stretching frequency to that of SiF$_3$SiFHBr (2216 cm^{-1}). A second absorption at 2198 cm^{-1} could be due to a compound such as SiF$_3$SiH$_2$Br, as this frequency lies between the Si–H stretches of SiF$_3$SiH$_3$ (2189 cm^{-1}) and SiF$_3$SiHBr$_2$ (2203 cm^{-1}).[16]

A low-temperature ^{19}F NMR experiment revealed a rather complex series of reactions. As was the case for SiF$_3$SiFHBr, this reaction is characterized by the initial F/Br redistribution of the starting SiF$_2$HSiF$_2$Br. A complicating factor is the availability of both ends of SiF$_2$HSiF$_2$Br for redistribution (for SiF$_3$SiFHBr, SiF$_3$ is inert with respect to redistribution). The redistribution of SiF$_2$HSiF$_2$Br leads to the formation of SiF$_3$SiF$_2$H, SiF$_2$BrSiFHBr, SiF$_3$SiFHBr, and SiF$_3$SiHBr$_2$.[11] Additionally, the direct reduction of the starting material to SiF$_2$HSiF$_2$H 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$_2$HSiF$_2$Cl, thus allowing the isolation of SiF$_2$HSiF$_2$H. However, comparable results were obtained in the reactions of SiF$_2$HSiF$_2$Br or SiF$_2$SiF$_2$Cl with Me$_3$SnH.

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$_3$SiHBr$_2$ with Me$_3$SnH was unaffected by the presence of CF$_2$=CF$_2$; under free-radical conditions, products attributable to the addition of Me$_3$SnH 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$_3$SnH[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$_3$SiH$_3$ is obtained in 90% yield from the reaction of SiF$_3$SiHX$_2$ (X = Br, Cl) with 2 equiv of Me$_3$SnH. F/Br redistribution precedes reduction in reactions between SiF$_3$SiFHBr and Me$_3$SnH, resulting in mixtures of SiF$_3$SiF$_2$H and SiF$_3$SiH$_3$ (1:1 ratio, 90% yield). The reaction of SiF$_2$HSiF$_2$X (X = Br, Cl) with Me$_3$SnH also led to mixtures of SiF$_3$SiF$_2$H and SiF$_3$SiH$_3$ (2:1 ratio) in 85–90% yield; small amounts of SiF$_2$HSiF$_2$H (<5%) were also observed.

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Registry No. SiF$_3$SiHBr$_2$, 56144-86-6; NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$, 22722-98-1; *i*-Bu$_2$AlH, 1191-15-7; SiH$_4$, 7803-62-5; SiF$_3$H, 13465-71-9; SiF$_4$, 7783-61-1; LiAlH$_4$, 16853-85-3; SiH$_3$SiH$_3$, 1590-87-0; SiF$_3$SiHCl$_2$, 119895-84-0; Me$_3$SnH, 1631-73-8; CF$_2$=CF$_2$, 116-14-3; SiF$_3$SiH$_2$Cl, 121097-51-6; SiF$_3$SiFHBr, 56144-87-7; SiF$_3$SiF$_2$H, 24628-33-9; SiF$_3$SiH$_3$, 15195-26-3; SiF$_2$HSiF$_2$Br, 51040-08-5; SiF$_2$HSiF$_2$Cl, 119895-86-2; SiF$_2$HSiF$_2$H, 34669-37-9; SiF$_2$BrSiFHBr, 56144-88-8; SiF$_3$SiH$_2$Br, 121097-52-7.

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

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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$_2$P)$_2$N$^+$ 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$_2$P)$_2$N$^+$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-ζ 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-ζ 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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Table I. Optimized Bond Lengths (Å), Bond Angles (deg), and Energies (au) of Isomeric NSO^- Anions

ion	prop	6-31G*	6-31+G*
NSO^-	r(SN)	1.459	1.462
	r(SO)	1.484	1.489
	∠NSO	123.0	122.4
	E_t	−526.740 00 (−527.227 47)[a]	−526.764 14 (−527.269 55)
SNO^-	r(SN)	1.715	1.706 (1.695)[a]
	r(NO)	1.195	1.196 (1.214)
	∠SNO	118.0	118.4 (120.5)
	E_t	−526.749 31 (−527.213 06)	−526.766 05 (−527.244 56)
SON^-	r(SO)	1.813	1.812
	r(NO)	1.214	1.211
	∠SON	121.3	121.5
	E_t	−526.669 38 (−527.115 89)	−526.686 58 (−527.146 23)
cy-NSO^-	r(SN)	1.799	1.760
	r(SO)	1.685	1.669
	r(NO)	1.440	1.460
	E_t	−526.629 15 (−527.101 39)	−526.648 50 (−527.139 80)

[a] MP2 energies obtained from single-point calculations and observed bond lengths and bond angles are in parentheses.

long-range behavior of molecular orbitals with energies close to the ionization limit. Hence, the relative stabilities of the isomeric anions obtained with the 6-31+G* basis set are more realistic than the 6-31G* values.

Results and Discussion

The optimized structures of the four isomeric NSO^- anions are listed in Table I. The calculated bond lengths and bond angle of the SNO^- anion are seen to be quite close to the X-ray values for this ion in $(Ph_2P)_2N^+SNO^-$.[2] It is noted that the addition of diffuse functions affects the geometry only very slightly. This is anticipated because the valence region of the 6-31G* basis set is inherently somewhat diffuse and able by itself to describe fairly properly the long-range behavior of the weakly bonded electrons.[8] Besides, molecular geometries are generally less basis set sensitive.

Comparison of the NO bond lengths of SNO^- (1.195 Å), SON^- (1.214 Å), and cy-NSO^- (1.440 Å) with those observed in some other molecules,[9] e.g. NO (1.1508 Å), NNO (1.1876 Å), NO_2 (1.193 Å), HCNO (1.207 Å), CH_2NOH (1.408 Å), and HONO (1.177 Å for N=O, 1.433 Å for N—OH), shows that the character of the NO bond changes from mainly double to mainly single across the series SNO^-, SON^-, and cy-NSO^-. As for the SO and SN bonds, the computed bond lengths (SO = 1.484 Å; SN = 1.459 Å) of NSO^- are comparable to those generally found experimentally in various molecules, e.g. SO (1.481 08 Å), SO_2 (1.4308 Å), S_2O (1.465 Å), $(CH_3)_2SO$ (1.477 Å), SN (1.4957 Å), and HNSO (SO = 1.45 Å, SN = 1.51 Å). However, the SO and SN bonds of SNO^- (SN = 1.715 Å), SON^- (SO = 1.813 Å), and cy-NSO^- (SO = 1.685 Å; SN = 1.799 Å) appear to be much longer, and only a few molecules have been found to have such long (still not as long as that of SON^-) SO/SN bonds, e.g. $(SO_3)_n$ (1.41–1.63 Å), S_4N_4 (1.62 and 1.74 Å for two different structures), H_2NSO_3 (SO = 1.44 Å; SN = 1.755 Å), and $SO_3(NO)_2^{2-}$ (NO = 1.284–1.286 Å; SO = 1.434–1.464 Å; SN = 1.791 Å).

Chivers et al.[3] optimized only the bond angles of NSO^- and SNO^- by the MNDO method and then did a single-point ab initio energy calculation using a DZ+d(S) basis set. Both methods favor SNO^- over NSO^- by about 418 kJ mol^{-1}. Ehrhardt and Ahlrichs[6] found that SNO^- was more stable than NSO^- by 15.4–19.8 kJ mol^{-1} and that a basis set extension in the polarization set (to include a second set d functions and a set of f functions) and in the valence set rendered SNO^- *less* stable by 69.9 and 65.2 kJ mol^{-1} with and without electron correlation correction, respectively. On the other hand, the present work shows that, at the SCF level of theory, both 6-31G* and 6-31+G* basis sets yield the following relative stability trend, with SNO^- being the most stable:

$$\text{cy-NSO}^- < \text{SON}^- < \text{NSO}^- < \text{SNO}^-$$

However, the inclusion of correlation energy correction reverses the order of stability of SNO^- and NSO^-:

$$\text{cy-NSO}^- < \text{SON}^- < \text{SNO}^- < \text{NSO}^-$$

Indeed, the MP2 (i.e. second-order perturbation theory with Møller–Plesset partitioning of the Hamiltonian in order to take into account the electron correlation) prediction of NSO^- to be more stable than SNO^- (by 37.8 and 65.7 kJ mol^{-1} with the 6-31G* and the 6-31+G* basis sets, respectively) may be considered to be supported by the fact that NSO^- was prepared about 10 years before SNO^- was synthesized.[1,2] Hence, this work indicates that correlation effects are important for a correct prediction of the relative stabilities of NSO^- and SNO^- if a basis set of medium size is used. It is interesting to note that ab initio calculations using the DZ+d(S), 6-31G* and MP2/6-31G* basis sets all indicate that the isoelectronic NSF is more stable than SNF.[10]

The agreement between theoretical and experimental vibrational frequencies is generally improved by scaling the raw theoretical values. The scale factor corrects both for the deficiencies in the theory and for the neglect of anharmonicity. Recently, the vibrational frequencies of quite a number of molecules have been computed at various levels of theory and compared with experiment.[11] The effect of scaling has been investigated. For 92% of the frequencies examined, the HF/6-31G* harmonic frequencies uniformly scaled by a factor of 0.89 lie within 100 cm^{-1} of experiment with a mean absolute error of 49 cm^{-1}. The vibrational frequencies and infrared intensities of NSO^-, SNO^-, SON^-, and cy-NSO^- calculated by using the 6-31G* basis set are listed in Table II. When uniformly scaled by a factor of 0.89, the calculated vibrational frequencies of NSO^- become 511, 1014, and 1284 cm^{-1}, compared favorably to the experimental values of 515, 990, and 1270 cm^{-1}. Thus, the agreement is within the expected accuracy, and the vibrational frequencies of the other three species after being scaled in this manner should therefore be rather realistic. The theoretical vibrational frequencies of the anions are all real. This shows that their optimized geometries are true equilibrium structures. As for infrared intensities, there is no experimental value available for comparison. However, data in Table II suggest that the infrared spectrum of SON^- will be weakest and that SNO^- and cy-NSO^- will each have one band and SON^- two bands probably too weak to be observed. Nevertheless, the theoretical spectra of the four anions are sufficiently different to be useful in the future identification of the yet unknown SON^- and cy-NSO^- species.

A bond between atom A and atom B may be described in terms of a covalent contribution (represented by the overlap population, q_{AB}) and an ionic contribution (represented by the charge separation, $\Delta q_{AB} = |q_A - q_B|$).[12] In similar molecules, these contributions should qualitatively parallel trends in bond lengths. Mulliken charge distributions, total atomic overlap populations, and charge separations for the isomeric NSO^- anions studied are given in Table III. As expected,[13] they are seen to be strongly dependent on the basis sets used, and thus their individual values should not be taken too literally. All the constituent atoms of the anions are found to carry some negative charge except NSO^- whose sulfur atom is positively charged, but the amount of charge on each atom and thus the charge separation between two bonded

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Table II. Calculated Vibrational Frequencies (cm^{-1}) and Infrared Intensities ($km\ mol^{-1}$) of Isomeric NSO^- Anions

NSO^-	freq	574 (515)[a]	1139 (990)[a]	1443 (1270)[a]
	intens	56	201	156
SNO^-	freq	547	811	1765
	intens	6	146	493
SON^-	freq	447	647	1619
	intens	4	3	42
cy-NSO^-	freq	380	764	1060
	intens	67	6	35

[a] Observed values.

Table III. Mulliken Charge Distributions (q_A), Total Atomic Overlap Populations (q_{AB}), and Charge Separations (Δq_{AB}) for Isomeric NSO^- Anions

ion	property	6-31G*	6-31+G*
NSO^-	q_N	−0.722	−0.736
	q_S	+0.542	+0.467
	q_O	−0.820	−0.730
	q_{SN}	+0.797	+0.342
	q_{SO}	+0.194	−1.086
	Δq_{SN}	1.264	1.203
	Δq_{SO}	1.362	1.197
SNO^-	q_S	−0.523	−0.612
	q_N	−0.037	−0.124
	q_O	−0.440	−0.264
	q_{SN}	+0.327	+0.006
	q_{NO}	+0.399	+0.207
	Δq_{SN}	0.486	0.488
	Δq_{NO}	0.403	0.140
SON^-	q_S	−0.466	−0.586
	q_O	−0.385	−0.048
	q_N	−0.149	−0.366
	q_{SO}	+0.065	−0.185
	q_{NO}	+0.313	−0.230
	Δq_{SO}	0.081	0.538
	Δq_{NO}	0.236	0.318
cy-NSO^-	q_N	−0.430	−0.572
	q_S	−0.007	−0.056
	q_O	−0.563	−0.373
	q_{SN}	+0.097	−0.292
	q_{SO}	+0.086	−0.129
	q_{NO}	−0.004	−0.252
	Δq_{SN}	0.423	0.516
	Δq_{SO}	0.556	0.317
	Δq_{NO}	0.133	0.199

atoms vary, from slightly to substantially, according to the basis sets used. On the other hand, the basis-set dependences of the total atomic overlap populations are more dramatic, the inclusion of diffuse functions changing half of the values of the total atomic overlap populations from positive to negative. Nevertheless, their relative values obtained with both the 6-31G* and the 6-31+G* basis sets correlate well with the calculated bond distances (Tables II and III) except for the SO bond of NSO^-. It is interesting to note that the bonds of NSO^- are most ionic in comparison to the bonds of the other three anions.

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Synthesis and Structural Characterization of a Mixed-Ring Rhenocene Hydride Complex, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ReH$

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Rhenocene hydride, Cp_2ReH (Cp = $\eta^5\text{-}C_5H_5$), the first carbonyl-free hydride,[2] the first hydride characterized by ^1H NMR spectroscopy, and the first bent metallocene,[3] has been quite important in the development of modern organometallic concepts since first reported in 1955. Despite this, the chemistry of this complex has remained relatively unexplored;[4] this neglect can perhaps be attributed to difficulties with its synthesis. Permethylrhenocene hydride, $Cp^*{}_2ReH$ (Cp^* = $\eta^5\text{-}C_5Me_5$), has only recently been reported,[5] and has been shown to exhibit reactivity significantly different from that observed for the cyclopentadienyl species. For example, the Re(II) species $Cp^*{}_2Re$ produced upon UV photolysis has been isolated and fully characterized.[6] The required metal vapor synthesis, however, of permethylrhenocene hydride is not amenable to general use. A solution synthesis of rhenocene derivatives based on the easily available Cp^*ReCl_4[7] (**1**) would afford an opportunity to explore the chemistry of this class of complexes. We now wish to report the synthesis, structural characterization, and some reactivity data of the new mixed-ring rhenocene hydride $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ReH$ (**2**).

Experimental Section

All manipulations were undertaken with use of standard Schlenk techniques under N_2. $NaBH_4$ (Aldrich) was used as received. Solvents were dried by refluxing over sodium wire under N_2 and stored over Davison 4-Å molecular sieves. Infrared spectra were recorded as Nujol mulls between NaCl plates with a Nicolet FT-5DX instrument. A JEOL-GLX400 spectrometer was used for ^1H and ^{13}C NMR measurements, and C_6D_6 was employed as a solvent (all spectra referenced to $SiMe_4$). Mass spectra were recorded with a Varian MAT A 311 instrument. Microanalyses were obtained from our microanalytical laboratory. Cp^*ReCl_4[8] (**1**) and NaCp[9] were prepared according to literature methods, with some modifications. In particular, yields of the reaction of $Cp^*Re(CO)_3$, available in 95% yield from $Re_2(CO)_{10}$,[10] with aqueous H_2O_2 (30%) in a two-phase benzene/water system can be improved by careful temperature control, i.e., a bath temperature not more than 80 °C, by addition of the H_2O_2 solution in two aliquots, one at the start of the reaction and one after the reaction mixture has turned deep red (ca. 3 h), by use of smaller amounts of H_2SO_4, ca. 0.1 mL for 10 g of the starting material, and by prompt termination of the reaction. It can be observed that the reaction solution first goes from clear to yellow, then to a deep red, and then back to a bright yellow. After the reaction is stopped at this point, the organic phase should be washed with a 5% aqueous $NaHCO_3$ solution before drying with $MgSO_4$ and solvent removal. Yields of 80–85% from $Cp^*Re(CO)_3$ have been consistently achieved on a 10-g scale. The raw product can be recrystallized from toluene/pentane or can be directly treated with 1 equiv of PPh_3 and excess $ClSiMe_3$ in toluene to yield >90% yields of Cp^*ReCl_4. Careful washing of the microcrystalline product from this reaction with toluene and ether directly yields Cp^*ReCl_4 of sufficient purity for further reactions. An alternative direct oxidation of $Cp^*Re(CO)_3$ to Cp^*ReO_3 in CCl_4 at −78 °C by slow addition of Mn_2O_7[11] (yield ca. 90%) has also recently been developed in this laboratory.[12] Preparation of the tetramethylethylcyclopentadienyl rhenocene hydride $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}$

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