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1,1,3,3-TETRAMETHYL-2,2,4,4-TETRAKIS(TRIMETHYLSILYL)-1,3-DISILACYCLOBUTANE AND ITS 1,3-DIGERMA AND 1,3-DISTANNA ANALOGS: UNEXPECTED PRODUCTS FROM THE REACTION OF BIS-(TRIMETHYLSILYL)BROMOMETHYLLITHIUM WITH DIMETHYLDIHALO DERIVATIVES OF SILICON, GERMANIUM AND TIN *

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Summary

The reaction of bis(trimethylsilyl)bromomethyllithium with the dimethyldihalo derivatives of silicon, germanium and tin in each case gave the respective 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-dimetallacyclobutane as the major product. Since the tin compound was the first 1,3-distannacyclobutane to be prepared, its structure was confirmed by ring cleavage reactions with bromine in CCl_4, to give $BrMe_2SnC(SiMe_3)_2SnMe_2C(SiMe_3)_2Br$, and with methyllithium, to give, after hydrolysis, $Me_3SnC(SiMe_3)_2SnMe_2C(SiMe_3)_2H$ and $(Me_3Si)_2(Me_3Sn)CH$. Trapping experiments with trimethyltin chloride and bromine showed intermediates of type $(Me_3Si)_2C(Li)MMe_2Cl$ to be involved in 1,3-dimetallacyclobutane formation.

Introduction

We have reported recently concerning the preparation and chemistry of hexamethylsilirane [2,3]. In view of the limited thermal stability of this compound, it seemed desirable to prepare a more stable hexasubstituted silacyclopropane ** which would be easier to handle. One such compound whose synthesis we considered undertaking was 1,1-dimethyl-2,2,3,3-tetrakis(trimethylsilyl)silirane (I). One might expect this molecule to be more stable thermally than hexamethylsilirane as a result of the steric bulk of the four trimethylsilyl substituents which might serve to hinder available decomposition pathways.

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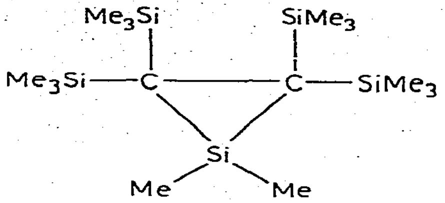
* Preliminary communication: ref. 1.

** Derivatives of the 7-siladispiro [2.0.2.1] heptane system are much more stable silacyclopropane compounds [2.4], principally as a result of electronic factors [5,6], but we were interested in simpler silacyclopropanes which did not enjoy such special stabilization.



(I)

The preparation of compound I via our route to siliranes [2,4] required the availability of $[(Me_3Si)_2CBr]_2SiMe_2$ (II) for the magnesium-effected ring closure reaction. In principle, the preparation of II should have been a routine task using the reaction of $(Me_3Si)_2CBrLi$, a reagent developed previously in these laboratories [7], with dimethyldichlorosilane. In practise, the reaction of this lithium reagent with dimethyldichlorosilane took an entirely different course which provided a new route to highly substituted 1,3-dimetallacyclobutanes.

Results and discussion

Bis(trimethylsilyl)bromomethyllithium is prepared by simultaneous addition of n-butyllithium in hexane and bis(trimethylsilyl)dibromomethane in tetrahydrofuran (THF) to dimethyl ether at —115°C. When the resulting orange solution was treated with one-half molar equivalent of dimethyldichlorosilane, color changes from pea green and then slowly to pale yellow were observed during the course of 90 min. A hydrolytic workup gave colorless crystals which contained carbon, hydrogen and silicon, but, unexpectedly, no bromine. The NMR spectrum of this product showed two singlets at δ 0.54 and 0.27 ppm with an intensity ratio of 1 : 3 (in contrast to the NMR spectrum of II, which should show two singlets in 1 : 6 intensity ratio). The mass spectrum of the crystalline product showed a molecular ion at m/e 432, as well as a prominent peak at m/e 216, which corresponds to a species $[M/2]^+$. The solution molecular weight of the product (vapor pressure osmometry in chloroform) was determined to be 427. On the basis of these results, the reaction product was determined to be 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (III) *. Based on the utilization of two moles of bis(trimethylsilyl)dibromomethane in the formation of one mole of III, the yield of III was 36%. Examination of the vola-

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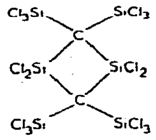
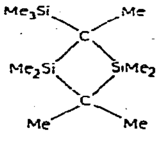
* A structurally similar perchlorinated 1,3-disilacyclobutane (IV) has been prepared by Müller and Müller [8] by reaction of $(Cl_3Si)_3CCl$ with Si/Cu, Si, Fe or Fe/Cu at elevated temperatures, and Fritz et al. [9] recently have reported the preparation of the highly substituted 1,3-disilacyclo-



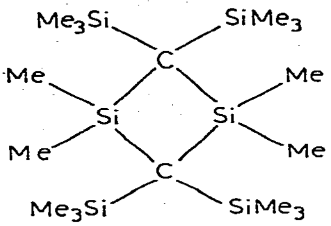
(IV)



(V)

butane V. For reviews covering the preparation, properties and chemical transformations of 1,3-disilacyclobutanes, see ref. 10 and 11.

tile components of the reaction mixture by gas chromatography (GLC) showed a 30% recovery of $(Me_3Si)_2CBr_2$ and the formation of $(Me_3Si)_2CHBr$ in 11% yield.

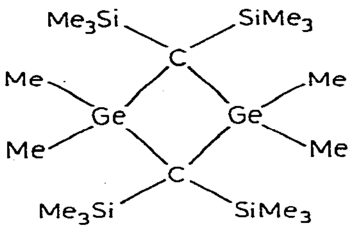


(III)

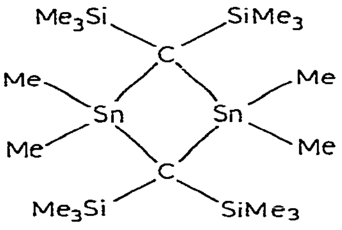
This reaction represents a novel route to 1,3-disilacyclobutanes, and how the reaction proceeds to give such a product was not immediately obvious. We will return to the question of mechanism later.

Of immediate interest was whether this reaction might be applicable to the preparation of other 1,3-dimetallacyclobutanes. One 1,3-digermacyclobutane was known [12], and no compound containing the 1,3-distannacyclobutane ring system had been prepared previously. In fact, the smallest well-characterized cyclic compounds containing only tin and carbon atoms as ring members were derivatives of the stannacyclopentane ring system *. Therefore, we continued our research with a study of the reactions of bis(trimethylsilyl)bromomethyllithium with one-half molar equivalent of dimethyldibromogermane and dimethyltin dichloride, respectively.

Addition of dimethyldibromogermane to two molar equivalents of $(Me_3Si)_2CBrLi$ at —115°C gave two products: the expected 1,3-digermacyclobutane (VI) in 17% yield and $(Me_3Si)_2C(GeMe_2Br)_2$ in 4.4% yield. Of greater interest was the success of a similar reaction with dimethyltin dichloride which did indeed give the expected 1,3-distannacyclobutane (VII) in 20% yield. Two other minor products were identified tentatively as $[(Me_3Si)_2CBr]_2SnMe_2$ (2%) and $(Me_3Si)_2C(SnMe_2Cl)_2$ (1%).



(VI)



(VII)

Since VII was the first compound of its class, special attention was given to its characterization. Its molecular weight in chloroform by vapor pressure osmometry was found to be 636 (vs. 614 calculated for VII). Its mass spectrum did not show a molecular ion, but the species which results form loss of a methyl group, [*M* —

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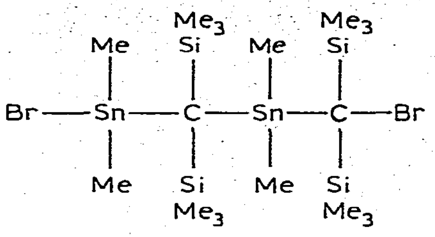
* For complete references relating to this question, see ref. 1.

$15]^+$, was observed, as was the $[M/2]^+$ fragment. The NMR spectrum showed the expected two singlets in 1 : 3 ratio, with tin satellites for the lower field signal. Chemical evidence also supported VII as the structure of the product. Combustion analysis gave satisfactory %C and %H values and the compound did not contain halogen. Brominolysis in carbon tetrachloride solution gave VIII, the product of the cleavage of an endocyclic tin—carbon bond, in 92% yield. In contrast, brominolysis of VII in methanol resulted in methyl group cleavage from tin to give IXa in 82% yield. Such a dramatic change in reaction site may be understood in terms of the observation reported by Boué et al. [13] that the $Br_2/MeOH$ reagent system cleaves methyl groups preferentially from methyl(alkyl)tin compounds, presumably because of the steric demand of the solvated bromine electrophile.



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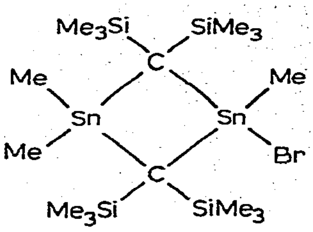


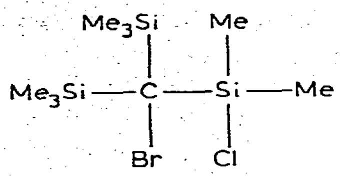
(IXa)

Nucleophilic cleavage of the 1,3-distannacyclobutane VII could be effected with methyllithium. A 1 : 1 reaction of this reagent with VII in refluxing THF followed by hydrolytic workup gave two products, IX and X in yields of 37% and 20%, respectively, thus establishing the reaction course shown in Scheme 1. When two molar equivalents of methyllithium were allowed to react with VII, a high yield of lithium reagent XI was obtained. Reactions of solutions of XI thus produced with water, trimethyltin chloride and trimethylchlorosilane gave $(Me_3Si)_2(Me_3Sn)CH$ (74%), $(Me_3Si)_2C(SnMe_3)_2$ (75%) and $(Me_3Si)_3CSnMe_3$ (86%), respectively.

The 1,3-disilacyclobutane III is considerably less reactive than VII, as demonstrated by the fact that it did not react with bromine in refluxing carbon tetrachloride during a 24 h reaction time. Cleavage did occur under harsher conditions. In contrast, 1,1,3,3-tetramethyl-1,3-disilacyclobutane reacts rapidly with Br_2 [11].

It has been reported [11] that less substituted 1,3-disilacyclobutanes do not react with organolithium reagents, and thus it was not unexpected that the much more hindered III was inert toward methyllithium in refluxing THF.

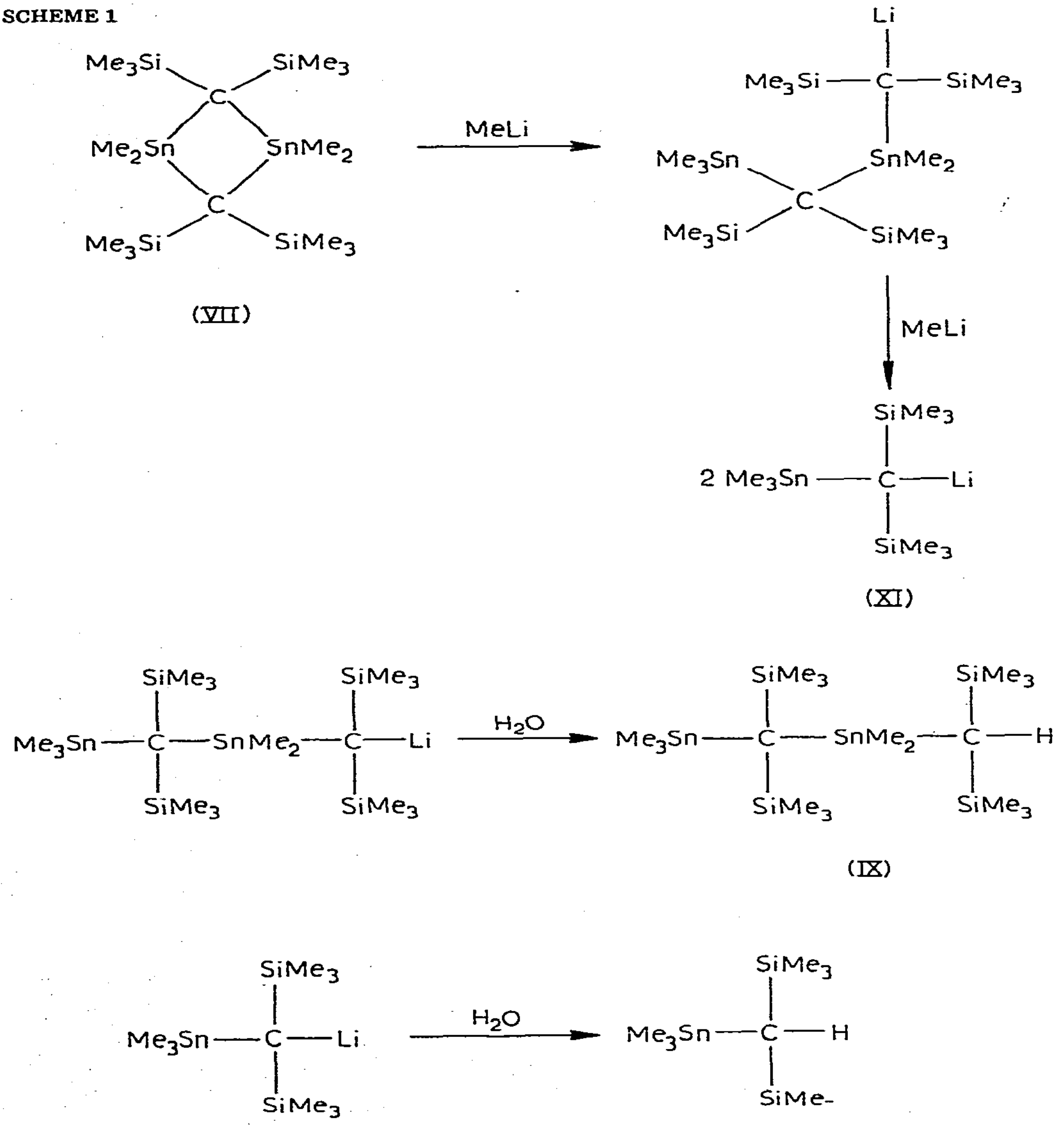
Further attention was devoted to the question of the mechanism of the process by which these novel 1,3-dimetallacyclobutanes were formed. It seemed reasonable to assume that the first step in the reaction sequence leading to III was the alkylation of dimethyldichlorosilane to give XII. It had been expected that this reaction would be followed by a second reaction at Si—Cl to give $[(Me_3Si)_2CBr]_2SiMe_2$. However, an alternate site of reactivity in XII with respect to organolithium reagents is its C—Br bond. Alkylation of an R_3SiCl compound is a relatively slow process, and, in fact, bromobenzene is more reactive toward n-butyllithium than is trimethylchlorosilane, as a competition experiment has



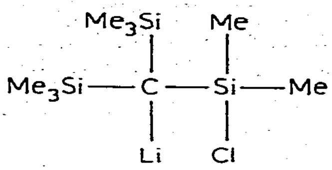
(XII)

shown [14]. Such nucleophilic attack at silicon will become even slower at the low temperatures used in our experiments, but it is well known that lithium—halogen exchange in alkyl halide systems (an electron-transfer process) is rapid even at low temperatures [15]. In XII, attack by the bulky $(Me_3Si)_2CBrLi$ re-

SCHEME 1



agent at the highly hindered silicon atom must be very unfavorable, so lithium—bromine exchange between $(Me_3Si)_2CBrLi$ and XII could well become the preferred process. An intermediate such as XIII, which would be formed in this



$$\begin{array}{ccccccc} & & Me_3Si & & Me & & \\ & & | & & | & & \\ Me_3Si & — & C & — & Si & — & Me \\ & & | & & | & & \\ & & Li & & Cl & & \end{array}$$

(XIII)

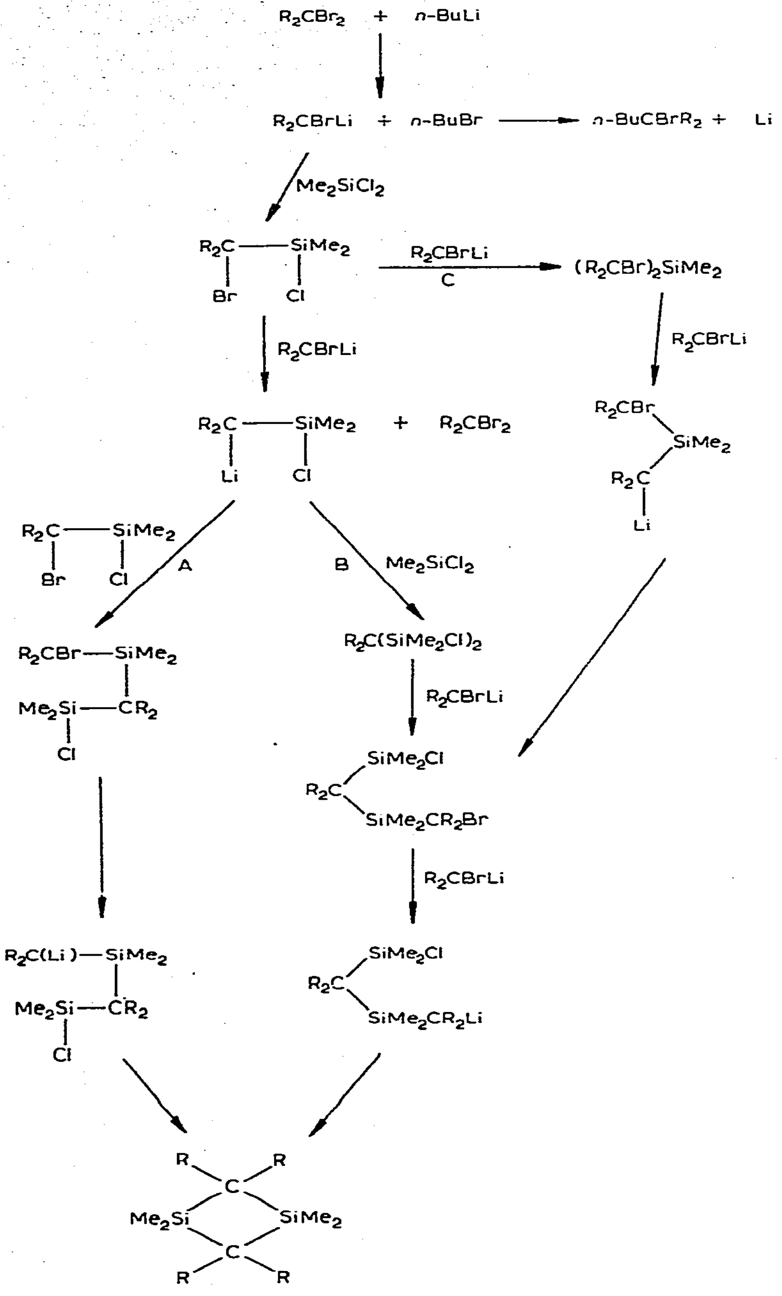
reaction, is not without precedence. Thus, evidence has been provided that the action of t-butyllithium on trimethylchlorosilane at —78° C gives some $LiCH_2SiMe_2Cl$, as well as the expected coupling product, Me_3SiCMe_3 [16]. More recently, the transient existence of $Ph_2ClSiCH(Li)Ph$ has been reported [17].

The lithium—bromine exchange reaction between $(Me_3Si)_2CBrLi$ and $(Me_3Si)_2CBrSiMe_2Cl$ to give XIII should be favored by several factors: First, the steric hindrance to nucleophilic substitution at silicon already mentioned. Second, the presence of three silyl groups on the carbon atom to which the bromine is bound. It has been shown that α-trimethylsilylalkyllithium reagents enjoy special stability which increases the more α-Me_3Si groups are present [18]. (The high kinetic acidity of $(Me_3Si)_3CH$ which forms the very stable $(Me_3Si)_3CLi$ is to be noted in this respect [19].)

If one assumes that reaction of XII with n-butyllithium gives lithium reagent XIII, then routes to the 1,3-disilacyclobutane product are available. One possible pathway involves a series of organometallic reaction steps (Scheme 2); another involves dimerization of $(Me_3Si)_2C{=}SiMe_2$ which possibly could have been formed via β-elimination of lithium chloride from XIII. (It may be noted that in the absence of a trapping agent, both in the gas phase [20] and in solution [21] "$R_2Si{=}CH_2$" intermediates dimerize to give 1,3-disilacyclobutanes.)

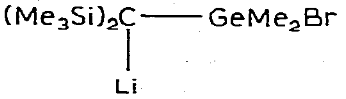
The formation of XIII by reaction of $(Me_3Si)_2CBrLi$ with XII would result in production of an equivalent amount of $(Me_3Si)_2CBr_2$. In all experiments in which a 1,3-dimetallacyclobutane was formed, this compound was found to be present in substantial amount. More direct evidence for the intermediacy of lithium reagent XIII was provided by experiments in which it was trapped by reaction with other substrates. Thus when one molar equivalent of dimethyldichlorosilane was added to the $(Me_3Si)_2CBrLi$ solution, a new product, $(Me_3Si)_2C(SiMe_2Cl)_2$ (XIV), was obtained in 7% yield, in addition to the 1,3-disilacyclobutane III (30% yield). The yield of XIV was increased to 31% when the $(Me_3Si)_2CBrLi$ solution was added to an excess of dimethyldichlorosilane. The formation of XIV is best explained in terms of a reaction of lithium reagent XIII with dimethyldichlorosilane. It was found that XIII could be intercepted with other substrates simply by keeping the reaction mixture obtained by addition of dimethyldichlorosilane to the $(Me_3Si)_2CBrLi$ solution at —120° C for 5 min and then adding the substrate. When trimethyltin chloride was added, $(Me_3Si)_2C(SnMe_3)(SiMe_2Cl)$ was obtained in 50% yield. In another experiment, the addition of bromine to the $(Me_3Si)_2CBrLi/Me_2SiCl_2$ reaction mixture gave $(Me_3Si)_2CBrSiMe_2Cl$ in 68% yield. The availability of this compound allowed us to test

SCHEME 2 (R = Me_3Si)



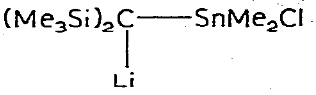
if the lithium reagent XIII could, in fact, be an intermediate in the formation of III in the absence of dimethyldichlorosilane. In a separate experiment, this compound was treated with one molar equivalent of t-butyllithium at −95°C. Disilacyclobutane III was formed in 14% yield. It would seem then that route B in Scheme 2 does not contribute importantly, if at all, to the formation of III.

In reactions of $(Me_3Si)_2CBrLi$ with dimethyldibromogermane and with dimethyltin dichloride it is very likely that similar intermediates are involved, i.e., XV and XVI. The isolation in low yield of $(Me_2Si)_2C(GeMe_2Br)_2$ and $(Me_3Si)_2C(SnMe_2Cl)_2$, respectively, in these experiments gives indirect indication of this. However, the trapping experiments which were successful in providing more direct evidence for the intermediacy of XIII failed in the case of the $(Me_3Si)_2CBrLi/Me_2SnCl_2$ reaction. Only the distannacyclobutane was isolated in an attempted interception experiment with trimethyltin chloride. An attempt to divert the assumed $(Me_3Si)_2CLiSnMe_2Cl$ intermediate in a reaction in which an excess of dimethyltin dichloride was used was only partially successful. The expected $(Me_3Si)_2C(SnMe_2Cl)_2$ was obtained, but only in 6% yield. Dimethyltin dichloride is not very soluble at these low temperatures and this may be the cause of the low yields in the reactions in which it was used.



$(Me_3Si)_2\underset{\substack{|\\ Li}}{C}{-}GeMe_2Br$

(XV)



$(Me_3Si)_2\underset{\substack{|\\ Li}}{C}{-}SnMe_2Cl$

(XVI)

This new route to highly substituted 1,3-dimetallacyclobutanes no doubt is capable of further extension, and we are investigating such possibilities.

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. The standard apparatus used consists of a three-necked, round-bottom flask of appropriate size equipped with a mechanical stirring assembly, a pressure-equalizing addition funnel and a Claisen adapter. The addition funnel is topped with a nitrogen inlet tube and the Claisen adapter is fitted with a septum cap and a low temperature thermometer.

Melting points were determined with a Mel-temp apparatus in capillary tubes which were sealed 0.75 in. or less above the sample and are uncorrected. This was necessary since most of the compounds prepared in this study, although they were high melting, were quite volatile and tended to sublime when heated in open melting point capillaries. Infrared spectra were recorded using a Perkin—Elmer Model 457A grating spectrometer. Proton NMR spectra were recorded on a Varian Associates T60 spectrometer. Mass spectra were obtained with an Hitachi—Perkin—Elmer RMU6 mass spectrometer at an ionizing potential of 70 eV.

Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl and stored under nitrogen. Dimethyl ether was passed through a drying tower containing P_2O_5 and Linde 4a molecular sieves and condensed directly into the reaction vessel.

Preparation of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane

Into the standard apparatus (1 liter flask) cooled to −115° C was condensed

500 ml of liquid dimethyl ether. Subsequently there were added simultaneously a solution of 45.41 g (0.143 mol) of bis(trimethylsilyl)dibromomethane [7] in 100 ml of dry THF from the addition funnel and 0.157 mol of n-butyllithium in 75 ml of hexane (Alfa/Ventron) by syringe. An addition time of 30 min was required so that the temperature did not rise above —115° C. The resulting dark orange homogeneous solution was stirred for 10 min at that temperature and then 10.7 ml (89.5 mmol) of dimethyldichlorosilane (Union Carbide Corp.) in 50 ml of THF was added during 15 min. A color change to pea green was noted. The mixture was stirred at —115° C for 90 min and then was allowed to warm slowly to room temperature. On warming, the color changed to light yellow and finally a colorless solution resulted. The mixture was hydrolyzed with 200 ml of distilled water. The organic layer was dried over anhydrous $MgSO_4$ and solvents were removed at reduced pressure, leaving a white solid and a yellow oil. The solid was filtered and recrystallized from pentane at —79° C to give 11.09 g (36% yield, based on $(Me_3Si)_2CBr_2$) of the title compound, m.p. (sealed capillary) 208—210° C. (Found: C, 49.96; H, 11.13; mol. wt. (vapor pressure osmometry (VPO) in chloroform), 427. $C_{18}H_{48}Si_6$ calcd.: C, 49.92; H, 11.17%; mol.wt., 433.1.) Its infrared spectrum (KBr disc) showed the following bands: 3003(sh), 2975m, 2945s, 2900m, 1398m, 1259vs, 884(sh), 843vs(br), 731w, 708w, 674s and 639w, cm^{-1}. The NMR spectrum ($CCl_4/CHCl_3$) showed singlets at δ 0.54 (12H, $SiMe_2$) and 0.27 ppm (36H, $SiMe_3$). The principal fragments observed in the mass spectrum were (m/e^+ (rel. intensity)): 432 (18, M^+), 216 (100, $1/2M^+$), 75 (77, $C_3H_{11}Si^+$) and 73 (70, Me_3Si^+).

Examination of the yellow oil from which the white solid was filtered by GLC (F & M 700, 6 ft UCW-98, 210° C) indicated the presence of $(Me_3Si)_2CHBr$ (11% yield, n_D^{25} 1.4657 (lit. [7] n_D^{25} 1.4659), and NMR [7]), $(Me_3Si)_2CBr_2$ (30%) and four other products in quantities too small for adequate characterization.

In another experiment carried out in similar fashion, $(Me_3Si)_2CBrLi$ was prepared by simultaneous addition of 40.73 g (0.128 mol) of bis(trimethylsilyl)dibromomethane in 100 ml of THF and 0.140 mol of n-butyllithium in hexane (64 ml) to 500 ml of dimethyl ether at —120° C. To the resulting solution was added 17 ml (0.134 mol) of dimethyldichlorosilane in 50 ml of THF. The color changed from orange to yellow when the chlorosilane was added, and the mixture became colorless while the temperature was allowed to increase slowly to 25° C. The reaction mixture was trap-to-trap distilled (70° C/0.1 mmHg) into a receiver cooled with liquid nitrogen. The solid residue was extracted with 300 ml of pentane and the extracts were evaporated to leave a colorless solid which was identified (IR, NMR, m.p.) as the 1,3-disilacyclobutane III (8.34 g, 30% yield).

The distillate from the trap-to-trap distillation was fractionally distilled. Two fractions were collected: (a) 35—70° C at 760 mmHg, and (b) 55—70° C at 0.1 mmHg. A solid residue was obtained. Examination of the volatiles showed the presence of $(Me_3Si)_2CHBr$ and $(Me_3Si)_2CBr_2$. Examination of the solid by thin layer chromatography (TLC) (silica, with hexane eluent) showed two compounds to be present. Column chromatography (silicic acid, hexane eluent) yielded a first fraction which was a mixture (by NMR) of the 1,3-disilacyclobutane III and another compound. A second fraction contained the pure compound $(Me_3Si)_2C(SiMe_2Cl)_2$ (3.23 g, 7.3% yield), a white solid which did not melt even when heated rapidly to 360° C. (Found: C, 38.12; H, 8.80; Cl, 20.42. $C_{11}H_{30}Cl_2Si_4$ calcd.: C, 38.23; H, 8.75; Cl, 20.52%.) NMR ($CCl_4/CHCl_3$): δ 0.79 (s, 12H, $SiClMe_2$) and 0.46 ppm (s, 18H, $SiMe_3$). IR (KBr disc): 2980(sh), 2960vs, 2900s, 2307w, 1925w, 1725m, 1403s, 1364w, 1293(sh), 1259vs, 1251vs, 1085w, 935(sh), 843vs(br), 760m, 725m, 705s, 672vs, 650s, 626w, 615w, 460vs and 309m, cm^{-1}.

A better yield of this product was obtained by carrying out the $(Me_3Si)_2CBrLi/Me_2SiCl_2$ reaction in a different manner. A solution of $(Me_3Si)_2CBrLi$ was prepared by simultaneous addition of 25.4 g (80 mmol) of $(Me_3Si)_2CBr_2$ in 50 ml of THF and 82 mmol of n-BuLi in hexane (34 ml) to 250 ml of dimethyl ether at —115° C in the standard reaction flask. The reagent solution was stirred at this temperature for 1 h while a second reaction flask was set up. The latter was charged with 0.242 mol of dimethyldichlorosilane in 500 ml of THF and then cooled to —105° C. The $(Me_3Si)_2CBrLi$ solution was transferred to the Me_2SiCl_2 via cannula and the resulting mixture was stirred at —105° C for 90 min before it was allowed to warm to room temperature. Trap-to-trap distillation of volatiles was followed by pentane extraction of the distillation residue. The extracts were evaporated to leave a white solid which was recrystallized from pentane to give in two crops 8.918 g of $(Me_3Si)_2C(SiMe_2Cl)_2$ (31% yield), which was identified by comparison of its IR and NMR spectra with those of the material from the previous experiment.

Preparation of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-digermacyclobutane

To a one-liter standard low temperature apparatus containing 500 ml of dimethyl ether at —115° C were added simultaneously solutions of 51.0 g (0.160 mol) of $(Me_3Si)_2CBr_2$ in 150 ml of THF and 0.167 mol of n-butyllithium in 75 ml of hexane during the course of 30 min. The resulting orange solution was stirred at —115° C for 15 min and then 22.0 g (83.8 mmol) of dimethyldibromogermane in 50 ml of THF was added during 10 min. The orange color darkened initially and then lightened to a bright yellow. The mixture was stirred at —110° C for 1 h and then allowed to warm slowly to room temperature, during which time the color faded to give finally a colorless solution. The reaction mixture was trap-to-trap distilled (70° C/0.01 mmHg) and the residue was extracted with 300 ml of pentane. The extracts were evaporated at reduced pressure to leave a solid and a small amount of an oil. Examination of the filtered solid by TLC (silica, hexane eluent) showed the presence of two compounds. These were separated by column chromatography (silicic acid, hexane eluent). First to be eluted with hexane (7.20 g, 13.8 mmol, 17% yield) was a colorless solid, the title compound, m.p. 225—226° C. (Found: C, 41.49; H, 9.26; mol. wt. (VPO in $CHCl_3$), 503. $C_{18}H_{48}Ge_2Si_4$ calcd.: C, 41.41; H, 9.27%; mol.wt., 522.) Its infrared spectrum (KBr disc) showed the following bands: 3024(sh), 3000(sh), 2972vs, 2946vs, 2901vs, 2806(sh), 1917w, 1798w, 1403s, 1255vs, 1249vs, 816vs(br), 718m, 671m, 604m, and 581m, cm^{-1}. The NMR spectrum ($CCl_4/CHCl_3$) showed singlets at δ 0.66 (12H, $GeMe_2$) and 0.19 ppm (36H, $SiMe_3$). The principal fragments observed in the mass spectrum were (*m/e* (rel. intensity)): 524 (8, M^+), 262 (68, $1/2M^+$), 247 (21, $[1/2M - 15]^+$) and 73 (100, Me_3Si^+).

A second, yellow band was eluted with acetone. The eluate was treated with decolorizing charcoal, filtered and evaporated at reduced pressure to give 3.69 g (4.4%) of colorless solid which did not melt even when heated rapidly to 360° C. (Found: C, 25.82; H, 5.95; Br, 29.73. $C_{11}H_{30}Br_2Ge_2Si_2$ calcd.: C, 25.24; H, 5.78; Br, 30.53%.) NMR ($CCl_4/CHCl_3$): δ 1.19 (s, 12H, $GeMe_2$) and 0.42 ppm (s, 18H, $SiMe_3$).

Preparation of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane

Dimethyl ether (450 ml) was condensed into a one-liter standard low temperature apparatus at −120° C and subsequently there were added simultaneously 50.9 g (0.160 mol) of bis(trimethylsilyl)dibromomethane in 100 ml of THF and 165 mmol of n-butyllithium in 75 ml of hexane. The resulting orange solution was stirred at −115° C for 10 min and then a solution of 18.1 g (82.5 mmol) of dimethyltin dichloride (Cincinnati Milacron) in 150 ml of THF was added during the course of 40 min, causing a color change from orange to yellow. The reaction mixture was stirred at −110° C for 90 min and then was allowed to warm slowly to room temperature; a colorless solution resulted. Trap-to-trap distillation (25° C/0.1 mmHg) to remove volatiles was followed by extraction of the oily residue with 600 ml of pentane. The extracts were evaporated at reduced pressure to leave a white solid and a light yellow oil. The solid was filtered and recrystallized from pentane at −20°C to give 9.794 g (16 mmol, 20% yield) of the title compound, m.p. 248—250° C. (Found: C, 35.26; H, 7.88; mol. wt. (VPO in $CHCl_3$), 636. $C_{18}H_{48}Sn_2Si_4$ calcd.: C, 35.19; H, 7.87%; mol. wt., 614.) The IR spectrum (KBr disc) showed bands at 2996(sh), 2973s, 2946s, 2904s, 1426(sh), 1400m(br), 1391w, 1263s, 1252s, 1248(sh), 841vs(br), 782s, 752m, 706m, 676(sh), 671s, 622w, 555s, 515m, 509m, cm^{-1}. The proton NMR spectrum ($CCl_4/CHCl_3$) showed singlets at δ 0.57 (12H, $J(^{119}Sn—^1H)$ 48 Hz, Me_2Sn) and 0.18 ppm (36H, $SiMe_3$). The principal fragments observed in the mass spectrum were (*m/e* (rel. intensity)) 597 (4, $[M-15]^+$), 539 (1), 451 (1), 306 (15, $1/2M^+$), 193 (8), 191 (5), 149 (12), 129 (13), 86 (100), 84 (>100, off scale) and 73 (46, Me_3Si^+).

The trap-to-trap distillate was distilled at atmospheric pressure to remove solvents. The residue was combined with the oily filtrate obtained from the pentane extracts and placed in the freezer at −20° C for 72 h. At the end of this time, a solid had formed (solid A), which was filtered. The filtrate was vacuum distilled (60—110° C at 0.9 mmHg) and the distillate was examined by GLC (F & M 700, 6 ft UCW-98, 170° C). The following compounds were present: $(Me_3Si)_2CHBr$ (15%), $(Me_3Si)_2CBr_2$ (15%) and $(Me_3Si)_2CBrC_4H_9$-n [7] (30%). The distillation residue solidified on cooling. TLC (silica, hexane eluent) showed this residue and solid A to be mixtures of two compounds. These were separated by column chromatography (silicic acid, elution with hexane and 70 : 30 hexane/dichloromethane). Both of the white solids obtained were recrystallized from pentane at −20° C. The first of these appeared to be $[(Me_3Si)_2CBr]_2SnMe_2$, which decomposed without melting at 330—345° C. (Found: C, 31.24; H, 7.04. $C_{16}H_{42}Br_2Si_4Sn$ calcd.: C, 30.73; H, 6.77%.) NMR (in $CDCl_3/CH_2Cl_2$): two singlets at δ 0.87 (6H, $J(^{119}Sn—^1H)$ 53 Hz and $J(^{117}Sn—^1H)$ 50 Hz) and 0.29 ppm (36H). The yield of this solid was 1.12 g (2.2%). The other solid, obtained in a yield of 0.953 g, appeared to be impure $(Me_3Si)_2C(SnMe_2Cl)_2$ on the basis of its NMR spectrum (in $CDCl_3/CH_2Cl_2$): 0.87 (s, 12H, $J(^{119}Sn-^1H)$ 57 Hz and $J(^{117}Sn-^1H)$ 54 Hz) and 0.32 ppm (s, 18H). (A pure sample of this compound was isolated in a later experiment; see below.) It was possible that the impure state of this product was due to partial exchange of Br for Cl on tin during the course of the reaction. In order to avoid such exchange, the reaction was repeated with dimethyltin dibromide.

Bis(trimethylsilyl)bromomethyllithium was prepared as described above from 100 mmol of bis(trimethylsilyl)dibromomethane and 104 mmol of n-butyllithium. The bright orange-yellow solution was stirred for 1 h at —115° C and then 15.50 g (50.2 mmol) of dimethyltin dibromide in 50 ml of THF was added. The reaction mixture was stirred under nitrogen for 1 h at —115° C to —100° C. During this time the color changed first to bright yellow and then faded slowly. The mixture was allowed to warm to room temperature and then was trap-to-trap distilled (25—150° C at 0.01 mmHg). The solid residue was extracted with 500 ml of pentane. Filtration was followed by concentration of the filtrate to about 5 ml. The residue was cooled to —20° C for several hours and filtered to remove 7.01 g of colorless crystals (22%) of the 1,3-distannacyclobutane VII. No minor byproducts of the expected type, $[(Me_3Si)_2CBr]_2SnMe_2$ and $(Me_3Si)_2C(SnMe_2Br)_2$, could be isolated.

In another reaction carried out in the standard manner using the lithium reagent prepared from 177 mmol of $(Me_3Si)_2CBr_2$ and 183 mmol of n-butyllithium, a smaller relative amount of dimethyltin dichloride, 60 mmol, was used. 1,3-Distannacyclobutane VII was obtained in 19% yield. The volatile products were $(Me_3Si)_2CHBr$ (13%) and $(Me_3Si)_2C(Br)(n\text{-}C_4H_9)$ (48%).

Reaction of bis(trimethylsilyl)bromomethyllithium with an excess of dimethyltin dichloride

The lithium reagent was prepared as usual from 14.53 g (45.7 mmol) of bis(trimethylsilyl)dibromomethane and 53 mmol of n-butyllithium at —120° C. The resulting bright orange-yellow solution was stirred at this temperature for 15 min. During this time a second apparatus (one-liter flask) equipped similarly to the first was set up and charged with 16.655 g (75.8 mmol) of dimethyltin dichloride, 150 ml of THF and 400 ml of dimethyl ether. This mixture was cooled to —135° C and the $(Me_3Si)_2CBrLi$ solution was added as rapidly as possible by means of a connecting cannula. The color of the lithium reagent was discharged within 1 min. After the mixture had been stirred for 1 h at —135° C to —110° C, the mixture was allowed to warm to room temperature. It then was concentrated to about 300 ml by rotary evaporation and the liquid remaining was trap-to-trap distilled. Strong heating was required to periodically remove plugs of the volatile Me_2SnCl_2 in the distillation apparatus. The residue was extracted with 200 ml of pentane. The extracts were concentrated to 5 ml at reduced pressure to leave a colorless solid in a colorless oil. This material, dissolved in a minimum of hexane was chromatographed on a 4.5 cm × 11 cm silicic acid column. Elution with hexane gave an oil which was combined with the trap-to-trap distillate. Further elution with 70 : 30 hexane/dichloromethane resulted in isolation of 2.135 g of colorless solid. The latter was recrystallized from pentane to give 1.4415 g (6%) of $(Me_3Si)_2C(SnMe_2Cl)_2$, m.p. 303.5—305° C (sealed capillary), with an NMR spectrum identical to that of the crude product isolated in the experiment above: singlets at 0.87 (12H, $J(^{119}Sn—^1H)$ 57 Hz and $J(^{117}Sn—^1H)$ 54 Hz) and 0.32 ppm (18H). (Found: C, 25.17; H, 5.68; Cl, 13.42. $C_{11}H_{30}Cl_2Si_2Sn_2$ calcd.: C, 25.08; H, 5.74; Cl, 13.46%.)

The combined volatiles were concentrated and examined by GLC. Only two compounds were present in high yield: $(Me_3Si)_2CHBr$ (36%) and $(Me_3Si)_2CBr_2$ (55%).

Brominolysis of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane

(a) In carbon tetrachloride. A 100 ml three-necked flask equipped with a nitrogen inlet tube, a magnetic stirring assembly and a 60 ml pressure-equalizing addition funnel was flame-dried under nitrogen and then charged with a solution of 1.976 g (3.22 mmol) of distannacyclobutane VII in 40 ml of carbon tetrachloride. A solution of 0.6 g (3.75 mmol) of bromine in 15 ml of carbon tetrachloride was added dropwise from the addition funnel at room temperature. All but the last drop was completely decolorized within this time. Addition of a few drops of pentane served to destroy the unconverted bromine. The reaction mixture was evaporated at reduced pressure, leaving 2.509 g of crude solid. This product was identified (NMR) as $BrSnMe_2C(SiMe_3)_2SnMe_2C(SiMe_3)_2Br$ contaminated with a very small amount of starting material. Recrystallization from pentane gave 2.299 g (92%) of pure material, m.p. (sealed capillary) 149.5—151°C. (Found: C, 28.08; H, 6.27; Br, 20.19. $C_{18}H_{48}Br_2Si_4Sn_2$ calcd.: C, 27.93; H, 6.25; Br, 20.64%.) NMR (CCl_4/CH_2Cl_2): δ 1.01 (s, 6H, Me_2SnBr), 0.63 (s, 6H, $SnMe_2$), 0.41 (s, 18H, $CBrSiMe_3$) and 0.03 ppm (s, 18H, $SiMe_3$).

(b) In methanol. The apparatus described in *a* above was connected to a liquid nitrogen trap and charged with 1.195 g (1.95 mmol) of the distannacyclobutane in 50 ml of anhydrous methanol. A solution of 0.70 g (4.37 mmol) of bromine in 20 ml of methanol was prepared in the addition funnel. The suspension of the tin compound was stirred and cooled to 0°C and then 2 ml of the bromine solution was added. The bromine color was not discharged after 30 min and therefore the mixture was warmed to room temperature. Subsequently the mixture was heated to 55°C for 15 h. Most of the bromine was consumed during this time and so the remainder of the bromine solution was added slowly in 2 ml portions to the heated reaction mixture over a 24 h period. The reaction mixture then was trap-to-trap distilled (25°C at 0.1 mmHg) into a trap cooled to —196°C. The residue was Soxhlet extracted into 100 ml of chloroform. Concentration of the extract produced, in three crops, 1.084 g (82%) of colorless, prismatic crystals, m.p. 245—250°C, identified as 1-bromo-1,3,3-trimethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane. (Found: C, 30.33; H, 6.66; Br, 11.41; mol.wt. (VPO in $CHCl_3$), 734. $C_{17}H_{45}BrSi_4Sn_2$calcd.: C, 30.06; H, 6.68; Br, 11.77%; mol.wt., 679.) NMR (in $CDCl_3$): δ 1.19 (s, 3H, MeBrSn), 0.71 (s, 3H, Me_2Sn), 0.62 (s, 3H, Me_2Sn), 0.29 (s, 18H, Me_3Si) and 0.23 ppm (s, 18H, Me_3Si).

Reaction of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane with methyllithium

(a) 1 : 1 Stoichiometry. A 100 ml three-necked round-bottom flask equipped with a thermometer, a nitrogen inlet tube, a septum stopper and a magnetic stir-

ring assembly was flame-dried under nitrogen and charged with 1.244 g (2.03 mmol) of the title tin compound and 40 ml of dry THF. A solution of 2.24 mmol of methyllithium (Alfa/Ventron) in 1.4 ml of diethyl ether was added slowly by syringe during 30 sec with vigorous stirring. A slightly exothermic reaction gave a yellow solution. This solution was stirred for 15 min and then 10 ml of saturated aqueous ammonium chloride solution was added, followed by 10 ml of distilled water. The orgainc layer was dried (Na_2SO_4) and then concentrated to 20 ml. Vacuum distillation gave a single fraction, b.p. 52—55° C/0.4 mmHg, n_D^{25} 1.4881, of a compound identified as bis(trimethylsilyl)(trimethylstannyl)methane. (Found: C, 36.92; H, 8.70. $C_{10}H_{28}Si_2Sn$ calcd.: C, 37.16; H, 8.73%.) The yield was 0.268 g (20.4%). NMR (in $CCl_4/CHCl_3$): δ 0.18 (s, 9H, $J(^{119}Sn—^1H)$ 52.5 Hz and $J(^{117}Sn—^1H)$ 49.5 Hz), 0.09 (s, 18H) and —0.69 ppm (s, 1H), in agreement with the formula $(Me_3Si)_2(Me_3Sn)CH$. Mass spectrum (*m/e* (rel. intensity): 307 (50), $[M-15]^+$, 191 (3), 165 (9), 129 (100) and 73 (38).

The residue from the distillation was a waxy solid which was purified by sublimation at 115° C/0.01 mmHg. This compound softened at 158—160° C and melted at 165—166° C. It was obtained in a yield of 0.343 g (37.3%). (Found: C, 36.68; H, 8.31. $C_{19}H_{52}Si_4Sn_2$ calcd.: C, 36.20; H, 8.32%.) NMR (in $CCl_4/CHCl_3$): singlets at δ 0.41 (6H, $J(^{119}Sn—^1H)$ 47.3 Hz and $J(^{117}Sn—^1H)$ 45.5 Hz), 0.30 (9H, $J(^{119}Sn—^1H)$ 50.0 Hz and $J(^{117}Sn—^1H)$ 47.5 Hz), 0.23 (18H), 0.18 (18H) and —0.15 ppm (1H); this in agreement with the structure $Me_3SnC(SiMe_3)_2SnMe_2C(SiMe_3)_2H$.

(b) 1 : 2 Stoichiometry. Using the procedure described above, 1.5684 g (2.56 mmol) of the distannacyclobutane was treated with 5.3 mmol of methyllithium in diethyl ether. The yellow reaction mixture was heated at reflux for 2 h and subsequently was hydrolyzed as described above. Vacuum distillation of the organic layer gave 1.2118 g (73.5%) of $(Me_3Si)_2(Me_3Sn)CH$, b.p. 48°C/0.4 mmHg.

Other reactions of bis(trimethylsilyl)trimethylstannylmethyllithium

(a) With trimethyltin chloride. The lithium reagent was prepared as described above by reaction of 2.0071 g (3.27 mmol) of the distannacyclobutane in 50 ml of THF with 6.74 mmol of methyllithium in 3.6 ml of pentane. The yellow solution of the reagent was treated with 1.5 g (7.5 mmol) of trimethyltin chloride (M & T Chemicals, Inc.). The reaction mixture was heated at reflux for a few hours and then was washed with aqueous-methanolic potassium fluoride solution to remove unconverted trimethyltin chloride. Removal of the solvent from the dried organic layer left a solid which was purified by sublimation at 110°C/0.05 mmHg to give 2.3824 g (75%) of $(Me_3Si)_2C(SnMe_3)_2$, which did not melt up to 360° C in a sealed capillary. (Found: C, 32.49; H, 7.46. $C_{13}H_{36}Si_2Sn_2$ calcd.: C, 32.13; H, 7.47%.) NMR (in CCl_4/CH_2Cl_2): δ 0.23 (s, 18H, $J(^{119}Sn—^1H)$ 50.5 Hz and $J(^{117}Sn—^1H)$ 47.5 Hz) and 0.17 (s, 18H).

(b) With trimethylchlorosilane. The lithium reagent was prepared from 2.066 g (3.37 mmol) of the distannacyclobutane in 50 ml of THF and 6.9 mmol of methyllithium and subsequently was treated with 10 mmol of trimethylchlorosilane in 5 ml of THF. The reaction mixture was heated at reflux for a few hours and then was hydrolyzed with saturated NH_4Cl solution. The organic layer was evaporated at reduced pressure to leave a crude solid which was sublimed at 120° C/0.04 mmHg to give 2.2864 g (86%) of $(Me_3Si)_3CSnMe_3$, a white solid

which, when freshly sublimed, did not melt up to 360° C when heated in a sealed capillary. Samples which had not been freshly sublimed tended to melt with partial decomposition at 354—360° C when heated in a sealed capillary. (Found: C, 39.55; H, 8.98. $C_{13}H_{36}Si_3Sn$ calcd.: C, 39.49; H, 9.18%.) NMR (CCl_4/CH_2Cl_2): δ 0.26 (s, 9H, $J(^{119}Sn—^1H)$ 50.5 Hz and $J(^{117}Sn—^1H)$ 47.7 Hz) and 0.21 ppm (s, 27H). This compound was prepared by Cook et al. [18] by reaction of $(Me_3Si)_3CLi$ with trimethyltin chloride; m.p. (sealed capillary) 354—356°C (dec.).

Reactions of $(Me_3Si)_2C(Li)SiMe_2Cl$

(a) With trimethyltin chloride. Bis(trimethylsilyl)bromomethyllithium was prepared as before by simultaneous addition of 25.44 g (80.0 mmol) of bis(trimethylsilyl)dibromomethane in 70 ml of THF and 82 mmol of n-butyllithium in hexane (41 ml) to 200 ml of dimethyl ether at —120° C. The resulting orange solution was stirred at this temperature for 5 min and then 42 mmol of dimethyldichlorosilane in 15 ml of THF was added. The reaction mixture turned green. It was stirred at —120° C for 5 min and then a solution of 9.54 g (47.8 mmol) of trimethyltin chloride in 80 ml of THF was added. The color of the reaction mixture quickly changed to pale yellow; slight warming to —95° C discharged the color completely. The mixture was stirred at —105° C for 1.5 h. Subsequently, it was allowed to warm to room temperature and was trap-to-trap distilled to remove volatiles. The residue was extracted with 350 ml of pentane. Evaporation of the extracts left a white solid which was recrystallized from pentane to give 8.781 g (50.3%) of $(Me_3Si)_2C(SnMe_3)(SiMe_2Cl)$, m.p. 364—366° C (sealed capillary). (Found: C, 34.59; H, 7.87; Cl, 8.89. $C_{12}H_{33}ClSi_3Sn$ calcd.: C, 34.66; H, 8.00; Cl, 8.53%.) NMR (in CCl_4/CH_2Cl_2): singlets at δ 0.58 (6H, $SiMe_2Cl$), 0.34 (9H, $J(^{119}Sn—^1H)$ 52.0 Hz and $J(^{117}Sn—^1H)$ 49.0 Hz), $SnMe_3$) and 0.26 ppm (18H, $SiMe_3$).

The trap-to-trap distillate was concentrated at reduced pressure and examined by GLC (6 ft UC-W98 silicone column at 150° C and 4 ft UC-W98 column at 90—180°C). The following were found to be present: $n\text{-}C_4H_9SnMe_3$ (35%), $(Me_3Si)_2CHBr$ (8.6%), $(Me_3Si)_2CBrCl$ (7.2%) and $(Me_3Si)_2CBr_2$ (34%).

(b) With bromine. The lithium reagent was prepared as in (a) by simultaneous addition of 23.0 g (75 mmol) of $(Me_3Si)_2CBr_2$ in 70 ml of THF and 80 mmol of n-butyllithium to 250 ml of dimethyl ether at —120° C. After 15 min, this mixture was treated with 37.5 mmol of dimethyldichlorosilane in 10 ml of THF. The resulting solution was stirred at —115° C for 15 min and then 6.4 g (40 mmol) of bromine in 10 ml of benzene was added slowly. The color of the reaction mixture was discharged within 1 min. The reaction mixture was allowed to warm to room temperature and then was trap-to-trap distilled. The residue was extracted with 300 ml of pentane. The extracts were evaporated to leave an oily solid. The latter was combined with the trap-to-trap distillate and the resulting solution was concentrated to about 50 ml at reduced pressure. Analysis of the concentrate by GLC (6 ft UC-W98 at 180° C) showed the presence of the following: $(Me_3Si)_2CHBr$ (6%), $(Me_3Si)_2CBr_2$ (74%) and the desired product, $(Me_3Si)_2(Me_2ClSi)CBr$ (68%). A sample of the latter was isolated for characterization by GLC; it is a solid which softens at 195—197° C and melts at 199—200° C. (Found: C, 32.94; H, 7.31; Br, 23.54; Cl, 10.44. $C_9H_{14}BrClSi_3$ calcd.: C,

32.57; H, 7.29; Br, 24.08; Cl, 10.68%.) NMR (in $CCl_4/CHCl_3$): singlets at δ 0.64 (6H) and 0.32 ppm (18H).

Isolation of $(Me_3Si)_2(Me_2ClSi)CBr$ from the reaction mixture in quantity proved to be a very difficult process. Samples for analysis and spectroscopic measurements could be collected by GLC, but strong heating of the collection capillary was necessary to keep the compound liquefied. Distillation was ruled out since the product and its major impurity, $(Me_3Si)_2CBr_2$, m.p. 68—70°C, are solids. Separation by elution chromatography was not feasible; the R_f values (TLC) of $(Me_3Si)_2(Me_2ClSi)CBr$ and $(Me_3Si)_2CBr_2$ are nearly identical. Sublimation was found to be applicable to the partial purification of the product. Repeated removal of $(Me_3Si)_2CBr_2$ from the cold-finger allowed the percentage of the product in the sublimate to be increased slowly. Sublimation at 30°C/0.01 mmHg finally resulted in the isolation of a waxy solid shown to contain $(Me_3Si)_2(Me_2ClSi)CBr$ and $(Me_3Si)_2CBr$ in 2.25 : 1 ratio (by NMR). This material was used in the experiment described below.

Reaction of bis(trimethylsilyl)(dimethylchlorosilyl)bromomethane with t-butyllithium

A 500-ml standard low temperature apparatus was charged with 9.741 g of a 2.25 : 1 mixture of the title silane and bis(trimethylsilyl)dibromomethane (see experiment above). This is equivalent to 20.6 mmol of $(Me_3Si)_2(Me_2ClSi)CBr$ and 9.15 mmol of $(Me_3Si)_2CBr_2$. THF (200 ml) was added and the solution was cooled to —90°C. t-Butyllithium (30.8 mmol in 2.5 ml of pentane) then was added. The yellow solution was cooled to —98°C and stirred for 15 min before being allowed to warm slowly to room temperature. The reaction mixture was hydrolyzed with 100 ml of water. The organic layer was dried and concentrated at reduced pressure to approximately 6 ml. The colorless solid which separated (1.0689 g, 12%) was identified spectroscopically as the 1,3-disilacyclobutane III. Further concentration of the filtrate and prolonged standing caused crystallization of another 0.2174 g of this product; total yield 14.4%. A small portion which had been recrystallized from toluene had a m.p. 213.5—215.5°C (sealed capillary).

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