is unexpectedly short. In addition, the N–C distance observed (1.386 (4) Å) is marginally shorter than the N(2)–C(25) bond (1.407 (6) Å) in **5**. Also, the average C–C distance in the phenyl ring in **7** (1.39 Å) is marginally longer than the corresponding distance in **5** (1.38 Å). This supports a stronger interaction between the nitrogen p orbital and an antibonding aromatic π orbital in the case of **7**. Irrespective of which effects (lone-pair–lone-pair repulsion, rehybridization, or delocalization) predominate in the hydrazine derivatives, it is a fact that the range of N–N bond lengths is 1.394 (7)–1.46 Å, which is less than 30% of the difference in length between an N–N single and an N–N double bond.

In summary, the data in this paper show that, in the case of N–N and P–P bonds, σ-orbital rehybridization effects become more important and P–P π-bonding contributions are considerably diminished in the heavier element pairs. Studies of the effects of rehybridization on bond distances in other heavier main-group element derivatives are continuing.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-8618739 and Instrumentation Grant CHE-8802721) for supporting this research.

Supplementary Material Available: Tables of atom coordinates, crystallographic data, and a summary of data collection and refinement and full tables of bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (20 pages); listings of structure factors (61 pages). Ordering information is given on any current masthead page.

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Cesium Fluoride Promoted Halogenation of Cyanogen by Chlorine and Bromine and Selected Reactions of Products[1]

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Received February 1, 1990

The reaction of cyanogen with Cl_2 and Br_2 in the presence of CsF gives rise to a series of compounds, $NCCF{=}NX$ (Cl, Br), $XN{=}CF{-}CF{=}NX$ (Br), and $NCCF_2NX_2$ (Cl). Subsequent reactions of $NCCF_2NCl_2$ with MF/Br_2 (M = Cs, K, Na) give rise to $X'N{=}CFCF{=}NX$, $XN{=}CFCF_2NXX'$, and $NCCF_2NXX'$ (X, X' = Cl, Br), involving oxidation and exchange of Cl by Br. Fourteen compounds were identified by ^{19}F NMR and mass spectrometry, and 10 of the compounds have not been previously reported. Photolysis of $NCCF{=}NX$ and $NCCF_2NXX'$ gives rise to the respective azine and diazene. The azine undergoes a fluoride ion induced cyclization to form a novel cyclic, 4-membered diazo compound. Thermal additions of $NCCF{=}NBr$ with C_2F_4 and $CF_2{=}CCl_2$ produced only traces of the expected adducts. New compounds identified were $NCCF{=}NCl$ (**1**), $NCCF_2NCl_2$ (**2**), $NCCF{=}NBr$ (**4**), $NCCF_2NBrCl$ (**14**), $NCCF_2NBr_2$ (**15**), $NCCF{=}N{-}N{=}CFCN$ (**16**), $NCCF_2N{=}NCF_2CN$ (**17**), and $NCCFN{=}NCFCN$ (**18**), and $ClN{=}CFCF{=}NBr$ (**7**), $BrN{=}CFCF_2NCl_2$ (**9**), $BrN{=}CFCF_2NClBr$ (**10**), $ClN{=}CFCF_2NClBr$ (**11**), and $ClN{=}CFCF_2NBr_2$ (**12**), which could only be identified in a mixture. Some evidence for $NCCF{=}NC_2F_4Br$ (**19**) and $NCCF{=}N(CF_2CCl_2)Br$ (**20**) was also found in the addition of **4** to the respective alkenes. Alternative routes to the previously known compounds $BrN{=}CFCF{=}NBr$ (**5**), $ClN{=}CFCF{=}NCl$ (**6**), $Cl_2NCF_2CF_2NCl_2$ (**3**), $ClN{=}CFCF_2NCl_2$ (**8**), and $BrN{=}CFCF_2NBr_2$ (**13**) were also identified.

Introduction

Cesium fluoride has been shown to be an effective reagent for the fluoride-promoted oxidation of $R_fCF{=}NF$ by Cl_2 and Br_2 to form R_fCF_2NFX, of R_fCN to $R_fCF_2NCl_2$ and $R_fCF{=}NBr$,[2,3] of $R_xN{=}CF_2$ to $R_xN(X)CF_3$,[4] of $CF_2{=}NX'$ (X' = F, Cl, Br) to $CF_3NX'X$,[2,5,6] of R_fCN by F_2 to R_fCFNF_2,[7] and of certain hindered imines $R_fN{=}CFR_f'$ by ClF to $R_fNClCF_2R_f'$.[8] These reactions are quite general with fluorinated imines and nitriles and are believed to occur via intermediate anions $R_fCF{=}N^-$, $R_fNX'^-$, and $R_xNCF_3^-$, although in most instances definitive evidence for the proposed anion intermediates is lacking. In an interesting extension of these fluoride-promoted reactions, we examined the reactivity of $N{\equiv}CCF{=}NF$ and found both multiple bonds were oxidized by Br_2 but only the imine function was reactive with Cl_2.[9] This work prompted us to examine the reactions of cyanogen under similar conditions to compare the reactivity of Cl_2 and Br_2 and to see if a selective and stepwise oxidation of the triple bonds was possible.[10] Of the 49 structural isomers possible in $X_2NCF_2CF_2CF_2NX_2$, $XN{=}CFCF{=}NX$, $XN{=}CFCF_2NX_2$, $NCCF_2{=}NX_2$, and $NCCF{=}NX$ for combinations of chlorine bromine and fluorine, at least 24 have now been positively identified.

Experimental Section

General Methods. All work was carried out in a conventional Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured on a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by *PVT* measurements.

IR spectra were taken on a Perkin-Elmer 1430 spectrometer connected to a 3600 data station using a 10-cm gas cell fitted with KCl windows and a glass–Teflon valve. ^{19}F NMR spectra were taken on a Jeol-FX-90Q Fourier transform spectrometer with ~80 mol % CCl_4 as solvent and ~20 mol % $CDCl_3$ as internal lock. $CFCl_3$ was used as an internal

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(1) Presented in part at the 8th European Symposium on Fluorine Chemistry, Jerusalem, Israel, August 1983; Abstract I-4. Southeastern Regional American Chemical Society Meeting, Charlotte, NC, Nov 1983; Abstract O-422.
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(9) Mir, Q.-C.; DesMarteau, D. D. *J. Fluorine Chem.* **1990**, *48*, 367.
(10) During the course of this work a related but different study on the oxidation of $(CN)_2$ by Br_2 and Cl_2 in the presence of HgF_2 was reported: Waterfeld, A.; Mews, R. *J. Chem. Soc., Chem. Commun.* **1982**, *839*.

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reference. Chemical shifts are negative to higher field of $CFCl_3$. Mass spectra were taken on a HP 5985B GC/MS instrument at 15 eV for EI and 50 eV for CI (CH_4). Samples were introduced into the source by direct gas inlet.

Melting points were taken by a modified Stock procedure.

Reagents. Cyanogen, chlorine, and bromine were obtained from commercial sources and were dried before using. Cesium fluoride, 99.9%, was activated by fusing it in a Pt dish, followed by grinding in a ball mill to a very fine powder under very anhydrous conditions. Potassium fluoride was similarly activated. Manipulation of KF and CsF was done exclusively in the drybox.

Reactions. All reactions except photolysis reactions were carried out in 100-mL glass bulbs fitted with a glass–Teflon valve. In the reaction of $(CN)_2$ with Br_2/CsF, the reactor was rotated to increase the surface contact of the reactants with CsF. The appropriate metal fluoride was added in the drybox, and the reactor was evacuated. The reactor was then cooled to −196 °C, and the gaseous reactants were condensed into it. The reactor was then warmed to an appropriate temperature and allowed to stand for several hours. The reactor contents were then separated by fractional condensation. The reactions are summarized in Tables I, II, and V. ^{19}F spectral data for compounds **7** ($ClN=CFCF=NBr$), **9** ($BrN=CFCF_2NCl_2$), **10** ($BrN=CFCF_2NClBr$), **11** ($ClN=CFCF_2NClBr$), and **12** ($ClN=CFCF_2NBr_2$), which could only be obtained as a mixture, are listed in Table IV. Characterization of other new compounds follow. The known products **3** ($Cl_2NCF_2CF_2NCl_2$), **5** ($BrN=CFCF=NBr$), **6** ($ClN=CFCF=NCl$), **8** ($ClN=CFCF_2NCl_2$), and **13** ($BrN=CFCF_2NBr_2$) were identified by their IR, MS, and ^{19}F NMR spectra, which agreed with the literature values.[10]

$NCCF=NCl$ (1). NMR: δ −20.4 (s). IR: 2257 (m), 1652 (s), 1641 (s), 1250 (s), 1238 (s), 883 (m), 873 (m), 759 (mw), 652 (mw) cm^{-1}. MS (CI): major *m/z* 107/109 (MH^+, 100%), 80/82 ($FCNCl^+$), 71 ($NCCFN^+$). Mp: −40 °C.

$NCCF_2NCl_2$ (2). NMR: δ −77.3 (s). IR: 2260 (m), 1199 (vs), 1157 (s), 1105 (vs), 826 (w), 803 (w), 782 (w), 734 (w), 675 (w) cm^{-1}. MS (EI): major *m/z* 160/162/164 (M^+, 25%), 134/136/138 ($M - CN^+$), 106/108 ($M - ClF^+$), 76 (CF_2CN^+, 100%). Mp: <−82 °C.

$NCCF=NBr$ (4). NMR: δ −4.6 (s). IR: 2256 (m), 1647 (vs), 1228 (s), 1218 (s), 868 (m), 860 (m), 735 (w), 700 (w), cm^{-1}. MS (CI): major *m/z* 151/153 (MH^+, 100%), 131/133 ($NCCNBr^+$), 106/108 ($CNBrH^+$), 93/95 (NBr^+), 71 ($M - Br^+$). Mp: −24 °C.

$NCCF_2NClBr$ (14). NMR: δ −74.1 (s). IR: 2259 (s), 1190 (vs), 1146 (vs), 1105 (vs), 819 (w), 771 (m), 737 (m), 659 (w) cm^{-1}. (Compound **15** was found to be present in a small amount in compound **14** via ^{19}F NMR and mass spectra; therefore the IR spectrum may contain bands due to compound **15**.) MS (CI): major *m/z* 204/206/208 (M^+, 100%), 178/180/182 ($M - CN^+$), 76 ($NCCF_2^+$).

$NCCF_2NBr_2$ (15). NMR: δ −70.3 (s). MS (CI): major *m/z* 229/231/233 ($M - F^+$, 70%). MS (EI): 248/250/252 (M^+, 5%). (Compound **15** was not separated from compound **14**.)

$NCCF=N-N=CFCN$ (16). NMR: δ −70.4 (s). IR: 2254 (m), 1658 (vs), 1293 (s), 1253 (s), 1149 (w), 1049 (w), 872 (w), 838 (w) cm^{-1}. MS (CI): major *m/z* 143 (MH^+, 100%), 86 $(NCCFN_2H)^+$, 71 ($NCCFN^+$), 53 $(C_2N_2H)^+$. MS (EI): 142 (M^+, 100%), 85 ($NCCFN_2^+$), 57 ($CFCN^+$), 52 ($C_2N_2^+$). Mp: −14 °C.

$NCCF_2N=NCF_2CN$ (17). NMR: δ −80.2 (s). IR: 2262 (m), 1201 (vs), 1101 (s), 1070 (m), 970 (w), 818 (w), 736 (m) cm^{-1}. MS (CI): major *m/z* 181 (MH^+, 100%), 152 ($M - N_2^+$), 105 ($NCCF_2N_2H^+$), 91 ($NCCF_2NH^+$), 76 ($NCCF_2^+$). Mp: −17 °C.

$NC\overbrace{CFN=NC}FCN$ (18). NMR: δ −80.2 (s). IR: 2261 (m), 1231 (m), 1186 (s), 1107 (m), 1068 (w), 969 (w), 901 (w), 733 (w) cm^{-1}. MS (CI): major *m/z* 143 (MH^+, 42%), 114 ($M - N_2^+$), 95 ($M - FN_2$), 76 ($CFCFN^+$), 69 ($NCCFC^+$), 59 (CFN_2^+), 53 ($C_2N_2H^+$, 100%).

$NCCF=NC_2F_4Br$ (19). IR: 2255 (m), 1737 (vs), 1312 (m), 1263 (vs), 1240 (vs), 1106 (vs), 946 (vs), 854 (vs), 812 (m), 767 (m), 739 (w) cm^{-1}. MS (CI): major *m/z* 251/253 (MH_+, 41%), 231/233 ($M - F^+$), 129/131 (CF_2Br^+), 121 ($NCCFNCF_2$, 100%)$^+$, 100 ($NCCFNCF^+$).

$NCCF=N(CF_2CCl_2)Br$ (20). IR: 2283 (m), 1734 (m), 1162 (s), 1026 (w), 1000 (m), 8955 (m), 808 (m), 747 (m), 696 (m) cm^{-1}. MS (CI): major *m/z* 255/257/259/261 ($M - CN^+$, 25%), 211/213/215/217 ($CF_2CCl_2Br^+$, 100%), 167/169 ($CNCF_2CBr^+$).

Results and Discussion

Reactions of $(CN)_2$ with CsF/Cl_2,Br_2. Representative reactions of cyanogen with Cl_2 and Br_2 in the presence of CsF are summarized in Table I. From these and many other trials, it is apparent that by suitable variation of reactant ratios and conditions, it is possible to carry out selective halofluorination of cyanogen. Chlorine oxidizes the $-C\equiv N$ bond almost exclusively to the dichloroamine species, whereas bromine stops at the bromoimine. This is consistent with previous results for a variety of related reactions with R_fCN.[2,3] The observed products can be rationalized by the reaction paths shown in Scheme I. Higher temperatures and excess X_2 clearly favor products **3** and **5**. We have no spectroscopic evidence for the proposed anion intermediates A–C, but since the reactions do not occur under the same conditions in the absence of CsF, such intermediates are certainly plausible.[11] Intermediates **6** and **8** are surely formed in these reactions, but under all conditions tried only **2** and **3** could be isolated. Except for **1** and **4**, the observed bromine and chlorine products are exclusive. In related work with reactions of $(CN)_2$ with HgF_2/Cl_2,Br_2, compounds **5**, **13**, **3**(Br), **3**, **6**, and **8** could be isolated but not **1**, **4**, **2**, and **14**.[10]

Table I. CsF-Promoted Reactions of $(CN)_2$ with Cl_2 and Br_2

mmol of reactants				conditions, °C/h	products (%)[a]
$(CN)_2$	Br_2	Cl_2	CsF		
1.0		1.2	10	−60/24	$NCCF=NCl$ (**1**) (trace)
				−60 to −20/48	$NCCF_2NCl_2$ (**2**) (19)
2.0		3.0	10	−10 to −5/20	**2** (30)
2.0		8.0	35	23/22	**2** (24), $(CF_2NCl_2)_2$ (**3**) (21)
5.2	10		10	−80 to −20/24	$NCCF=NBr$ (**4**) (50)
1.5	10		10	23/17	$BrN=CFCF=NBr$ (**5**) (95)
1.5	1.0	1.0	7	−196 to 23/4	**1** (10), **3** (~1), **2** (~1)

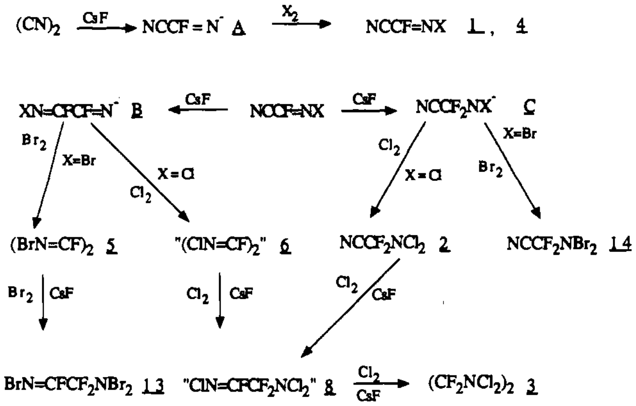
[a] Unreacted starting materials were recovered in each case.

Table II. Reactions of $NCCF_2NCl_2$ with MF/Br_2

reactants (mmol)	conditions, °C/h	products (%)
2 (2.0), Br_2 (4.0), CsF (10)	−196 to 23/5	**5**, **6**, **8**,[a] $ClN=CFCF=NBr$ (**7**), $BrN=CFCF_2NCl_2$ (**9**), $BrN=CFCF_2NClBr$ (**10**), $ClN=CFCF_2NClBr$ (**11**), $ClN=CFCF_2NBr_2$ (**12**)
2 (1.5), Br_2 (10), CsF (19)	−196 to 23/5	$BrN=CFCF_2NBr_2$ (**13**) (~80)
2 (1.0), Br_2 (3.0), NaF (4)	0 to 23/20	$NCCF_2NClBr$ (**14**) (15),[b] $NCCF_2NBr_2$ (**15**) (~1)

[a] Essentially 100% conversion to **5–12**. Substantial amounts of each were present, but individual yields could not be accurately determined. [b] **2** recovered.

Scheme I. Reaction Paths for $(CN)_2$ with CsF/X_2



Reactions of 2 with MF/Br_2. The conversion of N–Cl bonds to N–Br bonds by MF/Br_2 (M = Na, K, Cs) was previously shown to be an effective route to both $-NBr_2$ and $-NClBr$ derivatives from $-NCl_2$ compounds.[5,12] We hoped to use this as a means to prepare **11** and **14** as well as the mixed chlorine-bromine derivatives of **8** from compound **2**. This turned out to be a complex reaction resulting in a number of interesting new derivatives of cyanogen. Unfortunately, the complex mixture of products resulting from these reactions illustrated in Table II could not be

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(11) KF can sometimes be used in place of CsF for reactions of this type, but it was ineffective in promoting the reactions of cyanogen.

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

Scheme II. Possible Conversion Paths for $NCCF_2NCl_2$ to $BrN{=}CFCF_2NBr_2$

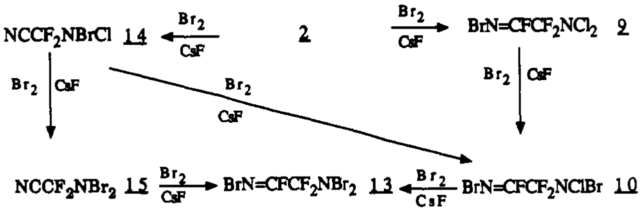

Table III. ^{19}F Chemical Shifts for Representative Chloro and Bromo Amines and Imines[a]

compd	δ(CF_3)	δ(CF_2)	δ(CF)
CF_3NCl_2[14]	-74.1[3]		
CF_3NClBr[5]	-72.3		
CF_3NBr_2[5]	-70.5		
$CF_3CF_2NCl_2$[14]	-78.4	-101.2	
CF_3CF_2NClBr[5]	-77.8	-96.3	
$CF_3CF_2NBr_2$[10]	-77.0	-91.8	
$(CF_2NCl_2)_2$[10]		-92.1	
$(CF_2NBr_2)_2$[10]		-80.2	
$NCCF_2NCl_2$[a]		-77.3	
$NCCF_2NBrCl$[a]		-74.1	
$NCCF_2NBr_2$[a]		-70.3	
$CF_3CF{=}NCl$[15]	-72.0		-42.1
$CF_3CF{=}NBr$[10]	-71.6		-26.9
$ClN{=}CFCF_2NCl_2$[10]		-90.6	-35.7
$BrN{=}CFCF_2NBr_2$[10]		-81.0	-19.9
$NCCF{=}NCl$[a]			-20.4
$NCCF{=}NBr$[a]			-4.6
$(CF{=}NCl)_2$[10]			-37.1
$(CF{=}NBr)_2$[10]			-20.1

[a] This work.

separated and, in general, conditions could not be found to favor a particular product except for **13**. Thus **7** and **9–12** were only identified in a mixture.

For the formation of **13** the reaction can be explained as shown in Scheme II. The high conversion to **13** is driven by the large excess of Br_2. When only a 2 to 1 excess of Br_2 to **2** is employed, one observes the complex mixture of products **5–12**, which contains the intermediates **9** and **10** of Scheme II. The products **8–12** can be explained by the conversion of $-NCl_2$ to NBrCl and $-NBr_2$ by the mixture of Br_2, BrCl, and Cl_2 that is present after the reaction begins.[13] As illustrated in Table I, BrCl (starting with a 1:1 mixture of Cl_2 to Br_2) converts -CN to $-CF{=}NCl$ and is apparently less reactive than Cl_2 or Br_2 alone. The presence of **5–7**, however, is not readily explained. The most likely route to these compounds is through an elimination under the reaction conditions of XF from **7–13** or from **2**, **14**, or **15**, followed by oxidation of $-C{\equiv}N$ to $-CF{=}NX$. However, in the absence of MF/X_2, all the compounds appear to be stable at 23 °C. Clearly, this is a complex reaction and highly dependent on the reaction conditions. It was somewhat fortuitous that **5–12** were observed in a single reaction.

Finally, the reaction of **2** with NaF/Br_2 is of interest since it clearly shows that NaF is effective in converting N—Cl to N—Br bonds by bromine but ineffective in promoting the oxidation of $-C{\equiv}N$. Both of these points were expected from previous results.[5,9]

Characterization of Halogen Derivatives of $(CN)_2$. Data for new compounds **1**, **2**, **4**, **14**, and **15** are contained in the Experimental Section. For those compounds that could be isolated in essentially pure form, the combination of IR, MS, and ^{19}F NMR spectra provides good proof of structure. The ^{19}F NMR spectra of these and related compounds show a remarkably regular variation in chemical shifts as a function of the halogens chlorine and bromine, and this can be used effectively to distinguish CF_3NX_2, $-CF_2NX_2$, and $-CF{=}NX$, for X = Cl, Br.

Table IV. ^{19}NMR: Mixed Fluoro–Chloro/Bromo Derivatives of $(CN)_2$

compd	δ(CF)	δ(CF_2)	$^3J_{FF}$, Hz
$ClN{=}CF^ACF^B{=}NBr$ (**7**)	-20.2 (B, d), -35.2 (A, d)[a]		11.6
$BrN{=}CFCF_2NCl_2$ (**9**)	~-20.7 (t)[b]	-90.2 (d)	7.3
$BrN{=}CFCF_2NClBr$ (**10**)	~-20.7 (t)[b]	-85.8 (d)	7.3
$ClN{=}CFCF_2NClBr$ (**11**)	~-35.1 (t)[b]	-86.5 (d)	7.3
$ClN{=}CFCF_2NBr_2$ (**12**)	~-35.1 (t)[b]	-82.3 (d)	7.3

[a] Overlaps with **11** and **12** but doublet clearly present. [b] Overlapping, but two triplets are evident.

Table V. Photolysis of Compounds **2**, **4**, and **14**

compd (mmol)	conditions, mL/h[a]	products (%)[b]
$NCCF{=}NBr$ (**4**) (2.0)	250/96	$NCCF{=}N{-}N{=}CFCN$ (**16**) (80), Br_2
$NCCF{=}NBr$ (**4**) (2.0)	15/200	**16** (10), Br_2
$NCCF_2NClBr$ (**14**) (0.5)	100/1	$NCCF_2N{=}NCF_2CN$ (**17**) (20), BrCl
$NCCF_2NCl_2$ (**2**) (1.0)	15/3	**17** (5), $NCCF_2Cl$, Cl_2
$NCCF_2NCl_2$ (**2**) (1.0)	500/3	**17** (50), Cl_2

[a] Direct South Carolina sunlight. [b] Balance of starting material was converted to nonvolatile residue.

Table III contains a summary of relevant compounds, and the regular shift of the fluorine signals to lower field in going from chlorine to bromine is clearly apparent.

With the aid of the data in Table III and mass spectrometry, good support for the structures of the new compounds **7** and **9–12** was obtained for a mixture of **5–12**. The mass spectrum of the mixture gave fairly intense molecular ions for $C_2N_2F_3ClBr_2$, $C_2N_2F_3BrCl_2$, and $C_2N_2F_2BrCl$ with the appropriate isotopic ratios as well as peaks that could be assigned to molecular ions of **5**, **6**, and **8**. Of course this cannot distinguish **9** from **11** or **10** from **12** but is very supportive when combined with the NMR data. The ^{19}F NMR data for **7** and **9–12** present in the mixture of **5–12** are summarized in Table IV. The overlapping peaks in the $XN{=}CF-$ region for **9–12** make assignment of accurate chemical shifts difficult, but the remainder of the spectra are well resolved.

Several of the reported new compounds **1**, **2**, **4**, **7**, and **9–11** could exist either as *E* or *Z* isomers or as a mixture of both isomers. From the available data, it is certain that **1**, **2**, and **4** are formed as a single isomer. The value of δ(CF) suggests that the observed isomer is *Z* in each case, and this has been confirmed for **4** by microwave spectroscopy.[16] On the basis of minimizing steric interactions, it is likely that **7** is *Z*,*Z* and that **9–11** are also the *Z* isomers. Compounds **11**, **14**, and **10** contain a chiral nitrogen atom, and the adjacent methylene fluorines are diastereotopic in related compounds in which one of the halogens on nitrogen is fluorine.[2] However, in agreement with other -NClBr derivatives, the nitrogen inversion is fast at near room temperature and first-order spectra are observed.[5]

Selected Reactions of 2, 4, and 14. All the *N*-halogen derivatives reported in this work appear to have reasonable thermal stability and are stable at 23 °C in glass in the absence of moisture and light. Pyrex-filtered sunlight is sufficiently energetic to cause rapid photolysis of the *N*-bromo derivatives and much less so for the *N*-chloro species. Previously, we and others have shown that photolysis or thermolysis often leads to an efficient coupling through nitrogen in both $-CF{=}N{-}Br$ and $-NBr_2$ and $-NCl_2$ derivatives.[3,5,17] We investigated the photolysis of **2**, **4**, and **14** by Pyrex-filtered sunlight to see if the respective azines and azo

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(13) BrCl is in equilibrium with Br_2 and Cl_2 at 25 °C: Mathau, H. C.; Pachuki, C. F.; Hawkins, N. J. *J. Chem. Phys.* **1954**, *22*, 1117.

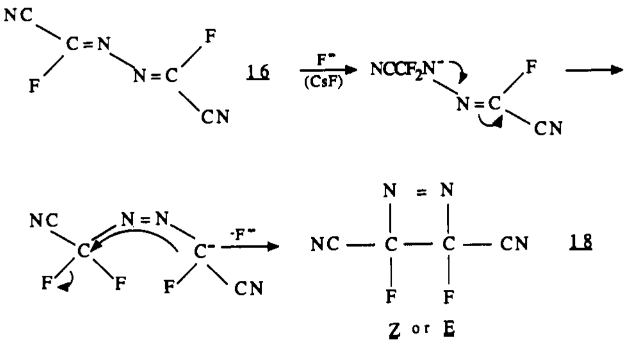
(14) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

(15) This compound was first prepared by: Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 2337. It was later prepared by an alternative route: Sekiya, A.; DesMarteau, D. D. *J. Org. Chem.* **1981**, *46*, 1277. The NMR of $CF_3CF{=}NCl$ was not reported in either of these references but was determined by the latter authors as δ(CF_3) -72.0, δ(CF) -42.1, J_{FF} = 5.2 Hz.

(16) DesMarteau, D. D.; Groner, P.; Nanaie, H.; Durig, J. R. To be published.

(17) Bauknight, C. W.; DesMarteau, D. D. *J. Org. Chem.* **1988**, *53*, 443.

Scheme III. Fluoride-Catalyzed Cyclization of the Azine **16**



compounds could be isolated. The results are summarized in Table V. High pressure decreased the yields of coupled products and led to greater formation of nonvolatile liquid and solid residues (presumably polymeric).

Both **16** and **17** were readily identified by their simple but indicative IR and NMR spectra and large parent ions in their mass spectra. The chemical shifts are reasonable for compounds of this structure, and the single resonance for each indicates only one of two possible geometric isomers is formed in each case, presumably *Z,Z* for **16** and *E* for **17**.[18]

Compound **16** is an unusual example of a conjugated system of double and triple C—N bonds. When **16** was condensed onto CsF at −196 °C and warmed to 22 °C, it underwent a rapid reaction (90% of **16** was absorbed by the CsF turning the CsF red-brown) with loss of the νC=N at 1658 cm^{-1} in the IR spectra of the volatile product and a shift in the single fluorine resonance from −70.4 to −80.2 ppm. The mass spectrum exhibits a large parent ion in the CI at *m/z* 143 (MH$^+$) identical with that of **16**, but the fragmentation pattern is much different. We explain this result on the basis of a fluoride-catalyzed cyclization of **16** to **18**, as shown in Scheme III.[19,20] **18** can exist as the *E* or *Z* isomer. Both isomers should exhibit only a single resonance in the ^{19}F NMR spectrum, and the presence of only one signal in the observed spectrum indicates that only one of the possible isomers is present. However, the configuration cannot be determined from the available data.

Finally, reactions of **4** with alkenes were carried out to see if this compound would undergo addition reactions as observed for other bromoimines.[3,17] Thermal reactions were carried out with C_2H_4, C_2F_4, and CF_2CCl_2 by combining equimolar amounts of the reactants in a 100-mL glass reactor in the dark at 80 °C. This procedure gave only traces of molecular adducts, and decomposition and polymer oils were the main products. At 22–25 °C the results were the same for C_2H_4 after 1 day, but C_2F_4 and CF_2CCl_2 showed small amounts of the adducts after 11 and 24 days, respectively.

$$\mathbf{4} + C_2H_4 \rightarrow \text{oil}, SiF_4$$

$$\mathbf{4} + C_2F_4 \rightarrow \underset{(\sim 5\%)}{NCCF{=}NCF_2CF_2Br\ (\mathbf{19})} + \text{other}$$

$$\mathbf{4} + CF_2CCl_2 \rightarrow \underset{(\sim 4\%)}{NCCF{=}N(CF_2CCl_2)Br\ (\mathbf{20})} + \text{other}$$

These products were only identified by IR spectroscopy and MS, and the regioisomer formed in the case of CF_2CCl_2 was not determined. The low yields of these additions compared to previous work with $CF_2{=}NX$ (Cl, Br) and $R_fCF{=}NBr$ reactions with a variety of alkenes must be due in part to the inherent tendency of **4** to polymerize under radical conditions, as shown by the photolysis of **4**.

Summary

The selective bromo- and chlorofluorination of cyanogen using CsF/Cl_2Br_2 has been demonstrated. Bromine forms only the bromoimines, whereas Cl_2 yields predominantly the dichloroamines. By selective control of reaction conditions, the stepwise oxidation of CN groups in cyanogen can be achieved. The substitution of Cl by Br and/or the bromofluorination of $NCCF_2NCl_2$ is a complex reaction resulting in 11 identifiable structural isomers of the possible bromo- and chlorofluorination products of cyanogen. Photolysis reactions of selected haloimine and haloamine derivatives of cyanogen provide routes to novel azines and azo compounds which are C-fluorinated derivatives of the dimer of cyanogen.

Acknowledgment. The support of this research by the U.S. Army Research Office (Grant DAAG-29-83-K-0173) is gratefully acknowledged.

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[18] See refs 3 and 9. See also: Perfluorohalogeno-Organo Compounds. *Gmelins Handbuch der Anorganische Chemie*, 8th ed.; Springer Verlag: West Berlin, 1980; Part 8.

[19] The internal nucleophilic displacement of fluoride ion from a saturated carbon is unusual, but precedent for such reactions in cyclizations exists: Chambers, R. D.; Lindley, A. A.; Philpot, P. D.; Fielding, H. C.; Hutchison, J.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 214.

[20] The related compound $CF_2{=}N{-}N{=}CF_2$ also reacts rapidly with CsF to give a brown oil and solid which has not been characterized (Ogden, P. H. *J. Chem. Soc. C*) **1971**, 2920). The known cyclic compound $\overline{CF_2N{=}NCF_2}$ is apparently not formed in the latter reaction but is readily prepared from $(CN)_2$ and AgF_2 which might be mechanistically similar to the formation of **18** from **16** (Emeleus, H. J.; Hurst, G. L. *J. Chem. Soc.* **1962**, 3021).

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Phenyl Substituents and Excited-State Lifetimes in Ruthenium(II) Terpyridyls

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Received January 30, 1990

Introducing phenyl substituents in the 4-, 4′-, and 4″-positions, para to the nitrogens, markedly enhances the excited-state lifetime of Ru(trpy)$_2^{2+}$, where trpy denotes 2,2′:6′,2″-terpyridine. The aryl groups conjugate with the low-lying π^* orbital of terpyridine and thereby stabilize the emissive charge-transfer excited state relative to a thermally accessible ^{3}d–d excited state that provides an efficient means of decay to the ground state. The barriers to deactivation via this channel are estimated to be 1500 cm^{-1} for Ru(trpy)$_2^{2+}$, 2200 cm^{-1} for Ru(4,4′-dpt)$_2^{2+}$, and 2300 cm^{-1} for Ru(tsite)$_2^{2+}$, where 4,4′-dpt denotes 4,4′-diphenyl-2,2′:6′,2″-terpyridine, and tsite denotes 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine.

Introduction

The metal-to-ligand charge-transfer (CT) excited states of polypyridine and polyimine complexes of ruthenium(II) can have reasonably long lifetimes in fluid solution; hence, they have been the subject of a great deal of experimental work.[1-3] We have

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[2] Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, P.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

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