closure and that the t product arises through ring closure in t-Co(tren)$(OH_2)(NH_2(CH_2)_2SCH_3)^{3+}$ formed by slow isomerization of the p isomer.

Registry No. p-*N*,*S*-Co(tren)-(*R*)-cysS^{2+}, 66495-52-1; t-*N*,*S*-Co(tren)-(*R*)-cysS^{2+}, 66609-59-4; t-[Co(tren)$(NH_2(CH_2)_2S)]Cl_2$, 66495-53-2; p-[Co(tren)$(NH_2(CH_2)_2S)]Cl_2$, 66537-70-0; p-*N*,*O*-[Co(tren)-(*R*)-cys$SCH_3]Cl_2$, 66574-20-7; t-*N*,*O*-[Co(tren)-(*R*)-cys$SCH_3]S_2O_6$, 66495-50-9; p-*N*,*S*-[Co(tren)$(NH_2(CH_2)_2SCH_3)]Cl_3$, 66495-51-0; t-*N*,*S*-[Co(tren)$(NH_2(CH_2)_2SCH_3)]Cl_3$, 66538-33-8; p-*N*,*S*-[Co(tren)-(*R*)-cys$SCH_3]Cl_3$, 66505-74-6; t-*N*,*S*-[Co(tren)-(*R*)-cys$SCH_3]Cl_3$, 66537-95-9; p-[Co(tren)$(NH_2(CH_2)_2SCH_3)]I_3$, 66505-75-7; t-[Co(tren)$(NH_2(CH_2)_2SCH_3)]I_3$, 66537-96-0; t-[Co(tren)-(*R*)-cys$SCH_3](NCS)_3$, 66537-98-2; p-[Co(tren)-(*R*)-cys$SCH_3](ClO_4)_3$, 66495-55-4; [Co(tren)$(OH_2)(OH)](ClO_4)_2$, 66495-57-6; [Co(tren)$(Me_2SO)_2](ClO_4)_3$, 66495-59-8; t-[Co(tren)$(NH_2(CH_2)_2SCH_3)]^{3+}$ (*S*), 66537-71-1; t-[Co(tren)$(NH_2(CH_2)_2SCH_3)]^{3+}$ (*R*), 66537-72-2; t-*N*,*S*-[Co(tren)-(*R*)-cys$SCH_3]^{3+}$ (*S*), 66537-73-3; t-*N*,*S*-[Co(tren)-(*R*)-cys$SCH_3]^{3+}$ (*R*), 66537-74-4; p-*N*,*S*-[Co(tren)-(*R*)-cys$SCH_3]^{3+}$ (*S*), 66537-75-5; p-[Co(tren)$(NH_2(CH_2)_2SCH_3)]^{3+}$ (*R*), 66537-76-6; p-[Co(tren)$(NH_2(CH_2)_2SCH_3)]^{3+}$ (*S*), 66537-77-7; ^{13}C, 14762-74-4.

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(24) This rate is not easily reproduced and hours may be necessary at ~20 °C. This irreproducibility is a kinetic characteristic of substitution reactions of such S-bound Co(III) complexes.[2]

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Nucleophilic Reactions of Lithium Bis(trifluoromethyl)sulfimide

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Lithium bis(trifluoromethyl)sulfimide, $LiN{=}S(CF_3)_2$, is a moderately stable precursor to several new bis(trifluoromethyl)sulfimides. With $(CH_3)_3SiCl$, $CF_3C(O)Cl$, CNCl, CF_3SO_2F, $ClSO_2F(SO_2Cl_2)$, and OPF_2Cl, $(CH_3)_3SiN{=}S(CF_3)_2$, $CF_3C(O)N{=}S(CF_3)_2$, $NCN{=}S(CF_3)_2$, $CF_3SO_2N{=}S(CF_3)_2$, $ClSO_2N{=}S(CF_3)_2$, and $OPF_2N{=}S(CF_3)_2$ are formed. The bis[bis(trifluoromethyl)sulfimides] $(CH_3)_2Si[N{=}S(CF_3)_2]_2$ and $CO[N{=}S(CF_3)_2]_2$ result with $(CH_3)_2SiCl_2$ and $COCl_2$. With the exception of the carbonyl compound which is a stable white crystalline solid, all of the sulfimides are moderately stable liquids of low volatility.

The reactive nucleophile lithium hexafluoroisopropylidenimine, $LiN{=}C(CF_3)_2$, is a valuable precursor to a large number of new compounds and interesting reactions.[1-11] Recently we reported the syntheses of bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$,[12,13] and its lithium salt.[12] Although

$$(CF_3)_2SF_2 + NH_3 \xrightarrow{RNH_2} (CF_3)_2S{=}NH \qquad 60\% \quad (1)$$

$$(CF_3)_2S{=}NH + n\text{-}C_4H_9Li \xrightarrow{\text{hexane}} (CF_3)_2S{=}NLi + C_4H_{10} \qquad 80\% \quad (2)$$

the route to this sulfimide salt is a multistep, moderate-yield process, the unusual opportunity for comparison of the reaction possibilities and properties of the products obtained with those of the carboimide, $(CF_3)_2C{=}NLi$, made further study of $(CF_3)_2S{=}NLi$ a worthwhile undertaking.

$$Cl_3CSCl + NaF \xrightarrow{\text{TMSO}} CF_3SCl \qquad 47\%$$

$$CF_3SCl + AgOC(O)CF_3 \rightarrow CF_3SOC(O)CF_3 + AgCl \qquad 90\text{–}100\%$$

$$CF_3SOC(O)CF_3 \xrightarrow[\text{Pyrex}]{h\nu} CF_3SCF_3 \qquad 90\text{–}100\%$$

$$CF_3SCF_3 + ClF \rightarrow CF_3SF_2CF_3 \qquad 75\%$$

+ reactions 1 and 2

While lithium bis(trifluoromethyl)sulfimide is less stable than its carbon analogue, it can be retained at 25 °C for brief periods without measurable decomposition. It undergoes reactions with a variety of molecules with electropositive centers but the stability of the products obtained is a function of the oxidation state of the elements at those centers. This is a difficulty inherent in sulfur(IV) systems which is not encountered with the much less easily reduced carbon compounds.

Results and Discussion

The trifluoromethyl groups bonded to carbon in $(CF_3)_2C{=}NH$ enhance the electrophilicity of the carbon–nitrogen double bond making it very susceptible to nucleophilic attack. This reactivity has been well studied.[14-30] Similarly in the case of $(CF_3)_2S{=}NH$, direct reaction with substrates does not permit the introduction of the $(CF_3)_2S{=}N-$ moiety. However, lithium bis(trifluoromethyl)sulfimide makes such synthetic reactions possible. Reaction 2 produces the golden yellow solid, $(CF_3)_2S{=}NLi$, and gives a quantitative amount of *n*-butane. A reddish black solid is obtained with concomitant lower yield of product in subsequent reaction when the $(CF_3)_2S{=}NH$ is added initially in greater than 0.25 mmol aliquots to the *n*-butyllithium solution. An excess of $(CF_3)_2S{=}NH$ is added and any unreacted sulfimide is removed under vacuum after reaction with the *n*-butyllithium is complete.

Although no formal decomposition studies of the lithium compound were undertaken, if allowed to remain at 25 °C for several days, its ability to introduce the $(CF_3)_2S{=}N-$ group was reduced markedly. However, no deleterious effects were noted after only several hours. The compound was not further characterized and its composition is based on products obtained in reactions described below.

When compounds with electrophilic centers and suitable leaving groups were condensed onto the lithium compound, metathetical reactions occurred, viz.

$$RX + (CF_3)_2S{=}NLi \rightarrow (CF_3)_2S{=}NR + LiX$$

$$RX = (CH_3)_3SiCl,\ CF_3C(O)Cl,\ CNCl,\ CF_3SO_2F,\ SO_2Cl_2,\ SO_2FCl,\ OPF_2Cl$$

$$RX_2 + 2(CF_3)_2S{=}NLi \rightarrow [(CF_3)_2S{=}N]_2R + 2LiX$$

$$RX_2 = (CH_3)_2SiCl_2,\ COCl_2$$

In general, these new bis(trifluoromethyl)sulfimides are liquids of low volatility with the exception of carbonyl bis[bis(trifluoromethyl)sulfimide], $CO[(CF_3)_2S{=}N]_2$, a colorless crystalline solid, which melts at 37.5 °C. All were handled in a standard vacuum line with slightly volatile liquids made accessible for analysis by manipulation via syringe in an inert atmosphere.

If the inlet temperature of the mass spectrometer is maintained at 25 °C, a molecular ion and a fragmentation pattern consistent with the proposed structure were observed in the mass spectrum of each molecule. The nuclear magnetic resonance spectra contain resonances of appropriate area ratios with little or no evidence of spin–spin coupling.

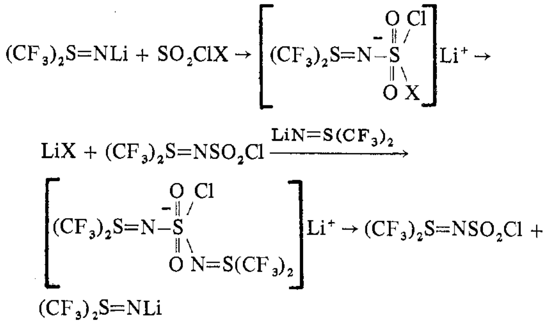
The thermal stability of these bis(trifluoromethyl)sulfimides varies over a wide range. For example, after 5 h at 78 °C in Pyrex glass, $(CF_3)_2S{=}NSi(CH_3)_3$ was decomposed. Similarly, $(CF_3)_2S{=}NC(O)CF_3$ was destroyed after 2 h at 75 °C. Even less stable was the $(CF_3)_2S{=}NSO_2CF_3$ which deteriorated after only a few days at 25 °C. Although it was possible to obtain mass, infrared, and NMR spectral data for $[(CF_3)_2S{=}N]_2Si(CH_3)_2$, attempts were unsuccessful to purify the compound adequately for elemental analysis. Extreme sensitivity toward hydrolysis made complete characterization of $(CF_3)_2S{=}NP(O)F_2$ difficult.

In contrast, the carbimides are much more stable; e.g., $(CH_3)_3SiC{=}N(CF_3)_2$ can be heated to 180 °C without change.[1] The disubstituted silyl compound $(CH_3)_2Si[C{=}N(CF_3)_2]_2$ can be distilled at 85 °C under reduced pressure.[31]

In the sulfonyl compounds, the sulfur is susceptible to nucleophilic attack by $(CF_3)_2S{=}N^-$. However, there is no evidence for any reaction with CF_3SO_2Cl at 25 °C without solvent. If, instead, CF_3SO_2F is reacted at 25 °C, the metathesis reaction proceeds as expected.

$$(CF_3)_2S{=}NLi \begin{array}{l} + CF_3SO_2Cl \rightarrow \text{no reaction} \\ + CF_3SO_2F \rightarrow (CF_3)_2S{=}NSO_2CF_3 + LiF \end{array}$$

The latter reaction occurs because of the greater positive character of the sulfur bonded to fluorine which enhances nucleophilic attack and the driving force provided by the high lattice energy of the product, LiF. Other sulfonyl halides, SO_2Cl_2 and SO_2ClF, react at 25 °C with $(CF_3)_2S{=}NLi$ to form $(CF_3)_2S{=}NSO_2Cl$ in each case. None of the disubstituted sulfonyl compound was isolated in either case even when the nucleophile was present in large excess. Our unsuccessful attempts to prepare the sulfonyl disulfimide may result from the decrease in the electrophilicity of the sulfur as chlorine or fluorine is replaced by the first bis(trifluoromethyl)sulfimide group making it less suitable for nucleophilic attack. On the other hand, it is possible that the monosubstituted sulfonyl sulfimide does undergo further nucleophilic attack to form a five-coordinate sulfur intermediate but under the conditions employed the $(CF_3)_2S{=}N^-$ unit is a better leaving group than Cl^- and disubstitution is precluded.



$$(CF_3)_2S{=}NLi + SO_2ClX \rightarrow \left[(CF_3)_2S{=}N-\overset{-}{S}(=O)_2(Cl)(X)\right]Li^+ \rightarrow LiX + (CF_3)_2S{=}NSO_2Cl \xrightarrow{LiN{=}S(CF_3)_2} \left[(CF_3)_2S{=}N-\overset{-}{S}(=O)_2(Cl)(N{=}S(CF_3)_2)\right]Li^+ \rightarrow (CF_3)_2S{=}NSO_2Cl + (CF_3)_2S{=}NLi$$

X = Cl, F

Sulfonyl difluoride does not react neat. This is likely due to kinetic rather than thermodynamic factors.

In contrast to the reaction with sulfonyl chloride fluoride, chlorine in OPF_2Cl is preferentially replaced by $(CF_3)_2S{=}N^-$. Here the high LiF lattice energy does not adequately compensate for the breaking of a very strong P–F bond and thus the weaker P–Cl link is severed with concomitant LiCl formation.

Reactions of $(CF_3)_2S{=}NLi$ with several compounds, particularly those in which the central atom is not present in its maximum oxidation state, result in the formation of decomposition products. In nearly all of the reactions studied at least small amounts of bis(trifluoromethyl) sulfide were observed and often it was the major volatile product formed in addition to dark, nonvolatile, intractable solids or liquids.

$$RX + (CF_3)_2S{=}NLi \rightarrow CF_3SCF_3 + \text{others}$$

$$RX = CF_3SCl,\ CF_3S(O)Cl,\ SF_5Cl,\ C(O)Cl_2,\ C(O)F_2,\ NOCl,\ NF_2Cl,\ Cl_2$$

Modifications of reaction conditions may enhance the success of formation of the various bis(trifluoromethyl)sulfimides.

The reaction of CF_3SCl with $(CF_3)_2S{=}NLi$ at −78 °C provides an excellent example of the elimination process which occurs when the nucleophile interacts with compounds which contain lower valent sulfur. If the product is removed below 25 °C and then allowed to warm to room temperature, CF_3SCF_3 is evolved and a white solid remains. Mass spectral analysis of this material indicates the formation of two interesting cyclic compounds, the trimer $(NSCF_3)_3$ and tetramer $(NSCF_3)_4$

$$(CF_3)_2S{=}NLi + CF_3SCl \rightarrow [(CF_3)_2S{=}NSCF_3] + LiCl$$

$$\hookrightarrow CF_3SCF_3 + (NSCF_3)_x \quad x = 3, 4$$

In this scheme the sulfur(IV) of the sulfimide is reduced to sulfur(II) in CF_3SCF_3 and the sulfur(II) of CF_3SCl is oxidized to sulfur(IV) in the cyclic compounds.

Similarly, elimination of CF_3SCF_3 occurs when COX_2 (X = Cl, F) and $(CF_3)_2S{=}NLi$ are reacted in equimolar amounts. It likely proceeds as follows.

$$\mathrm{COX_2 + (CF_3)_2S{=}NLi \rightarrow [(CF_3)_2S{=}NC(O)X] \xrightarrow{[1,3]F\sim}}$$
$$\mathrm{[(CF_3)_2S(X)NCO] \rightarrow CF_3SCF_3 + [XNCO]}$$

This shift, particularly in the case of X = F, has been observed by us when $(CF_3)_2C{=}NLi$ was reacted with COX_2[1] and by others with fluorophosphoranes[10] or when $(CF_3)_2C{=}NH$ was reacted with SOF_2 in the presence of CsF.[32] In these cases, the products remaining after the fluoride ion shift were isolable. Unfortunately in our reaction the interesting four-coordinate sulfur intermediate is unstable with respect to CF_3SCF_3. However, when an excess of $(CF_3)_2S{=}NLi$ is used in the carbonyl halide reaction, the disubstituted product is obtained which indicates that nucleophilic attack at the carbon in the $(CF_3)_2S{=}NC(O)X$ intermediate is the preferred or more rapid reaction compared to halide ion shift.

Experimental Section

Materials. $(CF_3)_2S{=}NH$,[29] CF_3SCl,[33] $CF_3S(O)Cl$,[34] SF_5Cl,[35] NF_2Cl,[36] and $P(O)F_2Cl$[37] were prepared according to the literature methods. $CF_3C(O)Cl$ (PCR), $C(O)F_2$ (PCR), ClCN (K and K Laboratories), $C(O)Cl_2$ (Matheson), NOCl (Matheson), and Cl_2 (J. T. Baker) were used as received without further purification.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively using *PVT* techniques. Many of the slightly volatile products were moved under dynamic vacuum into a removable "U" trap that was equipped so that liquid could be extracted through a rubber septum. Products were purified by fractional condensation (trap-to-trap distillation) or by use of an Aerograph A-90-P gas–liquid-phase chromatograph. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer with a 10-cm cell using KBr windows. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer by using CCl_3F as an internal standard. ^1H NMR spectra were obtained on either a Varian EM 360 or a Varian HA-100 spectrometer with tetramethylsilane as an internal standard, except in those cases where the sample signal is recorded at the same position as the reference. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer operating at an ionization potential of 15 or 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, or with the aid of a Perkin-Elmer 240 elemental analyzer. Boiling points and thermodynamic data were not determined because of the low thermal stability of most of the compounds. For gas chromatographic separations, the columns were constructed of 0.25-in. copper or aluminum tubing packed with 20% Kel-F oil (3M Co.) or FS-1265 (Varian) on Chromosorb P and SE 30 (Loenco) on Chromosorb W.

Preparation of Lithium Bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NLi$. One milliliter of 2 M (approximate) *n*-butyllithium in hexane solution was removed from the reagent bottle under anhydrous conditions by the use of a syringe and transferred to a clean, dry reaction flask equipped with a Kontes Teflon stopcock. About 0.125 mmol of $(CF_3)_2S{=}NH$ was condensed with liquid nitrogen onto the solution and the mixture was allowed to warm slowly from −196 °C to room temperature. The mixture was allowed to stand for several minutes to ensure complete reaction and then about 0.3 mmol of the sulfimide was condensed onto the solution. After this mixture was treated as above, approximately 0.7 mmol of sulfimide was measured and was added to the lithium salt solution. The procedure was repeated and the remainder of 2 mmol was added. After allowing the entire mixture to come to room temperature, the volatile portion of the reaction mixture was removed. This volatile portion contained primarily hexane, butane, and some unreacted bis(trifluoromethyl)sulfimide. For the best results the golden yellow solid that remained in the vessel was exposed to dynamic vacuum for several hours.

Preparation of Bis(trifluoromethyl)-*N*-(trimethylsilyl)sulfimide, $(CF_3)_2S{=}NSi(CH_3)_3$. To 1.25 mmol of $(CF_3)_2S{=}NLi$ prepared as above was added 1.25 mmol of chlorotrimethylsilane. The mixture was allowed to warm from −196 °C to room temperature over a period of several hours. Bis(trifluoromethyl)-*N*-(trimethylsilyl)sulfimide was recovered in 50% yield. A small amount (0.4 mmol) of unreacted chlorotrimethylsilane and fluorotrimethylsilane were recovered, also. $(CF_3)_2S{=}NSi(CH_3)_3$ was purified for analysis by fractional condensation only. The vapor pressure of this new compound is approximately 41 Torr at 26 °C. The ^{19}F NMR spectrum contains a resonance at 69.6 ppm and the ^1H NMR spectrum contains a resonance at 0.17 ppm. There is no F–H coupling. The infrared spectrum is as follows: 2960 (m), 2901 (w), 1301 (s), 1234 (vs, br), 1169 (s), 1105 (s), 850 (s), 750 (m), 562 (w), 456 cm^{-1} (w). The mass spectrum contained a molecular ion and an appropriate fragmentation pattern.

Anal. Calcd for $(CF_3)_2SNSi(CH_3)_3$: C, 23.34; N, 5.44; H, 3.53. Found: C, 23.71; N, 4.97; H, 3.61.

Preparation of Bis(trifluoromethyl)-*N*-(trifluoroacetyl)sulfimide, $(CF_3)_2S{=}NC(O)CF_3$. After 2.0 mmol of lithium salt was prepared, 2.0 mmol of trifluoroacetyl chloride was frozen onto the salt and allowed to warm to room temperature from −196 °C. The resulting compound, $(CF_3)_2S{=}NC(O)CF_3$, was isolated in approximately a 65% yield. The only other major volatile reaction component was unreacted $CF_3C(O)Cl$ (0.7 mmol). The $(CF_3)_2S{=}NC(O)CF_3$ was purified by fractional condensation and by gas chromatographic techniques. This molecule has a vapor pressure of 8 Torr at 26 °C. There are two resonance peaks in the ^{19}F NMR spectrum at 56.7 and 74.7 ppm. There is no coupling. The infrared spectrum is as follows: 1703 (s), 1350 (m), 1254 (vs), 1210 (s), 1181 (s), 1119 (vs), 1069 (vs), 841 (m), 758 (m), 737 cm^{-1} (m). The mass spectrum contained a molecular ion and appropriate fragmentation pattern.

Anal. Calcd for $(CF_3)_2SNC(O)CF_3$: C, 17.22; N, 4.98; F, 60.85. Found: C, 16.91; N, 5.05; F, 60.5.

Preparation of Bis(trifluoromethyl)-*N*-cyanosulfimide, $(CF_3)_2S{=}NC{\equiv}N$. By starting with 2.5 mmol of $(CF_3)_2S{=}NH$ and preparing the lithium salt as outlined above, $(CF_3)_2S{=}NC{\equiv}N$ can be synthesized in 60% yield. Cyanogen chloride was condensed onto the preformed lithium salt and the mixture was allowed to warm to room temperature slowly. This cyano derivative has a vapor pressure of 3 Torr at 26 °C. Purification was accomplished by allowing the more volatile components of the reaction mixture to vaporize from the less volatile portion. A gas chromatograph was used to purify the higher boiling fraction. $(CF_3)_2S{=}NH$ and ClCN were identified as the only other major contaminants. The single ^{19}F NMR resonance was observed at 57.6 ppm. The infrared spectrum is as follows: 2218 (w), 1255 (s), 1242 (s), 1198 (s), 1150 (s), 1120 (s), 1073 (s), 783 cm^{-1} (w). The mass spectrum contained a molecular ion and appropriate fragmentation patterns.

Anal. Calcd for $(CF_3)_2SNCN$: C, 17.14; N, 13.33. Found: C, 16.87; N, 13.12.

Preparation of Bis(trifluoromethyl)-*N*-(chlorosulfonyl)sulfimide, $(CF_3)_2S{=}NSO_2Cl$. In the usual procedure, the sulfimide lithium salt was made from 3.0 mmol of $(CF_3)_2S{=}NH$ and 1 molar equiv of *n*-butyllithium. More than a twofold excess of $ClSO_2F$ was frozen onto the lithium salt and the mixture was allowed to warm slowly to room temperature overnight. A 40% yield of $(CF_3)_2S{=}NSO_2Cl$ resulted from this reaction. Other major components were unreacted $ClSO_2F$ (3.5 mmol) and CF_3SCF_3 (~1.9 mmol). The $(CF_3)_2S{=}NSO_2Cl$ has less than 1 Torr vapor pressure at room temperature and was purified by gas chromatography after the more volatile compounds were removed on the vacuum line. The fluorine atoms on the CF_3– groups produce a single peak in the ^{19}F NMR spectrum at 57.8 ppm (singlet). The infrared spectrum is as follows: 1382 (s), 1257 (s), 1212 (s), 1180 (s), 1128 (s), 1053 (s), 980 (s), 762 (s), 584 cm^{-1} (w). The mass spectrum contained a molecular ion and appropriate fragmentation patterns.

Anal. Calcd for $(CF_3)_2SNSO_2Cl$: C, 8.47; N, 4.94; F, 40.19. Found: C, 8.50; N, 5.07; F, 40.0.

Preparation of Bis(trifluoromethyl)-*N*-(trifluoromethanesulfonyl)sulfimide, $(CF_3)_2S{=}NSO_2CF_3$. Following the procedure outlined earlier, 2.0 mmol of $(CF_3)_2S{=}NH$ was used to form the lithium sulfimido salt. After the solvent was removed, 3.0 mmol of CF_3SO_2F was condensed onto the solid and allowed to warm to room temperature in a Pyrex reaction vessel. The only volatile product of the reaction was unreacted CF_3SO_2F (2.0 mmol), but only 13% of the sulfimido moiety was isolated as $(CF_3)_2S{=}NSO_2CF_3$. The vapor pressure of the pure liquid is less than 1 Torr. After the more volatile material was removed by expansion into the vacuum line, the less volatile

$(CF_3)_2S{=}NSO_2CF_3$ was purified by gas chromatography. This molecule produced two singlets in the ^{19}F NMR spectrum at 58.3 and 76.2 ppm. The infrared spectrum is as follows: 1379 (s), 1210 (s), 1208 (s), 1150 (s), 1122 (s), 1059 (s), 983 (s), 787 (m), 759 cm^{-1} (m). The mass spectrum contained a molecular ion and appropriate fragmentation patterns.

Anal. Calcd for $(CF_3)_2SNSO_2CF_3$: C, 11.36; N, 4.42; F, 53.91. Found: C, 11.42; N, 4.58; F, 53.8.

Preparation of Carbonyl Bis[bis(trifluoromethyl)sulfimide], $CO[(CF_3)_2S{=}N]_2$. The lithium bis(trifluoromethyl)sulfimide salt was synthesized starting with 3.0 mmol of $(CF_3)_2S{=}NH$. Onto the solid lithium salt 1.5 mmol of phosgene $[C(O)Cl_2]$ was condensed and the mixture allowed to come to room temperature slowly. Approximately 0.4 mmol of unreacted $C(O)Cl_2$ was recovered in the volatile fraction along with an equal amount of CF_3SCF_3. The overall yield of the disubstituted carbonyl compound was 30%. Removal of the more volatile fraction was accomplished simply by expanding into the vacuum line and the purification of the low volatile product was completed by gas chromatography. The $CO[(CF_3)_2S{=}N]_2$ is a white, crystalline solid that melts at 37.5 °C. The ^{19}F NMR spectrum contains a resonance at 60.0 ppm which is a singlet. The infrared spectrum is as follows: 1608 (s), 1598 (m), 1250 (vbr, s), 1165 (s), 1134 (s), 1082 (s), 928 (m), 896 (m), 559 (m), 773 (m), 764 cm^{-1} (m). The mass spectrum contained a molecular ion and appropriate fragmentation patterns.

Anal. Calcd for $[(CF_3)_2SN]_2CO$: C, 15.15; N, 7.07. Found: C, 15.02; N, 7.23.

Preparation of Bis[bis(trifluoromethyl)sulfimido]dimethylsilane, $[(CF_3)_2S{=}N]_2Si(CH_3)_2$. The lithium salt was prepared by the standard method with the use of 4.0 mmol of $(CF_3)_2S{=}NH$.. The solvent was removed and 2.0 mmol of $(CH_3)_2SiCl_2$ was condensed onto the solid. After the reaction warmed slowly to room temperature, the $[(CF_3)_2S{=}N]_2Si(CH_3)_2$ was moved under dynamic vacuum into an accessible trap. Because of the low stability of this new silane, purification for elemental analysis was not successful. Decomposition occurred when purification by gas chromatography was attempted. The ^{19}F NMR spectrum contains a resonance at 74.4 ppm and the ^1H NMR spectrum contains a peak at 0 ppm. The infrared spectrum is low resolution and is as follows: 2960 (m), 2870 (w), 1295 (w), 1259 (s), 1220 (s), 1161 (s), 1077 (s, br), 1041 (s), 897 (m), 830 (m), 795 cm^{-1} (m). The mass spectrum contained a molecular ion and appropriate fragmentation patterns.

Preparation of Bis(trifluoromethyl)-*N*-(difluorophosphoryl)sulfimide, $(CF_3)_2S{=}NP(O)F_2$. Lithium bis(trifluoromethyl)sulfimide was prepared from 2.0 mmol of $(CF_3)_2S{=}NH$. The metathesis reaction occurred readily upon warming the reaction mixture of the lithium salt and 1.9 mmol of $P(O)F_2Cl$ slowly from −196 °C to room temperature. Phosphoryl fluoride (0.7 mmol) was recovered as the more volatile portion of the reaction products. The stability of $(CF_3)_2S{=}NP(O)F_2$ is low and collection of analytical data was difficult. Apparently the compound is sensitive to hydrolysis for although it could be purified by gas chromatography at 80 °C, subsequent manipulation led to decomposition even when care was taken to maintain anhydrous conditions.

Because of the problem of instability, the ^{19}F NMR spectrum of this compound was difficult to obtain. The ^{19}F resonance for the CF_3-groups is at 62.4 ppm and the fluorine atoms on phosphorus appear as a doublet whose center is at 70.2 ppm with a P–F coupling constant of 988 Hz. The infrared spectrum has low resolution and is as follows: 1314 (m), 1248 (s), 1196 (m), 1125 (m, br), 1059 (s), 910 (m), 761 cm^{-1} (m).

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Registry No. $(CF_3)_2S{=}NSi(CH_3)_3$, 61097-19-6; $(CF_3)_2S{=}NC(O)CF_3$, 61097-20-9; $(CF_3)_2S{=}NC{\equiv}N$, 66610-89-7; $(CF_3)_2S{=}NSO_2Cl$, 66610-88-6; $(CF_3)_2S{=}NSO_2CF_3$, 66610-87-5; $CO[(CF_3)_2S{=}N]_2$, 66610-86-4; $[(CF_3)_2S{=}N]_2Si(CH_3)_2$, 66610-85-3; $(CF_3)_2S{=}NP(O)F_2$, 66610-84-2; $(CF_3)_2S{=}NLi$, 61097-18-5; $(CF_3)_2S{=}NH$, 60646-40-4; $ClSi(CH_3)_3$, 75-77-4; $CF_3C(O)Cl$, 354-32-5; $ClC{\equiv}N$, 506-77-4; $ClSO_2F$, 13637-84-8; CF_3SO_2F, 335-05-7; $C(O)Cl_2$, 75-44-5; $(CH_3)_2SiCl_2$, 75-78-5; $P(O)F_2Cl$, 13769-75-0.

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