Synthesis of Boron Nitride via a Polymeric Vinylpentaborane Precursor

Sir:

In a recent communication,[1] we showed that 2-vinylpentaborane could undergo a thermally induced polymerization reaction to form either soluble or cross-linked poly(2-vinylpentaborane) oligomers. Furthermore, we demonstrated that these materials, when heated under an argon atmosphere, produced pure boron carbide (B_4C) in high ceramic yield. We have now found that when poly(alkenylpentaboranes) are pyrolyzed in the presence of a suitable reactant, they can serve as precursors to other important nonoxide ceramics. As an illustration, we report here the high-yield synthesis of boron nitride from the soluble oligomer poly(2-vinylpentaborane) (I).

There have been several previous reports of the use of polymer precursor routes as alternatives for the preparation of boron nitride (BN),[2–7] and these studies have resulted in the production of ceramic materials in a range of yields and purities. Recently, several studies have shown that the pyrolysis of certain boron polymers in the presence of ammonia can lead to enhanced yields and purity of boron nitride products. For example, Seyferth and Rees[8] recently reported that ammonia pyrolysis of diammine-linked decaborane polymers produced crystalline BN with reduced carbon contamination. Likewise, Ultrasystems[9] has described the synthesis of BN from ammonia pyrolysis of soluble polyborazine compounds.

Pentaborane(9) is known to react readily with ammonia and alkylated amines to form a variety of products.[10] Thus, depending on reaction conditions, simple deprotonation $[(NH_4^+)(B_5H_8^-)]$,[11] formation of a diammoniate $[(H_2B(NH_3)_2^+)(B_4H_7^-)]$,[11] or production of borazines may occur.[12] We have now found that I also readily reacts with ammonia at moderate temperatures to produce an intermediate that, when heated at higher temperatures, gives boron nitride in high yields.

The conversion of polymer I to boron nitride was accomplished by slowly heating (2 °C/min) a 470-mg sample of I from 25 to 350 °C under a flow of gaseous ammonia (~100 mL/min), followed by faster heating at the rate of 10 °C/min until a maximum temperature of 1000 °C was achieved. This temperature was then maintained for an additional 2 h, after which it was found that 472 mg of a light yellow solid was produced. Elemental analysis[13] of the material showed a B/N ratio of 1.05 with a measured level of carbon of 0.81%. The diffuse-reflectance IR spectrum[14] is consistent with spectra previously reported for boron nitride.[15] The material produced under these conditions was largely amorphous; however, crystalline BN (as determined by X-ray powder diffraction) was obtained when heating was continued for longer periods at 1450 °C.

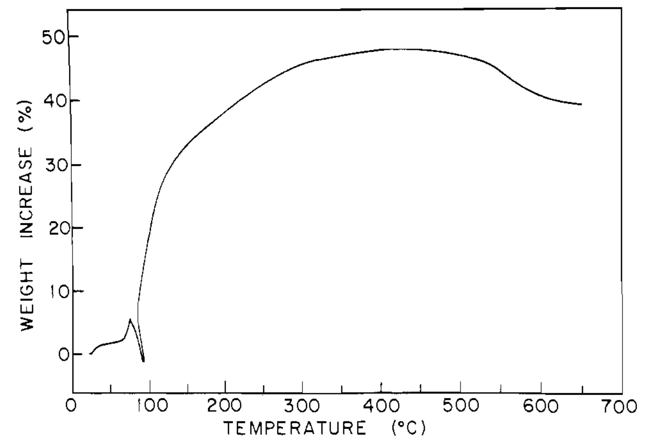
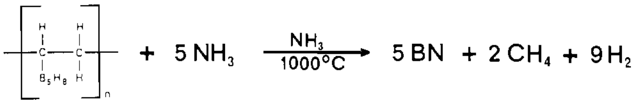


Figure 1. TGA analysis of polymer I under ammonia.[16]

Boron nitride prepared from I in the manner described above was obtained in 100.4% ceramic yield (based on a theoretical ceramic yield[21] of 139.0%) and a chemical yield of 72.2% based on the following equation:



$$\Big[-\underset{\underset{B_5H_8}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\Big]_n + 5\,NH_3 \xrightarrow[1000\,°C]{NH_3} 5\,BN + 2\,CH_4 + 9\,H_2 \qquad (1)$$

Thus, the addition of 5 equiv of NH_3 to I, followed by formation of boron nitride at higher temperatures, should result in a theoretical weight increase of 39%. This prediction is in excellent agreement with the thermogravimetric analysis[16] of I under an ammonia atmosphere (Figure 1), which showed a sharp weight increase in the range 75–400 °C (~48%) followed by a gradual weight loss from 475 to 650 °C (~10%).

In an effort to isolate the intermediate compound at the point of maximum weight gain, a 480-mg sample of I was placed in a tube furnace under a flow of gaseous ammonia (~100 mL/min). The sample was initially heated to 75 °C and then slowly heated (2 °C/min) through the temperature range 75–350 °C. Under these conditions a white, brittle material (640 mg) II was produced that was insoluble in a variety of polar and nonpolar organic solvents. A diffuse-reflectance IR spectrum[17] revealed the presence of N–H, C–H, B–H, and B–N bonds, while elemental analysis[18] is consistent with an empirical formula of $C_{2.0}B_{5.1}N_{4.8}H_{8.0}$. Since the B/C ratio in this material is identical with that of starting polymer I, the polymeric hydrocarbon backbone has probably remained intact. A UV–visible spectrum of the material showed a broad absorption with a maximum at 212 nm, similar to those that have been shown to arise from the π–π^* electronic transition in borazine and fused-borazine[19] polymers. This observation, coupled with the measured B/N ratio of ~1 in II, suggests that the pendant pentaborane cages in I have reacted with ammonia to form borazine-type ring systems in II. Indeed, the analytical data are in excellent agreement with the formation of a borazanaphthalene unit,[19] as shown in eq 2.

These results are thus consistent with the formation of BN from I in a two-step process. The initial step involves the formation

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(13) Anal. Calcd for BN: B, 43.55; N, 56.45; Found BN prepared by pyrolysis of I: B, 45.24; N, 55.88; C, 0.81; H, 0.46.

(14) IR (diffuse): 3640 m, 3420 s, 2800 w, 2560 m, 2320 w, 1440 vs, vbr, 1100 s, 940 w, 800 vs, 680 s, 620 s cm^{-1}.

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(16) TGA results were obtained by heating a sample of polymer I under ammonia from room temperature to 700 °C with a heating rate of 10 °C/min.

(17) IR (diffuse): 3420 vs, 3160 s, 2940 s, 2900 s, 2850 s, 2500 m, 1600 m, 1400 s, 1110 m, 700 m, 610 m cm^{-1}.

(18) Elemental analysis of polymer II: B, 33.15; N, 41.03; C, 14.70; H, 4.93.

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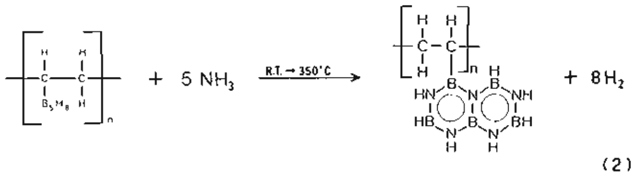
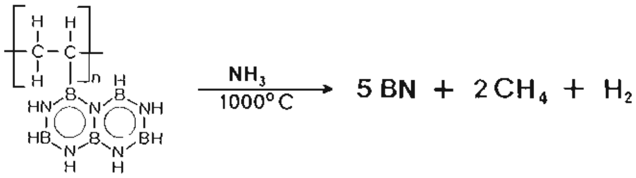


(2)

of a borazine polymer intermediate (eq 2), followed by a second decomposition reaction at higher temperatures to form BN as shown in eq 3. Indeed, it was also found that further treatment



(3)

of a pure sample of II under ammonia at higher temperatures resulted in formation of BN.

In summary, the results described herein demonstrate that poly(2-vinylpentaborane) oligomers are useful soluble ceramic precursors that can be readily converted to boron nitride in high yields. The potential applications for the processing of BN in this manner are numerous and include synthesis of composite materials[20] and the generation of thin films or coatings.[21] Furthermore, owing to the highly reactive nature of the pentaborane cage, these polymers may well serve as precursors to a wide variety of other important boron-containing ceramics and work exploring these possibilities is currently in progress.

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Department of Chemistry and
Laboratory for Research on the
Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Mario G. L. Mirabelli
Larry G. Sneddon*

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Synthesis of Thiomolybdenyl Complexes with $[Mo_2(S)_2(O)_2]^{2+}$ Cores and Substitutionally Labile Ligands. Crystal and Molecular Structure of the $[Mo_2O_2S_4(DMF)_3]$ Complex

Sir:

The reactivity characteristics of the Mo-coordinated S^{2-}, S_2^{2-}, and S_4^{2-} terminal ligands (L^{2-}) in the $[L_2Mo_2(\mu\text{-}S)_2S_nO_{2-n}]^{2-}$ complexes ($n = 0$–2) are greatly affected by the nature of the neighboring terminal ligands on the Mo atom.[1] A detailed study of neighbor-ligand effects in the relative nucleophilic properties of coordinated S^{2-}, S_2^{2-}, or S_4^{2-} ligands is expected to be useful in the evaluation of specific features that may be important in the catalysis of the hydrodesulfurization (HDS) reaction.[2] Among these features are included (a) the presence of proximal terminal oxo groups on the Mo atoms and (b) the interactions of the Mo atoms with oxides or hydroxides on the surface of the supporting γ-Al_2O_3 matrix.

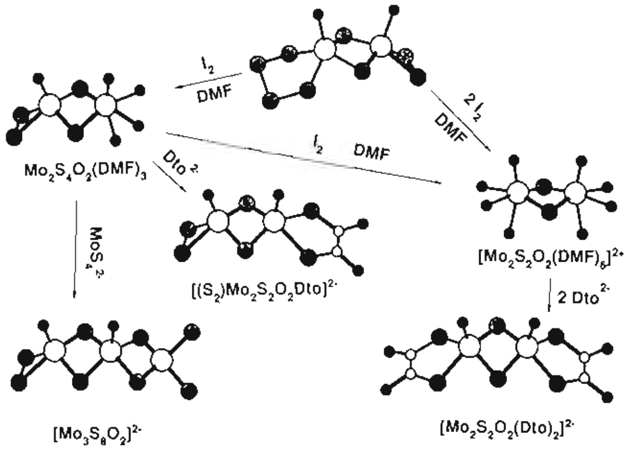

Figure 1. Synthesis and derivatives of the $[Mo_2O_2S_4(DMF)_3]$ and $[Mo_2O_2S_2(DMF)_6]^{2+}$ complexes.

The systematic synthesis of thiomolybdates with specific functional groups, and reactivity studies of such groups depend on the facile synthesis of simple derivatives of the $[Mo_2(\mu\text{-}S)_2S_nO_{2-n}]^{2+}$ cores, with substitution-labile terminal ligands. In the past, oxidative desulfurization reactions have been effective in the removal of coordinated S_x^{2-} ligands and their replacement by substitutionally labile ligands. Such reactions are exemplified in the synthesis of the $[Cp_2Fe_2(CH_3CN)_2(SEt)_2]^{2+}$ and $Os(I)_2(CO)_2(PPh_3)_2$ complexes. The former was obtained[3] by air oxidation of $[Cp_2Fe_2(S_2)(SEt)_2]^{0,+}$ in CH_3CN solution and the latter[4] by the I_2 oxidation of the $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ complex in CH_2Cl_2.

The reactions of $(Et_4N)_2[Mo_2O_2S_8]$[5] (I) with I_2 in dimethylformamide (DMF) are shown in Figure 1. The reaction of I with an equimolar amount of I_2 proceeds readily at ambient temperature and following unexceptional workup affords the orange crystalline $[Mo_2O_2S_4(DMF)_3]$ product[6] (II) in 70% yield. A similar reaction of I with 2 equiv of I_2 or the reaction of II with an equimolar amount of I_2 results in the formation of the $[Mo_2O_2S_2(DMF)_6]^{2+}$ cation in high yields. The latter can be isolated in crystalline form as the diiodide salt III.[6] The infrared spectra of the complexes show the Mo–O vibrations at 948 and 954 cm^{-1} for II and at 928 and 947 cm^{-1} for III. The C–O stretching vibrations of the coordinated DMF molecules appear as doublets at 1641, 1657 and 1647, 1664 cm^{-1} for II and III, respectively. The Mo–η^2–S_2 and Mo–S_b vibrations in II are found at 527 and 469 cm^{-1}, and the Mo–S_b stretching vibration in III occurs at 474 cm^{-1}. The conductivity of III in DMF solution (Λ

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(5) Hadjikyriacou, A.; Coucouvanis, D., manuscript in preparation. The synthesis of $[Mo_2O_2S_8]^{2-}$ is carried out, under aqueous aerobic conditions, by the reaction of $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$ (8.1 mmol in 400 mL of H_2O) with a sulfur-enriched, aqueous $(NH_4)_2S$ solution. The latter was obtained by the addition of 0.47 mmol of elemental sulfur to 65 mL of 22% $(NH_4)_2S$ solution obtained from Fisher Scientific. After a brief stirring at ambient temperature and standing for 24 h in air, the reaction mixture was treated with a solution of 50 mmol of Et_4NCl in 150 mL of water. The suspension of $(Et_4N)_2[Mo_2O_2S_8]$ that formed upon standing for 30 min was isolated, washed with ethanol, CS_2, and diethyl ether, and dried. The compound was recrystallized from 200 mL of DMF by the addition of 400 mL of 2-propanol. The yield of the yellow crystalline product was 9.6 g or 45%.

(6) Anal. Calcd for $Mo_2S_4O_5N_3C_9H_{21}$: C, 18.92; N, 7.35; H, 3.70; S, 22.44; Mo, 33.58. Found: C, 19.55; N, 7.43; H, 3.70; S, 21.70; Mo, 32.37. Calcd for $I_2Mo_2S_2O_8N_6C_{18}H_{42}$: C, 22.00; N, 8.57; H, 4.28; S, 6.53; Mo, 19.59; I, 25.92. Found: C, 22.00; N, 8.14; H, 4.53; S, 7.22; Mo, 17.75; I, 24.53. Severe twinning of the well-shaped orange crystals of this compound has prevented us from finding a single crystal suitable for an X-ray determination.