

# A facile synthesis of 2,4,6-trichloroborazine from boron trichloride–dimethylsulfide complex and ammonium chloride

Cheng Deng<sup>a,\*</sup>, Yong Cai Song<sup>a</sup>, Ying De Wang<sup>a</sup>, Yi He Li<sup>a</sup>,  
Yong Peng Lei<sup>a</sup>, Shu Wei Cao<sup>b</sup>

<sup>a</sup> State Key Laboratory of Advanced Ceramic Fibers & Composites, College of Aerospace and Materials Engineering,  
National University of Defense Technology, Changsha 410073, China

<sup>b</sup> Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China

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## Abstract

2,4,6-Trichloroborazine has been recognized as a desirable monomer for the preparation of high-performance boron nitride fibers through polymer derived ceramics route. So a high yield and facile synthesis of 2,4,6-trichloroborazine is essential in practice. Using boron trichloride–dimethylsulfide complex  $((\text{CH}_3)_2\text{S} \cdot \text{BCl}_3)$  and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) as starting materials and toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) as solvent, the synthesis of 2,4,6-trichloroborazine to give high yield is reported.

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**Keywords:** 2,4,6-Trichloroborazine; Boron trichloride–dimethylsulfide; Boron nitride precursor; Synthesis

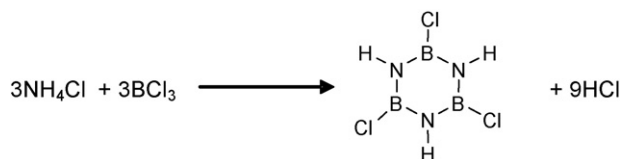
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Boron nitride fibers, in view of its unique properties, especially the absence of electrical conductivity, oxidation resistance, and optical transparency, offer advantages over other non-oxide ceramic fibers. Recently, 2,4,6-trichloroborazine ( $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ , TCB) with boron–nitrogen ring structure has been recognized as a desirable monomer for the preparation of high-performance boron nitride fibers through polymer derived ceramics (PDCs) route [1–5]. Over a period of years considerable effort has been devoted to the development of improved methods for the synthesis of 2,4,6-trichloroborazine and various of its derivatives. An improved method of preparation and purification has been accomplished by Brown and Laubengayer [6], who has also studied its chemical and certain physical properties. As reported in many literature [7,8], the compound  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$  was prepared by allowing boron trichloride ( $\text{BCl}_3$ ) to react with ammonium chloride ( $\text{NH}_4\text{Cl}$ ) at elevated temperatures (Scheme 1) and purified by recrystallization. Since the  $\text{BCl}_3$  is gaseous at room temperature, their reaction was somewhat inconvenient to control and the yield was low. So Jones and Kinney [9] thermally decomposed the addition compound of aniline and boron trichloride to obtain the corresponding substituted borazine. In a similar manner Rothgery and Hohnstedt [10] synthesized 2,4,6-trichloroborazine using acetonitrile adduct of boron trichloride instead of gaseous boron trichloride, and the yield was 57%. Therefore it is extremely desirable to have an easy and convenient preparation of 2,4,6-trichloroborazine at ambient pressure and easily obtained temperatures.

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\* Corresponding author.

E-mail address: [dcnudt@163.com](mailto:dcnudt@163.com) (C. Deng).



Scheme 1. Synthesis of 2,4,6-trichloroborazine.

In this article, one facile route for the preparation of 2,4,6-trichloroborazine is reported using boron trichloride–dimethylsulfide complex  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) as starting materials and toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) as solvent. Use of  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  in place of gaseous boron trichloride, this adduct could keep the low boiling boron trichloride in the reaction vessel at the reaction temperature and obtain 2,4,6-trichloroborazine in high yield.

## 1. Experimental

All experiments were performed under nitrogen atmosphere and anhydrous conditions using standard vacuumline, Schlenk techniques and an efficient dry box with solvents purified by standard methods.  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  (Guangzhou Ruihe Chemical Technology Co., CP) for the synthesis of  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$  was used as-received. Ammonium chloride (Sinopharm Chemical Reagent Co., AR) was dried under vacuum at  $110^\circ\text{C}$  for 12 h before the synthesis. Toluene was purified by distillation from metal sodium.

**Preparation of  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ .** 2,4,6-Trichloroborazine was prepared by refluxing a mixture of  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  and dry finely powdered ammonium chloride in toluene solution. The apparatus consisted of a 1-L two-necked flask fitted with a magnetic stirrer. One neck of the flask was provided with a water cooled reflux condenser which was attached in turn to a low temperature equipment. The outlet of the head was connected to a phosphoric oxide drying tower to prevent moisture from entering the apparatus. The other neck of the flask was fitted with an inlet tube imported dry nitrogen.

In a typical run 20 g (0.37 mol) of dry ammonium chloride, 66.3 g (0.37 mol) of  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  and 500 mL of dry toluene were all placed in the reaction flask. Dry nitrogen was passed through the apparatus to remove moisture, and the reflux head was cooled in an ethanol to  $-20^\circ\text{C}$ . The mixture was heated to gentle reflux for about 12 more hours until no HCl could be detected issuing from the reaction system.

At the end of reaction, the solution was filtered and the precipitate was extracted several times. The filtrate and the extract were combined, concentrated and dried at room temperature in a high vacuum ( $10^{-2}$  mbar) to get the crude product. The crude product was purified by recrystallization, and then the 15.0 g (0.082 mol) of white crystalline needles obtained indicated a yield of 66.3%.

The infrared spectra were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  on a FT-IR Nicolet Magna 550 spectrophotometer in KBr pellets.  $^{11}\text{B}$ - and  $^1\text{H}$  NMR spectra were recorded on a Bruker DMX 600, and the reference compound was  $\text{Et}_2\text{O}\cdot\text{BF}_3$  and tetramethylsilane, respectively. The solvent for all samples was  $\text{DMSO}-d_6$ .

Based on the chemical unstable property of  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$ , decompound reaction takes place at elevated temperatures. It would release  $(\text{CH}_3)_2\text{S}$  and  $\text{BCl}_3$  when heated at  $70\text{--}80^\circ\text{C}$  (Scheme 2).

At this experiment, when  $(\text{CH}_3)_2\text{S}\cdot\text{BCl}_3$  decompounded,  $\text{BCl}_3$  contacted the surface of  $\text{NH}_4\text{Cl}$  in toluene solution and  $(\text{CH}_3)_2\text{S}$  (b.p.  $36^\circ\text{C}$ ) fled the synthesis system. And simultaneity,  $\text{BCl}_3$  reacted vigorously with  $\text{NH}_4\text{Cl}$  powders in a highly exothermic manner to produce  $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$  and give HCl as by-product. So during the reaction violent evolution of hydrogen chloride was observed. Since the synthesis reaction is a gas–solid–liquid process, maintaining  $\text{BCl}_3$  vapor contacted  $\text{NH}_4\text{Cl}$  powders sufficiently is essential. However the velocity of decomposition reaction of the adduct was faster than the produce of TCB at the reaction temperature, so an efficient low temperature reflux system was necessary to retain the superfluous  $\text{BCl}_3$  in the reaction system in order to heighten the yield.



Scheme 2. The decompound reaction of boron trichloride–dimethylsulfide complex.

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