Inorg. Chem. **1989**, *28*, 2187–2189 **2187**

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Insertion of Tetrafluoroethylene and Trifluorochloroethylene into Nitrogen–Chlorine Bonds. A New Route to Perfluoroazaalkenes

Ghulam Sarwar, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

Received October 12, 1988

Insertion of olefins, $CF_2{=}CFX$ (X = Cl, F), into the nitrogen–chlorine bonds of dichloro(perfluoroalkyl)amines, R_fNCl_2 (R_f = CF_3, C_2F_5), occurs readily, providing an easy, straightforward route to secondary (polyfluoroalkyl)- or (perfluoroalkyl)chloroamines and tertiary (polyfluoroalkyl)- or (perfluoroalkyl)amines. At 65–70 °C, insertion into only one of the nitrogen–chlorine bonds occurs to give $R_fN(CF_2CFXCl)Cl$, while at 90–100 °C, insertion into both nitrogen–chlorine bonds produces the tertiary amine $R_fN(CF_2CFXCl)_2$ in good yield. Gas-phase photolysis of $R_fN(CF_2CFXCl)Cl$ results in essentially quantitative yields of the respective perfluoroazaalkenes, $R_fN{=}CF_2$, and fluorocarbons, $CFXCl_2$ (X = F, Cl).

Introduction

While the insertion of olefins into the nitrogen–halogen bond of secondary halo(perfluoroalkyl)amines is cited frequently in the literature, e.g., the insertion of hexafluoropropene or ethylene into the nitrogen–halogen bond of bromo- or iodobis(trifluoromethyl)amine,[1–5] a survey of the literature indicates that the analogous reaction with dichloro(perfluoroalkyl)amines to form secondary or tertiary (polyfluoroalkyl)- or (perfluoroalkyl)amines has not been reported. In only a single case has mention been made of the potential utility of dichloro(perhaloalkyl)amines for the synthesis of tertiary (perhaloalkyl)amines.[6] However, no results were given at that time, and no reports have appeared subsequently describing this chemistry for dichloro(perhaloalkyl)amines.

The reported chemistry of the dichloroamines is quite limited. The synthesis of diazo compounds is accomplished via pyrolysis[7] and photolysis[8,9] of dichloroamines. Dechlorination of $ClCF_2NCl_2$ by heating at 150 °C for 4 h results in an 80% yield of the chloroimine $CF_2{=}NCl$.[10] Similarly, $FN{=}CFCl$ is obtained by heating $Cl_2CFNFCl$ at 53 °C.[11] Reactions of compounds of the type $XCCl_2NF_2$ (X = Cl, F) with mercury generate fluoroimines in good yield,[12] while $Cl_2NCF_2CF_2NCl_2$ is dechlorofluorinated to yield cyanogen quantitatively in 0.5 h at 25 °C.[13] Attempts to insert CO or SO_2 into the nitrogen–chlorine bonds of the dichloroamines result primarily in the formation of the corresponding azo compounds.[14] The primary amine CF_3NH_2 is formed by reaction of CF_3NCl_2 with hydrochloric acid,[15] as well as by reaction with trimethylsilane.[16] Phosphorus trichloride reacts with $R_fCF_2NCl_2$ to give good yields of the corresponding phosphazenes, $R_fCF_2N{=}PCl_3$.[17] Fluorination of $ClCF_2NCl_2$ gives a 76% yield of $ClCF_2NClF$,[18] while CF_3NClBr is synthesized by the reaction of bromine with CF_3NCl_2.[19] The reactions of CF_3NCl_2 with $SeCl_2$ or Se and $SOCl_2$ to give $F_3CN{=}SeCl_2$ and CF_3NSO, respectively, have also been reported.[20]

In addition, the chlorobis(polyfluoroalkyl)amines are found to be particularly useful precursors in the synthesis of fluorinated azaalkenes. The per- or polyfluoroazaalkenes, $R_fN{=}CF_2$, are a class of compounds whose chemistry remains largely untouched primarily because of the paucity of high-yield routes to the aza compounds from commercially available or easily synthesized precursors.

We give here the first documented investigation of the insertion reactions of dichloro(perfluoroalkyl)amines with tetrafluoroethylene and chlorotrifluoroethylene. We describe a very straightforward route to the synthesis of new chlorobis(perfluoroalkyl)- and bis(polyfluoroalkyl)amines as well as new tris(perfluoroalkyl) and tris(polyfluoroalkyl)amines. Moreover, essentially quantitative yields of the perfluoroazaalkenes $R_fN{=}CF_2$ (R_f = CF_3, C_2F_5), are easily obtained by photolysis of chloroamines of the type $R_fN(CF_2CFXCl)Cl$ (R_f = CF_3, C_2F_5; X = Cl, F). Previously published synthetic routes to the perfluoroazaalkenes generally require high temperature and/or subsequent fluorination. These include preparation of $CF_3N{=}CF_2$ in 78% yield from fluorination of $CCl_3N{=}CCl_2$ with excess NaF in sulfolane at 150 to 160 °C over a period of 3 h.[21] Pyrolysis of CF_3NO at 160 °C for 1 day gives a 24% yield of $CF_3N{=}CF_2$.[22] Photolysis of $CF_3N{=}NCF_3$ results in a 10% yield of $CF_3N{=}CF_2$.[23] Perfluoro-2-aza-1-butene was prepared by passing $(C_2F_5)_3N$ through a graphite tube at 745 °C.[24] Similarly, pyrolysis of perfluoro-2-ethyl-1,2-oxazetidine) at 550 °C resulted in a nearly quantitative yield of $C_2F_5N{=}CF_2$.[25,26]

Results and Discussion

In the case of the secondary haloamines, Haszeldine and coworkers have suggested both free radical and ionic mechanisms for the insertion reaction with olefins.[4] They reported that heat or photolysis favors a radical mechanism, while reactions carried out at low temperatures in the absence of light follow an ionic pathway. The reaction of bromobis(trifluoromethyl)amine with chlorotrifluoroethylene to give $(CF_3)_2NCF_2CFClBr$ is consistent with a radical mechanism, where the intermediate radical $(CF_3)_2N^\bullet$ initially attacks the difluoromethylene carbon.

$$(CF_3)_2NBr \Leftrightarrow (CF_3)_2N^\bullet + Br^\bullet$$

$$(CF_3)_2N^\bullet + CF_2{=}CFCl \rightarrow (CF_3)_2NCF_2CFCl^\bullet$$

$$(CF_3)_2NCF_2CFCl + (CF_3)_2NBr \rightarrow (CF_3)_2NCF_2CFClBr + (CF_3)_2N^\bullet$$

We have found that chlorotrifluoroethylene as well as tetrafluoroethylene, upon heating, can be readily inserted into one or

---

(1) Young, J. A.; Tsoukalas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.

(2) Alexander, E. S.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. *J. Chem. Soc. C* **1968**, 796.

(3) Emeléus, H. J.; Tattershall, B. W. *Z. Anorg. Allg. Chem.* **1964**, *327*, 147.

(4) Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc.* **1965**, 6141.

(5) Barlow, M. G.; Fleming, G. L.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc. C* **1971**, 2744.

(6) Tullock, C. W. (E. I. du Pont). Br. Pat. 870,328, 1960.

(7) Young, D. E.; Anderson, L. R.; Fox, W. B. U.S. 3685563, 1972.

(8) Hynes, J. B.; Bishop, B. C.; Bigelow, L. A. *Inorg. Chem.* **1967**, *6*, 417.

(9) Geisel, M.; Waterfeld, A.; Mews, R. *Chem. Ber.* **1985**, *118*, 4459.

(10) Anderson, L. R.; Fox, W. B.; Young, D. E. *Chem. Commun.* **1970**, 395.

(11) Abe, T.; Nagase, S.; Kodaira, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 957.

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

(13) DeMarco, R. A.; Shreeve, J. M. *J. Fluorine Chem.* **1971/72**, *1*, 269.

(14) Hynes, J. B.; Bishop, B. C.; Bigelow, L. A. *Inorg. Chem.* **1966**, *5*, 488.

(15) Kloeter, G.; Lutz, W.; Seppelt, K.; Sundermeyer, W. *Angew. Chem.* **1977**, *89*, 754.

(16) Kumar, R. C.; Shreeve, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4958.

(17) Leidinger, W.; Sundermeyer, W. *J. Fluorine Chem.* **1981**, *19*, 85.

(18) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1981**, *20*, 1.

(19) Zheng, Y. Y.; Mir, Q. C.; O'Brian, B. A.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 518.

(20) Thrasher, J. S.; Bauknight, C. W., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1985**, *24*, 1598.

(21) Petrov, K. A.; Neimysheva, A. A. *Zh. Obshch. Khim.* **1959**, *29*, 2695.

(22) Yakubovich, A. Yu.; Ginsburg, V. A.; Makarov, S. P.; Privezentseva, N. F.; Martynova, L. L. *Dokl. Akad. Nauk SSSR* **1961**, *141*, 125.

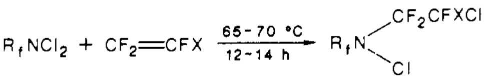
(23) Ogden, P. H. *J. Chem. Soc. C* **1971**, 2920.

(24) Emeléus, H. J.; Hurst, G. L. *J. Chem. Soc.* **1964**, 396.

(25) Barr, D. A.; Haszeldine, R. N.; Willis, C. J. *J. Chem. Soc.* **1964**, 1351.

(26) Klauke, E.; Holtschmidt, H.; Findeisen, K. (Farbenfabriken Bayer A.-G.). Ger. Offen. 210107, 1971/1972.

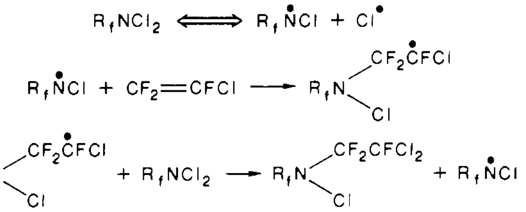
both of the nitrogen–chlorine bonds of dichloroamine, depending principally on the reaction temperature. Even in the presence of a large excess of olefin, only a one-to-one insertion reaction takes place with R_fNCl_2 ($R_f = CF_3$, C_2F_5) at 65–70 °C.



$$R_fNCl_2 + CF_2{=}CFX \xrightarrow[12-14\ h]{65-70\ ^\circ C} R_fN(CF_2CFXCl)Cl$$

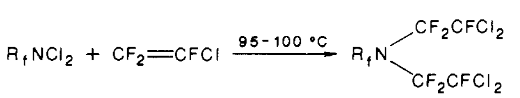
X = F, Cl

Although the reaction mechansim is believed to be free radical, only a single isomer is obtained from the reaction between R_fNCl_2 and chlorotrifluoroethylene. The mass spectrum, with a major fragment corresponding to $CFCl_2^+$, as well as ^{19}F NMR spectral data support the presence of only $R_fN(CF_2CFCl_2)Cl$, with no concomitant formation of $R_fN(CFClCF_2Cl)Cl$. The reaction apparently proceeds as follows:



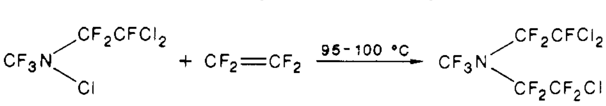
$$R_fNCl_2 \Longleftrightarrow R_f\dot{N}Cl + Cl^\bullet$$
$$R_f\dot{N}Cl + CF_2{=}CFCl \longrightarrow R_fN(CF_2\dot{C}FCl)Cl$$
$$R_fN(CF_2\dot{C}FCl)Cl + R_fNCl_2 \longrightarrow R_fN(CF_2CFCl_2)Cl + R_f\dot{N}Cl$$

Similarly, only a single insertion product is observed at 90–100 °C.



$$R_fNCl_2 + CF_2{=}CFCl \xrightarrow{95-100\ ^\circ C} R_fN(CF_2CFCl_2)_2$$

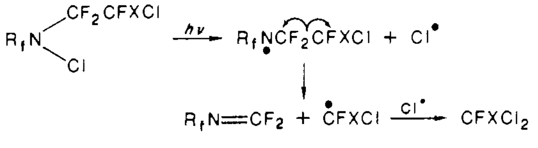
Treatment of $CF_3N(CF_2CFCl_2)Cl$ with tetrafluoroethylene at 90–100 °C results in the asymmetric tertiary amine as shown.



$$CF_3N(CF_2CFCl_2)Cl + CF_2{=}CF_2 \xrightarrow{95-100\ ^\circ C} CF_3N(CF_2CFCl_2)(CF_2CF_2Cl)$$

The formation of nitrene intermediates from the pyrolysis or photolysis of dichloroamines is proposed in the literature to account for the formation of $R_fN{=}NR_f$.[7-9,14,17] Diazenes were not formed, however, under the conditions used in the present study.

Gas-phase photolysis of the compounds $R_fN(CF_2CFXCl)Cl$ did not result in dimerization to the respective hydrazines, but instead the perfluoroazaalkenes $R_fN{=}CF_2$ were formed in nearly quantitative yield. The most probable mechanism involves free-radical formation and decomposition.



$$R_fN(CF_2CFXCl)Cl \xrightarrow{h\nu} R_f\dot{N}CF_2CFXCl + Cl^\bullet$$
$$R_f\dot{N}CF_2CFXCl \longrightarrow R_fN{=}CF_2 + \dot{C}FXCl \xrightarrow{Cl^\bullet} CFXCl_2$$

The chemistry of the perfluoro- or polyfuluoroazaalkenes has not been exploited as fully as that of perfluoro- or polyfluoroalkenes although their chemical behavior may be similar in many respects. An excellent review of synthetic methods for and reported chemistry of azaalkenes is available.[27]

Experimental Section

Materials. The reagents of CF_3NCl_2[20] and $C_2F_5NCl_2$[28] were prepared according to literature methods. Other chemicals were purchased as indicated: chlorine monofluoride (Ozark-Mahoning); BrCN (Aldrich Chemical Co., Inc.); CF_3CN, $CF_2{=}CF_2$, and $CF_2{=}CFCl$ (PCR).

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum system equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation). Most of the starting materials and products were quantitated by using *PVT* techniques. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer with a 10-cm gas cell equipped with KBr windows. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer using CCl_3F as an internal standard and $CDCl_3$ as solvent. Mass spectra were obtained with a VG HS7070 mass spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany. Photolysis reactions were carried out in quartz reaction vessels irradiated in a Rayonet photochemical reactor by using 3000-Å UV lamps.

Reactions of Olefins ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) with Dichloro(perfluoroalkyl)amines (CF_3NCl_2 or $C_2F_5NCl_2$). Preparation of $R_fN(CF_2CFXCl)Cl$. The *N,N*-dichloro compound R_fNCl_2 (CF_3NCl_2 or $C_2F_5NCl_2$) (10 mmol) and 12 mmol of olefin ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) were condensed at −196 °C into a 50-mL thick-walled Pyrex reaction tube. The tube was sealed and heated in an oven at 65–70 °C for 12–16 h. The products were separated by trap-to-trap distillation.

Properties of Chloro(2-chlorotetrafluoroethyl)(trifluoromethyl)amine, $CF_3N(CF_2CF_2Cl)Cl$. This compound was found in the trap cooled at −65 °C, having passed through a trap at −40 °C. It was obtained in ~60% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 255/253 (M^+), 1.1/1.6; 220/218 ($M^+ - Cl$) 5/15.1; 164 ($C_3F_6N^+$), 97; 137/135 ($C_2F_4Cl^+$), 18.4/57.9; 100 ($C_2F_4^+$), 12.2; 87/85 (CF_2Cl^+), 11.3/37.1; 69 (CF_3^+), 100; 50 (CF_2^+), 97. IR (gas): 1317–1160 br, 1110 vs, 985 vs, 868 vs, 827 vs, 724 s, 680 s, 652 s cm^{-1}. ^{19}F NMR: ϕ −59.89 (CF_3, tt), −68.69 (CF_2Cl, mult), −96.43 (CF_2N, qt); $J_{CF_3-CF_2N} = 13.43$ Hz, $J_{CF_3-CF_2Cl} = 3.66$ Hz, $J_{CF_2-CF_2} = 2.44$ Hz. Anal. Calcd for $C_3F_7Cl_2N$: C, 14.17; N, 5.51. Found: C, 14.60; N, 5.65.

Properties of Chloro(2,2-dichlorotrifluoroethyl)(trifluoromethyl)amine, $CF_3N(CF_2CFCl_2)Cl$. Under dynamic vacuum, this compound was found in the trap at −45 °C, having passed through a trap at −30 °C. It was obtained in ~80% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 236/234 ($C_3F_6NCl_2^+$), 0.4/0.8; 182/180 ($C_3F_5NCl^+$), 7.4/19.1; 170/168 ($C_2F_5NCl^+$), 4.6/13.8; 153/151 ($C_2F_3Cl_2^+$), 2.2/4.3; 132/130 ($C_2F_3NCl^+$), 3.8/11.8; 103/101 ($CFCl_2^+$), 40.2/64.9; 95 ($C_2F_3N^+$); 69 (CF_3^+), 100; 50 (CF_2^+), 7.6. IR (gas): 1293 vs, 1236 vs, 1170 vs, 1100 s, 955 s, 912 vs, 850 w, 810 vs, 714 s, 658 s cm^{-1}. ^{19}F NMR: ϕ −59.54 (CF_3, td), −71.12 (CF, mult), −93.59 (CF_2, qd); $J_{CF_3-CF_2} = 14.41$ Hz, $J_{CF_3-CF} = 4.52$ Hz, $J_{CF_2-CF} = 7.45$ Hz. Anal. Calcd for $C_3F_6Cl_3N$: C, 13.30; F, 42.14; N, 5.17; Cl, 39.37. Found: C, 13.48; F, 42.70; N, 5.14; Cl, 38.73.

Properties of Chloro(2-chlorotetrafluoroethyl)(pentafluoroethyl)amine, $CF_3CF_2N(CF_2CF_2Cl)Cl$. This compound was stopped in a trap at −60 °C, having passed through a trap at −40 °C. It was obtained in ~60% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 305/303 (M^+), 0.4/0.6; 270/268 ($M^+ - Cl$), 0.8/2.3; 220/218 ($C_3F_7NCl^+$), 12.7/39; 137/135 ($C_2F_4Cl^+$), 9.7/30.5; 119 ($C_2F_5^+$), 100; 114 ($C_2F_4N^+$), 26; 100 ($C_2F_4^+$), 7.7; 87/85 (CF_2Cl^+), 13.4/42.1; 69 (CF_3^+), 51.9. IR (gas): 1239 vs, 1209 w, 1182 w, 1118 s, 1081 s, 1029 s, 978 vs, 917 w, 830 w, 800 s, 741 s cm^{-1}. ^{19}F NMR: ϕ −68.57 (CF_2Cl, mult), −81.49 (CF_3, t), −93.76 (CF_2N, mult), −94.86 (CF_2N, multi); $J_{CF_3-CF_2} = 5.86$ Hz. Anal. Calcd for $C_4F_9Cl_2N$: C, 15.79; F, 56.25. Found: C, 16.02; F, 55.7.

Properties of Chloro(2,2-dichlorotrifluoroethyl)(pentafluoroethyl)amine, $CF_3CF_2N(CF_2CFCl_2)Cl$. This compound was stopped in the trap at −40 °C, having passed through a trap at −20 °C. It was obtained in ~80% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 286/284 ($M^+ - Cl$), 3.39/5.43; 220/218 ($C_3F_7NCl^+$), 24.50/75.44; 153/151 ($C_2F_3Cl_2^+$), 13.67/21.69; 137/135 ($C_2F_4Cl^+$), 6.92/21.14; 119 ($C_2F_5^+$), 100; 114 ($C_2F_4N^+$), 16.36; 103/101 ($CFCl_2^+$), 31.30/50.14; 69 (CF_3^+), 52.61; 50 (CF_2^+), 5.44. IR (gas): 1357 w, 1268 m, 1237 vs, 1198 s, 1165 s, 1105 s, 1082 vs, 1029 vs, 960 s, 907 vs, 847 w, 783 s, 731 vs cm^{-1}. ^{19}F NMR: ϕ −70.31 ($CFCl_2$, mult), −80.73 (CF_3, t), −90.69 (CF_2CF, tq), −93.82 (CF_2, td); $J_{CF_3-CF_2} = 6.23$ Hz, $J_{CF_2-CF_2CF} = 20.76$ Hz, $J_{CF_2-CF} = 8.3$ Hz. Anal. Calcd for $C_4F_8Cl_3N$: C, 14.97; F, 47.43. Found: C, 15.13; F, 47.20.

Preparation of $CF_3N(CF_2CFXCl)_2$ (X = F, Cl) and $C_2F_5N(CF_2CF_2Cl)_2$. To a 100-mL thick-walled Pyrex reaction vessel were added 25 mmol of olefin ($CF_2{=}CF_2$ or $CF_2{=}CFCl$) and 20 mmol of R_fNCl_2 ($R_f = CF_3$, C_2F_5). The tube was sealed and heated in an oven at 95–100 °C for 12–14 h. The products were separated and purified by trap-to-trap distillation.

Properties of $CF_3N(CF_2CF_2Cl)_2$. This compound was found in the trap at −40 °C, having passed through a trap at −20 °C. It was obtained in ~65% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 270/268 ($C_4F_9NCl^+$), 4.32/15.14; 182/180 ($C_3F_5NCl^+$), 4.92/15.15; 164 ($C_3F_6N^+$), 14.51; 137/135 ($C_2F_4Cl^+$), 32.26/100; 119 ($C_4F_3N^+$), 20.85; 87/85 (CF_2Cl^+), 16.08/49.76; 69 (CF_3^+); 60.44. IR (gas): 1342 vs, 1316 vs, 1272 s, 1229 s, 1210 vs, 1187 vs, 1155 s, 1121 s, 1016 s, 995 s, 905 s, 870 s, 813 vs, 797 vs, 747 s, 691

---

(27) Haas, A. *Gmelin Handbook of Inorganic Chemistry*; 8th ed.; Koschel, D., Ed.; Springer-Verlag: New York, 1979; part 9, Chapter 8.

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

s cm^{-1}. ^{19}F NMR: ϕ −50.27 (CF_3, mult), −69.27 (CF_2Cl, mult), −88.96 (NCF_2, mult). Anal. Calcd for $C_5F_{11}Cl_2N$: C, 16.95; F, 59.04. Found: C, 16.93; F, 58.80.

Properties of $CF_3N(CF_2CFCl_2)_2$. This compound was found in the trap at −10 °C, having passed through a trap at 0 °C. It was obtained in 60% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 286/284 ($C_4F_8NCl_2^+$), 5.98/9.53; 153/151 ($C_2F_3Cl_2^+$), 64.67/100; 137/135 ($C_2F_4Cl^+$), 5.22/16.18; 118/116 ($C_2F_3Cl^+$), 4.0/12.65, 103/101 ($CFCl_2^+$), 23.58/37.18; 87/85 (CF_2Cl^+), 4.65/14.23; 69 (CF_3^+), 22.20; 68/66 ($CFCl^+$), 1.49/4.61. IR (gas): 1324 vs, 1296 vs, 1239 s, 1213 s, 1149 s, 1105 vs, 982 vs, 899 vs, 829 vs, 765 vs, 737 vs, 657 s cm^{-1}. ^{19}F NMR: ϕ −49.06 (CF_3, pt), −69.73 ($CFCl_2$, qt), −83.74 (CF_2, qd); $J_{CF_3-CF_2} = 15.14$ Hz, $J_{CF_3-CF} = 20.39$ Hz, $J_{CF_2-CF} = 7.32$ Hz. Anal. Calcd for $C_5F_9Cl_4N$: C, 15.5; F, 44.2. Found: C, 15.61; F, 44.30.

Properties of $CF_3CF_2N(CF_2CF_2Cl)_2$. This compound was found in the trap at −10 °C. It was obtained in ∼55% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 320/318 ($C_5F_{11}NCl^+$), 6.73/18.60; 232/230 ($C_4F_7NCl^+$), 7.53/23.78; 214 ($C_4F_8N^+$), 14.78; 164 ($C_3F_6N^+$), 31.22; 135 ($C_2F_4Cl^+$), 100; 119 ($C_2F_5^+$), 98.88; 114 ($C_2F_4N^+$), 10.17; 87/85 (CF_2Cl^+), 23.23/72.66; 69 (CF_3^+), 46.11; 50 (CF_2^+), 5.56. IR (gas): 1310 s, 1290 s, 1240 vs, 1185 s, 1167 s, 1006 s, 839 s, 796 vs, 710 vs, 697 s cm^{-1}. ^{19}F NMR ϕ −66.95 (CF_2Cl, mult), −79.63 (CF_3, mult), −86.19 (CF_2N, mult), −87.86 (CF_2N, mult). Anal. Calcd for $C_6F_{13}Cl_2N$: C, 17.82; F, 61.1. Found: C, 18.28; F, 60.7.

Synthesis and Properties of $CF_3N(CF_2CFCl_2)(CF_2CF_2Cl)$. Five mmoles of $CF_3N(CF_2CFCl_2)Cl$ and 6 mmol of $CF_2{=}CF_2$ were condensed in a thick-walled Pyrex vessel. The tube was sealed and heated at 95–100 °C for 12–14 h. The product was purified by trap-to-trap distillation. This compound was found in a trap at −30 °C. It was obtained in ∼65% yield as a colorless liquid. Spectral data are as follows. EI MS (*m/e* (species), intensity): 286/284 ($C_4F_8NCl_2^+$), 3.64/5.64; 270/268 ($C_4F_9NCl^+$), 9.59/28.64; 182/180 ($C_3F_5NCl^+$), 6.21/19.45; 164 ($C_3F_6N^+$), 12.34; 153/151 ($C_2F_3Cl^+$), 60.70/96.75; 137/135 ($C_2F_4Cl^+$), 32.12/100; 119 ($C_2F_5^+$), 11.39; 114 ($C_2F_4N^+$), 417; 103/101 ($CFCl_2^+$), 30.01/47.65; 100 ($C_2F_4^+$), 13.02; 87/85 (CF_2Cl^+), 19.66/61.62; 69 (CF_3^+), 68.33; 50 (CF_2^+), 5.27. IR (gas): 1384 w, 1337 vs, 1312 vs, 1270 w, 1239 w, 1208 s, 1185 s, 1154 s, 1114 s, 1029 s, 1009 s, 907 s, 854 s, 780 vs, 744 s cm^{-1}. ^{19}F NMR: ϕ −49.81 (CF_3, mult), −68.28 (CF_2Cl, mult), −70.71 ($CFCl_2$), −84.84 (NCF_2CFCl_2), −87.74 (NCF_2CF_2Cl). Anal. Calcd for $C_5F_{10}Cl_3N$: C, 15.5; F, 44.2. Found: C, 15.61; F, 44.30.

Photolysis of $R_fN(CF_2CFXCl)Cl$. Five mmoles of $R_fN(CF_2CFXCl)Cl$ was condensed into a 500-mL quartz vessel and was photolyzed in the gas phase by using a Rayonet photochemical reactor at 3000 Å for 2–3 h. The products were separated by trap-to-trap distillation and identified by ^{19}F NMR and infrared spectral data. Photolysis of $CF_3N(CF_2CFXCl)Cl$ gave $CF_3N{=}CF_2$[27] and $CFXCl_2$. The azapropene (65–70% yield) was found in a trap at −120 °C, having passed through a trap at −100 °C. Photolysis of $CF_3CF_2N(CF_2CFXCl)Cl$ gave $CF_3CF_2N{=}CF_2$[27] and $CFXCl_2$. Perfluoro-2-aza-1-butene was found in the trap at −100 °C in ∼80% yield.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to NSF Grants CHE-8404974 and CHE-8703790, and to AFOSR Grant 87-0067.

Registry No. $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CFCl$, 79-38-9; CF_3NCl_2, 13880-73-4; $C_2F_5NCl_2$, 677-66-7; $CF_3N(CF_2CF_2Cl)Cl$, 120417-57-4; $CF_3N(CF_5CFCl_2)Cl$, 120417-58-5; $CF_3CF_2N(CF_2CF_2Cl)Cl$, 120417-59-6; $CF_3CF_2N(CF_2CFCl_2)Cl$, 120417-60-9; $CF_3N(CF_2CF_2Cl)_2$, 60940-98-9; $CF_3N(CF_2CFCl_2)_2$, 120417-61-0; $CF_3CF_2N(CF_2CF_2Cl)_2$, 63419-66-9; $CF_3N(CF_2CFCl_2)(CF_2CF_2Cl)$, 120417-62-1; $CF_3N{=}CF_2$, 371-71-1; CF_2Cl_2, 75-71-8; $CFCl_3$, 75-69-4; $CF_3CF_3N{=}CF_3$, 428-71-7.

Contribution from the Departments of Chemistry, University of the Witwatersrand,
Johannesburg, South Africa, and Texas A&M University, College Station, Texas 77843-3255

Metal Ion Recognition in Ligands with Negatively Charged Oxygen Donor Groups. Complexation of Fe(III), Ga(III), In(III), Al(III), and Other Highly Charged Metal Ions

Ann Evers,† Robert D. Hancock,† Arthur E. Martell,*,‡ and Ramunas J. Motekaitis‡

Received November 17, 1988

The existence of good linear relationships between the formation constant log values of complexes of ligands containing negative oxygen donor groups only and log $K_1(OH^-)$ values for the metal ions is demonstrated for a variety of ligands containing phenolate, carboxylate, and hydroxamate donor groups. The formation constants of DFB (desferriferrioxamine-B), BAMTPH (a synthetic trihydroxamate), and several dihydroxamic acids of the type $HONHCO(CH_2)_nCONHOH$ (n = 4, 6, 7, 8) with several metal ions are reported and used to demonstrate the general existence of linear relationships of the above type. The DFB constants are reported for Al(III), Ga(III), and In(III) and considered in relation to possible use of DFB for treating aluminum intoxication. The selectivity patterns of negatively charged oxygen donor ligands for metal ions are discussed in relation to the effect of chain length of the bridging groups connecting the donor groups, the presence of sulfonic acid groups, and how the selectivity patterns might be altered by the inclusion of other donor groups such as neutral oxygen and nitrogen donor groups.

Introduction

There is concurrently considerable interest in designing ligands for the complexation of metal ions that have in common a high affinity for the negatively charged oxygen donor atom. Types of donor groups of interest have been catecholates,[1,2] phenolates,[3] hydroxamates,[4,5] and phosphonates.[6] Areas of application of this type of ligand are removal of Fe(III) in the treatment of Cooley's anemia,[1-5] complexation of Al(III) in the treatment of aluminum intoxication,[7] development of complexes of In(III) and Ga(III) as imaging agents,[8] and complexation of actinide elements.[2] Also of interest here is use of complexes of lanthanide(III) ions as NMR imaging agents.[9]

In this paper the aim is to highlight some of the factors of importance in designing ligands that have predominantly negatively charged oxygen donor atoms. A consideration of importance in this regard is the type of correlation briefly discussed[10,11] for

---

† University of the Witwatersrand.

‡ Texas A&M University.

(1) Raymond, K. N.; Mueller, G.; Matzanke, B. F. *Top. Curr. Chem.* **1984**, *123*, 49.

(2) Raymond, K. N.; Freeman, G. E.; Kappel, M. J. *Inorg. Chim. Acta* **1984**, *94*, 193.

(3) (a) Harris, W. R.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 713. (b) Martell, A. E.; Motekaitis, R. J.; Clarke, E. T.; Harrison, J. J. *Can. J. Chem.* **1986**, *23*, 1188.

(4) Yoshida, I.; Murase, I.; Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1983**, *61*, 2740.

(5) Sun, Y.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chem.* **1985**, *24*, 4343.

(6) McMillan, D. T.; Murase, I.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1975**, *14*, 468.

(7) Martell, A. E.; Motekaitis, R. J. In *The Environmental Chemistry and Toxicology of Aluminum*; Lewis, T. E., Ed.; Lewis Publishers: Chelsea, MI, in press.

(8) Mathias, C. J.; Sun, Y.; Welch, M. J.; Green, M. A.; Thomas, J. A.; Wade, K. R.; Martell, A. E. *Nucl. Med. Biol.* **1988**, *15*, 69.

(9) Lauffer, R. C. *Chem. Rev.* **1987**, *87*, 901.

0020-1669/89/1328-2189$01.50/0