

Reactions of nitriles which contain the =NF or NF₂ functional group with boron halides

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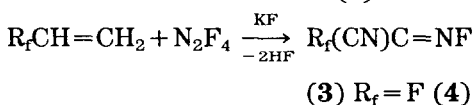
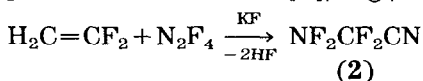
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Abstract

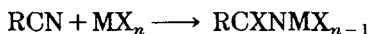
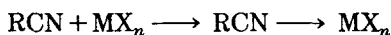
Dimeric insertion products [R_fCXNBX₂]₂ (R_f = F₂NCCIF, F₂NCF₂, CF₃C(=NF), FC(=NF); X = Cl, Br) are obtained when F₂NCCIFCN, F₂NCF₂CN, CF₃C(=NF)CN and FC(=NF)CN are reacted with boron trichloride or boron tribromide, respectively. The structures of these water-sensitive materials is supported by infrared, ¹⁹F and ¹¹B nuclear magnetic resonance and mass spectral data, and by elemental analyses.

Introduction

Compounds that contain nitrogen–halogen bonds, e.g., NF₂, =NF, >NF, NCl₂ or NCl are interesting materials and, in many cases, are valuable precursors to a variety of reaction products [1–5]. Tetrafluorohydrazine, N₂F₄, has played a major role in the initiation and growth of fluoronitrogen chemistry. By taking advantage of the addition of difluoroamino radicals across the double bond in selected olefins, followed by the loss of HF in the presence of alkali metal fluoride, difluoroamino or fluoroimino nitrile products are isolable [2], e.g.,



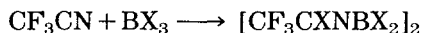
With metal and metalloid halides, nitriles react either as coordinating ligands or by insertion into the metal–halide bond [6–9]:



(X = halide or other anion; R = hydrocarbon)

With pentafluorobenzonitrile and boron trichloride or boron tribromide, only coordination compounds are formed and only [BBR₃(C₆F₅CN)] is suf-

ficiently stable to survive sublimation [6]. However, $[\text{BCl}_3(\text{C}_6\text{H}_5\text{CN})]$ and $[\text{BCl}_3(\text{CH}_3\text{CN})]$ are stable 1:1 adducts [8, 9]. The electrophilicity of the carbon atom of CF_3CN is greatly enhanced, thus encouraging migration of a nucleophilic ligand to that site which results in insertion into the B–X bond. Because of the strong electron-withdrawing power of the CF_3 group, the donor properties of CF_3CN are much weaker than those of either CH_3CN or $\text{C}_6\text{H}_5\text{CN}$, and as a consequence insertion reactions occur with boron trihalides to form *cis-trans* mixtures of dimeric products rather than 1:1 adducts [6]:



(X = Cl, Br)

Based on this earlier work and because of our continuing interest in the syntheses and reactions of NF_2 - and $=\text{NF}$ -containing nitriles, a study of the reactions of several such nitriles, i.e. NF_2CCIFCN , $\text{F}_2\text{NCF}_2\text{CN}$, $\text{FC}(=\text{NF})\text{CN}$ and $\text{CF}_3\text{C}(=\text{NF})\text{CN}$, with BX_3 (X = Cl, Br) was undertaken.

Experimental

CAUTION: Extreme care is absolutely essential when handling N_2F_4 and its derivatives. Contact with organic materials must be avoided. Adequate shielding should be utilized at all times. We have experienced several explosions when handling some of these new materials. Reaction quantities should not exceed a few millimoles.

Materials

Reagents were purchased or synthesized as indicated:

1-chloro-1-fluoroethene, trifluoroacetonitrile (PCR); boron trichloride (Union Carbide), boron tribromide (Aldrich). Difluoroamino(difluoro)acetonitrile (**2**), *syn*-fluoro(fluoroimino)acetonitrile (**4**) and *syn*-3,3,3-trifluoro-2-(fluoroimino)propane (**3**) were synthesized using literature methods [2].

General procedures

Spectral data were recorded using Perkin-Elmer 1710 Fourier transform infrared, JEOL FX90Q Fourier transform nuclear magnetic resonance and VG 7070HS mass spectrometers. A Pyrex vacuum system equipped with Heise–Bourdon tube and Televac thermocouple pressure gauges were used to handle volatile liquids and gases. Hygroscopic solids were characterized under an inert atmosphere. Elemental analysis were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Synthesis of $NF_2CCLFCN$ (1)

10 mmol each of 1-chloro-1-fluoroethene and N_2F_4 were condensed onto ~5 g of dry KF in a 75 ml stainless-steel Hoke cylinder at $-196^\circ C$. The cylinder was allowed to warm to $25^\circ C$ and then was heated at $160^\circ C$ for ~40 h. The product was trapped at $-110^\circ C$.

Spectral data for 1: IR (gas phase): 2265 m ($\nu_{C=N}$); 1306 m; 1293 m; 1187 vs; 1096 s; 1052 m; 1025 m; 987 s; 913 vs, cm^{-1} . ^{19}F NMR ($CDCl_3$) δ : 34.4, 36.6, 40.5, 42.7 (NF_2); -96.36 ; -96.41 ; -96.44 ; -96.50 (CF) ppm. Mass (CI) m/e (species) intensity: 147 ($M^+ + 3$) 27.6; 144 (M^+) 100; 125 ($M^+ - F$) 2.9; 94 ($C_2^{37}ClFN^+$) 19.8; 92 ($C_2^{35}ClFN$) 43.4; 57 (C_2FN) 14.2.

General method of synthesis of 5, 6, 7, 8, 9, 10 and 11

Into an evacuated 10 ml thick-walled glass vessel at $-196^\circ C$ were condensed 1.5 mmol of nitrile (1-4) and 1.5 mmol of boron halide (BCl_3 or BBr_3). The vessel was sealed, placed in a slush bath at $-136^\circ C$ and allowed to warm to $25^\circ C$ over a 24 h period. Unreacted starting materials were removed under vacuum and solids were characterized under inert conditions.

Spectral data for 5: IR (KBr): 1637 m; 1105 vs; 1038 vs; 985; 936 m; 875 vs; 810 vs; 591 s; 538 m; 463 s, cm^{-1} . ^{19}F NMR δ : 17.09; 24.44; 38.28; 45.63 (NF_2); -110.4 (CF) ppm. ^{11}B NMR δ : 5.26; 5.84 ppm. MS (CI) m/e (species) intensity: 260 ($M^+ / 2$) 0.3; ($M^+ / 2 - Cl$) 1.2; 207 ($M^+ / 2 + 1 - ClF$) 2.5. Analysis: Calcd. for $B_2C_4Cl_8F_6N_4$: C, 9.23; N, 10.77%. Found: C, 9.13; N, 10.66%.

Spectral data for 6: IR (KBr): 1680 m; 1628 vs; 1216 m; 1086 vs; 1014 s; 979 vs; 952 m; 927 s; 887 vs; 822 s; 811 s; 795 vs; 597 w; 522 w; 479 s; 430 s; 405 m, cm^{-1} . ^{19}F NMR δ : 16.97; 24.27; 38.23; 45.52 (NF_2); -108.5 (CF) ppm. ^{11}B NMR δ : -1.52 ; -2.41 ; -3.71 (br) ppm. Mass (CI) m/e (species) intensity: 396 ($M^+ / 2 + 1$) 1.0; 344 ($M^+ / 2 + 1 - NF_2$) 0.6; 316 ($M^+ / 2 - Br$) 10.3. Analysis: Calcd. for $B_2Br_6C_4Cl_2F_6N_4$: C, 6.07; N, 7.09%. Found: C, 6.14; N, 6.93%.

Spectral data for 7: IR (KBr): 1659 s ($\nu_{C=N}$); 1281 m; 1230 s; 1121 m; 1046 s; 975 s; 934 m; 883 s; 836 m; 773 vw; 658 vw; 599 m; 494 w; 476 m; 439 vw, cm^{-1} . ^{19}F NMR δ : 20.56 (NF_2); -101.5 (CF, on expansion two triplets, $J=3.4$ Hz and $J=3.6$ Hz, assignable to *cis* and *trans* isomers) ppm. ^{11}B NMR δ : 5.33; 5.92 ppm. Mass (CI) m/e (species) intensity: 245 ($M^+ / 2 + 1$) 6.9 (a pattern for 3 chlorine atoms was observed); 244 ($M^+ / 2$) 1.60; 209 ($M^+ / 2 - Cl$) 4; 192 ($M^+ / 2 - NF_2$) 23.1. Analysis: Calcd. for $B_2C_4Cl_6F_8N_4$: C, 9.84; N, 11.48%. Found: C, 9.84; N, 11.35%.

Spectral data for 8: IR (KBr): 1638 vs ($\nu_{C=N}$); 1508 w; 1474 w; 1267 vs; 1106 s; 1021 vs; 968 vs; 928 vs; 854 m; 795 vs; 755 m; 734 vw; 669 m; 632 vw; 490 m; 463 m; 438 m; 407 m, cm^{-1} . ^{19}F NMR δ : 20.10 (NF_2); -99.04 ; -99.21 (CF) ppm. ^{11}B NMR δ : 1.52, 2.31 ppm. Analysis: Calcd. for $B_2Br_6C_4F_8N_4$: C, 6.33; N, 7.39%. Found: C, 6.22; N, 7.29%.

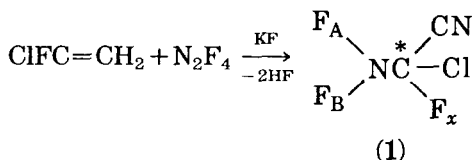
Spectral data for **9**: IR (KBr): 1672 s ($\nu_{C=N}$); 1618 m; 1322 m; 1220 m; 1181 vs; 1151 s; 1013 s; 932 s; 878 s; 743 m; 705 w; 669 w; 591 m; 556 m; 522 m; 421 m, cm^{-1} . ^{19}F NMR δ : 61.62 (=NF); -59.89 (CF_3 , $J_{\text{CF}_3-\text{F}}=9.76$ Hz) ppm. ^{11}B NMR δ : 5.54 ppm. Mass (CI) m/e (species) intensity: 221 ($\text{M}^+ / 2 - \text{Cl}$) 1.6. Analysis: Calcd. for $\text{B}_2\text{C}_6\text{Cl}_6\text{F}_8\text{N}_4$: C, 14.06; N, 10.94%. Found: C, 14.19; N, 10.90%.

Spectral data for **10**: IR (KBr): 1637 vs ($\nu_{C=N}$); 1579 m ($\nu_{C=NF}$); 1199 s, 1017 s; 945 s; 893 s; 874 vs; 795 m; 682 m; 647 w; 595 m; 555 w; 491 m; 464 m; cm^{-1} . ^{19}F NMR δ : 57.92; 58.90; 65.50 (=NF) ppm. ^{11}B NMR δ : 5.64 ppm. Mass (EI) m/e (species) intensity: 188 ($\text{M}^+ / 2 - \text{F}$) 2.9. Analysis: Calcd. for $\text{B}_2\text{C}_4\text{Cl}_6\text{F}_4\text{N}_4$: C, 11.65%. Found: C, 11.57%.

Spectroscopic data for **11**: IR (KBr): 1650–1550 m, br; 1168 vs; 1123 w; 1093 w; 1047 w; 989 s; 811 s; 792 s; 669 w; 631 w; 589 w; 482 m; 423 w; 414 w; 402 w, cm^{-1} . Analysis: Calcd. for $\text{B}_2\text{Br}_6\text{C}_4\text{F}_4\text{N}_4$: C, 7.04%. Found: C, 6.1%.

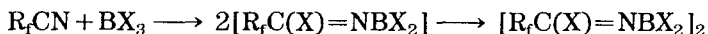
Results and discussion

The high-yield routes to (difluoroamino)difluoroacetonitrile, $\text{NF}_2\text{CF}_2\text{CN}$ (**2**), *syn*-3,3,3-trifluoro-2-(fluoroimino)propanenitrile, $\text{CF}_3\text{C}(=\text{NF})\text{CN}$ (**3**) and *syn*-fluoro(fluoroimino)acetonitrile, $\text{FC}(=\text{NF})\text{CN}$ (**4**), are well established [2]. We have now prepared (difluoroamino)chlorofluoroacetonitrile:



Because of the presence of an asymmetric carbon center in **1**, the fluorine atoms of the NF_2 moiety are magnetically nonequivalent, thus contributing to a ^{19}F NMR spectrum of the ABX type. The resonance bands in the fluorine NMR spectrum centered at δ -41.4 and -35.7 ppm are assigned to F_A and F_B . A large geminal coupling constant, $J_{AB}=625$ Hz, is observed. Quadrupole broadening of the nitrogen-fluorine signals precludes the observation of the fine structure in that region. However, the F_x resonance signal centered at δ -96.4 ppm has bands at δ -96.36, -96.40, -96.45 and -96.50 ppm ($J_{A-x}=27.5$ Hz; $J_{B-x}=9.0$ Hz). The experimental and computer-simulated spectra of **1** are identical. In the infrared spectrum, $\nu_{C=N}$ is observed at 2265 cm^{-1} and in the chemical ionization mass spectrum $\text{M}^+ + 1$ occurs at m/e 144.

Each of the nitriles gives solid dimeric insertion products with BCl_3 and BBr_3 :



R _f	X = Cl	Br
F ₂ NCClF	5	6
F ₂ NCF ₂	7	8
CF ₃ C(=NF)	9	
FC(=NF)	10	11
CF ₃ (ref. 6)	12	13

Just as earlier workers utilized the appearance of a new strong band in the infrared spectrum attributed to $\nu_{C=N}$ and the concomitant disappearance of the higher-energy band assigned to $\nu_{C\equiv N}$ to support the existence of dimeric structures, the analogous argument can be made here. For example, in **1**, $\nu_{C=N}$ at 2265 cm⁻¹ is shifted to $\nu_{C=N}$ at 1637 cm⁻¹ in **5**, and 1680, 1628 cm⁻¹ in **6**; in **2**, $\nu_{C\equiv N}$ at 2280 cm⁻¹ is shifted to $\nu_{C=N}$ at 1659 cm⁻¹ in **7**, and 1638 cm⁻¹ in **8**; in **3**, $\nu_{C\equiv N}$ at 2251 cm⁻¹ and $\nu_{C=N}$ at 1610 cm⁻¹ are shifted to $\nu_{C=N}$ at 1672 cm⁻¹ and $\nu_{C=NF}$ at 1618 cm⁻¹ in **9**; in **4**, $\nu_{C=N}$ at 2282 cm⁻¹ and $\nu_{C=NF}$ at 1650 cm⁻¹ are shifted to $\nu_{C=N}$ at 1637 cm⁻¹ and $\nu_{C=NF}$ at 1579 cm⁻¹ in **10**, and to $\nu_{C=N}$ at 1630 cm⁻¹ and $\nu_{C=NF}$ at 1573 cm⁻¹ in **11**. Thus, additions across the carbon–nitrogen triple bonds have occurred to form carbon–nitrogen double bonds. Molecular weights determined for **12** and **13** support their dimeric structures [6]. However, our mass spectral (CI) studies show only M⁺/2 as the largest m/e value for **5**, **6**, **7** and **8**, and M⁺/2 – Cl and M⁺/2 – F for **9**, **10** and **11**. Also, based on the resonance signals assigned to the CF₂ group in the ¹⁹F NMR spectra of **7** and **8**, it is likely that these compounds exist as mixtures of *cis* and *trans* isomers [6]. Both **5** and **6** have ABX type ¹⁹F NMR spectra with bands assigned to the diastereotopic NF₂ moiety centered at δ 17.09, 24.44, 38.28 and 45.63 ppm and at δ 16.96, 24.27, 38.23 and 45.52 ppm, respectively. Compound **10** showed an unusual ¹⁹F NMR spectrum with two sharp resonance peaks at δ 57.92 and 58.90 ppm (areas 4:1) assigned to CF and a very broad signal at δ 65.50 ppm (=NF).

The ¹¹B NMR resonance spectra for **12** and **13**, whose dimeric structures have been verified, occur at δ 5.6 and δ –2.3 ppm, respectively [6]. The analogous resonances for **5** and **6** are at δ 5.84, 5.26 and δ –1.52, –2.41 ppm; for **7** and **8** at δ 5.33, 5.92 and δ –1.52, –2.31 ppm; for **9** at δ 5.54 ppm; and for **10** at δ 5.64 ppm. Other compounds with dimeric structures, i.e. with tetra-coordinated boron atoms, have similar ¹¹B NMR shifts [9], while those with boron–nitrogen single bonds which contain tri-coordinated boron have chemical shifts at lower field values. For example, CF₃C[N(CH₃)₂]=NB[N(CH₃)₂]₂ formed from CF₃CN and B[N(CH₃)₂]₂ exhibits a ¹¹B NMR resonance at δ 27.6 ppm [10].

Comparison of our infrared and ¹⁹F and ¹¹B NMR spectral data for **5**–**11** with that of the earlier compounds **12** and **13** [6], supports the conclusion that these materials are dimeric compounds [R_fCXNBX₂]₂ which contain tetra-coordinated boron moieties and carbon–nitrogen double bonds. Elemental analyses confirm their purity. As might be expected the compounds have reasonable thermal stability but are readily hydrolyzed.

Acknowledgement

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References

- 1 E. O John, R. D Willett, B. Scott, R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, **28** (1989) 893.
- 2 H. M. Marsden and J. M. Shreeve, *Inorg. Chem.*, **26** (1987) 169, and references therein.
- 3 H. J. Emeléus, J. M. Shreeve and R. D. Verma, *Adv. Inorg. Chem.*, **33** (1989) 140.
- 4 C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80** (1958) 5004
- 5 E. O John and J. M. Shreeve, *Inorg. Chem.*, **27** (1988) 3100, and references therein.
- 6 J. Chatt, R. L. Richards and D. J. Newman, *J. Chem. Soc. (A)*, (1968) 126
- 7 R. A. Walton, *Q. Rev., Chem. Soc.*, **19** (1965) 126.
- 8 W. Gerrard, M. F. Lappert, H. Pyszora and J. W. Walls, *J. Chem. Soc.*, (1960) 2141
- 9 B. Swanson, D. F. Shriver and J. A. Ibers, *Inorg. Chem.*, **8** (1969) 2182
- 10 H. Noth and B. Wrackmeyer, in P. Diehl and E. Fluck (eds.), *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer-Verlag., New York, 1978, pp 240, 308.