

equipped with a Teflon stopcock (Fischer and Porter Co.). Liquid densities were measured in a pycnometer of calibrated volume of 0.1–0.2 ml. Separation of reaction products and subsequent purification of the desired product were performed with a dry, fractional codistillation apparatus⁷ using a coiled, unpacked, fluorinated copper column (12 ft. of 1/8-in. o.d. tubing). After separation, identification of known reaction products was made through infrared spectra. These spectra were obtained with a Perkin-Elmer Model 137B Infracord and a Pyrex cell with a 5-cm. path length and sodium chloride windows. The mass spectrum was recorded with a Consolidated Engineering Corp. Type 21-103 mass spectrometer. The nuclear magnetic resonance spectrum was obtained through the use of a Varian Model 4311B high-resolution spectrometer equipped with a 40-Mc. oscillator. Trichlorofluoromethane was used as an external reference. Since the compound is easily hydrolyzed, the synthesis and subsequent manipulations were carried out under anhydrous, vacuum conditions.

Reaction of Tetrafluorohydrazine and Carbon Monoxide.—Preliminary attempts to prepare difluoramino-carbonyl fluoride by mixing equimolar amounts of the starting materials at room temperature and at pressures not in excess of 1000 mm. and by slowly warming to various temperatures up to 200° in a static brass reactor resulted in a large number of decomposition products, including CF₄, N₂O, NO₂, CO₂, FNO, and COF₂. Some of these were present only as traces and all were not formed in every reaction. Reactions run in Monel tubes at pressures from 50 to about 200 atm. usually resulted in products similar to those in the lower pressure reactions described above.

In a typical run, 206 mm. of CO and 101 mm. of N₂F₄ were mixed in a 3-l. Pyrex bulb equipped with a quartz finger (water-cooled) and were irradiated for 2 hr. with a Hanau Type 81 high-pressure ultraviolet lamp. The yield of purified NF₂CFO was about 15% (2.6 mmoles) based on the initial amount of N₂F₄. Also recovered were about 15 mmoles of a roughly 50–50 mixture of N₂F₄ and COF₂. Large quantities of N₂F₂, accompanied by smaller amounts of SiF₄, NF₃, N₂O, and CO₂, were also found. These products suggest that the mechanism proposed for the reaction of N₂F₄ and SO₂⁸ would be applicable in this case.

Physical Properties of Difluoramino-carbonyl Fluoride.—(a) Experimental measurements gave an average vapor density of 100.3 g./mole compared to 99.0 for NF₂CFO. (b) The melting point was not determined since the pure material supercools to a glass (below –130°) which is stable at –183° for several months without crystallization. (c) The density of the glass is roughly 2.00 g./ml. at –183°. Liquid densities are given in Table I. In the range of –130 to –60°, the density (g./ml.) may be expressed as a function of the absolute temperature by the equation $d = 2.331 - 0.003577T$. (d) The vapor pressure values, measured over the temperature range from –130.0 to –56.2°, are given in Table II. The extrapolated boiling point is –52.0°. In the range –100 to –56°, these points lie on a Clausius-Clapeyron curve given by the equation $\log P_{\text{mm}} = 7.984 - 1129T^{-1}$. These data indicate a molar heat of vaporization of 5.17 kcal./mole and a Trouton constant of 23.4. (e) The infrared spectrum obtained at 10 mm. pressure consists of strong bands at 1900 (doublet, C–O stretch) and 1220 cm.⁻¹ (triplet, C–F stretch), moderate complex bands centered at 1045 and 968 cm.⁻¹ (N–F stretches), a weak triplet at 840 cm.⁻¹, and a moderate triplet at 768 cm.⁻¹. The latter two were not identified. (f) The nuclear magnetic resonance spectrum showed a sharp, well-resolved triplet (1:2:1) in the C–F region ($\delta_{\text{CCl}_3\text{F}} = 15.1$ p.p.m.; $J = 19.1$ c.p.s.) and a broad, single peak in the N–F region ($\delta_{\text{CCl}_3\text{F}} = -29.1$ p.p.m.). (g) In the mass spectrum, a parent peak, although weak, was observed at mass number 99. Extensive hydrolysis of the sample was also evident. Peaks attributed to the following species (with mass number and relative abundance) were observed: CO⁺, N₂⁺, 28, 18; NF⁺, 33, 13; CO₂⁺, 44, 39; CFO⁺, SiF⁺, 47, 100; NF₂⁺, 52, 8.5; FNCO⁺, 61, 1; F₂NC⁺, 64, 1.7; SiF₂⁺, 66, 2.3; F₂NCO, 80, 0.1; F₂NCF,

(7) G. H. Cady and D. P. Siegwath, *Anal. Chem.*, **31**, 618 (1959).

TABLE I
LIQUID DENSITIES OF NF₂CFO

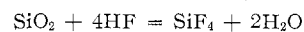
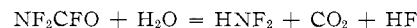
T, °C.	Density, g./ml.	T, °C.	Density, g./ml.
–130.0	1.817	–77.2	1.627
–115.5	1.764	–69.2	1.599
–97.7	1.704	–60.0	1.571
–87.3	1.665		

TABLE II
VAPOR PRESSURES OF NF₂CFO

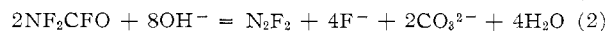
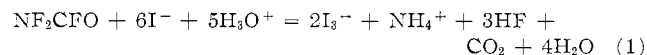
P, mm.	T, °K.	P, mm.	T, °K.
2	143.2	257.0	202.4
7.5	157.2	394.5	209.4
33.5	175.5	510.5	214.0
80.0	185.9	546	215.2
166.5	195.9	596	217.0
		(760)	(221.2)

83, 0.05; SiF₃⁺, 85, 3.3; F₂NCFO, 99, 0.05; SiF₄⁺, 104, 0.08. (h) *Anal.* Calcd. for NF₂CFO: C, 12.1; N, 14.2; F, 57.6. Found: C, 11.7; N, 14.4; F, 53.5.

Since the compound is hydrolyzed instantly by water, great care was exercised to maintain anhydrous conditions. An infrared spectrum indicated that HNF₂, CO₂, and SiF₄ were produced when a trace of water vapor was introduced into a sample of pure NF₂CFO. Hydrolysis apparently occurs according to



Gaseous difluoramino-carbonyl fluoride is also hydrolyzed rapidly and quantitatively at room temperature by acidic iodide or 0.6 N sodium hydroxide solutions according to



Equation 1 is analogous to the hydrolysis of HNF₂,⁸ and the N₂F₂ produced by eq. 2 is not hydrolyzed after 19 hr. at room temperature.⁹

Gaseous NF₂CFO does not attack mercury at room temperature. A sample was stored in CCl₃F in a sealed Pyrex tube at room temperature for 2 months with no appreciable alteration. The pure compound is stable for 2 hr. in glass at 100°.

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(8) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

(9) M. Schmeisser and P. Sartori, *Angew. Chem.*, **71**, 523 (1959).

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The B₉H₁₃NCS⁻ Ion

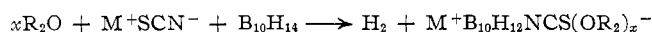
BY E. L. MUETTERTIES AND W. H. KNOTH

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We wish to correct an earlier¹ characterization of hydrolytic stability in B₁₀H₁₂X⁻ anions. Reaction

(1) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

of metal thiocyanates with decaborane in ethereal media is precisely described as



Earlier¹ we reported that such $B_{10}H_{12}X^-$ salts can be recrystallized from water; however, we find now that this is not a general property of these salts. Dissolution of the isothiocyanate derivative in water is accompanied by vigorous hydrogen evolution, and the only anionic species we have successfully isolated from aqueous solutions is $B_9H_{13}NCS^-$. We also found that this ion can be alternatively prepared in high yield through the reaction of decaborane with an aqueous dioxane solution of potassium thiocyanate.

Formation of $B_9H_{13}NCS^-$ in water-dioxane media must proceed through initial reaction of thiocyanate ion and decaborane. The alternative of decaborane ionization to $B_{10}H_{13}^-$ followed by thiocyanate ion addition can be rigorously excluded. We found no evidence of reaction between thiocyanate ion and $B_{10}H_{13}^-$ in aqueous dioxane. For example, dissolution of $(CH_3)_4N^+B_{10}H_{13}^-$ in water-dioxane and in water solutions of thiocyanate ion did not yield any borane species containing the NCS group. Salts of $B_{10}H_{13}^-$ were recovered on short solution exposures and $B_9H_{14}^-$ salts² on long (>1 min.) exposures. Thiocyanate ion does, however, add to $B_{10}H_{13}^-$ in anhydrous ethereal media to give $B_{10}H_{13}NCS^{2-}$.

This behavior of thiocyanate ion contrasts sharply with that of aqueous BH_4^- , CN^- , NH_3 , and OH^- , which react with $B_{10}H_{14}$ to yield $B_{10}H_{14}^{2-}$, $B_{10}H_{13}CN^{2-}$, $B_{10}H_{13}NH_3^-$, and $B_{10}H_{13}OH^{2-}$, respectively.³⁻⁶ Moreover, we found that addition of $B_{10}H_{13}^-$ salts to aqueous solutions of CN^- , BH_4^- , and OH^- gave $B_{10}H_{13}CN^{2-}$, $B_{10}H_{14}^{2-}$, and $B_{10}H_{13}OH^{2-}$, respectively.⁷ The rate of addition to $B_{10}H_{13}^-$ is very high for cyanide ion and relatively low for the other species.

Experimental

Potassium thiocyanate (0.02 mole) which had been rigorously dried under vacuum and decaborane (0.02 mole) were added to 60 ml. of dimethoxyethane, and the reaction mixture was stirred for 2 hr. During this time, hydrogen evolved (ca. 0.02 mole). Dioxane (60 ml.) was added, and the reaction mixture was concentrated until solid began to form. The solid was redissolved in warm dioxane which contained about 10% dimethoxyethane. This solution was filtered and then concentrated at about 10°

(2) $B_{10}H_{13}^-$ hydrolysis to $B_9H_{14}^-$ is relatively fast.

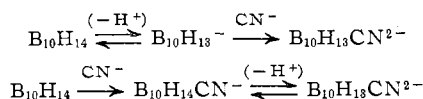
(3) E. L. Muettterties, *Inorg. Chem.*, **2**, 647 (1963).

(4) W. H. Knoch and E. L. Muettterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(5) E. L. Muettterties, to be published.

(6) L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Am. Chem. Soc.*, **85**, 2674 (1963).

(7) This establishes that these species can add to $B_{10}H_{13}^-$ but it does not distinguish between the two possible reaction sequences for the aqueous decaborane reactions, e.g.



In the cyanide and borohydride ion reactions there is no detectable yellow coloration attributable to a $B_{10}H_{13}^-$ intermediate but there is in the KOH reaction. The rate of CN^- addition to $B_{10}H_{13}^-$ is so fast that these data are not definitive. However, borohydride ion addition to $B_{10}H_{13}^-$ is slow. Therefore, we suggest that in the $B_{10}H_{14}-BH_4^-$ reaction $B_{10}H_{13}^-$ is the important intermediate.

until a crystalline phase separated. The solid was collected by filtration and vacuum dried for 24 hr. *Anal.* Calcd. for $KB_{10}H_{12}NCS \cdot 2.25OC_4H_8O$: C, 28.9; H, 7.28; K, 9.41; B, 26.1; N, 3.38; S, 7.70. Found: C, 29.0; H, 7.47; K, 8.72; B, 26.1; N, 3.41; S, 7.52.

The above reaction procedure was followed, and the reaction product was dissolved in water. There was an immediate and brisk evolution of hydrogen. A concentrated solution of tetramethylammonium chloride was added to the solution, and an oil formed. On warming, the oil solidified. The solid was collected by filtration and recrystallized from a hot water-methanol mixture. *Anal.* Calcd. for $(CH_3)_4NB_9H_{13}NCS$: C, 25.0; H, 10.4; B, 40.4; S, 13.3. Found: C, 25.2; H, 10.6; B, 40.1; S, 13.3. Major infrared absorptions of $(CH_3)_4NB_9H_{13}NCS$ in a Nujol mull, exclusive of Nujol bands, are at ~ 2500 (BH), 2150 (CN), 1470, 1060, 1040, 1020, 1005, 980, 950, 860, 735, and 715 cm^{-1} .

Decaborane (0.02 mole) was added to a mixture of 50 ml. of a saturated potassium thiocyanate solution in water and 35 ml. of water. Then 45 ml. of dioxane was added. On addition of the ether, decaborane dissolved rapidly with much hydrogen evolution to give a yellow solution. After 1 hr., the solution was diluted with 100 ml. of water and filtered. To the filtrate was added tetramethylammonium chloride solution to give a precipitate. The precipitate was collected and was recrystallized from hot water containing a small amount of methanol. *Anal.* Calcd. for $(CH_3)_4NB_9H_{13}NCS$: C, 25.0; H, 10.4; N, 11.6; B, 40.4; S, 13.3. Found: C, 25.4; H, 10.4; N, 11.6; B, 40.1; S, 13.4.

Anhydrous potassium thiocyanate (3.9 g., 0.02 mole) and the tetramethylammonium salt of $B_{10}H_{13}^-$ (1.94 g., 0.02 mole) were added to a mixture of dimethoxyethane (200 ml.) and dioxane (200 ml.). As the slurry was stirred, the B_{10} salt rapidly went into solution, leaving behind the large potassium thiocyanate crystals. After about 10 min. of stirring, the thiocyanate crystals were not visible, and a white solid had separated. Stirring was continued for 1 hr. and then the slurry was filtered. The solid was washed thoroughly with dimethoxyethane and dioxane. The solid was recrystallized from hot water containing a small amount of methanol, m.p. 295-300°. *Anal.* Calcd. for $[(CH_3)_4N]_2B_{10}H_{13}NCS$: C, 33.0; H, 11.4; B, 33.1; N, 12.8; S, 9.78. Found: C, 33.5; H, 11.5; B, 33.4; N, 12.8; S, 9.78. The infrared spectrum of this salt is quite rich; absorptions exclusive of the Nujol region are at ~ 2500 (BH), 2160 (CN), 1480, 1405, 1280, 1175, 1106, 1005, 970, 945, 793, 725, 698, and 665 cm^{-1} . This derivative of $B_{10}H_{14}^{2-}$ degrades in acidic media to $B_9H_{13}NCS^-$.⁸

(8) Analogous degradations in acidic media have been reported by B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

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Ligand Rearrangement in Cyclooctadiene by Palladium(II) and Platinum(II) π Complexes

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Information concerning the complexes of palladium(II) and platinum(II) with 1,5-cyclooctadiene is available in the papers of Chatt¹ and of Fischer and

(1) L. Chatt, *J. Chem. Soc.*, 3340 (1949); see also J. Chatt and L. Duncanson, *ibid.*, 2239 (1953), and J. Chatt, L. Vallarino, and L. Venanzi, *ibid.*, 2496 (1957).