authors also express their appreciation to Professor K. Caulton (Indiana University) for comments regarding the NMR data. Computer time for the X-ray diffraction data analysis was provided by the West Virginia Network for Educational Telecomputing.

Registry No. $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, 77965-67-4; $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$, 12109-71-6.

Supplementary Material Available: Listings of least-squares planes and calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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(*F*-Tetramethylene)sulfimide and (*F*-Tetramethylene)sulfoxyimide. Some *N*-Alkyl, *N*-(*F*-Alkyl), and *N*-Halo Derivatives

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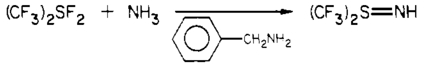
Received March 10, 1981

A new *F*-cyclic sulfimide, (*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NH, was formed when (*F*-tetramethylene)sulfur difluoride, $\overline{CF_2CF_2CF_2CF_2S}F_2$, and $LiNH_2$ were reacted in the presence of an excess of NH_3. With primary amines, $\overline{CF_2CF_2CF_2CF_2S}F_2$ gave the corresponding *N*-alkyl(*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NR (R = CH_3, C_2H_5). With LiN=C$(CF_3)_2$, $\overline{CF_2CF_2CF_2CF_2S}F_2$ results primarily in the formation of $\overline{CF_2CF_2CF_2CF_2S}$=NCF$(CF_3)_2$ and small amounts of $\overline{CF_2CF_2CF_2CF_2S}$=NC$(CF_3)$N=C$(CF_3)_2$. At reduced temperature, with the exception of *N*-(*F*-alkyl)-substituted *F*-cyclic sulfimides, the cyclic sulfimides $\overline{CF_2CF_2CF_2CF_2S}$=NR (R = H, CH_3, C_2H_5) are oxidized with *m*-chloroperbenzoic acid to the corresponding cyclic sulfoxyimides $\overline{CF_2CF_2CF_2CF_2S}$(O)=NR in high yields. *N*-Halo (Cl and Br) sulfimides were also synthesized by the reaction of $\overline{CF_2CF_2CF_2CF_2S}$=NH with Cl_2 or Br_2 in the presence of an alkali-metal fluoride (CsF or KF).

Introduction

Recently, there has been considerable interest in the chemistry of S(IV) compounds, $>SF_2$. For example, it has been shown that bis(*F*-methyl)sulfur difluoride, $(CF_3)_2SF_2$, will undergo metathesis reactions with primary amines to produce a series of new *N*-alkylbis(*F*-methyl)sulfimides, $(CF_3)_2S$=NR (R = CH_3, C_2H_5, *i*-C_3H_7).[2] The bis(*F*-methyl)sulfimide $(CF_3)_2S$=NH has also been shown to result from the reaction of $(CF_3)_2SF_2$ and NH_3 in the presence of a primary amine such as benzylamine[2] (eq 1). However, to date, no *F*-cyclic sulfimide nor its derivatives have been reported.



(1)

We have now synthesized (*F*-tetramethylene)sulfimide, *N*-alkyl(*F*-tetramethylene)sulfimides, and (*N*-*F*-alkyltetramethylene)sulfimides by the reaction of $\overline{CF_2CF_2CF_2CF_2S}F_2$ with $LiNH_2$, RNH_2 (R = CH_3, C_2H_5), and LiN=C$(CF_3)_2$, respectively, and also (*F*-tetramethylene)sulfoxyimide and *N*-alkyl(*F*-tetramethylene)sulfoxyimides by the oxidation of the corresponding cyclic sulfimides. The halogenation of $\overline{CF_2CF_2CF_2CF_2S}$=NH with Cl_2 and Br_2 in the presence of CsF or KF affords the corresponding *N*-chloro and *N*-bromo compounds which will be described also in this paper.

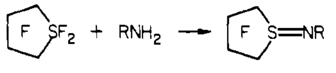
Results and Discussion

It has been shown that $(CF_3)_2SF_2$ and $\overline{CF_2CF_2CF_2CF_2S}F_2$ do not react with such weak nucleophiles as H_2O and NH_3 at ambient temperature.[3,4] In fact, $\overline{CF_2CF_2CF_2CF_2S}F_2$ does not react with NH_3 even at 100 °C for 5 h.[4] However, with excess amounts of primary amines, $(CF_3)_2SF_2$ has been shown to give *N*-alkylbis(*F*-methyl)sulfimide in reasonable yields[2] (eq 2). Furthermore, in the presence of primary amines,

$$(CF_3)_2SF_2 + 3RNH_2 \rightarrow (CF_3)_2S{=}NR + 2RNH_2HF \qquad (2)$$
$$R = CH_3,\ C_2H_5,\ CH(CH_3)_2$$

$(CF_3)_2SF_2$ has been found to react with NH_3 yielding bis(*F*-methyl)sulfimide, $(CF_3)_2S$=NH successfully.[2]

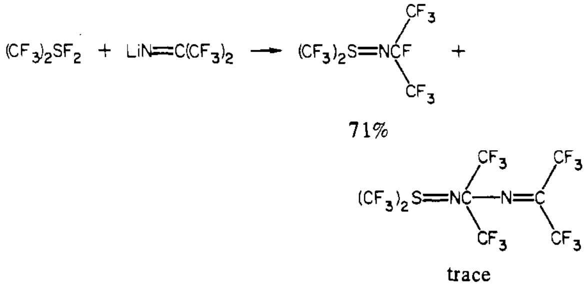
Similarly, we have found that when (*F*-tetramethylene)sulfur difluoride, $\overline{CF_2CF_2CF_2CF_2S}F_2$, was treated with primary amines, new *N*-alkyl(*F*-tetramethylene)sulfimides were formed (eq 3). These compounds are transparent liquids which are moderately stable at 25 °C.



(3)

R = CH_3 (70%), C_2H_5 (37%)

Lithium *F*-isopropylidenimine, $(CF_3)_2C$=NLi, has been used as a reactive nucleophile by workers here and elsewhere.[5,6] With $(CF_3)_2SF_2$, (*F*-isopropyl)bis(*F*-methyl)sulfimide was formed mainly together with small quantities of *N*-(*F*-isopropylidenimino)-*N*-(*F*-isopropyl)bis(*F*-methyl)sulfimide, viz eq 4.



(4)

Similarly, $\overline{CF_2CF_2CF_2CF_2S}F_2$ reacted smoothly with LiN=C$(CF_3)_2$, giving mainly *N*-(*F*-isopropyl)(*F*-tetra-

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[1] Visiting Research Scholar, Government Industrial Research Institute, Nagoya, Japan, 1979–1980.
[2] Morse, S. D.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 33.
[3] Sauer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971**, *1*, 1.
[4] Abe, T.; Shreeve, J. M. *J. Fluorine Chem.* **1973**, *3*, 17.
[5] Swindell, R. F.; Shreeve, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 5713.
[6] Swindell, R. F.; Babb, D. P.; Ouellette, T. J.; Shreeve, J. M. *Inorg. Chem.* **1972**, *11*, 242.

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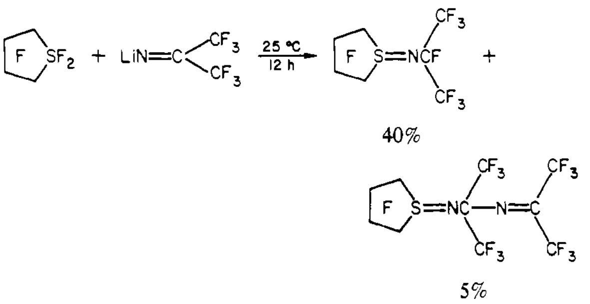
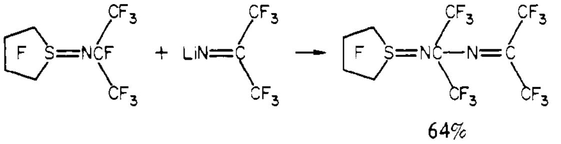
methylene)sulfimide, and small amounts of *N*-(isopropylidenimino)-*N*-isopropyl(*F*-tetramethylene)sulfimide (eq 5). When the former product was treated further with LiN=C(CF$_3$)$_2$, the latter product was obtained in a yield of 64% (eq 6). These new *N*-(*F*-alkyl) cyclic sulfimides are stable transparent colorless liquids. However, with other nucleophiles such as LiN=S(CF$_3$)$_2$[7] and NaOCH$_3$, no reaction took place. Although no comparative study of the relative reactivities of LiN=C(CF$_3$)$_2$ and LiN=S(CF$_3$)$_2$ has been reported, LiN=C(CF$_3$)$_2$ appears to behave as a stronger nucleophile than LiN=S(CF$_3$)$_2$ toward the highly electropositive isopropyl carbon.



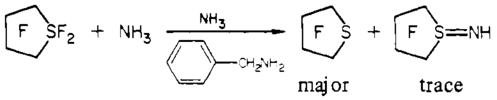
(5)



(6)

In order to compare the reactivity of LiN=C(CF$_3$)$_2$ toward S(IV) and S(VI) compounds, the reaction of the cyclic S(VI) compound $\overline{CF_2CF_2CF_2CF_2S}F_4$ with LiN=C(CF$_3$)$_2$ was also tried. It was found that $\overline{CF_2CF_2CF_2CF_2S}F_4$ did not react after 1 week at 25 °C. The inertness of the perfluorinated S(VI) compound $\overline{CF_2CF_2CF_2CF_2S}F_4$ was also demonstrated by the fact that no reaction occurred with ClF after 3 days at 25 °C.

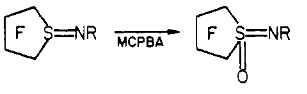
On the other hand, when the same procedure as was used for the preparation of (CF$_3$)$_2$S=NH was tried in order to obtain $\overline{CF_2CF_2CF_2CF_2S}$=NH, only traces of the new (*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NH, formed together with large quantities of the reduced product, i.e., $\overline{CF_2CF_2CF_2CF_2S}$ (eq 7). Modification of this method makes possible the preparation of the new (*F*-tetramethylene)sulfimide in a good yield.



(7)

When $\overline{CF_2CF_2CF_2CF_2S}F_2$ was treated with LiNH$_2$ in the presence of excess amounts of NH$_3$ at reduced temperature for a period of 3–4 days, the new sulfimide was found to be formed in a good yield (~80%). However, we attempted to prepare the new imide (i-C$_3$F$_7$)$_2$S=NH from (i-C$_3$F$_7$)$_2$SF$_2$ in a similar manner. We were not successful. The reason for this may be ascribed to the shielding of the central sulfur atom in (i-C$_3$F$_7$)$_2$SF$_2$ by the two i-C$_3$F$_7$ groups precluding nucleophilic attack. This new (*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}$=NH, is a colorless glass at 25 °C and was found to be a useful precursor to compounds which contain the $\overline{CF_2CF_2CF_2CF_2S}$=N group.[8] The IR spectrum of this new imide has a strong absorption band at 3315 cm^{-1} due to ν_{NH}.

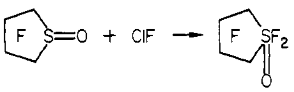
When these cyclic sulfimides (not *N*-(*F*-alkyl-substituted)) were treated with *m*-chloroperbenzoic acid (MCPBA) at reduced temperature for 3–4 days, a series of new cyclic sulfoxyimides was formed (eq 8). Acyclic sulfoxyimides, for example, bis(*F*-alkyl)sulfoxyimides, have been prepared either by the reaction of the bis(*F*-alkyl) sulfoxydifluoride with primary amines[9] or by the oxidation of bis(*F*-alkyl)sulfoxyimides with MCPBA.[2]



(8)

R = H (98%), CH$_3$ (79%), C$_2$H$_5$ (84%)

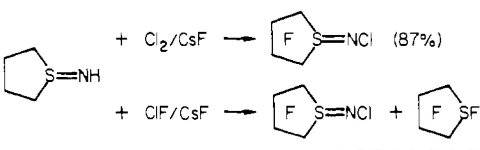
The *F*-cyclic sulfoxydifluoride $\overline{CF_2CF_2CF_2CF_2S}$(O)F$_2$ is known, having been prepared by the oxidative fluorination of $\overline{CF_2CF_2CF_2CF_2S}$=O with ClF[4] (eq 9).



(9)

However, the multistep synthesis which is required for the preparation of $\overline{CF_2CF_2CF_2CF_2S}$(O)F$_2$ and also its ease of hydrolysis limit access to $\overline{CF_2CF_2CF_2CF_2S}$(O)=NR by the first route. (*F*-Tetramethylene)sulfoxyimine, $\overline{CF_2CF_2CF_2CF_2S}$(O)=NH, is a colorless solid which freezes to a glass, while the *N*-alkyl-substituted derivatives are colorless liquids. These sulfoxyimides are stable at 25 °C for an extended period of time. The IR spectrum of $\overline{CF_2CF_2CF_2CF_2S}$(O)=NH contained a characteristic strong absorption band at 3395 cm^{-1} due to ν_{NH}.

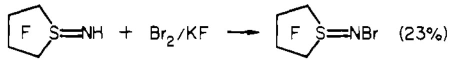
Since the alkali-metal fluorides have been shown to catalyze the halogenation of (CF$_3$)$_2$C=NH,[10] an attempt was made to extend this method to $\overline{CF_2CF_2CF_2CF_2S}$=NH. When $\overline{CF_2CF_2CF_2CF_2S}$=NH was treated with Cl$_2$ in the presence of CsF at 25 °C, the corresponding *N*-chloro derivative was formed in a good yield. The reaction of ClF with $\overline{CF_2CF_2CF_2CF_2S}$=NH in the presence of CsF was also found to give the *N*-chloro derivative. But, in this case, the chloro compound was contaminated with a considerable amount of (*F*-tetramethylene)sulfur difluoride, $\overline{CF_2CF_2CF_2CF_2S}F_2$, which was difficult to separate by trap-to-trap distillation (eq 10).



(10a)

(10b)

With Br$_2$ in the presence of KF, $\overline{CF_2CF_2CF_2CF_2S}$=NH afforded the corresponding *N*-bromo compound in a low yield (eq 11). The *N*-chloro(*F*-tetramethylene)sulfimide is a pale yellow liquid which solidifies near −40 °C, while the *N*-bromo derivative is a deeper yellow liquid.



(11)

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

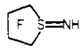
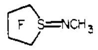
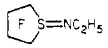
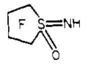
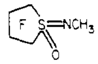
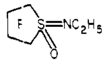
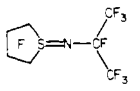
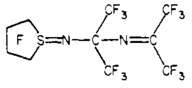
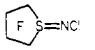
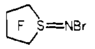
(8) Abe, T.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 242.

(9) Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* **1971**, *385*, 113.

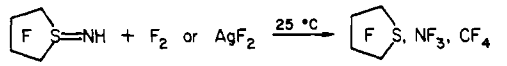
(10) Ruff, J. K. *J. Org. Chem.* **1967**, *32*, 1675.

(11) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

Table I. ^{19}F and ^{1}H NMR Spectra of (*F*-Tetramethylene)sulfimides and -sulfoxyimides

formula	α-CF_2	β-CF_2	others
	−116.8, −118.3 (1, J_{AB} = 231 Hz)	−130.8, −133.8 (1, J_{AB} = 266 Hz)	δ(H) 2.33
	−109.7 (s, 1)	−132.5, −135.9 (1, J_{AB} = 278 Hz)	δ(CH_3) 2.97
	−110.0 (d, 1), −110.3 (d, 1)	−133.1, −136.6 (1, J_{AB} = 265.6 Hz)	δ(CH_3) 1.17 (t), δ(CH_2) 3.25 (q, $J_{CH_3-CH_2}$ 7.1 Hz)
	−116.6, −117.6 (1, J_{AB} = 208.3)	−132.3 (s, 1)	δ(H) 4.60
	−117.3, −114.5 (1, J_{AB} = 210.0)	−132.7 (m, 1)	δ(CH_3) 3.22
	−116.1 (complex, 1)	−132.6 (complex, 1)	δ(CH_2) 1.32 (q), δ(CH_3) 3.5 (t, $J_{CH_3-CH_2}$ = 7.2 Hz)
	−111.0 (complex, 4)	−129.1, −133.1 (4, J_{AB} = 264.6 Hz)	φ(CF) −138.2 (1), φ(CF_3) −81.1 d (6), J_{CF_3-CF} 4.5 Hz)
	−110.5 (complex, 2)	−129.7, −134.2 (2, J_{AB} = 263.5 Hz)	φ(CF_3) −68.6 (3), φ($N{=}C(CF_3)_2$) −74.9 (3)
	−105.7, −131.1 (1, J_{AB} = 232.4 Hz)	−132.1, −135.8 (1, J_{AB} = 263.7 Hz)	
	−103.6, −107.7 (J_{AB} = 227.5 Hz)	−131.9, −135.3 (J_{AB} = 266.6 Hz)	

Several attempts were made to prepare the corresponding *N*-fluoro derivatives by the reaction of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$ with F_2 or with AgF_2 (eq 12). Unfortunately, only


(12)

cleaved products were found to be formed in appreciable quantities. No evidence was found for the formation of the *N*-fluoro derivative.

It has been demonstrated that perfluorinated *N*-chloro amines are susceptible to homolytic cleavage under thermolytic or photolytic conditions to give diazenes and Cl_2,[10] e.g., eq 13.

$$R_fNCl_2 \xrightarrow[\text{or }\Delta]{h\nu} R_fN{=}NR_f + Cl_2 \qquad (13)$$

Likewise, it has been shown that the photolysis of *N*-chlorobis(*F*-methyl)sulfimide results in the formation of a diazene.[12]

When the new *N*-chloro cyclic sulfimide $\overline{CF_2CF_2CF_2CF_2S}{=}NCl$ was photolyzed in a quartz vessel at 25 °C or below for 12 h, a yellow nonvolatile viscous liquid and Cl_2 were obtained. On the basis of spectroscopic (mass spectra, ^{19}F NMR) and elemental analyses, this liquid was shown to be a mixture of dimers containing approximately two chlorine atoms with or without the cyclic sulfide ring. A conclusive structural determination was not possible.

The ^{19}F NMR spectra of the (*F*-tetramethylene)sulfimides, (*F*-tetramethylene)sulfoxyimides, and *N*-halo(*F*-tetramethylene)sulfimides show resonances in the regions expected and integrate to the proper ratios. Due to the presence of an asymmetric center in the molecule, the geminal fluorines at the α- and β-carbons of the (*F*-tetramethylene)sulfimides and (*F*-tetramethylene)sulfoxyimides are nonequivalent and coupling occurs. We have reported earlier on the ^{19}F NMR spectra of *F*-tetramethylene sulfoxide which shows two sets of AB patterns at φ −114.7 and −118.3 with J_{AB} = 236 Hz, and at φ −128.1 and −131.8 with J_{AB} = 262 Hz due to the coupling of geminal fluorines at α- and β-carbons, respectively.[4]

In the present study, generally speaking, the following tendency was observed in the ^{19}F NMR spectra of the (*F*-tetramethylene)sulfimides and (*F*-tetramethylene)sulfoxyimides. In the case of the former, geminal fluorines both at the α- and β-carbons show an AB pattern or the geminal fluorines at the α-carbons show a complex multiplet and those at β-carbons show an AB pattern. On the other hand, in the case of the NMR spectra of the latter, geminal fluorines at the α-carbon show an AB pattern and those at the β-carbons show a complex singlet or geminal fluorines both at the α- and β-carbons show a complex singlet.

For example, in the case of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$, $\overline{CF_2CF_2CF_2CF_2S}{=}NCl$, and $\overline{CF_2CF_2CF_2CF_2S}{=}NBr$, typically two sets of AB patterns were observed, and in the case of the *N*-alkyl- and *N*-(*F*-alkyl)-substituted sulfimides, the complex resonance and an AB pattern were observed. In the case of $\overline{CF_2CF_2CF_2CF_2S}(O){=}NH$ and $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$, an AB pattern and a complex singlet were observed, while for $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$, two complex singlets were observed.

These ^{19}F NMR and ^{1}H NMR data are summarized in Table I.

Experimental Section

Materials. Literature methods were used to prepare $\overline{CF_2CF_2CF_2CF_2S}F_2$,[4] $(CF_3)_2SF_2$,[3] $(i\text{-}C_3F_7)_2SF_2$,[13] and $\overline{CF_2CF_2CF_2CF_2S}F_4$.[4] The other reagents were used as received from commercial suppliers without further purification. The reaction of anhydrous CH_3OH with metallic sodium was used to prepare $NaOCH_3$. The *m*-chloroperbenzoic acid (Aldrich) was used directly as received but was stored under refrigeration.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube gauge. All starting materials and products were

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(12) Kumar, R. C.; Shreeve, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 1951.

(13) Rosenberg, R. M.; Muetterties, E. L. *Inorg. Chem.* **1962**, *1*, 756.

purified by trap-to-trap distillation and gas chromatography. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cm cell equipped with KBr windows. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer and a JEOL FX-90 spectrometer by using CCl_3F as an internal standard. ^{1}H NMR spectra were obtained on a Varian EM-360 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 17 ev. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany, or at the University of Idaho.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$. Method A. In a 100-mL reaction vessel which contained 3.2 mmol of benzylamine, 3.27 mmol of $\overline{CF_2CF_2CF_2CF_2S}F_2$, and 13 mmol of NH_3 were condensed at −196 °C and warmed gradually to 25 °C. After 24 h, the volatile products were separated by trap-to-trap distillation. However, the compounds (0.27 g) which were retained in the trap at −78 °C after passing through a trap at −23 °C were found to be mainly $\overline{CF_2CF_2CF_2CF_2S}$ and small amounts of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$ by infrared spectroscopy.

Method B. Typically, into a 100-mL reaction vessel which contained 2.27 mL of 2.2 M *n*-BuLi–hexane solution (equivalent to 5.0 mmol of *n*-BuLi) was condensed at −196 °C 7 mmol of NH_3. The reaction mixture was warmed gradually to 25 °C over a 10–15-min period. The volatile products were removed under dynamic vacuum to leave a white solid, $LiNH_2$ (5.0 mmol). Onto this were condensed at −196 °C 10 mmol of isopentane, 4.90 mmol of $\overline{CF_2CF_2CF_2CF_2S}F_2$, and 10 mmol of NH_3. The reaction mixture was kept at −78 °C overnight and then at 0 °C for 2 days. Using a shorter reaction time resulted in contamination with small quantities of $\overline{CF_2CF_2CF_2CF_2S}F_2$ in the new cyclic imine. The product was separated by trap-to-trap distillation with use of a trap at −78 °C which retained $\overline{CF_2CF_2CF_2CF_2S}{=}NH$ (3.82 mmol; yield 78.0%). It is a colorless solid having a vapor pressure of 19 torr at 25 °C.

The ^{19}F and ^{1}H NMR spectra are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 3315 (m) (ν_{NH}), 1348 (ms), 1302 (ms), 1231 (vs), 1175 (s), 1060 (m), 989 (s), 951 (vs), 613 (m), 562 (m) cm^{-1}.

Anal. Calcd for C_4F_8SNH: C, 19.43; N, 5.67. Found: C, 19.80, N, 5.38.

Preparation of $(CF_3)_2S{=}NH$.[2] Onto 5.0 mmol $LiNH_2$ in a 100 mL reaction vessel were condensed at −196 °C 5.0 mmol of $(CF_3)_2SF_2$ and 10 mmol of NH_3. The reaction mixture was kept at −78 °C overnight and then at 0 °C for 2 days. The product was separated by trap-to-trap distillation by passing it through a −64 °C trap which retained $(CF_3)_2S{=}NH$ (2.38 mmol; 47.6% yield).

Reaction of $(i\text{-}C_3F_7)_2SF_2$ with $LiNH_2$. In a 100-mL flask which contained 3 mmol of $LiNH_2$, 10 mmol of isopentane, 3.13 mmol of $(i\text{-}C_3F_7)_2SF_2$, and 6 mmol of NH_3 were condensed at −196 °C. The reaction mixture was gradually warmed to −78 °C over an 11-h period and held at 0 °C for 2 days. The mixture was separated by trap-to-trap distillation. Only the starting $(i\text{-}C_3F_7)_2SF_2$ (2.54 mmol) was recovered, indicating that no reaction occurred.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$. Onto CH_3NH_2 (5.5 mmol) at −196 °C in a 50-mL Pyrex glass vessel equipped with a Kontes Teflon stopcock was condensed $\overline{CF_2CF_2CF_2CF_2S}F_2$ (1.6 mmol). The reaciton mixture was allowed to warm to 25 °C during 3 h and then kept at 0 °C. After 12 h, the product was separated by trap-to-trap distillation through a trap at −78 °C which retained the $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$ and small amounts of unreacted $\overline{CF_2CF_2CF_2CF_2S}F_2$. Final purification was accomplished by gas chromatography using a 90-cm column packed with 30% silicone QF-1 on chromosorb PAW. $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$ was obtained in a yield of 70.3%. It is a colorless liquid having a vapor pressure of 14 torr at room temperature.

The ^{19}F and ^{1}H NMR spectral data are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2820–2950 (w), 1343 (m), 1296 (ms), 1222 (vs), 1170 (s), 1095 (w), 1057 (m), 982 (s), 947 (w), 803 (m), 606 (w), 533 (w), 487 (w), 430 (w) cm^{-1}.

Anal. Calcd for $C_5F_8SNH_3$: C, 22.99; N, 5.36; H, 1.15. Found: C, 22.59; N, 5.17; H, 1.21.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$. Onto $C_2H_5NH_2$ (13.2 mmol) in a 100-mL reaction vessel was condensed 3.77 mmol of $\overline{CF_2CF_2CF_2CF_2S}F_2$. The reaction mixture was kept at −78 °C for 5 h, at 0 °C for 12 h, and then at 25 °C for 4 h. Purification of the product was accomplished by means of trap-to-trap distillation and gas chromatogrpahy. A yield of 37.4% of $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$ was obtained. It is a transparent liquid having a vapor pressure of 10.5 torr at 25 °C.

The ^{19}F and ^{1}H NMR spectral data are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2885–2985 (m), 1384 (w), 1342 (ms), 1298 (ms), 1221 (vs), 1205 (s, sh), 1170 (s), 1087 (w), 1056 (m), 981 (s), 944 (m), 765 (w), 605 (w), 537 (w) cm^{-1}.

Anal. Calcd for $C_8F_8SNH_5$: C, 26.18; N, 5.09; H, 1.82. Found: C, 26.20; N, 4.95; H, 2.00.

Reaction of $\overline{CF_2CF_2CF_2CF_2S}F_2$ with $LiN{=}C(CF_3)_2$. The literature method was used to prepare $LiN{=}C(CF_3)_2$ (2.0 mmol) in a rigorously flame-dried 100-mL reaction vessel.[5] The solvent was removed under dynamic vacuum, leaving a brown amorphous solid. Onto the solid was condensed $\overline{CF_2CF_2CF_2CF_2S}F_2$ (1.56 mmol), and the vessel was warmed slowly to 25 °C. After 12 h, products were separated by trap-to-trap distillation followed by gas chromatography. $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ (0.60 mmol) was obtained in a yield of 38.5%. The other product isolated was $\overline{CF_2CF_2CF_2CF_2S}{=}NC(CF_3)_2N{=}C(CF_3)_2$ (0.07 mmol; yield 4.5%). $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ is a colorless liquid with a boiling point of 97.5 °C obtained from the equation $\log P_{torr} = 7.64 - 1764.1/T$. The molar heat of vaporization is 8.1 kcal, and the Trouton constant is 21.8 eu.

The ^{19}F NMR spectral data are recorded in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 1499 (w), 1296 (ms), 1243–1252 (vs), 1192 (s), 1081 (m), 1060 (w), 986 (s), 948 (m), 733 (m), 701 (w), 675 (w) cm^{-1}.

Anal. Calcd for $C_7F_{15}SN$: C, 20.24; N, 3.37. Found: C, 20.30; N, 3.39.

Reaction of $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ with $LiNC(CF_3)_2$. A 1-mmol sample of $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ was condensed at −196 °C onto 1.54 mmol of $LiN{=}C(CF_3)_2$, and the reaction mixture was gradually warmed to 25 °C. After 14 h, the products were separated by trap-to-trap distillation. This transparent liquid which was retained in the −64 °C trap was found to be pure $\overline{CF_2CF_2CF_2CF_2S}{=}NC(CF_3)_2N{=}C(CF_3)_2$ (0.60 mmol; yield 63.8%). This compound is a colorless liquid with a boiling point of 115.9 °C obtained from the equation $\log P_{torr} = 6.83 - 1536.6/T$. The molar heat of vaporization is 7.0 kcal, and the Trouton constant is 18.1 eu.

The ^{19}F NMR spectral data are given in Table I. The mass spectrum does not have a molecular ion, but *m/e* 491 $[M - CF_3]^+$ and appropriate fragment ions are present. The infrared spectrum (capillary film) is as follows: 1732 (w), 1349 (w), 1318∼1327 (m), 1210–1235 (s–vs), 1160 (ms), 1039–1082 (w), 915–995 (w–m), 740 (m), 695 (m) cm^{-1}.

Anal. Calcd for $C_{10}F_{20}SN_2$: C, 21.43; N, 5.00. Found: C, 21.43; N, 5.04.

Reaction of $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ with $LiN{=}S(CF_3)_2$. The preparation of $LiN{=}S(CF_3)_2$ was slightly modified in this experiment.[7] In a rigorously flame-dried reaction vessel which contained 2 mL of dry ether and 0.55 mL of 2.2 M *n*-BuLi–hexane solution (equivalent to 1.2 mmol of *n*-BuLi), 1.5 mmol of $(CF_3)_2S{=}NH$ was condensed at −196 °C. The reaction mixture was gradually warmed to 25 °C during 10 min. The volatile compounds were removed under dynamic vacuum, leaving transparent yellow gelatinous $LiN{=}S(CF_3)_2$. Onto this was condensed at −196 °C 1.19 mmol of $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$, and the mixture was gradually warmed to 25 °C. After 17 h, the products were separated by trap-to-trap distillation, and the majority of the starting imide, $\overline{CF_2CF_2CF_2CF_2S}{=}NC$-

$F(CF_3)_2$ (1.04 mmol), was recovered. The other isolated compounds were CF_3SCF_3 (0.4 mmol) and a mixture of ether and F_2CF_2S (0.4 mmol).

Reaction of $CF_2CF_2CF_2CF_2S=NCF(CF_3)_2$ with $NaOCH_3$. Into a 50-mL reaction vessel which contained 2.11 mmol of $NaOCH_3$ was condensed 1.84 mmol of $CF_2CF_2CF_2CF_2S=NCF(CF_3)_2$. The reaction vessel was gradually warmed to 25 °C and agitated on a mechanical shaker for 3 days. The mixture was separated by trap-to-trap distillation, and the product retained at −40 °C was analyzed by IR. However, it was found that only the starting $CF_2CF_2CF_2CF_2S=NCF(CF_3)_2$ (1.50 mmol) was recovered.

Reaction of $CF_2CF_2CF_2CF_2SF_4$ with $LiN=C(CF_3)_2$. In a 50-mL flask, 2.98 mmol of $CF_2CF_2CF_2CF_2SF_4$ was condensed onto $LiN=C(CF_3)_2$ (3.0 mmol) at −196 °C and warmed slowly to 25 °C. After 10 days, the product was separated by trap-to-trap distillation. However, no reaction took place. Only unreacted $CF_2CF_2CF_2CF_2SF_4$ (2.86 mmol) was recovered.

Reaction of $CF_2CF_2CF_2CF_2SF_4$ with ClF. In a 30-mL Hoke cylinder, $CF_2CF_2CF_2CF_2SF_4$ (1.98 mmol) and ClF (2.3 mmol) were condensed at −196 °C and gradually warmed to 25 °C. After 70 h, the product was separated by trap-to-trap distillation. The majority of the starting $CF_2CF_2CF_2CF_2SF_4$ (1.87 mmol) was recovered, which indicated that no reaction took place.

Preparation of $CF_2CF_2CF_2CF_2S=NCl$. Method A. Into a 75-mL Hoke bomb which contained 5 g of CsF were condensed at −196 °C $CF_2CF_2CF_2CF_2S=NH$ (2.18 mmol) and Cl_2 (3.0 mmol). The reaction mixture was warmed slowly to 25 °C and allowed to remain for 4.5 h. Purification was conducted by trap-to-trap distillation using traps cooled at −98 and −40 °C. $CF_2CF_2CF_2CF_2S=NCl$ (1.90 mmol; yield 87.2%) was obtained in the trap in −40 °C. Small quantities of $CF_2CF_2CF_2CF_2S$ was found in the trap at −98 °C. This compound is a transparent light yellow liquid which has a vapor pressure of 8 torr at 25 °C and becomes a sherbet-like solid at −40 °C.

The ^{19}F NMR spectral data are recorded in Table I. The mass spectrum shows molecular ions with appropriate isotope ratios and appropriate fragment ions. The infrared spectrum is as follows: 1347 (s), 1304 (s), 1235 (vs), 1190 (s), 1170 (s), 1059 (ms), 986 (vs), 942 (s), 604 (m) cm^{-1}.

Anal. Calcd for C_4F_8SNCl: C, 17.05; N, 4.97. Found: C, 17.39; N, 5.18.

Method B. Into a 75-mL Hoke cylinder which contained 5 g of CsF were condensed at −196 °C $CF_2CF_2CF_2CF_2S=NH$ (3.34 mmol) and ClF (3.8 mmol). The reaction mixture was warmed gradually to 25 °C over a 12-h period. The product was separated by trap-to-trap distillaton using traps cooled at −98 and −40 °C. In the −40 °C trap, almost pure $CF_2CF_2CF_2CF_2S=NCl$ (1.24 mmol) was obtained. The product (0.86 g) which was retained at −98 °C was found to be a mixture of $CF_2CF_2CF_2CF_2S=NCl$ and $CF_2CF_2CF_2CF_2SF_2$ by IR spectroscopy. The product ratio is 62:38 as determined by ^{19}F NMR spectroscopy. The overall yield of $CF_2CF_2CF_2CF_2S=NCl$ was about 93%.

Photolysis of $CF_2CF_2CF_2CF_2S=NCl$. (1) At 25 °C for 11 h. When 2.09 mmol of $CF_2CF_2CF_2CF_2S=NCl$ in a 95-mL Quartz vessel was photolyzed by using a Hanovia utility model UV lamp for 11 h, a yellow viscous liquid was formed. The volatile products were separated by trap-to-trap distillation using traps at −196 and −98 °C. The compounds which were collected at −196 and −98 °C were Cl_2 (0.5 mmol) and $CF_2CF_2CF_2CF_2S$ (0.5 mmol), respectively. The viscous liquid in the quartz vessel was removed by washing with small amounts of CH_2Cl_2 several times, and the solvent was removed to give a dense yellow viscous liquid (0.20 g).

^{19}F NMR spectrum showed complicated resonances containing five major peaks (ϕ −60 to ϕ −131) and several small peaks. Although no conclusive assignment was made, among these peaks the strong resonance at ϕ −60.5 should be due to the $ClCF_2$ group. The mass spectrum shows such peaks assigned as *m/e* 531 $[C_7F_{15}S_2N_2{}^{35}Cl_2]^+$ as the largest ion together with *m/e* 496 $[C_7F_{15}S_2N_2{}^{35}Cl]^+$, 327 $[C_4F_8S_2N_2{}^{35}Cl]^+$, 247 $[C_5F_8{}^{35}Cl]^+$, and 231 $C_5F_9{}^+$. The IR spectrum (capillary film) is as follows: 1348 (m), 1303 (m), 1130–1230 (s–vs), 1062 (m), 989 (s), 948 (ms), 909 (s), 845 (w), 815 (w), 778 (w), 700 (m), 675 (w), 610 (w), 580 (w) cm^{-1}.

Elemental analysis of this compound shows C 19.20%, S 12.33%, and N 5.33%. These values are located between the expected compound of $C_8F_{16}S_2N_2$ ($CF_2CF_2CF_2CF_2S=NN=SCF_2CF_2CF_2CF_2$. Calcd: C, 19.51; S, 13.01; N, 5.69) and $C_8F_{16}S_2N_2Cl_2$ (($ClCF_2CF_2CF_2CF_2SN=)_2$. Calcd: C, 17.05; S, 11.37; N, 4.97).

(2) At 0 °C for 11 h. The quartz vessel (84 mL) which contained 2.66 mmol of $CF_2CF_2CF_2CF_2S=NCl$ was immersed in an ice bath to half of its height. Then, the contents were photolyzed for 11 h. Purification of the volatile product was conducted by trap-to-trap distillation where a trap at −196 °C retained the mixture of Cl_2 and $CF_2CF_2CF_2CF_2S$ (1.0 mmol), and a trap at −40 °C which retained unreacted $CF_2CF_2CF_2CF_2S=NCl$ (1.1 mmol). The product which was retained in the reaction vessel was handled as in method 1. Thus, 0.12 g of transparent yellow viscous liquid was obtained. The analysis of this compound by IR, ^{19}F NMR, and mass spectroscopy showed that this compound is the same as the one obtained in method 1.

Preparation of $CF_2CF_2CF_2CF_2S=NBr$. $CF_2CF_2CF_2CF_2S=NH$ (2.30 mmol) and Br_2 (6.3 mmol) were condensed in a 75-mL Hoke Cylinder which contained 7 g of KF at −196 °C. The reaction mixture was warmed gradually to 25 °C. After 12 h, the product was purified by trap-to-trap distillation using a trap at −40 °C which retained $CF_2CF_2CF_2CF_2S=NBr$ (yield 23.0%). This compound is a yellow liquid.

This ^{19}F NMR spectral data are given in Table I. Mass spectrum shows molecular ions with appropriate isotope ratios and appropriate fragmentation ions. The infrared spectrum (capillary film) is as follows: 1342 (s), 1295 (s), 1223 (vs), 1180 (s, sh), 1163 (vs), 1055 (s), 980 (vs), 936 (s), 850 (w), 669 (w), 638 (w), 608 (m), 555 (m), 542 (m), 487 (w), 442 (w) cm^{-1}.

Anal. Calcd for C_4F_8SNBr: C, 24.54. Found: C, 24.11.

Fluorination of $CF_2CF_2CF_2CF_2S=NH$. (1) With Elemental F_2. In a 150-mL Hoke cylinder which contained 7 g of KF, $CF_2CF_2CF_2CF_2S=NH$ (2.02 mmol) was condensed at −196 °C. Then, elemental F_2 (2.35 mmol) was expanded into it at −196 °C. The reaction mixture was warmed to 25 °C gradually during 3 h. Separation was conducted by trap-to-trap distillation through a trap at −196 °C which retained a mixture of CF_4, SiF_4, and NF_3 (0.62 mmol), a trap at −98 °C which retained $CF_2CF_2CF_2CF_2S$ (0.35 mmol), and a trap at −40 °C which retained unreacted $CF_2CF_2CF_2CF_2S=NH$ (1.02 mmol). No evidence was observed for the formation of $CF_2CF_2CF_2CF_2S=NF$.

(2) With AgF_2. In a 150-mL Hoke cylinder which contained 5 g of AgF_2, 3.20 mmol of $CF_2CF_2CF_2CF_2S=NH$ was condensed at −196 °C. The reaction mixture was warmed gradually to 25 °C. After 2.5 h, the products were transferred to the 75-mL Hoke bomd which contained 5 g of CsF to absorb HF. By trap-to-trap distillation using a trap cooled at −98 °C, $CF_2CF_2CF_2CF_2S$ (0.67 mmol) was obtained as the cleaved product. No other compound having a higher boiling point was obtained.

Preparation of $CF_2CF_2CF_2CF_2S(O)=NH$. In a 100-mL reaction vessel which contained 2.0 g of MPCBA, 4.87 mmol of $CF_2CF_2CF_2CF_2S=NH$ was condensed at −196 °C. The reaction vessel was kept at −78 °C for 16.5 h and then at 0 °C for 2 days. The product was collected by passing through a −64 °C trap which retained $CF_2CF_2CF_2CF_2S(O)=NH$ (4.72 mmol). Its yield was 96.9%. This compound is a white solid which freezes to a glass with a boiling point of 124.1 °C from the equation of $\log P_{torr} = 6.58 - 1469.5/T$. It melts near 75–78 °C. The molar heat vaporization is 6.7 kcal, and the Trouton constant is 16.9 eu.

The ^{19}F and ^1H NMR spectral data appear in Table I. The mass spectrum shows a molecular ion and appropriate molecular ions. The infrared spectrum is as follows: 3395 (ms), 1345 (vs), 1303 (ms), 1242 (s), 1195 (vs), 1152 (m), 1058 (m), 992 (vs), 955 (ms), 895 (w), 845 (w), 612 (w), 548 (m), 500 (ms) cm^{-1}.

Anal. Calcd for C_4F_8SNHO: C, 18.25; N, 5.32; H, 0.38. Found: C, 18.20; N, 5.51; H, 0.40.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$. Similarly, in a 100-mL reaction vessel which contained 0.88 g of MCPBA, 2.18 mmol of $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$ was condensed at −196 °C. The reaction vessel was held at −78 °C for 19 h, at 0 °C for 12 h, and at 25 °C for 10 h. The product was purified by trap-to-trap distillation through a trap at −64 °C. $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$ was obtained in a yield of 79.4%. This is a transparent liquid with a boiling point of 57.0 °C from the equation $\log P_{torr} = 2.27 - 1779.4/T$. The molar heat of vaporization is 8.1 kcal, and the Trouton constant is 24.7 eu.

The ^{19}F and ^1H NMR spectral data are found in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2867-3012 (w), 1447 (w), 1316 (vs), 1340 (s), 1303 (s), 1247 (s), 1190 (vs), 1061 (w), 992 (vs), 972 (s), 884 (w), 841 (m), 664 (w), 614 (w), 580 (w), 548 (w), 520 (m), 492 (m) cm^{-1}.

Anal. Calcd for $C_5F_8SNH_3O$: C, 21.66; N, 5.05; H, 1.08. Found: C, 21.20; N, 4.97; H, 1.21.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$. In a 100-mL reaction vessel which contained 0.43 g of MCPBA, 1.07 mmol of $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$ was condensed at −196 °C. Then, the reaction vessel was kept at −78 °C for 16 h, at 0 °C for 10 h, and at 25 °C for 8 h. The volatile product was found to be pure $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$ (0.90 mmol). Its yield was 83.6%. This is a transparent liquid with a boiling point of 60.2 °C from the equation $\log P_{torr} = 7.80 - 1640.0/T$. The molar heat of vaporization is 7.5 kcal, and the Trouton constant is 22.5 eu.

The ^{19}F and ^1H NMR spectral data are recorded in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum is as follows: 2893-2993 (w), 1386 (m s), 1337 (v s), 1303 (s), 1248 (s), 1192 (v s), 1063 (w), 994 (s), 954 (m s), 888 (w), 793 (w), 665 (w), 615 (w), 583 (w), 552 (w), 528 (m), 493 (w) cm^{-1}.

Anal. Calcd for $C_6F_8SNH_5O$: C, 24.74; N, 4.81; H, 1.72. Found: C, 24.54; N, 4.80; H, 1.70.

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Registry No. $\overline{CF_2CF_2CF_2CF_2S}{=}NH$, 77110-87-3; $\overline{CF_2CF_2CF_2CF_2S}{=}NCH_3$, 77984-24-8; $\overline{CF_2CF_2CF_2CF_2S}{=}NC_2H_5$, 77984-25-9; $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$, 77984-26-0; $\overline{CF_2CF_2CF_2CF_2S}{=}NC(CF_3)_2N{=}C(CF_3)_2$, 77984-27-1; $\overline{CF_2CF_2CF_2CF_2S}{=}NCl$, 77984-28-2; $\overline{CF_2CF_2CF_2CF_2S}{=}NBr$, 77984-29-3; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NH$, 77589-47-0; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NCH_3$, 77589-48-1; $\overline{CF_2CF_2CF_2CF_2S}(O){=}NC_2H_5$, 77984-30-6; $\overline{CF_2CF_2CF_2CF_2S}F_2$, 42060-60-6; $(CF_3)_2S{=}NH$, 60646-40-4; $\overline{CF_2CF_2CF_2CF_2S}$, 706-76-3; $LiNH_2$, 7782-89-0; $(CF_3)_2SF_2$, 30341-38-9; CH_3NH_2, 74-89-5; $C_2H_5NH_2$, 75-04-7; $LiN{=}C(CF_3)_2$, 31340-36-0.

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Crystal and Molecular Structure of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$, a Molecule with a Dinitrogen Ligand Behaving as a Diimido Group in a Ta=NN=Ta Bridge

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The complex $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$ has been studied by means of a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 9.712$ (2) Å, $b = 14.845$ (3) Å, $c = 18.448$ (4) Å, $\alpha = 67.278$ (14)°, $\beta = 84.812$ (15)°, $\gamma = 71.743$ (12)°, $V = 2328.5$ (7) $Å^3$, and $Z = 2$. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved via Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices are $R_F = 4.5\%$ and $R_{wF} = 3.1\%$ for all 4308 data (*none* rejected) and $R_F = 3.1\%$ and $R_{wF} = 3.0\%$ for those 3626 data with $|F_o| > 3\sigma(|F_o|)$. The binuclear complex contains two tantalum(V) atoms in trigonal-bipyramidal coordination environments. Each tantalum atom has two axial PMe_3 ligands; the equatorial sites are occupied by neopentylidene ligands [Ta(1)–C(1) = 1.932 (9) Å, Ta(2)–C(17) = 1.937 (9) Å], neopentyl ligands [Ta(1)–C(6) = 2.285 (10) Å, Ta(2)–C(22) = 2.299 (10) Å], and the bridging dinitrogen ligand. Bond lengths within the Ta–(μ-N_2)–Ta fragment [Ta(1)–N(1) = 1.837 (8) Å, Ta(2)–N(2) = 1.842 (8) Å, N(1)–N(2) = 1.298 (12) Å] indicate that it is best described as a Ta=NN=Ta system. The N(1)–N(2) distance of 1.298 (12) Å shows this molecule (with a pair of "14-electron" transition metal atoms) to have a far more activated μ-N_2 system that is observed in such other μ-N_2 derivatives of the early transition metals as $[(\eta^5\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (a "16-electron" complex) or $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$ (an "18-electron" complex).

Introduction

The preparation of the first terminal dinitrogen complexes, $[Ru(NH_3)_5N_2]X_2$ ($X = Br^-, I^-, BF_4^-, PF_6^-$), was reported in 1965.[1] This was followed, in 1968, by the synthesis[2] and crystallographic characterization[3] of a closely related species containing a bridging dinitrogen group, $[(NH_3)_5RuN{\equiv}NRu(NH_3)_5]^{4+}$.

Since this time a variety of other dinitrogen complexes has been synthesized, and their chemistry (including efforts to reduce the coordinated N_2 to NH_3 etc.) has been reviewed.[4-8]

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