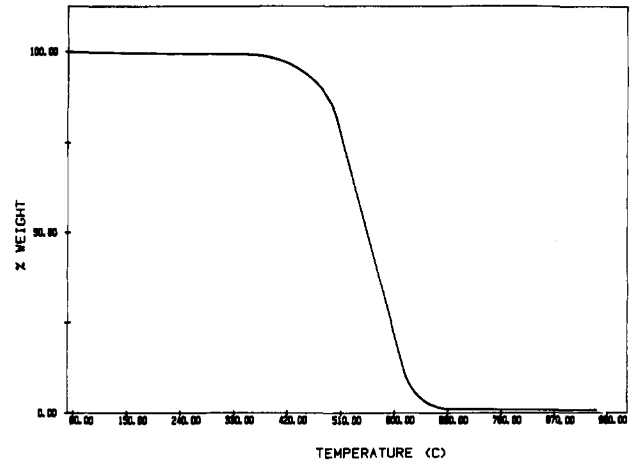


Figure 1. TGA trace of poly(dimethylsilene), $(Me_2SiCH_2)_n$ (under a stream of argon, at 10 °C/min).

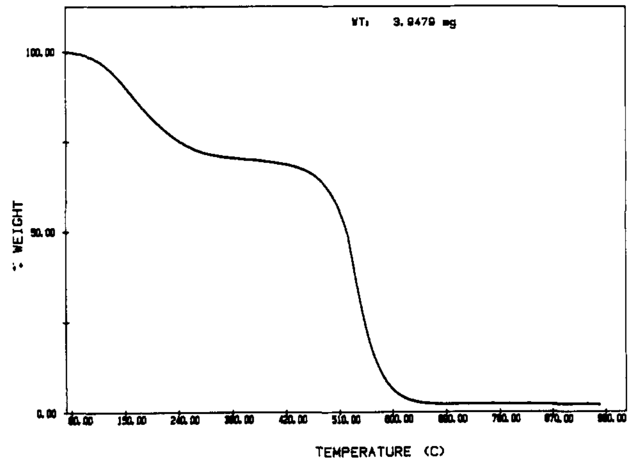


Figure 2. TGA trace of $\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$ (same conditions as in Figure 1).

That only every fourth Me_2SiCH_2 unit of the poly(dimethylsilene) is metalated can be understood in terms of charged dispersal from the metalated, negatively charged carbon atom along the $(Si\text{–}C)_n$ chain (polarization and inductive effects) that become sufficiently attenuated by the time of the fourth CH_2 group is reached.

The starting poly(dimethylsilene), $(Me_2SiCH_2)_n$, is thermally stable to almost 400 °C (TGA under argon; Figure 1), at which point rapid decomposition, which is complete at around 675 °C, begins. No ceramic residue remains. The TGA's of the silyl-substituted poly(dimethylsilenes) show a two-stage decomposition process: an initial 25% weight loss between 80 and 240 °C, followed by a rapid weight loss, which leaves about a 0–2% ceramic residue weight, between 450 and 625 °C (Figure 2). The initial 25% weight loss may represent cleavage of the organosilyl side groups.

Silicon Carbide Precursors Prepared by Modification of Silylated Poly(dimethylsilenes). The introduction of Me_2HSi and $Me_2(CH_2{=}CH)Si$ into poly(dimethylsilene) as described above provided the reactive functional groups required for the cross-linking needed in order to obtain a useful preceramic polymer. Conceptually, a hydrosilylation between these two polymers might provide a route to such a cross-linked polymer, and this was

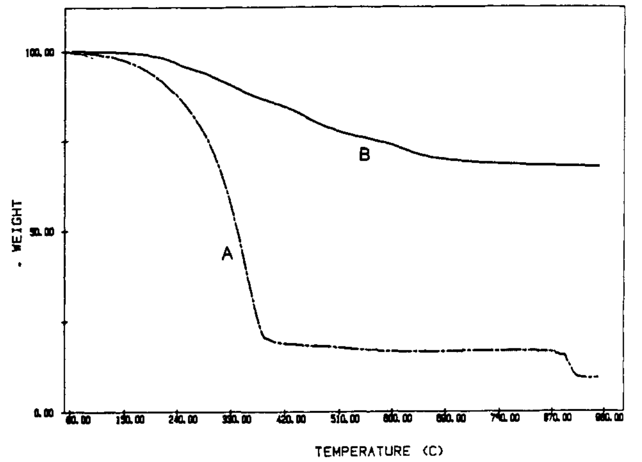


Figure 3. Comparison of the TGA traces of $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ (curve A) and the hybrid polymer resulting from the AIBN-catalyzed reaction of $\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$ (one part) and $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ (four parts) (curve B) (same conditions as in Figure 1).

the first possibility that was investigated. However, treatment of a mixture of the Me_2HSi- and the $Me_2(CH_2{=}CH)Si$-substituted poly(dimethylsilenes) with a catalytic amount of chloroplatinic acid or of azobis(isobutyronitrile) (AIBN), both effective hydrosilylation catalysts, did not lead to a high degree of cross-linking. The products of such reactions gave only very low yields of ceramic residue when they were pyrolyzed to 1000 °C under a stream of argon. It is possible that the rigidity of this polymer and steric factors were responsible for this lack of interpolymer reactivity. In any case, had this interchain cross-linking been successful, the resulting polymer still would have presented problems: its pyrolysis (under argon) would be expected to give a ceramic residue containing, in addition to the desired SiC, substantial amounts of elemental carbon.

More effective, but still insufficient, cross-linking occurred in the AIBN-catalyzed hydrosilylation of the Me_2HSi-substituted poly(dimethylsilene) with c-$[Me(CH_2{=}CH)SiNH]_3$, a compound that had proven useful in the hydrosilylative cross-linking of the $[(MeSiH)_x(MeSi)_y]_n$ polysilane.[13] Thus, when a mixture of these reactants (1:1 Si–H to Si–$CH{=}CH_2$ ratio) in benzene solution was heated at reflux in the presence of a catalytic amount of AIBN for 3 days (with incremental addition of the catalyst), a viscous oil was obtained. Pyrolysis of this product to 1000 °C under a stream of argon gave a ceramic residue yield of 24%.

The problems of low ceramic yield and the formation of elemental carbon in large amount in the pyrolysis of these poly(dimethylsilenes) were successfully addressed by another "hybrid polymer" approach. In earlier work, we[14] and, independently, Sinclair and Brown-Wensley[15] had studied the sodium condensation of $MeSiHCl_2$. In THF solvent this reaction gave a solid, THF-soluble polysilane of composition $[(MeSiH)_{0.4}(MeSi)_{0.6}]_n$; i.e., about 60% of the Si–H bonds had reacted with the sodium, generating cross-linking sites in which a silicon atom is bonded to three other silicon atoms. As a result of this extensive cross-linking, pyrolysis of this polysilane to 1000 °C under argon gave a fairly good (ca. 60%) ceramic yield.

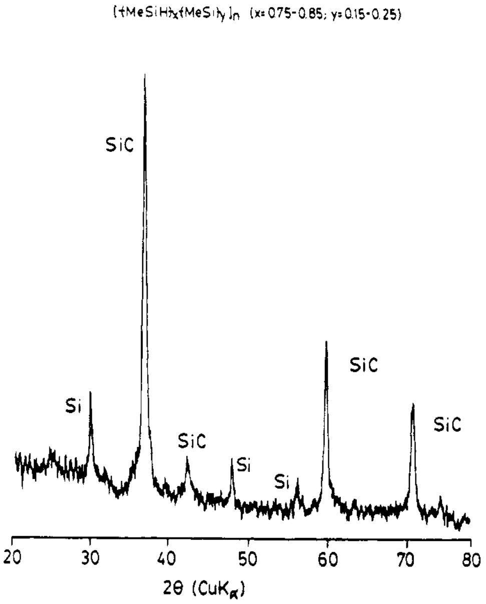


Figure 4. X-ray powder diffraction pattern of the ceramic obtained by pyrolysis of $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ to 1500 °C in argon.

However, this 40% weight loss included loss of many of the methyl groups (as CH_4), and the residue had a composition (by elemental analysis) of around 74 wt % SiC and 26 wt % elemental Si. A liquid polysilane, $[(MeSiH)_x(MeSi)_y]_n$ ($x = \sim 0.65-0.85$ and $y = 1 - x$), obtained by sodium condensation of $MeSiHCl_2$ in a solvent system of about 6 volumes of hexane + volume of THF, was less highly cross-linked, and its pyrolysis (same conditions) left a ceramic residue in only 15–20% yield (Figure 3, curve A). Again, the ceramic residue contained about 25 wt % of elemental silicon. When such a ceramic residue was heated at 1500 °C, crystallization occurred and the presence of β-SiC and elemental silicon was confirmed by X-ray powder diffraction (Figure 4). This defect of these polysilanes, the formation of elemental silicon on pyrolysis, can, however, be used to good advantage. In the present instance, we have made use of the abundant Si–H functionalities of the liquid polysilane in a hydrosilylation reaction with the $Me_2(CH_2{=}CH)Si$-substituted poly(dimethylsilane) $\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$, catalyzed by AIBN in refluxing benzene solution. A molar ratio of the polysilane to the $Me_2(CH_2{=}CH)Si$-substituted poly(dimethylsilene) of 1.5 gave a new organosilicon polymer as a waxy solid whose pyrolysis to 1000 °C under argon gave a 54% ceramic yield. When this molar ratio was 4.0, the ceramic yield obtained on pyrolysis of the resulting polymer was 68% (Figure 3, curve B). The composition of the ceramic product was, by elemental analysis, 91% by weight of SiC and 9% by weight of elemental carbon. Increasing the molar ratio (as defined above) of the two polymers to 7.5 gave a new organosilicon polymer whose pyrolysis resulted in a product of composition 94% by weight of SiC and 6% by weight of carbon.

The ceramic products obtained in this study were not examined in detail. All products of pyrolyses carried out to 1000 °C were amorphous; their X-ray powder diffraction (XRD) patterns showed only weak, very broad peaks. When the hybrid polymer samples were heated to 1000 °C at 10 °C/min under a stream of argon in a furnace, held at 1000 °C for 1 h, and then heated to 1500 °C at 10 °C/min and sintered at that temperature for 7 h, a further weight loss of between 3 and 9% usually was observed. The final products were crystalline, and XRD showed the presence of β-SiC; no lines due to elemental silicon were

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(13) Seyferth, D.; Yu, Y.-F.; Koppetsch, G. E. U.S. Patent 4,719,273, 1988.

(14) Wood, T. G. Ph.D. Dissertation, Massachusetts Institute of Technology, 1984.

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Table I. Reactions of Carbosilane-Derived Organoalkali-Metal Reagents with Chlorosilanes

M (amt of reagent mmol)	chlorosilane (amt, mmol)	product (% yield)
A. $(Me_3Si)_2CHM$ (M = Li, K)		
Li[a] (46.76)	Me_2HSiCl (58.5)	$(Me_3Si)_2CHSiMe_2H$ (78)
K (46.76)	Me_2HSiCl (117.0)	$(Me_3Si)_2CHSiMe_2H$ (85)
Li (46.76)	$Me_2(CH_2{=}CH)SiCl$ (58.5)	$(Me_3Si)_2CHSiMe_2CH{=}CH_2$ (84)
K (46.76)	$Me_2(CH_2{=}CH)SiCl$ (117.0)	$(Me_3Si)_2CHSiMe_2CH{=}CH_2$ (91)
Li (46.76)	Me_3SiCl (58.5)	$(Me_3Si)_3CH$ (69)
K (46.76)	Me_3SiCl (117.0)	$(Me_3Si)_3CH$ (78)
Li (46.76)	$Me_2PhSiCl$ (58.5)	$(Me_3Si)_2CHSiMe_2Ph$ (85)
K (46.76)	$Me_2PhSiCl$ (117.0)	$(Me_3Si)_2CHSiMe_2Ph$ (88)
Li (46.76)	$PhMeSiCl_2$ (58.5)	$(Me_3Si)_2CHSiPhMeCl$ (68)
Li (46.76)	Me_2SiCl_2 (58.5)	$(Me_3Si)_2CHSiMe_2Cl$ (45) + $[(Me_3Si)_2CH]_2SiMe_2$ (40)
Li (46.76)	$MeHSiCl_2$ (23.38)	$[(Me_3Si)_2CH]_2SiMeH$ (82)
Li (46.76)	Me_2SiCl_2 (23.38)	$[(Me_3Si)_2CH]_2SiMe_2$ (90)
Li (46.76)	$(ClMe_2SiCH_2)_2$ (23.38)	$[(Me_3Si)_2CHSiMe_2CH_2]_2$ (82)
B. $Me_3SiCH_2SiMe_2CHMSiMe_3$ (M = Li, K)		
Li (21.50)	Me_2HSiCl (26.90)	$Me_3SiCH_2SiMe_2CH(SiMe_3)SiMe_2H$ (88)
Li[b] (21.50)	Me_2HSiCl (26.90)	$Me_3SiCH_2SiMe_2CH(SiMe_3)SiMe_2H$ (76)
K (21.50)	Me_2HSiCl (53.8)	$Me_3SiCH_2SiMe_2CH(SiMe_3)SiMe_2H$ (91)
Li (21.50)	Me_3SiCl (26.90)	$Me_3SiCH_2SiMe_2CH(SiMe_3)_2$ (84)
Li[b] (21.50)	Me_3SiCl (26.90)	$Me_3SiCH_2SiMe_2CH(SiMe_3)_2$ (75)
K (21.50)	Me_3SiCl (53.8)	$Me_3SiCH_2SiMe_2CH(SiMe_3)_2$ (88)
C. $Me_2\overline{SiCH_2SiCH_2SiMe_2C}HM$ (M = Li, K)		
Li (23.09)	Me_2HSiCl (29.0)	$Me_2\overline{SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2H$ (73)
Li[b] (23.09)	Me_2HSiCl (29.0)	$Me_2\overline{SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2H$ (65)
K (23.09)	Me_2HSiCl (58.0)	$Me_2\overline{SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2H$ (77)
Li (23.09)	$Me_2(CH_2{=}CH)SiCl$ (29.0)	$Me_2\overline{SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2CH{=}CH_2$ (75)
K (23.09)	$Me_2(CH_2{=}CH)SiCl$ (58.0)	$Me_2\overline{SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2CH{=}CH_2$ (81)

[a] *t*-BuLi was used unless otherwise noted. [b] *sec*-BuLi was the RLi compound used.

observed (Figure 4). Thus, hybrid polymers based on the modified poly(dimethylsilene) are good candidates for further studies aimed at developing useful applications.

The available spectroscopic data do not allow us to say much about the detailed structure of these hybrid polymers. The reactions that form them must be more complicated than a simple hydrosilylation process, since treatment of the liquid $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ polysilane alone with a catalytic amount of AIBN in refluxing benzene solution gives a solid product with a melting range of 80–85 °C. Pyrolysis of this material (to 1000 °C under argon) results in a ceramic residue yield of 65.5%. Thus, two types of cross-linking processes appear to be operative when mixtures of this polysilane and the $Me_2(CH_2{=}CH)Si$-substituted poly(dimethylsilene) are treated with AIBN in refluxing benzene. Also noted in these reactions, in which AIBN was used as catalyst, was that some of the organic $Me_2(CN)C^{\bullet}$ radicals generated in the thermal decomposition of the catalyst had been incorporated into the polymer and could be detected in IR and ^1H NMR spectra of the polymers.

Experimental Section

General Considerations. All manipulations were carried out with use of oven-dried glassware under an inert atmosphere (argon or nitrogen) by following standard techniques. All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use.

NMR spectra were obtained by using a Varian XL-300 NMR spectrometer; IR spectra were gathered on a Perkin-Elmer Model 1430 spectrophotometer. Ceramic analyses were obtained from Galbraith Laboratories, Knoxville, TN, and C and H analyses on nonceramic materials were obtained from Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Lindberg tube furnaces with Eurotherm controllers were used for all preparative-scale (>1 g) pyrolyses (powder and bulk) to 1500 °C. For pyrolyses to 1000 °C, 1.5 in. o.d. quartz tubes and fused silica boats were used for all samplex; for those to 1500 °C, 2.5 in. o.d. mullite tubes and boron nitride boats supported on alumina dee tubes were used. All pyrolyses were carried out under an atmosphere of flowing argon. For experiments to 1000 °C the flow rate was ~6–8 L/h; for experiments to 1500 °C it was ~16–20 L/h.

TGA measurements were made on a Perkin-Elmer Model TGS2 instrument equipped with a Thermal Analysis System 4 controller.

The chlorosilanes used in this study were purchased from Petrarch and distilled from magnesium turnings prior to use.

Preparation and Reactions of Alkali-Metal Reagents, $(Me_3Si)_2CHM$ (M = Li, K). Reactions were carried out in three-necked, round-bottomed flasks of suitable size equipped with a pressure-equalizing addition funnel, a gas inlet/outlet tube connected to a Schlenk line, a rubber septum, and a magnetic stirbar. The reaction flask was flamed out under a stream of nitrogen prior to addition of reagents. All reactions were carried out under a dry nitrogen atmosphere.

(a) $(Me_3Si)_2CHLi$. To 7.5 g (46.8 mmol) of $(Me_3Si)_2CH_2$ was added 5.43 g (46.8 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The mixture was cooled to 0 °C, and then 27.5 mL of a 1.7 M solution of *t*-BuLi (46.8 mmol) in pentane was added dropwise with stirring. The reaction mixture was stirred at room temperature for 2.5–3.5 days. An orange to orange-brown solution resulted.

(b) $(Me_3Si)_2CHK$. To 7.5 g (46.8 mmol) of $(Me_3Si)_2CH_2$ was added 5.24 g (46.8 mmol) of *t*-BuOK in THF (or in hexane). This mixture was cooled to −70 °C, and then 19.5 mL of 2.4 M *n*-BuLi in hexane was added dropwise. The reaction mixture quickly became orange-brown. It was warmed slowly to 0 °C and stirred at that temperature for 30 min before the chlorosilane was added.

(c) Reactions of $(Me_3Si)_2CHM$ (M = Li, K) with Chlorosilanes. To the reagent solutions prepared as described above was added the chlorosilane (Table IA) at 0 °C with stirring. The reaction mixtures were stirred at room temperature for 14–16 h.

Those reaction mixtures in which complete alkylation of all Si–Cl bonds had been effected were worked up hydrolytically. To the reaction mixture, cooled to 0 °C, was added slowly 80 mL of distilled ice water. The organic phase was separated, and the aqueous phase was extracted with three 80-mL portions of diethyl ether. The combined organic phases were dried over $MgSO_4$. Subsequently, the solvents were distilled at atmospheric pressure and the residue was distilled (10-cm Vigreux column) at reduced pressure. A second distillation gave pure, colorless liquid products.

In those reactions in which the product still contained a Si-Cl bond, the reaction mixture, after addition of 100 mL of Et_2O, was passed through a nitrogen-flushed Celite column (5 × 2 cm). The eluted solution was distilled under nitrogen at atmospheric pressure to remove solvent. The product was isolated by double fractional distillation at reduced pressure (as above).

The following products were obtained in this manner.

$(Me_3Si)_2CHSiMe_2H$: bp 80–82 °C (28 mmHg); IR (KBr) ν(SiH) 2100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.80 (s, 1 H, methine H), 0.074 (s, 18 H, Me_3Si), 0.14 (d, J = 3.9 Hz, 6 H, Me_2Si), 4.09 (hept, J = 3.9 Hz, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ_C −0.57 (q, J = 120.1 Hz, Me_2Si), 2.03 (d, J = 99.1 Hz, methine C), 2.47 (q, J = 118.3 Hz, Me_3Si). Anal. Calcd for $C_9H_{26}Si_3$: C, 49.46; H, 11.99. Found: C, 49.50; H, 11.93.

$(Me_3Si)_2CHSiMe_2CH{=}CH_2$: bp 94–96 °C (20 mmHg); ^{1}H NMR ($CDCl_3$) δ −0.71 (s, 1 H, methine H), 0.09 (S, 18 H, Me_3Si), 0.16 (s, 6 H, Me_2Si), 5.59 (dd, J = 19.1, 4.9 Hz, 1 H, vinyl H trans to Si), 5.87 (dd, J = 14.7, 4.9 Hz, 1 H, vinyl H cis to Si), 6.28 (dd, J = 19.1, 14.7 Hz, 1 H, vinyl H gem to Si); ^{13}C NMR ($CDCl_3$) δ_C 1.24 (q, J = 119.2 Hz, Me_2Si), 2.98 (methine C), 3.33 (q, J = 118.2 Hz, Me_3Si), 130.2 (t, J = 154.6 Hz, $H_2C{=}$), 142.6 (d, J = 135.7, methine C). Anal. Calcd for $C_{11}H_{28}Si_3$: C, 54.02; H, 11.54. Found: C, 54.32; H, 11.58.

$(Me_3Si)_2CHSiMe_2Ph$: bp 88 °C (1 mmHg); very viscous liquid; ^{1}H NMR ($CDCl_3$) δ −0.37 (s, 1 H, methine H), 0.014 (s, 18 H, Me_3Si), 0.35 (s, 6 H, Me_2Si), 7.28–7.5 (m, 5 H, Ph); ^{13}C NMR (acetone-d_6) δ_C 2.28 (q, J = 118.8 Hz, Me_2Si), 3.03 (d, J = 100.0 Hz, methine C), 3.79 (q, J = 118.3 Hz, Me_3Si), 128.6 (d, J = 158.5 Hz), 134.4 (d, 153.9 Hz), 129.5 (d, J = 159.2 Hz), 143.3 (s) (Ph).

$(Me_3Si)_2CHSiPhMeCl$: mp 48 °C; bp 95 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 1 H, methine C), 0.06 (s, 9 H, Me_3Si), 0.1 (s, 9 H, Me_3Si), 0.73 (s, 3 H, MeSi), 7.3–7.6 (m, 5 H, Ph); ^{13}C NMR (CD_2Cl_2) δ_C 3.02, 3.13 (q, J = 119.7 Hz, Me_3Si), 5.05 (q, J = 122.0 Hz, MeSi), 6.50 (d, J = 101.8, methine C), 128.27, 133.57, 130.18, 139.51 (Ph). Anal. Calcd for $C_{14}H_{27}Si_3Cl$: C, 53.37; H, 8.64. Found: C, 53.50; H, 8.54.

$(Me_3Si)_2CHSiMe_2Cl$: bp 60–62 °C (7 mmHg); crystallizes on cooling to 0 °C; ^{1}H NMR ($CDCl_3$) δ −0.33 (s, methine H), 0.16 (s, 18 H, Me_3Si), 0.49 (s, 6 H, Me_2Si); ^{13}C NMR ($CDCl_3$) δ_C 3.24 (q, J = 118.9 Hz, Me_3Si), 6.97 (q, J = 121.2 Hz, Me_2Si), 8.62 (d, J = 100.7 Hz, methine H). Anal. Calcd for $C_9H_{25}Si_3Cl$: C, 42.73; H, 9.96. Found: C, 42.91; H, 9.97.

$[(Me_3Si)_2CH]_2SiMeH$: bp 93–95 °C (0.03 mmHg); viscous oil; ^{1}H NMR ($CDCl_3$) δ −0.57 (s, 1 H, methine H), 0.1 (s, 36 H, Me_3Si), 0.26 (d, J = 3.4 Hz, 3 H, MeSi), 4.16 (m, 1 H, SiH); ^{13}C NMR ($CDCl_3$) δ_C 1.27 (d, J = 127.0 Hz, methine C), 2.49 (q, J = 119.75 Hz, MeSi), 2.65 (q, J = 118.4 Hz, Me_3Si), 3.46 (q, J = 118.4 Hz, Me_3Si); EI MS (70 eV) M$^+$ at m/z 363, (M$^+$ − CH_3) (100). Anal. Calcd for $C_{15}H_{42}Si_5$: C, 49.64; H, 11.66. Found: C, 49.51; H, 11.77.

$[(Me_3Si)_2CH]_2SiMe_2$: bp 95–100 °C (0.02 mmHg); mp 50–51 °C; ^{1}H NMR ($CDCl_3$) δ −0.46 (s, 2 H, methine H), 0.11 (s, 36 H, Me_3Si), 0.22 (s, 6 H, Me_2Si); ^{13}C NMR ($CDCl_3$) δ_C 3.79 (q, J = 118.7 Hz, Me_3Si), 4.81 (q, J = 119.2 Hz, Me_2Si), 5.09 (d, J = 101.1 Hz, methine C). Anal. Calcd for $C_{16}H_{44}Si_5$: C, 50.98; H, 11.77. Found: C, 51.34; H, 11.67.

$[(Me_3Si)_2CHSiMe_2CH_2]_2$: bp 135–140 °C (0.07 mmHg); very viscous oil; ^{1}H NMR ($CDCl_3$) δ −0.73 (s, 2 H, methine H), 0.06 (s, 12 H, Me_2Si), 0.08 (s, 36 H, Me_3Si), 0.42 (s, 4 H, CH_2CH_2); ^{13}C NMR (C_6D_6) δ_C 0.43 (q, J = 118.2 Hz, Me_2Si), 2.30 (d, J = 99.9 Hz, methine C), 3.47 (q, J = 118.4 Hz, Me_3Si), 11.40 (t, J = 119.6 Hz, CH_2CH_2). Anal. Calcd for $C_{20}H_{54}Si_6$: C, 51.87; H, 11.75. Found: C, 51.71; H, 11.60.

Preparation and Reactions of $Me_3SiCH_2SiMe_2CHMSiMe_3$ (M = Li, K). These organolithium and organopotassium reagents were prepared by the procedure described above for $(Me_3Si)_2CHM$ (M = Li, K) with use of 5.0 g (21.5 mmol) of $(Me_3SiCH_2)_2SiMe_2$. Some experiments were carried out in which *sec*-BuLi was used in place of *t*-BuLi in the RLi/TMEDA reagent.

Only monometalation of $Me_3SiCH_2SiMe_2CH_2SiMe_3$ could be effected even when the *n*-BuLi/Me_3COK reagent was used in excess. Thus, when a reaction of 21.50 mmol of this carbosilane with 43 mmol of *n*-BuLi/Me_3COK was carried out under the usual conditions, reaction of the reagent solution with Me_3SiCl gave only $Me_3SiCH_2SiMe_2CH(SiMe_3)_2$ in 84% yield. Use of an even larger excess of the *n*-BuLi/Me_3COK reagent (86 mmol and 21.50 mmol of the carbosilane) was equally unsuccessful in effecting dimetalation.

Details of the reactions of these reagents with various chlorosilanes are given in Table IB. The following silylation products were isolated and characterized.

$Me_3SiCH_2SiMe_2CH(SiMe_2H)SiMe_3$: bp 71–72 °C (0.8 mmHg); IR (KBr) ν(SiH) 2097 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.79 (s, 1 H, methine H), −0.19 (s, 2 H, CH_2), 0.01 (s, 9 H, Me_3Si), 0.06 (s, 9 H, Me_3Si), 0.08 (s, 6 H, Me_2Si), 0.13 (d, J = 3.8 Hz, Me_2HSi), 4.10 (hept, J = 3.8 Hz, 1 H, SiH). Anal. Calcd for $C_{12}H_{34}Si_4$: C, 49.57; H, 11.79. Found: C, 49.59; H, 11.94.

$Me_3SiCH_2SiMe_2CH(SiMe_3)_2$: bp 68 °C (0.01 mmHg); ^{1}H NMR ($CDCl_3$) δ −0.77 (s, H, methine H), −0.18 (s, 2 H, CH_2), 0.01 (s, 9 H, Me_3Si), 0.09 (s, 18 H, Me_3Si), 0.11 (s, 6 H, Me_2Si). Anal. Calcd for $C_{13}H_{36}Si_4$: C, 51.23; H, 11.19. Found: C, 51.58; H, 11.83.

Reactions of $Me_3SiCH_2SiMe_2CM(SiMe_3)_2$ (M = Li, K). $Me_3SiCH_2SiMe_2CH(SiMe_3)_2$ (5.0 g, 16.41 mmol), prepared as described above, in separate experiments was treated with equimolar quantities of the *n*-BuLi/TMEDA and *n*-BuLi/Me_3COK reagents, respectively, as described in the preparation of $(Me_3Si)_2CHM$. Subsequently, an excess of Me_3SiCl was added, and after the reaction mixture was stirred for 16 h at room temperature, hydrolytic workup followed. The product, $Me_3SiCH_2SiMe_2C(SiMe_3)_3$, was distilled at 100–105 °C (0.015 mmHg). The viscous oil that was distilled crystallized to give a material with mp 41 °C. The yield of this product was 92% when the lithium reagent was used and 94% with the potassium reagent. ^{1}H NMR ($CDCl_3$): δ 0.014 (s, 9 H, Me_3Si), 0.20 (s, 27 H, Me_3Si), 0.074 (s, 2 H, CH_2), 0.24 (s, 6 H, Me_2Si). FD MS: m/z 377. Anal. Calcd for $C_{16}H_{44}Si_5$: C, 50.98; H, 11.77. Found: C, 51.21; H, 11.72.

Preparation and Reactions of $\overline{Me_2SiCH_2SiMe_2CH_2SiMe_2C}HM$ (M = Li, K). c-$(Me_2SiCH_2)_3$ was obtained as a byproduct in the synthesis of c-$(Me_2SiCH_2)_2$ by the method of Kriner.[16] Reactions of 5.0 g (23.09 mmol) of this compound with equimolar amounts of *n*-BuLi(TMEDA or *n*-BuLi/Me_3COK were carried out as described for the preparation of $(Me_3Si)_2CHM$ (M = Li, K). Reactions of the reagents thus formed with chlorosilanes followed. Hydrolytic workup gave the products listed in Table IC. The individual products were characterized.

$\overline{Me_2SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2H$: bp 80 °C (5 mmHg); IR (KBr) ν(SiH) 2099 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.84 (s, 1 H, methine H), −0.29 (s, 4 H, CH_2), 0.04, 0.09, 0.11 (s, 6 H each, Me_2Si in ring), 0.13 (d, J = 2.9 Hz, 6 H, exocyclic Me_2Si), 4.1 (hept, J = 2.9 Hz, 1 H, SiH). Anal. Calcd for $C_{11}H_{30}Si_4$: C, 48.10; H, 11.01. Found: C, 48.26; H, 11.03.

$\overline{Me_2SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2CH{=}CH_2$: bp 65–66 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ −0.764 (s, 1 H, methine H), −0.29 (s, 4 H, CH_2), 0.03, 0.09, 0.13, 0.135 (s, 24 H, Me_2Si), 5.58 (dd, J = 19.1, 4.9 Hz, 1 H, vinyl H trans to Si), 5.86 (dd, J = 14.7, 4.9 Hz, 1 H, vinyl H cis to Si), 6.26 (dd, J = 19.1, 14.7 Hz, 1 H, vinyl H gem to Si); EI MS: M$^+$ m/z 300. Anal. Calcd for $C_{13}H_{32}Si_4$: C, 51.92; H, 10.73. Found: C, 52.15; H, 10.69.

In these reactions also, use of an excess of the metalation system resulted only in monometalation. Thus, reaction of 23.09 mmol of c-$(Me_2SiCH_2)_3$ with 46.2 or even 69.3 mmol of *t*-BuLi/TMEDA, followed by addition of Me_2HSiCl in excess, gave only $\overline{Me_2SiCH_2SiMe_2CH_2SiMe_2C}HSiMe_2H$ in yields of 71 and 73%, respectively.

Preparation of 1,1,3,3-Tetramethyl-1,2-disilacyclobutane. This compound was prepared by the method of Kriner,[16] in which magnesium is added in portions to a solution of $Me_2(CH_2Cl)SiCl$ (Petrarch) in THF. In addition to the disilacyclobutane, formed in ca. 50% yield, the trimer c-$(Me_2SiCH_2)_3$, the tetramer c-$(Me_2SiCH_2)_4$, and higher oligomers $(Me_2SiCH_2)_n$ were formed in yields of 19%, 1.3%, and 13%, respectively.

$Me_2(CH_2Br)SiCl$ (Petrarch) also was used as starting material. Its use had the advantage that a faster reaction occurred.

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(16) Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601.

Table II. Metalation of Poly(dimethylsilene)

amt used for 0.5 g of $[Me_2SiCH_2]_n$				
Me_3COK, mg (mmol)	2.44 M n-BuLi, mL (mmol)	Me_2RSiCl added, R (amt, mmol)	polymer yield, %	polymer type and properties
130 (1.16)	0.48 (1.16)	H (4.6)	98	$\{[Me_2SiCH_2]_{15}[Me_2SiCH(SiMe_2H)]\}_n$; very viscous oil; soluble in C_6H_6, $C_6H_5CH_3$, $CHCl_3$, CH_2Cl_2, CCl_4; poorly soluble in hexane
776 (6.92)	2.84 (6.92)	H (20.0)	92	$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2H)]\}_n$; viscous oil; soluble in hexane
776 (6.92)	2.84 (6.92)	$CH{=}CH_2$ (20.3)	98	$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$; viscous oil; soluble in hexane
776 (6.92)	2.84 (6.92)	CH_2Cl (20.5)	95	$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH_2Cl)]\}_n$; viscous oil; soluble in hexane
776 (6.92)	2.84 (6.92)	CH_3 (20.5)	98	$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_3)]\}_n$; very viscous oil, forms a glass after a few days
776 (6.92)	2.84 (6.92)	Et_3SiCl (20.02)	98	$\{[Me_2SiCH_2]_3[Me_2SiCH(SiEt_3)]\}_n$; viscous oil; soluble in hexane
1550 (13.83)	5.67 (13.83)	H (42.2)		*a*
1550 (13.83)	5.67 (13.83)	$CH{=}CH_2$ (42.0)		*a*
2330 (20.8)	8.52 (20.8)	$CH{=}CH_2$ (61.6)		*a*
3880 (34.7)	14.22 (34.7)	CH_2Cl (106.3)		mobile liquid; complex NMR spectra

[a] Oil; complex NMR spectra due to chain scission by excess n-BuK.

A 500-mL three-necked, round-bottomed flask equipped with an addition funnel, a reflux condenser topped with a nitrogen inlet, and a mechanical stirrer was charged with a few milligrams of Mg powder in 5 mL of THF. A few drops of CH_2I_2 and then 1 mL of $Me_2(CH_2Br)SiCl$ were added. After the reaction had been initiated, 50 g (0.267 mol) of $Me_2(CH_2Br)SiCl$ and 50 mL of THF were added. Subsequently, 10.9 g (0.45 mol) of Mg powder was added portionwise, slowly during the course of 2 h while the reaction temperature was maintained between 35 and 50 °C. After about one-third of the Mg powder had been added, another 50 mL of THF was added in order to keep the reaction mixture stirrable. Another 50 mL of THF was added after about two-thirds of the Mg had been added. The reaction mixture was stirred for 2 h at 50 °C and then was cooled to 0 °C. Careful addition to 150 mL of water followed. The dried organic phase was distilled to give, after removal of solvent, 8.8 g (46%) of c-$(Me_2SiCH_2)_2$ (bp 122–124 °C (760 mmHg)). Further distillation at reduced pressure gave 2.1 g (11%) of $(Me_2SiCH_2)_3$ (bp 105–110 °C (45 mmHg)) and 0.5 g (2.6%) of $(Me_2SiCH_2)_4$ (bp 110 °C (2 mmHg)). The residue (3.5 g (18.2%)) was higher molecular weight $(Me_2SiCH_2)_n$. The physical and spectroscopic properties of the products agreed with literature data.[16]

Preparation of Poly(dimethylsilene). The procedure described by Levin and Carmichael[6e] was followed with use of 10 g of $(Me_2SiCH_2)_2$ and 2 μL of 5% $H_2PtCl_6{\cdot}6H_2O$ in 2-propanol. A colorless, rubbery material (9.6 g, 96%) was obtained. After several days of storage at room temperature it began to flow. IR (KBr): 2942 (s), 2886 (m), 2848 (w), 1416 (sh), 1400 (w), 1317 (w), 1245 (s), 1122 (sh), 1049 (s), 970 (sh), 820 (vs), 790 (vs), 749 (sh), 721 (sh), 685 (sh), 672 (m), 600 (vw) cm^{-1}. ^1H NMR (CD_2Cl_2): δ −0.28 (s, 2 H, CH_2), 0.1 (s, 6 H, Me_2Si). ^{13}C NMR ($CDCl_3$): δ 2.7 (q, J = 117.8 Hz, Me_2Si), 7.5 (t, J = 107.7 Hz, CH_2). Mol Wt: 2018 (vapor pressure osmometry); GPC (toluene solution, polystyrene standard) 50 000–200 000 Da (3 peaks, broad), 1000–3000 Da (2 peaks), the latter peaks predominated; TGA (in argon, 10 °C/min to 1000 °C) 100% weight loss.

Metalation of Poly(dimethylsilene) (PDMS). General Procedure. Poly(dimethylsilene), 0.500 g (6.93 mmol as Me_2SiCH_2), was dissolved in 80 mL of THF (reaction apparatus as in earlier metalation reactions), the solution was cooled to −78 °C, and the amount of Me_3COK indicated for each experiment in Table II was added. Subsequently, 2.44 M n-BuLi in pentane (quantity given in Table II) was added by syringe. An immediate yellow coloration was observed. The mixture was warmed to 0 °C during the course of 1 h, and then the chlorosilane indicated in Table II was added in the specified amount. The now colorless solution was stirred at room temperature for 12–14 h. Removal of volatiles at reduced pressure left a colorless residue of polymer and LiCl and KCl. This was extracted with 6;1 (v/v) benzene-/hexane. The extracts were filtered through a bed of Celite. The resulting clear solution was evaporated at 30 °C in vacuo to give the C-silylated poly(dimethylsilene). Details of these reactions are given in Table II.

The characterization of the individual polymeric procedures follows. The percent C values for all products are high, compared with those for the approximate formulas obtained by integration of the ^1H NMR spectra. This may be due in part to the inherent error in the integration and to the presence of some n-butyl groups resulting from minor cleavage of the Si–C bonds of the polymer by n-BuK.

$\{[Me_2SiCH_2]_{15}[Me_2SiCH(SiMe_2H)]\}_n$. Anal. Found: C, 50.72; H, 11.10. Mol wt (cryoscopy in benzene): 1574. Ceramic yield (TGA, Ar, 10 °C/*min to 950 °C*): *100% weight loss.* IR (KBr): ν(SiH) 2095 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.78 (s, 1 H, –CH–), −0.23 (s, 28 H), −0.12 (s, 2 H), −0.04 to +0.18 (m, with most intense peak at 0.06, 102 H, Me_2Si). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C −0.29, 2.78, 3.66, 3.82 (s, Me_2Si), 7.56 (s, $-CH_2-$) (–CH– osbscured).

$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2H)]\}_n$. Anal. Found: C, 51.95; H, 10.97. Mol wt (cryoscopy in benzene): 1180. GPC (in toluene, polystyrene standard): 3 peaks in the 1000–2000-Da range, a broad peak in the 50 000–150 000-Da range. Ceramic yield (TGA, Ar, 10 °C/min. to 950 °C): 100% weight loss. IR (KBr): ν(SiH) 2095 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.78 (s, 1 H, –CH–), −0.25 (s, 4 H, $-CH_2-$), −0.14 (s, 2 H, $-CH_2-$), 0.034, 0.04, 0.046 (s, 18 H, Me_2Si), 0.116, 0.122 (s, 6 H, Me_2Si), 0.16 (d, J = 3.7 Hz, 6 H, Me_2SiH), 0.85–1.25 (low intensity m, probably n-Bu), 4.1 (hept, J = 3.3 Hz, Si-H). ^{13}C NMR ($CDCl_3$): δ_C −0.37 (q, J = 119.0 Hz, Me_2SiH), 2.71 (q, J = 118.7 Hz, Me_2Si), 3.56 (q, J = 117.8 Hz, Me_2Si), 3.75 (q, J = 117.8 Hz, Me_2Si), 7.66 (t, J = 107.2, $-CH_2-$); –CH– signal in $^{13}C\{^1H\}$ NMR spectrum at δ 5.10 (s).

$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH{=}CH_2)]\}_n$. Anal. Found: C, 53.52; H, 10.86. Mol wt (cryoscopy in benzene): 1377. GPC (in toluene, polystyrene standard): 2 peaks in the 1000–3000-Da range, a broad peak in the 50 000–200 000-Da range. Ceramic yield (TGA, Ar, 10 °C/min to 950 °C): 2%. ^1H NMR ($CDCl_3$): δ −0.67 (s, 1 H, –CH–), −0.26 (s, 4 H, $-CH_2-$), −0.13 (s, 2 H, $-CH_2-$), 0.03 (s, 6 H, Me_2Si), 0.05 (s, 12 H, Me_2Si), 0.13 (s, 6 H, Me_2Si), 0.17 (s, 6 H, Me_2Si), 0.85–1.25 (low intensity m, probably due to n-Bu), 5.60 (dd, J = 20.2, 3.8 Hz, 1 H, vinyl H trans to Si), 5.86 (dd, J – 14.4, 3.8 Hz, 1 H, vinyl H cis to Si), 6.25 (dd, J = 20.2, 14.4 Hz, 1 H, vinyl H gem to Si).

$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH_2Cl)]\}_n$. Anal. Found: C, 51.49; H, 10.12; Cl, 9.07. Mol wt (cryoscopy in benzene): 1320. Ceramic yield (TGA, Ar, 10 °C/min to 950 °C): 100% weight loss. ^1H NMR ($CDCl_3$): δ −0.47 (s, 1 H, –CH–), −0.25 (s, 4 H, $-CH_2-$), −0.13 (s, 2 H, $-CH_2-$), 0.041 (s, 12 H, Me_2Si), 0.063 (s, 6 H, Me_2Si), 0.16 (s, 6 H, Me_2Si), 0.23, (s, 6 H, Me_2SiCH_2Cl), 0.83–1.23 (low intensity m, n-Bu), 2.8 (broad, s, 2 H, CH_2Cl).

$\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_3)]\}_n$. Anal. Found: C, 51.34; H, 11.09. Mol wt (cryoscopy in benzene): 1362. Ceramic yield (TGA, Ar, 10 °C/min to 950 °C): 100% weight loss. ^1H NMR ($CDCl_3$): δ −0.75 (s, 1 H, –CH–), −0.26 (S, 4 H, $-CH_2-$), −0.14 (s, 2 H, $-CH_2-$), 0.03 (s, 6 H, Me_2Si), 0.034 (s, 6 H, Me_2Si), 0.05 (s, 6 H, Me_2Si), 0.09 (s, 6 H, Me_2Si), 0.13 (s, 9 H, Me_3Si), 0.83–1.25 (low intensity m, n-Bu).

$\{[Me_2SiCH_2]_3[Me_2SiCH(SiEt_3)]\}_n$. Anal. Found: C, 56.53; H, 11.44. Mol wt (cryoscopy in benzene): 721. Ceramic yield (TGA, Ar, 10 °C/min to 950 °C): 16%. ^1H NMR ($CDCl_3$): δ −0.61 (s, 1 H, –CH–), −0.24 (s, 4 H, $-CH_2-$), −0.12 (s, 2 H, $-CH_2-$), 0.06 (s, 6 H, Me_2Si), 0.071 (s, 12 H, Me_2Si), 0.15 (s, 6 H, Me_2Si), 0.51, 0.66 (q, J = 7.7 Hz, 6 H, CH_2 of $SiEt_3$), 0.93, 0.96 (t, J = 7.7 Hz, 9 H, CH_3 of $SiEt_3$).

Other Products in Table II. When a 2-, or 3-, or 5-fold excess of the n-BuLi/Me_3COK reagent was used, scission of Si–C bonds of the $-Me_2Si-CH_2-$chain appeared to be extensive. The products were less viscous than when a 1:1 base:Me_2SiCH_2 ratio was used, their NMR spectra were too complex for interpretation, and their C, H analyses were not meaningful.

AIBN-Catalyzed Reaction of $\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH=CH_2)]\}_n$ with the Polysilane $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$. A Schlenk flask was charged with 1.5 g of the $Me_2(CH_2=CH)Si$-substituted poly(dimethylsilene), the polysilane (in separate experiments, 1.25, 2.08, 3.33, and 6.25 g, respectively), and 150 mL of benzene. To this solution was added 50 mg of α,α'-azobis(isobutyronitrile) (AIBN). The reaction flask was wrapped in aluminum foil to keep out the light, and the reaction mixture was heated at reflux for 1 day. After the mixture had been cooled to room temperature, another 50 mg of AIBN was added and the mixture was heated at reflux for another day. These steps were repeated another time, so that a total of 150 mg of AIBN had been added and the total reflux time was 3 days. The reaction mixture was filtered under nitrogen through a 5 × 2.5 cm nitrogen-flushed Celite column, and then the volatiles were removed under high vacuum. The nature of the residue depended on the ratio of $\{[Me_2SiCH_2]_3[Me_2SiCH(SiMe_2CH=CH_2]\}_n$ to $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ used. The products were readily soluble in benzene, toluene, chloroform, and dichloromethane and less soluble in hexane and ethers. The yields were quantitative. Characterization data are as follows.

(a) Product from reaction of 1.5 g of the $SiMe_2CH=CH_2$-substituted poly(dimethylsilene) and 1.25 g of $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$: waxy, colorless material. Anal. Found: C, 44.72; H, 9.27. Mol wt (cryoscopy in benzene): 585. IR (KBr, CCl_4): ν(SiH) 2098 cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.6 to -1.5 (multiplet due to Me_2Si, $SiCH_2$, SiCH, with maxima at -0.24, 0.1, 0.13, 0.3, 1.2), 1.52 (s, $Me_2C(CN)$), catalyst fragment incorporation), 3.3–4.0 (m, SiH); intensity ratio SiH:(Me_2Si + $SiCH_2$ + SiCH) = 1:12.5; very weak signals due to $Si-CH=CH_2$ also observed in the 5.3–6.3 ppm region. Ceramic yield (TGA, Ar, to 950 °C): 54%.

(b) Product from reaction of 1.5 g of the $SiMe_2CH=CH_2$-substituted poly(dimethylsilene) and 2.08 g of $[(MeSiH)_{0.8}(MeSi)_{0.2}$: colorless solid; mp 130–135 °C (softening range (TMA) 47–54 °C). Anal. Found: C, 38.73; H, 9.34. Mol wt. (cryoscopy in benzene): 606. IR (KBr, CCl_4): ν(SiH) 2100 cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.8 to +1.5 (m, $SiMe_2$, $SiCH_2$, SiCH), 1.52 (s, $Me_2C(CN)$), 3.4–4.2 (m, Si-H); SiH:(Me_2Si + $SiCH_2$ + SiH) = 1:14; no $Si-CH=CH_2$ signals. Ceramic yield (TGA, Ar, to 950 °C): 56%.

(c) Product from reaction of 1.5 g of the $SiMe_2CH=CH_2$-substituted poly(dimethylsilene) and 3.33 g of $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$: colorless solid; mp 120 °C (softening range (TMA) 62–85 °C). Anal. Found: C, 36.71; H, 9.03. Mol wt (cryoscopy in C_6H_6): 746. IR (KBr, CCl_4): ν(SiH) 2094 cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.9 to +1.5 (m, Me_2Si, $SiCH_2$, SiCH), 1.53 (s, $Me_2C(CN)$), 3.2–4.0 (m, SiH); no $Si-CH=CH_2$ signals. SiH/Me_2Si + $SiCH_2$ + SiCH = 1:12. Ceramic yield (TGA, Ar, to 950 °C): 68%. Furnace pyrolysis of a 1.300-g sample under a stream of argon to 1000 °C left an 870-mg (67%) residue. Further heating of a 300-mg sample of this residue under argon to 1500 °C resulted in a further 20-mg weight loss.

In these pyrolyses the samples were weighed into porcelain boats in a Vacuum Atmospheres intert-atmosphere box. The samples then were transferred to a quartz pyrolysis tube in a tube furnace and flushed well with argon. The heating program (10 °C/min) involved heating to 300 °C, with a 6-min hold, and further heating to 1000 °C, with a 2-h hold at that temperature. Slow cooling (under a stream of argon) left a black residue, which then was transferred to the inert-atmosphere box. The ceramic thus produced was amorphous by powder X-ray diffraction. In the pyrolyses carried out to 1500 °C, the initial heating was to 1000 °C at 10 °C/min; a 1-h hold was followed by further heating to 1500 °C at 10 °C/min. The sample was sintered at 1500 °C for 7 h. This produced a crystalline ceramic residue whose powder X-ray diffraction pattern showed only the lines due to β-SiC (none due to elemental silicon).

Elemental analysis of the ceramic residue of the pyrolysis to 1000 °C (33.83% C, 59.58% Si) allowed calculation of an approximate composition of 1 SiC + 0.33 C or 91.06% (by weight) of SiC and 8.94% of C.

(d) Product from 1.5 g of $SiMe_2CH=CH_2$-substituted poly(dimethylsilene) and 6.25 g of $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$: waxy material from which long fibers could be hand-drawn. Anal. Found: C, 33.50; H, 8.36. Mol wt (cryoscopy in C_6H_6): 720. IR (KBr, neat): ν(SiH) 2092 cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.8 to +1.5 (m, Me_2Si + $SiCH_2$ + SiCH); SiH:(Me_2Si + $SiCH_2$ + SiCH); no $Si-CH=CH_2$ signals. Ceramic yield (furnace, Ar, 10 °C/min to 1000 °C): 56% (a further 7.5% weight loss on heating to 1500 °C, followed by 7 h of sintering at 1500 °C). Analysis of the ceramic obtained in the 1000 °C pyrolysis (32.68% C, 63.81% Si) allowed calculation of an approximate composition of 1 SiC + 0.22 C or 94% by weight of SiC and 6% of C. The powder X-ray diffraction pattern of the material heated to 1500 °C showed only lines due to β-SiC.

Reaction of AIBN with Liquid $[(MeSiH)_{0.8}(MeSi)_{0.2}]_n$ (Control Experiment). The polysilane (3.0 g) was dissolved in 100 mL of benzene, and 50 mg of AIBN was added. The resulting solution was protected from the light with aluminum foil wrapping and heated at reflux under nitrogen for 24 h. Adding another 50 mg of AIBN and heating at reflux for 24 h followed. This procedure was repeated for a third time. The reaction mixture was filtered through silica gel and then was evaporated under high vacuum. A white solid (mp 80–85 °C) remained. Mol wt (cryoscopy in benzene): 635. Ceramic yield (TGA in argon, to 950 °C): 66%. The IR spectrum was identical with that of the starting material except for a weak band at 2250 cm^{-1}, presumably ν(CN). ^1H NMR ($CDCl_3$): δ 0.0–1.6 (m, strongest resonance at 0.18), 1.43 (s, $Me_2(CN)C$), 3.2–3.9 (m, SiH); SiH:$Me_2(CN)C$:SiMe intensity ratio 1:0.13:7.

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Registry No. $(Me_3Si)_2CHLi$, 41823-71-6; $(Me_3Si)_2CH_2$, 2117-28-4; t-BuLi, 109-72-8; $(Me_3Si)_2CHK$, 118111-55-0; t-BuK, 865-47-4; $Me_3SiCH_2SiMe_2CHLiSiMe_3$, 131544-56-4; $Me_3SiCH_2SiMe_2CHKSiMe_3$, 131544-57-5; $(Me_3Si)_2CHSiMe_2H$, 131544-58-6; $(Me_3Si)_2CHSiMe_2CH=CH_2$, 131544-59-7; $(Me_3Si)_2CHSiMe_2Ph$, 78907-68-3; $(Me_3Si)_2CHSiPhMeCl$, 131544-60-0; $(Me_3Si)_2CHSiMe_2Cl$, 78907-55-8; $[(Me_3Si(_2CH]_2SiMe_2$, 131544-61-1; $[(Me_3Si)_2CH]_2SiMeH$, 131544-62-2; $[(Me_3Si)_2CHSiMe_2CH_2]_2$, 131544-63-3; $Me_3SiCH_2SiMe_2CH(SiMe_3)SiMe_2H$, 131544-64-4; $Me_3SiCH_2SiMe_2CH(SiMe_3)_2$, 131544-65-5; $Me_3SiCH_2SiMe_2CLi(SiMe_3)_2$, 131544-66-6; $Me_3SiCH_2SiMe_2CK(SiMe_3)_2$, 131544-67-7; $Me_2SiCH_2SiMe_2CHKSiMe_2CH_2$, 131544-68-8; $Me_2SiCH_2SiMe_2CHLiSiMe_2CH_2$, 60799-18-0; $Me_2SiCH_2SiMe_2CH_2SiMe_2CHSiMe_2H$, 121007-51-0; $Me_2SiCH_2SiMe_2CH_2SiMe_2CHSiMe_2CH=CH_2$, 131544-69-9; Me_2HSiCl, 1066-35-9; $Me_2(CH_2=CH)SiCl$, 1719-58-0; Me_3SiCl, 75-77-4; $Me_2PhSiCl$, 768-33-2; $PhMeSiCl_2$, 149-74-6; Me_2SiCl_2, 75-78-5; $MeHSiCl_2$, 75-54-7; $(ClMe_3SiCH_2)_2$, 13528-93-3.