

Tris(triisopropylsilyl)silane and the Generation of Bis(triisopropylsilyl)silylene

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Tris(triisopropylsilyl)silane ($(iPr_3Si)_3SiH$) has been synthesized and studied by X-ray and neutron diffraction. It possesses an unusual structure in which the four silicon atoms are nearly coplanar, $\angle Si-Si-Si = 118.41(5)^\circ$. The Si-H distance is found to have a normal value of 1.506(2) Å. Thermal and room-temperature photochemical decomposition of $(iPr_3Si)_3SiH$ leads to the elimination of iPr_3SiH and the generation of bis(triisopropylsilyl)silylene, $[(iPr_3Si)_2Si:]$. Reactions of $(iPr_3Si)_2Si:$ include precedented insertions into H-Si bonds and addition to the π -bonds of olefins, alkynes, and dienes. Despite theoretical predictions of a triplet ground state for $[(iPr_3Si)_2Si:]$, stereospecific addition to *cis*- and *trans*-2-butene was observed.

Introduction

With no verified exceptions, all known silylenes $R_2Si:$, molecules containing divalent silicon atoms, possess singlet ground electronic states.^{1,2} We suggested in 1984³ that a fruitful approach to triplet ground states might be the generation of silylenes with such bulky substituents that the bond angle would be greatly enlarged from the 92° found for $H_2Si:$.⁴ With an increase in the bond angle at the divalent silicon atom, there is an increase in the p-character of the in-plane nonbonding orbital occupied by the unshared electrons of the lowest singlet. In the limit of linearity the nonbonding orbitals should be degenerate pure p-orbitals, and Hund's rule dictates a triplet ground state.

Our first experiments were guided by the results of ab initio calculations by Gordon which predicted for unsubstituted $H_2Si:$ that the potential energy curves for the lowest singlet and triplet states cross at ca. 129° , the triplet being lower in energy above this "crossover angle".⁵ $Ad_2Si:$ was generated in the optimistic belief that the energies of the lowest singlet and triplet states of a dialkylsilylene would mimic those of $H_2Si:$ in their variation with bond angle $H_2Si:$ and that adamantyl substituents would suffice to attain the "crossover angle" predicted by Gordon.⁶

In 1991 the stereospecificity of addition by $Ad_2Si:$ was interpreted as indicating the reaction of a singlet silylene, based on the empirical generalization from carbene chemistry known as the Skell rule.⁷ No triplet ESR signal was detected upon irradiation at 77 K of frozen organic glasses containing precursors for the successful ambient temperature photochemical genera-

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(2) Gaspar, P. P.; West, R. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig Y., Eds.; Wiley: Chichester, 1998; Chapter 51.

(3) Workshop on Organosilicon Reactive Intermediates, Sendai, Japan, Sept. 16–18, 1984, discussion following presentation by P. Boudjouk, "Ultrasonic Waves and Reactive Organosilanes".

(4) Dubois, I.; Herzberg, G.; Varma, R. D. *J. Chem. Phys.* **1967**, *47*, 4262.

(5) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348.

(6) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

(7) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. For an examination of the assumptions underlying the Skell rule, see: Gaspar, P. P.; Hammond, G. S. In *Carbene Chemistry*, 1st ed.; Kirmse, W., Ed.; Academic Press: New York, 1964; p 235.

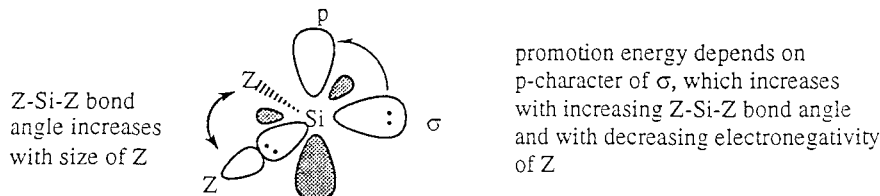


Figure 1. Effects of substituent size and electronegativity on the promotion energy of a nonbonding electron in a singlet silylene.

tion of Ad_2Si .^{6,8} Since Ad_2Si : appeared to possess a singlet ground state, it was clear that either we had overestimated the C-Si-C bond angle or the assumption that the potential surfaces for the lowest singlet and triplet states of Ad_2Si : would resemble those of H_2Si : was incorrect. Both turned out to be the case. The C-Si-C bond angle for the singlet silylene estimated by an STO/3G ab initio geometry optimization is 106.8° , which is well short of the "crossover angle" predicted by Gordon.^{5,9}

When Grev and Schaefer investigated substituent effects on the bending potential energy curves of silylenes by ab initio quantum mechanical methods, it became clear why even a congested dialkylsilylene is likely to possess a singlet ground state, and a new strategy for the generation of a triplet ground state was born.¹⁰ The "crossover angle" $\angle\text{Z-Si-Z}$, beyond which the triplet state lies below the singlet state, was found to increase in the series $(\text{SiH}_3)_2\text{Si}$: 115° , H_2Si : 130° , $(\text{CH}_3)_2\text{Si}$: 140° . Thus the "crossover angle" depends on the electronegativity as well as the size of the substituent Z. For a dialkylsilylene to possess a triplet ground state, the alkyl group must be sufficiently large to open up $\angle\text{C-Si-C}$ to $>140^\circ$, i.e., much bulkier than adamantyl.

The "crossover angle" can be regarded as representing the geometry of the molecule at which the one-electron orbital promotion energy required to convert the σ^2 configuration of the lowest singlet to the $\sigma\pi$ configuration of the lowest triplet is compensated by the reduction in the electron-electron repulsion attendant upon separating the nonbonding electrons, i.e., the release of

the "pairing energy". A decrease in the electronegativity of a substituent Z attached to the divalent silicon atom of a silylene leads to an increase in the s-character of the orbital contributed by the Si atom to the σ -bond, and this is accompanied by an increase in the p-character of the in-plane nonbonding orbital. This leads to a decrease in the orbital promotion energy that must be compensated by the release of the pairing energy of the lone pair in the singlet in order to achieve a triplet ground state. Since the promotion energy decreases with increasing bond angle, a reduction in the electronegativity of the substituents at the divalent silicon atom reduces the size of the "crossover angle".

The complementary effects of substituent size and electronegativity on the promotion energy of a singlet silylene are diagrammed in Figure 1.

It has been predicted that electronegativity effects alone can lead to triplet silylenes. Theoretical results have suggested that the very electropositive substituent Li leads to triplet ground-state silylenes even in the absence of a bulky substituent,¹¹⁻¹⁴ but experimental generation of a lithiosilylene has not yet succeeded.⁸

The results of Grev and Schaefer suggested that a successful strategy for the design of a ground-state triplet silylene would be to employ trialkylsilyl substituents R_3Si with R larger than methyl.¹⁰ Calculations on $(\text{Me}_3\text{Si})_2\text{Si}$: actually placed the triplet 1.2 kcal/mol lower in energy than the singlet, but the estimated error at the level of theory employed led to the prediction that for $(\text{Me}_3\text{Si})_2\text{Si}$: the singlet ($\angle\text{Si-Si-Si}$ 106.1°) is actually 3-4 kcal/mol more stable than the triplet ($\angle\text{Si-Si-Si}$ 127.8°).¹⁰

Encouraged by predictions from PM3 semiempirical calculations that $\angle\text{Si-Si-Si}$ in $(\text{iPr}_3\text{Si})_2\text{Si}$: would exceed the 115° "crossover angle" predicted by Grev and Schaefer for $(\text{H}_3\text{Si})_2\text{Si}$,¹⁵ bis(triisopropylsilyl)silylene, $(\text{iPr}_3\text{Si})_2\text{Si}$:, was chosen as a candidate for a silylene with a triplet ground state. Apeloig has recently, on the basis of density functional calculations, predicted that the triplet state of this silylene lies 1.7 kcal/mol below the lowest singlet state.¹⁶ This paper reports the synthesis and structure of $(\text{iPr}_3\text{Si})_3\text{SiH}$ and its use as a precursor for $(\text{iPr}_3\text{Si})_2\text{Si}$. The reactions of the silylene reported here do not reveal its ground-state multiplicity. Experi-

(8) Xiao, M. The Chemistry of Sterically Congested Organosilicon Compounds and the Quest for Triplet Ground-State Silylenes. Doctoral Dissertation, Washington University, St. Louis, Dec 1988.

(9) At STO-3G UHF $\angle\text{C-Si-C}$ for triplet Ad_2Si : is 120.8° and $\Delta E(\text{UHF T} - \text{RHF S}) = 16.6$ kcal/mol. Bond angle predictions for Ad_2Si : based on semiempirical calculations cannot be relied upon. The MNDO, AM1, and PM3 estimates of $\angle\text{C-Si-C}$ for singlet Ad_2Si : are 119.3° , 117.1° , and 111.9° , respectively, but these methods produce rather large errors when applied to Me_2Si : with estimated singlet-(UHF triplet) $\angle\text{C-Si-C}$ (deg): MNDO 105.8(131.7), AM1 107.0(126.4), PM3 103.7(129.9). Ab initio calculations at the DZ(d) TCSCF level predict $\angle\text{C-Si-C}$ (deg) = 98.8 (singlet), 117.9 (triplet), and STO-3G calculations predict 95.5 (singlet), 114.7 (UHF triplet). For Me_2Si STO-3G calculations give the same order of energies as the split basis TCSCF calculations and (fortuitously) the same energy gap: $\Delta E(\text{T-S})$ (kcal/mol) = 24.4 (STO-3G), 24.2 (TCSCF). In contrast, the semiempirical methods all predict triplet ground states, $\Delta E(\text{UHF T} - \text{RHF S})$ (kcal/mol) = -5.9 (MNDO), -21.3 (AM1), -1.4 (PM3). Comparison of the calculated UHF ΔH_f° of the triplet state with that of the RHF ΔH_f° of the singlet state of Ad_2Si : gives $\Delta E(\text{T-S})$ (kcal/mol) and $\angle\text{C-Si-C}(\text{T})$ at MNDO, AM1, and PM3: -7.5 (139.0°), -22.7 (129.4°), and -2.2 (130.8°), respectively. There was very little spin contamination of the UHF triplet Ad_2Si : wave function, $\langle S^2 \rangle = 2.0123$ (MNDO), 2.0315 (AM1), 2.0278 (PM3), and 2.0019 (STO-3G). The semiempirical and STO-3G calculations reported here were carried out employing the Spartan molecular modeling program, version 5.0, supplied by Wavefunction, Inc., Irvine, CA.

(10) Grev, R. S.; Schaefer, H. F., III; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638.

(11) Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537.

(12) Colvin, M. E.; Breulet, J.; Schaefer, H. F. *Tetrahedron* **1985**, *41*, 1429.

(13) Colvin, M. E.; Schaefer, H. F.; Bicerano, J. *J. Chem. Phys.* **1985**, *83*, 4581.

(14) Gordon, M. S.; Schmidt, M. W. *Chem. Phys. Lett.* **1986**, *132*, 294.

(15) The PM3 predictions for $\angle\text{Si-Si-Si}$ are 114.9° singlet, 130.0° triplet, $\Delta E(\text{T-S}) = 7.6$ kcal/mol. We are grateful to Dr. Daniel J. Berger for these calculations.

(16) Apeloig, Y. 30th Organosilicon Symposium, London Ontario, Canada, May 30-31, 1997, Abstract C-4. Holthausen, M. C.; Koch, W.; Apeloig, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2623.

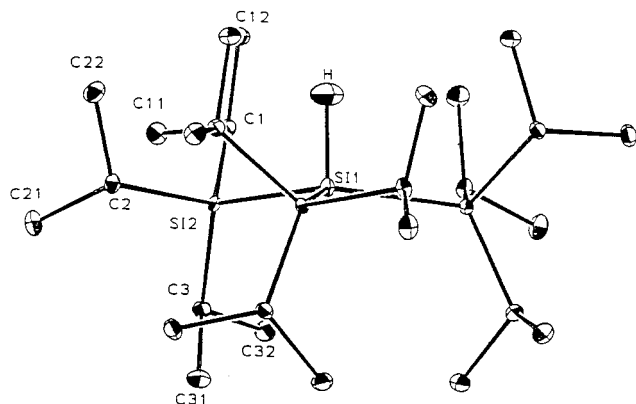
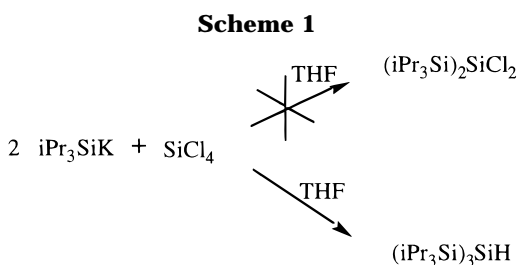


Figure 2. Neutron diffraction structure for tris(triisopropylsilyl)silane.



ments to resolve this critical issue are under way and will be reported separately.

Results

Tris(triisopropylsilyl)silane ($(\text{iPr}_3\text{Si})_3\text{SiH}$): Preparation, Structure, and Synthesis. Established routes for the generation of the target silylene by photochemical means, needed for spectroscopic studies of $(\text{iPr}_3\text{Si})_2\text{Si}$, required a silirane precursor whose synthesis called for a dihalosilane $(\text{iPr}_3\text{Si})_2\text{SiX}_2$ ($X = \text{Cl}$ or Br). In attempting the following preparation of $(\text{iPr}_3\text{Si})_2\text{SiCl}_2$, a crystalline substance was obtained whose X-ray structure revealed it to be tris(triisopropylsilyl)silane, $(\text{iPr}_3\text{Si})_3\text{SiH}$ (Scheme 1).¹⁷ A single step synthesis of $(\text{iPr}_3\text{Si})_3\text{SiH}$ in 3% yield has recently been published with an X-ray crystal structure.¹⁸

The neutron diffraction structure of $(\text{iPr}_3\text{Si})_3\text{SiH}$ is shown in Figure 2, and selected bond lengths and angles from the three independent structure determinations are shown in Chart 1. For structural comparison, a neutron diffraction structure of hexaisopropylidisilane $\text{iPr}_3\text{SiSiPr}_3$ was determined and is shown in Figure 3.¹⁹

A more efficient synthesis of $(\text{iPr}_3\text{Si})_3\text{SiH}$ was developed and is shown below. Work by Kira et al. indicated that the attachment of two iPr_3Si groups to a silicon

(17) The synthesis and X-ray crystal structure of $(\text{iPr}_3\text{Si})_3\text{SiH}$: have been presented: The Sendai International Symposium on The Frontiers of Organosilicon Chemistry, Sendai, Japan, Nov. 4–6, 1994. Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Klooster, W. T.; Koetzle, T. F. 29th Central Regional ACS meeting, Midland, MI, May 28–30, 1997, abstract 179. Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Klooster, W. T.; Koetzle, T. F.; Lei, D.; Lin, T. S.; Winchester, W. R. 30th Organosilicon Symposium, London, Ontario, Canada, May 30, 31, 1997, abstract A-16. The neutron diffraction structure was also presented at Midland and London.

(18) Kyushin, S.; Sakurai, H.; Matsumoto, H. *Chem. Lett.* **1998**, 107. No synthetic details are given.

(19) An X-ray structure has recently been reported: Antomettei, A.; Soderquist, J. A.; Huang, S. D. *Z. Kristallogr.-N. W. Cryst. Struct.* **1999**, 214, 43; *Chem. Abstr.* **1999** 130, 117682f.

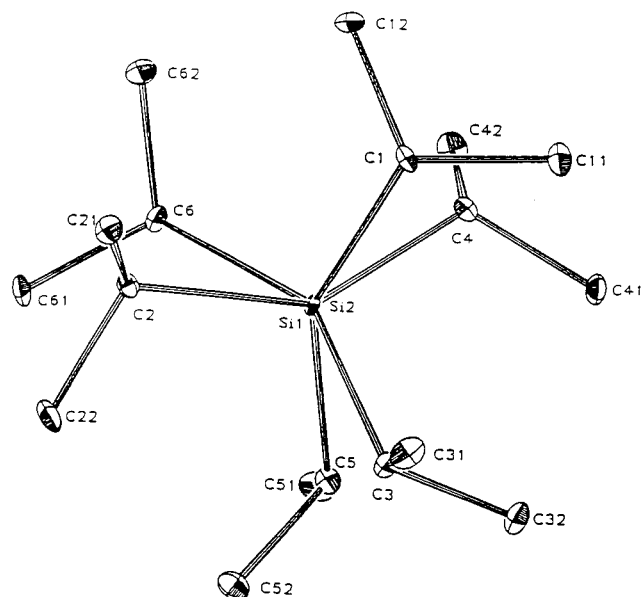
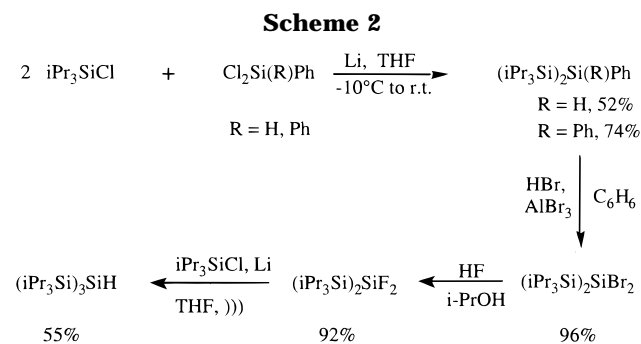


Figure 3. Neutron diffraction structure for hexaisopropylidisilane.



atom could be accomplished via cross-coupling of $\text{iPr}_3\text{SiSiCl}$ with dihalosilanes using established techniques.²⁰ In our hands attachment of a third iPr_3Si group succeeded with $(\text{iPr}_3\text{Si})_2\text{SiF}_2$ but *not* with $(\text{iPr}_3\text{Si})_2\text{SiBr}_2$. The efficient and inexpensive but often overlooked fluorination procedure of Eaborn employing aqueous HF was employed (Scheme 2).²¹

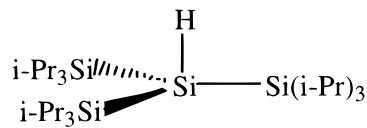
Thermal Decomposition of $(\text{iPr}_3\text{Si})_3\text{SiH}$. Trapping agents provided strong evidence for the generation of the target silylene. Pyrolysis of $(\text{iPr}_3\text{Si})_3\text{SiH}$ in the presence of a diene and two alkynes, respectively, led to the isolation in high yields of the products expected from the trapping of $(\text{iPr}_3\text{Si})_2\text{Si}$, together with the iPr_3SiSiH coproduct of silylene generation (Scheme 3). The X-ray crystal structure of 1,1-bis(triisopropylsilyl)-2,3-bis(trimethylsilyl)silirene is shown in Figure 4. The large $\angle\text{Si-Si-Si} = 129.44(3)^\circ$ provided additional encouragement for the hope that $(\text{iPr}_3\text{Si})_2\text{Si}$ would prove to possess a triplet ground state. This silirene is stable in air, in marked contrast to the first silacyclopentene 1,1,2,3-tetramethylsilirene, whose extreme reactivity toward oxygen and moisture made it extremely difficult to handle.²²

(20) $(\text{iPr}_3\text{Si})_2\text{SiBr}_2$ is mentioned in: Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1489. We are grateful to Professor Kira for his private communication of the experimental procedures for the synthesis of $(\text{iPr}_3\text{Si})_2\text{SiPh}_2$ and $(\text{iPr}_3\text{Si})_2\text{SiBr}_2$.

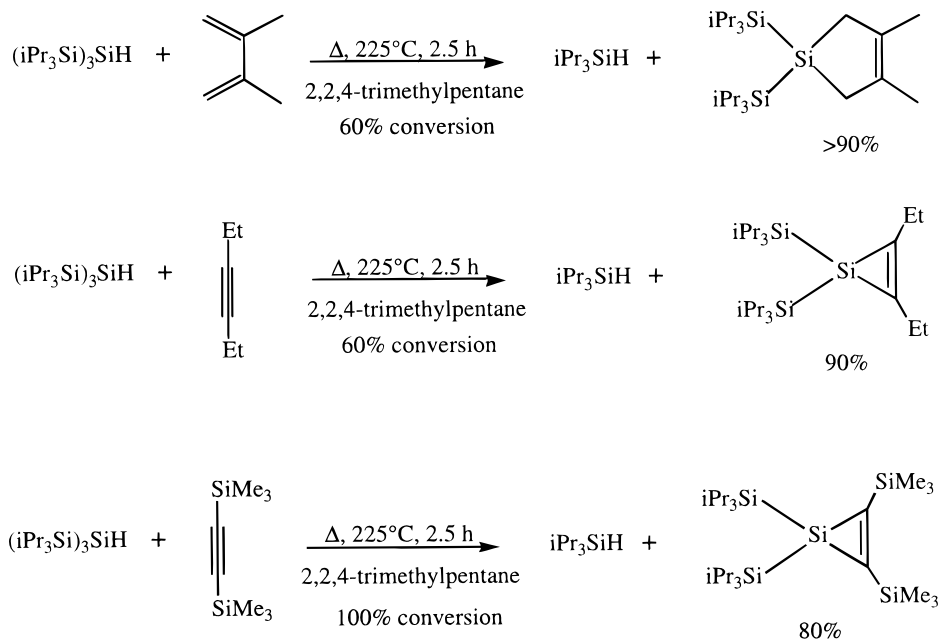
(21) Eaborn, C. *J. Chem. Soc.* **1952**, 2846.

(22) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, 98, 3715.

Chart 1

	by x-ray diffraction	by x-ray diffraction ¹⁸	by neutron diffraction
	r(SiSi) 2.405(1) Å r(Si-H) 1.61(1) Å	2.405(1) Å 1.39(7) Å	2.398(2) Å 1.506(2) Å
	∠Si-Si-Si 117.9(1)° ∠Si-Si-H 98.3(1)°	118.10(3)° 97.99(7)°	118.41(5)° 97.30(9)°

Scheme 3

**Photochemical Decomposition of (iPr₃Si)₃SiH.**

The need for a photochemical route to (iPr₃Si)₂Si: led to experiments on the 254 nm irradiation of (iPr₃Si)₃SiH. Generation of (iPr₃Si)₂Si: was evidenced by the formation of the expected trapping products when the

photodecomposition was carried out in the presence of substrates containing H–Si and C=C bonds, as indicated by the examples in Scheme 4.

Addition of the photochemically generated silylene to *cis*- and *trans*-2-butene is discussed below. With a detection limit of ca. 6% by ²⁹Si and ¹³C NMR spectroscopy, addition was >94% stereospecific. For purposes of comparison, the *cis*- and *trans*-1,1-bis(trimethylsilyl)-2,3-dimethylsilanes were also produced via the “organometallic” route shown in Scheme 5. In the lithium-mediated dehalogenation of Ad₂SiI₂ the selectivity among pairs of substrates differed from that of both thermally and photochemically generated Ad₂Si.⁶ Thus it is likely that the stereospecific formation of siliranes in this lithium-mediated dehalogenation reaction is a silylenoid process rather than a silylene reaction.

Attempted photolysis of (iPr₃Si)₃SiH in a frozen glass at 77 K failed. A frozen degassed 0.07 M solution in methylcyclohexane was irradiated for 1 h, then thawed, and again frozen and irradiated further. After 5 h total irradiation time in five such cycles, GC–MS analysis indicated no more than 1% conversion.

Discussion

Structure of (iPr₃Si)₃SiH and iPr₃SiSiPr₃. The most dramatic structural feature of (iPr₃Si)₃SiH is the near coplanarity of the four silicon atoms (the three symmetry-equivalent Si–Si–Si angles sum to ca. 355°).

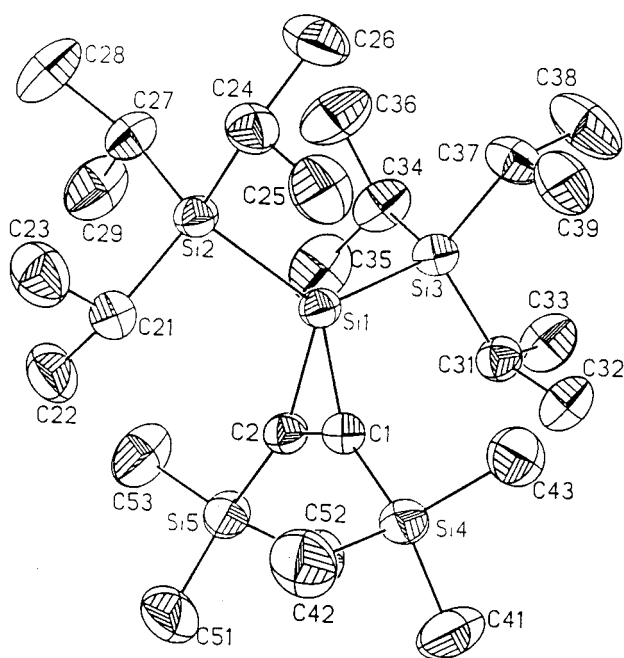
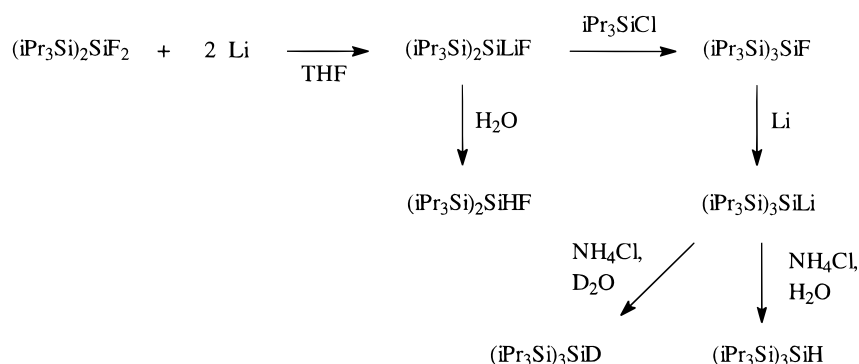


Figure 4. X-ray diffraction structure for 1,1-bis(trimethylsilyl)-2,3-bis(trimethylsilyl)silene.

Scheme 6



of iPr_3SiCl with $(\text{iPr}_3\text{Si})_2\text{SiF}_2$ is of considerable interest. The most probable mechanism is shown in Scheme 6.

The first step, metalation of $(\text{iPr}_3\text{Si})_2\text{SiF}_2$, has been demonstrated in the absence of iPr_3SiCl by quenching the resulting $(\text{iPr}_3\text{Si})_2\text{SiLiF}$ with water to yield $(\text{iPr}_3\text{Si})_2\text{SiHF}$. Reaction of separately formed $(\text{iPr}_3\text{Si})_2\text{SiLiF}$ with iPr_3SiCl has been found to yield $(\text{iPr}_3\text{Si})_3\text{SiF}$, which is formed as a byproduct when less than 2 equiv of lithium are employed in the reaction of $(\text{iPr}_3\text{Si})_2\text{SiF}_2$ with iPr_3SiCl . The presence of $(\text{iPr}_3\text{Si})_3\text{SiLi}$ in the reaction mixture before aqueous workup was revealed by use of D_2O .

In an alternative mechanism the initial metalation forms iPr_3SiLi , which acts as a nucleophile toward $(\text{iPr}_3\text{Si})_2\text{SiF}_2$, forming $(\text{iPr}_3\text{Si})_3\text{SiF}$. Indeed the formation of a ca. 20% yield of $\text{iPr}_3\text{SiSiPr}_3$ as a byproduct along with $(\text{iPr}_3\text{Si})_3\text{SiH}$ suggests that some iPr_3SiLi is formed. Use of fluoride leaving groups is a well-known device in organosilicon chemistry for easing the attachment of bulky groups by nucleophilic substitution. The steric congestion of $(\text{iPr}_3\text{Si})_2\text{SiF}_2$ should however prevent this molecule from competing with iPr_3SiCl for iPr_3SiLi , thus requiring both $(\text{iPr}_3\text{Si})_2\text{SiLiF}$ and iPr_3SiLi intermediates.

Photolysis of $(\text{iPr}_3\text{Si})_3\text{SiH}$. Silylene generation in the photolysis of permethylated linear and branched-chain polysilanes has been known since the 1970s.²³ From these precursors silylenes are formed exclusively by the extrusion of $:\text{SiR}_1\text{R}_2$ units from $\text{Si}-(\text{SiR}_1\text{R}_2)-\text{Si}$ chains. Irradiation of $(\text{Me}_3\text{Si})_3\text{SiOMe}$, however, led to the elimination of Me_3SiOMe (the only process observed in pyrolysis) as well as $\text{Me}_3\text{SiSiMe}_3$, thus forming both $(\text{Me}_3\text{Si})_2\text{Si}:$ and $\text{Me}_3\text{Si}(\text{MeO})\text{Si}:$.²⁴

Thus, on the basis of these precedents, photolysis of $(\text{iPr}_3\text{Si})_3\text{SiH}$ might have been expected to form $\text{iPr}_3\text{Si}(\text{H})\text{Si}:$ if exclusive elimination of $\text{iPr}_3\text{SiSiPr}_3$ occurred, or both $\text{iPr}_3\text{Si}(\text{H})\text{Si}:$ and $(\text{iPr}_3\text{Si})_2\text{Si}:$, if elimination of both $\text{iPr}_3\text{SiSiPr}_3$ and iPr_3SiH took place. In the event, irradiation of $(\text{iPr}_3\text{Si})_3\text{SiH}$ at room temperature has proved to be a clean source of $(\text{iPr}_3\text{Si})_2\text{Si}:$. Elimination of $\text{iPr}_3\text{SiSiPr}_3$ is presumably unfavorable due to the geometry of $(\text{iPr}_3\text{Si})_3\text{SiH}$, the distance between two iPr_3Si groups being greater than that necessary for silicon-silicon bond formation between two triisopropylsilyl groups in the excited state of $(\text{iPr}_3\text{Si})_3\text{SiH}$.

Reactions of $(\text{iPr}_3\text{Si})_2\text{Si}:$. The addition of silylenes to 1,3-dienes to form 1-silacyclopent-3-enes and to alkynes to form silirenes has ample precedent.^{1,2} Thus the formation of 1,1-bis(triisopropylsilyl) derivatives of these silacycles when $(\text{iPr}_3\text{Si})_3\text{SiH}$ was pyrolyzed at 225 °C in the presence of 2,3-dimethylbutadiene, 3-hexyne, and bis(trimethylsilyl)acetylene, respectively, provided strong evidence for the generation of $(\text{iPr}_3\text{Si})_2\text{Si}:$. The formation of Si-H/Si-D insertion products when $(\text{iPr}_3\text{Si})_3\text{SiH}$ was irradiated with low-pressure Hg lamps in the presence of the triethylsilanes $\text{Et}_3\text{SiH}/\text{Et}_3\text{SiD}$, respectively, also points to the generation of the silylene. None of these reactions speaks to the question of the electronic state of the reacting silylene.

The formation of $(\text{iPr}_3\text{Si})_2\text{SiH}_2$, if it is a product derived from $(\text{iPr}_3\text{Si})_2\text{Si}:$, would provide chemical evidence for the reactions of a triplet state. This product could result from H-abstraction, a process unknown for singlet silylenes,^{1,2} but well-established for triplet carbenes.²⁵ However, the low deuterium incorporation (0.13) in the $(\text{iPr}_3\text{Si})_2\text{SiH}_2$ that accompanied the $(\text{iPr}_3\text{Si})_2\text{DSiSiEt}_3$ when DSiEt_3 was employed as reaction substrate requires that these products be formed by quite different reactions. One possibility is of course that $(\text{iPr}_3\text{Si})_2\text{DSiSiEt}_3$ is formed by direct insertion of the silylene into the D-Si bond.

The least contorted scenario that attributes both $(\text{iPr}_3\text{Si})_2\text{DSiSiEt}_3$ and $(\text{iPr}_3\text{Si})_2\text{SiH}_2$ to the reactions of $(\text{iPr}_3\text{Si})_2\text{Si}:$ assigns the former product to concerted insertion by a singlet silylene and the latter to unselective abstraction by a triplet.²⁶

Stereospecific *cis* addition to olefins has been reported for dimethylsilylene, $\text{Me}_2\text{Si}:$,²⁷⁻²⁹ phenyltrimethylsilylsilylene, $\text{Ph}(\text{Me}_3\text{Si})\text{Si}:$,³⁰ diphenylsilylene, $\text{Ph}_2\text{Si}:$,²⁸ and diadamantylsilylene, $\text{Ad}_2\text{Si}:$,⁶ all presumed to have reacted from their ground singlet electronic states.

According to the dictates of the Skell rule,⁷ stereospecific addition of $(\text{iPr}_3\text{Si})_2\text{Si}:$ to *cis*- and *trans*-2-butene

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(26) Formation of $(\text{iPr}_3\text{Si})_2\text{SiH}_2$ in the room-temperature photolysis of 2,3-diethyl-1,1-bis(triisopropylsilyl)silirene (W. R. Winchester, results to be published) suggests that this product is indeed derived from $(\text{iPr}_3\text{Si})_2\text{Si}:$.

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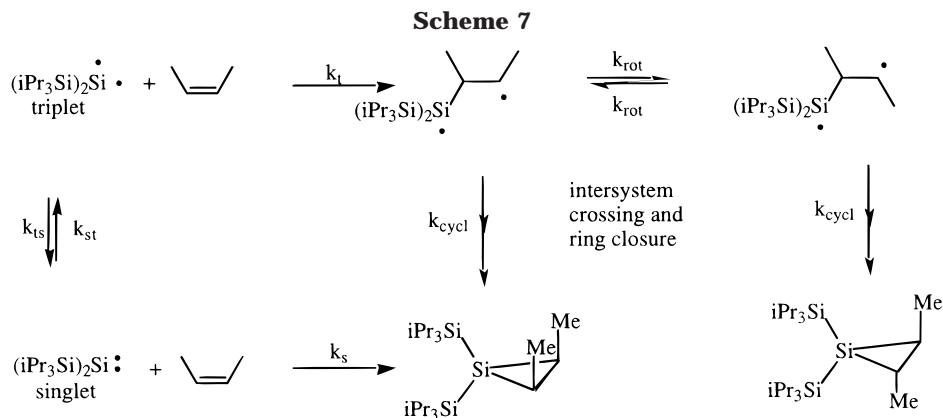
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indicates the participation of a singlet silylene in a concerted addition. Does this constitute chemical evidence for a *singlet ground state* for $(iPr_3Si)_2Si$? Not necessarily, since alternative explanations for stereospecific addition include the following:

1. A triplet ground state is siphoned off via a reaction of the low-lying first excited singlet state. If Apeloig's estimate¹⁶ of $\Delta E(S-T) = 1.7$ kcal/mol is correct, then the equilibrium constant $K = [S]/[T]$ is approximately 1/50 at room temperature. Then, with reference to Scheme 7, if the rate constant for addition of singlet $(iPr_3Si)_2Si$: k_s is much larger than 50 times that for addition of the triplet silylene k_t , stereospecific addition of the silylene would be observed despite a triplet ground state, if interconversion of the spin states is more rapid than the triplet addition reaction, $k_{ts}, k_{st} \gg k_t$, $K = k_{ts}/k_{st}$.

While the formation of the coproduct $(iPr_3Si)_2SiHCH(CH_3)CH=CH_2$ upon addition of $(iPr_3Si)_2Si$: to both *cis*- and *trans*-2-butene is consistent with a diradical intermediate, that intermediate may be formed from the silirane rather than intervene in its formation. There is precedent for silirane to allylsilane ring openings.³¹

2. The Skell rule breaks down because conformational equilibration of the biradical intermediate in the addition of triplet silylene is *not* rapid compared to cyclization. For addition of triplet silylene to be nonstereospecific, rotation about the C-C single bond formed when the triplet silylene adds to one end of the π -bond of an olefin diastereomer must be more rapid than intersystem crossing and ring closure, $k_{rot} \gg k_{cycl}$. As discussed in case 1 above, triplet addition will only be *observable* if $k_t > Kk_s$ or k_{ts} is less than or equal to k_t .

The observation that nonstereospecific addition by some triplet carbenes does occur makes it clear that in all 1-carbon systems the condition $k_{rot} \gg k_{cycl}$ can be met. But it has been suggested that silyl substituents β to radical centers $R_3SiCH_2CHR^\bullet$ cause an increase in the barrier height for rotation about the $C_\alpha-C_\beta$ bond.³² For a β -trimethylsilylallyl radical the increase in the barrier height over that for a β -ethyl was estimated to be 1.1 ± 1.0 kcal/mol.³² Both hyperconjugation and p-d homo-

conjugation were believed to contribute to the increase in barrier height.

Since the addition of a triplet carbene to the E- and Z-isomers of a given olefin rarely gives the same E/Z product ratio,²⁵ it seems that even in optimal cases k_{rot} is not much larger than k_{cycl} . Therefore an increase in the barrier height by 1 kcal/mol that reduces k_{rot} by a factor of ca. 5 is likely to tip the scales in favor of stereospecific addition. For triplet silylene addition k_{cycl} is also likely to be larger than for the case of triplet carbenes because spin-orbit coupling is much greater in silicon than in carbon, enhancing the rate of intersystem crossing.

It should be noted that the only known failure of the Skell rule involves a heavy atom. Both 3P and 1D sulfur atoms add stereospecifically to *cis*-2-butene,³³ and evidence was found for a diradical intermediate in the triplet addition.³⁴ But calculations suggested that stereospecific addition by 3P S atoms may be due to initial formation of a triplet sulfur-olefin complex that correlated with an excited triplet thiirane, and this could relax to the singlet ground state.³⁵ That concerted additions of triplet silylenes are not thermodynamically allowed is indicated by calculations on triplet siliranes.³⁶

Both the reactions of an excited singlet in equilibrium with a triplet ground state and a failure of the Skell rule are plausible explanations for stereospecific addition by $(iPr_3Si)_2Si$: even if this silylene has a triplet ground state. Direct observation of the ground state by ESR or electronic spectroscopy will be required to assign the ground-state multiplicity. Electronic spectroscopy that would also be useful may be frustrated by an absence of absorptions at wavelengths greater than 300 nm according to theoretical predictions by Apeloig.³⁷ ESR experiments in frozen glasses require precursors whose photolysis yields the silylene at 77 K. $(iPr_3Si)_3SiH$ is not photolabile at 77 K. Results from other precursors will be presented separately.³⁸

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Conclusions

The synthesis of $(iPr_3Si)_3SiH$ has provided a molecule whose novel structure, in which the four silicon atoms are nearly coplanar, suggests that the iPr_3Si group provides a test for a calculation-based strategy for the design of a silylene with a triplet ground electronic state. The ca. $118^\circ \angle Si-Si-Si$ in $(iPr_3Si)_3SiH$ found by X-ray and neutron diffraction to be larger than the "crossover angle" beyond which the lowest triplet state of $(H_3Si)_2Si$: is predicted to be the ground state, and density functional calculations by Apeloig predict that the ground state of $(iPr_3Si)_2Si$: is a triplet. Pyrolysis and photolysis of $(iPr_3Si)_3SiH$ in the presence of established trapping agents for silylenes lead to products indicative of the generation of the target silylene, $(iPr_3Si)_2Si$:. The reaction products do not, however, establish conclusively the ground-state multiplicity. A product $(iPr_3Si)_2SiH_2$ whose formation from $(iPr_3Si)_2Si$: requires H atom abstraction processes is consistent with one's expectations for the chemistry of triplet silylenes, but the mechanism by which $(iPr_3Si)_2SiH_2$ arises has not been established. Although stereospecific addition of $(iPr_3Si)_2Si$: to the 2-butenes can be reconciled with a triplet ground state by special pleading, this observation would normally be attributed to the reactions of a singlet state. Further work with other precursors of $(iPr_3Si)_2Si$:, including direct spectroscopic detection, will be required to identify the ground electronic state.

Experimental Section

General Data. All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Unless otherwise specified, photolyses were carried out in a Rayonet type RS photochemical reactor (model number RPR-208, 120 W radiated power) equipped with low-pressure mercury lamps emitting 254 nm radiation. Benzene, THF, and ether were dried by and distilled from benzophenone sodium ketyl under a nitrogen atmosphere.

1H , ^{13}C , and ^{29}Si NMR spectra were recorded on Varian XL-300 and Gemini-300 FT spectrometers. Combined gas chromatography-mass spectrometry was performed on a Hewlett-Packard Model 5890 Series II instrument employing a 25m 5%-OVS capillary column.

For photolyses the reported yields are based on the unrecovered silylene or silylenoid precursor and were determined by integration of the gas chromatogram with the use of dodecane as an internal standard.

Materials. Bis(trimethylsilyl)acetylene (Aldrich, 99%), *cis*-butene (Aldrich, >95%), *trans*-butene (Aldrich, 99%), 2,3-dimethylbutadiene, (Aldrich, 99%), 3-hexyne (Aldrich, 99%), trichlorosilane (Petrach, 99%), and triethylsilane (Aldrich, 99%) were used.

Neutron Diffraction Structure Determination for Hexaisopropyldisilane. Crystals were obtained by recrystallization from a saturated hexane solution. A colorless specimen of volume 6.1 mm^3 was mounted on an aluminum pin with halocarbon grease and sealed under a helium atmosphere inside an aluminum container. This container was placed in a closed-cycle helium refrigerator³⁹ and mounted on the four-circle diffractometer at port H6M of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by Be (002) planes in transmission geometry, was of wavelength $1.0462(1) \text{ \AA}$, as calibrated against a KBr crystal ($a_0 = 6.6000 \text{ \AA}$ at 295 K). The sample temperature was maintained at $15.0 \pm 0.5 \text{ K}$ during the experiment,

and unit cell dimensions were determined by least-squares fit of $\sin^2 \theta$ values for 63 reflections in the range $50^\circ \leq 2\theta \leq 59^\circ$. Intensity data were obtained over one quadrant of reciprocal space by means of $\omega:2\theta$ scans. The intensities of two reflections were monitored during the data collection and showed no systematic variations throughout. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles as described previously.⁴⁰ Lorentz factors were applied, as well as an absorption correction.^{41,42} Transmission factors were in the range 0.515–0.721. Averaging over 248 symmetry-related pairs of reflections resulted in an internal agreement factor of 0.010 and yielded 8149 independent observations, of which 3082 had $F_0^2 > 3\sigma(F_0^2)$. Further details are given in Supplementary Table 5.

Since this was an unknown compound, the structure had to be solved. That was done using direct methods.⁴³ The full expected molecule $(iPr_3Si)_3SiH$ was used as a search fragment, expanded according to the 3-fold symmetry. Only the Si and C atoms were used, since H has a negative scattering length. This method located all non-hydrogen atoms without any difficulty. The molecule turned out to be $iPr_3SiSiPr_3$. The atomic positions determined from direct methods were then used as the starting point for the refinements.

Coherent neutron-scattering lengths (fm) for H (−3.7406), C (6.646), and Si (4.149) were taken from the International Tables.⁴⁴ Least-squares refinements were carried out by a full-matrix procedure⁴⁵ minimizing $\sum w(F_0^2 - k^2 F_c^2)^2$, where $w = [\sigma^2(F_0^2)]^{-1}$, using all independent data minus 25 reflections that were affected by the powder lines from the aluminum container. The final model included the scale factor k and positional and anisotropic displacement parameters β_{ij} for all atoms except for the off-diagonal terms for atoms Si1. The extinction parameter⁴⁶ was omitted after it failed to assume a significant value. This gave a total of 556 variable parameters. The refinement converged $\Delta\rho/\sigma(\rho) < 0.1$ with fit indices $R(F_0^2) = 0.190$, $R_w(F_0^2) = 0.110$, $R_w(F_0) = 0.063$, $S = 1.03$, based on 8124 reflections. In the final difference Fourier, the largest $|\Delta\rho|$ errors were about 4% of the maximum peak in the ρ_0 map (C1). Bond lengths and angles are listed in Supplementary Table 8.

Neutron Diffraction Structure Determination for Tris-(triisopropylsilyl)silane. A colorless irregular crystal of maximum dimensions $2.1 \times 3.0 \times 4.4 \text{ mm}$, calculated volume 25.0 mm^3 , was glued to a 1 mm diameter vanadium pin using the two-component glue Kwikfill and mounted on a Displex cryorefrigerator⁴⁷ on the thermal-beam 4-circle diffractometer D19 at ILL equipped with a 4×64 position-sensitive detector.⁴⁸ The wavelength was $1.2691(2) \text{ \AA}$ from a Cu (220) monochromator in reflection. The crystal was cooled at 1.25 deg/min to 20 K while monitoring the strong (0 4 4) reflection. The space group $Pa\bar{3}$ was confirmed at 20 K. Reflections were measured to preset monitor counts in equatorial geometry (in

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the $+h+k+l$ octant) up to 40° in 2θ , and in normal-beam geometry at higher angles, the time increasing with scattering angle from 6 to 12 s per step in ω (ILL programs Hklgen and Mad). Three standard reflections were measured regularly and showed no significant variation. The unit cell dimensions were calculated as $a = 18.6893(5)$ Å, from the centroids in three dimensions of 3328 strong reflections (ILL program Rafd19), min and max. 2θ used 8.71° and 104.45° . Bragg intensities were integrated in 3D using the ILL program Retreat.⁴⁹

The intensities were corrected for attenuation by the cryo-refrigerator cans (minimum and maximum transmission factors 0.8359 and 0.8997), and by the crystal (calculated $\mu = 3.52$ cm⁻¹, minimum and maximum transmission coefficients 0.3718 and 0.5385) with the program D19abs, based on the ILL version of the CCSL system;⁵⁰ the crystal was described by seven faces, some imperfect. The final data set included almost all unique reflections up to 2θ of 90° , and a significant number to 100° . In all, 8348 reflections were recorded, yielding 2151 unique reflections after averaging.

(iPr₃Si)₃SiH from an Attempted Synthesis of (iPr₃Si)₂-SiCl₂. A 0.782 g (20.0 mmol) sample of potassium and 1.93 g (10.0 mmol) of iPr₃SiCl in 25 mL of dry heptane were refluxed 6 h. The solution turned yellow and a gray precipitate formed. The mixture was cooled to room temperature and filtered through glass wool to give a clear yellow solution, which was frozen at 77 K. A 0.084 g (0.5 mmol) portion of SiCl₄, dried over P₂O₅ and distilled, was added to the frozen iPr₃SiK solution, and the mixture was allowed to warm to room temperature and then stirred overnight. A white precipitate was removed by filtration, and volatiles were removed under vacuum from the filtrate. The light yellow residue was dissolved in a minimum of pentane and placed overnight in a freezer. The crystals that formed were removed by filtration and found to be iPr₆Si₂, of which a second crop was obtained upon prolonged cooling of the filtrate. Further cooling of the filtrate deposited a 30% yield of (iPr₃Si)₃SiH, identified by X-ray crystallography. This synthesis was unreliable.

Preparation of 2-Phenyl-1,1,1,3,3,3-hexaisopropyltrisilane, (iPr₃Si)₂SiHPh. A suspension of lithium (1.4 g, 0.20 mol) in THF (100 mL) under nitrogen was cooled with an acetone/ice bath to -10° C. A solution of phenyldichlorosilane (7.2 g, 0.041 mol) and chlorotriisopropylsilane (15.7 g, 0.082 mol) in THF (100 mL) was added dropwise to this stirred suspension over 3 h. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into a separatory funnel containing hexanes (200 mL) and water (50 mL). After the layers were separated and the aqueous layer was washed two more times with hexanes, the organic layer was dried over sodium sulfate, filtered, and concentrated. This gummy material had a mass of 16.9 g, and GC indicated there were two major components: the desired product and hexaisopropylidisilane in the ratio of 64:36. Careful purification using chromatography on silica gel (1 g compound to 20 g silica), eluting with hexane, led to the isolation of 9.0 g (52%) of 2-phenyl-1,1,1,3,3,3-hexaisopropyltrisilane, 98% pure by GC. ¹H NMR (CDCl₃, ppm): 1.05 (d, $J = 7.1$ Hz, 36H), 1.17 (m, 6H), 4.13 (s, 1H), 7.17 (m, 3H), 7.54 (m, 2H). ¹³C NMR (CDCl₃, ppm): 13.2, 19.7, 19.9, 127.51, 127.53, 136.1, 137.2. ²⁹Si NMR (C₆D₆, ppm): -73.2 ($^1J_{\text{SiH}} = 146$ Hz), 6.5. HREI MS (m/e , ri %): 420 (13), 377 (30), 262 (41), 157 (49), 59 (100). HRMS for C₂₄H₄₈Si₃ calcd 420.3064, found 420.3062. Hexaisopropylidisilane: ¹H NMR (C₆D₆, ppm): 1.18 (d, $J = 6.3$ Hz, 36H), 1.27 (m, 6H). ¹³C NMR (C₆D₆, ppm): 13.19, 20.55. ²⁹Si NMR (C₆D₆, ppm): -1.4 .

Preparation of 2,2-diphenyl-1,1,1,3,3,3-hexaisopropyltrisilane. A suspension of lithium (0.7 g, 0.10 mol) in THF

(10 mL) under dry nitrogen was prepared in a Schlenk flask, and a few drops from a solution of diphenyldichlorosilane (5.0 g, 0.02 mol) and chlorotriisopropylsilane (4.5 g, 0.02 mol) in THF (100 mL) were added to this stirred suspension. Addition was stopped, and the mixture was treated with ultrasound until the reaction had started, as evidenced by the formation of a light green color. Then, the Schlenk flask was placed in a dry ice/acetone cooling bath, and the addition continued dropwise over 3 h. The solution was allowed to warm to room temperature and stirred overnight. At this point the mixture is a dark red, and there has been significant formation of diphenyl(triisopropylsilyl)silyllithium, as indicated by GC/MS of a sample quenched with D₂O. After stirring for another 24 h, the silyllithium was quenched with a second equivalent of chlorotriisopropylsilane (4.5 g, 0.02 mol) in THF (20 mL). The reaction mixture was poured into a separatory funnel containing hexanes (200 mL) and water (50 mL). After the layers were separated and the aqueous layer washed two more times with hexanes, the organic layer was dried over sodium sulfate, filtered, and concentrated. This mixture was dissolved in hexane (100 mL) and cooled to -20° C, yielding crystals (2.6 g) of the desired compound. Careful purification using chromatography on silica gel (1 g of compound to 20 g of silica), eluting with hexane, led to the isolation of an additional 4.6 g of material, for a total yield of 74%. ¹H NMR (CDCl₃, ppm): 0.99 (d, $J = 7.1$ Hz, 36H), 1.37 (m, 6H), 7.3 (m, 6H), 7.7 (m, 4H). ¹³C NMR (CDCl₃, ppm): 13.5, 20.1, 127.3, 127.9, 137.0, 137.8. ²⁹Si NMR (C₆D₆, ppm): -36.9 , 1.01. HRMS for C₃₀H₅₂Si₃: calcd 496.3377, found 496.3367.

Preparation of 2,2-Dibromo-1,1,1,3,3,3-hexaisopropyltrisilane. (Similar results were obtained when the reaction was carried out using 2-phenyl-1,1,1,3,3,3-hexaisopropyltrisilane.) An oven-dried 250 mL round-bottom flask was fitted with a gas bubbler, reflux condenser, and magnetic stirbar. A gas outlet was prepared, which went to a trap, followed by a mineral oil bubbler and finally an Erlenmeyer flask containing 500 mL of 10% NaOH as a trap for unreacted HBr. Freshly distilled benzene (50 mL) was added along with 2,2-diphenyl-1,1,1,3,3,3-hexaisopropyltrisilane (4.1 g, 8.3 mmol) and aluminum bromide (0.5 g, 0.2 mmol). HBr, from a lecture bottle, was added, and the solution became slightly warm to the touch. HBr bubbling was continued for 20 min, followed by 20 min of nitrogen. Acetone (2 mL) was added, and the aluminum bromide-acetone complex coated the bottom of the flask as a gum. The benzene solution of the product was decanted from this gum.

The benzene and residual HBr were removed in-vacuo, and the product was dissolved in 5 mL of hexanes. The hexane solution was filtered through a pipet with a small plug of silica gel to remove traces of HBr and aluminum bromide. Placement of this solution in a freezer yielded white crystals of pure 2,2-dibromo-1,1,1,3,3,3-hexaisopropyltrisilane (3.0 g, 6.0 mmol, 72%). Concentration of the filtrate yields material that is slightly less pure, but typically suitable for use in further reactions (approximately 1 g) for a total yield of 96%: mp $44-45^\circ$ C. ¹H NMR (C₇D₈, ppm): 1.26 (d, 36H, $J = 7.5$ Hz), 1.60 (m, 6H, $J = 7.5$ Hz). ¹³C NMR (C₇D₈, ppm): 13.24, 20.18. ²⁹Si NMR (C₇D₈, ppm): 3.6, 25.1. HRMS for C₁₈H₄₂Si₃Br₂: calcd 500.0961, found 500.0948.

Preparation of 2,2-Difluoro-1,1,1,3,3,3-hexaisopropyltrisilane. To a solution of 5.03 g (10.0 mmol) of 2,2-dibromo-1,1,1,3,3,3-hexaisopropyltrisilane in 60 mL of 2-propanol was added 10 mL of 49% HF aqueous solution. The reaction mixture was stirred at room temperature for 4 h. The mixture was then poured into a separatory funnel with 150 mL of hexanes and extracted three times with water. After the organic phase was dried over anhydrous Na₂SO₄, the volatiles were removed to afford 3.70 g (97%) of colorless product. This was purified by kugelrohr distillation at 100° C and 0.1 mm. Yield: 3.50 g (92%). ¹H NMR (C₆D₆, ppm): 1.16 (d, $J = 6$ Hz, 36H), 1.31 (m, $J = 6$ Hz, 6H). ¹³C NMR (C₆D₆, ppm): 12.1 (t,

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$^3J_{CF} = 1$ Hz), 19.8. ^{29}Si NMR (C_6D_6 , ppm): -0.4 (t, $^2J_{\text{SiF}} = 15.5$ Hz), 44.8 (t, $^1J_{\text{SiF}} = 390$ Hz). ^{19}F NMR (C_6D_6 , ppm): -122.3 (d, $^1J_{\text{SiF}} = 391$ Hz). HRMS for $\text{C}_{18}\text{H}_{42}\text{F}_2\text{Si}_3$: calcd 380.2562, found 380.2564.

Preparation of Tris(triisopropylsilyl)silane. Lithium (0.14 g, 20 mmol) was weighed into an oven-dried 250 mL Schlenk flask and freshly distilled THF added (50 mL). Chlorotriisopropylsilane (0.96 g, 5.0 mmol) and 2,2-difluoro-1,1,1,3,3,3-hexaisopropyltrisilane (1.90 g, 5.00 mmol) were dissolved in THF (50 mL) and added dropwise to the lithium suspension while irradiating with ultrasound using an ultrasonic washer. After complete addition, the reaction progress was monitored by GC, to ensure complete reduction of the intermediate monofluorotrisilylsilane to the lithiotrisilylsilane. When the reaction was complete, the mixture was poured into hexane/ammonium chloride solution to protonate the silyl-lithium and quench unreacted lithium. The hexane solution was washed with water, dried, and concentrated to yield a mixture of hexaisopropylidisilane and the desired tris(triisopropylsilyl)silane. Recrystallization from 5 mL of pentane at -20 °C yielded 1.33 g (55%) of clear blocks of tris(triisopropylsilyl)silane: mp 206–209 °C (uncorrected). ^1H NMR (C_6D_6 , ppm): 1.18 (d, 54H, $J = 7.2$ Hz), 1.26 (h, 9H, $J = 7.2$ Hz), 3.0 (s, 1H). ^{13}C NMR (C_6D_6 , ppm): 16.0, 20.93. ^{29}Si NMR (C_6D_6 , ppm): 13.7, -146.3 ($^1J_{\text{Si-H}} = 136$ Hz). HRMS for $\text{C}_{27}\text{H}_{64}\text{Si}_4$: calcd 500.4085, found 500.4040.

Reaction of Difluorobis(triisopropylsilyl)silane with Lithium. A suspension containing difluorobis(triisopropylsilyl)silane (0.6 g, 1.58 mmol) and lithium (0.05 g, 7.1 mmol) in THF (40 mL) was stirred at room temperature for 15 h. Water (15 mL) was added, followed by pentane (50 mL) to extract the organic products. The aqueous layer was extracted twice more with pentane (20 mL), and the organic layers were combined and dried over sodium sulfate. After removal of the solvent, GC/MS and NMR analysis indicated that no starting material remained. The only products observed were fluorobis(triisopropylsilyl)silane and 1,1,1,3,3,3-hexaisopropyltrisilane in the ratio of 80:20. Fluorobis(triisopropylsilyl)silane: ^1H NMR (C_6D_6 , ppm): 1.12 (d, 18H, $J = 6.8$ Hz), 1.16 (d, 18H, $J = 6.6$ Hz), 1.25 (m, 6H), 6.02 (d, 1H, $J = 37.8$ Hz, Si-H). MS (EI): *m/e* (relative intensity) 362 (M⁺), 235, 204, 193, 156, 157, 115, 73, 59. **1,1,1,3,3,3-Hexaisopropyltrisilane.** ^1H NMR (C_6D_6 , ppm): 1.15 (m, 42H), 2.97 (s, 2H). ^{13}C NMR (C_6D_6 , ppm): 13.40, 19.98. ^{29}Si NMR (C_6D_6 , ppm): 11.6, -131.1 ($^1J_{\text{Si-H}} = 160$ Hz). HRMS for $\text{C}_{18}\text{H}_{44}\text{Si}_3$: calcd 344.2751, found 344.2742.

Pyrolysis of Tris(triisopropylsilyl)silane in the Presence of 2,3-Dimethylbutadiene. Preparation of 1,1-Bis(triisopropylsilyl)-3,4-dimethylsilacyclopent-3-ene. Into a pyrolysis tube attached to a Teflon stopcock was placed a mixture of tris(triisopropylsilyl)silane (59 mg, 0.12 mmol) and 2,3-dimethylbutadiene (81 mg, 1.0 mmol) dissolved in freshly dried 2,2,4-trimethylpentane (0.8 mL). After being degassed on a vacuum line to 0.02 Torr and five freeze-pump-thaw cycles, the tube was sealed with a torch and then heated to 225 °C for 3 h. After cooling, the ampule was opened and the pyrolysate was transferred into a 5 mL round-bottom flask under an atmosphere of nitrogen. Volatiles, including solvent, unreacted dimethylbutadiene, and one coproduct, triisopropylsilane, were evaporated in vacuo, and the oily residue was recrystallized from pentane. The crystals were removed and identified as unreacted tris(triisopropylsilyl)silane. After removal of the pentane from the mother liquor, the oily product was identified as 1,1-bis(triisopropylsilyl)-3,4-dimethylsilacyclopent-3-ene. GC/MS indicated that the purity of the product was about 95%. The yield was almost quantitative, based on the conversion of the starting material (75%). 1,1-Bis(triisopropylsilyl)-3,4-dimethylsilacyclopent-3-ene: ^1H NMR (CDCl_3 , ppm): 1.10 (d, 36H, $J = 7.0$ Hz), 1.26 (m, 6H), 1.67 (bs, 6H), 1.88 (bs, 4H). ^{13}C NMR (CDCl_3 , ppm): 13.50, 19.30, 20.17,

25.85, 132.06. ^{29}Si NMR (C_6D_6 , ppm): 1.48, -45.91 . HRMS for $\text{C}_{24}\text{H}_{52}\text{Si}_3$: calcd 424.3377, found 424.3359.

Pyrolysis of Tris(triisopropylsilyl)silane in the Presence of 3-Hexyne. Preparation of 1,1-Bis(triisopropylsilyl)-2,3-diethylsilirene. Into a pyrolysis tube attached to a Teflon stopcock was placed a mixture of tris(triisopropylsilyl)silane (75 mg, 0.15 mmol) and hexyne (184 mg, 2.24 mmol) dissolved in freshly dried 2,2,4-trimethylpentane (0.7 mL). After being degassed on a vacuum line to 0.02 Torr and five freeze-thaw pump cycles, the sample tube was sealed with a torch and then heated to 225 °C for 3 h. After cooling the ampule was opened, and the pyrolysate was transferred into a 5 mL round-bottom flask under an atmosphere of nitrogen. Volatiles, including solvent, unreacted 3-hexyne, and one coproduct, triisopropylsilane, were evaporated in vacuo, and the oily residue was recrystallized from pentane. The crystals were removed and identified as unreacted tris(triisopropylsilyl)silane. After removal of the pentane, the oily product was identified as 1,1-bis(triisopropylsilyl)-2,3-diethylsilirene. The material could be further purified by kugelrohr distillation at 120 °C and 0.1 mm. GC/MS indicated that the purity of the product was greater than 99%. The yield was 95% (51 mg) based on the conversion of the starting material (85%). 1,1-Bis(triisopropylsilyl)-2,3-diethylsilirene: ^1H NMR (CDCl_3 , ppm): 1.07 (bs, 42H), 1.18 (h, 6H), 2.58 (q, 4H, $J = 7.6$ Hz). ^{13}C NMR (CDCl_3 , ppm): 13.07, 14.02, 19.93, 23.47, 137.33. ^{29}Si NMR (C_6D_6 , ppm): -155.58 , 6.57. HRMS for $\text{C}_{24}\text{H}_{52}\text{Si}_3$: calcd 424.3377, found 424.3379.

Pyrolysis of Tris(triisopropylsilyl)silane in the Presence of Bis(trimethylsilyl)acetylene. Preparation of 1,1-Bis(triisopropylsilyl)-2,3-bis(trimethylsilyl)silirene. Into a pyrolysis tube equipped with a Teflon stopcock was placed a mixture of tris(triisopropylsilyl)silane (75 mg, 0.15 mmol) and bis(trimethylsilyl)acetylene (200 mg, 1.2 mmol) dissolved in freshly dried 2,2,4-trimethylpentane (0.6 mL). After being degassed on a vacuum line to 0.02 Torr and five freeze-pump-thaws, the sample tube was sealed and then heated to 225 °C for 18 h. After cooling the ampule was opened, and the pyrolysate was transferred into a 25 mL round-bottom flask under an atmosphere of nitrogen. Volatiles, including solvent, unreacted alkyne, and one coproduct, triisopropylsilane, were evaporated in vacuo, and the crystalline residue was recrystallized from pentane. GC/MS indicated that the purity of the product was greater than 99%, and the yield was 73 mg (95%) after recrystallization. 1,1-Bis(triisopropylsilyl)-2,3-bis(trimethylsilyl)silirene: ^1H NMR (C_6D_6 , ppm): 0.37 (s, 18H), 1.14 (m, 6H), 1.18 (d, $J = 5.4$ Hz, 36H). ^{13}C NMR (C_6D_6 , ppm): 0.76, 13.56, 20.21, 166.38. ^{29}Si NMR (C_6D_6 , ppm): -186.5 , -8.5 , 7.7. HRMS for $\text{C}_{26}\text{H}_{60}\text{Si}_5$: calcd 512.3541, found 512.3525.

Preparation of *trans*-1,1-Bis(triisopropylsilyl)-2,3-dimethylsilirene. Working in a glovebox, lithium (50 mg, 7 mmol) and 5 mL of THF were placed into a 250 mL round-bottom Schlenk flask. The flask was removed from the glovebox and attached to a Schlenk line, and the solution was frozen with liquid nitrogen. After the flask was evacuated, *trans*-2-butene (2.5 mL, 1.2 g, 21 mmol) was added by vacuum transfer and the solution allowed to warm to room temperature. A solution of the dibromobis(triisopropylsilyl)silane in THF was prepared (50 mg, 0.1 mmol) and added to the butene solution. The mixture was placed in an ultrasound bath until the reaction between the dibromide and the lithium had started, as indicated by coloring of the solution. Then the addition of the remaining dibromobis(triisopropylsilyl)silane (200 mg, 0.4 mmol in 25 mL of THF) solution was started and continued dropwise over 2 h.

When the reaction was complete, as indicated by the complete loss of the starting dibromide by GC/MS, the THF and 2-butene were removed in vacuo. The flask was brought into the glovebox, pentane (5 mL) added, and the excess lithium removed by filtration through a piece of glass wool contained in a pipet. The solvent was removed in vacuo and a

sample prepared for NMR analysis in benzene- d_6 . Analysis of the ^{13}C NMR spectrum of this mixture showed the presence of bis(triisopropylsilyl)silane, tetrakis(triisopropylsilyl)disilene, and the desired *trans*-2,3-dimethyl-1,1-bis(triisopropylsilyl)silirane.

The *trans*-2,3-dimethyl-1,1-bis(triisopropylsilyl)silirane (50 mg, 20% yield) was isolated by kugelrohr distillation at 0.1 Torr and 120 °C. NMR analysis showed a binary mixture of bis(triisopropylsilyl)silane and *trans*-1,1-bis(triisopropylsilyl)-2,3-dimethyl-silirane: ^1H NMR (C_6D_6 , ppm): 0.75 (m, 2H), 1.15–1.24 (bm, 42H), 1.55 (d, 6H). ^{13}C NMR (C_6D_6 , ppm): 14.50 (iPr, CH), 19.42 (CH), 19.69 (CH_3), 19.99 (iPr, CH_3), 20.56 (iPr, CH_3). ^{29}Si NMR (C_6D_6 , ppm): 11.68, –149.6.

***cis*-1,1-Bis(triisopropylsilyl)-2,3-dimethylsilirane** was prepared in an analogous fashion. ^1H NMR (C_6D_6 , ppm): 1.08–1.14 (bm, 44H), 1.46 (d, 6H). ^{13}C NMR (C_6D_6 , ppm): 13.21, 13.65, 14.06 (CH, iPr), 14.95 (CH, iPr), 20.26 (CH_3 , iPr), 20.35 (CH_3 , iPr). ^{29}Si NMR (C_6D_6 , ppm): –159.1, 8.2, 14.5.

Photolysis of Tris(triisopropylsilyl)silane in the presence of *cis*-Butene at Room Temperature. Tris(triisopropylsilyl)silane (98.7 mg, 0.2 mM) was weighed into a large diameter photolysis tube equipped with a vacuum stopcock, and dried pentane (5 mL) was added, followed by 10 μL of dodecane. A sample was taken for GC analysis, and then 2 mL of *cis*-butene was added by vacuum transfer. Following this, the solution was degassed to 1 μmHg by five freeze–thaw cycles. The sample was irradiated for 3 h, and GC analysis indicated 30% reaction, so the reaction mixture was irradiated for an additional 3 h. The photolysis tube was taken into the glovebox, and the entire contents transferred to a 50 mL flask and sealed with a stopcock. The volatiles were removed in vacuo, taking care to exclude air. The nonvolatile component was dissolved in benzene- d_6 for analysis by ^1H , ^{13}C , and ^{29}Si NMR. *Within the limits of the NMR analysis the only silirane formed had a cis configuration.* In addition to the *cis*-silirane, the compounds 1,1,1,3,3,3-hexaisopropyltrisilane and 3-bis(triisopropylsilyl)silyl-1-butene were observed. 3-Bis(triisopropylsilyl)silyl-1-butene: MS (EI): *m/e* (relative intensity) 398 (M+, 0.6), 355 (0.9), 313 (0.5), 301 (0.5), 271 (1.2), 259 (1.8), 240 (83.4), 197 (100). ^1H NMR (C_6D_6 , ppm): 0.9–1.4 (bm, 46H), 3.83 (s, 1H, Si–H), 4.92 (d, $\text{CH}=\text{CHH}$, $J = 10.0$ Hz), 4.96 (d, $\text{CH}=\text{CHH}$, $J = 16.9$ Hz), 6.19 (ddd, $\text{C}=\text{CH}_2$, $J = 7.1, 10.0$ Hz, 17.1 Hz). 1,1,1,3,3,3-Hexaisopropyltrisilane: ^1H NMR (C_6D_6 , ppm): 1.15 (m, 42H), 2.97 (s, 2H). ^{13}C NMR (C_6D_6 , ppm): 13.40, 19.98. ^{29}Si NMR (C_6D_6 , ppm): 11.6, –131.1 ($^1J_{\text{Si-H}} = 160$ Hz). HRMS for $\text{C}_{18}\text{H}_{44}\text{Si}_3$: calcd 344.2751, found 344.2742.

NMR Analysis. The ^{29}Si NMR spectrum of the *cis*-2,3-dimethylsilirane contains peaks at 14.5, 8.2, and –159.1 ppm. The *trans*-2,3-dimethylsilirane has peaks at 13.1 and –149.6 ppm. The lower field peaks are much more intense and are therefore the better signals to use when looking for small quantities of material. Given a peak height of 32 cm for the *cis*-silirane at 14.5 pm, noise = ± 1 cm, one can calculate that the maximum amount of *trans*-silirane that could be present and not observed is 6%. (1:16, conservatively measured) In a like manner, using the peak at 14.98 in the *cis*-silirane as the standard, one may estimate the maximum amount of *trans*-silirane that could be present and not observed as (4/21) or 20%.

Photolysis of Tris(triisopropylsilyl)silane in the Presence of Triethylsilane at Room Temperature. Tris(triisopropylsilyl)silane (21.9 mg, 0.044 mmol) was weighed into a vial and transferred into a glovebox along with an oven-dried quartz photolysis tube equipped with a rotflo stopcock. Once in the glovebox the silane was dissolved in methylcyclohexane (MCH, 1 mL). Once the crystals had dissolved, dodecane (5.5 μL) was added as an internal standard. Triethylsilane that had been dried, distilled, and vacuum transferred into a tube with a rotflo stopcock was weighed (45 mg, 34 mmol) in the glovebox. One-half of the silane solution (0.5 mL) was added

to the triethylsilane, a drop of this solution was set aside for an initial analysis, and the rest was placed in the photolysis tube. The rotflo stopcock was closed and the tube removed from the glovebox and attached to a high-vacuum line with an O-ring joint. The solution was frozen and degassed to less than 1 μmHg pressure; this required five cycles of freeze–thaw degassing.

The solution was then irradiated for 15 min, upon which GC/MS analysis (true-total-ion, TTI, method) indicated that there was 52% conversion of the starting material, with 97% of the resulting products being bis(triisopropylsilyl)triethylsilylsilane and 3% bis(triisopropylsilyl)silane. Bis(triisopropylsilyl)triethylsilylsilane: ^1H NMR (C_6D_6 , ppm): 0.94 (q, $J = 7.5$ Hz, 6H), 1.24 (d, 36H, isopropyl methyls), 1.1–1.3 (isopropyl CH and ethyl CH_3), 2.90 (s, Si–H). ^{13}C NMR (C_6D_6 , ppm): 7.16, 8.81, 15.29, 20.63. ^{29}Si NMR (C_6D_6 , ppm): –146.0, 0.2, 14.3. HRMS for M–iPr: $\text{C}_{21}\text{H}_{51}\text{Si}_4$ calcd 415.3068, found 415.3063.

Preparation of Deuteriotriethylsilane. There have been several reports for the synthesis of deuteriotriethylsilane.^{51,52} In our hands, either they had low yields because of the difficulty of separation of product from the solvent used, or they employed expensive precursors. The neat reaction of lithium aluminum deuteride with chlorotriethylsilane lead to quantitative conversion in high yields. Lithium aluminum deuteride (0.42 g, 0.01 mol) was added to neat chlorotriethylsilane (3.0 g, 0.02 mol) at room temperature and stirred overnight. GC analysis showed complete reduction of the chlorosilane to the deuteriosilane, which was then distilled under nitrogen into a Schlenk flask. It was freeze–thaw degassed three times and vacuum transferred into a sealed transfer flask. Proton NMR integration showed the deuterium incorporation to be 95.2%. This material was identical in all ways with that reported in the literature.

Preparation of 2,2-Dideutero-1,1,1,3,3,3-hexaisopropyltrisilane. (iPr₃Si)₂SiBr₂ (100 mg, 0.2 mmol) was weighed into a 25 mL Schlenk flask and dissolved in THF. The solution was cooled to 0 °C and lithium aluminum deuteride (8.4 mg, 0.2 mmol) added. After stirring 1 h and warming to room temperature, GC/MS analysis showed complete reaction, and the reaction was stopped by pouring the reaction mixture into a separatory funnel containing hexanes (50 mL) and ammonium chloride solution (50 mL, 5%). After the layers were separated, the hexane layer was washed three times with water, dried, and concentrated, yielding 53 mg (77%) of pure material. The product had spectral data identical to those reported above for 1,1,1,3,3,3-hexaisopropyltrisilane, except the MS and the ^1H NMR spectrum, which did not contain a SiH₂ signal. MS (EI): *m/e* (relative intensity) 346 (M+, 6), 303 (53), 261 (24), 219 (39), 177 (25), 157 (100). For the analysis of deuterium incorporation in the photolysis of tris(triisopropylsilyl)silane with deuteriotriethylsilane the peak intensities used were: MS (EI) *m/e* (relative intensity obsd, calcd) 346 (100,100), 347 (35.8, 35.8), 348 (16.1,15.9), 349 (3.7, 3.7).

Photolysis of Tris(triisopropylsilyl)silane in the Presence of Deuteriotriethylsilane at Room Temperature. Tris(triisopropylsilyl)silane (8.5 mg, 0.017 mmol) was weighed into a vial and transferred into a glovebox along with an oven-dried quartz photolysis tube equipped with a rotflo stopcock. Once in the glovebox the silane was dissolved in methylcyclohexane (MCH, 0.5 mL). Once the crystals had dissolved, dodecane (4.8 mg) was added as an internal standard. Deuteriotriethylsilane, which had been dried, distilled, and vacuum transferred into a tube with a rotflo stopcock, was weighed (27 mg, 0.23 mmol) in the glovebox. The silane solution (0.5 mL) was added to the deuteriotriethylsilane, a drop of this solution was set aside for an initial analysis, and the rest was

(51) Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.

(52) Brown, J.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866.

placed in the photolysis tube. The rototflow stopcock was closed and the tube removed from the glovebox and attached to a high-vacuum line with an O-ring joint. The solution was frozen and degassed to less than 1 μmHg pressure; this required five cycles of freeze–thaw degassing.

The solution was then irradiated for 10 min, upon which GC/MS analysis (total ion integration) indicated there was 23% conversion of the starting material with 94% of the resulting products being bis(triisopropylsilyl)triethylsilylsilane and 6% 1,1,1,3,3,3-hexaisopropyltrisilane. For the analysis of deuterium incorporation in 1,1,1,3,3,3-hexaisopropyltrisilane GC/MS analysis was carried out in single-ion monitoring mode for increased sensitivity, monitoring only the parent ions and the contributing isotopic peaks 344–350. The normalized relative intensities were as follows: mass (intensity) 344 (100), 345 (41.2), 346 (20.4), 347 (8.0), 348 (3.91).

Using I_{mw} for each of the intensities and $\text{SiH}_2 = (\text{iPr}_3\text{-Si})_2\text{SiH}_2$, etc.,

$$I_{\text{tot}} = I_{\text{SiH}_2} + I_{\text{SiHD}} + I_{\text{SiD}_2} = I_{344} + I_{345} + I_{346} + I_{347} + I_{348} \quad (1)$$

$$\% \text{SiH}_2 = I_{\text{SiH}_2}/I_{\text{tot}} \quad \% \text{SiHD} = I_{\text{SiHD}}/I_{\text{tot}} \\ \% \text{SiD}_2 = I_{\text{SiD}_2}/I_{\text{tot}} \quad (2)$$

Recognizing that there are three Si atoms and 18 C atoms, one can calculate from the isotopic abundances the relative intensities for $M + 1$ (0.358), $M + 2$ (0.159), $M + 3$ (0.037) for each of the HH, HD, and D_2 compounds. Assuming I_{344} is solely due to SiH_2 , then we can easily calculate the total intensity due to SiH_2 using the known isotopic abundances (eq 3). To calculate the SiHD intensity, we look at the intensity for mass 345, but must subtract the contribution from $M + 1$ for SiH_2 (eq 4). For SiD_2 we look at mass 346, but subtract contributions from $M + 2$ of the SiH_2 and $M + 1$ of the SiHD (eq 5).

$$I_{\text{SiH}_2} = I_{344} + 0.358 \times I_{344} + 0.159 \times I_{344} + 0.037 \times I_{344} = \\ 1.554 \times I_{344} \quad (3)$$

$$I_{\text{SiHD}} = (I_{345} - (0.358 \times I_{344})) \times 1.554 \quad (4)$$

$$I_{\text{SiD}_2} = (I_{346} - (0.159 \times I_{344}) - (I_{345} - (0.358 \times I_{344}))) \times \\ 1.554 \quad (5)$$

Using these equations and the observed intensities, we calculate 90% (iPr_3Si) SiH_2 , 5% (iPr_3Si) SiHD , and 2% (iPr_3Si) SiD_2 .

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for tris(triisopropylsilyl)silane, hexaisopropylidisilane, and 1,1-bis(triisopropylsilyl)-2,3-(bistrimethylsilyl)silirene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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