### Contribution to the Chemistry of Boron, 241[1] Improved Synthesis of 2,4,6-Trichloroborazine

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2,4,6-Trichloroborazine

2,4,6-Trichloroborazine is an important starting material for the preparation of many borazine derivatives, particularly for the parent borazine (HB=NH)<sub>3</sub>. Both are precursors for the CVD of boron nitride. Improved conditions for the synthesis of (ClB=NH)<sub>3</sub> to give high yields are reported.

### Introduction

In order to study mechanistic details of the formation of boron nitride from the gas phase, suitable single source precursors are needed which decompose thermally into BN. One prerequisit is sufficient volatility to get good growths rates on the substrate, the second, that they contain the corresponding element atoms – in our case boron and nitrogen – in the correct proportion, as well as with good leaving groups, in order that these will not contaminate the film built up by the CVD process (e. g. silylgroups may lead to a contamination of BN films by Si-atoms) [2].

For the formation of BN films by a CVD-process borazine and 2,4,6-trichloroborazine, (henceforth called trichloroborazine), are suitable precursors [2c, 3]. The parent borazine is obtained from trichloroborazine by reduction with NaBH<sub>4</sub> in diglyme [4, 5], and a new and efficient synthesis from  $(NH_4)_2SO_4$  and NaBH<sub>4</sub> in tetraglyme has recently been reported [6]. If one chooses the trichloroborazine route to B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> then a high yield synthesis of the trichloroborazine is essential. Yields described for the synthesis of (ClB=NH)<sub>3</sub> are in the range between 40 and 60% [3b, 5]. With the aim to improve the synthesis of trichloroborazine, we investigated two methods of its preparation: i) from NH<sub>4</sub>Cl and BCl<sub>3</sub> [5, 7] in chlorobenzene, and ii) from hexamethyldisilazane and BCl<sub>3</sub> in hexane [8].

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Laubengayer *et al.* [7] developed the synthesis of (ClB=NH)<sub>3</sub> from BCl<sub>3</sub> and [NH<sub>4</sub>]Cl in boiling chlorobenzene according to eq. (1).

$$3 \operatorname{BCl}_3 + 3 \operatorname{[NH_4]Cl} \rightarrow (\operatorname{ClB=NH})_3 + 9 \operatorname{HCl}$$
(1)

Although yields up to 70% are reported these can be achieved only with difficulties [5, 7]. In order to keep the low boiling boron trichloride in the reaction vessel at the reaction temperature, it is applied as its acetonitrile adduct H<sub>3</sub>C-CN·BCl<sub>3</sub> [5b] ( $\delta^{11}B =$ 2,2), which is, however, only sparingly soluble in chlorobenzene.

# Synthesis of Trichloroborazine from BCl<sub>3</sub> and [NH<sub>4</sub>]Cl

The course of reaction (1) has, as far as we are aware, not been investigated in detail. It is conceivable that several steps are needed until chloroborazine results. Therefore, we considered an <sup>11</sup>B NMR study as necessary in order to derive reaction conditions that might reliably improve the yield.

<sup>11</sup>B NMR spectra of samples taken during reaction (1) showed four signals for tetracoordinated boron species at  $\delta^{11}B = 6.9$ , 3,7, 1,7 and 0,8 besides the signals for CH<sub>3</sub>CN·BCl<sub>3</sub> ( $\delta^{11}B = 2.2$ ) and (ClB=NH)<sub>3</sub> ( $\delta^{11}B = 30.6$ ). The latter increases at the expense of the others as the reaction proceeds. Attempts to isolate reaction intermediates, in order to use these for the assignment of the signals, failed. However, it is not unreasonable to make the following assumptions. The sharp signal at  $\delta^{11}B =$ 6,9 is due to BCl<sub>4</sub><sup>-</sup> ( $\delta^{11}B = 6.5 - 8.9$ ) [9] while the signal at  $\delta^{11}B = 3.7$  can be assigned to H<sub>3</sub>N·BCl<sub>3</sub>

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[10a]. The remaining to two signals may result from  $[H_2N\text{-BCl}_2]_n$  (n = 2, 3) or from a species of type **1**.



Since a comparatively large amount of nonsublimable material results, it is quite likely that polymers of type Cl<sub>2</sub>B(NH-BCl)<sub>n</sub>NH<sub>2</sub>BCl<sub>3</sub> are formed. Thus, in order to improve the yield of (ClB=NH)<sub>3</sub> it seemed advisable to choose conditions that prevent the formation of any kinds of intermediates responsible for the formation of higher oligomers and/or polymers of type  $(ClB=NH)_n$ . We assumed that this can be achieved by using an excess of BCl<sub>3</sub> in the form of CH<sub>3</sub>CN·BCl<sub>3</sub>. Indeed, using a twofold excess of CH3CN·BCl3 over the stoichiometry required by eq. (1) a yield in excess of 80 % of (ClB=NH)<sub>3</sub> is obtained [10b]. Under these conditions an additional <sup>11</sup>B NMR signal at 37,7 ppm is observed. This signal points to the formation of  $HN(BCl_2)_2 (\delta^{11}B = 38.4 \text{ for } {}^{t}BuN(BCl_2)_2 [11].$ 

As far as the various steps in the formation of (ClB=HN)<sub>3</sub> are concerned, we assume that CH<sub>3</sub>CN·BCl<sub>3</sub> reacts with NH<sub>4</sub>Cl to give an ammonium tetrachloroborate which in turn loses HCl to generate  $H_3N \cdot BCl_3$ , a compound only recently characterized [10]. This adduct eliminates HCl at elevated temperatures with formation of H<sub>2</sub>N-BCl<sub>2</sub>, a reaction that is well known for the analogous decomposition of R<sub>2</sub>HN·BCl<sub>3</sub> or RNH<sub>2</sub>·BCl<sub>3</sub>, particularly in the presence of an auxiliary base [12], or for arylamino-BCl<sub>3</sub> adduct thermolysis [13]. H<sub>2</sub>NBCl<sub>2</sub> either dimerizes, trimerizes or oligomerizes, and these "adducts" loose HCl to arrive at products  $(ClB=NH)_n$  as shown in eq. (2). Reactions (3) to (5) represent the formation of intermediates on the way to trichloroborazine.

$$(Cl_2B-NH_2)_n \to nHCl + (ClB=NH)_n$$
(2)

$$H_2N$$
- $BCl_2 + BCl_3 \rightarrow Cl_3B \cdot NH_2$ - $BCl_2$ 

$$Cl_3B-NH_2-BCl_2 \rightarrow Cl_2B-NH-BCl_2 + HCl$$
 (4)

$$Cl_2B-NH-BCl_2 \rightarrow Cl_3B + ClB \equiv NH$$
 (5)

 $3 \text{ ClB} \equiv \text{NH} \rightarrow (\text{ClB} = \text{NH})_3 \tag{6}$ 

We assume that the excess of BCl<sub>3</sub> successfully prevents the formation of long chain polymers  $(Cl_2BNH_2)_n$  or of  $Cl_2B-(NH-BCl)_m-NH_2 \cdot BCl_3$ , and

thus drives the reaction to the formation of the chloroborazine.

The excess of BCl<sub>3</sub> can be recovered at the end of the reaction. Yields of 40-60% reported in the literature [1, 2] for a stoichiometric reaction of NH<sub>4</sub>Cl with BCl<sub>3</sub> show that at the end of the reaction no BCl<sub>3</sub> is present to achieve the cleavage of the polymers. An excess of BCl<sub>3</sub> prevents the formation of polymers and helps to increase the yield of trichloroborazine.

As demonstrated, the yield of  $(ClB=NH)_3$  can be raised to 83% and more in far less time than by the classical method, but the low volatility of the solvent is still a problem for the isolation of  $(ClB=NH)_3$  [14]. For this reason the reaction of BCl<sub>3</sub> with HN(SiMe<sub>3</sub>)<sub>2</sub> has been reinvestigated.

## Synthesis of Trichloroborazine from $BCl_3$ and $(Me_3Si)_2NH$

The Si-N-cleavage of hexamethyldisilazane with BCl<sub>3</sub> provides an alternative method to prepare the borazine (ClB=NH)<sub>3</sub>. The reported yields of 30% are unsatisfactory particularly if larger amounts of the trichloroborazine are required [8]. So, we investigated reaction (7) in more detail in order to find optimal conditions for the formation of (ClB=NH)<sub>3</sub>.

 $HN(SiMe_3)_2 + BCl_3 \rightarrow 1/3 (ClB=NH)_3 + 2 Me_3SiCl (7)$ 

$$HN(SiMe_3)_2 + BCl_3 \longrightarrow Me_3Si - N - B - Cl = (8)$$

$$Me_3Si - N - B - Cl = (8)$$

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If reaction (7) is performed in hexane at -78 °C, the formation of a voluminous precipitate can be noted, and the amount of Me<sub>3</sub>SiCl formed according to NMR spectra ( $\delta^{29}$ Si = 30,5) is very small. This leads to the conclusion that an amine-BCl<sub>3</sub> adduct is formed according to eq. (8). It can be detected by <sup>11</sup>B NMR ( $\delta$  = 6 ppm). When the reaction mixture was allowed to a reach ambient temperature, the adduct decomposes, conceivably to the dichloro(trimethylsilylamino)borane **2** as shown

(3)

in eq. (9). This aminoborane can form dimeric or oligomeric species by  $Me_3SiCl$  or HCl elimination. The excess of BCl<sub>3</sub> can trap intermediates by preventing the formation of polymeric (ClB=NH)<sub>n</sub>. This should lead to the diborylamine HN(BCl<sub>2</sub>)<sub>2</sub> which provides (ClB=NH)<sub>3</sub> as described by eq. (5) and (6).

The formation of the dimer of **2**,  $[(Me_3Si)HNBCl_2]_2$  is indicated by the <sup>11</sup>B NMR signal at  $\delta = 4,6$ . Further heating of the reaction mixture can then lead to the formation of a polymer with elimination of Me<sub>3</sub>SiCl and/or HCl.

This fact explains the low yield of the chloroborazine because under these conditions the formation of the polymer is competing with the formation of (ClB=NH)<sub>3</sub>. But if there is an excess of BCl<sub>3</sub> the dimerisation of the silylated dichloroaminoborane can be suppressed (eq. (10)):

$$2 \xrightarrow{Me_3Si}_{H} \xrightarrow{Cl} + BCl_3 \longrightarrow Cl_3B - NH(SiMe_3) - BCl_2$$
(10)

Nevertheless, if reaction (7) is performed with a 100% excess of BCl<sub>3</sub> in hexane at -78 °C some dimeric dichloroaminoborane [(Me<sub>3</sub>Si)HN-BCl<sub>2</sub>]<sub>2</sub> can still be detected in the <sup>11</sup>B NMR spectrum ( $\delta^{11}$ B = 4,6), but the amount of the precipitate is much less as compared to a reaction using stoichiometric conditions. Furthermore, the monomeric species  $(Me_3Si)HN-BCl_2$  ( $\delta^{11}B = 38,6$  ppm) is clearly seen in the <sup>11</sup>B NMR spectrum with an amount up to 25%; the main product in solution is the borazine  $(ClB=NH)_3$  ( $\delta^{11}B = 30.6$  ppm; 75%). After the mixture was heated to reflux the chloroborazine was isolated in 96% yield. However, if the silizane is added at ambient temperature under the same conditions (100% excess BCl<sub>3</sub>) in such a way that the reaction temperature reaches 60 °C, the <sup>11</sup>B NMR spectrum of the solution indicated the quantitative formation of (ClB=NH)<sub>3</sub>. Thus, a complete conversion of (Me<sub>3</sub>Si)<sub>2</sub>NH into (ClB=NH)<sub>3</sub> is possible. Solvent, excess BCl3 and the Me3SiCl formed during the reaction can be easily removed in vacuo. (CIB=NH)<sub>3</sub> is obtained spectroscopically pure. However, sublimation reduces the yield due to further condensation.

### Conclusion

Two independent routes have been investigated with the aim to improve the yield of trichloroborazine. In both cases an excess of BCl<sub>3</sub> is necessary to prevent or suppress competing reactions, and to achieve high yields.

#### Experimental

All reactions were performed under nitrogen gas in anhydrous solvents to prevent hydrolysis.

#### Synthesis of B-Trichloroborazine

a) From NH<sub>4</sub>Cl and BCl<sub>3</sub>·NCMe: Into a 21 three necked flask with a mechanical stirrer and reflux condenser was added MeCN (16,4 g, 0,40 mol) and chlorobenzene (300 ml). The flask was cooled to -20 °C. Then BCl<sub>3</sub> (32 ml, 0.40 mol) was distilled into the reaction vessel under vigorous stirring. The acetonitrile-BCl<sub>3</sub> adduct ( $\delta^{11}B = 2,2$ ) separated as a white mass. When the addition of BCl<sub>3</sub> was complete, powdered, dry NH<sub>4</sub>Cl (21,5 g, 0,40 mol) was added. The mixture was then heated for 5 h to reflux. At about 120 °C the formation of HCl set in quite vigorously and gas evolution took place for ca. 30 min (ca. 83% of the theoretical amount was released). Heating was continued for 5 h. As the reaction proceeded the ammonium chloride dissolved and some insoluble brown material formed. The <sup>11</sup>B NMR spectrum of the solution showed besides the signal for (ClB=NH)<sub>3</sub>, ( $\delta$  = 30,6 ppm, 45%) four more signals at  $\delta = 6.9 (11\%), 3.7 (5\%), 1.7 (22\%)$  and 0,8 (17%). The insoluble material was removed by filtration and the solvent and any other volatiles were removed in vacuum from the solution. Trichloroborazine (6,6 g, 27%) was recovered from the residue by sublimation in vacuo at 60 °C/0.01 mm Hg, m. p. 86 °C.

b) The reaction was performed analogously with a twofold excess of BCl<sub>3</sub> (64 ml, 0,8 mol), and a condenser cooled with dry ice was used. The yield of (ClB=NH)<sub>3</sub> of the sublimed compound was 20,3 g (83%).

c)  $From(Me_3Si)_2NH$  and  $BCl_3$ : Boron trichloride (200 ml, 2,66 mol) was condensed into a 2l three necked flask fitted with a dropping funnel, CO<sub>2</sub> condenser and a mechanical stirrer. 400 ml of hexane were added to the BCl<sub>3</sub>. At -10 °C (ice/NaCl cooling) HN(SiMe\_3)<sub>2</sub> (283 ml, 1,33 mol) was then added from a dropping funnel to the stirred solution at a rate which allows BCl<sub>3</sub> to fully condense at the CO<sub>2</sub> condenser. (The reaction temperature may reach 60 °C.) The course of the reaction could be controlled by <sup>11</sup>B NMR spectroscopy ( $\delta^{11}B$ : 4,6

[Me<sub>3</sub>SiN(H)-BCl<sub>2</sub>]<sub>2</sub>; 6,0 Cl<sub>3</sub>B-NH(SiMe<sub>3</sub>)<sub>2</sub>; 30,6

(ClB=NH)<sub>3</sub>; 38,6 Me<sub>3</sub>SiN(H)-BCl<sub>2</sub>. If there was some Me<sub>3</sub>SiN(H)-BCl<sub>2</sub> remaining in the solution, it could be decomposed to (ClB =NH)<sub>3</sub> by heating to reflux. All volatile compounds were removed after 6 h in a vacuum. The oily residue crystallized completely after 2d and consisted of pure trichloroborazine ( $\delta^{11}$ B = 30,6). Yield: 78g (96%).

d) When the same reaction was performed at -78 °C, a large amount of a white precipitate was formed on adding BCl<sub>3</sub>, and the amount of Me<sub>3</sub>SiCl according to the NMR spectra ( $\delta^{29}$ Si = 30,5) was very small after the addition was completed. The <sup>11</sup>B NMR spectrum exhibited a signal at  $\delta$  = 38,6 due to Cl<sub>2</sub>B-N(H)SiMe<sub>3</sub>) besides a large signal due to BCl<sub>3</sub>( $\delta$  = 46). After the solution was allowed

to attain ambient temperature, the <sup>11</sup>B NMR spectrum of the solution showed resonances for (ClB=NH)<sub>3</sub> ( $\delta^{11}$ B = 30,6, 75%) and monomeric Cl<sub>2</sub>B-N(H)SiMe<sub>3</sub> ( $\delta$  = 38,6, 25%) as well as of [Me<sub>3</sub>SiN(H)-BCl<sub>2</sub>]<sub>2</sub> ( $\delta$  = 4,6 ~ 4%). After heating to reflux the solid disappeared with formation of (ClB=NH)<sub>3</sub>. All volatiles were then removed in vacuo. The yield was comparable to that of the previous method (74g, 93%). Purification by sublimation was not necessary.

e) If the reaction was performed stoichiometrically under analogous conditions [10 ml of BCl<sub>3</sub> (0,133 mol), 28,3 ml of HN(SiMe<sub>3</sub>)<sub>2</sub>(0,133 mol), 200 ml of hexane], a large amount of a white precipitate was formed. Although the mixture was heated to reflux for 6h, only 2,6 g (34%) of trichloroborazine was isolated by sublimation.

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