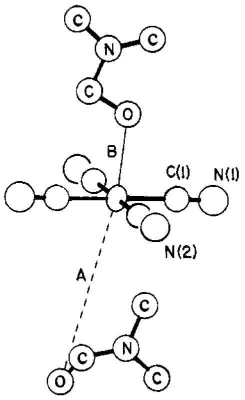


Figure 1. View of the $Co(CN)_4^{2-}$ molecular anion and the associated pair of disordered DMF molecules (see text). Co–O distances are indicated by letter (*A*, 5.89; *B*, 2.64 Å).

by absorptions assigned to the known *tetrahedral* $[Co(CN)_3CH_3CN]^-$ anion.[14]

Owing to the unusual stereochemistry suggested by our spectral and magnetic measurements and the ambiguity of the spectral measurements resulting from the aforementioned equilibria, we decided to carry out an X-ray structure determination on the salt. Very small single crystals could be obtained only from DMF solution. The crystals are monoclinic, space group $P2_1/c$, with $a = 11.188$ (3) Å, $b = 12.423$ (4) Å, $c = 29.142$ (9) Å; $\beta = 98.31$ (3)°. The observed density,[15] 1.26 (1) g cm^{-3}, implied that DMF solvate was contained in the crystals; the resultant formulation is $(PNP)_2Co(CN)_4{\cdot}4DMF$ (for $Z = 2$, $d_{calcd} = 1.270$). Full-matrix least-squares refinement of positional and thermal parameters for all atoms, using 2025 data for which $F > 3.92\sigma(F)$ and $2\theta_{Mo\ K\alpha} < 40°$, gave $R = 0.084$ and $R_w = 0.105$. The structure of the anion (Figure 1) consists of a crystallographically centrosymmetric square-planar $Co(CN)_4^{2-}$ moiety, associated with a pair of disordered DMF molecules. This disorder is such that the NC_3 skeleton of the DMF is similar for each molecule, but the oxygen atoms occupy two different positions of equal probability. In one (A) the Co–O distance is 5.89 Å, while in the other (B), a significant contact, 2.64 (3) Å, occurs. This interaction represents a bond order of ~0.1, as discussed by Raymond et al.[16] The shortest distances from Co to the P and N atoms of the PNP cation are ~9 Å. This suggests formulation of the complex as square-planar $Co(CN)_4^{2-}$ *weakly coordinated*[16] to one DMF molecule. The remaining DMF molecules in the unit cell, which arise from one symmetry-independent DMF, are ordered and do not approach the Co atom. The Co–C(1) and –C(2) distances (1.869 (15), 1.875 (14) Å, respectively) are among the shortest observed for Co(II)–CN distances;[16,17] the C(1)–Co–C(2) angle is 91.1 (6)°.[18]

Besides being a textbook demonstration of the great ligand field strength of cyanide, the existence and structure of $(PNP)_2Co(CN)_4$ emphasizes the complexity of cobalt–cyanide chemistry. The sensitivity of the catalytically active[19] $Co(II)-CN^-$ system to counterion (as well as to solvent[3,10]) predicts a significant dependence of reactivity on counterion. This and the effects of other choices of counterion are under active study in our laboratory.

Acknowledgment. We thank Professor R. Holm and Dr. J. J. Girerd (Harvard) for their kind assistance in measurement of the solid-state magnetic moment data. This research was supported by the National Science Foundation under Grant CHE-8209006, the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Three tables of atomic coordinates, temperature factors, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

---

[14] ESR, electrochemical, and magnetic moment data provide good evidence for the existence of this species.[3,9]

[15] The density was measured by neutral buoyancy in 1-bromopentane/2-bromoprop-1-ene mixtures.

[16] Jurnak, F. A.; Greig, D. R.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 2585–2589.

[17] Simon, G. C.; Adamson, A. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 7654–7663. Brown, L. D.; Raymond, K. N.; Goldberg, S. Z. *Ibid.* **1972**, *94*, 7664–7674.

[18] Other distances and angles in the anion: N(1)–C(1), 1.15 (2); N(2)–C(2), 1.17 (2) Å; C(1)–Co–O(1B), 90.6 (9)°; C(2)–Co–O(1B), 92.8 (8)°; Co–C(1)–N(1), 178 (1)°; Co–C(2)–N(2), 177 (1)°.

[19] Kwiatek, J. *Catal. Rev.* **1967**, *1*, 37–72. Funabiki, T.; Yamazaki, Y.; Sato, Y.; Yoshida, S. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1915–1918. Funabiki, T.; Hosomi, H.; Yoshida, S.; Tarama, K. *J. Am. Chem. Soc.* **1982**, *104*, 1560–1568.

N-Bromodifluoromethanimine

Brian A. O'Brien, Joseph S. Thrasher,
Charles W. Bauknight, Jr., Mark L. Robin, and
Darryl D. DesMarteau*

Department of Chemistry, Clemson University
Clemson, South Carolina 29631

Received February 22, 1984

The fascinating chemistry of the simple imines $CF_2{=}NX$ (X = F, Cl) has provided routes to many novel fluorinated materials.[1-5] These compounds have also provided an opportunity to compare the reactivities of the carbon–nitrogen double bonds affected only by the halogen substituent on nitrogen and to compare the reactivities of the N–X bonds. Perfluoromethanimine is considerably more electrophilic than $CF_2{=}NCl$, but the N—X bond in the latter is considerably more reactive.

In the course of research with $CF_2{=}NX$ (X = Cl, F), we became increasingly interested in preparing the *N*-bromo analogue. It was obvious that the latter would have the most reactive N–X bond and would represent an extremely useful synthon. However, all attempts to prepare it by methods analogous to the preparation of $CF_2{=}NCl$[6] and $CF_2{=}NF$[7] failed. We speculated that the fluoride-promoted oxidation of $FC{\equiv}N$ by Br_2 might yield the desired compound. However, $FC{\equiv}N$ is quite difficult to prepare,[8] and this reaction remained untried until an unexpected source of $FC{\equiv}N$ became available. Pyrolysis of $CF_3CF_2CF{=}NBr$ at 450 °C gives $FC{\equiv}N$ and C_2F_5Br in excellent yield.[9] This provided the needed $FC{\equiv}N$, and our first attempt at the preparation of $CF_2{=}NBr$ was successful.

$$FC{\equiv}N + MF \rightarrow F_2C{=}N^-M^+ \xrightarrow{Br_2} F_2C{=}NBr + MBr \qquad M = K, Rb, Cs$$

Some of the $CF_2{=}NBr$ is further oxidized to CF_3NBr_2, which was previously prepared from the metal fluoride catalyzed conversion of CF_3NClBr to CF_3NBr_2 by Br_2.[4]

$$CF_2{=}NBr + MF \rightarrow CF_3NBr^-M^+ \xrightarrow{Br_2} CF_3NBr_2 + MBr$$

In a typical reaction, a 100-mL flask fitted with a glass–Telfon valve is charged with 15 mmol of active KF in a drybox.[10] The

---

[1] Chang, S.-C.; DesMarteau, D. D. *Inorg. Chem.* **1983**, *22*, 805.

[2] Chang, S.-C.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 771.

[3] Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 4844.

[4] Zheng, Y. Y.; Mir, Q.-C.; O'Brien, B. A.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 518.

[5] Zheng, Y. Y.; Bauknight, C. W.; DesMarteau, D. D. *J. Org. Chem.* in press.

[6] Young, D. E.; Anderson, L. R.; Fox, W. B. *J. Chem. Soc., Chem. Commun.* **1970**, 395.

[7] Sekiya, A.; DesMarteau, D. D. *J. Org. Chem.* **1981**, *46*, 1277.

[8] Fawcett, F. S.; Lipscomb, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 2576.

[9] O'Brien, B. A.; DesMarteau, D. D. *J. Org. Chem.* **1984**, *49*, 1467.

[10] Both CsF and RbF are effective in this reaction. However, KF appears to give higher yields. Metal fluorides are activated by fusing in a platinum crucible, followed by grinding to a fine powder in a ball mill under very anhydrous conditions. No reaction was observed with NaF.

0002-7863/84/1506-4266$01.50/0 © 1984 American Chemical Society

Table I. Vibrational Assignments for $CF_2{=}NX$

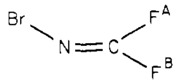
	$CF_2{=}NF^a$		$CF_2{=}NCl$		$CF_2{=}NBr^c$	
	IR	Raman	IR^b	Raman^c	IR	Raman
C=N	1740.3 s	1733 m, p	1728 vs	1731 m, p	1742R vs^e 1732P	1731 w, p
CF_2(as)	1385.5 s	1388 vw, p	1322 s	1322 vw, p	1305R vs^e 1293P	1305 vw, p
NX	1021.2 s	1013 w, p	771 m	777 vs, p	726R m^e 718P	727 s, p
CF_2(s)	932.9 s	932 vvs, p	981 s	989 m, p	981R 976Q s 972P	981 w, p
δ-CF_2	640	644 vs, p	598 w	598 s, p	578 w	587 m, p
ρ-CF_2	520.0 w	522 s, p	465 w	465 vs, p	391 w	390 vs, p
δ-NX	285.7 w	291 w, p	228 m^{c,d}	237 m, p	200?^{f}	199 m, p
β-CF_2	643.2 m	649 m, dp	658 m	659 m, dp	673R 665Q m 657P	663 w, dp
tors	302.5 w	306 m, dp	234 m^{c,d}	245 sh, dp?	213 vw^g	225 vs, dp?

[a] Reference 12. [b] Reference 11. [c] This work. IR taken on a Perkin-Elmer 1430 Data System using a 10-cm cell fitted with CsI windows. Raman spectra were taken on a Spex 1403 Ramalog Double Spectrometer with a Scamp data system. Samples were contained in a low-temperature liquid cell; excitation was by the 514.5 nm line of an argon ion laser ($CF_2{=}NCl$, 400 mW; $CF_2{=}NBr$, 100 mW). [d] Two overlapping bands. [e] Q branches clearly evident but not readily resolved. [f] Low-wavenumber limit of instrumentation was 200 cm^{-1}. Comparison of background and sample spectrum indicates presence of a medium absorption just below 200 cm^{-1}. [g] Presence of a weak band at 300 torr is clearly evident. At higher pressures, attack of $CF_2{=}NBr$ on the CsI windows is rapid.

flask is then evacuated and cooled to −196 °C, and Br_2 (4.8 mmol) and $FC\equiv N$ (3.5 mmol) are added by vacuum transfer. The reactor is then warmed to 22 °C in a water bath while agitating the contents by shaking. Reaction is rapid near 22 °C, and after 1 h, the volatile materials are pumped through a series of cold traps yielding (mmol) CF_3NBr_2 (−75 °C, 1.3) $CF_2{=}NBr$ (−111 °C, 1.3), and small amounts of $FC\equiv N$ and C_2F_5Br (−196 °C), the latter present as an impurity in the starting $FC\equiv N$.

N-Bromodifluoromethanimine is a pale yellow gas (bp 14.5 °C, log P(torr) = 6.5472 − (642.38/T) − (118 655/T^2), ΔH_{vap} = 6.71 kcal/mol, ΔS_{vap} = 23.3 eu), which freezes to a pale yellow solid (mp −93 to −92 °C). A UV–vis spectrum (210–780 nm) of the gas at 5 torr (10 cm) exhibits an intense absorption at 240 nm (ϵ_{max} 651 M^{-1} cm^{-1}) with a weak shoulder near 340 nm. At 20 torr, absorption begins at 600 nm. Under the same conditions, $CF_2{=}NCl$ shows evidence of strong absorption below 210 nm.

The mass spectrum of $CF_2{=}NBr$ exhibits intense molecular ions in both EI (100%) and CI (100%) at 143/145 and 144/146, respectively. A vapor-density molecular weight determination gave a value of 144 (calcd 143.923). The ^{19}F NMR (1% in 80:20:1/CCl_4:$CDCl_3$:$CFCl_3$) gave the expected AB spin system with A −31.3, B −54.3, and $^2J_{AB}$ = 68 Hz.



The infrared (g) and Raman (l) spectra allow a good assignment of the fundamental vibrational modes in $CF_2{=}NBr$ based on C_s symmetry. These assignments were easily made by comparison with the spectra of $CF_2{=}NF$ and $CF_2{=}NCl$.[11,12] For $CF_2{=}NCl$, previous assignments based on only a partial infrared spectrum must be revised in view of Raman data obtained in this work. The assignments for the compounds are compared in Table I by using the description previously given for $CF_2{=}NF$.[12] Within the resolution limit of our instrument, the band contours for $CF_2{=}NBr$ appear to be nearly identical with those of $CF_2{=}NF$. For both $CF_2{=}NBr$ and $CF_2{=}NCl$, the assignment of the torsional frequency is tentative. Neither molecule exhibits a distinct Raman band for this mode. However, very weak features at a somewhat higher frequency than δ-NX are evident in the spectra. In the case of $CF_2{=}NF$, the torsion is the second least intense Raman band, and this provides support for the assignments in $CF_2{=}NCl$ and $CF_2{=}NBr$. Taken together, the assignments in Table I provide very reasonable values for the three compounds.

The chemistry of $CF_2{=}NBr$ is under active investigation and will be reported separately. Other reactions of $FC\equiv N$ suggested by this work are also being explored.

Acknowledgment. Financial support of this research by the U.S. Army Research Office (DAAG29-83-K0173) and the National Science Foundation (CHE-8217217) is gratefully acknowledged.

---

(11) Hirschmann, R. P.; Simon, H. L.; Yound, D. E. *Spectrochim. Act., Part A* **1971**, *27A*, 421.

(12) Christen, D.; Oberhammer, H.; Hammaker, R. M.; Chang, S.-C.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 6186.

Testing for Symmetry in Neighboring Group Participation in Carbocation Formation. An Insight into Double-Bond Participation via Trifluoromethyl Group Substitution

Paul G. Gassman* and Joyce Breitweiser Hall

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received February 22, 1984

As part of our extensive studies of neighboring group participation in carbocation formation, we have made use of two tests for the nature of the interaction of a neighboring group in the stabilization of an incipient carbocation. One of these tests[1] has become known as the "tool of increasing electron demand" and has been extensively used.[2,3] The other involved changing the substituents on the neighboring group to enhance its electron density and hence its ability to act as a neighboring group.[4] This test has not been widely used because the observed rate differences

---

(1) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545; **1970**, *92*, 2549, 2551.

(2) For a detailed discussion, see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 101, 163–175.

(3) For a recent leading reference, see: Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146.

(4) Gassman, P. G.; Patton, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 2160. For the historical background to the controversy concerning the nature of the transition state involved in the ionization of **1a**, see: Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183. Winstein, S.; Shatavsky, M. *Ibid.* **1956**, *78*, 592. Woods, W. G.; Carboni, R. A.; Roberts, J. D. *Ibid.* **1956**, *78*, 5653. Winstein, S.; Lewin, A. H.; Pande, K. C. *Ibid.* **1963**, *85*, 2324. Diaz, A.; Brookhart, M.; Winstein, S. *Ibid.* **1966**, *88*, 3133. Brown, H. C.; Bell, H. M. *Ibid.* **1963**, *85*, 2324.

0002-7863/84/1506-4267$01.50/0 © 1984 American Chemical Society