elemental composition, and infrared and ^{1}H NMR spectral data. The three bands in the N–H stretch region of the infrared spectrum in conjunction with the absorption at 1111 cm^{-1} (found to be characteristic of the NHSiMe$_3$ group)[19] support the presence of two types of amino hydrogens. The ^{1}H NMR spectrum shows three different methyl proton environments with the two very close together, δ 0.40 and 0.35, being assigned to the trimethylsilyl groups on the ring nitrogens. Protons on nitrogen are known to produce broad NMR peaks at varied locations. The signals at –0.44 and 0.87 ppm are ascribed to the NH protons. Their relative ratio, 1:2, is in agreement with the assignments; however, the ratio of the methyl protons to the nitrogen protons, 25.7:1, is much higher than the calculated value of 9:1. This could be due to peak broadening of the NH protons. The molecular weight of 2300 indicates the compound exists in solution in a polymeric form. Difficulty was experienced in solvent removal, and efforts to obtain crystals for X-ray structure determination were unsuccessful. The material exhibited only a single endotherm in the differential scanning calorimetry analysis at ~275 °C. No endotherm was observed within the melting range. Thermolysis at 280 °C gave (Me$_3$Si)$_2$NH and ammonia; the ratio of the starting material to HN(SiMe$_3$)$_2$ to NH$_3$ was found to be 1:0.6:0.1. From the above ratios, the large decrease in the infrared 1110-cm^{-1} absorption, and the retention of the doublet at 3380 and 3290 cm^{-1}, one is tempted to speculate that condensation took place via the NHSiMe$_3$ substitutents.

Pyrolysis up to 1000 °C of the low-temperature thermolysis product, using TGA, resulted in a black, shiny residue, pointing to carbon retention in agreement with the high ceramic yield. Conducting the final pyrolysis in a tube furnace, under an ammonia atmosphere, at 280–990 °C, gave a 37.7% ceramic yield, which is higher than the 24.65% calculated for pure AlN production.

One of the objectives of this investigation was to prepare precursors for BN·AlN ceramics. Reaction of Al[N(SiMe$_3$)$_2$]$_3$ with BCl$_3$, on the basis of literature data,[20-22] offered a potential approach, i.e.

$$\mathrm{BCl_3 + Al[N(SiMe_3)_2]_3 \rightarrow Cl_2BN(SiMe_3)Al[N(SiMe_3)_2]_2 + Me_3SiCl}$$

Unreacted starting materials were recovered at 50 °C; at 71 °C partial reaction took place; at 100 °C all BCl$_3$ was consumed and Me$_3$SiCl, Me$_4$Si, and Me$_3$B were liberated. The isolation of the last two compounds shows that exchange between methyl and chloro groups occurred. Formation of (CH$_3$)$_x$(Cl)$_y$SiN units is proposed on the basis of the reactions of N(SiMe$_3$)$_3$ and [(Me$_3$Si)$_2$NBNSiMe$_3$]$_2$ with boron trichloride.[23] The ratio of Al[N(SiMe$_3$)$_2$]$_3$:Si liberated:B incorporated:Me liberated:Cl liberated (in Me$_3$SiCl) was found to be 1:1.5:1.2:1.9:0.3. The methyl group calculation includes all the methyl groups from Me$_3$B and one from Me$_4$Si. From the above ratio, we calculate that the formation of N–B–N bridges takes place to the extent of ~20%. Therefore, the resultant system contains BCl and SiCl linkages and consequently should be amenable to reactions with (Me$_3$Si)$_2$NH and ammonia and lead to potential candidate precursors to ceramics containing B, Al, and Si.

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[19] Paciorek, K. J. L.; Kratzer, R. H.; Kimble, P. F.; Nakahara, J. H.; Wynne, K. J.; Day, C. S. *Inorg. Chem.* **1988**, *27*, 2432.

[20] Steinberg, H.; Brotherton, R. J. In *Organoboron Chemistry*; John Wiley and Sons: New York, 1966; Vol. II; pp 85–86.

[21] Ebsworth, E. A. V. *Volatile Silicon Compounds*; International Series of Monographs on Inorganic Chemistry; Pergamon Press: Oxford, England, 1963.

[22] Janik, J. Fr.; Narula, C. K.; Gulliver, E. G.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1988**, *27*, 1222 and references therein.

[23] Paciorek, K. J. L.; Kratzer, R. H.; Nakahara, J. H.; Krone-Schmidt, W. *Inorg. Chem.* **1989**, *28*, 2896.

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Fluorinated Three- and Four-Nitrogen Compounds and Their Reactions

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Insertion of trifluoroacetonitrile into the nitrogen–chlorine bond of CF$_3$(C$_2$F$_5$)NN(Cl)C$_2$F$_5$ gives CF$_3$(C$_2$F$_5$)NN(C$_2$F$_5$)N=C(Cl)CF$_3$ in low yield. Polyfluorodiazanes containing an ether functionality CF$_3$(C$_2$F$_5$)NN=C(CF$_3$)OR$_f$ [R$_f$ = CH$_2$CF$_3$, CH(CF$_3$)$_2$] are prepared by reacting CF$_3$(C$_2$F$_5$)NN=C(Cl)CF$_3$ with LiOR$_f$. Chlorine fluoride adds readily to the carbon–nitrogen double bond in CF$_3$(C$_2$F$_5$)NN=C(CF$_3$)OR$_f$ to give CF$_3$(C$_2$F$_5$)NN(Cl)CF(CF$_3$)OR$_f$. Photolysis of the latter compounds results in the formation of tetrazanes [CF$_3$(C$_2$F$_5$)NNCF(CF$_3$)OR$_f$]$_2$. The tetrazane [CF$_3$(C$_2$F$_5$)NN(C$_2$F$_5$)]$_2$ when heated with polyfluoroolefins (CF$_2$=CFCl, CFCl=CFCl, CF$_2$=CH$_2$, CF$_2$=CFH) forms CF$_3$(C$_2$F$_5$)NN(C$_2$F$_5$)CX$_2$CY$_2$N(C$_2$F$_5$)N(C$_2$F$_5$)CF$_3$.

Introduction

At first glance, with the exception of compounds of carbon, it would appear that molecules containing catenated atoms of other elements are relatively unstable. While there is no element that can compete with carbon in numbers of catenated atoms, it should be noted that it is possible to prepare stable catenated species of other elements, especially if fluorine atoms or fluorinated groups or other electronegative species are present in the molecule; e.g., compare CF$_3$O$_n$CF$_3$ (n = 1–3) and O$_n$F$_2$ (n = 1, 2, 4, and perhaps 5 and 6) or CF$_3$S$_n$CF$_3$ (n = 1–6), HS$_n$H (n = 1–6), and Cl S$_n$Cl (n = 1–100). Thus, it is expected that stable catenated nitrogen compounds should exist, since (CF$_3$)$_3$N and CF$_3$N$_2$CF$_3$ are both extremely stable molecules.

We[1] and others[2,3] have been able to synthesize highly stable perfluoroalkyl-substituted tetrazanes (R$_f$)$_2$NN(R$_f$)N(R$_f$)N(R$_f$)$_2$. The earlier syntheses[3] were accomplished in low yield by the photolysis of diazanes, e.g., $\mathrm{R_fN{=}NR_f \xrightarrow{h\nu} [(R_f)_2NNR_f]_2}$, or from the photolysis or thermolysis of a halogen (Cl$_2$ or Br$_2$) with [(CF$_3$)$_2$NN(CF$_3$)]$_2$Hg.[2] The former reaction is assumed to proceed

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[1] Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 3345 and references therein.

[2] Dobbie, R. C.; Emelêus, H. J. *J. Chem. Soc. A* **1966**, 933.

[3] Dacey, J. R.; Young, D. M. *J. Chem. Phys.* **1955**, *23*, 1302. Pritchard, G. O.; Pritchard, H. O.; Schutt, H. I.; Trotman-Dickenson, A. F. *Trans. Faraday Soc.* **1956**, *52*, 849. Ginsburg, V. A.; et al. *Dokl. Chem.* (*Engl. Transl.*) **1962**, *142*, 4.

0020-1669/90/1329-4255$02.50/0

via either the hydrazo or tetrazo radical. Interestingly, although fluorinated two-nitrogen and four-nitrogen compounds have long been known, heretofore very few stable fluorinated three-nitrogen compounds have been reported.

In our work,[1] the insertion of nitriles, e.g., ClCN and CF_3CN, into the nitrogen–chlorine bonds of bis(polyfluoroalkyl)- or bis(perfluoroalkyl)chloroamines, followed by the facile addition of chlorine fluoride to the resulting double bond, gave rise to a new family of chlorotris(polyfluoroalkyl)hydrazines. Photolysis of the latter compounds formed the highly stable tetrazanes and chlorine concomitantly, viz.

$$R_f(CF_3)NCl + RC{\equiv}N \xrightarrow{h\nu} R_f(CF_3)NN{=}CClR$$

$$R_f(CF_3)NN{=}CClR + ClF \rightarrow R_f(CF_3)NN(Cl)CClFR$$

$$2R_f(CF_3)NN(Cl)CClFR \xrightarrow{h\nu} [R_f(CF_3)NNCClFR]_2 + Cl_2$$

We have now extended our work with fluorinated catenated nitrogen compounds to (1) prepare a stable three-nitrogen species, (2) utilize $CF_3(C_2F_5)NN{=}C(Cl)CF_3$ as a precursor to more highly substituted tetrazanes, and (3) examine the reaction chemistry of our previously reported tetrazanes with polyfluoroolefins.

Results and Discussion

Building on the successful insertions of both fluorinated and nonfluorinated olefins into the nitrogen–halogen bond, e.g., hexafluoropropene or ethylene into the N—X bond of bromo- or iodobis(trifluoromethyl)amine[4-8] or olefins into chlorobis(trifluoromethyl)amine,[9,10] we reported the stepwise insertion of $CF_2{=}CFX$ (X = Cl, F) into the N–Cl bonds of dichloro(perfluoroalkyl)amines.[11] Insertions of CNCl and/or CF_3CN into the element–chlorine bonds of $(CF_3)_2NCl$,[2] $(R_f)R_f'NCl$,[1] SF_5Cl,[12] and CF_3SF_4Cl[13] form compounds such as $(R_f)R_f'NN{=}CClR$ and $R'N{=}CClR$ (R = Cl, CF_3; R′ = SF_5, CF_3SF_4).

We now have extended the insertion of nitriles into the N–Cl bonds of chlorotris(perfluoroalkyl)hydrazines. In so doing, we can report the low-yield synthesis of a stable, highly fluorinated three-nitrogen compound.

$$CF_3(C_2F_5)NN(Cl)C_2F_5{}^{1} + CF_3CN \xrightarrow[6\text{–}10\ h]{h\nu} \underset{\text{I; 5–10\%}}{CF_3(C_2F_5)NN(C_2F_5)N{=}C(Cl)CF_3} + \underset{60\text{–}70\%}{[CF_3(C_2F_5)NN(C_2F_5)]_2}$$

I is a viscous, water-white, slightly volatile liquid that is stable for long periods at 25 °C. Attempts to saturate the carbon–nitrogen double bond of I with chlorine fluoride led only to fragmentation. In our experiments, I was not a satisfactory precursor to more highly catenated nitrogen compounds. However, chlorine fluoride can add to the double bond of $CF_3(C_2F_5)NN{=}C(Cl)CF_3$ (II), which, when photolyzed, loses chlorine to form $CF_3(C_2F_5)NN{=}CFCF_3$. The latter was converted successfully to a perfluorinated tetrazane by the above procedure.

In an effort to prepare more highly substituted tetrazanes with concomitantly differing densities, we concluded that II would be a useful precursor when the C–Cl bond was replaced through nucleophilic reaction. Thus, with lithium polyfluoroalkoxides, II forms stable derivatives:

$$\text{II} + LiOR_f \xrightarrow{-196\ ^\circ C \rightarrow \text{room temp}} \underset{\text{III, IV}}{CF_3(C_2F_5)NN{=}C(OR_f)CF_3} + LiCl$$

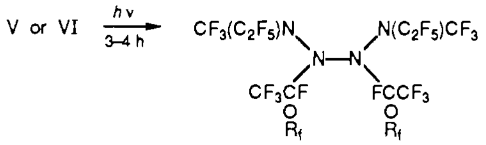
$$R_f = CH_2CF_3\ (\text{III}),\ C(CF_3)_2H\ (\text{IV})$$

Now, when III and IV are reacted with ClF at −78 °C for 10–12 h, addition across the carbon–nitrogen double bond occurs smoothly:

$$\text{III or IV} + ClF \xrightarrow[10\text{–}12\ h]{-196 \rightarrow -78\ ^\circ C} \underset{\text{V, VI}}{CF_3(C_2F_5)NN(Cl)CF(OR_f)CF_3}$$

$$R_f = CH_2CF_3\ (\text{V}),\ C(CF_3)_2H\ (\text{VI})$$

Both V and VI are viscous liquids that are stable indefinitely at 25 °C. On photolysis, two new tetrazanes with polyfluoro ether functionalities are obtained:



$R_f = CH_2CF_3$ (VII), $C(CF_3)_2H$ (VIII)

Compound VII is stable at 60 °C for at least 11 h but undergoes significant decomposition at 80 °C in a shorter time, while VIII is considerably decomposed after 8 h at 60 °C. At 25 °C, the densities of VII and VIII are 2.1 and 2.2 g/mL, respectively. While these new diether tetrazanes are a novel new compound type, perhaps the most interesting occurrence in these synthetic steps is the chlorine fluoride addition to form V and VI. For instance, while $R_fN{=}CF_2$ can be reacted with ClF to give chloroamines, $R_f(CF_3)NCl$,[14] $R_fN{=}SF_2$ + ClF results in breaking of the $-N{=}S$ bond to form $R_fNCl_2 + SF_4$.[15] Also, when $R_fN{=}EF_2$ is reacted with alkoxides, followed by ClF, a similar cleavage occurs:

$$R_fN{=}EF_2 + LiOR_f' \rightarrow \underset{\text{IX}}{R_fN{=}E(OR_f')_2}$$

$$E = C,^{16}\ S^{17}$$

$$R_fN{=}E(OR_f')_2 + ClF \rightarrow R_fNCl_2 + EF_n(OR_f')_2$$

$$E = C,\ n = 2^{16} \qquad E = S,\ n = 4^{17}$$

The case with $R_fN{=}S(OR_f')R_f''$ has not yet been studied, but with IX (E = C or S), regardless of the conditions employed, the double bond was cleaved with ClF to give stable diethers or sulfuranes. While it would have been useful to prepare $R_fN{=}E(F)OR_f$ for use in ClF addition studies, in our experiments, nucleophilic displacement of both fluorine atoms invariably occurs. However, at −78 °C chlorine monofluoride can be added to $CF_3N{=}CFN(CF_3)_2$ to give the stable secondary *N*-haloamine.[16]

Perhaps not surprisingly, given the radical-based formation of tetrazanes,[3] it is possible to insert olefins into the N2–N3 bond of tetrazane under quite mild conditions. Thus, at 100–110 °C, $[CF_3(C_2F_5)NN(C_2F_5)]_2$ can be reacted readily with $CF_2{=}CFCl$, $CFCl{=}CFCl$, $CF_2{=}CH_2$, and $CF_2{=}CFH$ to form $CF_3(C_2F_5)$-

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(4) Young, J. A.; Tsoukalas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.
(5) Alexander, E. S.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. *J. Chem. Soc. C* **1968**, 796.
(6) Emeléus, H. J.; Tattershall, B. W. *Z. Anorg. Allg. Chem.* **1964**, *327*, 147.
(7) Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc.* **1965**, 6141.
(8) Barlow, M. G.; Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 2744.
(9) Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 3829.
(10) Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 3833.
(11) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28*, 2187.
(12) Tullock, C. W.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 357.
(13) Yu, S.-L.; Shreeve, J. M. *Inorg. Chem.* **1976**, *15*, 743.
(14) Sprenger, G. H.; Shreeve, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1770.
(15) DeMarco, R. A.; Shreeve, J. M. *J. Fluorine Chem.* **1971/72**, *1*, 269; *J. Chem. Soc. D* **1971**, 788.
(16) Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. *J. Fluorine Chem.* **1990**, *40*, 395.
(17) Marsden, H. M.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 4021.

$NN(C_2F_5)\underset{|}{\overset{|}{C}}\underset{|}{\overset{|}{C}}N(C_2F_5)N(C_2F_5)CF_3$ in ~30–40% yield, e.g.

$$CF_3(C_2F_5)NN(C_2F_5)N(C_2F_5)N(C_2F_5)CF_3 \xrightarrow{100\text{–}110\ ^\circ C} 2CF_3(C_2F_5)N\dot{N}(C_2F_5)$$

$$CF_3(C_2F_5)N\dot{N}(C_2F_5) + CF_2{=}CFCl \rightarrow$$

$$CF_3(C_2F_5)NN(C_2F_5)CFCl\dot{C}F_2 \xrightarrow{[CF_3(C_2F_5)NN(C_2F_5)]_2} CF_3(C_2F_5)NN(C_2F_5)CFClCF_2N(C_2F_5)N(C_2F_5)CF_3$$

Unfortunately, under the conditions (thermal) attempted, it was not possible to add to SO_2, SF_4, or $CF_3CF{=}CF_2$. These insertion compounds are stable, colorless liquids that are purified by removing all volatile materials under vacuum.

Experimental Section

Materials. The literature method was used for the synthesis of $CF_3(C_2F_5)NN(C_2F_5)Cl$ and $CF_3(C_2F_5)NN{=}C(CF_3)Cl$.[1] Trifluoroacetonitrile, $CF_2{=}CFCl$, $CFCl{=}CFCl$, and $(CF_3)_2CHOH$ (PCR), CF_3CH_2OH and *n*-butyllithium (Aldrich), and chlorine fluoride (Ozark-Mahoning) were purchased and used as received. Japan Halon Co. Ltd. provided $CF_2{=}CH_2$ and $CF_2{=}CFH$.

General Procedures. A Pyrex glass vacuum system, including a Heise Bourdon tube and Televac thermocouple gauges, was used for gases and volatile liquids. Conventional *PVT* techniques were used to quantify volatile starting materials and products. A Perkin-Elmer Model 1710 infrared Fourier transform spectrometer equipped with an IBM PS/2 data station was used to record infrared spectra. ^{19}F NMR spectra were obtained with a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer (CCl_3F as reference). In some cases $CDCl_3$ or a mixture of $CDCl_3$ and $CFCl_2CF_2Cl$ (10:1) was employed as solvent. A VG 7070 mass spectrometer was used to obtain either electron impact (17 eV) or chemical ionization mass spectra. A Rayonet reactor with 3000-Å UV lamps was used for photochemical reactions. Elemental analyses were obtained from Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $CF_3^A(CF_3^BCF_2^C)NN(CF_3^DCF_2^E)N{=}C(CF_3^F)Cl$. A 5-mmol sample of $CF_3(C_2F_5)NN(C_2F_5)Cl$ and 40 mmol of $CF_3C{\equiv}N$ were condensed into a 2-L quartz vessel at −196 °C. After the temperature of the vessel reached 25 °C, the mixture was photolyzed (3000 Å) for 6–8 h, and the contents of the vessel were separated by trap-to-trap distillation. The desired product $CF_3(C_2F_5)NN(C_2F_5)N{=}C(CF_3)Cl$ was found in the trap cooled at −45 °C in 5–10% yield, having passed through a trap at −10 °C that contained $[CF_3(C_2F_5)NN(C_2F_5)]_2$ (60–70% yield). Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 467/465 (M^+) 0.6/1.5, 385 ($C_6F_{15}N_2^+$) 5.6, 348/346 ($C_5F_{11}N_3Cl^+$) 1.8/5.9, 335 ($C_5F_{13}N_2^+$) 4.2, 316 ($C_5F_{12}N_2^+$) 0.6, 297 ($C_5F_{11}N_2^+$) 6.9, 247 ($C_4F_9N_2^+$) 5.0, 119 ($C_2F_5^+$) 55.3, 69 (CF_3^+) 100. IR (liquid): 1673 s (C=N), 1359 s, 1309 s, 1244 vs, 1173 s, 1143 s, 1093 s, 976 vs, 932 s, 843 s, 750 s, 535 s cm^{-1}. ^{19}F NMR: ϕ −58.21 (A, mult), −70.83 (F, s), −80.56 (B, mult), −82.24 (D, mult), −95.27, −97.12 (C, mult), −99.67, −100.6 (E, mult). Anal. Calcd for $C_7F_{16}N_3Cl$: C, 18.04; F, 65.31; N, 9.02; Cl, 7.63. Found: C, 18.07; F, 65.50; N, 8.95; Cl, 7.74.

General Method for the Preparation of $CF_3(C_2F_5)NN{=}C(CF_3)OR_f$ (R_f = CF_3CH_2, $(CF_3)_2CH$). To a dry 500-mL Pyrex round-bottomed flask, equipped with a Kontes Teflon stopcock, 5 mL (~10 mmol) of 1.6 M BuLi in hexane was added under an inert atomosphere. The vessel was evacuated at −196 °C, and a slight excess (~12 mmol) of the alcohol was condensed into the flask. The mixture was allowed to warm to room temperature and left for several hours. The volatile materials (hexane, butane, and unreacted alcohol) were removed under vacuum, leaving the alkoxide salt, $R_fO^-Li^+$, in the flask. Into the flask at −196 °C was then condensed 5 mmol of $CF_3(C_2F_5)NN{=}C(Cl)CF_3$. The reactants were allowed to warm slowly to room temperature over a 2-h period. After 24 h the resulting product mixture was separated by trap-to-trap distillation.

Properties of $CF_3^A(CF_3^BCF_2^C)NN{=}C(CF_3^D)OCH_2CF_3^E$. This compound was found in the trap cooled to −30 °C, having passed through a trap at −10 °C. It was obtained in 47% yield as a colorless liquid. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 397 (M^+ + 1) 25.7, 396 (M^+) 24.8, 377 (M^+ − F) 100, 327 ($M^+ - CF_3$) 5.3, 297 ($M^+ - OCH_2CF_3$) 12.3, 149 ($C_3F_5OH_2^+$) 21.6, 119 ($C_2F_5^+$) 8.6, 83 ($CF_3CH_2^+$) 20.8, 69 (CF_3^+) 51.0. IR (gas): 2989 m, 1667 vs, 1428 s, 1373 s, 1288 vs, 1242 vs, 1198 vs, 1171 vs, 1108 s, 892 s, 752 s cm^{-1}. ^{19}F NMR: ϕ −61.91 (A, tq), −67.30 (D, qt), −73.8 (E, t), −81.66 (B, mult), −102.92 (C, qq). ^1H NMR: δ −4.70 (CH_2, q); J_{A-C} = 11.47 Hz, J_{A-D} = 3.67 Hz, J_{C-D} = 2.68 Hz, J_{CH_2-E} = 7.81 Hz.

Properties of $CF_3^A(CF_3^BCF_2^C)NN{=}C(CF_3^D)OCH(CF_3^E)_2$. This compound was found in the trap cooled to −50 °C, having passed through a trap at −20 °C. It was obtained in 33% yield as a colorless liquid. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 465 (M^+ + 1) 15.7, 464 (M^+) 26.1, 445 (M^+ − F) 100, 395 ($M^+ - CF_3$) 7.7, 297 ($M^+ - OCH(CF_3)_2$) 12.1, 217 ($C_4F_8HO^+$) 9.3, 119 ($C_2F_5^+$) 17.7, 69 (CF_3^+) 72.9. IR (gas): 2996 s, 1679 (C=N) vs, 1383 vs, 1293 vs, 1238 vs, 1172 vs, 1122 s, 898 s, 755 s, 692 s cm^{-1}. ^{19}F NMR: ϕ −61.80 (A, tq), −67.41 (D, qt), −73.26 (E, d), −82.01 (B, s), −103.73 (C, qq). ^1H NMR: δ 6.04 (CH, septet); J_{A-C} = 11.82 Hz, J_{A-D} = 3.76 Hz, J_{C-D} = 2.15 Hz, J_{CH-E} = 5.37 Hz.

Reaction of Chlorine Fluoride with $CF_3(C_2F_5)NN{=}C(CF_3)OR_f$ (R_f = CF_3CH2, $(CF_3)_2CH$). A 3-mmol sample of $CF_3(C_2F_5)NN{=}C(CF_3)OR_f$ and 5 mmol of ClF were condensed at −196 °C into a 75-mL stainless steel vessel fitted with a Whitey high-pressure stainless steel valve. The mixture was allowed to warm from −196 to −78 °C and held at that temperature for 10–12 h. The desired product, $CF_3(C_2F_5)NN(Cl)CF(CF_3)OR_f$, was isolated by trap-to-trap distillation.

Properties of $CF_3^A(CF_3^BCF_2^C)NN(Cl)CF^F(CF_3^D)OCH_2CF_3^E$. This compound was found in the trap cooled to −20 °C in 75% yield as a colorless liquid. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 433/431 (M^+ − F) 2.5/7.7, 415 (M^+ − Cl) 0.7, 396 (M^+ − ClF) 49.5, 377 ($M^+ - ClF_2$) 100, 353/351 ($M^+ - OCH_2CF_3$) 2.3/5.1, 297 ($C_5F_{11}N_2^+$) 88, 247 ($C_4F_9N_2^+$) 17.5, 199 ($C_4F_7OH_2^+$) 46.5, 149 ($C_3F_5OH_2^+$), 49.3, 119 ($C_2F_5^+$) 47.2, 83 ($CF_3CH_2^+$) 73.7, 69 (CF_3^+) 100. IR (gas): 2996 w, 1312 s, 1250 vs, 1185 s, 1100 s, 1030 s, 912 w, 737 w cm^{-1}. ^{19}F NMR: ϕ −55.98, −56.06 (A, q, mult), −74.59, −74.94 (E, D, t, mult), −78.36, −78.59 (D, mult), −81.43 to −82.87 (B, mult), −102.57 (C, q, mult), −109.23 (F, mult). ^1H NMR: δ 2.95 (q, mult); J_{CH_2-E} = 7.57 Hz, J_{E-F} = 26.37 Hz, J_{A-E} = 12.94 Hz.

Properties of $CF_3^A(CF_3^BCF_2^C)NN(Cl)CF^F(CF_3^D)OCH(CF_3^E)_2$. This compound was found in the trap cooled to −30 °C. It was obtained in 79% yield as a colorless liquid. Spectral data were as follows. IR (liquid): 3008 w, 1364 s, 1304 s, 1214 s, 1115 s, 1042 s, 903 s, 728 s, 712 s, 693 s cm^{-1}. ^{19}F NMR: ϕ −56.47, −57.74 (A, mult), −73.09 (E, mult), −77.95 (D, mult), −82.01, −83.16 (B, mult), −99.33 to −105.8 (C and F, mult). ^1H NMR: δ 4.86 (mult).

Photolysis of $CF_3(CF_3CF_2)NN(Cl)CF(CF_3)OR_f$ (R_f = CF_3CH_2, $(CF_3)_2CH$). A 2-mmol sample of $CF_3(C_2F_5)NN(Cl)CF(CF_3)OR_f$ was condensed at −196 °C into a 200-mL quartz vessel. Afer warming to room temperature over a period of 1 h, the contents were photolyzed for 2–3 h at 3000 Å. The volatile products were removed under vacuum, and the tetrazane $[CF_3(CF_3CF_2)NNCF(CF_3)OR_f]_2$ was found in the reaction vessel as an involatile compound.

Properties of $[CF_3^A(CF_3^BCF_2^C)NNCF^F(CF_3^D)OCH_2CF_3^E]_2$. This product was isolated as an involatile, colorless liquid in the reaction vessel in 80–85% yield. Spectral data were as follows. MS (EI^+) [*m/e* (species) intensity]: 791 ($M^+ - HF_2$) 1.8, 790 (M^+ − 2HF) 3.7, 771 ($M^+ - H_2F_3$) 1.8, 721 ($M^+ - CH_2F_5$) 0.5, 515 ($C_9F_{19}N_2OH_2^+$) 4.9, 514 ($C_9F_{19}N_2HO^+$) 9.5, 477 ($C_9F_{17}N_2OH_2^+$) 55.7, 415 ($C_7F_{15}N_2OH_2^+$) 39.1, 316 ($C_5F_{12}N_2^+$) 7.8, 297 ($C_5F_{11}N_2^+$) 70.8, 199 ($C_4F_7OH_2^+$) 100, 133 ($C_2F_5N^+$) 82.8, 83 ($CF_3CH_2^+$) 100, 69 (CF_3^+) 100. IR (liquid): 2993 s, 1465 w, 1427 s, 1299 s, 1240 s, 1166 s, 1073 s, 937 s, 737 s cm^{-1}. ^{19}F NMR: ϕ −54.50 (A, mult), −74.13, −75.35 (E, mult), −77.08, −78.59, −79.34 (D, mult), −80.56, −81.77 (B, mult), −89.76 to −105.4 (C and F, mult). ^1H NMR: δ 4.28 (mult). Anal. Calcd for $C_{14}F_{30}N_4O_2H_4$: C, 20.24; H, 0.48; N, 6.77. Found: C, 20.28; H, 0.54; N, 6.76. Density at 25 °C: 2.1 g/mL.

Properties of $[CF_3^A(CF_3^BCF_2^C)NNCF^F(CF_3^D)OCH(CF_3^E)_2]_2$. This compound was obtained as an involatile colorless liquid in the reaction vessel in 75–80% yield. Spectral data were as follows. MS (CI) [*m/e* (species) intensity]: 966 (M^+) 6.6. IR (liquid): 3025 s, 1363 s, 1304 s, 1218 s, 1115 s, 1072 s, 1040 s, 940 s, 902 s, 884 s, 739 s, 694 s cm^{-1}. ^{19}F NMR: ϕ −54.50, −55.31 (A, mult), −71.75 to −82.76 (B, D, E, mult), −101 to −106 (C and F, mult). ^1H NMR: δ 5.03 (mult). Anal. Calcd for $C_{16}F_{36}N_4O_2H_2$: C, 19.87; H, 0.21; N, 5.80. Found: C, 20.22; H, 0.34; N, 5.73. Density at 25 °C: 2.2 g/mL.

Reactions of Olefins ($CF_2{=}CFCl$, $CFCl{=}CFCl$, $CF_2{=}CH_2$, $CF_2{=}CFH$) with the Tetrazane $[CF_3(C_2F_5)NN(C_2F_5]_2$. A 2-mmol sample of perfluorotetrazane was weighed into a thick-walled Pyrex glass tube. The tube was evacuated at −196 °C, and 4 mmol of olefin was condensed into the tube. The tube was sealed and heated at 100–110 °C for 10–12 h. The products were purified by trap-to-trap distillation.

Properties of $CF_3(C_2F_5)NN(C_2F_5)CF_2CFClN(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the trap cooled at −10 °C in 35–40% yield as a colorless liquid. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 769/767 (M^+ − F) 4.6/15.0, 751 (M^+ − Cl) 9.8, 530 ($C_9F_{20}N_3^+$) 39.7, 451 ($C_7F_{16}N_2Cl^+$) 22.6, 403/401 ($C_6F_{14}N_2Cl^+$) 10.5/17.9, 385 ($C_6F_{15}N_2^+$) 40.5, 297 ($C_5F_{11}N_2^+$) 71, 119 ($C_2F_5^+$) 95.5, 69 (CF_3^+) 54.1. IR (liquid): 1219 vs, 1166 vs, 1137 s, 1095 s, 1074 s, 1033 s, 995 s, 951 vs, 932 s, 867 s, 844 s, 822 s, 806 s, 777 s, 755 s, 739 s, 709 s, 676 s, 650 s, 617 s, 534 s cm^{-1}. ^{19}F NMR: ϕ −57.51, −58.55 ($C\mathit{F}_3N$, mult), −80.67, −81.89, −82.18 ($C\mathit{F}_3CF_2$, mult), −94.9 to −106

(CF_2, CF_3CF_2N, CFCl, mult). Anal. Calcd for $C_{12}F_{29}N_4Cl$: C, 18.32; N, 7.12. Found: C, 18.32; N, 7.39.

Properties of $CF_3(C_2F_5)NN(C_2F_5)$ $CFClCFClN(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the reaction vessel as a nonvolatile liquid. It was obtained in ~40% yield. Spectral data were as follows. MS [*m/e* (species) intensity]: 785/783 ($M^+ - F$) 4.6/7.3, 543/541 ($M^+ - C_2F_{10}Cl$) 2.6/8.5, 366 ($C_6F_{14}N_2^+$) 2.6, 297 ($C_5F_{11}N_2^+$) 9.9, 247 ($C_4F_9N_2^+$) 17.6, 164 ($C_3F_6N^+$) 24.9, 119 ($C_2F_5^+$) 100, 69 (CF_3^+) 85.7. IR (liquid): 1223 s, 1134 w, 1087 w, 1071 s, 951 w, 939 w, 887 w, 874 w, 828 w, 812 w, 771 w, 752 s, 738 s, 680 s cm^{-1}. ^{19}F NMR: ϕ −56.6, −57.22 (CF_3N, mult), −80.91, −81.72 (CF_3CF_2, mult), −91.04 to −97.3 (CF_3CF_2, CFCl, mult). Anal. Calcd for $C_{12}F_{28}N_4Cl_2$: C, 17.96; N, 6.98. Found: C, 17.98; N, 6.95.

Properties of $CF_3(C_2F_5)NN(C_2F_5)CF_2CFHN(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the trap cooled at −10 °C as a colorless liquid in ~30% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 734 [(M^+ + 1) − F] 16.97, 683 ($M^+ - CF_3$) 1.3, 417 ($C_7F_{16}N_2H^+$) 28.4, 385 ($C_6F_{15}N_2^+$) 4.8, 367 ($C_6F_{14}N_2H^+$) 78.2, 297 ($C_5F_{11}N_2^+$) 5.6, 279 ($C_5F_{10}N_2H^+$) 22.0, 229 ($C_4F_8N_2H^+$) 21.1, 119 ($C_2F_5^+$) 74.9, 69 (CF_3^+) 77.4. IR (liquid): 1362 s, 1230 s, 1142 s, 1121 s, 1104 s, 1079 s, 1040 s, 946 s, 931 s, 890 s, 783 w, 739 s, 712 s cm^{-1}. ^{19}F NMR: ϕ −58.9 (CF_3N, mult), −82.7 to −84.38 (CF_3CF_2, mult), −95.79 to −101.87 (CF_2CF_3, CF_2, CFH, mult). ^1H NMR: δ 5.9 (d, mult). Anal. Calcd for $C_{12}F_{29}N_4H$: C, 19.15; N, 7.45. Found: C, 19.18; N, 7.38.

Properties of $CF_3(C_2F_5)NN(C_2F_5)CF_2CH_2N(C_2F_5)N(C_2F_5)CF_3$. This compound was found in the trap cooled at −10 °C. It was a colorless liquid obtained in 30–35% yield. Spectral data were as follows. MS (CI^+) [*m/e* (species) intensity]: 665 ($M^+ - CF_3$) 6.0, 627 ($M^+ - CF_5$) 1.1, 463 ($C_8F_{17}N_3H_2^+$) 6.5, 399 ($C_7F_{15}N_2H_2^+$) 29.7, 385 ($C_6F_{15}N_2^+$) 8.8, 349 ($C_6F_{13}N_2H_2^+$) 100, 311 ($C_6F_{11}N_2H_2^+$) 9.5, 261 ($C_5F_9N_2H_2^+$) 11.4, 119 ($C_2F_5^+$) 14.3, 69 (CF_3^+) 14.6. IR (liquid): 1359 w, 1224 s, 1142 s, 1109 s, 1072 s, 1035 s, 951 s, 938 s, 916 w, 878 w, 751 w, 736 s, 702 w cm^{-1}. ^{19}F NMR: ϕ −58.03 (CF_3N, mult), −81.66 to −85.77 (CF_3CF_2, mult), −94 to −100.72 (CF_3CF_2, CF_2, mult). ^1H NMR: δ 3.63 (CH_2, t), $J_{CH_2-CF_2}$ = 14.9 Hz. Anal. Calcd for $C_{12}F_{28}N_4H_2$: C, 19.62; N, 7.63. Found: C, 19.69; N, 7.65.

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Electron Transfer. 103. Reactions of Aqueous Chromium(IV)[1]

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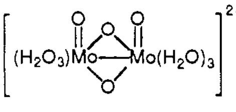
Reduction of $HCrO_4^-$ with the bridged dimer of Mo^V ($Mo_2O_4^{2+}$) in aqueous solutions buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its salt (Lig^-) yields a pink Cr(IV) complex (ϵ_{max}^{510} = 1.3×10^3 M^{-1} cm^{-1} when [Lig^-] = 0.05 M). This species is reduced to a bichelate of Cr^{III} with excess $(Mo^V)_2$ but oxidized to a bichelate of Cr^V with excess $Cr_2O_7^{2-}$, indicating that it too is bischelated. The formation of Cr^{IV} from Cr^{VI} and $(Mo^V)_2$ proceeds through two routes, with the activated complex for the second featuring one more H^+ and one more carboxylate group than that for the first. The comproportionation reaction, $Cr^{IV} + Cr^{VI} \rightarrow 2Cr^V$, appears to entail a $Cr^{IV}Cr^{VI}$ complex (K_{assn} = 40 ± 7 M^{-1}), which reacts via both an acid-independent and a [H^+]-proportional path. Data for the reaction of Cr^{IV} with $(Mo^V)_2$ are in accord with the sequence (6)–(9) in which the key step is the reversible, unimolecular conversion to the principal $(Mo^V)_2$ species to an activated form ($k = 5 \times 10^2$ s^{-1} at 25 °C) that reacts rapidly with Cr^{IV}. To form a Cr^{IV} complex of this type stable enough to be examined in conventional mixing experiments, it is necessary that the carboxylate ligand be attached to the Cr^{IV} center prior to reduction and that the usual 1e⁻ reductants, which rapidly reduce Cr^{IV}, be avoided.

In 1949 Westheimer presented kinetic evidence that oxidations of alcohols with $HCrO_4^-$ passed through the atypical oxidation state Cr(IV).[2] Further indications accumulated in the 1960s that this state was an intermediate in the reactions of Cr(VI) with 1e⁻ metal-center reductants.[3] A small array of Cr(IV) derivatives have been characterized,[4] but these are generally not stable in aqueous media. Notable exceptions are a group of chromium(IV) diperoxo ammines, which were first prepared near the turn of the century[5] and were eventually examined in detail by Garner and co-workers.[6] Mechanistic studies of complexes of this type[7] are complicated by the presence of three oxidizing functions in a single molecule.

Reports in 1985 mentioned the formation of Cr(IV) complexes devoid of peroxo ligands when α-hydroxy carboxylato chelates of Cr(V) were reduced with Fe^{2+}, VO^{2+}, or U(IV).[8] Although specific rates of a few reactions of such transients could be estimated, study was limited by the competing decay of Cr(IV) in the presence of 1e⁻ reagents.

We here describe the preparation of aqueous Cr(IV) solutions of greatly improved stability by treatment of $HCrO_4^-$ with the dimeric molybdenum(V) cation, I (abbreviated $(Mo^V)_2$), in solutions buffered by excess 2-ethyl-2-hydroxybutanoic acid (II) and its anion. This acid is the most effective member of a group



I

$(C_2H_5)_2C(OH)COOH$

II

of α-hydroxy carboxylic acids known to stabilize Cr(V) via chelation.[9] We find that it is likewise useful in stabilizing Cr(IV) and, on the basis of earlier evidence,[8a,b] suggest that it is bidentate here as well. In addition to data pertaining to the formation of this unusual state, we include information on its reduction with

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(2) See, for example: Watanabe, E.; Westheimer, F. H. *J. Chem. Phys.* **1949**, *17*, 61.

(3) See, for example: (a) Espenson, J. H.; King, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3328. (b) Sullivan, J. C. *Ibid.* **1965**, *87*, 1495. (c) Espenson, J. H. *Ibid.* **1964**, *86*, 1883. (d) Birk, J. P. *Ibid.* **1969**, *91*, 3189. (e) MacKnight, G. F.; Haight, G. P. *Inorg. Chem.* **1973**, *12*, 1619. (f) For an early critical review, see: Espenson, J. H. *Acc. Chem. Res.* **1970**, *2*, 347.

(4) (a) Clark, H. C.; Sandana, Y. N. *Can. J. Chem.* **1964**, *42*, 50. (b) Wilhelmi, K.; Jonson, O. *Acta Chem. Scand.* **1961**, *15*, 1415. (c) Hagihara, N.; Yamazaki, H. *J. Am. Chem. Soc.* **1959**, *81*, 3160. (d) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 772. (e) Dyracz, G.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 4756.

(5) (a) Weide, O. F. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2178. (b) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181.

(6) (a) House, D. A.; Garner, C. S. *Nature*, **1965**, *208*, 776. (b) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840. (c) House, D. A.; Hughes, R. G.; Garner, C. S. *Ibid.* **1967**, *6*, 1077.

(7) Ghosh, S. K.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4224.

(8) (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Ibid.* **1985**, *24*, 4679. (c) Bose, R. N.; Gould, E. S. *Ibid.* **1986**, *25*, 94.

(9) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.