is the nature of the $2e_1$ orbital as an in-phase (pseudo ungerade) combination of ring e_1 and nitrogen $p\pi$ orbitals with probably only a small combination of metal 6p to stabilize it. Thus, the $2e_1$ orbital may be regarded as approaching nonbonding character. This should also lead to a relative weakening of the bond and a further thermodynamic factor leading to its reactivity. The PES study has demonstrated that the $2e_1$ orbital is to a considerable extent localized on the nitrogen. It has also established an IE for this orbital which is compatible with significant proton affinity. Thus, a reaction pathway of electrophilic attack on the nitrogen suggests itself for an imido exchange reaction.

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Cleavage of Carbon–Silicon Bonds in the Presence of Silicon–Silicon Bonds by Electron-Transfer Reagents

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The unexpected undecamethylcyclohexasilyl anion, $Si_6Me_{11}^-$, was obtained in solution from the reactions of electron-transfer reagents including methyllithium, alkali metals, or trimethylsilyl anion with dodecamethylcyclohexasilane, Si_6Me_{12}, in the presence of either hexamethylphosphoramide or of 18-crown-6 in ether solvents. $Si_6Me_{11}^-$ was also prepared from Si_6Me_{12} in hexamethylphosphoramide by electrolytic reduction. $Si_6Me_{11}^-$ is a stable and useful intermediate that can be derivatized with a variety of electrophiles.

Introduction

Examples of the well-known cleavage of silicon–silicon bonds with alkali metals to give organosilanyl derivatives include the preparation of 1,4-dilithiooctaphenyltetrasilane from octaphenylcyclotetrasilane and lithium metal[1] and the cleavage of decamethyltetrasilane by sodium–potassium alloy to give a mixture of products of varying chain lengths.[2] Dodecamethylcyclohexasilane (Si_6Me_{12}, 1) has been cleaved by both sodium–potassium alloy[3] and lithium metal,[4] and in both cases the products were reported to be the linear chain compounds $M(SiMe_2)_nM$ (n = 2–6; M = Li, Na, K).

Alkylsilanyl anions may be prepared by several other routes. Bis(trialkylsilyl)mercury compounds have been cleaved by alkali metal to give $MSiR_3$ (M = Li, Na, K; R = Me, Et).[5] $LiSiMe_3$ is more easily prepared by the reaction of hexamethyldisilane with methyllithium in the presence of hexamethylphosphoramide (HMPA).[6] In a similar manner $KSiMe_3$ is prepared from hexamethyldisilane and potassium methoxide in a hexane solution of 18-crown-6.[7] In these reactions both HMPA and crown ether appear to enhance the reactivity by strongly solvating the alkali metals. Peralkylpolysilanyl anions such as $LiSi(SiMe_3)_3$ have been prepared by the cleavage of $Si(SiMe_3)_4$, or related compounds, by methyllithium.[8] The observed high stability of $LiSi(SiMe_3)_3$ was attributed to charge delocalization over contiguous silicon atoms.

Permethylcyclopolysilanes can also be reduced chemically and electrochemically at low temperatures to form anion radicals.[9] ESR spectra of $(SiMe_2)_n^{\bullet -}$ (n = 5–7) indicate that the unpaired electron density is delocalized over the ring, with hyperfine splitting showing equivalent interaction with all of the ring methyl groups. Several substituted methylcyclopolysilanes have also been reduced,[10] but in no case was carbon–silicon bond cleavage reported.

Apparently, facile cleavage by metallic or organometallic reagents of Si–alkyl bonds in compounds containing Si–Si bonds has not been reported. The Si–aryl bond in $SiPh_4$ is readily cleaved with potassium metal.[11] The resultant triphenylsilanyl anion bonds to a methyl group from the dimethoxyethane solvent to give $SiPh_3Me$, and subsequent reactions proceed to generate $SiPhMe_3$ and thus reflect the relative stability of the Si–alkyl bond.

To prepare synthetically useful organopolysilane intermediates, including α,ω-dilithiopermethylpolysilanes and related alkali metal derivatives of methylsilanes, we started an investigation of ring cleavage of dodecamethylcyclohexasilane (1) using organometallic and alkali metal reagents known to break silicon–silicon bonds. Observation of an unexpected reaction led to the synthesis and utilization of a cyclic methylpolysilane reagent, $Si_6Me_{11}^-$, as described herein.

Results

Preparation and Derivatization of $Si_6Me_{11}^-$ (2). The reaction of Si_6Me_{12} (1) with lithium metal in $HMPA/Et_2O$ solution did not proceed with silicon–silicon bond cleavage as expected to give $Li(SiMe_2)_6Li$ but instead gave a red intermediate, $Si_6Me_{11}^-$ (2), the product of Si–C bond cleavage. Evidence that the formation of this product

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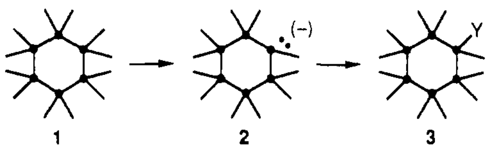
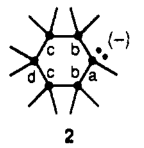
resulted from the major reaction pathway includes derivatization to form substituted cyclohexasilanes as well as analysis by NMR. In HMPA solution, 2 was stable in the absence of air and water.

The product 2 was readily derivatized to give substituted cyclohexasilanes, ($Si_6Me_{11}Y$) (3). For example, derivatization with bromoethane gave **3a** (Y = Et) with an overall yield of 46% based on starting silane as shown by GC/MS. In addition, 2 was derivatized with $ClSiMe_3$ and with dimethyl sulfate to give **3b** (Y = $SiMe_3$, 46% yield) and 1 (50% yield), respectively. Proton NMR of **3a** gave no definitive structural information for these compounds due to overlap of the methylsilicon peaks. The ^{13}C NMR spectrum, however, did differentiate six of the seven nonequivalent ring methyl groups in **3a** and **3b**. The ^{29}Si NMR spectra of **3a**, **3b**, and **3f** (Y = $CH_2Si(CH_3)_3$) exhibited sharp singlets in the expected 1:1:2:2, 1:1:1:2:2, and 1:1:1:2:2 ratios, respectively. The assumed structure shown of 2 was confirmed by ^{29}Si NMR. Neither ^1H nor ^{13}C NMR gave resolved spectra of 2, but the ^{29}Si NMR spectrum showed four sharp singlets with a 1:2:2:1 intensity pattern as expected. The high-field peak (−108.1) can be assigned definitely to the negatively charged silicon, and the other assignments are consistent with literature values for related organosilane compounds.[12]





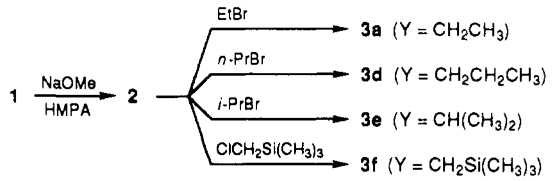
2
a, −108.1 ppm
b, −33.8 ppm
c, −40.7 ppm
d, −41.6 ppm

Electrochemical Generation of 2. Cyclic voltammetry and controlled-potential electrolysis were performed on HMPA solutions of 1 to study the electrochemical generation of $Si_6Me_{11}Li$. The initial cyclic voltammogram of 1 in HMPA shows the formation of the solvated electron at −3.0 V.[13] A small reductive current observed at −1.9 V may be due to the direct reduction of 1. Upon electrolysis experiments, the potential necessary to maintain an adequate electrolysis current drops from −3.0 to −1.9 V. This change is most likely due to a surface effect that comes about upon electrolysis. The surface of the electrode may be conditioned to facilitate the direct reduction of 1. During electrolysis a red species was produced at the surface of the working electrode and the resulting solution became red-orange. The electrosynthesis of 2 was verified by GC analysis of a derivatization product, **3a**.

Additional Routes to 2. The combination of 1 with certain other reagents, specifically HMPA solutions of methyllithium, butyllithium, sodium and potassium alkoxides, sodium and potassium metal, sodium trimethylsilanate, and phenyllithium as well as THF solutions of sodium and potassium methoxide, sodium and potassium metal, and trimethylsilylpotassium in the presence of a cyclic polyether, 18-crown-6, also gave dark red solutions. The presence of 2 as the major reaction product was inferred from a variety of derivatization reactions.

Methyllithium was combined with 1 to give a red solution of 2, which was readily derivatized with iodomethane or bromoethane to give 1 or **3a**, respectively. To further substantiate that the active intermediate leading to the regeneration of 1 is indeed 2, derivatization was carried out with an excess of CD_3I. This reaction gave the expected product **3c** (Y = CD_3), as determined by GC/MS.

The series of metal alkoxides NaOR (R = Me, Et) and KOR (R = Me, Et, *t*-Bu) all gave 2 upon reaction with 1 in HMPA. In all cases derivatization with bromoethane gave **3a** (Y = Et). The product 2 from NaOMe was also derivatized with bromopropane, 2-bromopropane, and chloromethyltrimethylsilane. Derivatization with bulky groups including *tert*-bromobutane gave low yields and numerous side products.



When a red-brown solution of phenyllithium was added to an HMPA solution of 1, the reaction mixture became dark green. Derivatization with bromoethane gave **3a** as the major product, indicating that 2 was present in the dark green solution. As in all of the previous reactions, the yield of **3a** from 1 was less than 50%. Since ring cleavage was expected to be the competing reaction and since the reaction with phenyllithium might give easily identifiable linear phenyl silanes, the side products of derivatization with bromoethane were studied by GC/MS. The products identified by molecular-ion peaks were $Ph(SiMe_2)_nEt$ (n = 4–6) and $Ph(SiMe_2)_nH$ (n = 5, 6) as well as a small amount of biphenyl. The observed dark green color apparently was a consequence of the biphenyl anion radical. The linear species observed indicate that ring cleavage is probably the major competing reaction and is most likely responsible for the low yields of 3.

The reaction of 1 with $KSiMe_3$ is without preparative utility since considerable amounts of $Si_6Me_{10}Et_2$, $Si_6Me_9Et_3$, $Si_6Me_{11}H$, and short-chain products are obtained.

Effects of the Reaction Medium and of Variation of the Ratios of Reactants. The minimum concentration of HMPA required for the reaction of methyllithium with 1 was investigated. It was found that the solvent must be nearly 20% (v/v) HMPA for the dark red color of 2 to appear fully. The choice of cosolvent is not critical for any of the reactions involving HMPA. Almost any inert cosolvent may be used as long as the solution is at least 20% HMPA. In addition, pure HMPA may be used as solvent for the reaction since 1 is sparingly soluble and 2 is fully soluble in HMPA. The reaction of methyllithium with 1 in THF, with no HMPA present, followed by derivatization with bromoethane gave a low yield of short-chain derivatives and no **3a**.

A few reagents were found to react with 1 to give 2 in the absence of HMPA. Sodium metal, potassium metal, KOMe, and $KSiMe_3$ all gave 2 in the presence of the crown ether 18-crown-6.

In separate experiments, 1 was allowed to react with lithium or NaOMe, in 1:4 or 1:2.6 mole ratios, respectively, to determine if multiple substitutions on the ring would occur. After derivatization with bromoethane, GC/MS demonstrated that in neither case was the disubstituted

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$Si_6Me_{10}Et_2$ a significant reaction product. Thus, **2** is a relatively stable species. To test whether the reaction of **1** to form **2** might be catalytic with respect to the organometallic reagent, two separate experiments were run. Reactions involving either 12 mol % lithium or 5 mol % NaOMe led to less than a 1% yield of **3a** upon derivatization. The yields of **3a** from the reaction of Si_6Me_{12} with lithium in ethyl ether/HMPA were approximately constant with molar ratios for Si_6Me_{12}/Li being either 7:15 or 1:1.

Other Attempts at Si–C Bond Cleavage. To determine whether Si–C cleavage could be similarly induced in other organosilanes, several other alkyl- and arylsilanes were allowed to react under reaction conditions similar to that for **1** above. From the addition of decamethylcyclopentasilane (Si_5Me_{10}) contaminated by a small amount of **1** to MeLi in HMPA followed by addition of bromoethane, no observable Si_5Me_9Et was obtained. The product mixture did contain an amount of **3a** greater than the amount of contaminant **1** originally present, consistent with previously reported[2] ring–chain–ring equilibria depleting Si_5Me_{10}.

Decamethyltetrasilane, $Me(SiMe_2)_4Me$, was allowed to react with both methyllithium and lithium metal in HMPA to determine whether Si–Si bond cleavage or Si–C bond cleavage is the major pathway for linear methylsilanes. Analysis of the products of derivatization with bromoethane showed that a range of products $R(SiMe_2)_nR'$ (R, R′ = Me, Et; n = 3–5) were produced. Since Si_4Me_9Et is present as only a minor reaction product, Si–Si bond cleavage and chain scrambling appear to be the major reaction pathways.[14-16]

Octaphenylcyclotetrasilane, $(SiPh_2)_4$, was allowed to react with lithium in HMPA to determine whether silicon–silicon bond cleavage or silicon–carbon bond cleavage is the major reaction pathway for cyclic phenylsilanes under the reaction conditions used for **1**. Derivatization with iodomethane and subsequent analysis by direct-inlet MS showed the presence of $Me(SiPh_2)_4Me$ but no indication of *cyclo*-$(SiPh_2)_3SiPhMe$. Thus, as in other solvents,[17] the major reaction pathway with this cyclic phenylsilane is the silicon–silicon bond cleavage to give the α,ω-disubstituted linear tetrasilane.

Analysis of Gaseous Reaction Products. To gain insight into possible mechanistic pathways, the gaseous reaction products of **1** with lithium, methyllithium, and potassium methoxide were analyzed. Since the reaction involves the loss of a CH_3 group, a simple mechanism might lead to production of methane, ethane, or dimethyl ether. None of these compounds were detected. However, molecular hydrogen was detected in each reaction. Both lithium and methyllithium in pure HMPA gave only small amounts of H_2 (0.01–0.04 mol of H_2/mol of Li or MeLi) which were found to be independent of the quantity of **1** present; similar small amounts were observed even in the absence of **1**. With the reaction of $KOCH_3$ and **1** in either HMPA or 18-crown-6/THF solution, molecular hydrogen was produced in larger amounts (15–18 mol of H_2/mol of $KOCH_3$). However, the amount of H_2 produced was again dependent on the amount of alkali metal-containing reagent present and independent of the amount of **1** present. In separate reactions using $KOCD_3$ and C_6D_6, small amounts of H–D were also produced indicating that the hydrogen probably is a product of a reagent solvent reaction and not an integral part of the reaction leading to **2**.

ESR. Searches by ESR were made for stable radical species either present in solution or as long-lived intermediates in the preparation of **2**. Neither a dilute solution of **2** nor a solution of the two reactants **1** and MeLi, as they were allowed to warm from −75 to 0 °C, exhibited an ESR spectrum.

Discussion

Contrary to expectations, the silicon–carbon bond in dodecamethylcyclohexasilane is cleaved preferentially to the silicon–silicon bond by alkali metals and alkyllithium reagents. This observed stability of the silicon–silicon bond is remarkable and makes possible new synthetic pathways in organosilicon chemistry. Some previously reported syntheses of cyclic derivatives of Si_6Me_{12} also reflect the stability of the silicon–silicon bond.[18-20] Tentatively, the preferred route to the intermediate $Si_6Me_{11}^-$ is the reaction of methyllithium and Si_6Me_{12} in $HMPA/Et_2O$ solutions. To successfully prepare $Si_6Me_{11}^-$, the presence of a metal-complexing agent such as HMPA or 18-crown-6 is important. $Si_6Me_{11}^-$ is a convenient reagent since sealed solutions of it in HMPA persist for weeks at room temperature in the absence of light. By contrast, methyllithium reacts preferentially with the silicon–silicon bond in hexamethyldisilane in HMPA[6] and in n-decamethyltetrasilane. Electron delocalization onto contiguous silicons may contribute to the stability of $Si_6Me_{11}^-$, consistent with the increasing order of thermal stability and decreasing chemical reactivity:[8,21]

$$Me_3SiLi < Me_2(Me_3Si)SiLi < Me(Me_3Si)_2SiLi < (Me_3Si)_3SiLi$$

Electron transfer appears to be a common feature in the various pathways to $Si_6Me_{11}^-$ (**3a**). Electrochemical reduction of Si_6Me_{12} at ambient temperatures leads to $Si_6Me_{11}^-$, which presumably is a decomposition product of $(Si_6Me_{12})^{\bullet -}$. Solvent-mediated electron transfer is known to occur in reactions of lithium, sodium, potassium, or methyllithium in hexamethylphosphoramide,[22,23] and in nonpolar solvents complexation of metal ions by 18-crown-6 also is known to facilitate electron transfer.[7,24] The trimethylsilyl anion, obtainable from the reaction

$$MOMe + Me_3SiSiMe_3 = MSiMe_3 + Me_3SiOSiMe_3$$

reacts readily as an electron-transfer agent,[25,26] and presumably the linear species $MeO(SiMe_2)_6^-$ and $Ph(SiMe_2)_6^-$ are obtained from the reactions of cyclic Si_6Me_{12} with MOMe or phenyllithium and are capable of acting as electron-transfer agents in HMPA. However, since sodium isopropoxide or *tert*-butoxide in HMPA transfers electrons to benzophenone,[27,28] direct electron transfer from meth-

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oxides in HMPA to Si_6Me_{12} also is conceivable. Mechanistic details, including the fate of the methyl group lost in the formation of $Si_6Me_{11}^-$, and the nature of silicon-containing noncyclic products remain unknown. Reactions with the solvent HMPA[29,30] have not been excluded and may obscure mechanistic information.

The cyclic anion radical $Si_6Me_{12}^{\bullet-}$ was first prepared by electrolytic reduction of Si_6Me_{12} below −120 °C in dimethyl ether/glyme solvent, was investigated at that temperature, and was observed to decompose rapidly at slightly higher temperatures.[9] From observed ^{13}C and ^{29}Si hyperfine coupling constants and theoretical calculations, the singly occupied molecular orbital in some $(SiR_2)_n^{\bullet-}$ radicals has been inferred to be an admixture of Si–C σ^* and Si–Si σ^* or pπ orbitals.[31] Thus, the unpaired electron is to some extent in the region of silicon–carbon antibonding atomic orbitals, and propensity for cleavage of a silicon–carbon bond in preference to a silicon–silicon bond can be rationalized.

Experimental Section

Materials. Tetrahydrofuran (THF, Aldrich), diethyl ether, hexanes (Aldrich), and 1,2-dimethoxyethane (DME, Mallinckrodt) were distilled from CaH_2 under N_2 and stored over 4-Å molecular sieves. Hexamethylphosphoramide was distilled (bp 70–75 °C, 0.3 mm) from either CaH_2 or P_2O_5 and stored over molecular sieves. *Caution! HMPA is a suspected carcinogen and therefore always was handled carefully with gloves in an efficient hood.*[32]

Lithium wire (0.02% Na, Alfa), dimethyl sulfate (MCB), and iodomethane (Aldrich) were purchased and used without further purification. Bromoethane (Eastman) and chlorotrimethylsilane (a gift from the Dow Corning Corp.) were dried over 4-Å molecular sieves and distilled under an atmosphere of dry nitrogen prior to use. Halide-free methyllithium and MeLi·LiBr (Aldrich) were used as received. The molarities were checked periodically by acidiometric titration.[33] All other reagents were appropriately purified prior to use.

Dodecamethylcyclohexasilane (**1**) was prepared readily by a literature[34] procedure. Essentially oxide-free Na/K alloy (22/78) was used as received from Callery Chemical Co. and was transferred with a stainless steel cannula under a positive pressure. Octaphenylcyclotetrasilane[1] and decamethyltetrasilane were prepared by literature procedures.[35]

Dry sodium methoxide was prepared from oxide-free metallic sodium and methanol which had been freshly distilled from magnesium.[36] Potassium methoxide was prepared in an analogous manner. All reactions were performed under an atmosphere of dry nitrogen or helium unless otherwise noted.

Teflon-coated stirring bars were observed to react with some of the above alkali and organoalkali reagents, and therefore for reactions reported below exclusive use was made of glass-encased stirring bars. Greaseless Teflon valves and Teflon sleeves for glass tapered joints were used but with minimum contact time with reactive solutions.

Equipment. Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard Model 5750 instrument using an 8 ft × $^1/_8$ in. column packed with 10% Apiezon L on 80–100 mesh NAW Chromosorb W. Gas chromatography/mass spectra data were obtained with a Hewlett-Packard Model 5985 GC/MS instrument, and other mass spectral data were obtained with a Consolidated Electrodynamics Corp. 21-104 spectrometer operating at an ionizing energy of 70 or 20 eV. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Cyclic voltammetry and controlled-potential electrolysis were performed with equipment and by methods described elsewhere.[37] ESR spectra were obtained on a Varian Associates Model E-4 spectrometer. Elemental analyses were performed either by Galbraith Laboratories (Knoxville, TN) or by the Analytical Services Laboratory, Northwestern University (Evanston, IL).

^1H NMR spectra were obtained with either a Perkin-Elmer R-20B or Varian T-60 spectrometer. Cyclohexane was used as an internal standard [$\delta(Me_4Si) = \delta(C_6H_{12}) + 1.42$ ppm] in CCl_4 solutions. $^{13}C\{^1H\}$ NMR spectra were obtained in natural abundance at ambient probe temperature (32 °C) either at 20.00 MHz on a Varian Associates CFT-20 or at 22.50 MHz on a JEOL FX-90Q Fourier transform spectrometer. A 5-mm NMR tube containing 10% TMS/C_6D_6 (v/v) was coaxially fitted into a regular 10-mm NMR tube which contained ca. 5–15 wt % of sample in CCl_4. The internal tube served both as the deuterium field lock for the spectrometer and the external standard. The ^{13}C chemical shifts are referenced to TMS in CCl_4 [$\delta = \delta$(TMS in C_6D_6) − 0.94 ppm], where a positive δ is downfield from TMS.

All ^{29}Si NMR spectra were obtained (21.1 kG field at 17.76 MHz) with a JEOL FX-90Q NMR spectrometer. The air/water-sensitive samples were charged into 10-mm NMR tubes via syringe techniques into which a 4- or 5-mm tube was coaxially fitted. All chemical shifts are referenced to internal TMS. The inner tube was filled with an appropriate deuterated lock solvent (C_6D_6, $CDCl_3$). After careful placement of the inner concentric tube this arrangement was sealed with parafilm. Standard Teflon spacers were used to stabilize the inner glass tube but kept out of contact with the reactive solutions. The spectra were obtained rapidly at ambient temperature (37 °C). Typical spectral widths of 3000–5000 Hz (i.e., 170–282 ppm) were utilized in these studies. A 90° flip angle (pulse width 17 μs) was used, whereas the repetition rate (acquisition time + pulse delay) was varied between 10 and 200 s to achieve the maximum signal-to-noise ratio. A gated-decoupled pulse train was used to minimize the nuclear Overhauser effect. Quantitative observations of relative intensities in the ^{29}Si spectra were facilitated by 0.04 M $Cr(acac)_3$, which reduces spin–lattice relaxation times to approximately the same value.

Preparation of Ethylundecamethylcyclohexasilane ($Si_6Me_{11}Et$) (3a) from Si_6Me_{12} and Lithium. To a stirred solution of **1** (5.0 g, 14 mmol) in 25 mL of ethyl ether and 25 mL of HMPA was added lithium wire (3-mm lengths, 0.21 g, 30 mmol). After 10 min the lithium started to react and the solution began to turn red. After 12 h all of the lithium had reacted giving a dark red solution containing intermediate **2**. The ^1H NMR spectrum of this solution had two unresolved peaks at 0.04 and 0.00 ppm. The ^{13}C NMR spectrum, in the 1.13 to −3.56 ppm region, was complex. This solution was added dropwise to bromoethane (5.0 mL, 65 mmol) in 50 mL of hexane cooled by an ice bath. Workup was accomplished by extracting the reaction mixture with 2 × 250-mL portions of water to remove the HMPA and the LiBr salts. The solvents from the organic layer were removed by rotary evaporation leaving 3.1 g of a white solid. GC/MS analysis indicated that 77% of the material was a species with a molecular ion and fragmentation pattern corresponding to the compound **3a**: selected *m/e* (relative intensity) 365 (4), 364 (26), 363 (42), 362 (100, M^+), 259 (18), 201 (18), 199 (4). Thus, the overall yield based on starting silane was 46%. Recrystallization from methanol–acetone (or 7:1 95% EtOH/THF) gave **3a**, a white solid: mp 225–228 °C (sealed tube), sublimes at 90 °C, 0.1 mm; M_r 366 (calcd 363); ^1H NMR δ 0.12 and 0.14 (33 H, $SiCH_3$), 0.40–1.2 (br m, 5 H, $SiCH_2CH_3$) ppm; ^{13}C NMR δ 10.26 (1 C), 4.86 (1 C), −4.99 (2 C), −5.42 (2 C), −5.70 (3 C), −6.09 (1 C), −6.18 (2 C), −8.29 (1 C) ppm; IR (KBr disk) 2950, 2880, 1400, 1250, 1010, 960, 800, 730, 680, 650, 410, 395 cm^{-1}. Anal. Calcd for $C_{13}H_{38}Si_6$: C, 43.02; H, 10.55; Si, 46.43. Found: C, 43.02; H, 10.71; Si, 45.48.

In another experiment, a 1/1 molar ratio of **1** to lithium was allowed to react. Here, lithium (0.08 g, 12 mmol) was added to a stirred solution of **1** (4.0 g, 12 mmol) in 20 mL of ethyl ether and 20 mL of HMPA. After 18 h of reaction followed by 18 h

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of additional stirring, the red solution was added to bromoethane (5.0 mL, 65 mmol) in 40 mL of hexane cooled by an ice bath. Workup gave 2.4 g of a white solid. GC/MS analysis indicated that 74% of this material (43% overall yield from 1) was $Si_6Me_{11}Et$ (m/e 362, M^+) with only 8% (5% overall) being unreacted 1 (m/e 348, M^+).

Preparation of $Si_6Me_{11}Et$ from Si_6Me_{12} and Methyllithium. To a stirred solution of 1 (5.0 g, 14 mmol) in 25 mL of ethyl ether and 25 mL of HMPA cooled by an ice bath was added methyllithium (15 mmol) dropwise. After addition of a few drops, the solution immediately became faint red and then darkened upon further addition. After 1 h of stirring, this solution was added to bromoethane (4.0 mL, 52 mmol) in 25 mL of hexane cooled by an ice bath. Workup gave 3.0 g of a white solid. GC/MS analysis indicated that 67% of this material (40% overall yield) was a species with m/e 362 (M^+). Recrystallization from methanol–acetone gave a white solid which analyzed as above for $Si_6Me_{11}Et$.

For a study of the effect of solvent composition, methyllithium (2.9 mmol) was added to a stirred solution of 1 (1.0 g, 2.9 mmol) in 10 mL of ethyl ether cooled by an ice bath. This solution remained colorless. A 1/1 (v/v) mixture of HMPA/ethyl ether was then slowly added. The originally clear solution changed to light yellow, then orange, and finally to the previously observed typical red color. At this point 6 mL of solvent mixture had been added and the solvent composition was 17% HMPA. Increasing the HMPA concentration further did not noticeably alter the reaction mixture.

Preparation of Intermediate 2 and of $Si_6Me_{11}Et$ from Si_6Me_{12} and Metal Alkoxides, Alkali Metals, or $KSiMe_3$. The series of metal alkoxides NaOR (R = Me, Et) and KOR (R = Me, Et, *t*-Bu) all gave 2 upon reaction with 1 in HMPA. The following procedure involving standard Schlenk techniques is typical: A 100-mL flask equipped with a side-arm stopcock was charged with 1.0 g (19 mmol) of NaOMe in a glovebox. The flask was fitted with a septum through which 20 mL (115 mmol) of nitrogen-purged HMPA was added. To this slurry was added 10 mL of Et_2O. Stirring was accomplished using a glass-encased stirring bar. A solution of 5.0 g (14 mmol) of 1 in 10 mL of Et_2O was added at room temperature. The reaction mixture became a light red-orange color after the additon of ca. 10 drops, and a deep red color developed with subsequent addition. The ^1H NMR of solution included the following: δ 0.20, 0.10, 0.08, and 0.04. The red intermediate was derivatized with bromoethane, and the products were identified, generally by GC/MS. In a typical preparation, the above solution was slowly added to 80 mL of hexane containing EtBr (5 mL, 67 mmol), and the reaction mixture was stirred for 2 h and hydrolyzed with 50 mL of dilute HCl. Workup involved hexane (100 mL) addition, extraction with water (3 × 400 mL), separation and drying the hexane layer over $MgSO_4$, flash evaporation, drying at 0.01 Torr, and crystallizing the white waxy solid from 95% EtOH/THF (7:1) to obtain a white powder with properties listed above for **3a**. Yield: 38%. GLC showed >98% purity with 1 as the primary impurity.

Under similar reaction conditions 2 was prepared from 1 with sodium metal, potassium metal, or KOMe each in the presence of 18-crown-6 and either HMPA/THF or HMPA/Et_2O. From 1 and phenyllithium, as the active reagent in HMPA/benzene/Et_2O, a complex mixture of products resulted. After derivatization of this mixture with ethyl bromide, the following products were identified by GC/MS: **3a**, $C_6H_5(SiMe_2)_nEt$ (n = 4–7), and $C_6H_5(SiMe_2)_5H$. The combination of 1 with $KSiMe_3$[25] followed by derivatization with bromoethane gave the following products as shown by GC/MS: 1, $Me_3Si(SiMe_2)_nEt$ (n = 4, 5), $Si_6Me_{10}Et_2$, $Si_6Me_9Et_3$, and $Si_6Me_{11}H$.

Electrochemical Generation of Intermediate 2. Cyclic voltammetry was performed in a three-compartment electrochemical cell from 0.0 to −3.5 V in an HMPA solution that was 0.1 M in 1 and 0.1 M in $LiClO_4$ as supporting electrolyte. The counter and working electrodes were platinum foil (0.5 cm × 0.5 cm) and platinum wire, respectively. The reference electrode was silver wire. The voltammogram showed a small reductive current at −1.9 V and a large reductive current at −3.0 V.

Controlled-potential electrolysis of the above solution was run for 5 h at room temperature. The working electrode was platinum foil (1 cm × 1 cm), and N_2 gas was slowly bubbled through the solution. The initial potential was −3.0 V, giving a current of 1 mA. However, the potential necessary to maintain this current began to drop, and after 15 min only −1.9 V was needed to give 1 mA of current. The remainder of the electrolysis was performed at −1.9 V. A red species was produced at the surface of the working electrode giving the solution a red-orange color. After electrolysis, this solution was added to a stirred solution of bromoethane (0.5 mL, 6.7 mmol) in 10 mL of hexane. Workup included adding 25 mL of H_2O and separating off the organic layer.

The organic layer was then analyzed by gas chromatography (230 °C, 45 mL/min of He, 8 ft × $^1/_8$ in., 8% SF-96 silicone on 80–100 mesh Chromosorb W-HP). The presence of both unreacted 1 and $Si_6Me_{11}Et$ was confirmed by comparing the retention times of the two observed peaks to those of a reference containing authentic samples of the two compounds.

Reaction of 1 with Excess Li or NaOMe. To a stirred solution of 1 (4.0 g, 12 mmol) in 20 mL of ethyl ether and 20 mL of HMPA was added lithium (0.33 g, 48 mmol). All of the lithium reacted within 24 h, and the solution was stirred for an additional 12 h (additional stirring probably not necessary). The red solution was added to bromoethane (5.0 mL, 65 mmol) in 40 mL of hexane cooled by an ice bath. Workup gave 2.2 g of a white solid. GC/MS analysis indicated that 83% of this material (44% overall yield) was $Si_6Me_{11}Et$ (m/e 362, M^+) with no indication of any $Si_6Me_{10}Et_2$ (m/e 376, M^+). A similar experiment beginning with a 2.6 mol of NaOMe to 1.0 mol of 1 ratio gave similar results.

Preparation of Undecamethyl(trimethylsilyl)cyclohexasilane ($Si_6Me_{11}SiMe_3$) (3b). To a stirred solution of 1 (4.0 g, 12 mmol) of 25 mL of ethyl ether and 25 mL of HMPA was added lithium (0.17 g, 24 mmol). After 12 h the red solution was added to chlorotrimethylsilane (4.0 mL, 32 mmol) in 25 mL of THF cooled by an ice bath. Workup gave 3.0 g of a white solid. GC/MS analysis indicated that 72% of this material was $Si_6Me_{11}SiMe_3$. Impurities were mostly starting material 1 and $Si_6Me_{11}H$. Thus, the overall yield of **3b** based on 1 was 46%. Three recrystallizations from ethanol–THF gave a white solid identified as **3b**, mp 114–116 °C (sealed tube); M_r 418 (calcd 407); ^1H NMR δ 0.14 ppm (m, Si–Me); ^{13}C NMR δ 1.31 (3 C), −3.16 (2 C), −4.63 (2 C), −4.83 (2 C), −5.15 (1 C), −6.49 (3 C), −11.22 (1 C); ^{29}Si NMR −9.4 (1 Si), −38.9 (2 Si), −40.9 (2 Si), −42.3 (1 Si), −82.2 (1 Si) ppm; GC/MS selected m/e (relative intensity) 406 (87, M^+), 333 (18), 318 (9), 259 (100). Anal. Calcd for $Si_7C_{14}H_{42}$: C, 41.31; H, 10.40; Si, 48.29. Found: C, 41.02; H, 10.77; Si, 48.44.

Conversion of 2 Back to 1. To a stirred solution of 1 (4.0 g, 12 mmol) in 25 mL of ethyl ether and 25 mL of HMPA was added lithium (0.17 g, 25 mmol). After 12 h an ^1H NMR of the red solution showed only the peaks due to 2. The solution was then added to dimethyl sulfate (5.0 mL, 53 mmol) in 50 mL of THF cooled by an ice bath. Workup followed by sublimation gave 2.0 g (50% yield) of a white solid identified as 1: mass spectrum m/e 348 (M^+); ^1H NMR 0.13 ppm (sharp singlet);[20] ^{13}C NMR −5.94 ppm.

In a second experiment, methyllithium (15 mmol) was added dropwise to a stirred solution of 1 (5.0 g, 14 mmol) in 20 mL of ethyl ether and 25 mL of HMPA cooled by an ice bath. After 1 h of stirring, the red solution was added to iodomethane (5.0 mL, 76 mmol) in 20 mL of ethyl ether cooled by an ice bath. Workup followed by recrystallization from ethanol–THF gave 2.0 g (40% yield) of a white solid which analyzed as above for 1.

Additional Derivatives of 2. The intermediate 2 was derivatized with a number of other reagents using procedures similar to those above.

Addition of CD_3I to a reactive solution prepared from MeLi and 1 in HMPA/Et_2O led to a 35% yield of (trideuteriomethyl)undecamethylcyclohexasilane, **3d**. GC/MS: 94% $Si_6Me_{11}CD_3$, m/e 351 (M^+); 6% Si_6Me_{12} (unreacted).

Addition of *n*-bromopropane to a reaction mixture from the combination of NaOMe, HMPA, Et_2O, and 1 led to a 36% yield of undecamethyl(*n*-propyl)cyclohexasilane, **3d**: mp 180–182 °C; GLC >98% purity; ^1H NMR δ 0.10 and 0.12 (33 H, $SiCH_3$), 0.40–1.90 (br m, 7 H, $CH_3CH_2CH_2Si$) ppm; ^{13}C NMR δ 20.2 (1 C), 18.8 (1 C), 15.6 (1 C), −5.0 (2 C), −5.5 (2 C), −5.7 (3 C), −6.1 (1 C), −6.2 (2 C), −7.8 (1 C) ppm; GC/MS, selected m/e (relative intensity) 379 (16), 378 (38), 377 (74), 376 (100, M^+), 260 (79), 259 (30), 201 (22), 199 (4). Anal. Calcd for $C_{14}H_{40}Si_6$: C, 44.60; H, 10.70. Found: C, 44.95; H, 10.92.

With isopropyl bromide, analogous reactions gave a 22% yield of undecamethylisopropylcyclohexasilane, **3e**: mp 102–104 °C; GLC >97% purity; ^{1}H NMR δ 0.40–2.00 (br m, 7 H, $CH_3)_2CHSi$); 0.25, 0.18, and 0.11 (3 br s, 33 H, $SiCH_3$) ppm; ^{13}C NMR δ 21.03 (2 C), 14.58 (1 C), −4.02 (2 C), −5.09 (2 C), −5.33 (2 C), −6.37 (1 C), −6.6 (3 C), −8.81 (1 C) ppm; GC/MS selected *m/e* (relative intensity) 379 (5), 378 (28), 377 (32), 376 (65, M$^+$), 333 (39), 259 (100), 201 (3), 199 (7) and impurities Si_6Me_{12} and $Si_6Me_{11}H$, 334 (M$^+$).

With chloromethyltrimethylsilane analogous reactions gave ((trimethylsilyl)methyl)undecamethylcyclohexasilane, **3f**: bp 120 °C/0.5 Torr, 16% yield; ^{1}H NMR δ 0.182 and 0.122 (33 H, $SiCH_3$), 0.03 (9 H, $Si(CH_3)_3$), −0.16 (2 H, $SiCH_2Si$) ppm; ^{13}C NMR δ 1.92 (3 C), −3.02 (1 C), −4.72 (1 C), −5.06 (2 C), −5.51 (1 C), −5.57 (2 C), −5.72 (2 C), −6.10 (2 C), −6.26 (1 C) ppm; ^{29}Si NMR δ 1.81 (1 Si), −40.6 (1 Si), −41.6 (2 Si), −42.0 (2 Si), −42.5 (1 Si); GC/MS selected *m/e* (relative intensity) 413 (7), 422 (32), 421 (52), 420 (100), 347 (22), 332 (3), 373 (57). Anal. Calcd for $C_{15}H_{44}Si_7$: C, 42.78; H, 10.53; Si, 46.69. Found: C, 42.87; H, 10.61; Si, 46.62.

Reaction of Si_5Me_{10} with MeLi. Under typical reaction conditions, Si_5Me_{10} was allowed to react with MeLi and then derivatized with EtBr. No Si_5Me_9Et was observed by GC/MS although a significant amount (~20%) of **3a** was detected.

Reactions of Decamethyltetrasilane (Si_4Me_{10}). To a stirred solution of Si_4Me_{10} (2.8 g, 11 mmol) in 7.0 of ethyl ether and 7 mL of HMPA cooled by an ice bath was added methyllithium (11 mmol) dropwise over 20 min. After approximately half of the methyllithium was added, the solution had the typical red color. Upon further addition the color faded until at the end of the addition the solution was pale orange-red. After 30 min of stirring, the solution was unchanged in color and was added to bromoethane (2.0 mL, 27 mmol) in 25 mL of hexane cooled by an ice bath. Workup followed by vacuum distillation (25–70 °C, 0.1 Torr) gave 0.6 g of an oily liquid. GC/MS analysis indicated that the product mixture contained a number of acyclic species including apparent isomers whose formulas and *m/e* for M$^+$ (with relative intensities) are summarized: $Me(SiMe_2)_3Me$, 204 (17); $Me(SiMe_2)_3Et$, 218 (25, 2 isomers); $Et(SiMe_2)_3Et$, 232 (5, 2 isomers); $Me(SiMe_2)_4Me$, 262 (27, unreacted starting material and one isomer); $Me(SiMe_2)_4Et$, 276 (12); $Et(SiMe_2)_4Et$, 290 (2, 3 isomers); $Me(SiMe_2)_5Me$, 320 (3); $Me(SiMe_3)_5Et$, 334 (2). Similar results were obtained from lithium metal and **1** as the initial reagents.

Reactions of Lithium with Octaphenylcyclotetrasilane (Si_4Ph_8). To a stirred solution of Si_4Ph_8 (3.0 g, 4.1 mmol) in 20 mL of ethyl ether and 20 mL of HMPA was added lithium (0.06 g, 8.6 mmol). After 12 h all of the lithium had reacted to give a dark purple solution. This solution was added to iodomethane (2.0 mL, 30 mmol) in 40 mL of hexane cooled by an ice bath. Workup including back-extraction of the aqueous layer with 40 mL of benzene gave 1.2 g of a white solid. Because of low volatility, analysis was done by direct inlet mass spectroscopy. The MS analysis indicated the presence of $Me(SiPh_2)_4Me$ (*m/e* 758, M$^+$) with no indication of *cyclo*-$(SiPh_2)_3SiPhMe$ (calcd *m/e* 666, M$^+$).

Analysis of Gaseous Reaction Products. For reactions with lithium metal, specified amounts of **1** and HMPA were added to a 50- or 100-mL Schlenk flask, and a storage vessel containing lithium was fitted to the top of the flask. This apparatus was evacuated (HMPA has negligible vapor pressure at room temperature), closed, and then tilted so that the lithium fell into the solution. The mixture was stirred, and the pressure was monitored. After completion of the reaction, some of the gas sample was allowed to expand into an evacuted flask and analyzed by mass spectroscopy. Runs included the following: (A) 2.0 g of **1** (5.7 mmol), 45 mL of HMPA, and 0.04 g of lithium (5.8 mmol); (B) 2.0 g of **1** (5.7 mmol), 20 mL of HMPA, and 0.005 g of lithium (0.7 mmol); (C) a blank involving the addition of 0.03 g of lithium (4.3 mmol) to 10 mL of pure HMPA.

The analysis of gaseous products from the reaction of **1** with methyllithium followed a similar procedure except that the ethyl ether from the methyllithium solution was condensed out prior to evacuation and the order of addition was reversed. In the reaction, **1** (1.0 g, 2.9 mmol) was added to methyllithium (3.1 mmol) in 16 mL of HMPA. An ^{1}H NMR of the solution after reaction showed that only 75% of the starting material **1** reacted indicating the destruction of some of the methyllithium prior to reaction. Indeed, evolution of gas was observed when 0.1 mL of methyllithium solution was added to 0.1 mL of HMPA in a 2-mm i.d. glass tube.

For the reaction involving KOMe/HMPA, a slightly different apparatus was used. Into a 50-mL flask was charged 0.27 g (3.8 mmol) of KOMe, 1.0 g (3.8 mmol) of 18-crown-6, and 10 mL of THF. This flask was connected to a 10-mL storage tube which had been charged with 1.1 g (3.2 mmol) of **1**. This apparatus was subject to two freeze–pump–thaw cycles and then allowed to equilibrate at room temperature, whereupon the pressure of the THF reached 0.18 atm. With stirring, **1** was quickly added (before THF absorption could make it sticky). Within 2 min the pressure increased to 0.36 atm in a volume of 223 mL. Accounting for the THF, 1.6 mmol of a gas was produced. The deep red reaction mixture was stirred for an additional 10 min. A portion of the gas was examined by MS (CEC). The THF masked all ions with *m/e* > 10, but *m/e* 2 had increased by a 14-fold factor relative to the background, confirming the presence of H_2.

Electron Spin Resonance. To prepare a sample of **2** for the ESR study, 100 μL of a 0.1 M solution of **1** (0.01 mmol) in 1/1 (v/v) HMPA/ethyl ether was added to a capped 1-mm i.d. ESR quartz sample tube. Into the tube was syringed 40 μL (0.08 mmol) of methyllithium solution. The mixture turned light yellow-red. No ESR signal could be observed.

In a low-temperature run, 100 μL of a 0.01 M solution of **1** (0.001 mmol) in 4:1 (v/v) ethyl ether/HMPA was added to the quartz sample tube. The capped tube was then placed in the ESR cavity and adjusted so that the measurement would be taken just below the solvent interface level. The cavity and tube were then cooled to −75 °C and 20 μL of a 0.2 M methyllithium (0.004 mmol) in ether solution was syringed into the tube. Repeated scans were taken as the cavity was allowed to warm to 0 °C. No ESR signals were observed. Upon removal of the tube, the solution interface region had the expected light yellow-red color indicating that reaction had taken place.

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