Notes

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(Perfluoroalkylimino)selenyl Chlorides

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Very few examples of compounds containing discrete nitrogen–selenium double bonds exist. The first of these was reported in 1967 and involved the preparation of ((arylsulfonyl)imino)selenyl chlorides.[2]

$$RSO_2NCl_2 + Se \rightarrow RSO_2N{=}SeCl_2 \qquad (1)$$

Other examples such as $TeF_5N{=}SeCl_2$[3] and $SF_5N{=}SeCl_2$[4] have appeared only more recently.

$$TeF_5NH_2 + SeCl_4 \rightarrow TeF_5N{=}SeCl_2 + 2HCl \qquad (2)$$

$$3SF_5NCl_2 + 2Se_2Cl_2 \rightarrow 3SF_5N{=}SeCl_2 + SeCl_4 \qquad (3)$$

Both the arylsulfonyl and the pentafluorosulfanyl derivatives decompose upon standing in sharp contrast to the pentafluorotellurium compound. Thus, it was our interest to attempt the preparation of more $-N{=}Se<$ systems and to compare their stabilities to those of the above-mentioned compounds.

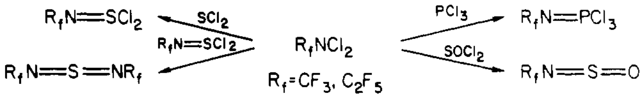
In order to prepare perfluoroalkyl analogues, one would envision either the free amines or the dichloroamines as starting materials. However, it is well documented that perfluoroalkylamines with fluorine in the α-position relative to the nitrogen readily eliminate HF to give the corresponding nitriles.[5] In fact this problem has[6] and can be circumvented by using the dichloramines as starting materials (see Scheme I). Our investigation has also led to a new one-step, high-yield synthesis of (trifluoromethyl)dichloramine.

Experimental Section

Materials. ClF,[7] $C_2F_5NCl_2$,[8] and $FC(O)NCl_2$[9] were prepared by literature methods; BrCN, CF_3CN, Se, Se_2Cl_2, and H_2SeO_3 were obtained from commercial sources and used without further purification. *Caution*! Many *N*-halo compounds are known to be powerful explosives; therefore, suitable safety precautions should be kept in mind. We advise that the preparations and reactions of these materials be done on a small scale.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 1430 Data System, while Raman spectra were taken on a Spex 1403 Ramalog double spectrophotometer with a Scamp data system. Mass spectra were obtained on a HP 5985A GC/MS system. The mass numbers are given for ^{80}Se and ^{35}Cl; the intensities include all isotopes. Fluorine-19 NMR spectra were recorded on a JEOL FX-90Q spectrometer at 84.25 MHz and referenced to internal CCl_3F. Selenium-77 NMR spectra were taken at 17.06 MHz and referenced to external H_2SeO_3.

Scheme I



Preparation of (Trifluoromethyl)dichloramine. Cyanogen bromide (10.0 mmol, 1.06 g) was condensed into the bottom of a 95-mL Monel cylinder chilled to liquid-nitrogen temperature. The level of the liquid nitrogen was then raised, and ClF (65 mmol) was added slowly so that it would condense into the upper portion of the cylinder. The reaction vessel was placed in a slush bath at −130 °C and allowed to warm slowly to room temperature overnight. The volatile materials were then transferred to the vacuum system and passed through a series of traps at −50, −125, and −196 °C. The trap at −50 °C stopped 1.14 g of a pale yellow solid with properties characteristic of BrF_3.[10] The contents of the −125 °C trap, consisting primarily of CF_3NCl_2 and Cl_2, were then shaken over mercury until complete removal of the Cl_2. Repeated distillation gave CF_3NCl_2 (9.5 mmol) in 95% yield, stopping in the trap at −125 °C.

Preparation of ((Trifluoromethyl)imino)selenyl Dichloride. Method A. Diselenium dichloride (1.14 g, 5.0 mmol) was loaded into an FEP tube reactor with a metal valve in the drybox. After evacuation and cooling to −196 °C, approximately 10 mL of dry CCl_3F was condensed into the reactor. This mixture was warmed to room temperature and stirred to form a homogeneous solution before being refrozen in liquid nitrogen. An additional 1 mL of CCl_3F was then condensed in followed by 1.25 g of CF_3NCl_2 (8.1 mmol). The reaction mixture was placed in a −50 °C bath and maintained at the temperature overnight. Over the next 24-h period, the temperature of the bath was allowed to rise slowly to room temperature. During this time, a white precipitate formed and the color of the solution changed from dark red to light yellow. The volatile materials were then transferred to the vacuum line and passed through a series of traps at −15, −55, and −196 °C. The pale yellow, milky liquid that stopped in the trap at −55 °C was further purified by reaction with fresh CF_3NCl_2 for short periods of time between distillations. This process was repeated until the product was obtained as a clear liquid (1.55 g, 89% yield). The white solid (>0.45 g) was identified as $SeCl_4$ through its Raman spectrum.[11]

Method B. Selenium (0.47 g, 6.0 mmol) and CF_3NCl_2 (0.95 g, 6.2 mmol) were reacted under the same conditions as above. The 0.70 g of material stopping in the −55 °C trap was found to contain $CF_3N{=}SeCl_2$ along with other products ($CF_3N{=}NCF_3$, Se_2Cl_2).

$CF_3N{=}SeCl_2$: IR (gas) 1280 (w), 1237 (vs), 1200 (s), 1174 (s), 1038 (m), 771 (w), 651 (w), 610 (w) cm^{-1}; IR (liquid) 1220 (vs b), 1145 (vs b), 1024 (m), 962 (w), 764 (m), 650 (m), 609 (m), 515 (w) cm^{-1}. Raman (liquid) 1028.5 (6), 769 (23), 523? (6), 379 (59), 356.5 (100), 331 (52), 246 (25), 195 (27), 165 (44), 114 (17) cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 233 M^+ (3), 198 $[M - Cl]^+$ (100), 179 $[M - Cl - F]^+$ (20), 163 CF_3NSe^+ (25), 150 $SeCl_2^+$ (6), 144 CF_2NSe^+ (26), 115 $SeCl^+$ (19), 94 NSe^+ (34), 80 Se^+ (24); chemical ionization mass spectrum (methane) *m/z* (relative intensity) 234 $[M + H]^+$ (100), 214 $[M - F]^+$ (33), 199 $[M + H, -Cl]^+$ (10), 198 $[M - Cl]^+$ (24), 180 $[M + H, -Cl - F]^+$ (7), 179 $[M - Cl - F]^+$ (8), 150 $SeCl_2^+$ (7); ^{19}F NMR δ −50.6 (s, CF_3); ^{77}Se NMR δ 1073 (q, N=Se, $^3J_{Se-F}$ = 35 Hz).

Decomposition of $CF_3N{=}SeCl_2$. Samples of $CF_3N{=}SeCl_2$ were observed to begin to decompose within 30 min at room temperature. At first, a white precipitate formed followed by a progressive reddening in color of the remaining liquid. A 1.53-g sample of $CF_3N{=}SeCl_2$ left standing in an FEP tube reactor for 9 days gave 0.33 g of $CF_3N{=}NCF_3$ (IR, NMR)[12] as the principal, volatile, decomposition product following reaction workup. Although not identified in this experiment (see below), the white solid and red liquid that formed were believed to be $SeCl_4$ and Se_2Cl_2, respectively.

In a separate experiment $CF_3N{=}SeCl_2$ (0.16 g, 0.7 mmol) was hydrolyzed with H_2O (0.0270 g, 1.5 mmol). The volatile products, which were identified by infrared spectroscopy, included HCl, CO_2, and SiF_4.

Preparation of ((Pentafluoroethyl)imino)selenyl Dichloride. Diselenium dichloride (1.37 g, 6.0 mmol) and $C_2F_5NCl_2$ (2.12 g, 10.4

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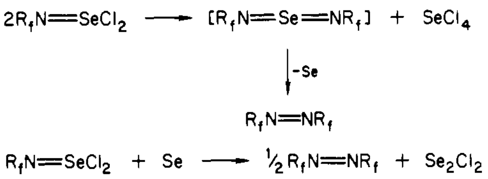
Scheme II



mmol) were reacted under the same conditions given in method A for $CF_3N{=}SeCl_2$. The product $C_2F_5N{=}SeCl_2$ (1.8i g, 6.8 mmol) was isolated as a clear, pale yellow liquid in 76% yield. IR (gas) 1233 (vs), 1212 (vs), 1134 (s), 1097 (vs), 929 (m), 754 (w), 704 (m) cm^{-1}; IR (liquid) 1203 (vs b), 1116 (m), 1084 (s), 933 (m), 753 (w), 704 (m) cm^{-1}; Raman (liquid) 933 (3), 755 (26), 704 (3), 373 (100), 367 (66), 360 (74), 331 (53), 314 (44), 265 (10), 168 (53), 142 (35) cm^{-1}; mass spectrum (70 eV) m/z (relative intensity) 248 $[M - Cl]^+$ (61), 229 $[M - Cl - F]^+$ (35), 214 $[M - CF_3]^+$ (46), 213 $C_2F_5NSe^+$ (23), 194 $C_2F_4NSe^+$ (29), 179 $[M - CF_3 - Cl]^+$ (27), 150 $SeCl_2^+$ (23), 115 $SeCl^+$ (100), 94 NSe^+ (20), 80 Se^+ (34), 69 CF_3^+ (71), 50 CF_2^+ (7); chemical ionization mass spectrum (methane) m/z (relative intensity) 284 $[M + H]^+$ (100), 264 $[M - F]^+$ (71), 248 $[M - Cl]^+$ (65), 214 $[M - CF_3]^+$ (20); ^{19}F NMR δ −86.1 (s, CF_3), −89.5 (s, CF_2); ^{77}Se NMR δ 1088 (t, N=Se, $^3J_{Se-F} = 36.7$ Hz).

Decomposition of $C_2F_5N{=}SeCl_2$. The pentafluoroethyl derivative was found to decompose in a fashion similar to that of $CF_3N{=}SeCl_2$. Analysis by Raman spectroscopy revealed that the white solid formed in the decomposition was $SeCl_4$.[11] A sample of $C_2F_5N{=}SeCl_2$ (1.90 g, 7.0 mmol) left standing in an FEP tube reactor for 4 days gave $C_2F_5N{=}N\text{-}C_2F_5$[12] (0.53 g, 2.0 mmol) as the principal, volatile, decomposition product. A small quantity of CF_3CN (<0.25 mmol) was also found in the product mixture.

Results and Discussion

The reaction of BrCN with ClF gives a new, efficient method for producing (trifluoromethyl)dichloramine. Previously the best method of preparing CF_3NCl_2 relied on first preparing $CF_3N{=}SF_2$ and then reacting this material with ClF.[9]

$$BrCN + 6ClF \rightarrow CF_3NCl_2 + 2Cl_2 + BrF_3 \qquad (4)$$

$$SF_4 + (FCN)_3 \xrightarrow[155\ °C]{CsF} CF_3N{=}SF_2 \xrightarrow{2ClF} CF_3NCl_2 \qquad (5)$$

The yield in the BrCN reaction is substantially higher, but we have not attempted to scale this reaction beyond 10 mmol.

The dichloramines CF_3NCl_2 and $C_2F_5NCl_2$ react readily with Se_2Cl_2 to give the corresponding iminoselenyl dichlorides and $SeCl_4$.

$$3R_fNCl_2 + 2Se_2Cl_2 \xrightarrow{CCl_3F} 3R_fN{=}SeCl_2 + SeCl_4 \qquad (6)$$

Both reactions proceed at a somewhat higher temperature than does that of the sulfur analogue $SF_5N{=}SeCl_2$ and without the intermediate blackening (elemental Se?).[4] The trifluoromethyl derivative is also formed in the reaction of CF_3NCl_2 with elemental selenium; however, one cannot rule out the initial formation of Se_2Cl_2 in this reaction.

$$CF_3NCl_2 + Se \rightarrow CF_3N{=}SeCl_2 \qquad (7)$$

Diselenium dichloride was also found to react with $FC(O)NCl_2$, but the reaction product was too unstable to be isolated and characterized.

The instability of the (perfluoroalkylimino)selenyl halides is not totally unexpected. It is surprising that the major products of the decomposition are not analogous to those observed in the decomposition of $SF_5N{=}SeCl_2$.[4] Only a small quantity of CF_3CN observed in the decomposition of $C_2F_5N{=}SeCl_2$ gave evidence for an analogous pathway.

$$2SF_5N{=}SeCl_2 \rightarrow 2SF_3{\equiv}N + SeCl_4 + SeF_4 \qquad (8)$$

$$2C_2F_5N{=}SeCl_2 \rightarrow 2CF_3C{\equiv}N + SeCl_4 + SeF_4 \qquad (9)$$

Other evidence indicates that the major decomposition reaction is that shown in eq 10. A possible mechanism for this decomposition is shown in Scheme II. This mechanism is supported by the early appearance of $SeCl_4$ in the decomposition and by the fact that both $CF_3N{=}SeCl_2$ and $C_2F_5N{=}SeCl_2$ react with elemental selenium to give the respective perfluoroazoalkane and a heavy, red liquid believed to be Se_2Cl_2. Sharpless and co-workers have also previously proposed selenium diimides as reactive intermediates in organic syntheses.[13]

$$6R_fN{=}SeCl_2 \rightarrow 3R_fN{=}NR_f + 2SeCl_4 + 2Se_2Cl_2 \qquad (10)$$

The Raman stretching frequencies at 1028.5 cm^{-1} in $CF_3N{=}SeCl_2$ and at 933 cm^{-1} in $C_2F_5N{=}SeCl_2$ have been assigned to the N=Se stretch. A similar, unexpectedly large difference in the N=Se stretching frequencies of $SF_5N{=}SeCl_2$ and $TeF_5N{=}SeCl_2$ (~80 cm^{-1}) has previously been observed.[4] A possible explanation for this variation could be the degree of association and/or association mechanism in these compounds.[14] The selenium-77 NMR spectra reported herein are consistent with Se(IV) species, and the observed couplings to fluorine strongly support the identity of the new compounds.

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Nephelauxetic Effect in Metal Ion Paramagnetic Shielding of Spin-Paired d^6 Transition-Metal Complexes

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Electronic configuration of the spin-paired $3d^6$, $4d^6$, and $5d^6$ transition-metal complexes is properly described by the strong-field ligand field scheme, as has been well documented in the study of their electronic absorption spectra.[1] Therefore, magnetic shielding of metal ions in such complexes may be evaluated by the same general approach of Griffith and Orgel[2] that has been first applied to the cobalt(III) complexes.[3] Thus, magnetic shielding in all spin-paired d^6 complexes is expected to be dominated by the large paramagnetic shielding term arising through mixing of the excited $^1T_{1g}(t_{2g}{}^5e_g)$ state with the ground $^1A_{1g}(t_{2g}{}^6)$ state. This term is also strongly influenced by ligands (unlike the diamagnetic shielding term) and contains valuable information about metal–ligand bond covalency.[4,5] The effect of covalency has been conveniently quantified by introduction of the circulation removing ratio (η), which allows the paramagnetic shielding term (σ^P) to be expressed as[6]

$$\sigma^P = -\frac{\mu_0}{4\pi}(32\mu_B{}^2)\langle r^{-3}\rangle_{d_F}\frac{\eta}{\Delta E} \qquad (1)$$

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