ported to be 99.99% pure after calcination to remove the carbon content.

However, there is another factor which may contribute to the anomalous behavior of Pt/Filtros. Unlike the other catalysts, Pt/Filtros cooled in hydrogen gave a value of $N_{\rm cp}$ only 0.7 that of the catalyst cooled in helium. A similar difference between cooling this catalyst in hydrogen vs. helium was observed in the hydrogenation of ethylene at temperatures below 0 °C.[31] This may be the manifestation of a higher solubility of hydrogen in large particles of platinum than in small ones.

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Silicon Substitution for the Stabilization of Silicenium Ions

Joseph B. Lambert*[1] **and Hsiang-ning Sun**

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received May 14, 1976*

Abstract: Systems have been examined in which a silicenium ion, if produced by hydride transfer ($R_3Si\text{-}H + (C_6H_5)_3C^+\ ClO_4^-$), would be stabilized inductively by tetravalent silicon attached directly to the electron-deficient silicon. The systems examined in this fashion (triphenylsilane, methyldiphenylsilane, pentaphenyldisilane, pentamethyldisilane, and tris(trimethylsilyl)silane) all exhibited hydride transfer in CH_2Cl_2 or CH_3CN/1,4-dioxane at −20 to −30 °C, by observation of the production of $(C_6H_5)_3C\text{-}H$ and (after reaction with $NaBD_4$) of recovered $R_3Si\text{-}D$. The NMR spectrum of methyldiphenylsilane after reaction with $(C_6H_5)_3C^+\ ClO_4^-$ and prior to reaction with $NaBD_4$ showed loss of the methyl doublet and the Si-H multiplet and appearance of a methyl singlet and a C-H peak. None of the systems exhibited conductance prior to reaction with $NaBD_4$. On the basis of the lack of conductance and the common behavior of all systems, including those such as $(C_6H_5)_3SiH$ known not to produce silicenium ions, we conclude that the intermediates in these reactions have the covalent structure $R_3Si\text{-}O\text{-}ClO_3$ or are tight ion pairs. Free silicenium ions are not produced, and silicon substitution offers no special stabilization under these conditions.

Trivalent, positively charged silicon (R_3Si^+) has been an elusive chemical species.[2] Although there is evidence from appearance potentials and mass spectral fragmentation that silicenium[3] ions exist in the gas phase,[4] evidence in the condensed phase is very rare. The chemistry of silicon is characterized by coordination expansion rather than contraction because of the availability of low-energy d orbitals. Thus, pentavalent siliconium[3] ions have been prepared and studied.[5]

Traditional attempts to stabilize silicenium ions have been through p_π-p_π ($C \rightarrow Si^+$) donation, which has been successful in carbenium ion chemistry ($C \rightarrow C^+$). There are two drawbacks to this approach. First, carbon is more electronegative (2.55) than silicon (1.90), so that a carbon substituent automatically destabilizes a silicenium ion inductively. Second, p_π-p_π overlap between carbon and silicon is considerably poorer than between carbon and carbon because of the differences in orbital dimensions. Thus, phenyl should have at best a poor stabilizing effect through conjugation and at worst a destabilizing effect through induction. A more viable approach we felt was to choose substituents on silicon that can offer inductive stabilization and to ignore conjugative substituents that stabilize carbenium ions. The types of substituents we have examined to date contain silicon as the atom attached to the silicon that will bear charge in the silicenium ion ($R_3Si\text{-}Si^+$). The principal stabilizing influence of the silicon substituent is intended to be electrostatic induction of charge. It is also possible that σ delocalization, which has been established to exist in polysilanes,[6] can provide some stabilization. The series we have chosen to examine is R_3SiX, R_3SiR_2SiX, and $(R_3Si)_3SiX$, in which the central silicon atom progressively bears zero, one, and three silicon substituents and X is a group capable of being removed to generate trivalent, positive silicon.

Generation of a silicenium ion must be attempted in a medium of extremely low nucleophilicity in order to avoid coordination expansion to pentavalent silicon. For this reason, we have chosen to avoid reactions that attempt the generation via loss of halogen ($R\text{-}X \rightarrow R^+ + X^-$) because of the difficulty of masking the nucleophilicity of the leaving group (X^-). Hydride exchange reactions (eq 1), which have also been used

$$R_3SiH + (C_6H_5)_3CClO_4 \rightarrow (C_6H_5)_3CH + R_3SiClO_4 \quad (1)$$

widely to generate carbenium ions, offer distinct advantages. The anion can be selected to have very low nucleophilicity. This procedure has been used recently in studies of reported silicenium ion generation.[7] Both starting materials and products give clear NMR spectra that can be used to follow the reaction. In the present investigation we report the results of the hydride exchange reaction on silicon hydrides in which the central silicon atom bears silyl substituents.

Results and Discussion

Three types of experiments were performed to test for the existence of silicenium ions in the reactions of these silicon hydrides. (1) Reaction of the silicon hydrides with triphenylmethyl perchlorate (eq 1) and examination of the products formed from quenching the reaction with sodium borodeuteride (eq 2) (the method of Corey).[7]

$$R_3SiClO_4 + NaBD_4 \rightarrow R_3SiD \quad (2)$$

Production of triphenylmethane (eq 1) and regeneration of the starting material, with hydride replaced by deuteride (eq 2), would indicate that hydride had indeed been abstracted.[7] (2) Examination of the NMR spectrum at all stages of the reaction (eqs 1 and 2). This experiment gives information about destruction of the starting material and formation of the final product, as well as direct data on the intermediate formed by eq 1. (3) Examination of the conductance of the solutions produced by the hydride abstraction reaction in order to obtain specific information about the ionic nature of the intermediate formed in eq 1.

Product Studies. Triphenylsilane (**1**), methyldiphenylsilane (**2**), pentaphenyldisilane (**3**), pentamethyldisilane (**4**), and

$(C_6H_5)_3SiH$ **1**	$CH_3(C_6H_5)_2SiH$ **2**
$(C_6H_5)_3Si(C_6H_5)_2SiH$ **3**	$(CH_3)_3Si(CH_3)_2SiH$ **4**
$[(CH_3)_3Si]_3SiH$ **5**	$(C_6H_5)_2SiH_2$ **6**

tris(trimethylsilyl)silane (**5**) were allowed to react with triphenylmethyl perchlorate in methylene chloride and in 1/1 acetonitrile/1,4-dioxane. The former solvent is relatively noninteracting, and the latter is capable of considerable stabilization of ionic intermediates. The reaction mixtures were quenched in excess $NaBD_4$, and the organics were isolated. In all cases, about 80% or more of triphenylmethane could be obtained, and the corresponding silane-*d* was produced. We also examined the reaction with diphenylsilane (**6**) and found that *both* hydrogen atoms were abstracted under these conditions. There is a host of evidence that simple silanes such as **1**, **2**, and **6** do not form silicenium ions, so that we were loathe to conclude from the successful hydride abstraction in all six systems that free ionic trivalent silicon was produced. The other admissible conclusion is that such an intermediate was formed in none, but that the hydride abstraction reaction passes through nonionic intermediates. To clarify the situation, we examined the hydride abstraction reaction of these silanes in detail through their NMR spectra and their conductance titration curves.

NMR Spectra. The spectrum of methyldiphenylsilane in 1/1 acetonitrile/1,4-dioxane is given in Figure 1 (top). The methyl peak is a doublet centered at δ 0.76, and the Si-H peak is a quartet at 5.08. The hydride abstraction reaction of eq 1 should result in the appearance of the C-H singlet of triphenylmethane and in the disappearance of the methyl doublet and the Si-H quartet of the silane. All reactions were carried out at −20 to −30 °C, but NMR spectra were recorded at room temperature.

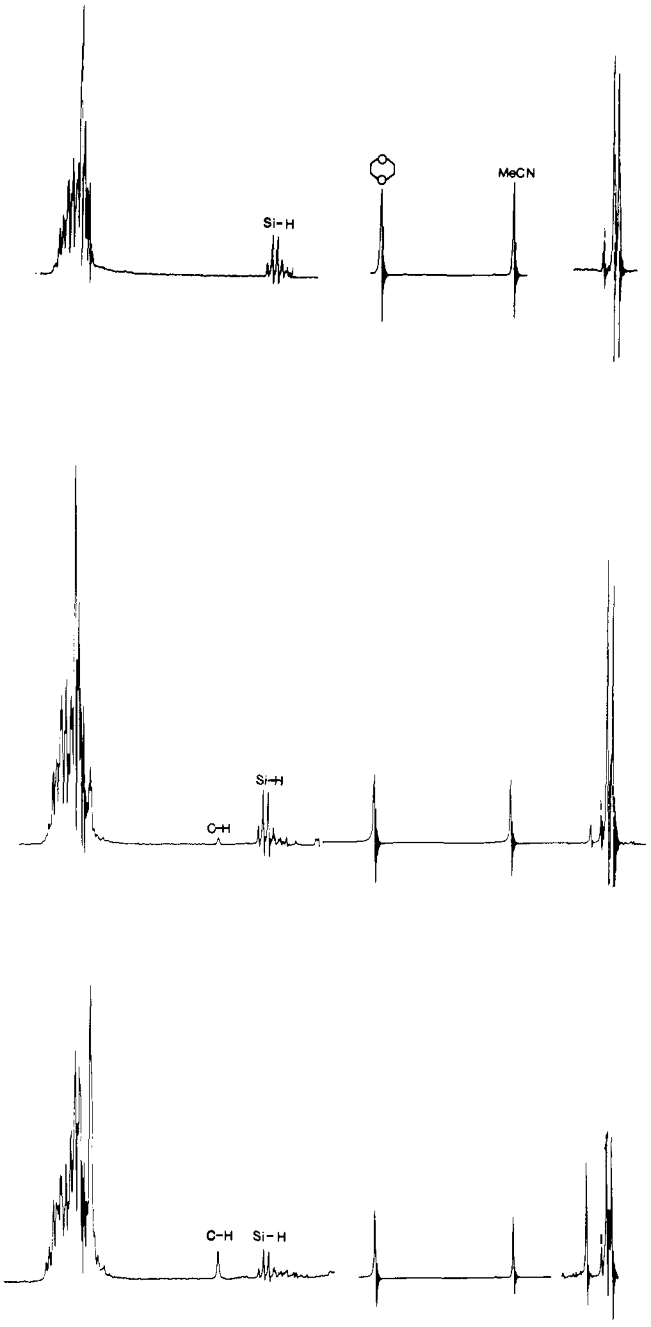

Figure 1. (Top) The 60-MHz proton NMR spectrum of methyldiphenylsilane (**2**) in 1/1 acetonitrile/1,4-dioxane at room temperature. An impurity is indicated by the letter i. (Middle) The proton spectrum of the same solution, following the addition of 0.05 equiv of triphenylmethyl perchlorate. (Bottom) The proton spectrum of the same solution, following the addition of a total of 0.3 equiv of triphenylmethyl perchlorate.

Figure 1 (middle) shows the spectrum produced by the addition of 0.05 equiv of triphenylmethyl perchlorate to methyldiphenylsilane in the same solvent. The C-H resonance of triphenylmethane is just visible at δ 5.7. In addition, a singlet has appeared just to the left (downfield) of the methyl doublet. This singlet must be due to the methyl group in whatever intermediate is produced from the silane by hydride abstraction. The fact that the doublet splitting has disappeared in the resonance of the intermediate demonstrates that the Si-H bond has been broken. In Figure 1 (bottom), the addition of about 0.3 equiv of the perchlorate has clearly increased the C-H peak of triphenylmethane and the methyl singlet of the intermediate silyl species at the expense of the Si-H singlet and the methyl doublet of the starting silane. The reaction is extremely clean, and no other product peaks are observed.

Thus, the reaction of methyldiphenylsilane with triphenylmethyl perchlorate does result in hydride abstraction to form an intermediate whose NMR spectrum is consistent with the material on the right side of eq 1. Conversion of an alkane to a carbenium ion normally results in a considerable downfield shift of a methyl group attached to the charge-bearing carbon, e.g., 2.1 ppm for $CH_3(C_6H_5)_2CH \rightarrow CH_3(C_6H_5)_2C^+$.[8] The new methyl resonance formed by hydride abstraction of methyldiphenylsilane, however, is shifted downfield only a modest amount (~0.4 ppm) from the methyl resonance of the starting material (best seen in Figure 1, bottom). Because the solvent, acetonitrile/1,4-dioxane, is able to provide coordination, it is possible that the intermediate is a complex of the type $CH_3(C_6H_5)_2Si\text{-}S^+$, where S is the solvent. In such an intermediate, the positive charge resides not on silicon but on the oxygen of dioxane or the nitrogen of acetonitrile. Such a complex would explain the small downfield shift of the methyl resonance and the common behavior of all the silanes (**1-5**).

This hypothesis can be readily tested by carrying out the same experiments as those illustrated in Figure 1, but with a very poorly coordinating solvent. For this purpose we chose methylene chloride. Although this solvent obscures the Si-H and C-H resonances, the methyl resonances are easily observed. Figure 2 (top) presents the result of the addition of about 0.4 equiv of triphenylmethyl perchlorate to methyldiphenylsilane. The conditions are similar to those of Figure 1 (bottom), and the results are essentially the same. The methyl doublet of the starting material has declined in intensity, and the methyl singlet of the intermediate has appeared at nearly the same chemical shift as in the coordinating solvent. We conclude therefore that the intermediate is not coordinated to solvent in either acetonitrile/1,4-dioxane or in methylene chloride, because of the similarity of the results. Figure 2 (middle) shows the final product from the addition of an excess of triphenylmethyl perchlorate to methyldiphenylsilane. The methyl doublet has disappeared entirely, and the methyl singlet of the intermediate is the only observable highfield resonance. Because of the relatively small downfield shift on hydride abstraction, it is doubtful that appreciable charge buildup has taken place on silicon. If the solvent is not involved in coordination, then we must conclude that the gegenion perchlorate is coordinated to or otherwise closely associated with silicon, despite its extremely low nucleophilicity. We tentatively assign the covalent structure **6** or the tight ion pair **7** as the structure of the intermediate.

$R_3Si\text{-}O\text{-}ClO_3$ **6**

$[R_3Si^+][^-OClO_3]$ **7**

Quenching of the intermediate (Figure 2, middle) with sodium borodeuteride and isolation (in CS_2/dimethoxyethane) gave materials with the proton spectrum shown in Figure 2 (bottom). There are resonances from the C-H of triphenylmethane and from an unsplit methyl. Isolation of the starting material, methyldiphenylsilane, proved that the methyl singlet must come from this molecule. The absence of splitting indicates that the Si-H bond has been replaced by Si-D. The Si-H quartet is also missing. These results are consistent with those discussed in the previous section.

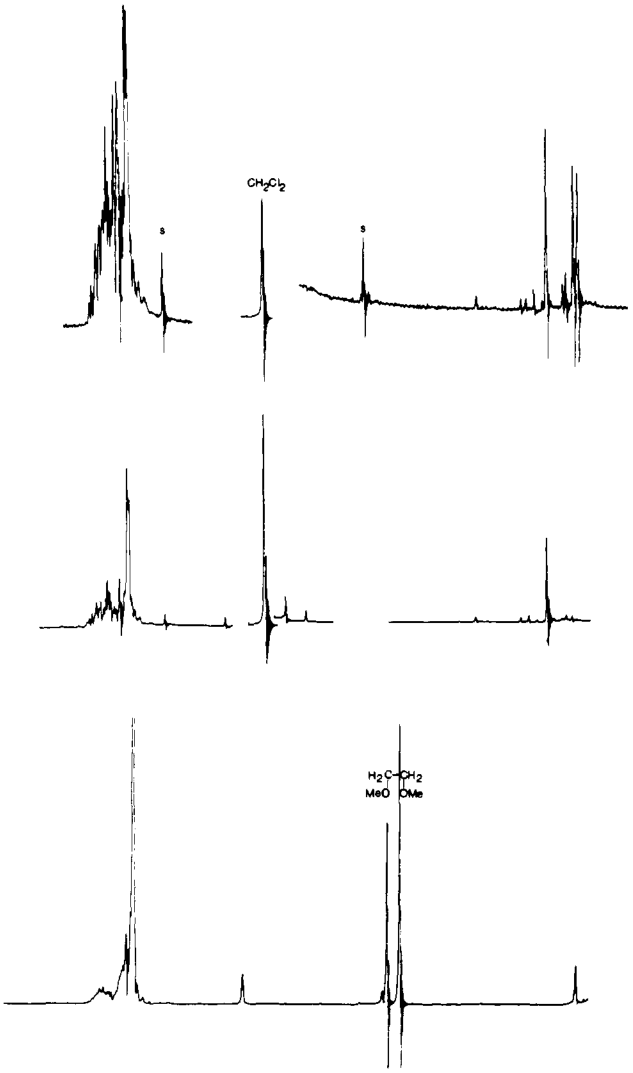

Figure 2. (Top) The 60-MHz proton NMR spectrum of methyldiphenylsilane (**2**) in CH_2Cl_2 at room temperature, following the addition of 0.4 equiv of triphenylmethyl perchlorate. Spinning sidebands of the solvent are indicated by the letter s. (Middle) The proton spectrum of the same solution, following the addition of an excess of triphenylmethyl perchlorate. (Bottom) The products from the reaction of the above solution and $NaBD_4$, isolated and placed in CS_2/1,2-dimethoxyethane.

It should be noted that the spectra of Figures 1 and 2 show distinct methyl resonances for the starting silane and for the intermediate. Thus, at room temperature the equilibrium of

$$R_3Si\text{-}H + R_3SiClO_4 \rightleftharpoons R_3SiClO_4 + R_3Si\text{-}H \quad (3)$$

eq 3 is slow on the NMR time scale. Rapid interchange of hydride would have produced an averaged methyl signal (and hydride signal).

The intermediate (Figure 2, middle) was also quenched in water, and a mixture of triphenylmethane and triphenylsilanol was produced. The silanol is the expected product from hydrolysis of the perchlorate complex **6**. The result is not definitive, however, because of the possibility of acid-induced hydride shift during hydrolysis.[9]

Analogous NMR results were also obtained with triphenylsilane (**1**), pentaphenyldisilane (**3**), and the tetrasilane (**5**).

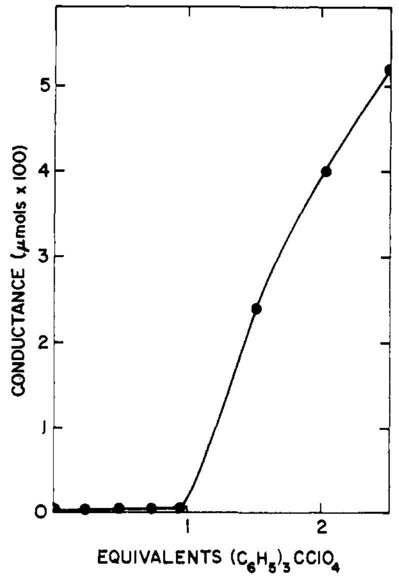

Figure 3. The conductance of a solution of methyldiphenylsilane (2) in CH_2Cl_2 at −20 °C, as a function of added triphenylmethyl perchlorate.

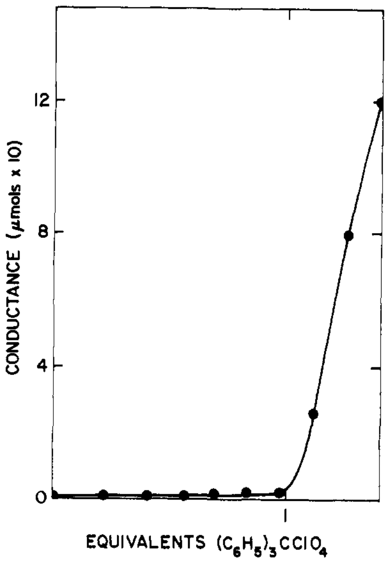

Figure 4. The conductance of a solution of tris(trimethylsilyl)silane (5) in CH_2Cl_2 at −20 °C, as a function of added triphenylmethyl perchlorate.

Conductance Studies. The product and the NMR studies show that treatment of silanes **1–5** with triphenylmethyl perchlorate results in hydride abstraction. The common behavior of all substrates and the small downfield shift of the CH_3-Si resonance suggests that very little charge is present on silicon. The data therefore favor a covalent or ion pair structure of the type **6** or **7**, rather than a truly ionic silicenium ion **8**. To

$$R_3Si^+ \quad ClO_4^-$$

8

distinguish these possibilities further, we examined the conductance of solutions identical with those studied by NMR (Figure 2). Conductometric titrations were carried out at −20 to −30 °C by the slow addition of triphenylmethyl perchlorate in CH_2Cl_2 to the silanes **1–5**, also in CH_2Cl_2. The titration curves for methyldiphenylsilane (**2**) and tris(trimethylsilyl)silane (**5**) are given, respectively, in Figures 3 and 4. The other three silanes produced essentially identical curves. No appreciable conductance was observed until an equiv of triphenylmethyl perchlorate had been added. Above the equivalence point, conductance was observed from dissociation of the titrant, triphenylmethyl perchlorate, itself. It is clear from these results that the intermediate formed in the hydride abstraction reaction has little ionic character, consistent with a covalent species (**6**) or with nonconducting tight ion pairs (**7**).

Conclusions

Silyl substitution offers no palpable stabilization of positive charge on trivalent silicon. Abstraction of a proton from pentaphenyldisilane (**3**) or pentamethyldisilane (**4**) would produce a silicenium ion with a single silyl substituent on the charge-bearing silicon, and tris(trimethylsilyl)silane (**5**) would produce an ion with three silyl substituents. Nonetheless, these three substrates exhibit the same behavior as the two simple alkyl- or aryl-substituted systems, triphenylsilane (**1**) and methyldiphenylsilane (**2**). This behavior consists of reaction with triphenylmethyl perchlorate to produce a single intermediate no longer possessing a Si-H bond. The intermediate from **2** exhibits a methyl resonance that is shifted downfield about 0.4 ppm; reaction with $NaBD_4$ regenerates the starting material, with the Si-H bond replaced by Si-D. Identical behavior is observed in acetonitrile/1,4-dioxane and in methylene chloride. The intermediate is essentially nonconducting. On the basis of previous studies,[2] it is unlikely that the simple alkyl and aryl systems (**1** and **2**) produce a silicenium ion. The common behavior of all five substrates, the small methyl shift in the proton NMR spectrum on formation of the intermediate, and the absence of conductance indicate that hydride abstraction of **1–5** leads to the formation of a covalent or tight ion pair silicenium perchlorate (**6** or **7**), despite the low nucleophilicity of perchlorate. Reaction of $NaBD_4$ with this material, rather than with a free silicenium ion, regenerates the starting material.

Recent reports[7] of the formation of silicenium ions were based on hydride abstraction from a silane to produce an intermediate that regenerates the starting material on reaction with $NaBD_4$. We have demonstrated that such observations alone are not sufficient to prove the existence of a free silicenium ion. Until specific evidence on the nature of the intermediate by conductance or magnetic resonance is reported, the actual structure of the intermediates recently reported must be considered unproved, as the authors themselves point out.[7,20]

Experimental Section

Proton magnetic resonance spectra were recorded at 60 MHz on a Perkin-Elmer R20B spectrometer. Conductances were measured with an Industrial Instruments Inc. conductance bridge, Model RC 16B2. All reactions were carried out under dry N_2. Solvents and reagents were distilled from appropriate drying agents and stored over molecular sieves. Dimethoxyethane (DME) was distilled first from Na then from $NaBH_4$ prior to use. Melting points (uncorrected) were determined with a Thiele tube.

Triphenylsilane (1) was obtained by reduction of triphenylchlorosilane (Ventron) in ethyl ether with $LiAlH_4$.

Methyldiphenylsilane (2). The addition of 0.22 mol of C_6H_5MgBr to 11.5 g (0.1 mol) of methyldichlorosilane (Ventron) followed by hydrolysis with 50 ml of 10% HCl gave 14.0 g (72%) of the desired product, bp 116–117 °C (2.5 mm) [lit.[18] 152–154 °C (25 mm)].

Hexaphenyldisilane. Triphenylchlorosilane (18 g, 0.06 mol) and 1.5 g (0.065 mol) of Na were refluxed in 50 ml of dry xylene for 12 h with vigorous stirring. The purple-white solid was filtered under N_2 and then added in small portions to 150 ml of absolute ethanol to destroy the excess Na. The white solid was filtered and washed with 2 × 15 ml of 20% ethanol to leave 14 g (90%) of the desired product, mp >360 °C (lit.[10] 368–370 °C).

Sodium–Potassium Alloy. To 100 ml of xylene was added 40 g (1.02 mol) of K and 8 g (0.35 mol) of Na. The reaction mixture was heated until both metals melted. The molten metals were forced to coalesce with the aid of a glass rod. The liquid alloy was ready for use after cooling to room temperature.

Triphenylsilylpotassium. To a solution of 5.2 g (0.01 mol) of hexaphenyldisilane suspended in 5.0 ml of dry ether was added slowly 1.3 ml of the Na-K alloy via a syringe. A green color developed after the reaction mixture was stirred for about 5 min. Another 50 ml of ether was added, and the mixture was stirred at room temperature for 48 h. At the end of this period, a tan-colored suspension was formed. Small portions of Hg were added to destroy the excess alloy. The solution was then ready for use.

Pentaphenylchlorodisilane. A triphenylsilylpotassium solution prepared according to the procedure described above was added fairly rapidly to 4 g (0.016 mol) of diphenyldichlorosilane (Ventron) dissolved in 40 ml of ether. After all the reagent had been added, the reaction mixture was stirred at room temperature for 4 h and then filtered under N_2. The solvent was removed at reduced pressure to leave a semisolid, which was recrystallized from pentane to give 3.3 g (45%) of the desired product, mp 155-156 °C (sealed tube) (lit.[11] 154-155 °C).

Pentaphenyldisilane (3).[12] Pentaphenylchlorodisilane (1.0 g, 2.2 mmol) was dissolved in 50 ml of dry ether. This solution was added to a suspension of 1.0 g (2.8 mmol) of $LiAlH_4$ in 100 ml of ether. The solution was refluxed for 24 h. The reaction mixture was then hydrolyzed with a mixture of 3.0 g of ice and 0.5 ml of 36% HCl. The organic layer was separated and dried (Na_2SO_4). Removal of the solvent left a semisolid. Recrystallization from a 1/1 mixture of CS_2 and hexane afforded 0.4 g (40%) of the desired product, mp 126 °C (lit.[12] 128-129 °C). A Si-H stretching frequency at 2130 cm^{-1} was observed in the ir spectrum, and the NMR spectrum showed a singlet at δ 5.10 for Si-H.

Hexamethyldisilane.[13,14] Potassium metal (39 g, 1 mol) in a three-necked flask equipped with a condenser was heated under dry N_2 to melt, and 217 g (2.0 mol) of trimethylchlorosilane (Aldrich) was added dropwise. After all the chlorosilane had been added, the reaction mixture was refluxed overnight. Vacuum distillation condensed all low-boiling liquids in a dry ice-acetone bath. These materials were then fractionated through a 20-cm Vigreaux column to give 54 g (74%, based on K consumed) of the desired product, bp 112-113 °C (lit.[13] 112-113 °C).

Pentamethylchlorodisilane.[15] Hexamethyldisilane (20.0 g, 0.135 mol) and $AlCl_3$ (18.0 g, 0.135 mol) were mixed at 0 °C. To this solution was added 10.0 g (0.135 mol) of acetyl chloride with vigorous stirring below 20 °C. After all the CH_3COCl had been added, the reaction mixture was stirred at room temperature overnight. All volatile liquids were collected in a dry ice-acetone bath at reduced pressure. The mixture was then fractionated through a 20-cm Vigreaux column to give 16.0 g (74%) of the desired product, bp 134-136 °C [lit.[14] 92 °C (204 mm)].

Pentamethyldisilane (4).[14] To a suspension of 1.0 g (0.026 mol) of $LiAlH_4$ in 40 ml of *n*-hexyl ether was added dropwise 3.2 g (0.020 mol) of pentamethylchlorodisilane dissolved in 15 ml of *n*-hexyl ether. After all the chlorosilane had been added, the reaction mixture was stirred at room temperature for 1 h. Excess $LiAlH_4$ was destroyed with a mixture of 5 g of ice and 0.5 ml of 36% HCl. The organic layer was separated, dried, and distilled to give 1.7 g (64%) of the desired product, bp 100 °C [lit.[14] 97.5 °C (715 mm)].

Tetrakis(trimethylsilyl)silane.[16] To 94.2 g (0.86 mol) of trimethylchlorosilane, dissolved in 200 ml of THF, and 15.1 g (2.15 mol) of Li wire was added 20 ml of a solution of 30 g (0.18 mol) of $SiCl_4$ (Ventron) dissolved in 150 ml of THF. After 3 h of stirring at room temperature, dropwise addition of the $SiCl_4$ was completed, and the reaction mixture was stirred overnight at room temperature. Unreacted Li wire and insoluble salts were removed by filtration under N_2. The homogeneous dark brown solution was hydrolyzed by addition to a mixture of 40 g of crushed ice and 15 ml of 36% HCl. The organic layer was separated and dried (Na_2SO_4), and the solvent was removed under reduced pressure to give a residue of solid and semisolid. Sublimation [85 °C (1 mm)] gave 37.0 g (65%) of the pure product, mp 319 °C (sealed tube) (lit.[16] 319-322 °C).

Tris(trimethylsilyl)silane (5). The pentasilane (10 g, 0.031 mol) was dissolved in a mixture of 32 ml of THF and 8.0 ml of ether. To this solution was added slowly 16 ml of 2.0 M CH_3Li solution via a syringe with vigorous stirring. The resulting yellow solution was stirred for another 2 h and then hydrolyzed with a mixture of 25 g of crushed ice and 5 ml of 36% HCl. The organic layer was separated and dried (Na_2SO_4). After removal of the solvent, the residue was distilled to give 6.4 g (70%) of the desired product, bp 78-85 °C (7-9 mm) [lit.[17] 80-83 °C (8 mm)].

Triphenylmethyl Perchlorate.[19] Triphenylcarbinol (Aldrich, 1.0 g, 3.8 mmol) was dissolved in 15.0 ml of acetic anhydride. To this solution was added dropwise 1.25 ml of 70% $HClO_4$ with the temperature kept below 20 °C. After all the $HClO_4$ had been added, the solution was kept in an ice bath for 1 h. After removal of the supernatant with a pipet, the residue was washed with 5 × 20 ml of dry ether. The solid was then dried under vacuum for 3 h to give 1.20 g (70%) of the desired product. The product was kept in the dark at −17 °C in a refrigerator for later use.

Conductometric Titrations. A premeasured amount of the appropriate silyl hydride was dissolved in 140 ml of CH_2Cl_2 in an oven-dried flask under N_2. The solution in the conductance cell was immersed in a cold bath containing ether and dry ice (about −20 °C). The temperature of the bath was controlled by constantly adding dry ice during the titration process. The solution was allowed to reach equilibrium temperature by stirring for 5 min. A triphenylmethyl perchlorate solution was prepared in the same solvent with known concentration. After each addition (about 10% of the total silane), the solution was stirred for 5 min to assure completion of the reaction and attainment of thermal equilibrium, and the conductance was then measured (Figures 3 and 4).

The trapping experiment (eq 1 and 2)[7] utilized 0.4475 g (2.26 mmol) of methyldiphenylsilane (**2**) dissolved in 10 ml of dry CH_2Cl_2 and cooled at −20 to −30 °C. To this solution was added dropwise 0.7692 g (2.26 mmol) of triphenylmethyl perchlorate in 35 ml of CH_2Cl_2. The color of the perchlorate was discharged immediately. After all the perchlorate had been added, the reaction mixture showed a very faint brown color. This solution was quickly added to an ice-cold DME solution (25 ml) containing excess $NaBD_4$ (0.5 g). The faint brown color was discharged immediately. All solvents were then removed under high vacuum. Another 50 ml of CH_2Cl_2 was added to the residue, and the excess $NaBD_4$ was filtered off. The CH_2Cl_2 solution was then added to 5 ml of H_2O, and the solution was stirred at room temperature for 30 min. The organic layer was separated and dried (Na_2SO_4). After removal of the solvent, the residue was dissolved in CS_2 with 10% DME. The NMR spectrum of this residue is shown in Figure 2 (bottom). Another separate run was carried out on a tenfold larger scale with $NaBH_4$. The products were separated by vacuum distillation and identified by melting point and NMR. The NMR spectra were also recorded for aliquots taken with different amounts of added perchlorate from this reaction and another similar reaction performed in a 1/1 mixture of CH_3CN and 1,4-dioxane (Figures 1 and 2). These hydride extractions were very exothermic, so that temperature control (<−20 °C) was essential. Otherwise, various decomposition products could be observed. It seems, however, that once the silyl perchlorate is formed, it is stable up to 35 °C for several hours.

References and Notes

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(20) NOTE ADDED IN PROOF: These same conclusions have been reached independently by Professors T. J. Barton and K. Mislow.