(10) J. H. Teuben, *J. Organomet. Chem.,* **57**, 159 (1973).
(11) D. Ytsma, J. G. Hartsuiker, and J. H. Teuben, *J. Organomet. Chem.,* **74**, 239 (1974).
(12) H. H. Brintzinger, *J. Am. Chem. Soc.,* **89**, 6871 (1967).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Difluoroborane, an H–D Exchange Catalyst for the Preparation of B-Trideuterioborazines

Anthony J. DeStefano and Richard F. Porter*

The purpose of this note is to describe a relatively simple procedure for preparing B-deuterioborazines. The method involves direct deuteration of a borazine derivative in the gas phase with a deuterium–HBF_2 mixture. In the reaction HBF_2 acts as an H–D exchange catalyst. The method appears to have advantages over conventional synthetic techniques which require specially deuterated starting materials.

Experimental Section

Mixtures of HBF_2–BF_3 were prepared by a method similar to that of Coyle, Cooper and Ritter.[1] In a typical synthesis a mixture of BF_3 and B_2H_6 in a molar ratio of 2:1 at a total pressure of 200 mm was heated to 200 °C for 0.5 h in a 1-l. stainless steel vessel. Under these reaction conditions HBF_2–BF_3 product mixtures contained 30–40% HBF_2 with less than 1% B_2H_6. Mixtures of DBF_2–BF_3 were prepared by reaction of HBF_2–BF_3 mixtures with deuterium gas.[2] Sample purities were checked by ir and mass spectra.

The preparation of borazine followed the procedure of Hohnstedt and Haworth.[3] N-Trimethylborazine and N-triethylborazine were prepared by the method used by Beachley.[4] Ether solvent remaining in the products after trap-to-trap distillation was removed by reaction with BCl_3. Sample purities were checked by ir and mass spectra.

Mass spectra were obtained on a CEC-21-103A mass spectrometer with probe temperature at 50 °C and on a previously described photon impact mass spectrometer employing the Lyman α line of hydrogen as the source of ionizing radiation.[5] Infrared spectra were obtained on Perkin-Elmer 337 and 521 grating spectrophotometers.

Results

Preparation of $D_3B_3N_3H_3$. Mixtures of $H_3B_3N_3H_3$ and DBF_2 containing some BF_3 were allowed to react for periods up to 1500 s in an 80-ml stainless steel vessel. The reaction was quenched by immersion of the reaction vessel into liquid nitrogen. The percent H–B converted to D–B in borazine was then determined by mass spectral analysis. Results of the analyses are shown in Table I. The data indicate that the deuteration reaction probably occurs through homogeneous and heterogeneous pathways, making the determination of specific rate constants difficult. It can be noted that the rate of formation of the deuterated borazine is comparable to the rate of DBF_2 formation from the reaction

$$HBF_2 + D_2 \rightarrow DBF_2 + HD \qquad (1)$$

under similar reaction conditions.[2]

For qualitative determinations of the rate of borazine deuteration a number of mixtures with different DBF_2:$H_3B_3N_3H_3$:D_2:BF_3 ratios were allowed to react for periods of 1.0, 2.33, and 16 h. The results of mass spectral analysis of the products are shown in Table II. At short times the rate of deuteration of borazine is quite rapid and dependent, to a first approximation, on the DBF_2:$H_3B_3N_3H_3$ ratio. At longer times back-reactions became more important and the net rate of deuteration decreased markedly. A change from Pyrex to stainless steel reaction vessels did not appear to alter the results

Table I. Results of Isotope Exchange Experiments in Mixtures of $H_3B_3N_3H_3$, DBF_2, and BF_3 (T = 297 K)

Sample compn, $H_3B_3N_3H_3$: DBF_2:BF_3	Pressure, mm	Time, s	% H–B converted to D–B in borazine samples
1:0.24:0.40	40	1500	5.2
1:0.19:0.35	54	1500	6.9
1:0.14:0.26	45.5	1500	1.8
1:0.16:0.29	52	1500	5.5
1:0.10:0.18	73.5	1500	1.3
1:0.06:0.12	65	1500	1.4
1:0.04:0.08	56	1500	0.77
1:0.05:0.09	109.5	500	0.92

Table II. Results of Isotope Exchange Experiments in Mixtures of DBF_2, $H_3B_3N_3H_3$, D_2, and BF_3 (T = 297 K)

Sample compn, DBF_2: $H_3B_3N_3H_3$:D_2: BF_3	Pressure, mm	Time, h	% H–B converted to D–B in borazine samples	Vessel
1:1:28.7:1.8	192	1	34	Pyrex
1:2.1:28.7:1.8	130	1	16	Pyrex
1:1:23.7:1.9	268	1	31	Stainless
1:1.7:23.6:1.9	95	1	12	Stainless
1:2.4:28.7:1.8	113	2.33	31	Pyrex
1:0.8:24.5:1.8	183	2.33	23	Pyrex
1:0.8:23.6:1.9	155	2.33	56	Stainless
1:2.2:24.5:1.8	67	16	65	Pyrex
1:4.7:24.5:1.8	184	16	65	Stainless
0:1:33:0	274	16	5	Stainless

Table III. Parent Regions of the 70-eV Electron Impact Spectra of $H_3B_3N_3H_3$ and Deuterium-Enriched Borazines

Mass no.	D_3B_3-$N_3H_3{}^a$	D_3B_3-$N_3H_3{}^b$	D_3B_3-$N_3H_3{}^c$	H_3B_3-N_3H_3
85	1.00	0.87	0.72	
84	50.0	51.1	50.0	
83	40.5	40.9	38.8	
82	100	100	100	0.51
81	66.7	68.9	68.3	39.3
80	19.8	20.0	17.0	100
79	9.0	8.9		62.4
78	7.4	7.4		21.4
77	6.2	6.2		11.3
76	4.8	5.0		8.5
75	2.1	2.3		4.0
74	0.48	0.60		0.85

^{a} Prepared using DBF_2–D_2. ^{b} Prepared photochemically.
^{c} Calculated from the $H_3B_3N_3H_3$ spectrum (see text).

significantly. The final entry in Table II shows the result of allowing an $H_3B_3N_3H_3$–D_2 sample to react at 297 K for 16 h in the stainless steel container. This puts an upper limit of about 5% on the amount of borazine deuterated thermally[6,7] after 16 h under our experimental conditions.

B-Trideuterioborazine of isotopic purity comparable to that produced photochemically[6] was obtained as follows. A mixture containing $H_3B_3N_3H_3$, DBF_2, BF_3, and D_2 at partial pressures of 7, 5, 9, and 453 mm, respectively, was allowed to react in an 80-ml stainless steel vessel. At intervals of 9, 14.5, and 5.5 h the H_2–HD–D_2 mixture in the products was removed and replaced with pure D_2 at pressures of 520, 430, and 456 mm, respectively. The final mixture was then allowed to react for 18 h prior to mass spectral and infrared analysis. The ir spectrum of the deuterated borazine was identical with that reported in the literature.[8,9] Shown in Table III are the 70-eV electron impact mass spectra of deuterated borazine samples prepared by the above procedure and by the photochemical

Table IV. Results of Isotope Exchange Experiments in Mixtures of DBF_2, $H_3B_3N_3(CH_3)_3$, D_2, and BF_3 ($T = 297$ K; Pyrex Vessel)

Sample compn, DBF_2: $H_3B_3N_3(CH_3)_3$: D_2:BF_3	Pressure, mm	Time, h	% H–B converted to D–B in $H_3B_3N_3$-$(CH_3)_3$ samples
1:1.1:9.5:2.9	103	1	7
1:1:29.5:1.8	100	2.33	33
1:1.8:24.5:1.8	110	16	71
1:0.2:9.5:2.9	280	16	92
0:1:54:0	434	16	28
0:1:16:0	103	16	4

Table V. The 10.2-eV Photon Impact Spectra of $H_3B_3N_3(CH_3)_3$ and $H_3B_3N_3(C_2H_5)_3$ and Their B-Deuterated analogues

Mass no.	$D_3B_3N_3$-$(CH_3)_3$	$H_3B_3N_3$-$(CH_3)_3$	Mass no.	$D_3B_3N_3$-$(C_2H_5)_3$	$H_3B_3N_3$-$(C_2H_5)_3$
127	4.7		169	8.5	
126	100		168	100	
125	82		167	71.8	
124	26.8	5.5	166	20.5	8.1
123		100	165		100
122		81.5	164		71.4
121		24.7	163		17.4

procedure previously described.[6] Also shown in Table III are the parent regions of an $H_3B_3N_3H_3$ mass spectrum and a $D_3B_3N_3H_3$ spectrum calculated by assuming the only ions in the $H_3B_3N_3H_3$ parent region are the $H_3B_3N_3H_3^+$ parent ions and the $H_2B_3N_3H_3^+$ ions obtained through hydride extraction from a boron site.[5,10] The results indicate that the preparation of $D_3B_3N_3H_3$ from DBF_2–D_2–BF_3 mixtures yields $D_3B_3N_3H_3$ samples of isotopic purity comparable to those obtained photochemically.

Preparation of $D_3B_3N_3(CH_3)_3$ and $D_3B_3N_3(C_2H_5)_3$. The effectiveness of D_2–DBF_2 mixtures for deuteration of N-trimethylborazine was observed by allowing DBF_2–H_3B_3-$N_3(CH_3)_3$–D_2–BF_3 mixtures of different composition to react for periods of 1.0, 2.33, and 16 h prior to mass spectral analysis. The results are shown in Table IV. Also shown in Table IV are the results of two D_2–$H_3B_3N_3(CH_3)_3$ mixtures allowed to react thermally for 16 h. Correction for the rate of reaction 2 shows the rate of N-trimethylborazine deuteration

$$H_3B_3N_3(CH_3)_3 + D_2 \rightarrow H_2DB_3N_3(CH_3)_3 + HD \qquad (2)$$
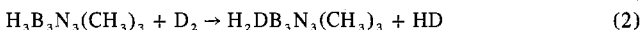
in the presence of DBF_2 is accelerated. Preparation of moderately pure $D_3B_3N_3(CH_3)_3$ samples was achieved by the following procedure. A mixture containing $H_3B_3N_3(CH_3)_3$, DBF_2, BF_3, and D_2 at pressures of 8, 18, 52, and 144 mm, respectively, was allowed to react in an 80-ml stainless steel vessel. After the initial reaction period of 6 h, the reaction mixture was replenished with pure D_2 (350 mm), allowed to react for 13.5 h, replenished again with pure D_2 (374 mm), and allowed to react for 19 h prior to ir and mass spectral analysis. The 10.2-eV photon impact mass spectrum of the B-deuterated N-trimethylborazine obtained by this procedure is shown in Table V. Comparison of the mass spectral intensity patterns of the deuterated product with those for the pure $H_3B_3N_3(CH_3)_3$ (Table V) indicates the sample is at least 97% enriched in deuterium atoms. The ir spectrum obtained from the deuterated sample (Figure 1) shows that the molecule is deuterated extensively at the boron site (strong B–D stretching vibration at 1875 cm^{-1}). The weak band at 2480 cm^{-1} which may be due to the B–H stretching vibrations places an upper limit of about 5% on residual hydrogenated borazine.
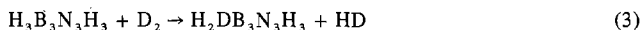
Moderately pure *B*-trideuterio-*N*-triethylborazine was prepared by allowing several drops of liquid $H_3B_3N_3(C_2H_5)_3$ (vapor pressure at 298 K is ~ 2 mm) to react with a mixture
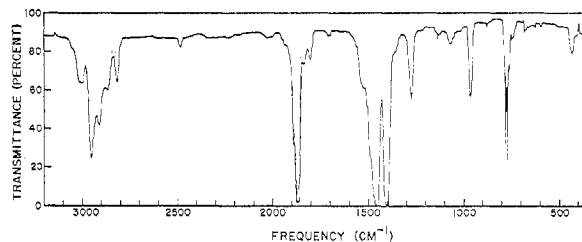
Figure 1. Infrared spectrum of B-deuterated *N*-trimethylborazine at a pressure of 8 mm.
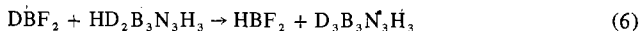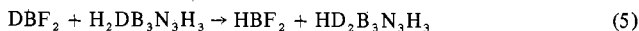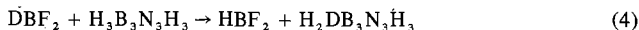
containing DBF_2, BF_3, and D_2 at pressures of 37, 70, and 270 mm, respectively, in a 500 ml Pyrex vessel. After the reaction had proceeded for 22 h, the reacted deuterium was removed from the mixture and replaced by pure deuterium ($P_{D_2} \approx 300$ mm). This process was repeated three times at intervals of 27, 48, and 120 h. The 10.2-eV photon impact spectra of $H_3B_3N_3(C_2H_5)_3$ and the B-deuterated *N*-triethylborazine obtained are shown in Table V. We note that the relative intensities of peaks in the parent regions of the two compounds are essentially identical, indicating that the D-enriched sample is better than 95% deuterated on an atomic basis.

Discussion

The mechanism for the formation of $D_3B_3N_3H_3$ in DBF_2–$H_3B_3N_3H_3$–D_2 mixtures is complicated by competing and sequential steps involving reaction (1), the exchange reaction

$$H_3B_3N_3H_3 + D_2 \rightarrow H_2DB_3N_3H_3 + HD \qquad (3)$$

and the three-step exchange process

$$DBF_2 + H_3B_3N_3H_3 \rightarrow HBF_2 + H_2DB_3N_3H_3 \qquad (4)$$

$$DBF_2 + H_2DB_3N_3H_3 \rightarrow HBF_2 + HD_2B_3N_3H_3 \qquad (5)$$

$$DBF_2 + HD_2B_3N_3H_3 \rightarrow HBF_2 + D_3B_3N_3H_3 \qquad (6)$$

The bimolecular rate constant reported for reaction 1 is $k(1)$ = $(7.4 \pm 2.0) \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} at 298 K.[2] Our data indicate that the rate constant for reaction 3 could be about 2 orders of magnitude less than $k(1)$ if reaction 3 is treated by a second-order rate expression. However, regardless of the order for reaction 3, this competing step is too slow under our experimental conditions to control the extent of H–D exchange with borazine. Reaction 4 and, presumably, reactions 5 and 6 are faster than (3) under all of the experimental conditions tested. Thus we conclude that the rate of H–D exchange with borazine is controlled by the speed of reaction 1. The reaction sequence for deuteration of $H_3B_3N_3(CH_3)_3$ follows a similar analysis. A multicentered intermediate involving bridging hydrogens
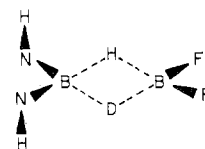
may explain why reactions 4–6 proceed by direct processes involving exchange exclusively at boron sites.

Advantages of this new procedure for preparing B-deuterated borazine derivatives over the photochemical method include the general convenience of working with moderately large samples of material under room-temperature reaction conditions and the absence of competing radical reactions[11] that may diminish the yield of desired product.

References and Notes

(1) T. D. Coyle, J. Cooper, and J. J. Ritter, *Inorg. Chem.*, **7**, 1014 (1968).
(2) P. M. Curtis and R. F. Porter, *Chem. Phys. Lett.*, **37**, 153 (1976).
(3) L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).
(4) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 981 (1969).
(5) A. DeStefano and R. F. Porter, *Inorg. Chem.*, **14**, 2882 (1975).
(6) M. P. Nadler and R. F. Porter, *Inorg. Chem.*, **8**, 599 (1969).
(7) G. H. Dahl and R. Schaeffer, *J. Am. Chem. Soc.*, **83**, 3034 (1961).
(8) K. Niedenzu, W. Sawodny, H. Watanabe, J. Dawson, T. Totani, and W. Weber, *Inorg. Chem.*, **6**, 1453 (1967).
(9) A. Kaldor and R. F. Porter, *Inorg. Chem.*, **10**, 775 (1971).
(10) R. F. Porter and J. J. Solomon, *J. Am. Chem. Soc.*, **93**, 56 (1971).
(11) L. J. Turbini, T. J. Mazanec, and R. F. Porter, *J. Inorg. Nucl. Chem.*, **37**, 1129 (1975).

Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

Isotopic Exchange and Substitution Reactions of Sulfitopentaamminecobalt(III) and cis-Disulfitotetraamminecobalt(III). Direct Evidence for the Specific Trans-Labilizing Influence of the Sulfito Ligand

Lynne Richards and Jack Halpern*[1]

The S-bonded sulfito ligand ($SO_3{}^{2-}$) has been reported to exert a marked trans-labilizing influence in a variety of cobalt(III) complexes.[2-7] Evidence for such an influence has been deduced from either (i) synthetic studies in which it was found that only the ligands trans to $SO_3{}^{2-}$ are readily replaced by other ligands[4,5,8] or (ii) the observation of enhanced rates of substitution for complexes containing $SO_3{}^{2-}$ ligands.[2,3,6,7] In some instances, kinetic studies have provided evidence for a limiting S_N1 mechanism for the substitution reactions of such complexes.[2,3,6,7]

While the results of the studies cited above can be accommodated most plausibly in terms of explanations involving a specific trans-labilizing influence of the sulfito ligand, such an interpretation is not in every case unequivocal. In some cases, at least, the observations are also consistent with a general labilizing influence of the sulfito ligand, the formation of the monosubstituted trans product (e.g., [*trans*-Co-$(NH_3)_4(SO_3)(H_2O)$]$^+$ from [Co$(NH_3)_5(SO_3)$]$^+$ [3] and [*trans*-Co$(CN)_4(SO_3)(H_2O)$]$^{3-}$ from [*trans*-Co$(CN)_4$-$(SO_3)(NH_3)$]$^{3-}$ [6]) being thermodynamically, rather than purely kinetically, favored. In order to distinguish between these two possibilities and establish unequivocally whether $SO_3{}^{2-}$ exhibits a specific trans-labilizing influence in cobalt(III) complexes, two investigations were undertaken, namely, (1) determination of the extent of exchange of [Co$(NH_3)_5(SO_3)$]$^+$ with $^{15}NH_3$[9] and (2) examination of the substitution reactions of [*cis*-Co$(NH_3)_4(SO_3)_2$]$^-$ with $^{15}NH_3$ and with other ligands. The results of these studies, reported in this paper, do serve to confirm unambiguously the specific trans-labilizing influence of the sulfito ligand.

Experimental Section

[Co$(NH_3)_5(SO_3)$]$_2SO_3\cdot2H_2O$ (1) and NH$_4$[*cis*-Co$(NH_3)_4$-$(SO_3)_2$]$\cdot3H_2O$ (2) were prepared and isolated according to literature procedures.[4,10] Anal. Calcd for **1**: Co, 20.9; S, 17.0; O, 31.2. Found: Co, 20.6; S, 16.8; O, 30.9. Calcd for **2**: S, 17.8; N, 19.5; H, 6.2. Found: S, 17.9; N, 19.4; H, 6.2.

[Co$(NH_3)_4(^{15}NH_3)(SO_3)$]$_2SO_3\cdot H_2O$ and NH$_4$[*cis*-Co$(NH_3)_2$-$(^{15}NH_3)_2(SO_3)_2$]$\cdot3H_2O$ were prepared by dissolving the corresponding

Table I. Exchange of [Co$(NH_3)_5(SO_3)$]$^+$ and [*cis*-Co$(NH_3)_4(SO_3)_2$]$^-$ with $^{15}NH_3$

Complex	Amt, mmol	Vol of 1.2 M $^{15}NH_3$ soln,^{a} ml	No. of NH_3 ligands exchanged^c
[Co$(NH_3)_5SO_3$]$^+$	0.07	2.0	1.21
	0.07	2.0	1.18
	0.07	2.0	1.18
	0.07	2.0	0.96
	0.14	1.0	1.05
	0.035	4.0	0.99
	0.07	2.0^b	0.98
		Mean	1.08 ± 0.1
[*cis*-Co$(NH_3)_4(SO_3)_2$]$^-$	0.06	2.0	2.33
	0.06	2.0	1.97
	0.06	2.0	2.31
	0.06	2.0	1.70
	0.03	4.0	1.98
	0.03	4.0	1.92
	0.06	2.0^b	1.70
	0.06	2.0^b	1.63
		Mean	1.94 ± 0.2

^{a} 49% $^{15}NH_3$ enrichment unless otherwise noted. ^{b} 12.5% $^{15}NH_3$ enrichment. ^{c} After approximately 10 min at 25 °C.

unlabeled salts in aqueous solutions of $^{15}NH_3$. Following equilibration for approximately 10 min, the labeled products were isolated, washed with ethanol and ether, and dried.

$^{15}NH_4NO_3$, containing 49% $^{15}NH_4{}^+$, was obtained from Nuclear Equipment Chemical Corp. and analyzed mass spectrometrically. An aqueous solution of $^{15}NH_3$ (1.2 M, pH 11–12) was prepared by distilling a solution of 1 g of $^{15}NH_4NO_3$ in 10 ml of 1 M NaOH and collecting the distillate in distilled water.

NaOBr was prepared by slowly adding Br_2 to an aqueous solution of NaOH (40 wt %) at 0 °C. The resulting solution was stored at 0 °C.

$NaClO_4$ was prepared by neutralizing an aqueous $HClO_4$ solution with reagent grade Na_2CO_3. The resulting solution was boiled to remove CO_2, filtered while hot, and analyzed by evaporating aliquots at 140 °C to constant weight.

Determinations of ^{15}N content were made mass spectrometrically using an AEI MS9 dual-focus mass spectrometer. NH_3 was liberated from the complex by adding 1 M NaOH, distilling the resulting mixture, and collecting the distillate in 0.25 M H_2SO_4. Argon was bubbled through the solution during distillation to ensure complete liberation of NH_3. The distillate solution was placed in one arm of a Y-tube. A solution of NaOBr was placed in the other arm and the solutions were frozen by immersion in liquid nitrogen. The system was evacuated to below 5 μ for 15 min. To convert the NH_3 to N_2, the solutions were allowed to melt and were mixed. When N_2 liberation ceased, the solution was frozen and all of the N_2 was introduced into the mass spectrometer. The peak heights corresponding to $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ were measured and the percent of ^{15}N was computed. In each case the known amount of nitrogen initially present agreed with the amount recorded by the mass spectrometer.

The kinetics of the substitution reactions were determined at 25.0 °C in solutions in which the ionic strength was held constant at 1.05 M with $NaClO_4$. The reactions were followed spectrophotometrically using a stopped-flow spectrometer in those cases where the rate was too fast for conventional measurement.

Results and Discussion

The results of experiments on the exchange of [Co-$(NH_3)_5SO_3$]$^+$ and [*cis*-Co$(NH_3)_4(SO_3)_2$]$^-$ with $^{15}NH_3$ are summarized in Table I.

The observation that only *one* (1.08 ± 0.10) NH_3 ligand in [Co$(NH_3)_5SO_3$]$^+$ exchanges with $^{15}NH_3$ demonstrates unequivocally the specific trans-labilizing influence of the $SO_3{}^{2-}$ ligand. The product of this exchange reaction must be the specifically trans-labeled complex [*trans*-Co$(NH_3)_4$-$(^{15}NH_3)(SO_3)$]$^+$ and the reaction, accordingly, has provided a unique route for the preparation of this and other specifically trans-$^{15}NH_3$-labeled pentaamminecobalt(III) complexes.[11]