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# Silaethylene Intermediates from α-Lithiosilanes. 2. Reactions with Chlorosilanes and 1,3-Butadiene

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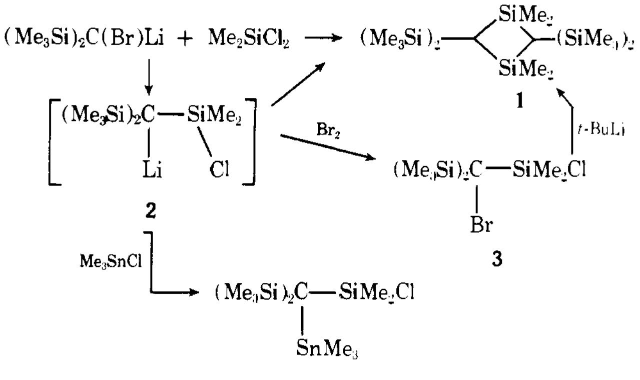
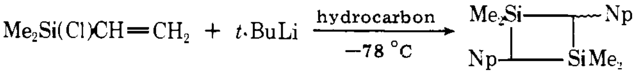
**Abstract:** Evidence is presented which indicates that silaethylene intermediates can be produced by the elimination of lithium chloride from α-lithiochlorosilanes under appropriate experimental conditions. The reaction of *tert*-butyllithium with vinyldimethylchlorosilane at low temperatures in hydrocarbon solvents gives high yields of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutanes. Trapping and competition experiments with various chlorosilanes indicate that coupling reactions of the initially produced α-lithiochlorosilane, **5**, are slower than the reactions leading to the 1,3-disilacyclobutanes. When the reaction is carried out in the presence of 1,3-butadiene apparent [2 + 2] and [2 + 4] cycloadducts are produced by the reaction of the silaethylene intermediate with butadiene. Among them is 1,1-dimethyl-2-neopentyl-3-vinylsilacyclobutane, a compound which cannot be formed by the addition of **5** to butadiene followed by ring closure.

In 1974 Seyferth and Lefferts reported that the reaction of bis(trimethylsilyl)bromomethyllithium with dimethylchlorosilane at low temperature in ether solvents gave moderate yields of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**1**).[1] Subsequently, they demonstrated that an α-lithiochlorosilane, **2**, could be the precursor of **1** by



trapping experiments with trimethyltin chloride. When the reaction mixture was treated with bromine the α-bromo compound **3** was obtained. Furthermore, when **3** was treated with *tert*-butyllithium, a 17% yield of **1** was obtained, presumably by lithium-halogen exchange to re-form **2**.[2] While other workers have investigated the chemistry of α-lithiohalosilanes produced by metalation,[3] and have used such compounds as synthetic intermediates,[4] the observation of 1,3-disilacyclobutane products from these intermediates was not reported.

We recently discovered that the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in hydrocarbon solvents at low temperature gives high yields of the *cis*- and *trans*-1,3-disilacyclobutanes, **4**.[5] We suggested at that time that **4** arises from



**4**. Np = neopentyl

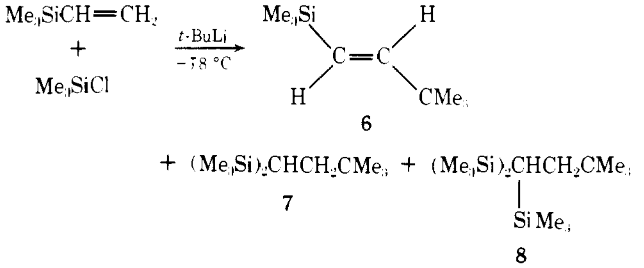
the dimerization of a silaethylene intermediate formed by the elimination of lithium chloride from an α-lithiochlorosilane precursor. We now wish to present further evidence that this is the case.

## Results and Discussion

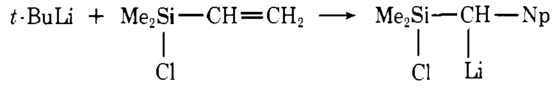
It seems reasonable that the first step in the reaction of vinyldimethylchlorosilane with *tert*-butyllithium leading to **4** is an addition reaction leading to the α-lithiochlorosilane, **5**. While such additions are known,[6] the only example of the addition of an organolithium reagent to a vinylsilane bearing substituents susceptible to nucleophilic displacement on silicon is contained in the original report of the reaction.[6a] In order to gain a better understanding of the relative rates of the coupling reaction of *tert*-butyllithium with chlorosilanes and the addition to vinylsilanes, competition experiments in which equimolar mixtures of vinyltrimethylsilane and trimethylchlorosilane were treated with 1 equiv of *tert*-butyllithium in hydrocarbon, ether, or tetrahydrofuran solvents were performed. In these experiments three products were isolated after hydrolytic workup: *trans*-1-trimethylsilyl-3,3-dimethylbutene (**6**); 1,1-bis(trimethylsilyl)-3,3-dimethylbutane (**7**); and 1,1,3-tris(trimethylsilyl)-5,5-dimethylhexane (**8**), all of which clearly arise from the initial addition of *tert*-butyllithium to the vinylsilane. In none of the experiments was any *tert*-butyltrimethylsilane, the anticipated product from an initial coupling reaction, observed. Table I gives the yields of the products in the three solvent systems studied.

**Table I.** Results of the Competition Experiments between Vinyltrichlorosilane and Trimethylchlorosilane for *tert*-Butyllithium

| Solvent | Yields of the products, % | | |
|---|---|---|---|
| | 6 | 7 | 8 |
| Hexane | 30 | 40 | 10 |
| Ether | 60 | 30 | 5 |
| Tetrahydrofuran | 0 | 76 | 0 |



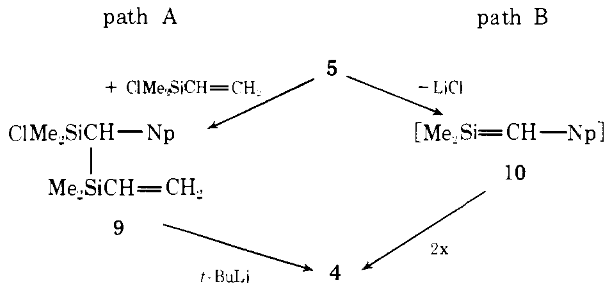
Product **6** evidently arises from loss of lithium hydride from the initial adduct to vinyltrimethylsilane. Cunico observed **7** as the major product when the *tert*-butyllithium adduct to vinyltrimethylsilane was derivatized with trimethylchlorosilane.[6c] The addition of the initial *tert*-butyllithium adduct to a second mole of vinyltrimethylsilane prior to coupling with trimethylchlorosilane gives rise to **8**. While the reasons for the variations in product distribution are not clear, the results indicate that, in hydrocarbon or ether solvents, elimination or addition reactions of the initial adduct compete with its derivatization by trimethylchlorosilane. In tetrahydrofuran the preferred reaction of the initial adduct is coupling with trimethylchlorosilane. The experiments do show that, in these three solvent systems, trimethylchlorosilane cannot compete with trimethylvinylsilane for *tert*-butyllithium. Inasmuch as chloro and alkoxy groups on silicon have been found to activate vinylsilanes toward addition of Grignard reagents,[7] one would anticipate that the addition of *tert*-butyllithium to vinyldimethylchlorosilane should be even more facile than the addition to vinyltrimethylsilane. All of these considerations not only confirm our suggestion that the first step in the reaction of *tert*-butyllithium with vinyldimethylchlorosilane is an addition to give the $\alpha$-lithiochlorosilane, **5**, but also suggest that the same reaction may occur in ether or tetrahydrofuran.



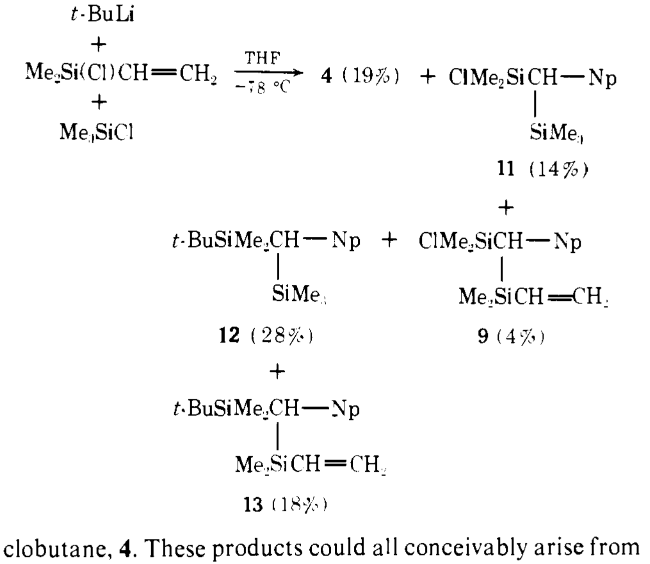
$$t\text{-BuLi} + \underset{\displaystyle \text{Cl}}{\text{Me}_2\text{Si}}\text{—CH=CH}_2 \longrightarrow \underset{\displaystyle \text{Cl}}{\text{Me}_2\text{Si}}\text{—}\underset{\displaystyle \text{Li}}{\text{CH}}\text{—Np}$$

**5**

**Trapping Experiments with Chlorosilanes.** Two possible routes can be suggested for the formation of the disilacyclobutane, **4**, from **5**. In path A, **5** couples with vinyldimethylchlorosilane to give 3,3,6,6-tetramethyl-4-(chlorodimethylsilyl)-3-silahept-1-ene (**9**), which could react with *tert*-butyllithium to give **4**. In path B, loss of lithium chloride from **5** gives rise to the silaethylene intermediate, **10**. Such intermediates are known to dimerize Path A requires that the coupling of vinyldimethylchlorosilane with **5** must compete favorably with other possible reactions of **5**, viz., addition or elimination reactions. To test this possibility the following competition experiments were performed. An equimolar mixture of vinyldimethylchlorosilane and trimethylchlorosilane in hexane was treated with 1 equiv of *tert*-butyllithium at −78 °C. The resulting mixture was warmed to room temperature. After workup only the disilacyclobutane, **4**, was obtained. No trace of 2,2,5,5-tetramethyl-3-(chlorodimethylsilyl)-2-silahexane (**11**), the anticipated coupling product of **5** with trimethylchlorosilane, could be detected. In another experiment, the solution resulting from the addition of 1 equiv of vinyldimethylchlorosilane to *tert*-butyllithium in hexane at −78 °C was warmed to −40 °C for 15 min. The solution was the bright yellow color which we believe to be associated with the $\alpha$-lithiosilane. No precipitation of lithium chloride, a process which always accompanies the formation of **4** in hydrocarbon solvents, had occurred. When the reaction mixture was cooled to −78 °C and excess trimethylchlorosilane in THF was added, the immediate formation of a white precipitate was observed probably resulting from the increased polarity of the reaction mixture when THF was added. Workup gave a 74% yield of **4** and no detectable **11** or other products arising from coupling with trimethylchlorosilane. These experiments indicate that, in hydrocarbon solvents, the coupling of the $\alpha$-lithiochlorosilane, **5**, with other chlorosilanes is slower than the reactions leading to the disilacyclobutane, and tend to mitigate against path A for disilacyclobutane production. They do not rule out the possibility that **5** could undergo self-condensation within an organolithium aggregate to form **4**, a process which might be promoted by THF.



Because the competition experiments between vinyltrimethylsilane and trimethylchlorosilane showed that we could trap $\alpha$-lithiosilanes in THF, the reaction of *tert*-butyllithium with vinyldimethylchlorosilane and trimethylchlorosilane was investigated using THF as the solvent. When the reagents were mixed at −78 °C a deep brownish yellow color developed which faded rapidly at −78 °C. Anhydrolytic workup gave four products, **9**, **11**, **12**, and **13**, in addition to the disilacyclobutane, **4**. These products could all conceivably arise from coupling of the $\alpha$-lithium compound, **5**, with the chlorosilanes available in the reaction mixture. Because we have shown that *tert*-butyllithium preferentially adds to vinylsilanes rather than coupling with chlorosilanes, compounds **12** and **13**, with *tert*-butyl substitution at silicon, must have been formed after the initial addition of *tert*-butyllithium to vinyldimethylchlorosilane. It could be that they are formed by addition of the alkyllithium reagent across the Si=C double bond in **10**, or that the silicon atom in the $\alpha$-lithiochlorosilane is activated toward nucleophilic substitution.[9] This point, and the solvent effects



on these reactions, are currently under investigation in our laboratories.

The isolation of **9** in the preceding experiment permitted the testing of its intermediacy in the formation of the 1,3-disilacyclobutanes, **4**. Indeed, when a hexane solution of **9** was treated with 1 equiv of *tert*-butyllithium, **9** was converted to **4** in 63% yield. However, it was noted that the lithium chloride precipitate formed more slowly than in the reactions with vinyldimethylchlorosilane. This observation prompted a competition experiment in which a mixture of **9**, contaminated with some **4** and **13**, and vinyldimethylchlorosilane was treated with *tert*-butyllithium. GLC analysis of the mixture using an internal standard before and after the reaction showed that only vinyldimethylchlorosilane was converted to **4**. The amounts of **9** and **13** present in the reaction mixture remained essentially unchanged. This experiment verifies our suggestion that *tert*-butyllithium should add to vinyldimethylchlorosilane faster than to a trialkylvinylsilane, e.g., **9**. It also demonstrated that **9** cannot be a precursor of **4** in the reaction of *tert*-butyllithium with vinyldimethylchlorosilane, in hydrocarbon solvents, because the overall rate of a series of reactions cannot exceed the rate of one of the steps.

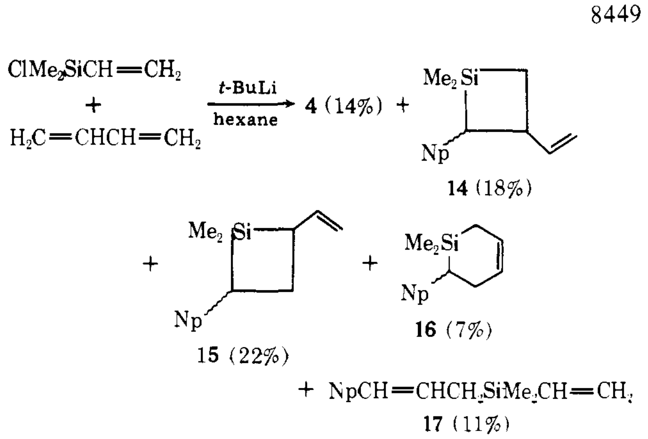
The above experiments rule out a sequential addition/coupling pathway in the formation of the disilacyclobutanes from vinyldimethylchlorosilane. The sluggishness of coupling reactions between organolithium reagents and chlorosilane has been observed by ourselves and others.[11] The preponderance of evidence points to path B, involving loss of lithium chloride from the α-lithiosilane, **5**, to give a silaethylene intermediate, **10**, which dimerizes to produce the 1,3-disilacyclobutanes. Further support for this conclusion has been obtained in the reactions of **10** with 1,3-butadiene.

**Reaction with 1,3-Butadiene.** It has been established that silaethylenes, generated by the thermolysis of silacyclobutanes, will give apparent [2 + 2] and [2 + 4] cycloaddition products with alkenes[12] and dienes.[13] In an attempt to utilize analogous traps in our system, the reaction of *tert*-butyllithium with vinyldimethylchlorosilane was carried out in the presence of vinyltrimethylsilane, styrene, and 1,3-butadiene.

In typical experiments 1 equiv of *tert*-butyllithium in *n*-pentane was added to an 0.1 M solution of vinyldimethylchlorosilane in dry hexane cooled to −78 °C which contained the trapping reagent. The resulting solutions were allowed to warm to room temperature and stirred overnight. After hydrolytic workup (water), the product mixtures were analyzed by gas chromatography. With a 3.5-fold molar excess of vinyltrimethylsilane, only **4** and polymeric material were obtained. The reaction in the presence of 1 equiv of styrene produced only a large amount of polymeric material.

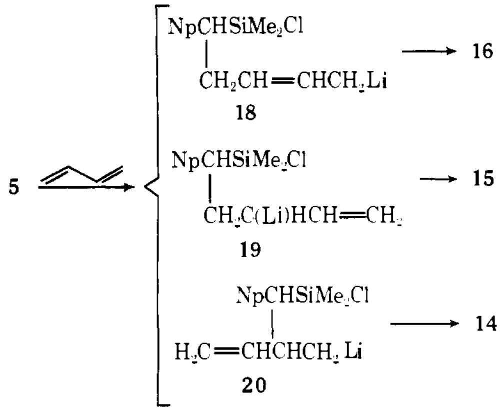
However, when an equimolar mixture of vinyldimethylchlorosilane was treated with 1 equiv of *tert*-butyllithium using 1,3-butadiene as the trap under the typical conditions, a mixture of five silicon-containing products, accounting for 72% of the original silane, was obtained. In addition to the 1,3-disilacyclobutane mixture, **4** (14% yield), 1,1-dimethyl-2-neopentyl-3-vinylsilacyclobutane (**14**, 18% yield), 1,1-dimethyl-2-neopentyl-4-vinylsilacyclobutane (**15**, 22% yield), 1,1-dimethyl-6-neopentylsilacyclohex-3-ene (**16**, 7% yield), and 3,3,9,9-tetramethyl-3-silanona-1,5-diene (**17**, 11% yield) were obtained.

Compound **17** apparently arises from the addition of *tert*-butyllithium to butadiene followed by coupling with vinyldimethylchlorosilane. A similar reaction has been reported in which the adduct of 1,3-butadiene and *tert*-butyllithium in hydrocarbon solvent was derivatized with trimethylchlorosilane to give only the cis and trans isomers of 5,5-dimethyl-1-trimethylsilyl-2-hexene.[14] Unfortunately, with **17**, the near chemical equivalence of the vinyl protons of the internal double bond precludes the determination of stereochemistry at this site by $^1$H NMR. The other four products of the reaction are derived from **5**. Among them **14**, **15**, and **16** incorporate one butadiene unit.



The isomers **14** and **15** gave satisfactory elemental analyses and mass spectra. They were distinguished by their $^1$H NMR spectra. The allylic proton of **14** occurred in the usual allylic region of the spectrum, a multiplet centered at δ 3.28, and a singlet for both of the methyl groups on silicon appeared at δ 0.52. In **15**, the resonance for the allylic proton, adjacent to the dimethylsilyl group, occurred further upfield as a multiplet centered at δ 2.39, and showed splittings of ca. 7, 11, and 18 Hz due to coupling with the two methylene protons in the ring and the α proton of the vinyl group. In addition the silylmethyl protons showed two distinct resonances at δ 0.48 and 0.54, consistent with their cis and trans relationship to the adjacent vinyl group in **15**. While both **14** and **15** should exist as cis, trans isomers, we were unable to separate stereoisomers by GLC.

It might be suggested that products **14**, **15**, and **16** arise from the addition of the α-lithiochlorosilane **5** to butadiene followed by ring closure:



However, the formation of the 3-vinylsilacyclobutane **14** cannot be rationalized by such a reaction path as it requires the precursor **20**, which can only be formed by a 2,1-addition of **5** to butadiene. It is known that organolithium reagents do not undergo 2,1-additions to butadiene in hydrocarbon solvents.[14] Such an addition requires the formation of a terminal organolithium while 1,4-addition gives an allyllithium intermediate. Furthermore, in additions of *tert*-butyllithium to 1,3-butadiene, no evidence has been found for 1,2-addition.[15] Derivatization of the adduct with trimethylchlorosilane gave only the 1,4 products. Even on protonation less than 6% of the terminal olefin was observed.[15] These observations seem to mitigate against the possibility that **19** is the precursor of the 4-vinylsilacyclobutane **15**, if intramolecular reactions of allyllithiums are similar to their intermolecular reactions. The silacyclohexene, **16**, could arise by an addition/cyclization pathway involving the intermediate lithium compound, **18**. But it should be noted that the [2 + 4] cycloadduct analogous to **18** is produced in the reaction of 1,3-butadiene with 1,1-dimethylsilaethylene generated by the thermolysis of 1,1-dimethylsilacyclobutane.[12]

While both compounds **15** and **16** could be produced by an addition/cyclization pathway, the only reasonable alternative path for the formation of **14** appears to be the [2 + 2] cycloaddition of the highly reactive 1,1-dimethyl-2-neopentylsilaethylene (**10**) with butadiene. It is interesting to note, if **14**, **15**, and **16** are assumed to be cycloadducts of **10**, that the ratio of [2 + 2] to [2 + 4] cycloadducts is 85/15. This ratio is consistent with what one would expect for a reactive species undergoing cycloaddition with butadiene. It is known that the s-trans conformation of 1,3-butadiene, which would lead to the [2 + 2] cycloadducts, is about 2.9 kcal/mol more stable than the s-cis form, the only conformation which can undergo [2 + 4] cycloaddition.[16] It has been estimated that, at room temperature, the ratio of the s-trans to s-cis form of butadiene is 93/7.[17] Our slightly lower ratio of 85/15 might be due to competition between the addition/cyclization pathway and the cycloaddition pathway, or to the lack of concertedness in the cycloaddition of the polar silaethylene intermediate.[18]

Thus, the products obtained from the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in the presence of butadiene in hydrocarbon solvents at low temperatures, and the trapping and competition experiments with chlorosilanes, support the hypothesis that, under appropriate reaction conditions, $\alpha$-lithiochlorosilanes do eliminate lithium chloride to give silaethylene intermediates. Recently Barton and coworkers have presented evidence for an analogous elimination reaction. When they metalated 1-chloro-1-methyl-1-silacyclohexa-2,4-diene in the presence of excess perfluoro-2-butyne, an adduct was obtained which could arise from the reaction of the alkyne with silabenzene formed by the elimination of lithium chloride from 5-lithio-1-chloro-1-methyl-1-silacyclohexa-2,4-diene.[19] Similar reactions have also been observed in the metalation of monoalkylaminofluoro- (or chloro-) silanes wherein the elimination of lithium halide gives "silicon–nitrogen ylide" type species which dimerize to give cyclic disilazanes.[20]

After this report was submitted for publication a communication by Wiberg and Preiner which indicates that an analogous elimination of lithium salts from $\alpha$-lithiosilyl phosphates, phosphites, or tosylates gives rise to 1,1-dimethyl-2,2-bis(trimethylsilyl)silaethylene appeared.[23]

## Experimental Section

**Materials.** Solvents were dried by distillation from lithium aluminum hydride prior to use. All glassware was oven dried prior to use, assembled hot, and cooled while flushing with dry nitrogen. All reactions were conducted under an atmosphere of dry nitrogen or argon. Olefins, with the exception of 1,3-butadiene, were distilled prior to use. Solutions of *tert*-butyllithium were standardized using the diphenylacetic acid titration method of Kofron.[21] For the GLC analyses a 5 ft × 1/4 in. stainless steel column containing 10% SE-30 on 60–80 mesh acid-washed Chromosorb W was used for products other than chlorosilanes. For the chlorosilanes a 5 ft × 1/4 in. stainless steel 1 QF-1 column pretreated with silicon tetrachloride was used. Columns (20 ft × 1/2 in.) of the same types were used for the preparative work. Yields were determined in most cases by GLC analyses of the concentrated product solutions using hydrocarbon or diglyme as an internal standard. NMR spectra were obtained with a Jeolco PS-100 or a Hitachi Perkin-Elmer R24B 60-MHz spectrometer, using $Me_4Si$ or chloroform as internal standards and carbon tetrachloride as the solvent. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer. Elemental analyses were performed by C. F. Geiger, Ontario, Calif., or by Galbraith Laboratories, Inc., Knoxville, Tenn.

***cis*- and *trans*-1,1,3,3-Tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane (4).** The preparation of these compounds by the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in hydrocarbon solvents at −78 °C and their characterization have been described previously.[5]

**Competition Experiments between Vinyltrimethylsilane and Trimethylchlorosilane for *tert*-Butyllithium. A. Hexanes.** To a solution of 20 mmol of vinyltrimethylsilane and 20 mmol of trimethylchlorosilane in 50 mL of hexanes cooled to −78 °C was slowly added 20 mmol of *tert*-butyllithium in 13 mL of pentane. As the resulting solution was warmed slowly to room temperature a white precipitate formed slowly. After stirring at room temperature for 3 h and refluxing for 10 h, the yellow color had faded. Hydrolytic workup (water) gave the yields of **6**, **7**, and **8** shown in Table I. No *tert*-butyltrimethylsilane could be detected by GLC.

***trans*-1-Trimethylsilyl-3,3-dimethyl-1-butene (6).**[6e] MS *m/e* ($M^+$) 156. NMR $\delta$ 0.11, s, 9 H ($Me_3Si$); 1.05, s, 9 H ($Me_3C$); 5.45, d, 1 H and 6.08, d, 1 H (vinyl protons), $J = 18$ Hz.

**1,1-Bis(trimethylsilyl)-3,3-dimethylbutane (7).**[6e] MS *m/e* ($M^+$) 230. NMR $\delta$ −0.15, t, 1 H, $J = 4.5$ Hz (methine proton); 0.11, s, 18 H (trimethylsilyl protons); 0.93, s, 9 H (*t*-Bu protons); and 1.50, d, 2 H, $J = 4.5$ Hz (methylene protons).

**1,1,3-Tris(trimethylsilyl)-5,5-dimethylhexane (8).** MS *m/e* ($M^+$) 330. NMR $\delta$ −0.20 to −0.36, m, 1 H (methine adjacent to two silicons); 0.12, s, 18 H and 0.18, s, 9 H (trimethylsilyl protons); 0.68–0.84, m, 1 H (methine adjacent to one silicon); 1.01, s, 9 H (*t*-Bu protons); and 1.17–1.83, m, 4 H (methylene protons).

Anal. Calcd for $C_{17}H_{42}Si_3$: C, 61.73; H, 12.80. Found: C, 61.93; H, 12.87.

**B. Diethyl Ether.** The same amounts of reagents described in the hexane run above were mixed at −78 °C in 50 mL of diethyl ether. The resulting yellow solution was warmed slowly to room temperature. As the temperature rose, the yellow color faded slowly and a white precipitate formed. The mixture was stirred at room temperature for 1 h. Hydrolytic workup gave the yields of **6**, **7**, and **8** shown in Table I. No *tert*-butyltrimethylsilane could be detected.

**C. Tetrahydrofuran.** The same amounts of reagents as described in the hexane run above were combined in 50 mL of THF at −78 °C. A brownish-yellow color developed immediately as the *tert*-butyllithium was added, and this color rapidly changed to pale yellow. The reaction solution was allowed to warm slowly to room temperature. The pale yellow color faded after 1 h. After 12 h a small amount of white precipitate had formed. Hydrolytic workup gave a 76% yield of **7**. No *tert*-butyltrimethylsilane could be detected in the reaction mixture.

**Attempt to Trap 5 with Trimethylchlorosilane in Hydrocarbon Solvent.** A mixture of 5 mmol of vinyldimethylchlorosilane and 5 mmol of trimethylchlorosilane was added slowly to 5 mmol of *tert*-butyllithium in 4.2 mL of pentane and 20 mL of hexane cooled to −78 °C. The resulting yellow solution was allowed to warm slowly to room temperature. A white precipitate formed as the temperature of the reaction mixture approached room temperature. After stirring at room temperature for 1 h, the reaction mixture was analyzed by GLC. Only a 48% yield of **4** was obtained. No trace of **11**, the expected derivatization product of **5** with trimethylchlorosilane, could be detected.

**Reaction of Vinyldimethylchlorosilane and Trimethylchlorosilane with *tert*-Butyllithium in THF.** To a solution of 20 mmol of vinyldimethylchlorosilane and 20 mmol of trimethylchlorosilane in 50 mL of THF was added a solution of 20 mmol of *tert*-butyllithium in 13 mL of pentane at −78 °C. The reaction solution turned to a brownish-yellow color as the *tert*-butyllithium was added, but this color faded rapidly. The reaction mixture was warmed to room temperature and stirred for 4 h. Workup gave a 19% yield of **4** and four other products: **9**, **11**, **12**, and **13** in 9, 14, 28, and 18% yields, respectively. These compounds were separated and analyzed by preparative GLC.

**3,3,6,6-Tetramethyl-4-(chlorodimethylsilyl)-3-silahept-1-ene (9).** MS *m/e* ($M^+$) 262 and 264, ca. 3:1. NMR $\delta$ −0.10 to 0.10, m, 1 H (methine proton); 0.20, s, 6 H (dimethylsilyl protons); 0.47, s, 6 H (chlorodimethylsilyl protons); 0.88, s, 9 H (*t*-Bu protons); 1.57, d, $J = 4.3$ Hz, 2 H (methylene protons); and 5.62–6.48, m, 3 H (vinyl protons).

Anal. Calcd for $C_{12}H_{29}Si_2Cl$: C, 54.81; H, 10.35. Found: C, 54.85; H, 10.44.

**2,2,5,5-Tetramethyl-3-(chlorodimethylsilyl)-2-silahexane (11).** MS *m/e* ($M^+$) 250 and 252, ca. 3:1. NMR $\delta$ 0.10, s, 9 H (trimethylsilyl protons); 0.08–0.12, m, 1 H (methine proton); 0.47, s, 6 H (chlorodimethylsilyl protons); 0.90, s, 9 H (*t*-Bu protons); 1.50, d, $J = 4$ Hz, 2 H (methylene protons).

Anal. Calcd for $C_{11}H_{27}Si_2Cl$: C, 52.65; H, 10.85. Found: C, 52.79; H, 10.90.

**2,2,3,3,6,6-Hexamethyl-4-trimethylsilyl-3-silaheptane (12).** MS *m/e* ($M^+$) 272. NMR δ 0.02, s, 6 H (dimethylsilyl protons); 0.08, s, 9 H (trimethylsilyl protons); 0.89, s, 9 H, and 0.93, s, 9 H (*t*-Bu protons); 1.38–1.69, m, 2 H (methylene protons); −0.10 to 0.10, m, 1 H (methine proton).

Anal. Calcd for $C_{15}H_{36}Si_2$: C, 66.09; H, 13.31. Found: C, 65.91; H, 13.33.

**2,2,3,3,6,6-Hexamethyl-4-(dimethylvinylsilyl)-3-silaheptane (13).** MS *m/e* ($M^+$) 284. NMR: δ −0.10 to 0.10, m, 1 H (methine proton); 0.07, s, 6 H, and 0.18, s, 6 H (dimethylsilyl protons); 0.90, s, 9 H, and 0.94, s, 9 H (*t*-Bu protons); 1.58, d, $J$ = 4.5 Hz, 2 H (methylene protons); and 5.55–6.32, m, 3 H (vinyl protons).

Anal. Calcd for $C_{16}H_{36}Si_2$: C, 67.52; H, 12.72. Found: C, 67.41; H, 12.07.

**Reaction of 9 with *tert*-Butyllithium in Hydrocarbon Solvent.** To a solution of 8.8 mmol of **9** in 40 mL of hexane was added slowly 8.8 mmol of *tert*-butyllithium in 5.5 mL of pentane at −78 °C. The resulting solution was warmed to room temperature and stirred for 2 h, during which time a white precipitate slowly formed.[22] Hydrolytic workup gave a 63% yield of the 1,3-disilacyclobutanes, **4**. No **13**, the anticipated coupling product between **9** and *tert*-butyllithium, could be detected.

**Reaction of 9 and Vinyldimethylchlorosilane with *tert*-Butyllithium in Hydrocarbon Solvent.** A mixture containing 2.4 mmol of **9**, 1.2 mmol of **4**, and 1.0 mmol of **13** was combined with 4.0 mmol of vinyldimethylchlorosilane in 30 mL of pentane. The resulting solution was analyzed by GLC and the relative peak areas established. The solution was cooled to −78 °C and 3.0 mmol of *tert*-butyllithium in 21 mL of pentane was added. The clear solution was warmed to room temperature. After stirring for 1 h, a large amount of white precipitate had formed. The reaction solution was then analyzed using the same GLC conditions and found to contain 1.6 mmol of vinyldimethylchlorosilane, 2.3 mmol of **9**, 2.2 mmol of **4**, and 1.0 mmol of **13**. The changes correspond to the consumption of 2.4 mmol of vinyldimethylchlorosilane, the production of 1.0 mmol of **4**, and essentially no change in the amounts of **9** or **13**.

**General Method for the Reaction of Vinyldimethylchlorosilane with *tert*-Butyllithium in the Presence of an Olefin.** To a solution of 10 mmol of vinyldimethylchlorosilane and the trapping olefin in 100 mL of hexane cooled to −78 °C was added 10 mmol of *tert*-butyllithium in 13 mL of pentane. The resulting solution was warmed to room temperature and stirred overnight. After hydrolytic workup, the concentrated product mixture was analyzed by GLC.

**A. Trimethylvinylsilane as the Trapping Olefin.** This experiment was performed with a 3.5-fold excess of trimethylvinylsilane using the general method described above. The disilacyclobutanes, **4**, were the only products obtained.

**B. Styrene as the Trapping Olefin.** This experiment was performed as described above using 1 equiv of freshly distilled styrene. Only a large amount of polymeric material was obtained.

**C. 1,3-Butadiene as the Trapping Olefin.** When the experiment was performed as described in the general method using 1 equiv of 1,3-butadiene as the trapping olefin, 1.13 g of product was obtained, bp 60–73 °C (8 Torr). Analysis of the mixture by GLC showed five major components, **4**, **14**, **15**, **16**, and **17**, in 14, 18, 22, 7, and 11% yields, respectively.

**1,1-Dimethyl-2-neopentyl-3-vinylsilacyclobutane (14).** MS *m/e* ($M^+$) 196. NMR δ 0.52, s, 6 H (dimethylsilyl protons); 1.02, s, 9 H (*t*-Bu protons); 1.20–1.84, m, 5 H (methylene and methine protons); 3.08–3.48, m, 1 H (allylic proton); 4.72–5.10, m, 2 H, and 5.64–6.10, m, 1 H (vinyl protons).

Anal. Calcd for $C_{12}H_{24}Si$: C, 73.34; H, 12.32. Found: C, 73.41; H, 12.34.

**1,1-Dimethyl-2-neopentyl-4-vinylsilacyclobutane (15).** MS *m/e* ($M^+$) 196. NMR δ 0.48, s, 3 H, and 0.54, s, 3 H (dimethylsilyl protons); 1.04, s, 9 H (*t*-Bu protons); 1.00–1.68, m, 5 H (methylene and methine protons); 2.16–2.62, m, 1 H (allylic proton); 4.88–5.14, m, 2 H, and 5.80–6.20, m, 1 H (vinyl protons).

Anal. Calcd for $C_{12}H_{24}Si$: C, 73.34; H, 12.32. Found: C, 72.97, H, 12.13.

**1,1-Dimethyl-6-neopentylsilacyclohex-3-ene (16).** MS *m/e* ($M^+$) 196. NMR δ 0.08, s, 3 H, and 0.16, s, 3 H (dimethylsilyl protons); 1.02, s, 9 H (*t*-Bu protons); 1.00–1.64, m, 5 H, 1.80–2.20, m, 1 H, and 2.36–2.76, m, 1 H (methylene and methine protons); 5.50–5.96, m, 2 H (vinyl protons).

Anal. Calcd for $C_{12}H_{24}Si$: C, 73.34; H, 12.32. Found: C, 73.52; H, 12.10.

**1-Neopentyl-3-(dimethylvinylsilyl)-1-propene (17).** MS *m/e* ($M^+$) 196. NMR δ 0.20, s, 6 H (dimethylsilyl protons); 1.00, s, 9 H (*t*-Bu protons); 1.58, d, $J$ = 5 Hz, 2 H (methylene protons); 1.95, d, $J$ = 5 Hz, 2 H (methylene protons of the neopentyl group); 5.17–5.55, m, 2 H, and 5.65–6.37, m, 3 H (vinyl protons).

Anal. Calcd for $C_{12}H_{24}Si$: C, 73.34; H, 12.32. Found: C, 73.08; H, 12.16.

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## References and Notes

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