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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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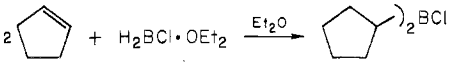
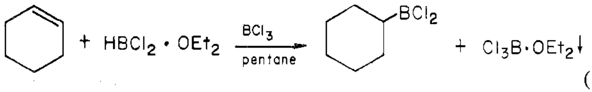
Representative haloborane–methyl sulfide complexes, $Cl_3B{\cdot}SMe_2$ and $Br_3B{\cdot}SMe_2$, undergo rapid redistribution with $H_3B{:}SMe_2$ providing a simple, general synthetic route to the substituted haloborane derivatives $HBCl_2{\cdot}SMe_2$, $H_2BCl{\cdot}SMe_2$, $HBBr_2{\cdot}SMe_2$, and $H_2BBr{\cdot}SMe_2$. 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.



(1)



(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

N_2 gas. All the reactions were carried out in N_2 atmosphere to protect the reactive boron compounds from air and moisture. The special experimental techniques used in handling air-sensitive materials are described elsewhere.[26] The BF_3 and BCl_3 obtained from Matheson Gas Co. and BBr_3 from Alfa-Ventron, certified >99% pure, were used directly.

The ^1H NMR spectra were recorded on Varian T-60 and the ^{11}B NMR on XL-100 instruments. The ^1H and ^{11}B NMR chemical shifts are in δ ppm with reference to Me_4Si and $BF_3{\cdot}OEt_2$ standards, respectively. All melting points are uncorrected and determined in evacuated, sealed capillary tubes using the Thomas Hoover capillary melting point apparatus.

Preparation of Boron Trihalide–Methyl Sulfide Complexes. (1) $F_3B{\cdot}SMe_2$. A 200-mL reaction flask[26] cooled in an ice bath was charged with 30 mL (25.07 g, 404 mmol) of SMe_2 and, while stirring the contents of the flask, BF_3 gas was passed in to saturation. A total of 28.3 g (417.6 mmol) was absorbed. The mixture was allowed to attain room temperature and excess BF_3 was passed through a mercury bubbler into a NaOH solution. A quantitative yield of the 1:1 complex (BF_3:SMe_2 = 1.03:1) was obtained as a colorless liquid, indefinitely stable at 25 °C under N_2, fuming in air: ^1H NMR δ 2.21 (CCl_4, singlet), 1.53 (benzene, singlet); ^{11}B NMR δ −2.3 (singlet).

Free SMe_2 shows ^1H NMR δ 2.06 (CCl_4) and 1.78 (benzene), both singlets.

(2) $Cl_3B{\cdot}SMe_2$. In a 500-mL reaction flask cooled in ice bath, 75.0 mL (62.7 g, 1 mol) of SMe_2 and 150 mL of pentane were placed. From the cylinder, 45.0 mL (61.4 g, 523 mmol) of BCl_3 was condensed into a graduated tube maintained at −20 °C with a liquid–solid CCl_4 bath. The BCl_3 was then allowed to distill slowly into the reaction flask, with the contents of the flask being stirred vigorously. The complex precipitated instantaneously. When all the BCl_3 had been transferred into the reaction flask, the mixture was brought to room temperature. Pentane and excess SMe_2 were pumped off (water aspirator, 15-mm pressure). The product was a white solid, 94.0 g (100% yield), mp 86–87 °C (lit.[24] 90 °C), ^1H NMR δ 2.51 (CCl_4, singlet) and 1.47 (benzene, singlet).

(3) $Br_3B{\cdot}SMe_2$. A 100-mL reaction flask cooled in an ice bath was charged with 14.9 mL (12.4 g, 200 mmol) of SMe_2 and 50 mL of pentane. While stirring the contents of the flask vigorously, 9.5 mL (25.34 g, 100 mmol) of liquid BBr_3 was added dropwise through a syringe (exothermic!). The flask was brought to room temperature and solvent pumped off. A white amorphous powder, 31.5 g (99% yield), was obtained, mp 106–107 °C (lit.[24] 108 °C), ^1H NMR δ 2.56 (CCl_4, singlet) and 1.51 (benzene, quartet, J = 3 Hz).

Preparation of Haloborane–Methyl Sulfide Complexes. (1) $HBCl_2{\cdot}SMe_2$. To 132 g (737 mmol, 5% excess) of the $Cl_3B{\cdot}SMe_2$ powder and 50 mL of SMe_2 taken in a 500-mL reaction flask was added 35.0 mL (350 mmol) of $H_3B{\cdot}SMe_2$ at 25 °C and stirred for 16 h. Excess SMe_2 was pumped off to afford 147 g (~100% yield) of a clear viscous liquid, ^1H NMR δ 2.42 (CCl_4, singlet) and ^{11}B NMR δ −2.2 (doublet, J_{BH} = 157 Hz). Hydrolysis[26] revealed that it is 8.12 M in active hydride.

(2) $HBBr_2{\cdot}SMe_2$. The procedure is the same as above but requires 12 h at 40 °C for completion of the reaction. The product is a colorless, viscous liquid (at 40 °C), ^1H NMR δ 2.48 (CCl_4, singlet) and ^{11}B NMR δ 7.3 (doublet, J_{BH} = 160 Hz). Hydrolysis indicated 7.8 M in active hydride.

(3) $H_2BCl{\cdot}SMe_2$. The procedure is the same as in (1), but $Cl_3B{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$ were mixed in a 1:2 molar ratio and stirred for 6 h at 25 °C. The resulting colorless viscous liquid shows ^1H NMR δ 2.34 (CCl_4, singlet) and ^{11}B NMR δ 6.7 (triplet, J_{BH} = 131 Hz). Small amounts (2–3%) of $HBCl_2{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$ were present as impurities. Even heating to 50 °C did not reduce the amounts of these species. The product was 18.0 M in active hydride as revealed by hydrolysis.

(4) $H_2BBr{\cdot}SMe_2$. The procedure is the same as in (3), except that $Br_3B{\cdot}SMe_2$ was used, and it was necessary to heat the mixture at 65 °C for 6 h to ensure completion of the reaction. No observable disproportionation takes place even in 12 h at 25 °C. The product is a clear liquid, ^1H NMR δ 2.38 (CCl_4, singlet), ^{11}B NMR δ 10.5 (triplet, J_{BH} = 132 Hz).

Results and Discussion

Boron Trihalide–Methyl Sulfide. The addition compounds were prepared by bringing together equimolar quantities of boron halides and methyl sulfide. Literature does not record the isolation of $F_3B{\cdot}SMe_2$ in pure form. We prepared it as a colorless liquid, stable at room temperature when stored under nitrogen. The preparations of $Cl_3B{\cdot}SMe_2$,[24] $Br_3B{\cdot}SMe_2$,[24] and $I_3B{\cdot}SMe_2$[25] have been previously described in the literature. These are white solids indefinitely stable at room temperature (under N_2).

Redistribution between $X_3B{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$. It was observed during this study that on mixing $H_3B{\cdot}SMe_2$ does not undergo redistribution with $F_3B{\cdot}SMe_2$. This corresponds to the behavior earlier observed for diborane and BF_3 in the presence of ethyl ether.[2] However, on mixing under appropriate conditions, $H_3B{\cdot}SMe_2$ reacted readily with $Cl_3B{\cdot}SMe_2$ and $Br_3B{\cdot}SMe_2$ to give the corresponding haloborane addition compounds.

$$H_3B{\cdot}SMe_2 + 2X_3B{\cdot}SMe_2 \rightarrow 3HBX_2{\cdot}SMe_2 \qquad (3)$$

$$2H_3B{\cdot}SMe_2 + X_3B{\cdot}SMe_2 \rightarrow 3H_2BX{\cdot}SMe_2 \qquad (4)$$

$HBCl_2{\cdot}SMe_2$. One part of $H_3B{\cdot}SMe_2$ was added to two parts of solid $Cl_3B{\cdot}SMe_2$ at 0 °C under nitrogen where no appreciable reaction was observed. Upon keeping the mixture at 25 °C, a slow exothermic reaction took place and the mixture became a thick slurry. The slurry was stirred for 24 h at 25 °C when it became a clear liquid. The product was characterized as $HBCl_2{\cdot}SMe_2$ by ^{11}B NMR and ^1H NMR. Whenever large amounts of $HBCl_2{\cdot}SMe_2$ were prepared for use in hydroboration studies, a 2–3% excess of $Cl_3B{\cdot}SMe_2$ was used in order to ensure the quantitative conversion of $H_3B{\cdot}SMe_2$ to the product.

$HBBr_2{\cdot}SMe_2$. Two parts of liquid BBr_3 were added to a mixture of one part of $H_3B{\cdot}SMe_2$ and two parts of SMe_2 at 0 °C and stirred at 40 °C for 12 h. A homogeneous liquid was obtained (at 40 °C) which was characterized as the desired $HBBr_2{\cdot}SMe_2$ (eq 5) by ^{11}B NMR and ^1H NMR. No other boron species were detected in significant amounts by ^{11}B NMR.

$$2BBr_3 + H_3B{\cdot}SMe_2 + 2SMe_2 \rightarrow 3HBBr_2{\cdot}SMe_2 \qquad (5)$$

$H_2BCl{\cdot}SMe_2$. Two parts of $H_3B{\cdot}SMe_2$ were added to one part of solid $Cl_3B{\cdot}SMe_2$ taken in a flask under nitrogen at 0 °C where little or no reaction was observed. However, warming the mixture to 25 °C resulted in a slow dissolution of the solid $Cl_3B{\cdot}SMe_2$. The mixture was stirred for 6 h at 25 °C. ^{11}B NMR and ^1H NMR spectroscopic examination of the product showed that it was >90% pure $H_2BCl{\cdot}SMe_2$ (eq 4, X = Cl). Small amounts of unconverted $HBCl_2{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$ were present as impurities in the product (as indicated by ^{11}B NMR). Heating the mixture to 50 °C did not reduce the amount of these two species.

$H_2BBr{\cdot}SMe_2$. One part of liquid BBr_3 was added to a mixture of two parts of $H_3B{\cdot}SMe_2$ and one part of SMe_2 at 0 °C and stirred at 25 °C. After 12 h reaction at 25 °C, the reaction product consisted of a mixture of $HBBr_2{\cdot}SMe_2$, $H_2BBr{\cdot}SMe_2$, and $H_3B{\cdot}SMe_2$ in the ratio 1:2:1 (as indicated by ^1H NMR). Almost quantitative conversion of the reactants to $H_2BBr{\cdot}SMe_2$ was achieved by heating the mixture at 65 °C for 6 h (eq 6). The product was characterized as $H_2BBr{\cdot}SMe_2$ by ^{11}B NMR and ^1H NMR. Only traces of $HBBr_2{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$ were detected in the product, which was >95% pure $H_2BBr{\cdot}SMe_2$.

$$2H_3B{\cdot}SMe_2 + BBr_3 + SMe_2 \rightarrow 3H_2BBr{\cdot}SMe_2 \qquad (6)$$

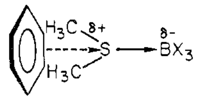
Neat $HBCl_2{\cdot}SMe_2$, $H_2BCl{\cdot}SMe_2$, and $H_2BBr{\cdot}SMe_2$ are liquids at 25 °C, whereas $HBBr_2{\cdot}SMe_2$ is a solid (mp ~30–35 °C). All of these compounds are stable indefinitely when stored under nitrogen at 25 °C. These compounds fume in air and eventually leave a white deposit in the container. The neat materials are 8.05 M in $HBCl_2{\cdot}SMe_2$, 7.8 M in $HBBr_2{\cdot}SMe_2$ (liquid), 9.0 M in $H_2BCl{\cdot}SMe_2$, and 9.1 M in

$H_2BBr{\cdot}SMe_2$. The strength of the neat materials was determined by hydrolyzing a known aliquot and measuring the hydrogen evolved according to the standard procedure.[26]

NMR Spectral Behavior. The proton NMR spectra in CCl_4 indicate that the methyl protons of $F_3B{\cdot}SMe_2$, $Cl_3B{\cdot}SMe_2$, and $Br_3B{\cdot}SMe_2$ appear at δ 2.21, 2.51, and 2.56, respectively, as compared to δ 2.06 for free SMe_2. The corresponding values for $H_2BCl{\cdot}SMe_2$, $H_2BBr{\cdot}SMe_2$, $HBCl_2{\cdot}SMe_2$, and $HBBr_2{\cdot}SMe_2$ are δ 2.34, 2.38, 2.42, and 2.48, respectively. The increase in downfield shift corresponds to the order of increase in acidities of Lewis acids: $BF_3 < BCl_3 < BBr_3$.[27] This is supported by the extensive NMR studies of Bula and Hartman.[17] As we move along this series, an increasingly strong S→B coordinate bond is formed, as reflected in the three-bond coupling between the methyl protons and the boron atom.[17,25] This also explains the fast exchange of SMe_2 between the added SMe_2 and $F_3B{\cdot}SMe_2$ and $Cl_3B{\cdot}SMe_2$ but the absence of such exchange in the case of $Br_3B{\cdot}SMe_2$. The latter complex is strong enough to prevent the exchange at room temperature.

In benzene solution, these addition compounds exhibit the methyl sulfide shifts opposite to those in CCl_4 solution. Thus the methyl protons of SMe_2, $F_3B{\cdot}SMe_2$, $Cl_3B{\cdot}SMe_2$, and $Br_3B{\cdot}SMe_2$ appear at δ 1.78, 1.53, 1.47, and 1.51, respectively. The appearance of $Br_3B{\cdot}SMe_2$ as a quartet while methyl protons in other complexes are singlets is attributable to the fact that $Br_3B{\cdot}SMe_2$ is a relatively stronger complex. It has been reported that such a quartet exists in the NMR of this complex in dichloromethane solution at lower temperature (<14 °C).[17] The appearance of a clear quartet at 35 °C (NMR probe temperature) in benzene solution but not in CCl_4 nor CH_2Cl_2 solution suggests that the complex is much more stabilized in benzene than in the latter solvents.

The upfield shift in methyl proton signals in benzene solution is quite interesting. One explanation may be that the addition compounds have charge separation which leads to the attraction of positively charged sulfur atoms toward the π cloud of the benzene ring, thus bringing the methyl protons within the shielding region of the aromatic ring:



No attempt was made to investigate further in this direction.

An interesting feature of haloborane–methyl sulfide addition compounds is the enormously different behavior of the chloroborane and bromoborane derivatives in their exchange of methyl sulfide molecules between themselves and the added free SMe_2. The chloroborane derivatives exchange their SMe_2 molecules very readily, whereas the bromoborane derivatives do not undergo such exchange. Thus, in the ^1H NMR spectrum of a CCl_4 solution of a mixture of $H_3B{\cdot}SMe_2$, $H_2BCl{\cdot}SMe_2$, and $HBCl_2{\cdot}SMe_2$, the methyl proton signals appear as a single peak. Upon addition of a small amount of SMe_2 to this mixture, the peak position is shifted upfield slightly. Still only a single peak is observed in the ^1H NMR spectrum. On the other hand, the CCl_4 solution of a mixture of $H_3B{\cdot}SMe_2$, $H_2BBr{\cdot}SMe_2$, and $HBBr_2{\cdot}SMe_2$ gives ^1H NMR signals attributable to each individual species, establishing the absence of a rapid exchange of the methyl sulfide molecules. The addition of a small amount of SMe_2 to this mixture causes the $H_3B{\cdot}SMe_2$ peak to broaden but has no effect on the signals due to the other species, showing that only the $H_3B{\cdot}SMe_2$ is exchanging with the methyl sulfide molecues but not the bromoborane derivatives. This is the first report of such a difference between $Cl_3B{\cdot}SMe_2$ and the corresponding chloroborane derivatives, and $Br_3B{\cdot}SMe_2$ and the corresponding bromoborane compounds, in their exchange with added SMe_2.

Conclusions

This study describes an investigation of redistribution reactions between boron trihalide–methyl sulfides and the readily available borane–methyl sulfide as a simple, general route for the synthesis of haloborane–methyl sulfide complexes. The exchange behavior of these complexes throws some light on the relative strength of S→B coordinate bonds in various boron trihalide–methyl sulfides and haloborane–methyl sulfides.

The excellent stability of haloborane adducts combined with their reactivity and ease of preparation makes them a new class of convenient hydroborating and reducing agents. As we hoped, these stable chloroborane– and bromoborane–methyl sulfide addition compounds turn out to be excellent reagents for hydroboration of olefins and acetylenes. The results of this study will be published subsequently.

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Registry No. $F_3B{\cdot}SMe_2$, 15403-85-7; $Cl_3B{\cdot}SMe_2$, 5523-19-3; $Br_3B{\cdot}SMe_2$, 29957-59-3; $HBCl_2{\cdot}SMe_2$, 63462-42-0; $HBBr_2{\cdot}SMe_2$, 55671-55-1; $H_2BCl{\cdot}SMe_2$, 63348-81-2; $H_2BBr{\cdot}SMe_2$, 55652-52-3; SMe_2, 75-18-3; BF_3, 7637-07-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $H_3B{\cdot}SMe_2$, 13292-87-0.

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