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 apparatus[7] 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 difluoraminocarbonyl 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 CF_4, N_2O, NO_2, CO_2, FNO, and COF_2. 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 N_2F_4 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 NF_2CFO was about 15% (2.6 mmoles) based on the initial amount of N_2F_4. Also recovered were about 15 mmoles of a roughly 50–50 mixture of N_2F_4 and COF_2. Large quantities of N_2F_2, accompanied by smaller amounts of SiF_4, NF_3, N_2O, and CO_2, were also found. These products suggest that the mechanism proposed for the reaction of N_2F_4 and SO_2[3] would be applicable in this case.

Physical Properties of Difluoraminocarbonyl Fluoride.—(a) Experimental measurements gave an average vapor density of 100.3 g./mole compared to 99.0 for NF_2CFO. (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 ($\delta_{CCl_3F} = 15.1$ p.p.m.; $J = 19.1$ c.p.s.) and a broad, single peak in the N–F region ($\delta_{CCl_3F} = -29.1$ 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^+, N_2^+, 28, 18; NF^+, 33, 13; CO_2^+, 44, 39; CFO^+, SiF^+, 47, 100; NF_2^+, 52, 8.5; $FNCO^+$, 61, 1; F_2NC^+, 64, 1.7; SiF_2^+, 66, 2.3; F_2NCO, 80, 0.1; F_2NCF, 83, 0.05; SiF_3^+, 85, 3.3; F_2NCFO, 99, 0.05; SiF_4^+, 104, 0.08. (h) *Anal.* Calcd. for NF_2CFO: C, 12.1; N, 14.2; F, 57.6. Found: C, 11.7; N, 14.4; F, 53.5.

TABLE I

LIQUID DENSITIES OF NF_2CFO

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 NF_2CFO

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)

Since the compound is hydrolyzed instantly by water, great care was exercised to maintain anhydrous conditions. An infrared spectrum indicated that HNF_2, CO_2, and SiF_4 were produced when a trace of water vapor was introduced into a sample of pure NF_2CFO. Hydrolysis apparently occurs according to

$$NF_2CFO + H_2O = HNF_2 + CO_2 + HF$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

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

$$NF_2CFO + 6I^- + 5H_3O^+ = 2I_3^- + NH_4^+ + 3HF + CO_2 + 4H_2O \quad (1)$$

$$2NF_2CFO + 8OH^- = N_2F_2 + 4F^- + 2CO_3^{2-} + 4H_2O \quad (2)$$

Equation 1 is analogous to the hydrolysis of HNF_2,[8] and the N_2F_2 produced by eq. 2 is not hydrolyzed after 19 hr. at room temperature.[9]

Gaseous NF_2CFO does not attack mercury at room temperature. A sample was stored in CCl_3F 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°.

Acknowledgments.—This work was supported in part by the Advanced Research Projects Agency through a contract administered by the Office of Naval Research. The authors are indebted to Mr. B. J. Nist of the University of Washington for the mass and nuclear magnetic resonance spectra.

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The $B_9H_{13}NCS^-$ Ion

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Received April 22, 1965

We wish to correct an earlier[1] characterization of hydrolytic stability in $B_{10}H_{12}X^-$ anions. Reaction

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(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

$$x\mathrm{R_2O} + \mathrm{M^+SCN^-} + \mathrm{B_{10}H_{14}} \longrightarrow \mathrm{H_2} + \mathrm{M^+B_{10}H_{12}NCS(OR_2)_x^-}$$

Earlier[1] 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 $B_9H_{14}^-$ salts[2] 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° 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]

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

[3] E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

[4] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

[5] E. L. Muetterties, 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.*

$$\mathrm{B_{10}H_{14}} \overset{(-\mathrm{H^+})}{\rightleftharpoons} \mathrm{B_{10}H_{13}^-} \xrightarrow{\mathrm{CN^-}} \mathrm{B_{10}H_{13}CN^{2-}}$$

$$\mathrm{B_{10}H_{14}} \xrightarrow{\mathrm{CN^-}} \mathrm{B_{10}H_{14}CN^-} \overset{(-\mathrm{H^+})}{\rightleftharpoons} \mathrm{B_{10}H_{13}CN^{2-}}$$

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 $B_{10}H_{15}^-$ is the important intermediate.

[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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Received April 30, 1965

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

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[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).