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Tri-*tert*-butylsilyl(triisopropylsilyl)silylene $(t\mathrm{Bu})_3\mathrm{Si{-}Si{-}Si}(i\mathrm{Pr})_3$ and Chemical Evidence for Its Reactions from a Triplet Electronic State

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Evidence is presented for the generation of a silylene reacting from a triplet electronic state. This has proven to be a formidable task.[1−3] A conceptual basis for a successful strategy was provided in 1991 when it was recognized that the "crossover angle" $\angle\mathrm{Z{-}Si{-}Z}$, beyond which the lowest triplet state lies below the lowest singlet, decreases with decreasing electronegativity of Z.[4] With Z = trialkylsilyl the predicted crossover angle of 115−120° should be accessible, and bis(tri-isopropylsilyl)silylene $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ was generated in the hope that it would possess a triplet ground electronic state.[2] Density functional calculations by Apeloig and co-workers predict a $\Delta E_{\mathrm{S-T}} = 1.4{-}1.7$ kcal/mol for $(i\mathrm{Pr_3Si})_2\mathrm{Si}$.[5] The EPR experiment that could establish a triplet ground state has been limited by a scarcity of precursors for the photochemical generation of $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ in an organic glass.[6]

With one exception, the formation of a product of hydrogen acquisition $(i\mathrm{Pr_3Si})_2\mathrm{SiH_2}$ whose possible origin from a triplet silylene was speculative,[2] the reactions observed for $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ were those addition and insertion processes already well-known from the study of singlet silylenes.[1] This suggested that, even if $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ has a triplet ground state, reactions of the lowest singlet state might siphon off the silylene, thus preventing study of triplet silylene *chemistry*. Therefore, attention has turned to silylenes more likely to react from a triplet state, that is, silylenes predicted to have triplet ground states *and* a larger singlet−triplet splitting than $(i\mathrm{Pr_3Si})_2\mathrm{Si}$. Attempts by Wiberg to generate bis(tri-*tert*-butylsilyl)silylene $(t\mathrm{Bu_3Si})_2\mathrm{Si}$ by a silylenoid route suggested that this silylene, while predicted to possess a triplet ground state, might be too sterically hindered to undergo intermolecular reactions.[7] For tri-*tert*-butylsilyl(triisopropylsilyl)silylene $(t\mathrm{Bu})_3\mathrm{Si{-}Si{-}Si}(i\mathrm{Pr})_3$, **1**, $\Delta E_{\mathrm{S-T}}$ is likely to lie between the values predicted by Apeloig for $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ (1.4−1.7 kcal/mol) and for $(t\mathrm{Bu_3Si})_2\mathrm{Si}$ (4.1−7.1 kcal/mol).[5,8] Thus, **1** seemed to be a likely candidate for a silylene with a triplet ground state that would undergo reactions from that state. Synthesis of the key starting material for **1**, $(t\mathrm{Bu})_3\mathrm{Si{-}SiBr_2{-}Si}(i\mathrm{Pr})_3$, **2**, was straightforward after recognition of a useful generalization for the formation of sterically congested Si−Si bonds by salt-elimination reactions: $\mathrm{Y_3SiM + XSiZ_3 \rightarrow Y_3Si{-}SiZ_3 + MX}$. If one reaction partner is more sterically hindered than the other, it should be the nucleophile $\mathrm{Y_3SiM}$.[9,10]

The most useful precursor of **1**, 3-phenyl-1-tri-*tert*-butylsilyl-1-triisopropylsilyl-1-silacyclopent-3-ene, **3**, was synthesized by condensation of **2** with a reagent prepared by reduction of 2-phenylbutadiene with activated magnesium (Scheme 1).

Previous reports of selectivity inversions between metal-free and organometallic reaction systems for the generation of silylenes and their equivalents,[11,12] suggest that insertion product **5** and addition product **6** are the results of *silylenoid* reactions (the latter seemingly the first magnesium-induced addition to be reported). Room-temperature photolysis of **3** and **6** in methylcyclohexane solutions containing 2,3-dimethylbutadiene or trimethylsilane serving as trapping agents gave rise to the products of π-addition, **4**, and H−Si insertion, **5**, associated with previously investigated silylenes (Scheme 2).[1,13]

In the absence of added trapping agents, photolysis of **3** leads to a mechanistically suggestive product **7** that results formally from intramolecular insertion of silylene **1** into an H−C bond of a *tert*-butyl group (Scheme 3).[14]

Formation of **7** at room temperature from a species whose H−Si and π-addition reactions reveal it to be a silylene is consistent with the reaction of an accessible triplet state. H−C insertion by a *singlet* silylene is predicted to require ca. 20 kcal/mol activation energy and has most commonly been observed as an intramolecular reaction at high temperatures.[15,16] However, intramolecular H-atom abstraction by *triplet* 1, followed by radical coupling, is a feasible pathway to **7** (Scheme 4). Intermolecular H-atom abstraction from a suitable hydrogen donor should compete with the intramolecular process. The results (Scheme 5) from photolysis of **3** in the presence of triisopropylsilane lend support to such a mechanism.

The presence of $\mathrm{HSi}(i\mathrm{Pr})_3$ leads to a marked decrease in the yield of **7**. With $\mathrm{DSi}(i\mathrm{Pr})_3$ deuterium is not incorporated in **7**.[17]

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(1) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds II*; Rappoport, Z., Apeloig, Y. Eds.; Wiley: Chichester, 1998; Chapter 43, pp 2463−2569.

(2) Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Winchester, W. R.; Braddock-Wilking, J.; Rath, N. P.; Klooster, W. T.; Koetzle, T. F.; Mason, S. A.; Albinati, A. *Organometallics* **1999**, *18*, 3921−3932.

(3) An EPR-active species formed upon irradiation of a dipropylsilicon porphyrin with visible light was reported to be a long-lived silicon diradical: Zheng, J. Y.; Konishi, K.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 9838−9843. Its relationship to triplet silylenes remains to be established.

(4) Grev, R.; Schaefer, H. F., III; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638−5643.

(5) Holthausen, M. C.; Koch, W.; Apeloig, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2623−2624.

(6) Only $(i\mathrm{Pr_3Si})_3\mathrm{SiBr}$ has been successfully photolyzed to $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ at 77 K (in a 3-methylpentane glass), and an EPR signal was observed at 9750 G (*x*-band) at 8 K that may be due to $(i\mathrm{Pr_3Si})_2\mathrm{Si}$, but that assignment remains to be confirmed: Gaspar, P. P.; Chen, T.; Haile, T.; Lei, D.; Lin, T.-S.; Smirnov, A. I.; Winchester, W. R. 31st Organosilicon Symposium, New Orleans, May 29−30, 1998, C-3.

(7) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217−252.

(8) $\Delta E_{\mathrm{S-T}}$ should increase with increasing $\angle\mathrm{Si{-}Si{-}Si}$. A reliable prediction for **1** is not yet available, but the series of X-ray crystallographic angles for the model compounds $\mathrm{R_3Si{-}SiBr_2{-}SiR'_3}$ is encouraging: 129° for R = R′ = *i*Pr (Winchester, W. R.; Rath, N. P.; Gaspar, P. P. to be published), 136.0° for R = *t*Bu, R′ = *i*Pr (Jiang, P.; Rath, N. P.; Gaspar, P. P. to be published), 141.5° for R = R′ = *t*Bu (Wiberg, N. private communication).

(9) Gaspar, P. P.; Autry, M. E.; Beatty, A. M.; Braddock-Wilking, J.; Chen, T.; Chen, Y.-S.; Chiang, M. Y.; Haile, T.; Jiang, P.; Klooster, W. T.; Koetzle, T. F.; Lei, D.; Mason, S. A.; Rath, N. P.; Winchester, W. R.; Xiao, M. New Synthetic Methods in Organosilicon Chemistry, Seoul, Korea, May 22, 1999; L-13.

(10) $t\mathrm{Bu_3SiNa + SiHCl_2Ph}$ yielded $t\mathrm{Bu_3Si{-}SiHClPh}$ whose Li salt reacted with $\mathrm{ClSi}(i\mathrm{Pr})_3$ forming $(t\mathrm{Bu})_3\mathrm{Si{-}SiHPh{-}Si}(i\mathrm{Pr})_3$. Dephenylation with HBr/$\mathrm{AlBr_3}$ led to **2**.

(11) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281−1288.

(12) Boudjouck, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.

(13) Gel permeation chromatography indicated the formation of oligomers with peaks at 1100 D and ca. 32000 D.

(14) Other products include $t\mathrm{Bu_3Si}(i\mathrm{Pr_3Si})\mathrm{SiH_2}$ **8** (≤0.5%), $i\mathrm{Pr_3SiH}$ (6.8%), $t\mathrm{Bu_3SiH}$ (6.5%).

(15) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1985**, *106*, 5421−5425; Davidson, I. M. T.; Scampton, R. J. *J. Organomet. Chem.* **1984**, *271*, 249−260; Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698−707.

(16) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, pp 335−385.

(17) In the presence of triisopropylsilane the yield of $t\mathrm{Bu_3Si}(i\mathrm{Pr_3Si})\mathrm{SiH_2}$ **8** rises slightly to 1.7% ($\mathrm{HSi}(i\mathrm{Pr})_3$, 1.1% $\mathrm{DSi}(i\mathrm{Pr})_3$), and with $\mathrm{DSi}(i\mathrm{Pr})_3$ mass spectroscopy indicates an isotopic composition: 17% $\mathrm{RR'SiH_2}$, 58% $\mathrm{RR'SiHD}$, 25% $\mathrm{RR'SiD_2}$. While **8** may be due to hydrogen acquisition by silylene **1**, there is insufficient evidence for such an interpretation.

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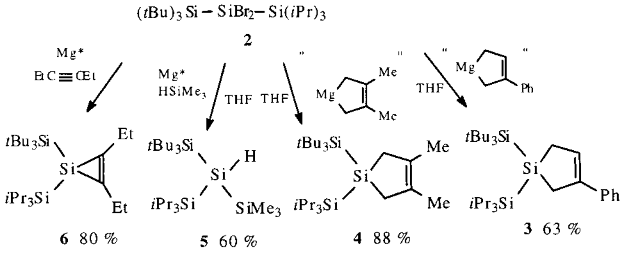
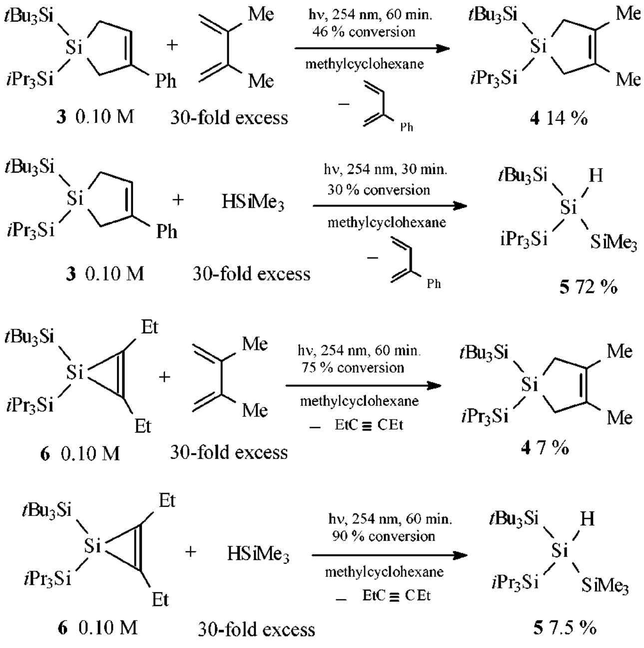
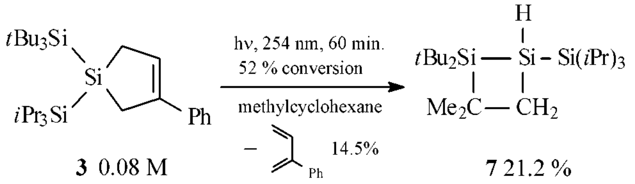
Scheme 1



Scheme 2

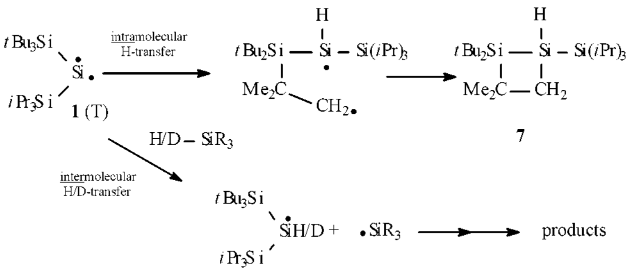


Scheme 3

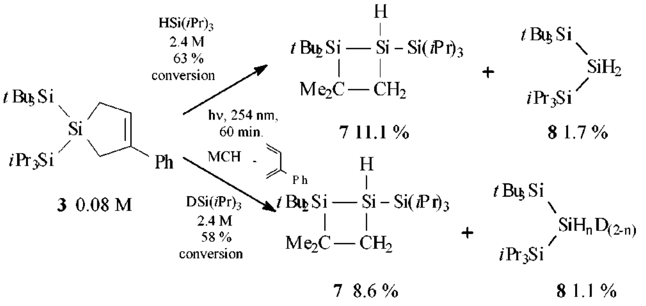


The mechanism of Scheme 4 is consistent with both of the following observations: (1) Trapping agent $HSiMe_3$ leads to a high yield of the product of formal intermolecular H−Si insertion by silylene **1**. (2) In the presence of triisopropylsilane no product of formal H−Si insertion is found, but the yield of a product of formal intramolecular H−C insertion decreases.

Scheme 4



Scheme 5



According to the mechanism of Scheme 4, the difference between $HSiMe_3$ and $HSi(iPr)_3$ as trapping agents is that the steric encumbrance of the triisopropylsilyl radical prevents coupling of the radical pair formed upon H-atom abstraction. In the case of $HSiMe_3$ the radical pair can couple to form the formal insertion product **5**. Experiments are underway to confirm reactions from a triplet state of **1** by CIDNP, while confirmation of a triplet ground state awaits discovery of a photochemical precursor for **1** that will function in a glass.

In 1997 Wiberg made a suggestion,[7] repeated recently,[18] that a product analogous to **7** from the metal-induced dehalogenation of $(tBu_3Si)_2SiX_2$ (X = F, Cl, Br) is formed via the *triplet* silylene $(tBu_3Si)_2Si$. While the suggestion is not implausible, no evidence for the intermediacy of a free silylene in the reactions studied by Wiberg has been presented, and the silylenoid intermediates that intervene in these reactions can be expected to yield similar products. Banaszak-Holl has recently activated a stable germylene toward intermolecular H−C insertion,[19] and intramolecular H−C insertion by a diarylgermylene has been promoted by Lewis acids.[20]

In conclusion, the observation that photolysis of a precursor to silylene $(tBu)_3Si{-}Si{-}Si(iPr)_3$, **1**, leads to the formation of a product of formal intramolecular H−C insertion in addition to products from intermolecular H−Si insertion and diene π-addition suggests that free silylene **1** reacted from its predicted triplet ground state. The intramolecular H−C insertion product is unlikely to arise from a singlet silylene at room temperature.

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Supporting Information Available: Experimental procedures for the synthesis of compounds **2**−**6**, the photochemical experiments on the generation of silylene **1**, and the characterization of **7** and **8**. (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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