effect of the hydrophobic pocket, however, is to hinder the entry of the H^+ and Cl^- ions, leading to a slower rate for the second reaction than in case of ethylenediamine.

Registry No. $[Cr(tren)ox]^+$, 57719-00-3; $[Cr(trenH)ox(H_2O)]^{2+}$,, 75234-31-0; $[Cr(trenH_2)ox(H_2O)_2]^{3+}$, 75234-32-1; $[Cr(trenH_3)ox(H_2O)_3]^{4+}$, 75234-33-2; $[Cr(H_2O)_4ox]^+$, 24777-95-5.

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Difluoroborane, a Hydrogen–Deuterium Exchange Catalyst. Application to Pentaborane(9) and Methylpentaborane(9)

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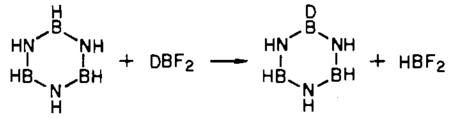
An interesting chemical property of difluoroborane (HBF_2) is its reactivity with deuterium gas to undergo H–D exchange. The reaction

$$HBF_2(g) + D_2 \xrightarrow{k_2} DBF_2 + HD \tag{1}$$

proceeds with a second-order rate constant $k_2 = (7.4 \pm 2.0) \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} at 25 °C. This reaction, which is quite rapid at 100 °C, has an apparent activation energy of 17.8 ± 1.2 kcal/mol. Curtis and Porter[1] proposed that the process involves an activated intermediate formed by a three-center interaction of D_2 with the electron-deficient boron atom in HBF_2. The possibility of using HBF_2 as an H–D exchange catalyst is evident in the thermodynamic investigation of DeStefano and co-workers.[2] Results of that study showed that mixtures of H_2 and D_2, which do not exchange at a perceptible rate at 25 °C, reach an equilibrium mixture of H_2, HD, and D_2 with 24 h when HBF_2 is present in the gas mixture. The rate of scrambling is increased significantly at higher temperatures. Borazine ($H_3B_3N_3H_3$) reacts with DBF_2 at ordinary temperatures by H–D exchange. The process shown in eq 2 is accelerated when borazine is present in a D_2–DBF_2 mixture by the replacement of the deuterated reactant in reaction 1. The process is site selective at the B–H bonds, and consecutive H–D exchange reactions lead to tri-*B*-deuterioborazine as the final product. Coyle and co-workers[3] found that process 3 proceeds rapidly at ordinary temperatures.



(2)

$$B_2H_6 + DBF_2 \rightarrow B_2H_5D + HBF_2 \tag{3}$$

From these observations and the nature of reaction 1, it is clear that B_2D_6 could be obtained directly from a mixture of B_2H_6, HBF_2, and and D_2 in excess. These considerations have suggested the use of HBF_2 as an H–D exchange catalyst for preparing partially or totally deuterated boron hydrides. In this paper we report experimental results for B_5H_9, 1-$CH_3B_5H_8$, and 2-$CH_3B_5H_8$.

The exchange of hydrogens between diborane and pentaborane(9) was studied by Koski and co-workers.[4–6] They applied infrared, mass, and NMR spectroscopy to their investigations of the reaction. The exchange was reported to occur by a bimolecular collision between borane and pentaborane (eq 4 and 5).

$$B_2D_6 \rightarrow 2BD_3 \tag{4}$$

$$BD_3 + B_5H_9 \rightarrow B_5H_8D + BD_2H \tag{5}$$

At 80 °C the reaction was complicated by the pyrolytic formation of pentaborane from deuterated diborane. When the B_5D_9 fraction was subtracted in the spectra of the pentaborane product, they observed that the exchange of B_2D_6 and B_5H_9 involved preferential deuteration of the terminal positions of the pentaborane.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using 3-in. gas cells with KBr optics. The cells were thoroughly purged with dry nitrogen after cleaning, and background spectra were run before and after use. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103A spectromter at 70-eV ionizing voltage.

B_5H_9 (Callery Chemical Co.) was repurified by vacuum distillation through U-tube traps. Slow passage of the B_5H_9 through a −78 °C trap removed the higher molecular weight impurities. Pure B_5H_9 was recovered in a −98 °C trap. D_2 was obtained from Air Products and Chemicals, Inc., research grade. 1-Methylpentaborane(9) was prepared from B_5H_9 and CH_3Br under Friedel–Crafts conditions with aluminum chloride catalyst.[7] 2-Methylpentaborane(9) was prepared from the rearrangement of 1-$CH_3B_5H_8$ by employing the base catalyst 2,6-lutidine.[8] The product purities were confirmed by their mass, infrared, and proton NMR spectra.

Samples of DBF_2 were prepared from mixtures of B_2D_6 and BF_3 by a method similar to that of Coyle et al.[3] A 3:1 mixture of BF_3:B_2D_6 was heated to 180 °C in $^1/_2$ h at a total pressure of 250 torr (1 torr = 133.3 N m^{-2}) in a 1-L stainless-steel vessel equipped with a Whitey 1KS6 valve. The products, a mixture of BF_3 and DBF_2, were separated from small amounts of B_5D_9 by slow passage through a −98 °C trap. Quantitative determination of DBF_2 in the reagent mixture was accomplished by measuring the amount of HD and D_2 formed when the sample was exposed to an excess of H_2. Mixtures of HBF_2 and DBF_2 may be analyzed by absorbance measurements at 924 cm^{-1} (A_H) and 787 cm^{-1} (A_D), respectively.

Results and Discussion

The DBF_2–B_5H_9 Exchange Reaction. A mixture of reagents in the molar proportion B_5H_9:DBF_2:BF_3 = 1:0.7:1.6 at a total pressure of 400 torr was heated for 24 h at 98 °C in a 100-mL Pyrex vessel. The products that were recovered in a −98 °C trap indicated partial deuteration of B_5H_9 by the infrared absorption at 1950 cm^{-1} corresponding to a B–D stretching vibration. The infrared analysis of the products recovered at −198 °C indicated that nearly all of the DBF_2 had been converted to HBF_2. Several more 24-h runs were made with the sample of pentaborane. The reaction vessel was maintained at 100 °C with approximately 100 torr of D_2 added between runs. Infrared analyses indicated progressive deuteration of the pentaborane fraction (observed in the relative intensities of the absorptions at 2600 and 1950 cm^{-1}). Due to the exchange reaction with deuterium (eq 1), the difluoroborane remained highly deuterated. A second sample with composition B_5H_9:DBF_2:BF_3:D_2 = 1.0:0.43:1.0:2.5 at a total pressure of 440 torr was heated for 48 h at 80 °C. The products were

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Table I. Rate Constant Data for the DBF_2-B_5H_9 Hydrogen Exchange Reaction

	initial reactant pressure, torr					B_5H_9 [a]
T, °C	B_5H_9	DBF_2	D_2	k_2, cm^3/(molecule s)	reacn time, h	fraction reacted
78	2	8	17	5.43×10^{-24} [b]	39.55	0.194
100	2.5	9	20	3.53×10^{-23}	0.42	0.016
120	1	4	8.5	1.91×10^{-22}	2.08	0.185
138	1	4	8.5	8.75×10^{-22}	0.88	0.350

[a] Determined from the mass spectral analysis of m/e 64/65 and the normal isotopic distribution of boron. [b] A least-squares fit from four determinations.

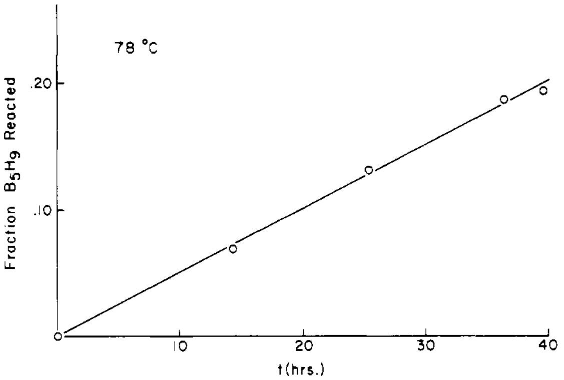


Figure 1. Fractional yield of B_5H_8D in the DBF_2–B_5H_9 exchange reaction. Initial pressures in torr (T = 78 °C): B_5H_9, 2; BF_3, 26.5; HBF_2, 8; D_2, 17.

separated by vacuum distillation through U-tube traps at −98 and −196 °C. Mass spectral analysis of the pentaborane recovered from the −98 °C trap indicated H–D exchange had occurred, without significant loss of material by pyrolysis. The difluoroborane was recovered in the deuterated form from the −196 °C trap. In a blank experiment with DBF_2 absent, H–D exchange was not observed.

DBF_2–Methylpentaborane(9) Exchange Reactions. Observations of the H–D exchange products in the DBF_2–B_5H_9 system suggested a possible selectivity for the exchange at the apical boron of pentaborane. So that this possibility could be explored, 1- and 2-methylpentaboranes were used in an H–D exchange experiment with DBF_2. Two identical 100-mL Pyrex reaction vessels were prepared and were each filled with a DBF_2–BF_3 mixture (approximately 30% DBF_2) to a pressure of 68 torr. 1-$CH_3B_5H_8$ (P = 50 torr) was added to one vessel, and 2-$CH_3B_5H_8$ (P = 50 torr) was added to the other. The vessels were simultaneously immersed in a 90 °C bath and removed after 3.5 h. The products were vacuum distilled through U-tube traps at −98 and −196 °C. Infrared analyses of the difluoroborane covered in the −196 °C traps gave absorbance ratios $A_D/A_H = 0.265/0.14$ and $0.34/0.075$ for the products of the 2-methyl- and 1-methylpentaborane reactions, respectively. Due to the cancellation of concentration effects, the ratio $(A_H/A_D)_{2\text{-methyl}}/(A_H/A_D)_{1\text{-methyl}} = 2.4$ gave a direct comparison of the rates of H–D exchange with apical and basal H's in the pentaborane derivatives. When this result is normalized to a per atom basis, the ratio of rates of exchange of an apical/basal H atom is about 6/1 (counting the terminal H's only).

Rate Measurements. A mixture in the molar ratio B_5H_9:DBF_2:BF_3:D_2 = 2:8:18:17 was maintained at 78 °C, and the progress of the reaction was noted by withdrawing small samples for mass spectral analysis. The fraction (f) of B_5H_9 converted to B_5H_8D in the reaction

$$DBF_2 + B_5H_9 \rightarrow HBF_2 + B_5H_8D \qquad (6)$$

was obtained directly from mass spectral ion intensities of $^{11}B_5H_9^+$ and $^{11}B_5H_8D^+$ and the relationship

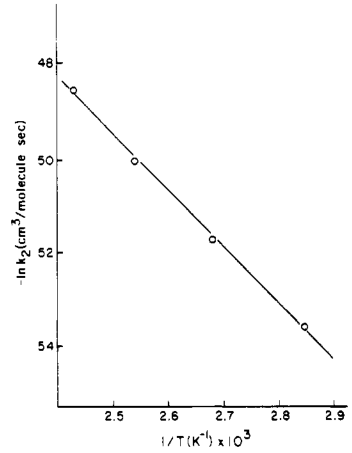


Figure 2. Plot of $-\ln k_2$ vs. + $1/T$ for the DBF_2–B_5H_9 exchange reaction.

$$f = I_{B_5H_8D^+}/(I_{B_5H_8D^+} + I_{B_5H_9^+}) \qquad (7)$$

Measurements were taken under conditions where the quantity of $B_5H_7D_2$ due to consequentive exchange processes was small. A nearly linear dependence of f on reaction time was observed from data obtained at 78 °C (Figure 1). This behavior is consistent with a pseudo-first-order process with the concentration of DBF_2 remaining constant due to reaction 1. For low conversions to B_5H_8D, integration of the rate expression

$$d[B_5H_9]/dt = -k'[B_5H_9] \qquad (8)$$

gives

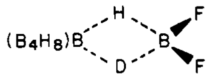
$$-\ln (1 - f) = k't \simeq f \qquad (9)$$

For strict second-order behavior, $k_2' = k_2[DBF_2]$. With the assumption of this relationship, rate data from a series of measurements at different reaction temperatures and starting conditions are given in Table I.

Figure 2 is a plot of $-\ln k_2$ vs. $1/T$ for the values in Table I. From the Arrhenius rate expression under initial rate conditions, $A = (5.9 \pm 0.2) \times 10^9$ cm^3 molecule^{-1} s^{-1} and E_a = 24.2 ± 0.4 kcal mol^{-1}. An activation energy of 27 kcal mol^{-1} was reported for the B_2D_6–B_5H_9 exchange reaction.[9]

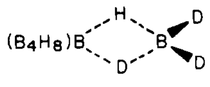
Conclusions

The hydrogen exchange reaction of pentaborane with difluoroborane suggests the existence of a multicentered intermediate (I) similar to that proposed by DeStefano and Porter[2]



I

for the difluoroborane–borazine exchange reaction. A similar intermediate (II) may apply to the borane–pentaborane exchange reaction. The intermediate II may in fact have a finite existence. In mass spectrometric studies of the reaction of borane with pentaborane, Fridmann and Fehlner[10,11] observe a six-boron ion with an uncertain number of hydrogens. This



II

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ion may be the ionization product of the proposed exchange intermediate II.

There are several advantages for the use of difluoroborane in the study of the reactions of borane. (1) The relative abundance of difluoroborane at equilibrium is high compared to that of borane in the dissociation of diborane. (2) The gas-phase reactions in the diborane system involve the formation of triborane.[12] (3) The pyrolysis of diborane produces the higher boron hydrides. In isotopic studies, this may lead to confusing side products. Pyrolysis products of difluoroborane are not observed in this study.

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Registry No. DBF_2, 13709-79-0; B_5H_9, 19624-22-7; 1-$CH_3B_5H_8$, 19495-55-7; 2-$CH_3B_5H_8$, 23753-74-4.

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Long-Wavelength Excitation of Hexacyanocobaltate(III), $Co(CN)_6^{3-}$, in Aqueous Solution. Questions Regarding Intersystem-Crossing Efficiencies

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The photochemistry and spectroscopy of the $Co(CN)_6^{3-}$ ion have been extensively investigated.[1] Comparison of the photochemical properties of this ion and monosubstituted derivatives $Co(CN)_5X^{(2+n)-}$ (where X^{n-} is an anion or neutral) to those of analogous pentaamminecobalt(III) derivatives $Co(NH_3)_5X^{(3-n)+}$ indicates very different behaviors.[1] Irradiation of the pentacyano derivatives in the wavelength region of the LF bands results in ligand photosubstitution, generally replacement of X^{n-} or CN^- by solvent. Quantum yields are moderately large (~0.1–0.4 mol/einstein) and essentially independent of irradiation wavelength (λ_{irr}) in the LF region. For example $Co(CN)_6^{3-}$ in aqueous solution undergoes CN^- photoaquation (eq 1) with a wavelength-independent Φ_{CN} =

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + CN^- \quad (1)$$

0.31 when irradiated at wavelengths (254–365 nm) corresponding to spin-allowed LF absorptions.[2] In contrast, for the pentaammine derivatives photosolvation quantum yields are much smaller and are sharply λ_{irr} dependent, photoaquation of NH_3 from $Co(NH_3)_6^{3+}$ occurring with $\Phi_{NH_3} = 5.4 \times 10^{-3}$ and 3.1×10^{-4} at λ_{irr} = 365 and 472 nm, respectively.[3] An attractive rationalization of these photoreactivity differences is the interpretation that the lowest excited state (ES) of the pentacyano complexes has triplet character while that of the pentaammine series has quintet character.[4] This argument is consistent with the greater ligand field strength of CN^- and with parallels in the LF photoreactivity patterns of the pentacyanocobalt(III) species with other strong-field d^6 complexes such as the pentaammine complexes of Rh(III), Ir(III), and Ru(II) which have been concluded to undergo ligand labilization primarily from lowest energy triplet LF states.[5–7]

Table I. Photoaquation Quantum Yields for $Co(CN)_6^{3-}$ as a Function of Irradiation Wavelength[a]

λ_{irr}, nm	Φ_{CN^-}, mol/einstein	ref
254	0.31 ± 0.01	2
313	0.31 ± 0.01	2
365	0.31 ± 0.01	2
405	0.29 ± 0.02	this work
436	0.34 ± 0.05	this work

[a] In aqueous pH 2 solution, at 25 °C.

There is one major difference between the accepted models for the LF photochemistries of $Co(CN)_5X^{(2+n)-}$ and the heavier metal complexes. The latter complexes are generally viewed to undergo rapid internal conversion/intersystem crossing from initially populated single LF states to the lowest energy LF ES (a triplet) with unitary or near unitary efficiency. This property is reflected in the λ_{irr} quantum yields (including, in some cases, direct singlet to triplet excitations)[5a,b] and in the coincidence of limiting quantum yields obtained by triplet sensitization with values derived by direct singlet to singlet excitation.[7] In contrast, triplet sensitization experiments for $Co(CN)_6^{3-}$ have been interpreted as indicating that CN^- labilization from the lowest triplet state occurs with a very high yield (Φ(limiting) $\cong$ 0.8) and that intersystem crossing from initially excited singlets is relatively inefficient ($\Phi_{isc} \cong 0.4$).[8] Recently, two spectroscopic studies[9] have identified an absorption band for the $Co(CN)_6^{3-}$ ion at ~390 nm which has been assigned a singlet to triplet ($^3T_{1g} \leftarrow {}^1A_{1g}$) transition. Furthermore, plots of log ϵ vs. energy for the room-temperature aqueous solution spectrum of $K_3Co(CN)_6$ demonstrate the presence of a shoulder ($\epsilon = 0.38\ M^{-1}\ cm^{-1}$) at ~24.600 cm^{-1} (406 nm) which may be assigned to this spectral feature.[10] The present study examines the intersystem crossing efficiencies by measuring quantum yields for excitation in these spectral regions representing direct triplet excitation.

Experimental Section

The salt $K_3Co(CN)_6$ was prepared by the published method[11] and recrystallized twice from hot water. The photolysis apparatus has been described before[12] and consisted of a high-pressure mercury-lamp light source with λ_{irr} isolated with mercury-line interference filters. Light intensities were determined by ferrioxalate actinometry. The electronic spectrum of $K_3Co(CN)_6$ in dilute (pH 2) aqueous solution gave extinction coefficients of 2.0, 0.38, and 0.080 $M^{-1}\ cm^{-1}$ at the wavelengths 380, 405, and 436 nm, respectively. In comparison, the spectrum of $Co(CN)_5(H_2O)^{2-}$, obtained in situ by exhaustive photolysis, gave the respective ϵ's of 260 (λ_{max}), 164, and 37 $M^{-1}\ cm^{-1}$ at these wavelengths. Solution concentrations used for long-wavelength photolysis were 0.06 (λ_{irr} = 405 nm, initial absorbance at 405 nm $\cong$ 0.05, 2-cm cell) and 0.12 M (λ_{irr} = 436 nm, initial absorbance at 436 nm $\cong$ 0.02, 2-cm cell). Product yields were calculated for very small percent conversion to products (~0.5%) by monitoring absorbance

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