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Borazines: Molecules Which Do Not Exhibit Hydrogen Bonding

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Received May 10, 1977 AIC70338R

A series of B-monosubstituted borazines $H_2XB_3N_3H_3$ (X = $N(CH_3)_2$, OCH_3, CH_3CO_2, and Cl) have been studied intensively in order to identify properties consistent with hydrogen bonding. Our data include comparisons of infrared spectra of low-pressure gas-phase samples with spectra for the condensed phases at low temperatures, variable temperature, and concentration-dependent ^{1}H-NMR studies and physical properties. The investigation of the infrared and NMR spectra of $B(NHCH_3)_3$ with added $N(C_2H_5)_3$ is also presented. Our results are consistent with the conclusion that hydrogen bonding between a hydrogen bonded to a nitrogen in a substituted borazine ring and a basic atom does not occur or is exceedingly weak. The major reason that borazines and $B(NHCH_3)_3$ do not exhibit properties consistent with hydrogen bonding is the hydrogen bonded to the nitrogen has insufficient partial positive charge. The origin of this behavior is related to π bonding and electronegativity effects.

Hydrogen bonding is considered to be responsible for some characteristic but unusual macroscopic and spectroscopic properties of compounds which have a hydrogen bonded to an electronegative atom. The borazines have the potential for hydrogen bonding as they have N–H bonds. However, the existence of hydrogen bonding in or between borazine molecules has never been confirmed nor denied by careful experiments. We felt that the results from a study designed to identify hydrogen bonding could also be used to aid our understanding of the bonding in borazines. There are very few, if any, molecules with N–H bonds which do not form hydrogen bonds under appropriate conditions, provided an interaction is not prevented by steric effects. Thus, if borazine molecules did not exhibit properties consistent with hydrogen bonding, there could be two fundamental explanations: the hydrogen bonded to nitrogen might not have sufficient positive charge, or the nitrogen atoms might not have sufficient basic character. Hydrogen bonding would not be expected to be prevented by steric effects in the planar borazine molecule.

The question of the existence of hydrogen bonding in borazine chemistry has had a mixed history. Some researchers have used hydrogen bonding to account for observed properties, while others have considered intermolecular hydrogen bonding to be either very weak or absent. There have not been any papers which have been concerned with intramolecular hydrogen bonding in borazines. In a study of the separations of borazines by chromatography,[1] Phillips, Powell, and Semlyen observed that borazines which have free N–H groups are retarded by Carbowax more than borazines without N–H groups. These workers attributed their observations to hydrogen bonding between borazine NH groups and the oxygen atoms of Carbowax. Other researchers used hydrogen-bonded interactions to account for the unusual ^{35}Cl NQR spectrum[2] of $Cl_3B_3N_3H_3$ which had two lines instead of the one expected. In contrast, Kaldor and Porter[3] considered the close correlation of the gaseous and liquid Raman spectra of $H_3B_3N_3H_3$ surprising, because it indicated to them that in liquid borazine there was very little association. Other workers also concluded that the borazines, $F_3B_3N_3H_3$,[4] $Cl_3B_3N_3H_3$,[5] $Br_3B_3N_3H_3$,[5] $(OCN)_3B_3N_3H_3$,[6] and $(SCN)_3B_3N_3H_3$,[6] interact weakly in the solid state. However, only Lappert and Pyszora[6] have attempted to account for the observation that intermolecular hydrogen bonding is either very weak or absent in these borazines. They considered that the boron–nitrogen double-bond character in the ring makes the nitrogen atoms insufficiently basic to have hydrogen bonding. Alternative explanations for the lack of hydrogen bonding could have been presented but were not. For example π bonding between a substituent and the borazine ring might prevent the substituent from being the primary basic site for hydrogen bonding. Another possibility is that the hydrogen bonded to the nitrogen of the ring does not have sufficient positive character to lead to those interactions called hydrogen bonds. There are many unanswered questions regarding hydrogen bonding in borazines.

In this paper we report the results of our studies which were designed to identify properties consistent with hydrogen bonding in borazines. Our results are consistent with the conclusion that hydrogen bonding between a hydrogen bonded to nitrogen in a substituted borazine ring and a basic atom does not occur or is exceedingly weak. The major reason that borazines do not exhibit properties consistent with hydrogen bonding is the hydrogen bonded to the nitrogen has insufficient partial positive charge. We have intensively investigated the properties of monosubstituted borazine derivatives $H_2XB_3N_3H_3$ (X = $N(CH_3)_2$, OCH_3, CH_3CO_2, and Cl) as well as reviewed the data for some other borazines. These derivatives have (1) basic atoms bonded directly to the borazine ring, (2) basic atoms separated by intervening atoms, or (3) the possibility for intramolecular hydrogen bonding through the formation of a six-membered ring as in $H_2(CH_3CO_2)B_3N_3H_3$. In addition we have studied the properties of an aminoborane, $B(NHCH_3)_3$. Our data include comparisons of infrared spectra of low-pressure gas-phase samples with spectra for the condensed phases at low temperatures, variable temperature, and concentration-dependent ^{1}H NMR studies and physical properties. The investigation of the infrared and NMR spectra of $B(NHCH_3)_3$ with added $N(C_2H_5)_3$ is also informative.

For systems which exhibit hydrogen bonding, the frequencies of the NH stretching and bending vibrations are sensitive to the state of molecular aggregration. Usually, the NH stretching frequency decreases and the NH bending frequency increases as the extent of hydrogen bonding increases upon going from the gas to the condensed phase. Weak hydrogen bonding is considered to cause changes of about 200 cm^{-1} for stretching frequencies and 25 cm^{-1} for bending frequencies.[7] The spectral data for the NH stretching and bending modes are given in Table I. The NH stretching frequencies decreased by about 50 cm^{-1} upon going from the gas to the condensed phase. However, many other, but not all, bands in the spectra also decreased in frequency by about 30 cm^{-1}. Furthermore, the decrease in the NH stretching frequency does not depend upon the substituent, as one would expect, if hydrogen bonding were responsible. In addition the appearances of the spectra of the condensed phases do not indicate hydrogen bonding. The NH stretching bands for the condensed phases are very sharp as they have average widths at half-height of 20 ± 3 cm^{-1} compared to 23 ± 3 cm^{-1} for the gas phase. Our spectral observations upon warming the cell from low temperatures are also informative. We observed the spectrum to change abruptly rather than gradually. These observations might suggest that minor structural changes or structural constraints upon molecular motion could be responsible for spectral changes. It is also interesting to note

Table I. Infrared Spectral Data (cm^{-1})

H_2XB_3-N_3H_3, X =	NH stretching frequencies for phase		NH bending frequencies for phase	
	Gas[a]	Condensed[b]	Gas[a]	Condensed[b]
H	3476	3427	710	709
F	3496	*c*	704	*c*
Cl	3485, 3475	3440, 3430	707	700
Br	3495	*c*	711	*c*
OCH_3	3486	3437	687	672
$N(CH_3)_2$	3492	3448, 3418	662	646
NH_2[d]	3482	3440 (l)[b]	677	669 (l)[b]
OCN	3480	3440	707	707
SCN	3472	3442 (l)[b]	719	712 (l)[b]
CN	*c*	3403 (m)[b]	*c*	707 (m)[b]
CH_3CO_2	3486, 3466	3445, 3427, 3415	686	655
CH_3SO_3	*c*	3435, 3052	*c*	717

[a] Pressure of samples was 3–5 mm in a 10-cm cell. [b] Spectra observed in low-temperature cell with cold finger at −196 °C except where indicated as liquid (l) or mull (m) at room temperature. [c] Data not available. [d] Data from R. F. Porter and E. S. Yeung, *Inorg. Chem.*, 7, 1306 (1968).

Table II. Variable-Temperature NMR Data[a] (Solvent, Toluene-d_8)

H_2XB_3-N_3H_3, X =	δ =			
	Ortho NH		Para NH	
	20 °C	−82 °C	20 °C	−82 °C
H	5.32	5.14	5.32	5.14
Cl	5.10	4.81	5.10	*b*
OCH_3	4.49	4.82	4.97	5.10
CH_3CO_2	5.45	5.70	5.45	5.70
$N(CH_3)_2$	4.29	4.41	4.77	4.98

[a] All data are given in ppm downfield from TMS. [b] Resonance NH was not resolved but appeared as a bump on the downfield side of the line.

Table III. Vapor-Pressure Data[9]

$H_2XB_3N_3H_3$		$H_2XB_3N_3H_3$	
X =	P(0 °C), mm	X =	P(24 °C), mm
F	35.6	F	116
Cl	8.4	OCH_3	6
Br	<1	$N(CH_3)_2$	2

Table IV. ^1H NMR Data for $B(NHCH_3)_3$[a] (Solvent, CCl_4)

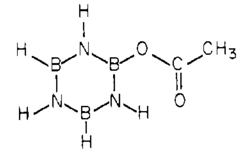
% by wt	NH	CH
46.1	1.48	2.45
25.1	1.44	2.42, 2.48
7.2	1.42	2.46, 2.50
6.5 + 7.9% $N(C_2H_5)_3$	1.43	*b*

[a] All resonances are given in ppm downfield from TMS. [b] Resonance obscured by those of $N(C_2H_5)_3$.

that the absolute frequency (NH stretch) is not significantly influenced by the single substituent in these monosubstituted borazines. The dependence of the NH bending frequencies[3] (out-of-plane) on phase does not indicate hydrogen bonding in the condensed phase either. If hydrogen bonding occurred, the frequency should have increased, but it decreased (or remained constant) in all cases upon going from the gas to the condensed phase. All of our infrared data suggest that hydrogen bonding is either absent or exceedingly weak in borazines.

Our ^1H NMR data are also consistent in demonstrating only very weak, if any, hydrogen bonding for the borazine derivatives. In variable temperature studies (20 to −82 °C), Table II, the chemical shift of the NH protons moved downfield for $H_2(CH_3O)B_3N_3H_3$, $H_2(CH_3CO_2)B_3N_3H_3$, and $H_2[N(CH_3)_2]B_3N_3H_3$ while the lines for $H_3B_3N_3H_3$ and $H_2ClB_3N_3H_3$ moved upfield upon cooling. The maximum observed downfield shift was only 0.33 ppm for the ortho NH protons of $H_2(CH_3O)B_3N_3H_3$. (The NH lines of borazine compounds are broad due to quadrupolar effects. Consequently there is a ±0.05 ppm error in estimating chemical shifts.) One might have expected $H_2[N(CH_3)_2]B_3N_3H_3$ to exhibit properties consistent with the most hydrogen bonding but the downfield shift was only 0.12 ppm. Compounds which are involved in hydrogen bonding usually undergo changes in proton chemical shifts[7] on the order of 2–4 ppm. Thus, the small changes in chemical shifts that we observe could be due to exceedingly weak hydrogen bonds or they might be related to line broadening which results in part from relaxation effects involving the nuclear quadrupole moments of the high-spin nitrogen nucleus.[8] Other aspects of our ^1H NMR data are consistent with the absence of significant hydrogen bonding. Hydrogen-bonded systems usually undergo proton exchange. In contrast, there is no exchange that we can detect by NMR. Finally, the previous observations that NH chemical shifts are independent of concentration[8–11] in CCl_4 or $Si(CH_3)_4$ solutions over the concentration range from 10 to 95% confirm the absence of significant hydrogen bonding between borazine molecules. Additional studies of the spectral properties with added strong bases or weak acids were prevented as decomposition or reaction was observed.

The NMR spectrum of $H_2(CH_3CO_2)B_3N_3H_3$ is particularly informative for confirming the absence of significant hydrogen bonding. The acetato derivative has the potential for hydrogen bonding between the hydrogen bound to nitrogen and (1) a ring nitrogen, (2) the acetate oxygen atom bound to the boron atom of the ring, or (3) the double-bonded oxygen of the carbonyl group. Furthermore, there is the potential for either inter- or intramolecular hydrogen bonding. Intramolecular hydrogen bonding would result in the formation of a six-membered ring. All of our spectra data indicate that the two NH groups ortho to the acetato group are equivalent at temperatures down to −82 °C, the lowest we could study.



Neither low-temperature ^1H NMR nor infrared spectral data indicate any nonequivalence of the ortho NH groups. In fact the ortho and para NH protons are magnetically equivalent and move downfield by only 0.25 ppm upon cooling from +20 to −82 °C in toluene-d_8. Qualitatively identical observations were made for a cyclopentane solution $H_2(CH_3CO_2)B_3N_3H_3$. The ortho and para NH protons are magnetically equivalent and move downfield by 0.19 ppm upon cooling from +20 to −33 °C, the lowest temperature we could achieve because of solubility.

The vapor-pressure data for series of borazines do not indicate properties indicative of hydrogen bonding. The changes in vapor pressures for appropriate series of compounds (Table III) are best explained by changes in dispersion forces rather than hydrogen bonding. Similar trends have been observed for the trihaloborazines.[12] It is of interest to note that $F_3B_3N_3H_3$ has no liquid phase at pressures less than 1 atm.[12]

In order to learn more about the apparent lack of hydrogen bonding in boron–nitrogen systems, we also studied the spectral properties of $B(NHCH_3)_3$ under a variety of conditions. The ^1H NMR spectrum of $B(NHCH_3)_3$ in CCl_4 has no significant dependence upon concentration over the range of 7.2 to 46.1

wt % (Table IV). Even stronger evidence for the absence of hydrogen bonding for $B(NHCH_3)_3$ is shown by our NMR data for a solution which had 6.5% $B(NHCH_3)_3$ and 7.9% $N(C_2H_5)_3$ in CCl_4. The NH chemical shift was 1.43 ppm compared to 1.42 ppm for the 7.2% solution without the added strong base, $N(C_2H_5)_3$. Our infrared data are just as conclusive in demonstrating the absence of hydrogen bonding. The spectrum of $B(NHCH_3)_3$ in the condensed phase in our low-temperature cell indicated the NH stretching frequency to be a sharp band at 3407 cm^{-1}. Upon adding $N(C_2H_5)_3$ to the sample, the NH stretching frequency remained a sharp band but moved to 3402 cm^{-1}, a strong indication for no hydrogen bonding. For comparison, the NH stretching frequency for the gas phase of $B(NHCH_3)_3$ occurs at 3464 cm^{-1}. It is interesting that the difference in frequency between gas and condensed phase is about the same as for borazines, about 50 cm^{-1}.

Borazines and aminoboranes exhibit properties which are consistent with the absence of significant hydrogen bonding. According to all of the available data in borazine chemistry, hydrogen bonding does not occur because the hydrogen bonded to the ring nitrogen does not have sufficient partial positive charge to lead to those interactions called hydrogen bonds. This lack of sufficient partial positive charge on the hydrogen bonded to the ring nitrogen atoms is related to the existence of π bonding in the borazine ring. As has been pointed out previously by Hoffmann[13] π bonding *initially* gives the boron atoms a partial negative charge and nitrogen a partial positive charge. However, the nitrogen atoms compensate for their donation of π-electron density by withdrawing electron density through the σ system. Thus, a small partial negative charge is maintained on nitrogen,[13] and the hydrogen bonded to nitrogen has less positive charge than a normal NH. Similarly, the hydrogen bonded to boron has less negative charge than a normal BH. The decreased partial negative charge on the BH has been experimentally demonstrated by reactivity studies.[10,14] The lack of properties indicative of hydrogen bonding is consistent with the decreased partial positive charge on the NH. There is no evidence to suggest that the absence of significant hydrogen bonding is due to steric hindrance or the absence of an appropriate basic site. In the derivative $H_2[N(CH_3)_2]B_3N_3H_3$ the dimethylamino group is sufficiently basic[15] to form a stable adduct with B_2H_6. Thus, it should be basic enough to give some hydrogen-bonded interactions if there was an NH with sufficient positive charge. The acetato derivative provides another example. In $H_2[CH_3CO_2]B_3N_3H_3$, there are two potentially basic oxygen atoms. The oxygen bonded to the boron of the borazine ring might loose some electron density through π bonding to the borazine ring. However, the carbonyl oxygen of the acetate group should have sufficient basicity for hydrogen bonding, if there were a hydrogen with sufficient positive charge. Carbonyl oxygen atoms in acetates and even amides are known to form hydrogen bonds.[7] Furthermore, an intramolecular hydrogen bond between an NH and the carbonyl oxygen could be formed through the least loss of entropy for the system as a simple six-membered ring would exist. We have no evidence for intramolecular hydrogen bonding in $H_2(CH_3CO_2)B_3N_3H_3$, even at low temperatures. We regret that hydrogen-bonding studies with added bases or other protonic acid systems are impossible because of complicating reactions which destroy or change the borazines.

The properties of $B(NHCH_3)_3$ are also consistent with the absence of significant hydrogen bonding. These observations greatly aid our understanding of the origins of this most unusual behavior. Our conclusion is that the absence of hydrogen bonding in this aminoborane is due to the absence of protons with sufficient positive charge, a consequence of π bonding. If π-electron density is donated from nitrogen to boron, there must be withdrawal of electron density by nitrogen through the σ system to maintain a partial negative charge on nitrogen.[13] Consequently, the hydrogen bonded to nitrogen in boron–nitrogen π-bonded systems has less partial positive charge than a normal NH. The boron–nitrogen σ bond might be weakened but it is compensated by the π bond and the resultant coulombic interactions. Our experiments with added $N(C_2H_5)_3$ further demonstrate that the absence of significant hydrogen bonding in boron–nitrogen π-bonded systems is related to the lack of a hydrogen with sufficient positive charge rather than an appropriate base site. An altenative explanation for the absence of hydrogen bonding in the $B(NHCH_3)_3 \cdot N(C_2H_5)_3$ system might be related to steric effects. However, complete steric hindrance to hydrogen bonding would require a planar molecule. Aminoboranes with nitrogen–hydrogen substituents should have particularly low barriers to rotation. In addition, the observation that amino-group exchange reactions occur readily would not be consistent with large amounts of steric hindrance or the lack of basic sites in the molecule.

Boric acid molecules are considered to have some π bonding but also show properties indicative of hydrogen bonding. Our spectroscopic studies also confirm hydrogen bonding in $B(OH)_3$. These observations are consistent with our hypothesis that the absence of hydrogen bonding in boron–nitrogen π-bonded systems is due to the absence of a hydrogen with sufficient positive charge. The boron–oxygen bond compared to the boron–nitrogen bond should have a much smaller degree of π bonding, due to the higher electronegativity of oxygen compared to nitrogen. Thus, less withdrawal of electron density through the σ system is needed to maintain the partial negative charge on oxygen, and consequently the hydrogen bonded to oxygen in $B(OH)_3$ has a much higher positive charge and is capable of hydrogen bonding.

B-monosubstituted borazines and the aminoborane $B(NHCH_3)_3$ exhibit most unusual behavior. These classes of compounds have NH bonds but exhibit macroscopic and spectroscopic properties indicative of no significant hydrogen bonded interactions.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a standard vacuum system. Solvents were dried and purified by conventional means. The borazines, $H_2ClB_3N_3H_3$,[16] $H_2(CH_3CO_2)B_3N_3H_3$,[10] $H_2(CH_3O)B_3N_3H_3$[9] and $H_2[N(CH_3)_2]B_3N_3H_3$,[9] and $B(NHCH_3)_3$,[17] were prepared according to previously described procedures. Purity of samples was confirmed by vapor-pressure measurements and spectral data.

Infrared Spectra. The infrared spectra were recorded in the range of 4000–250 cm^{-1} using a Perkin-Elmer Model 457 spectrometer. Gas-phase spectra were observed from samples at 3–5-mm pressure in a 10-cm cell equipped with KBr optics. Condensed phase spectra were observed using a low-temperature cell.[18] The sample was cooled by a cold finger which contained liquid nitrogen.

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz using a JEOLCO MH-100 spectrometer equipped with variable-temperature capability. In all variable-temperature studies, the solvent for the 20% borazine solutions was toluene-d_8.

Registry No. $H_3B_3N_3H_3$, 6569-51-3; $H_2FB_3N_3H_3$, 29601-24-9; $H_2ClB_3N_3H_3$, 15061-65-1; $H_2BrB_3N_3H_3$, 28019-98-9; $H_2(OCH_3)B_3N_3H_3$, 18277-68-4; $H_2(N(CH_3)_2)B_3N_3H_3$, 15127-53-4; $H_2(OCN)B_3N_3H_3$, 34154-39-7; $H_2(SCN)B_3N_3H_3$, 33926-68-0; $H_2(CN)B_3N_3H_3$, 33926-69-1; $H_2(CH_3CO_2)B_3N_3H_3$, 33926-70-4; $H_2(CH_3SO_3)B_3N_3H_3$, 33926-71-5; $B(NHCH_3)_3$, 7397-44-6.

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Molecular Addition Compounds. 3. Redistribution of Borane–Methyl Sulfide with Boron Trichloride–Methyl Sulfide and Boron Tribromide–Methyl Sulfide as Convenient Routes to the Corresponding Haloborane–Methyl Sulfides[1,2]

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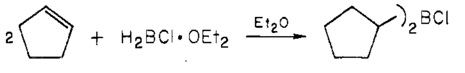
Received March 18, 1977 AIC70217R

Representative haloborane–methyl sulfide complexes, $Cl_3B{\cdot}SMe_2$ and $Br_3B{\cdot}SMe_2$, undergo rapid redistribution with $H_3B{:}SMe_2$ providing a simple, general synthetic route to the substituted haloborane derivatives $HBCl_2{\cdot}SMe_2$, $H_2BCl{\cdot}SMe_2$, $HBBr_2{\cdot}SMe_2$, and $H_2BBr{\cdot}SMe_2$. However, $F_3B{\cdot}SMe_2$ does not show such redistribution. In contrast to the corresponding etherates, these compounds are remarkably stable. In CCl_4 solution, at room temperature, $F_3B{\cdot}SMe_2$, $Cl_3B{\cdot}SMe_2$, and the chloroborane complexes exchange rapidly with added SMe_2, but $Br_3B{\cdot}SMe_2$ and the bromoboranes do not exhibit such exchange under these conditions. The unusual chemical shifts of methyl protons in the ^1H NMR spectra of boron trihalide–methyl sulfide in benzene solution are also discussed.

Introduction

Diborane readily undergoes disproportionation with boron trichloride in the presence of ethers to give the corresponding chloroborane etherates,[2] which have proven to be valuable hydroborating agents, providing simple synthetic routes to R_2BCl and $RBCl_2$ derivatives[4] (eq 1, 2). However, they suffer from several disadvantages. First, the syntheses of chloroborane etherates proceed from lithium borohydride,[4] a relatively expensive reagent. Second, the products are relatively unstable. Thus chloroborane–ethyl ether can be prepared in dilute ethyl ether, but loses diborane when the excess ether is removed. Neat dichloroborane–ethyl ether can be prepared but undergoes relatively rapid decomposition on storage. Consequently, it must be synthesized and used shortly thereafter.



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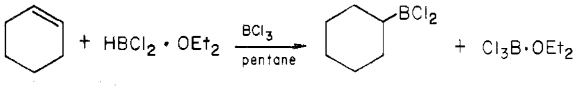

(2)

Stable addition compounds of haloboranes with amines have been prepared and characterized.[5-10] However, they do not possess the desired properties as hydroborating and reducing agents.[9,11] In view of the recent developments in the applications of dialkylchloroboranes and alkyldichloroboranes in organic syntheses,[12] it is highly desirable to have stable derivatives of haloboranes which could be conveniently used as hydroborating agents. Therefore, we directed our efforts to synthesize new addition compounds of haloborane which would be stable at room temperature but would still possess the desirable hydroboration properties.

During the past few years, a great deal of progress has been made in the preparation and spectral characterization of the molecular addition compounds of mixed boron trihalides (BX_2Y). The amine complexes are stable,[13-15] whereas the corresponding dimethyl ether adducts are unstable to disproportionation.[16] The methyl sulfide complexes have also been characterized by ^1H NMR.[17] Therefore, it appeared reasonable to explore the methyl sulfide complexes of haloboranes as possible derivatives with the desired stability and characteristics.

Borane–methyl sulfide is a remarkably stable borane addition compound and a useful hydroborating agent.[18-21] The preparation and characterization of $F_3B{\cdot}SMe_2$ and $Cl_3B{\cdot}SMe_2$ in solution were previously reported.[22,23] Recently the methyl sulfide complexes of BCl_3, BBr_3, and BH_3 have been prepared in pure form in good yields.[24] However, a search of the literature failed to reveal any evidence for the preparation and characterization of haloborane–methyl sulfide complexes. Accordingly, we undertook to establish whether $F_3B{\cdot}SMe_2$, $Cl_3B{\cdot}SMe_2$, and $Br_3B{\cdot}SMe_2$ would undergo disproportionation with $H_3B{\cdot}SMe_2$ to provide relatively stable addition compounds of the corresponding haloboranes. While the detailed investigation of the synthetic applications of these haloborane–methyl sulfide complexes was in progress, the preparation of the iodoborane and bromoborane complexes was reported.[25] This makes iodoboranes also available for synthetic purposes, which is complementary to our work on chloroboranes and bromoboranes.

This paper reports the first preparation and characterization of $F_3B{\cdot}SMe_2$ in pure form and also a detailed study of the disproportionation reactions between boron trihalide–methyl sulfide and borane–methyl sulfide in different stoichiometric ratios leading to the preparation of various stable haloborane–methyl sulfide complexes. These complexes are characterized by ^1H NMR, ^{11}B NMR, and active hydride analysis.

Experimental Section

Materials. The reaction flasks and other glass equipment used for experiments were dried in an oven and assembled in a stream of dry