positions of the remaining hydrogen atoms were calculated (P–C–H and H–C–H = 109.5°). Refinement of all non-hydrogen atoms anisotropically resulted in $R_w = 0.068$; this small improvement (for 85 extra variables) combined with the large deviations in the anisotropic thermal parameters indicated that the data were not sufficiently accurate to warrant this degree of refinement. At this point a correction for the 1.5% decay of the three standard reflections was applied, but as expected, the effect was small. Final refinement with anisotropic thermal parameters for tungsten, antimony, and phosphorus only and recalculation of the hydrogen atom positions gave the residuals in Table X. The largest peaks on the final difference map were all due to heavy-atom noise, being randomly oriented about the tungsten and antimony atoms at distances of 1.01–1.21 and 0.96–1.10 Å, respectively. Finally, there is one relatively short intermolecular contact of 2.30 Å between F(6) and H(10) (the hydrogen atom on C(10)).

**Structure Determination of 3c.** Crystals were obtained by layering hexanes onto a cold solution of **3c** in $CH_2Cl_2$ and allowing the mixture to stand at −40 °C overnight. The successful solution of the structure ultimately justified the initial assumption of space group $P\bar{1}$. A 1.0% decay in the intensities of the three standard reflections was observed over the course of the data collection, but no correction was applied. Positions and isotropic thermal parameters for the 35 non-hydrogen atoms refined as above to $R_w = 0.076$. Positions for the hydrogen atoms were calculated (C–H = 1.00 Å), and further isotropic refinement gave $R_w = 0.063$. An absorption correction was then applied by using an 8 × 8 × 8 grid. Refinement with anisotropic thermal parameters for all non-hydrogen atoms gave the residuals in Table X. The largest peaks on the final difference map were all due to heavy-atom noise, being randomly oriented about the tungsten and antimony atoms at distances of 0.99–1.10 Å and 1.10–1.16 Å, respectively.

**Structure Determination of 5.** Crystals of **5** were grown at −40 °C as described above for **3c**. Inspection of the data showed that reflections having $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, were systematically absent, consistent only with space group $P2_1/n$. A correction for the 3.7% decay of the three standard reflections was applied. Positions and isotropic thermal parameters for the 18 non-hydrogen atoms refined as above to $R_w = 0.062$. An absorption correction was then applied by using an 8 × 8 × 8 grid. Refinement with anisotropic thermal parameters for all non-hydrogen atoms was carried out. A difference map allowed the location of five hydrogen atoms on the three methyl carbons, and the positions of the remaining hydrogen atoms were calculated (P–C–H and H–C–H = 109.5°). Final refinement of all non-hydrogen atoms using anisotropic thermal parameters gave the residuals in Table X. The largest peaks on the final difference map were all due to heavy-atom noise, being randomly oriented about the tungsten atom at distances of 0.97–1.56 Å.

**Structure Determination of 6.** Crystals of **6** were grown at −40 °C as described above for **3c**. Inspection of the data showed that reflections having $0k0, k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, were systematically absent, consistent only with space group $P2_1/n$. A correction for the 2.5% decay of the three standard reflections was applied. Positions and isotropic thermal parameters for the 20 non-hydrogen atoms refined as above to $R_w = 0.103$. An absorption correction was then applied by using an 8 × 8 × 8 grid. Refinement with anisotropic thermal parameters for the three heaviest atoms gave $R_w = 0.078$. A difference map was used to locate one hydrogen atom on each of the methyl groups, and the positions of the remaining hydrogen atoms were then calculated as above. Refinement of all non-hydrogen atoms using anisotropic thermal parameters gave the residuals in Table X. The largest peaks on the final difference map were all due to heavy-atom noise, being randomly oriented about the tungsten atom at distances of 0.09–1.16 Å.

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**Supplementary Material Available:** Tables of full crystallographic data for **3b**, **3c**, **5**, and **6**, positional parameters, bond distances and angles, and temperature factors for **3c**, **5**, and **6**, and input frequencies and output force constants for 13 compounds and details of the calculation of the Cotton–Kraihanzel force constants (25 pages); tables of structure factors for **3c**, **5**, and **6** (33 pages). The X-ray data for **3b** is available as supplementary material to ref 15. Ordering information is given on any current masthead page.

# Notes

Contribution from Dow Corning Corporation,
Midland, Michigan 48686

## A New Synthetic Route to Fluorodisilanes via Selective Reduction of Halofluorodisilanes

John J. D'Errico[†] and Kenneth G. Sharp*

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Our primary interest in fluorodisilanes was as potential molecular precursors to amorphous silicon films[1,2] containing hydrogen and fluorine. The use of fluorodisilanes for this purpose eliminates the need for precursor gas mixtures such as $SiF_4/SiH_4$.[3] In addition, lower deposition temperatures are required when compared to the case for compounds such as $SiF_2H_2$.[4]

Several routes to fluorodisilanes have been reported. Mixtures of $SiF_2HSiH_3$ and $SiF_3SiH_3$ were generated from the reaction of $SiCl_2HSiH_3$ with $SbF_3$.[5] Fluorodisilane is obtained via the cleavage of Si–O or Si–N bonds in $(Si_2H_5)_2O$ or $(Si_2H_5)_3N$ by $BF_3$.[6,7] Also, direct current ("ozonizer") plasma synthesis of the symmetrical disilanes 1,2-difluorodisilane and 1,1,2,2-tetrafluorodisilane via coupling reactions of the radicals derived from the monosilanes $SiH_3F$ and $SiH_2F_2$ has been reported.[5] This route has the disadvantages of involving slow, low-yield reactions and the difficulty of preparing pure $SiFH_3$.[8]

This report describes the reactions of bromofluoro- or chlorofluorodisilanes with $Me_3SnH$. These reactions are characterized by the selective reduction of Si–Cl or Si–Br bonds without cleavage of Si–F or Si–Si bonds.

### Experimental Section

**Materials and Manipulations.** All manipulations were conducted by using a recirculating drybox ($N_2$ atmosphere), Schlenk techniques (Ar atmosphere), and a grease-free glass vacuum line (background pressure $<10^{-4}$ Torr). Trimethyltin chloride, $SbF_3$, $[(CH_3)_2CHCH_2]_2AlH$ (DIBAL-H, Aldrich Chemical Co.), and VITRIDE (70% $NaAlH_2(OCH_2CH_2OCH_3)_2$ in toluene, Hexcel Specialty Chemicals) were used as obtained. Trimethyltin hydride was prepared from the $LiAlH_4$ reduction

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[†] Present address: Indian Orchard Plant, Monsanto Chemical Co., Springfield, MA 01151.

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of $Me_3SnCl$.[9] $SiF_2HSiF_2Br$ was obtained from the reaction of $SiF_2$[10] with HBr;[11] the redistribution of $SiF_2HSiF_2Br$ yielded $SiF_3SiF_2H$, $SiF_3SiFHBr$, and $SiF_3SiHBr_2$.[11] $SiF_3SiHCl_2$ and $SiF_2HSiF_2Cl$ were obtained from the reaction of $SnCl_4$ with $SiF_3SiHBr_2$ and $SiF_2HSiF_2Br$, respectively.[12] Unless otherwise noted, reactions involving $Me_3SnH$ were performed on a vacuum line in the absence of solvent. The tin byproduct of these reactions was shown to be $Me_3SnX$ (X = Br, Cl) by $^1H$ NMR and IR spectroscopy.[13] $Me_3SnX$ was removed from the disilanes by passing the mixtures through a trap cooled to −95 °C (toluene), at which temperature the disilanes are volatile.

**Spectral Measurements.** The NMR tubes (5 mm o.d., wall thickness 0.77 mm) were flamed out under vacuum prior to loading. High-resolution $^1H$ and $^{19}F$ NMR spectra (toluene-$d_8$) were obtained on a Varian XL200 spectrometer operating at 200 and 188 MHz, respectively. Infrared spectra (gas cell, KBr windows, 2-cm$^{-1}$ resolution) were obtained on a Nicolet 5SXB Fourier transform spectrometer.

**Reduction of $SiF_3SiHBr_2$ Using VITRIDE ($NaAlH_2(OCH_2CH_2OCH_3)_2$) or DIBAL-H (*i*-$Bu_2AlH$).** The same procedure was used with each reducing agent. $SiF_3SiHBr_2$ (0.15 mmol) was condensed into a flask at −196 °C and then warmed to −78 °C (2-propanol/$CO_2$). The reducing agent (0.15 mmol, in 15 mL of toluene) was added in portions over 30 min; no volatile compounds could be removed under vacuum at this point. The mixture was warmed to room temperature for 15 min. The volatile compounds were then removed under vacuum; an IR spectrum indicated the presence of $SiH_4$ (40%), $SiF_3H$ (40%), and $SiF_4$ (20%; yields estimated from IR measurements). There were no disilanes present in the mixture.

**Reduction of $SiF_3SiHBr_2$ Using $LiAlH_4$.** $SiF_3SiHBr_2$ (0.2 mmol) and $LiAlH_4$ (0.2 mmol) were allowed to react at room temperature for 15 min. An IR spectrum of the volatile material indicated the presence of $SiF_3H$ (45%), $SiH_4$ (45%), $SiH_3SiH_3$ (5%),[14] and unreacted $SiF_3SiHBr_2$ (5%; yields estimated from IR measurements).

**Reduction of $SiF_3SiHX_2$ (X = Br, Cl) Using $Me_3SnH$.** $SiF_3SiHBr_2$ (0.2 mmol) and $Me_3SnH$ (0.4 mmol) were warmed to room temperature for 30 min; IR spectra indicated that the $SiF_3SiHBr_2$ had been consumed. Pure $SiF_3SiH_3$, as determined from $^1H$ and $^{19}F$ NMR and IR spectra,[11,15] was isolated in 90% yield. Comparable results were obtained with $SiF_3SiHCl_2$.

$SiF_3SiHBr_2$, $Me_3SnH$, and $CF_2{=}CF_2$ (1:2:7 ratio) at −196 °C were warmed to room temperature for 10 min. An IR spectrum indicated the presence of only $SiF_3SiH_3$ and unreacted $CF_2{=}CF_2$.

One equivalent of $SiF_3SiHCl_2$ and 2 equiv of $Me_3SnH$ were condensed into an NMR tube at −196 °C. No reaction was observed via $^{19}F$ NMR as the tube was warmed to −10 °C for 25 min. The tube was then warmed to 0 °C and maintained at this temperature for 30 min. Very little $SiF_3SiHCl_2$ was observed in the mixture, the major component being $SiF_3SiH_3$. There were also small peaks due to $SiF_3SiH_2Cl$.[12] After 1 h at 0 °C, $SiF_3SiHCl_2$ and $SiF_3SiH_2Cl$ were consumed, with the major product being $SiF_3SiH_3$ (90% yield).

**Reaction of $SiF_3SiFHBr$ with $Me_3SnH$.** $SiF_3SiFHBr$ (0.2 mmol) and $Me_3SnH$ (0.2 mmol) were allowed to react at room temperature for 10 min. $^1H$ and $^{19}F$ NMR and IR spectra indicated the presence of $SiF_3SiF_2H$[11] and $SiF_3SiH_3$ in approximately equimolar amounts (90% isolated yield).

Equimolar quantities of $SiF_3SiFHBr$ and $Me_3SnH$ were condensed into a 5-mm medium-wall NMR tube at −196 °C. The mixture was warmed to −80 °C for 30 min. The $^{19}F$ NMR spectrum contained peaks due to $SiF_3SiFHBr$ (major), $SiF_3SiH_3$, $SiF_3SiF_2H$, and $SiF_3SiHBr_2$. A triplet centered at −122.9 ppm (relative to external $CFCl_3$) with $^3J_{H-F} = 7.7$ Hz was also present. The mixture was gradually warmed to 10 °C; the major products were $SiF_3SiH_3$ and $SiF_3SiF_2H$ (1:1 ratio, 90% yield), with small amounts of $SiF_3SiFHBr$ and $SiF_3SiHBr_2$ remaining.

**Reaction of $SiF_2HSiF_2X$ (X = Br, Cl) with $Me_3SnH$.** Equimolar quantities of $SiF_2HSiF_2Br$ and $Me_3SnH$ were allowed to react at room temperature for 10 min. An IR spectrum indicated the major products of the reaction to be $SiF_3SiF_2H$ and $SiF_3SiH_3$ (2:1 ratio, 90% yield). There were also absorptions in the Si–H stretching region at 2214 and 2198 cm$^{-1}$. Similar results were observed for $SiF_2HSiF_2Cl$.

Equimolar quantities of $SiF_2HSiF_2Br$ and $Me_3SnH$ were condensed into a 5-mm medium-wall NMR tube at −196 °C. The sample was gradually warmed to −40 °C and held there for 20 min. Peaks due to $SiF_3SiF_2H$, $SiF_2HSiF_2H$,[5] $SiF_3SiFHBr$, $SiF_3SiHBr_2$, and $SiF_2BrSiFHBr$[11] were observed. Most of the $SiF_2HSiF_2Br$ was gone after the mixture had been held at 10 °C for 20 min. After 30 min at 20 °C, the major products of the reaction were $SiF_3SiF_2H$ and $SiF_3SiH_3$ (2:1 ratio, 85% yield), together with equimolar quantities of $SiF_3SiHBr_2$, $SiF_3SiH_2Br$, $SiF_3SiFHBr$, and $SiF_2HSiF_2H$.

## Results and Discussion

Fluorodisilanes of the general formula $Si_2F_xH_{6-x}$ were desired as precursors for the deposition of amorphous silicon films containing both hydrogen and fluorine. Our approach to these compounds involved the initial synthesis of bromofluoro- or chlorofluorodisilanes and the subsequent selective conversion of Si–Br or Si–Cl into Si–H.

The reactions between $SiF_3SiHBr_2$ and various conventional reducing agents ($LiAlH_4$, VITRIDE ($NaAlH_2(OCH_2CH_2OCH_3)_2$), and DIBAL (*i*-$Bu_2AlH$)) resulted in the cleavage of the Si–Si bond and reduction of some Si–F bonds. Although $SiH_3SiH_3$ was observed in the reactions with $LiAlH_4$, no evidence was obtained for the formation of fluorodisilanes.

The reaction between $SiF_3SiHX_2$ (X = Br, Cl) and $Me_3SnH$ (1:2 molar ratio) proceeded smoothly at room temperature to yield $SiF_3SiH_3$ in 90% yield. There was no evidence for further reaction of $SiF_3SiH_3$ with $Me_3SnH$. A low-temperature $^{19}F$ NMR experiment (where X = Cl) indicated that these reductions proceed in a stepwise manner, as evidenced by observation of $SiF_3SiH_2Cl$.[12] $SiF_3SiH_3$ has previously been observed as a member of a complex mixture of products resulting from the reaction of $SiF_2$ and $B_2H_6$.[15] A two-step separation process then had to be used to obtain pure $SiF_3SiH_3$.

The corresponding reaction of $SiF_3SiFHBr$ with $Me_3SnH$ was expected to provide the previously unknown molecule $SiF_3SiFH_2$. However, when equimolar amounts of $SiF_3SiFHBr$ and $Me_3SnH$ were allowed to react at room temperature, the products consisted of $SiF_3SiF_2H$ and $SiF_3SiH_3$ in a 1:1 molar ratio (90% yield). There was no evidence of other disilanes in the product mixture. A possible explanation for this behavior is that $SiF_3SiFH_2$ is initially formed but that it quickly undergoes redistribution to give the observed products. Such behavior would parallel that of fluorosilane, which has been described as being very susceptible to F/H bond redistribution.[8]

Mechanistic insight into this reaction was provided by a low-temperature $^{19}F$ NMR experiment. $SiF_3SiFHBr$ and $Me_3SnH$ were condensed into an NMR tube at −196 °C and warmed to −80 °C for 30 min. An NMR spectrum obtained at this point indicated the presence of $SiF_3SiFHBr$, $SiF_3SiH_3$, $SiF_3SiF_2H$, and $SiF_3SiHBr_2$. A triplet centered at −122.9 ppm (relative to external $CFCl_3$) with $^3J_{H-F} = 7.7$ Hz is very similar to that observed for $SiF_3SiH_2Cl$[12] and is assigned to $SiF_3SiH_2Br$. There was no direct evidence for the formation of $SiF_3SiFH_2$ even at this low temperature. The presence of $SiF_3SiHBr_2$ indicates that the starting material undergoes F/Br redistribution reactions prior to reduction by the tin hydride (eq 1). $SiF_3SiHBr_2$ could then undergo stepwise

$$2SiF_3SiFHBr \rightarrow SiF_3SiF_2H + SiF_3SiHBr_2 \qquad (1)$$

reduction (via $SiF_3SiH_2Br$) to the observed $SiF_3SiH_3$.

In the absence of $Me_3SnH$, $SiF_3SiFHBr$ requires several hours at room temperature to undergo redistribution to form $SiF_3SiF_2H$ and $SiF_3SiHBr_2$. This observation suggests that $Me_3SnH$ is promoting redistribution (eq 1), even at −80 °C. Conversion of Si–Br into Si–H by the tin hydrides occurs only after this redistribution has occurred.

The reaction between $SiF_2HSiF_2Br$ and $Me_3SnH$ was also investigated. An infrared spectrum of the products of a room-temperature reaction indicated the presence of $SiF_3SiF_2H$ and $SiF_3SiH_3$ (2:1 ratio, 90% yield). There was also an absorption in the Si–H stretching region at 2214 cm$^{-1}$; this feature is tentatively assigned to $SiF_2BrSiFHBr$, given the similarity of this

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stretching frequency to that of $SiF_3SiFHBr$ (2216 cm$^{-1}$). A second absorption at 2198 cm$^{-1}$ could be due to a compound such as $SiF_3SiH_2Br$, as this frequency lies between the Si–H stretches of $SiF_3SiH_3$ (2189 cm$^{-1}$) and $SiF_3SiHBr_2$ (2203 cm$^{-1}$).[16]

A low-temperature $^{19}F$ NMR experiment revealed a rather complex series of reactions. As was the case for $SiF_3SiFHBr$, this reaction is characterized by the initial F/Br redistribution of the starting $SiF_2HSiF_2Br$. A complicating factor is the availability of both ends of $SiF_2HSiF_2Br$ for redistribution (for $SiF_3SiFHBr$, $SiF_3$ is inert with respect to redistribution). The redistribution of $SiF_2HSiF_2Br$ leads to the formation of $SiF_3SiF_2H$, $SiF_2BrSiFHBr$, $SiF_3SiFHBr$, and $SiF_3SiHBr_2$.[11] Additionally, the direct reduction of the starting material to $SiF_2HSiF_2H$ appears to proceed at a competitive rate, as a small amount of this compound was observed in the early stages of this reaction.

It was thought that the corresponding redistribution reactions would be slower for $SiF_2HSiF_2Cl$, thus allowing the isolation of $SiF_2HSiF_2H$. However, comparable results were obtained in the reactions of $SiF_2HSiF_2Br$ or $SiF_2SiF_2Cl$ with $Me_3SnH$.

Organotin hydrides typically react with organic halides and unsaturated bonds via a free-radical mechanism. These reactions require heating, irradiation, or initiation by a free-radical source.[17] However, in the case of the bromofluoro- or chlorofluorodisilanes, the reactions proceeded below room temperature and in the absence of free-radical initiators. There was no evidence of Si–Si bond cleavage or products attributable to coupling of free radicals. Additionally, the reaction of $SiF_3SiHBr_2$ with $Me_3SnH$ was unaffected by the presence of $CF_2{=}CF_2$; under free-radical conditions, products attributable to the addition of $Me_3SnH$ to the olefin should be apparent.[18] A mechanism that is consistent with these observations involves a four-centered transition state in which there is a pairwise exchange of atoms between the silicon and tin. This type of transition state has been postulated for other reductions involving $Me_3SnH$[19] and for the F–Br exchange observed between disilane molecules.[11]

Other reactions of alkyltin hydrides have been suggested to proceed via nucleophilic attack of the tin hydride, resulting in a polar transition state.[20] However, these reactions are promoted by the presence of polar solvents. Since the reactions involving halofluorodisilanes can occur in the gas phase, we do not feel that polar transition states play an important role in these reactions.

## Conclusions

$SiF_3SiH_3$ is obtained in 90% yield from the reaction of $SiF_3SiHX_2$ (X = Br, Cl) with 2 equiv of $Me_3SnH$. F/Br redistribution precedes reduction in reactions between $SiF_3SiFHBr$ and $Me_3SnH$, resulting in mixtures of $SiF_3SiF_2H$ and $SiF_3SiH_3$ (1:1 ratio, 90% yield). The reaction of $SiF_2HSiF_2X$ (X = Br, Cl) with $Me_3SnH$ also led to mixtures of $SiF_3SiF_2H$ and $SiF_3SiH_3$ (2:1 ratio) in 85–90% yield; small amounts of $SiF_2HSiF_2H$ (<5%) were also observed.

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**Registry No.** $SiF_3SiHBr_2$, 56144-86-6; $NaAlH_2(OCH_2CH_2OCH_3)_2$, 22722-98-1; *i*-$Bu_2AlH$, 1191-15-7; $SiH_4$, 7803-62-5; $SiF_3H$, 13465-71-9; $SiF_4$, 7783-61-1; $LiAlH_4$, 16853-85-3; $SiH_3SiH_3$, 1590-87-0; $SiF_3SiHCl_2$, 119895-84-0; $Me_3SnH$, 1631-73-8; $CF_2{=}CF_2$, 116-14-3; $SiF_3SiH_2Cl$, 121097-51-6; $SiF_3SiFHBr$, 56144-87-7; $SiF_3SiF_2H$, 24628-33-9; $SiF_3SiH_3$, 15195-26-3; $SiF_2HSiF_2Br$, 51040-08-5; $SiF_2HSiF_2Cl$, 119895-86-2; $SiF_2HSiF_2H$, 34669-37-9; $SiF_2BrSiFHBr$, 56144-88-8; $SiF_3SiH_2Br$, 121097-52-7.

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Contribution from the Chemistry Department,
The Chinese University of Hong Kong,
Shatin, NT, Hong Kong

# Theoretical Study of the Structures, Relative Stabilities, and Infrared Spectra of the Isomeric NSO$^-$ Anions

Suk Ping So

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The potassium salt of the NSO$^-$ anion was first prepared and characterized by vibrational spectroscopy about 10 years ago by Armitage and Brand.[1] They suggested that this anion be called the thiazate ion. However, the synthesis, spectroscopic data, and X-ray structure of the isovalent thionitrite anion SNO$^-$ (as the $(Ph_2P)_2N^+$ salt) were reported only recently.[2]

To compare the structures, stabilities, and spectroscopic properties of the above two isomeric anions, Chivers et al.[3] have carried out a calculation on their structures. They optimized the bond angles of NSO$^-$ and SNO$^-$ by the MNDO method, fixing the bond lengths at those for $(Ph_2P)_2N^+SNO^-$ obtained from X-ray diffraction analysis. Then a single-point ab initio calculation was done to compute the orbital eigenvalues and Mulliken's populations by using the double-$\zeta$ basis (i.e. each atomic orbital is represented by two basis functions) of Clementi and Roetti[4] augmented with a 3d polarization function on sulfur (DZ+d(S)).[5] In fact, the equilibrium geometries and relative stabilities of NSO$^-$ and SNO$^-$ have been computed earlier by Ehrhardt and Ahlrichs[6] using the ab initio SCF method and basis sets of better than double-$\zeta$ plus polarization functions quality.

To the author's knowledge, the other isomeric anions SON$^-$ and cyclic cy-NSO$^-$ are still not known. In addition, infrared data for SNO$^-$ are lacking. Hence, a theoretical study on the structures and infrared spectra of these four isomeric anions was carried out in the hope that this work may be helpful to their future experimental identification. The optimized geometries of NSO$^-$ and SNO$^-$, though reported earlier,[6] were recalculated because it is more consistent to discuss and compare results of these anions obtained with the same basis set.

## Calculations

The structures of NSO$^-$, SNO$^-$, SON$^-$, and cy-NSO$^-$ were fully optimized by the energy gradient method using the GAUSSIAN 82 and Gaussian 86 packages of programs.[7] The standard 6-31G* and 6-31+G* basis functions were used. (A 6-31G split-valence basis set utilizes the expansion of six Gaussian functions for each inner-shell atomic orbital and, for each valence atomic orbital, two valence shells comprising three and one Gaussian functions, respectively. A 6-31G* basis set results when a set of six d-type functions for the second-row atom is added.) The extra electron in an anion is usually weakly bound. Even large basis sets such as 6-31G* do not incorporate functions with significant amplitude at a distance from their center and thus do not provide a completely adequate description of molecular species in which a large portion of the valence electron density is allocated to diffuse lone-pair or to antibonding orbitals. One way to overcome problems associated with anion calculations is to include in the basis set one or more highly diffuse functions, such as the 6-31+G* set, which is the 6-31G* set augmented by a single set of diffuse Gaussian s- and p-type functions for each of the constituent atoms.[8] These basis functions are then able to describe properly the

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