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Tris(trimethylsilyl)sulfonium and Methylbis(trimethylsilyl)sulfonium Ions: Preparation, NMR Spectroscopy, and Theoretical Studies[1]

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Tris(trimethylsilyl)sulfonium **1** and methylbis(trimethylsilyl)sulfonium **2** ions were prepared as long-lived species by reacting trimethylsilane and trityl tetrakis(pentafluorophenyl)borate (Ph_3C^+ TPFPB) in the presence of precursor sulfides and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy at −78 °C. Attempted preparation of dimethyl(trimethylsilyl)sulfonium ion under similar conditions failed as a result of the formation of the more stabilized trimethylsulfonium ion. Structures, and ^{13}C and ^{29}Si NMR chemical shifts were calculated by density functional theory (DFT)/IGLO methods. The calculated results agree well with the experimental data.

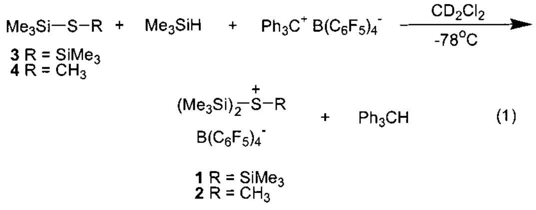
Introduction

Sulfonium salts containing a tricoordinated sulfur atom attached to three carbon atoms have been well-known since the early 1900s. Trialkylsulfonium ions are more stable than the corresponding trialkyloxonium ions and can be easily prepared by the alkylation of saturated dialkyl sulfides under mild conditions because of sufficient nucleophilicity of the sulfur atom.[2] Sulfonium salts and the ylides derived from them have become increasingly useful in organic synthesis,[3] and more recently sulfonium ions have found specific industrial applications as cationic initiators for polymerization.[4] Although there has been increasing interest in the chemistry of heterosulfonium salts in which one or more of the ligand is a heteroatom (halogen, sulfur, oxygen, or nitrogen), silyl-substituted sulfonium ions are rare and their structures have not been confirmed.[5]

Hydride transfer of organohydrosilane to trityl cations, known as Corey hydride transfer,[6] has been well adopted for the production of silyl cation[7] and synthesis of silylated onium ions.[8] We previously reported the preparation and NMR spectroscopic characterization of long-lived trisilyloxonium ions.[8c] In our continuing studies of silyl-substituted onium ions,[8a−c] we now wish to report the preparation and NMR (^{1}H, ^{13}C, ^{29}Si) spectroscopic characterization of long-lived trisilylsulfonium and methyldisilylsulfonium ions. We have also calculated the structure of the sulfonium ions using density functional theory (DFT) method. ^{13}C and ^{29}Si NMR chemical shifts of the ions were also computed using the IGLO method, and the results were compared with the experimental data.

Results and Discussion

Synthesis of Trisilylsulfonium Ion and NMR Studies. In contrast to studies on trisilyloxonium ion reported by Olah and Prakash,[8c] when the hydride abstraction from trimethylsilane by trityl TPFPB was carried out in the presence of 3−5 equiv of hexamethyldisilathiane **3** at −78 °C, trisilylsulfonium was not formed. In a separate experiment, it was shown that hexamethyldisilathiane undergoes fast exchange with trityl TPFPB in CD_2Cl_2 even at −78 °C, as shown by ^{1}H, ^{13}C, and ^{29}Si NMR. To avoid this exchange, hexamethyldisilathiane and trityl TPFPB were used in equimolar amount, so that all hexamethyldisilathiane could react with the in-situ-generated trimethylsilyl cation. Thus when trityl TPFPB in CD_2Cl_2 solution was added to a mixture of trimethylsilane and 1 equiv of hexamethyldisilathiane at −78 °C under argon in a NMR tube, successful formation of tris(trimethylsilyl)sulfonium ion **1** was observed (eq 1).



$$\mathrm{Me_3Si{-}S{-}R} + \mathrm{Me_3SiH} + \mathrm{Ph_3C^+\,B(C_6F_5)_4^-} \xrightarrow[-78^{\circ}\mathrm{C}]{\mathrm{CD_2Cl_2}} \underset{\mathrm{B(C_6F_5)_4^-}}{\mathrm{(Me_3Si)_2\overset{+}{S}{-}R}} + \mathrm{Ph_3CH} \tag{1}$$

3 R = $SiMe_3$
4 R = CH_3

1 R = $SiMe_3$
2 R = CH_3

^{1}H NMR spectrum recorded at −78 °C shows a peak at δ 0.75 corresponding to the methyl groups of trisilyl-

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[1] Considered Onium Ions. Part 53. For Part 52, see: Olah, G. A.; Prakash, G. K. S.; Rasul, G. *Proc. Natl. Acad. Sci., U.S.A.* **1999**, *96*, 3494.

[2] Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; John Wiley & Sons: New York, 1998.

[3] Stirling, C. J. M., Ed. The Chemistry of Sulphonium Group. In *The Chemistry of Functional Groups*; Patai, S., Series Ed.; Wiley: New York, 1981; Parts 1 and 2.

[4] (a) Sundell, P.-E.; Jönsson, S.; Jult, A. *J. Polym. Sci. Polym. Chem.* **1991**, *29*, 1535. (b) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J. Polym. Sci. Polym. Chem.* **1991**, *29*, 1845. (c) Decker C.; Le Xuam, H.; Nguyen Thi Viet, T. *J. Polym. Sci. Polym. Chem.* **1995**, *33*, 2759. (d) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1.

[5] Although there have been two reports on the preparation of silylsulfonium ions, the claims are not true; see refs 10 and 11.

[6] (a) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *92*, 3237. (b) Corey, J. Y.; West R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.

[7] Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191.

[8] (a) Olah, G. A.; Rasul, G.; Prakash, G. K. S. *J. Organomet. Chem.* **1996**, *521*, 271. (b) Prakash, G. K. S.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Organomet. Chem.* **1998**, *550*, 119. (c) Olah, G. A.; Li, X.-Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962. (d) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697.

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Table 1. NMR Chemical Shifts of Some Silylsulfonium Ions and Their Precursors[a]

	^{1}H ($SiCH_3$) ppm	^{13}C ($SiCH_3$) ppm		^{29}Si ppm	
compounds	exp	exp	calcd	exp	calcd
Me_3SiH	0.11	−2.6	−2.2	−16.3	−16.3
$(Me_3Si)_2S$ (**3**)	0.33	4.1	3.7	12.9	15.3
$(Me_3Si)_3S^+$ (**1**)	0.75	2.9	3.0	38.8	42.9
Me_3SiSCH_3 (**4**)	0.30	0.3	0.3	15.9	16.0
$(Me_3Si)_2S^+CH_3$ (**2**)	0.68	−0.2	−0.3	40.8	46.8

[a] Experimental and calculated chemical shifts are referenced to TMS.

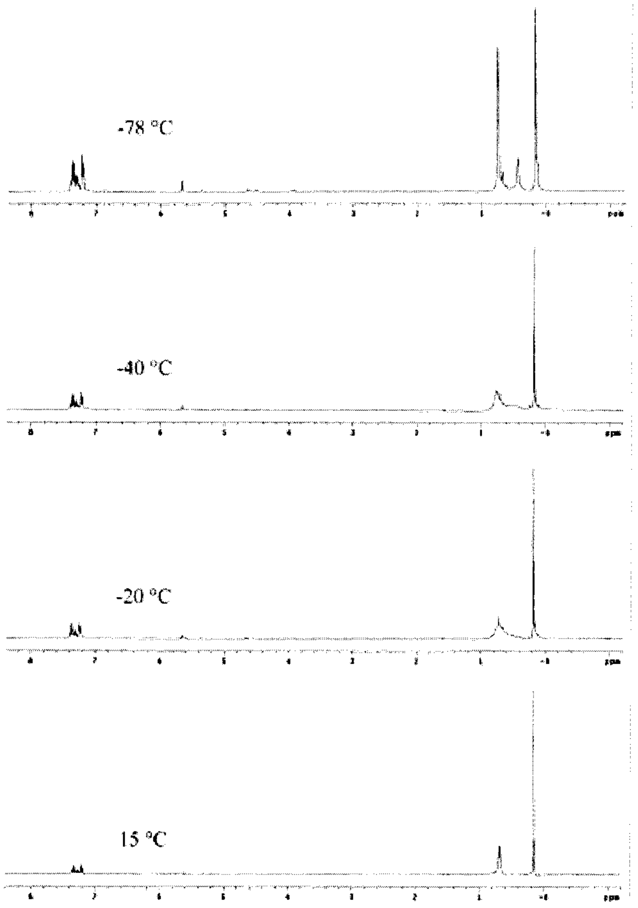


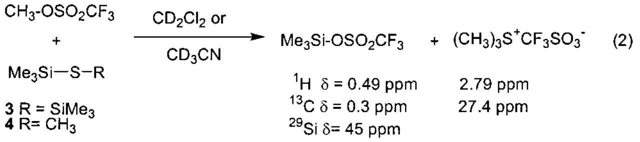
Figure 1. ^{1}H NMR spectra of $(Me_3Si)_3S^+$ at variable temperatures.

sulfonium ion. ^{13}C and ^{29}Si NMR resonances for the trisilylsulfonium ion appeared at 2.9 and 38.8 ppm, respectively (see Table 1). The ^{29}Si NMR shift of **1** is deshielded by 26 ppm compared to that of hexamethyldisilathiane (^{29}Si δ 13). Even though the chemical shifts cannot be directly related to positive charge density, the results qualitatively indicate that the positive charge of the trisilylsulfonium ion is delocalized on both S and Si atoms. To examine the stability of **1** in the solution, we further recorded the NMR spectra of the trisilylsulfonium ion at different temperatures. The NMR spectra of the trisilylsulfonium ion reaction mixture did not change below −60 °C. However, the signals of **1** and a small amount of remaining hexamethyldisilathiane coalesced on raising the temperature above −60 °C (Figure 1). This exchange was clearly indicated by the observed averaged peaks in ^{1}H, ^{13}C, and ^{29}Si NMR at room temperature; the resonances were 0.68, 3.4, and 8.7 ppm, respectively. It is interesting to note that this exchange process is thermally reversible, and a sharp singlet resonance at δ 38.8 was obtained in the ^{29}Si NMR spectrum upon cooling the solution back to −78 °C.

We treated trimethylsilyl trifluoromethanesulfonate **(**TMSOTf**)** with hexamethyldisilathiane in CD_2Cl_2 to study the effect of other low nucleophilicity counteranions. However, we observed only the starting materials by ^{1}H, ^{13}C, and ^{29}Si NMR with no evidence for the formation of trisilylsulfonium ion. This result can be explained by the strength of the stronger Si−O bond in TMSOTf compared to the Si−S bond in **1**.

Synthesis of Methyldisilylsulfonium Ion and NMR Studies. Similarly, methylthiotrimethylsilane **4** and trimethylsilane in the presence of 1 equiv of trityl TPFPB formed the corresponding methylbis(trimethylsilyl)sulfonium ion **2**, whose NMR data are also shown in Table 1. A solution of ion **2** was found to be more stable than that of ion **1**, and ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of **2** did not show any temperature dependence up to room temperature. The ^{1}H NMR chemical shifts of **2** at δ 0.68 ($Si-CH_3$) and δ 2.37 ($S-CH_3$) were found deshielded compared to the progenitor, methylthiotrimethylsilane at δ 0.30 ($Si-CH_3$) and δ 2.02 ($S-CH_3$). The ^{13}C NMR resonances at −0.2 ($Si-CH_3$) and 10.8 ppm ($S-CH_3$) also confirm the formation of **2**. ^{29}Si NMR chemical shift of **2** was found be at 40.8 ppm.

Attempted preparation of **2** either by reacting methylthiotrimethylsilane and TMSOTf or by reacting hexamethyldisilathiane and methyl iodide did not proceed; only starting materials were observed in both cases. Independent reaction of hexamethyldisilathiane and methyl triflouromethanesulfonate **(**MeOTF**)** in either CD_2Cl_2 or CD_3CN resulted in trimethylsulfonium triflate and TMSOTF quantitatively (eq 2). The products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.



Attempted Synthesis of Dimethylsilylsulfonium Ion. When dimethyl sulfide was allowed to react with trimethylsilane in the presence of 1 equiv of trityl TPFPB in CD_2Cl_2 at −78 °C, we observed a white precipitate that was characterized as trimethylsulfonium ion and triphenylmethane by NMR spectroscopy. Even under a variety of conditions no evidence for the formation of dimethylsilylsulfonium ion was found. In CD_3CN solvent, in the above experiment at −40 °C, the NMR data showed only the formation of trimethylsulfonium ion (^{1}H δ 2.79, ^{13}C δ 27.4 ppm) and triphenylmethane as well as few unidentified silyl compounds.

Attempts to prepare dimethylsilylsulfonium ion by reacting thiomethyltrimethylsilane **4** and MeOTF in either CD_2Cl_2 or CD_3CN also resulted in TMSOTf and trimethylsulfonium ion. The formation of trimethylsulfonium ion instead of dimethylsilylsulfonium ion is presumably due to displacement of the Me_3Si group in the initially formed dimethylsilylsulfonium ion to produce the more stable trimethylsulfonium ion.[9] Since the sulfonium ions are known to disproportionate, the dimeth-

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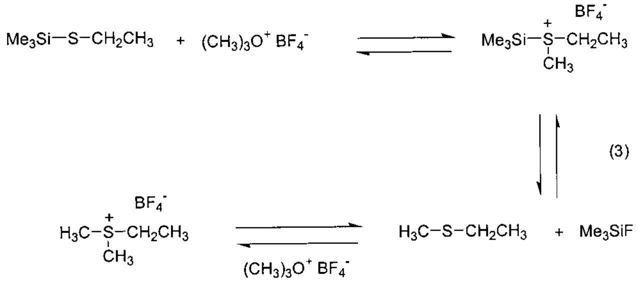
[9] Ray, F. E.; Levine, I. *J. Org. Chem.* **1937**, *2*, 267.

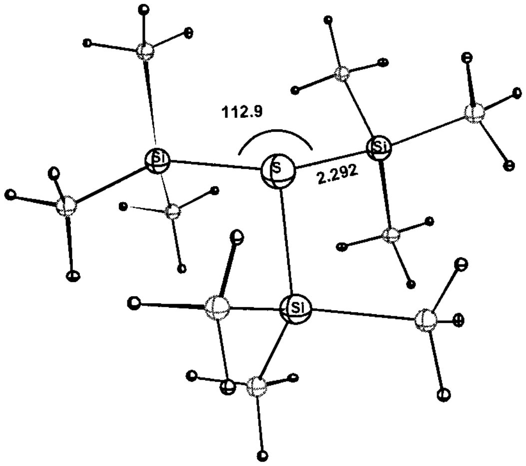
ylsilylsulfonium ion appears to desilylate and react with another molecule of MeOTf, giving trimethylsulfonium ion in all cases.

Abel et al. have claimed that a mixture of *n*-butylthiotrimethylsilane and methyl iodide upon standing in the dark for several days resulted in *n*-butylmethyl(trimethylsilyl)sulfonium iodide as a fine white precipitate.[10] The evidence for the formation of silylsulfonium ion was based on poor elemental analysis data. We have repeated the work of Abel et al. by reacting methylthiotrimethylsilane and methyl iodide in either CD_2Cl_2 or CD_3CN. The precipitation did occur in both solvents after 2 days; however, no evidence for the formation of dimethylsilylsulfonium ion was obtained by ^{13}C and ^{29}Si NMR spectroscopy. The white precipitate was found to be only the trimethylsulfonium ion (^{1}H δ 2.73, ^{13}C δ 27.4). Recently Franek and El-Sayed reported the first preparation of dialkylsilylsulfonium ions by reacting ethyl- or propylthiotrimethylsilane and Meerwein's trimethyloxonium salt. The claim for the purported silylsulfonium ions was based on the ^{1}H NMR data.[11] Repetition of this work by treating ethylthiotrimethylsilane and trimethyloxonium tetrafluoroborate in CD_3NO_2 at −10 °C gave almost identical reported ^{1}H NMR resonances (δ 0.22, 1.50, 2.91, 3.34) with a product yield of 50%.[12] However, ^{1}H NMR integration and ^{13}C NMR data (δ_{obs} 8.9, 24.7, 38.9) suggest that the observed species is actually ethyldimethylsulfonium tetrafluoroborate (eq 3). The presence

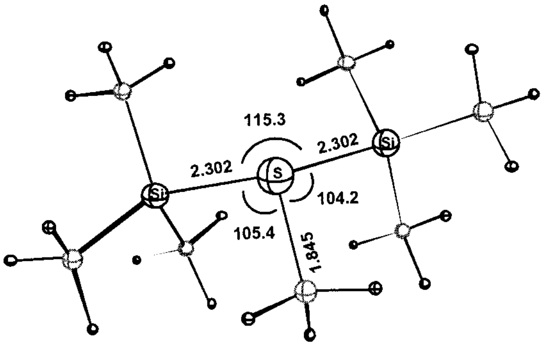


of trimethylfluorosilane[13] was also confirmed by ^{29}Si and ^{19}F NMR spectra (lit.[14] ^{29}Si, δ 32.9 in acetone-d_6 relative to internal TMS, doublet, $J = 274$ Hz; ^{19}F, δ −156 relative to internal $CFCl_3$). Trimethylfluorosilane is produced by the reaction of initially formed ethylmethyl(trimethylsilyl)sulfonium ion with the F^- ions of BF_4^- moiety. Since ethylthiotrimethylsilane requires 2 equiv of $(CH_3)_3O^+BF_4^-$ to form the ethyldimethylsulfonium ion (eq 3), when both reagents were mixed in 1:1 ratio, only half of the sulfide reacted. This result is consistent with the Franek and El-Sayed's work wherein roughly 56% yield of the product was observed.

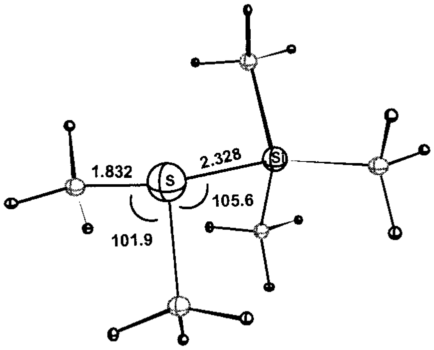
When a similar silylonium ion, trimethylsilylnitrilium tetrafluoroborate ($Me_3SiNCCH_3^+$ BF_4^-) was reported by Wenkert et al.,[15] Bassindale refuted their claim,[14] concluding that the reported preparation of silylnitrilium tetrafluoroborate actually gave trimethylfluorosilane and boron trifluoride coordinated acetonitrile complex.



$[(CH_3)_3Si]_3S^+$ **1** (C_3)



$[(CH_3)_3Si]_2S^+CH_3$ **2** (C_1)



$(CH_3)_3SiS^+(CH_3)_2$ **5** (C_s)

Figure 2. DFT B3LYP/6−3 1 G* optimized structures of **1**, **2**, and **5**.

Density Functional Theory (DFT)/IGLO Studies. To substantiate the observed experimental results we have calculated the structures and ^{13}C and ^{29}Si NMR chemical shifts of tris(trimethylsily)sulfonium **1** and methylbis(trimethylsilyl)sulfonium **2,** as well as dimethyl(trimethylsilyl)sulfonium **5** ions. The structures were fully optimized at the density functional theory (DFT) B3LYP/6−31 G* level. The minimum energy structure of tris(trimethylsilyl)sulfonium ion was found to be of C_3 symmetry, as shown in Figure 2, with Si−S bond distance of 2.292 Å. The sulfur atom in **1** is modestly pyramidal.

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[10] Abel, E. W.; Armitage, D. A.; Bush, R. P. *J. Chem. Soc.* **1964**, 2455.

[11] Franek, W.; El-Sayed, I. *Sulfur Lett.* **1996**, *19*, 181.

[12] Reported ^{1}H NMR resonances ($CDCl_3$) are δ 0.18, 1.44, 2.85, 3.30. Yield 56%.

[13] Observed Me_3SiF has ^{1}H δ 0.22 (d, $J = 7.8$ Hz), ^{13}C δ −0.1 ($J = 15.1$ Hz), ^{29}Si δ 34.3 ($J = 273$ Hz), ^{19}F δ −156 ppm.

[14] Bassindale, A. R.; Stout, T. *Tetrahedron Lett.* **1984**, *25*, 1631.

[15] Caputo, R.; Ferreri, C.; Palumbo, G.; Wenkert, E. *Tetraheron Lett.* **1984**, *25*, 577.

The pyramidalization level is about 16°, expressed as the out-of-plane bending angle of the central sulfur atom relative to the plane defined by its three bonding partners. Optimized structures of methylbis(trimethylsilyl)sulfonium and dimethyl(trimethylsilyl)sulfonium ions were found to be of C_1 and C_s symmetry, respectively, with pyramidalization levels of 19° and 21° (Figure 2).

The relative stability of trisilylsulfonium and trisilyloxonium ions were compared by using the following isodesmic reaction (eq 4). Trimethylsilyl group transfer from silylated sulfonium ion $(Me_3Si)_3S^+$ **1** to $(Me_3Si)_2O$ giving silylated oxonium ion $(Me_3Si)_3O^+$ and $(Me_3Si)_2S$ was computed to be endothermic by 11.8 kcal/mol. This again indicates that trialkylsulfonium ions are more stable than the corresponding trialkyloxonium ions. In comparison, the methyl group transfer from methylated sulfonium ion $(CH_3)_3S^+$ to $(CH_3)_2O$ giving methylated oxonium $(CH_3)_3O^+$ and $(CH_3)_2S$ was also calculated to be endothermic by 16.4 kcal/mol (eq 5).

$$(Me_3Si)_3S^+ + (Me_3Si)_2O \longrightarrow (Me_3Si)_3O^+ + (Me_3Si)_2S \tag{4}$$

$$(CH_3)_3S^+ + (CH_3)_2O \longrightarrow (CH_3)_3O^+ + (CH_3)_2S \tag{5}$$

We have also reproduced the ^{13}C and ^{29}Si NMR chemical shifts of **1** and **2** at the IGLO II//B3LYP/6-31G* level with reasonable degree of accuracy (Table 1). The calculated ^{29}Si δ of **1**, 42.9 ppm, agrees well with the experimental value of 38.8 ppm. The calculated ^{13}C δ of **1** is 3.0 ppm, also very close to the experimental value of 2.9 ppm. The calculated average ^{29}Si δ of **2** is 46.8 ppm, 6.0 ppm more deshielded than the experimental value of 40.8 ppm. On the other hand, the calculated average ^{13}C δ of Si$-$CH$_3$ in **2** is -0.3 ppm, close to the experimental value of -0.2 ppm. The ^{29}Si δ of **5** was computed to be 54.4 ppm.

Conclusions

The first silylsulfonium ions, tris(trimethylsilyl)sulfonium and methylbis(trimethylsilyl)sulfonium ions, were prepared as long-lived species and unequivocally characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The strong tendency for formation of the more stable trimethylsulfonium ion in solution has prevented successful synthesis of the dimethylsilylsulfonium ion. The structural parameters and chemical shifts of the ions were also computed by DFT/IGLO methods. The calculated results agree reasonably well with the experimental data.

Experimental Section

Apparatus and Materials. Trimethylsilane (Gelest), hexamethyldisilathiane, methylthiotrimethylsilane, and CD_2Cl_2 (Aldrich) are commercially available and were used as received. Trityl tetrakis(pentafluorophenyl)borate (Ph_3C^+ TPFPB**)** was prepared according to a literature method.[16] All NMR spectra were obtained on a Varian 300 spectrometer equipped with a variable temperature probe, and chemical shifts (^1H, ^{13}C, and ^{29}Si) were referenced to tetramethylsilane.

Tris(trimethylsilyl)sulfonium Ion. Trimethylsilane (0.1 mL, ca. 0.8 mmol) was condensed in a 5 mm J. Young NMR tube and cooled to -78 °C in a dry ice/acetone bath. Hexamethyldisilathiane (0.24 mmol) and trityl TPFPB (0.23 mmol) in CD_2Cl_2 (0.75 mL) were added subsequently to the NMR tube. The NMR tube sealed off at -78 °C, and the NMR spectra of the sample were recorded at -78 °C.

Methylbis(trimethylsilyl)sulfonium Ion. By using a similar procedure as described above, the reaction of trimethylsilane (0.1 mL) and methylthiotrimethylsilane (0.17 mmol) in the presence of 1 equiv of trityl TPFPB (0.17 mmol) in CD_2Cl_2 at -78 °C gave a solution of methylbis(trimethylsilyl)sulfonium TPFPB with triphenylmethane.

Calculation Methods, Basis Set, and Geometry. Calculations were carried out with the Gaussian 98 program system.[17] The geometry optimizations were performed using the DFT[18] method at the B3LYP[19]/6-31G* levels.[20] Vibrational frequencies at the B3LYP/6-31G*//B3LYP/6-31G* level were used to characterize stationary points as minima and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.96. Isodesmic energies were calculated at the B3LYP/6-31G*//B3LYP/6$-$31G* + ZPE level. ^{13}C and ^{29}Si NMR calculations were performed according to the reported method using IGLO programs[21] at the IGLO II′ levels using B3LYP/6-31G* geometries. Huzinaga[22] Gaussian lobes were used as follows. Basis II″: Si, 11s 7p 2d contracted to [5111111, 211111, 11], d exponent = 1.4 and 0.35; C, O: 9s 5p 1d contracted to [51111, 2111, 1], d exponent: 1.0; H: 3s contracted to [21]. The ^{13}C and ^{29}Si NMR chemical shifts were referenced to TMS (calculated absolute shift, i.e., $\delta(Si) = 380.6$ and $\delta(C) = 196.4$).

Acknowledgment. Partial support of our work by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: ^1H, ^{13}C, and ^{29}Si NMR spectra of tris(trimethylsilyl)sulfonium and methylbis(trimethylsilyl)sulfonium ions at -78 °C and room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Chien, J. C. W.; Tsai, W.-M.; Ransch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

[17] *Gaussian 98* (Revision A.5); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon, M.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1998.

[18] Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

[19] Becke's three parameter hybrid method using the LYP correlation functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[20] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

[21] Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR* **1991**, *91,* 651. Kutzelnigg, W. *Isr. J. Chem.* **1980**, *27,* 789. Fleischer, U.; Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1987**, *86,* 6337. Schindler, M. *J. Am. Chem. Soc.* **1987**, *109,* 5950.

[22] Huzinaga, S. *Approximate Atomic Wave Function*; University of Alberta: Edmonton, Alberta, Canada, 1971.