

this series of closely related metal clusters, an *n* methyl substitution in place of a hydrogen atom on a cyclopentadienyl ring gives rise to a relatively constant charge donation to the trimetal core thereby electrostatically destabilizing the LUMO (which is mainly of antibonding trimetal orbital character). The greater instability of the LUMO (to which the electron is added upon formation of the monoanion) is then deemed to be responsible for the increased difficulty of reduction upon methyl substitution of the cyclopentadienyl ligands in this series. This observation may allow one to tailor the electrochemical properties of similar compounds by suitable choice of substituents on the cyclopentadienyl ligands.

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Supplementary Material Available: Three tables listing the observed and calculated structure factor amplitudes for $(\eta^5\text{-C}_5\text{H}_5)_2\text{CoNi}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_3\text{-CO})_2$, $\text{Ni}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-CO})_2$, and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{CoNi}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_3\text{-CO})_2$, (16 pages). Ordering information is given on any current masthead page.

Bis[bis(*F*-methyl)sulfimide], *N*-Chlorobis(*F*-methyl)sulfimide, and *N*-Fluorobis(*F*-methyl)sulfimide

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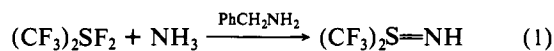
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Abstract: The first member of a new class of stable sulfimides, bis[bis(*F*-methyl)sulfimide], $(\text{CF}_3)_2\text{S}=\text{NN}=\text{S}(\text{CF}_3)_2$, results from the photolysis of $(\text{CF}_3)_2\text{S}=\text{NCl}$. The latter is prepared by reacting $(\text{CF}_3)_2\text{S}=\text{NH}$ with ClF in the presence of CsF. Under similar conditions, $(\text{CF}_3)_2\text{S}=\text{NH}$ reacts with SF_4 to give $(\text{CF}_3)_2\text{S}=\text{NF}$.

The simplest *N*-halo sulfur difluoride imides, $\text{XN}=\text{SF}_2$ ($\text{X} = \text{F, Cl, Br, I}$), have been synthesized via the mercurial $\text{Hg}(\text{NSF}_2)_2$ in reaction with the respective halogen under mild conditions¹ or from the appropriate *N*-halogen hexamethyl disilazanes and SF_4 .¹ The chloro compound is also formed when NSF is treated with chlorine in the presence of CsF.² However, the formal parent sulfimide, $\text{HN}=\text{SF}_2$ has not been prepared. Earlier we reported the synthesis of bis(*F*-methyl)sulfimide, $(\text{CF}_3)_2\text{S}=\text{NH}$ ^{3,4} and some nucleophilic reactions of its lithium derivative.^{3,5} It now has been possible to synthesize the fluoro and chloro analogues of $(\text{C-F}_3)_2\text{S}=\text{NH}$ as well as the bis[bis(*F*-methyl)sulfimide] $(\text{CF}_3)_2\text{S}=\text{NN}=\text{S}(\text{CF}_3)_2$.

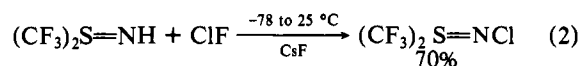
Results and Discussion

When a primary amine is added to a mixture of NH_3 and $(\text{CF}_3)_2\text{SF}_2$, bis(*F*-methyl)sulfimide, $(\text{CF}_3)_2\text{S}=\text{NH}$, is formed in 50%–60% yield (eq 1).^{3,4} It is stable in Pyrex glass under ambient



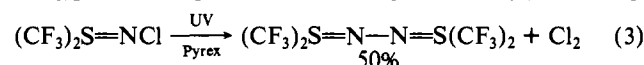
conditions for extended periods. Although the lithiated salt $\text{LiN}=\text{S}(\text{CF}_3)_2$ behaves as a useful transfer reagent for the $(\text{C-F}_3)_2\text{S}=\text{N}$ - moiety, prior to this report the parent imine has not been used successfully as a precursor to new $(\text{CF}_3)_2\text{S}=\text{N}$ containing compounds.

At first glance, it is somewhat surprising that when an equimolar mixture of ClF and $(\text{CF}_3)_2\text{S}=\text{NH}$ in the presence of CsF is allowed to warm from -78 to 25°C over a 12-h period, the product is the slightly yellow *N*-chloro imide, viz.



rather than a saturated derivative or molecules of decomposition. The carbon analogue $(\text{CF}_3)_2\text{C}=\text{NCl}$ is synthesized similarly although saturation of the $>\text{C}=\text{N}$ bond occurs if the reaction temperature is allowed to approach 25°C .⁶ In a qualitative comparative study of the relative ease of saturating the double bond in $\text{CF}_3\text{SF}_3=\text{NCF}_3$ and $\text{CF}_3\text{SF}_4\text{N}=\text{CFCF}_3$, it was found that ClF did not saturate at a temperature lower than 50 and 70°C , respectively.⁷ In the presence of CsF, saturation occurred at or below 25°C . Thus, as would be expected, the polarity of the $\text{S}^{\text{IV}}\text{-N}$ bond in $(\text{CF}_3)_2\text{S}=\text{NCl}$ is much reduced over that of the $\text{S}^{\text{VI}}\text{-N}$ bond in $\text{CF}_3\text{SF}_3=\text{NCF}_3$, and addition does not occur. The new chloro imide is stable for a few hours in Pyrex glass at 25°C and decomposes to the volatile $(\text{CF}_3)_2\text{S}$ and other unidentified material. In the mass spectrum, an intense molecular ion is observed where the appropriate ^{35}Cl – ^{37}Cl isotope ratio is present. Preliminary electron diffraction studies indicate that the bond angles and bond distances in $(\text{CF}_3)_2\text{S}=\text{NCl}$ differ markedly from those of $\text{F}_2\text{S}=\text{NCl}$. These data will be published upon completion of the study.

As is typical of compounds which contain positive halogen atoms, i.e., O-Cl or $>\text{NCl}$, photolysis, even through Pyrex glass, results in the generation of chlorine and a second compound which contains an O-O or $>\text{N-N}<$ bond. Such is the case for $(\text{CF}_3)_2\text{S}=\text{NCl}$ (eq 3). The novel bis[bis(*F*-methyl)sulfimide],



which is a colorless liquid, is stable in Pyrex glass for indefinite periods. Although a molecule ion is not observed in the mass spectrum, determination of molecular weight with use of PVT

(1) Glemser, O.; Mews, R. *Adv. Inorg. Chem. Radiochem.* **1972**, *11*, 238 and references therein.

(2) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1787.

(3) Morse, S. D.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1976**, 560.

(4) Morse, S. D.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 33.

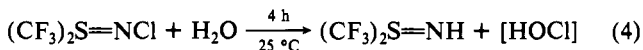
(5) Morse, S. D.; Shreeve, J. M. *Inorg. Chem.* **1978**, *17*, 2169.

(6) Swindell, R. F.; Zaborowski, L. M.; Shreeve, J. M. *Inorg. Chem.* **1971**, *10*, 1635.

(7) Yu, S. L.; Shreeve, J. M. *Inorg. Chem.* **1976**, *15*, 14.

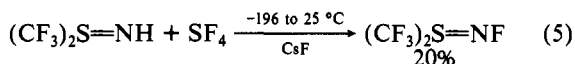
techniques gives a value of 360 (theoretical 368). Elemental analysis supports the proposed composition. The carbon analogue $(CF_3)_2C=N-N=C(CF_3)_2$ is known,⁶ but we believe this to be the first such sulfur-nitrogen compound.

N-Chlorobis(*F*-methyl)sulfimide is sensitive to moisture as is demonstrated by its slow hydrolysis in an infrared cell when the contents were exposed to relatively dry Idaho air, viz.



This reaction was monitored with infrared studies by observing the appearance and growth of ν_{N-H} .

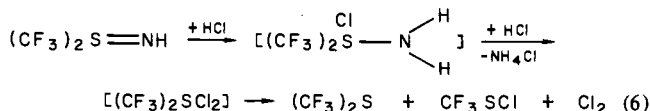
When $(CF_3)_2C=NH$ is reacted with $SF_4(CsF)$, a double-bond shift occurs to form $(CF_3)_2C(F)N=SF_2$.⁸ In sharp contrast, $(CF_3)_2S=NH$ with $SF_4(CsF)$ undergoes only a hydrogen displacement reaction and no 1,3 shift is observed.



The latter shift is a very characteristic reaction mode where $(CF_3)_2C=NX$ ($X = H, Li$) is involved, and dozens of examples are available in the literature. The driving force must be the formation of the strong C-F bond with concomitantly little change in energy involved in the shift from $>C=N$ to $N=S<$ in the SF_4 case. However, in reaction with $(CF_3)_2S=NH$, there are no energy gains to be made by the formation of another S-F bond which would be accompanied by a change in the coordination number of sulfur(IV) from 3 to 4 and a double-bond shift to form another $>S=N$ bond if $(CF_3)_2SFN=SF_2$ were synthesized. Comparison of the known three- and four-coordinate sulfur(IV) compounds indicates that the three-coordinate systems tend to have greater stability. If the isomer $(CF_3)_2S(F)N$ were formed, because of the driving force of the strong $S=N$ bond, the $N=S$ stretching frequency should appear at $\sim 1500\text{ cm}^{-1}$ (NSF_2NR_2 at $\sim 1475\text{ cm}^{-1}$). No infrared bond is observed at such energy. Again because of the unpredictability of the position for the $=N-F$ ^{19}F NMR signal it is not a firm basis for argument, but, on the other hand, it is unlikely that the S-F ^{19}F NMR band would occur as high as $\phi -50$ when it is found at $\phi +66.9$ and $+79.0$ for NSF_3 and NSF_2NR_2 , respectively. Therefore, it must be concluded that this isomer is not formed. In this case, SF_4 behaves strictly as a fluorinating reagent.

The new *N*-fluorobis(*F*-methyl)sulfimide is a colorless compound which can be separated from the reaction mixture by trap-to-trap distillation where it is retained at $-116^\circ C$. A molecular ion as well as a peak at 134 (CF_3SNF^+) and others appropriate to this structure are found in the mass spectrum. The ^{19}F NMR spectrum contains two singlets at $\phi -66.4$ (CF_3) and at $\phi -50.0$ (NF) in the ratio of 6:1. $(CF_3)_2S=NF$ is stable in Pyrex glass at $25^\circ C$ for limited periods.

When equimolar quantities of $(CF_3)_2S=NH$ and anhydrous HCl were reacted at $-78^\circ C$, a white crystalline solid, NH_4Cl , and volatile products, identified as $(CF_3)_2S$, CF_3SCl , CF_3Cl , and Cl_2 , were observed. The products suggest that the initial reaction was one of addition of HCl to the $>S=N$ bond with loss of NH_3 , leaving the unstable $(CF_3)_2S_2Cl_2$ which spontaneously decomposed, viz.



(8) Glemser, O.; von Halasz, S. P. *Chem. Ber.* **1969**, *102*, 3333.

(9) Glemser, O.; Koch, W. *Z. Naturforsch. B.* **1968**, *23*, 745.

Experimental Section

Materials. $(CF_3)_2S=NH$ was prepared according to the literature method.⁴ Chlorine monofluoride (Ozark-Mahoning) and SF_4 (Matheson) were used as received.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourden tube gauge. Most of the starting materials and products were measured quantitatively with use of PVT techniques. Products were purified by fractional condensation (trap-to-trap distillation). Infrared spectra were recorded with a Perkin-Elmer 457 or 599 spectrometer with a 10-cm cell with use of KBr windows. ^{19}F NMR spectra were obtained on a Varian HA-100 Spectrometer by using CCl_3F as an internal standard. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer operating at an ionization potential of 17 eV. Elemental analysis were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of *N*-Chlorobis(*F*-methyl)sulfimide. Bis(*F*-methyl)sulfimide, $(CF_3)_2S=NH$ (1 mmol), and ClF (1 mmol) were condensed into a Pyrex reaction vessel containing cesium fluoride at $-196^\circ C$. The mixture was allowed to warm slowly to $-78^\circ C$, and then it was warmed from $-78^\circ C$ to $25^\circ C$ over 12 h. After trap-to-trap distillation, $(CF_3)_2S=NCl$ was found in a trap at $-78^\circ C$ in about 70% yield. Its infrared spectrum (gas phase) shows bands at 1280 sh, 1250 s, 1230 s, 1195 s, 1140 vs, 1075 vs, 990 vs, 730 vs, and 670 cm^{-1} . A molecular ion is observed at m/e 219 (M^+ , 36%) in the mass spectrum. In addition, other peaks were recorded at m/e 170 ($(CF_3)_2S^+$, 11.5%), 150 (CF_3SNCl^+ , 25.6%), 120 (CF_3SF^+ , 15.4%), 115 (CF_3SN^+ , 15.4%), 101 (CF_3S^+ , 6.4%), 82 (CF_2S^+ , 10.2%), 69 (CF_3^+ , 100%), and 46 (SN^+ , 20.5%). The ^{19}F NMR spectrum showed a singlet at $\phi -66.8$. After about 6 h at ambient temperature, $(CF_3)_2S=NCl$ decomposes to $(CF_3)_2S$ as the main volatile compound (identified from its infrared spectrum).

Preparation of *N*-Fluorobis(*F*-methyl)sulfimide. Equimolar amounts (1 mmol) of $(CF_3)_2S=NH$ and SF_4 were condensed into a Pyrex glass reactor at $-196^\circ C$ which contained an excess of CsF. The mixture was warmed to $25^\circ C$ over a period of 4 h. After trap-to-trap distillation, $(CF_3)_2S=NF$ was collected in a trap at $-116^\circ C$ in about 20% yield. The infrared spectrum is as follows: 1280 w, 1240 vs, 1180 vs, 1100 vs, 740 m, 670 cm^{-1} . A molecular ion is observed at m/e 203 (M^+ , 10%). The other principal peaks are observed at 170 ($(CF_3)_2S^+$, 5%), 134 (CF_3SNF^+ , 5%), 120 (CF_3SF^+ , 30%), 101 (CF_3S^+ , 15%), 82 (CF_2S^+ , 5%), 69 (CF_3^+ , 100%), and 46 (SN^+ , 17.5%). The ^{19}F NMR spectrum showed two singlets at $\phi -66.4$ and $\phi -50.0$ in the ratio of 6:1.

Preparation of $((CF_3)_2S=N)_2$. *N*-Chlorobis(*F*-methyl)sulfimide, $(CF_3)_2S=NCl$, was condensed into a Pyrex reaction vessel at $-196^\circ C$, and then it was photolyzed at room temperature overnight. After trap-to-trap distillation, $((CF_3)_2S=N)_2$ stopped in a trap at $-66^\circ C$ in about 50% yield. Its infrared spectrum shows peaks at 1250 s, 1220 s, 1140 s, 990 m, 745 m, 605 m, and 450 cm^{-1} . A molecular peak is not observed in the mass spectrum but peaks at m/e 303 ($(CF_3)_2SNCF_2CF_3^+$, 1.2%), 253 ($(CF_3)_2SNCF_3^+$, 1.2%), 203 ($(CF_3)_2SNF^+$, 28.9%), 170 ($(CF_3)_2S^+$, 14.5%), 120 (CF_3SF^+ , 41.1%), 101 (CF_3S^+ , 13.3%), 69 (CF_3^+ , 100%), and 46 (SN^+ , 15%) are observed. The ^{19}F NMR spectrum showed a singlet at $\phi -67.3$. Anal. Calcd. for $((CF_3)_2S=N)_2$: C, 13.04; N, 7.60; F, 61.95. Found: C, 12.26; N, 7.23; F, 61.2.

Reaction of $(CF_3)_2S=NH$ and Anhydrous HCl. Equimolar amounts (1 mmol) of $(CF_3)_2S=NH$ and anhydrous HCl were condensed into a Pyrex reaction vessel at $-196^\circ C$. The mixture was slowly warmed to $-78^\circ C$. After keeping it at this temperature for 15 min, a white crystalline solid which was identified to be NH_4Cl along with the volatiles $(CF_3)_2S$, CF_3SCl , CF_3Cl , and Cl_2 were observed. These products were identified from their infrared spectra and in the case of Cl_2 from color and the cold trap in which it was retained after trap-to-trap distillation.

Hydrolysis of $(CF_3)_2SNCl$. Atmospheric air was introduced into the gas infrared cell containing $(CF_3)_2S=NCl$ to study the hydrolysis. The infrared spectrum showed the formation of $(CF_3)_2S=NH$.

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