10^{-3} M 2-acetylnaphthalene ($OD_{337} = 3.8$). The concentration of PhCN was varied from 1.96×10^{-3} to 8.64 M, and the ΔOD was determined in the usual fashion.

Triplet quenching experiments used $[CpFePyr]^+PF_6^-$ at typical concentrations for laser irradiation at 532 nm. The samples contained 3.92×10^{-3} M PhCN and 10^{-5}–10^{-3} M perylene. Typical ΔOD determinations were made, and a plot of ΔOD versus perylene concentration was flat.

Conductivity measurements were performed in the flow cell of a Dionex CDM-1 conductivity detector by pumping, via syringe, 5 mL of solution through the cell. A series of solutions of increasing conductivity were measured without removing the previous solution. The narrow bore tubing and small volume of the cell ensured that the previous solution was displaced by the first 1–1.5 mL of the succeeding solution. The remaining solution resulted in very stable readings which were rather insensitive to the flow rate of 5–10 mL/min.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 12.[1] Syntheses, Polymerizations, and Ceramic Conversion Reactions of *B*-Alkenylborazines

Anne T. Lynch and Larry G. Sneddon*

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

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Abstract: High yield synthetic routes for the production of new *B*-alkenylborazines and poly(*B*-alkenylborazine) polymers and oligomers as well as the use of the poly(*B*-alkenylborazines) as polymeric precursors to boron nitride ceramics are reported. The syntheses of the *B*-alkenylborazines are based on the use of transition-metal reagents to activate the B–H bonds of borazine for either alkyne-addition or olefin-dehydrocoupling reactions and are the first examples of transition-metal-catalyzed reactions of borazine to be reported. Thus, the complexes $RhH(CO)(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ were found to activate borazine/alkyne-addition reactions with acetylene, propyne, 1-butyne, and 2-butyne to give the previously unknown B-substituted alkenylborazines, *B*-$(RHC{=}CR')$-$B_3N_3H_5$ (R, R′ = H, Me, or Et). For reactions employing $RhH(CO)(PPh_3)_3$, typical yields of *B*-alkenylborazines range from 70 to 85% with the catalyst undergoing 25–50 turnovers an hour. Palladium bromide was found to catalyze the dehydrocoupling reactions of either borazine or *N*-trimethylborazine with olefins, such as ethylene and propene, to give the corresponding *B*-alkenyl- and *B*-alkylborazine products. The *B*-alkenylborazines were found to readily undergo thermally induced polymerizations to produce insoluble poly(*B*-alkenylborazines). Soluble, low molecular weight (<1500) oligomers were formed when the thermal polymerization reactions were carried out in the presence of additional borazine. The spectroscopic data for the soluble oligomers confirm that they have structures composed of carbon backbones containing pendant borazines. The ceramic conversion reactions of both the soluble and insoluble polymers were explored as potential routes to boron nitride ceramics. It was found that pyrolysis of these polymers yielded ceramic materials with B/N ratios of ~1.0 which, depending upon the polymer and pyrolysis conditions, ranged from black, high carbon materials to white, crystalline h-boron nitride. In all cases, the polymer/ceramic conversions were found to take place with both high ceramic and chemical yields.

Interest in the use of polymer precursor[2] routes to ceramics has initiated new studies of the design and synthesis of inorganic polymer systems. In our own work we have been interested in the development of synthetic pathways for the construction of new boron-containing polymers which might serve as precursors to nonoxide ceramics, such as boron carbide or boron nitride. For example, we have previously shown[3,4] that transition-metal reagents can be used to catalyze the reactions of pentaborane(9) with acetylenes to form 2-alkenylpentaboranes in high yields. Subsequent work[5] then demonstrated that 2-vinylpentaborane can be readily polymerized and that soluble oligomers of poly(2-vinylpentaborane) can, depending upon pyrolysis conditions, be converted in high yields to either boron carbide or boron nitride. Other workers have also studied polymer precursor routes to these materials.[6-16]

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[1] For part 11, see: Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 592–597.

[2] For current work in the use of precursors to ceramic materials, see: (a) Wynne, K. J.; Rice, R. W. *Ann. Rev. Mater. Sci.* **1984**, *14*, 297–334. (b) Rice, R. W. *Am. Cer. Soc. Bull.* **1983**, *62*, 889–892. (c) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. (d) *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984; pp 235–312, and references therein.

[3] (a) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449–453. (b) Mirabelli, M. G. L.; Sneddon, L. G., to be submitted for publication.

[4] (a) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857–2858. (b) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955–3962.

[5] (a) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 3305–3307. (b) Mirabelli, M. G. L.; Sneddon, L. G. *Inorg. Chem.* **1988**, *27*, 3271–3272. (c) Mirabelli, M. G. L.; Lynch, A. T.; Sneddon, L. G. *Solid State Ionics* **1989**, *32/33*, 655–660.

[6] Narula, C. K.; Schaeffer, R.; Paine, R. T. *J. Am. Chem. Soc.* **1987**, *109*, 5556–5557.

[7] Narula, C. K.; Paine, R. T.; Schaeffer, R. *Polymer Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1987**, *28*, 454.

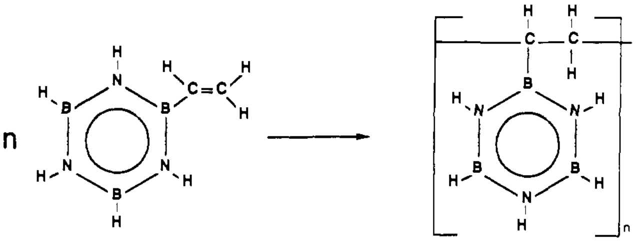
[8] Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Better Ceramics through Chemistry II*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; MRS Symposia Proceedings 73; Materials Research Society: Pittsburgh, PA, 1986; pp 383–388.

[9] Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 378–384.

[10] (a) Rees, W. S., Jr.; Seyferth, D. Presented at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Sept 1987; Paper INOR 446. (b) Rees, W. S., Jr.; Seyferth, D. *J. Am. Ceram. Soc.* **1988**, *71*, C194–C196.

One particularly attractive precursor to h-BN is the ring compound borazine, $B_3N_3H_6$, since the compound is readily made[17] and has both the correct boron/nitrogen ratio and a hexagonal structure. Indeed, Paine[6-9] and Ultrasystems[11-13] have each recently demonstrated the use of linked polyborazine gels or polymers as precursors for boron nitride.

An alternative type of preceramic borazine polymer would be one in which the borazine is bound as a pendant group on a conventional organic polymer backbone. For example, a compound such as vinylborazine, which could be considered the inorganic analogue of styrene, could serve as the repeating unit in the construction of the new polystyrene-type polymer, poly(vinylborazine). Furthermore, because of their similarity to conventional organic vinyl polymers, these types of borazine polymers might be both soluble and processable.



(1)

Owing to the absence of general synthetic routes for the formation of suitable *B*-alkenylborazine monomers, the production of poly(vinylborazine) polymers has not been possible. Thus, although vinyl derivatives of alkylated borazines have been prepared,[18-20] including *B*-vinylpentamethylborazine and *B*-trivinyl-*N*-triphenylborazine, the presence of the ring substituents was found to inhibit polymerization. Furthermore, even if polymers based on these compounds could be made, their high carbon contents would make them undesirable as boron nitride precursors. The parent *B*-trivinylborazine has also been synthesized, in 45% yields by thermolysis of bis(trimethylamino)-vinylborane.[21] Although the polymerization reactions of this compound have not been reported, it would be expected, due to the three vinyl substituents, to form only insoluble crosslinked polymers and have little preceramic utility.

In a preliminary communication[22] we recently reported the development of a general, transition-metal-catalyzed, synthetic route for the high yield production of *B*-alkenylborazines. In this paper we report full details of these and related metal-catalyzed reactions as well as the synthesis and ceramic conversion reactions of the new inorganic polymer, poly(vinylborazine).

Table I. NMR Data of Alkenylborazines and Poly(alkenylborazines)

compd[a]	nucleus	δ^b J (Hz), assignment
I	$^{11}B^c$	31.2 (s, B2), 31.5 (d, J_{BH} = 129 Hz, B4,6).
	$^1H^d$	4.4 (q, J_{BH} = 136 Hz, BH, 2), 5.26 (t, J_{NH} = 51 Hz, NH, 3), 5.85 (m, $CH_{a,b,c}$, 3)
	$^{13}C^e$	130.4 (s, 1), 136.5 (q, J_{CB} = 67 Hz, 1)
II	$^{11}B^c$	31.4 (d, J_{BH} = 138 Hz, B6), 31.7 (s, B2,4)
	$^1H^f$	5.0 (s, br, NH, 3), 5.84 (m, $CH_{a,b,c}$, 6)
III	$^{11}B^c$	31.3 (s, B2), 31.6 (d, J_{BH} = 136 Hz, B4,6)
	$^1H^f$	1.65 (d of d, $J_{CH_3CH_a}$ = 6.4 Hz, $J_{CH_3H_b}$ = 1.5 Hz, CH_3, 3), 4.52 (q, J_{BH} = 119 Hz, BH, 2), 5.04 (t, J_{NH} = 44.9 Hz, NH, 3), 5.44 (d of d, $J_{H_bH_a}$ = 17.7, $J_{H_bCH_3}$ = 1.2, CH_b, 1), 5.95 (d of q, $J_{H_aH_b}$ = 18.0, $J_{H_aCH_3}$ = 6.1, CH_a, 1)
IV	$^{11}B^c$	31.6 (d, J_{BH} = 132 Hz, B4,6), 32.0 (s, B2)
	$^1H^f$	1.63 (s, CH_3, 3), 4.76 (q, J_{BH} = 127 Hz, BH, 2), 5.19 (t, J_{NH} = 50 Hz, NH, 3), 5.27 (s, br, CH, 1), 5.43 (s, br, CH, 1)
V	$^{11}B^c$	31.6 (d, J_{BH} = 137 Hz, B4,6), 31.6 (s, B2)
	$^1H^g$	0.90 (t, $J_{CH_3CH_2}$ = 7.3 Hz, CH_3, 3), 2.0 (p, J = 7.1, CH_2, 2), ~4.4 (q, J_{BH} = 110 Hz, BH, 2), 5.08 (t, J_{NH} = 45 Hz, NH, 3), 5.43 (d, $J_{H_aH_b}$ = 18 Hz, CH_a, 1), 6.06 (d of t, $J_{H_bH_a}$ = 17 Hz, $J_{H_aCH_2}$ = 6.1 Hz, CH_2, 1)
VI	$^{11}B^c$	31.6 (d, J_{BH} = 146 Hz, B4,6), 32.2 (s, B2)
	$^1H^{f,h}$	0.91 (t, $J_{CH_3CH_2}$ = 7.4 Hz, CH_3, 3), 1.94 (q, $J_{CH_2CH_3}$ = 7.4, CH_2, 2), 5.21 (t, J_{NH} = ~45 Hz, NH, 3), 5.29 (s, H_a, 1), 5.40 (s, H_b, 1)
VII	$^{11}B^c$	31.6 (d, J_{BH} = 140 Hz, B4,6), 32.3 (s, B2)
	$^1H^f$	1.48 (s, br, CH_3, 3), 1.55 (d, J_{CH_3H} = 7.0 Hz, CH_3, 3), ~4.5 (q, br, J_{BH} = 116 Hz, BH, 2), 5.19 (t, J_{NH} = 49 Hz, NH, 3), 5.80 (q, J_{CH_3H} = 7.5 Hz, CH, 1)
VIII	$^{11}B^c$	31.5 (d, J_{BH} = 135 Hz, B4,6), 36.7 (s, B2)
	$^1H^d$	0.62 (q, $J_{CH_3CH_2}$ = 7.6 Hz, CH_3, 3), 0.80 (t, $J_{CH_2CH_3}$ = 7.8 Hz, CH_2, 2), 4.57 (q, br, J_{BH} = 131 Hz, BH, 2), 4.82 (t, J_{NH} = 50 Hz, NH, 2), 4.99 (t, J_{NH} = 40 Hz, NH, 1)
IX	$^{11}B^c$	31.4 (d, J_{BH} = 144 Hz, B4,6), 36.4 (s, B2)
	^1H	0.64 (t, $J_{CH_3CH_2}$ = 8 Hz, CH_3, 3), 0.88 (d, $J_{CH_2CH_3}$ = 5 Hz, CH_2, 2), 1.22 (m, J = 6 Hz, CH_2), 4.5 (q, J_{BH} = 123 Hz, BH, 2), 4.9 (t, J_{NH} = 49 Hz, NH, 3)
X	$^{11}B^c$	34.9 (d, J_{BH} = 144 Hz, B4,6), 34.1 (s, B2)
	$^1H^{d,h}$	2.93 (s, CH_3, 6), 2.97 (s, CH_3, 3), 5.78 (m, $H_{a,b,c}$, 3)
XII	$^{11}B^c$	30.6 (d, J_{BH} = 129 Hz, B4,6), 35.8 (s, B2)
	$^1H^d$	0.9 (m, br), 4.9 (br)

[a] All spectra obtained in C_6D_6. [b] Key: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, all shifts are in ppm. [c] Boron-11 NMR at 160.5 MHz. [d] Proton NMR at 500 MHz. [e] Proton spin decoupled, carbon-13 NMR spectrum at 125.8 MHz, at 62 °C. [f] Proton NMR at 250.15 MHz. [g] Proton NMR at 200.13 MHz. [h] Because of overlap, BH protons could not be identified.

Experimental Section

All manipulations were carried out by using standard high vacuum or inert atmosphere techniques as described by Shriver.[23]

Materials. Ammonia was purchased from Aldrich or Matheson and used as received. Acetylene and ethylene were obtained from Matheson and borazine from Callery Chemical Co. Acetylene, ethylene, and borazine were purified by vacuum line fractionation prior to use. $PdBr_2$ was obtained from Aldrich and 1-butyne from Columbia Organic Chemicals and were used as received. The N-$(CH_3)_3B_3N_3H_3$,[24] $RhH(CO)(PPh_3)_3$,[25] and $IrCl(CO)(PPh_3)_2$[26] were prepared by standard literature methods.

Physical Measurements and Instrumentation. Boron-11 NMR spectra at 160.46 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. Proton NMR at 200.13 MHz and boron-11 NMR at 64.02 MHz were obtained on an IBM AF-200 Fourier transform spectrometer. Proton NMR spectra at 250.15 MHz were obtained on an IBM AF-250 Fourier transform spectrometer. Chemical shifts for ^{11}B NMR spectra are relative to external $BF_3{\cdot}O(C_2H_5)_2$, with a negative sign indicating an upfield shift. Chemical shifts for ^1H NMR spectra are in

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(11) Paciorek, K. J. L.; Harris, D. H.; Krone-Schmidt, W.; Kratzer, R. H. Technical Report No. 4; Ultrasystems Defense and Space Inc.: Irvine, CA, 1987.

(12) Paciorek, K. J. L.; Krone-Schmidt, W.; Harris, D. H.; Kratzer, R. H.; Wynne, K. R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 392–406.

(13) (a) Paciorek, K. L.; Harris, D. H.; Kratzer, R. H.; Smythe, M. E.; Kimble, P. F. Technical Report No. SN-2022-F; Ultrasystems Defense and Space Inc.: Irvine, CA, 1985. (b) Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci., Polym. Chem. Educ.* **1986**, *24*, 173–185.

(14) Walker, B. E., Jr.; Rice, R. W.; Becher, P. F.; Bender, B. A.; Coblenz, W. S. *Am. Cer. Soc. Bull.* **1983**, *62*, 916–923.

(15) Gonsalves, K. E.; Agarwal, R. *Appl. Organomet. Chem.* **1988**, *2*, 245–249.

(16) Shaw, S. Y.; Dubois, D. A.; Nielson, R. H. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 385–391.

(17) For a review of borazine syntheses and chemistry, see: *Gmelin Handbush der Anorganishen Chemie, Borazine and Its Derivatives*; Springer-Verlag: New York, 1978; Vol. 17.

(18) Klancia, A. J.; Faust, J. P.; King, C. S. *Inorg. Chem.* **1967**, *6*, 840–842.

(19) Klancia, A. J.; Faust, J. P. *Inorg. Chem.* **1968**, *7*, 1037–1038.

(20) Pellon, J.; Deichert, W. G.; Thomas, W. M. *J. Polym. Sci.* **1961**, *55*, 153–160.

(21) Fritz, P.; Niedenzu, K.; Dawson, J. W. *Inorg. Chem.* **1964**, *3*, 626–627.

(22) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867–5868.

(23) Shriver, D. F.; Drezdzon, M. A. *Manipulations of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(24) Schaeffer, G. W.; Anderson, E. R. *J. Am. Chem. Soc.* **1949**, *71*, 2143–2145.

(25) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 59–60.

(26) Vrieze, K.; Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101–104.

Table II. Infrared Spectra (cm^{-1}) of Alkenylborazines

I[a]	3480 s, 3080 sh, m, 3070 m, 2980 m, 2970 m, 2600 m, 2520 vs, 2440 m, 1910 w, br, 1620 s, 1540 m, 1475 vs, br, 1425 s, sh, 1380 vs, 1350 s, sh, 1290 w, br, 1140 w, sh, 1125 m, 1120 m, 1015 m, 955 s, 930 vs, 920 vs, 735 s, 720 vs, 690 m, 680 m
III[b]	3440 vs, 3000 m, 2960 m, 2930 m, 2910 m, 2880 m, sh, 2850 m, 2600 sh, w, 2580 m, 2500 vs, 2440 m, sh, 2420 m, 1640 vs, 1460 vs, br, 1390 s, 1370 vs, 1340 s, 1310 m, 1280 w, 1270 w, 1145 w, 1125 m, 1075 w, 1055 w, 1035 w, 980 s, 920 s, 900 vs, 785 m, 715 s, 620 m
IV[b]	3440 s, 3050 m, 2950 m, 2930 m, 2910 m, sh, 2850 w, 2580 w, sh, 2500 s, 2420 w, 1625 m, 1615 m, 1505 s, sh, 1460 vs, br, 1410 s, 1395 s, 1380 s, 1345 m, sh, 1330 m, 1260 w, 1080 w, 1040 w, 980 w, 920 s, 900 vs, 740 m, 715 s, 625 m
V[b]	3440 vs, 2990 sh, m, 2960 s, 2920 s, 2870 s, 2850 sh, m, 2580 m, 2500 vs, 2440 m, 2420 m, 2280 m, 2200 w, 1905 w, 1865 w, 1810 w, 1725 w, 1635 vs, 1410 vbr, vs, 1395 s, 1375 vs, 1345 s, 1320 sh, m, 1275 m, 1255 m, 1145 m, 1130 m, 1100 m, 1070 m, 1015 m, 985 s, 920 sh, vs, 905 vs, 860 w, 825 m, 810 m, 785 w, 715 s, 630 m, 610 m
VI[b]	3440 vs, 3050 m, 2960 vs, 2930 s, 2910 s, 2870 s, 2580 m, 2510 vs, 2440 m, 2420 m, 2390 w, 2330 w, 2280 w, 2260 w, 2200 w, 2190 w, 2140 w, 1850 w, 1810 w, 1635 m, 1615 s, 1465 vs, vbr, 1420 vs, 1410 vs, 1375 vs, 1350 sh, s, 1330 s, 1310 m, 1270 m, 1230 m, 1215 w, 1130 w, 1110 w, 1085 m, 1075 m, 1015 m, 1035 m, 1010 w, 985 m, 920 sh, vs, 905 vs, 865 w, 815 w, 800 w, 735 s, 715 vs
VII[b]	3450 s, 3020 w, 2990 w, 2970 m, 2930 m, 2910 m, 2860 m, 2580 sh, w, 2510 s, 2440 w, 1660 s, 1470 vs, br, 1440 vs, br, 1385 s, 1340 m, 1325 m, 1275 w, 1230 w, 1090 w, 1070 w, 1030 w, 980 w, 920 s, 910 vs, 820 w, 715 s, 655 s
VIII[b]	3440 vs, 2950 vs, 2910 s, 2870 s, 2840 sh, m, 2800 m, 2580 s, 2500 vs, 2430 s, 2340 w, 1910 w, 1810 w, 1620 w, 1530 sh, s, 1465 vbr, vs, 1410 vs, 1375 vs, 1345 vs, 1290 m, 1270 m, 1125 m, 1105 s, 1055 m, 990 m, 960 m, 910 vs, 815 w, 765 s, 720 s
IX[b]	3420 s, 2940 s, 2900 m, 2860 m, 2500 s, 1475 vs, br, 1390 s, 1105 w, 920 sh, m, 910 s, 715 m
X[b]	3050 m, 2950 vs, 2900 s, 2880 sh, m, 2850 m, 2810 m, 2560 sh, m, 2520 m, 2480 vs, 1610 s, 1460 vbr, vs, 1400 br, vs, 1285 m, 1260 m, 1210 m, 1115 s, 1080 s, 1060 m, 1050 sh, m, 1010 s, 940 s, 925 m, 900 m, 875 vs, 730 m, 710 s

[a] Gas cell, NaCl windows, 10 cm. [b] Thin film NaCl plates.

Table III. Infrared Spectra of Poly(alkenylborazines) and Ceramic Materials

polymer	
XI[b]	3450 s, 2950 s, 2925 s, 2900 s, 2500 s, 1460 vs, br, 1100 s, 1000 s, 900 vs, 700 s
XII[a]	3440 vs, 2940 vs, 2900 vs, 2860 vs, 2730 w, 2580 s, sh, 2500 vs, 2420 s, 2280 w, 1905 w, 1810 w, 1600 m, 1420 vs, br, 1265 vs, 1220 vs, br, 1170 s, 1085 vs, 1065 s, 1000 vs, 920 vs, 900 vs, 865 s, sh, 845 s, 820 s, 750 vs, sh, 710 vs, br
XIII[a]	3430 vs, 2940 vs, 2920 vs, 2890 vs, 2860 vs, 2720 w, 2580 s, 2500 vs, 2430 s, 2270 w, 2200 w, 1905 w, 1805 w, 1635 s, 1600 m, 1400 vs, vbr, 1140 s, br, 1115 s, br, 1065 s, 1015 s, 980 s, 920 s, sh, 900 s, 840 m, sh, 820 s, 700 vs, br
XIV[a]	3430 vs, 2950 vs, 2910 vs, 2950 vs, 2720 w, 2580 s, 2500 vs, 2420 s, 2260 w, 2200 w, 2140 w, 1905 w, 1805 w, 1630 s, 1600 s, 1400 vs, vbr, 1270 vs, 1225 br, s, 1140 vs, br, 1080 br, s, 1090 sh, s, 1015 br, s, 985 s, 970 s, sh, 920 vs, sh, 900 vs, 850 m, 825 m, 700 vs, vbr
XV[b]	3445 s, 2952 s, 2867 s, 2583 sh, m, 2509 s, 2432 sh, m, 1644 w, 1458 vs, 1377 vs, 1280 s, 1241 s, 1140 s, 985 s, 908 vs, 712 vs
ceramic	
XVI[b]	3368 sh, s, 3233 s, 3092 s, 1649 sh, m, 1578 sh, m, 1440 vs, 1347 vs, 1241 s, 1099 s, 1028 s, 943 sh, s, 927 vs, 863 sh, m, 783 s, 698 s
XVII[b]	3450 m, sh, 2800 w, 2550 w, 2350 w, 1450 vs, br, 1100 m, 850 w, 720 s, 700 m, 625 m
XVIII[b]	3450 m, sh, 2825 w, 2560 w, 2375 w, 1450 br, vs, 1150 w, 1110 w, 820 s, 700 m, 640 w
XVIII[b,c]	3300 br, m, 2575 w, 2375 w, 1420 vs, br, 1160 w, 820 s

[a] Thin film, NaCl plates. [b] Diffuse reflectance IR, KBr. [c] Ceramic heated at 1450 °C. [d] Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, sharp.

ppm based on 7.15 ppm for C_6D_6 (relative to Me_4Si at 0.00 ppm). NMR data are listed in Table I.

Gas-liquid chromatography was conducted on either a Varian Aerograph Model 920 gas chromatograph or a Gow Mac 550P gas chromatograph. Unit and high-resolution mass spectra were obtained on a VG-7070H high-resolution mass spectrometer interfaced to a VG 11-250J data system. Infrared spectra were recorded on a Perkin-Elmer 1465 infrared spectrophotometer. Diffuse reflectance infrared spectra were performed at the DuPont Marshall Laboratories on a Perkin-Elmer Fourier transform instrument with the proper diffuse reflectance attachment. UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Infrared spectral data for *B*-alkenylborazines are in Table II; IR data for the poly(alkenylborazines) and ceramic materials are in Table III.

Gel permeation chromatography was also performed at the DuPont Marshall Laboratories on a Waters GPC-2 high-pressure liquid chromatograph equipped with two Waters 100 Å ultrastyragel columns with tetrahydrofuran as the eluting solvent (flow rate = 1 mL/min). The columns were calibrated with poly(ethyleneglycol) and poly(propyleneglycol) standards.

Thermogravimetric analyses were performed on a Dupont 2100 thermal analyzer with a 951 TGA. Differential scanning calorimetry was performed on a Dupont 910 thermal analyzer with a 910 DSC cell base. X-ray powder diffraction spectra were recorded on a Rigaku Geigerflex X-ray powder diffractometer. Densities were measured by flotation in a mixture of dichloromethane and diiodomethane.

Polymer pyrolyses were carried out in a Lindberg 58000 series tube furnace oven with an Eurotherm 818 temperature control unit. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN.

Preparation of Alkenylborazines. Reactions with $RhH(CO)(PPh_3)_3$. $B_3N_3H_6$ and Acetylene. In a typical reaction, 9 mg of $RhH(CO)(PPh_3)_3$ (9.8×10^{-3} mmol) was placed in an 88-mL Fischer-Porter glass pressure reaction vessel (part no. 100-205-0003) which was then evacuated. Borazine (2.218 g, 27.5 mmol) and 30 mmol of acetylene were condensed into the flask at −196 °C. The reaction mixture was then allowed to warm to room temperature, and within minutes the yellow solution turned reddish brown and became completely homogeneous. After 4 h the reaction flask was attached to the vacuum line, frozen at −196 °C, and degassed to remove a small amount of noncondensable gas. The volatile materials were then fractionated through a −30, −70, −116, −196 °C trap series, resulting in the isolation of 306 mg (2.87 mmol) of pure *B*-(CH_2=CH)-$B_3N_3H_5$ (I) in the −70 °C trap and 1.890 g of unreacted $B_3N_3H_6$ in the −116 °C trap. This corresponds to a 71.8% yield of I, based on consumed borazine, and 293 catalyst turnovers in the 4-h period.

Higher reaction temperatures (50 °C, for example) caused extensive polymerization of the *B*-(CH_2=CH)-$B_3N_3H_5$, as evidenced by the formation of a ball of intractable residue in the reaction flask, reducing the yield of the reaction. Allowing the reaction to continue for extended periods of time or increasing the acetylene/borazine ratio caused the formation of *B*-$(CH_2{=}CH)_2$-$B_3N_3H_4$ (II), a pure sample of which was obtained by preparative GLC. For example, when the reaction was carried out for 10 h, a ~4% yield of *B*-$(CH_2{=}CH)_2$-$B_3N_3H_4$ was observed.

Exact mass calcd for I $^{11}B_3{}^{14}N_3{}^{12}C_2{}^{1}H_8$ 107.0997, fd 107.1000; for II $^{11}B_3{}^{14}N_3{}^{12}C_4{}^{1}H_{10}$ 133.115, fd 133.114. The UV spectrum of I shows a broad absorption centered at 212 nm.

$B_3N_3H_6$ and Propyne. In an analogous reaction, borazine (2.47 g, 30.7 mmol) and 30 mmol of propyne were reacted in the presence of 6.6 mg (0.0072 mmol) of $RhH(CO)(PPh_3)_3$ at 55 °C for 10 h. Fractionation of the reaction mixture through a −20, −65, −196 °C trap series gave 364 mg (3.02 mmol) of *B*-propenylborazines stopping in a −65 °C trap and 2.187 g (27.2 mmol) of unreacted borazine. This corresponds to an 85.2% yield, based upon consumed borazine, and 419 catalyst turnovers during the 10 h period. GLC analysis (6 ft, 6% TCP column, 120 °C) of the product indicated that it was composed of a 4:1 mixture of *B*-*trans*-(1-MeCH=CH)-$B_3N_3H_5$ (III, Rv = 6.4) and *B*-2-(CH_2=CMe)-$B_3N_3H_5$ (IV, Rv = 4.9). Pure samples of each isomer were obtained by preparative GLC. Exact mass calcd for $^{11}B_3{}^{14}N_3{}^{12}C_3{}^{1}H_{10}$ 121.115, fd III 121.113; IV 121.116.

$B_3N_3H_6$ and 1-Butyne. Borazine (1.68 g, 20.9 mmol) and 20 mmol of 1-butyne were reacted in the presence of 11.7 mg (0.013 mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 6 h. Fractionation of the volatile materials gave 184 mg (1.37 mmol) of *B*-butenylborazine products stopping in a −60 °C trap, corresponding to 105 catalyst turnovers during the 6-h period. The exact yield could not be calculated since unreacted borazine could not be quantitatively separated from 1-butyne. GLC analysis of the product (3 ft, 3% TCP column, 110 °C) showed it to be composed of a 4.5:1 mixture of *B-trans*-(1-(EtCH=CH))-$B_3N_3H_5$ (V, Rv = 17.9) and 2-(1-(CH_2=CEt))-$B_3N_3H_5$ (VI, Rv = 11.4). Pure samples of each isomer were obtained by preparative GLC. Exact mass calcd for $^{11}B_3{}^{14}N_3{}^{12}C_4{}^{1}H_{12}$ 135.1308, fd V 135.1314; VI, 135.1310.

$B_3N_3H_6$ and 2-Butyne. Borazine (1.618 g, 20.1 mmol) and 20 mmol of 2-butyne were reacted with 16.5 mg (0.018 mmol) of RhH(CO)(PPh_3)$_3$ at room temperature for 4 h. Fractionation of the volatiles gave 270 mg (2.01 mmol) of *B*-butenylborazines stopping in a −55 °C trap, corresponding to 112 catalyst turnovers during the 4-h period. Again, the product yield could not be accurately calculated since unreacted borazine and 2-butyne could not be quantitatively separated. GLC analysis of the product (3 ft, 3% TCP column, 110 °C) indicated that it was composed of a 3:2 mixture of *B-trans*-(2-*cis*-(MeCH=CMe))-$B_3N_3H_5$ (VII, Rv = 17.7) and V. A pure sample of VII was obtained by preparative GLC. Exact mass calcd for VII, $^{11}B_3{}^{14}N_3{}^{12}C_4{}^{1}H_{12}$, 135.1308, fd 135.132.

***N*-Me$_3$-$B_3N_3H_3$ and Acetylene.** *N*-Me$_3$-$B_3N_3H_3$ (1.234 g, 10.1 mmol) and 30 mmol of acetylene were reacted with 15.3 mg of RhH(CO)(PPh_3)$_3$ for 24 h at room temperature. Fractionation of the volatiles showed no alkenylborazine products. Heating at higher temperatures (70 °C) also gave no reaction.

Reactions with IrCl(CO)(PPh_3)$_2$. $B_3N_3H_6$ and Propyne. In a typical reaction, 0.055 g of IrCl(CO)(Ph_3)$_2$ (0.071 mmol) was reacted with borazine (8.9 mmol) and propyne (30 mmol) in an 88-mL Fischer-Porter reaction flask at 55 °C for 1 h. Fractionation of the volatile materials through a −65, −195 °C trap series gave 117 mg (0.96 mmol) of *B*-propenylborazines and 7.03 mmol of unreacted borazine. This corresponds to 51.5% yield, based upon consumed borazine, and 14 catalyst turnovers. GLC analysis indicated that the product was a 4:1 mixture of III and IV, with a 5% *B*-propylborazine IX impurity. Exact mass calcd for IX, $^{11}B_3{}^{14}N_3{}^{12}C_3{}^{1}H_{12}$, 123.131, fd 123.131.

$B_3N_3H_6$ and 1-Butyne. Borazine (20 mmol) and 1-butyne (40 mmol) were reacted with 0.051 g (0.065 mmol) of IrCl(CO)(PPh_3)$_2$ at room temperature for 24 h. Fractionation of the volatile materials gave 363 mg (2.69 mmol) of *B*-butenylborazines stopping in a −60 °C trap, corresponding to 42 catalyst turnovers. The yield could not be calculated since the borazine could not be quantitatively separated from the 1-butyne. GLC analysis showed the product to be a 3:2 mixture of V and VI, with an ~5% *B*-butylborazine impurity.

Reactions with PdBr$_2$. $B_3N_3H_6$ and Ethylene. A 0.115-g (0.43 mmol) sample of PdBr$_2$ powder was stirred in vacuo with 40 mmol of ethylene and 1.65 g (20.5 mmol) of borazine in an 88-mL Fischer-Porter pressure reactor at room temperature. The reaction was stopped after 6 h and fractionated through a −70 °C trap resulting in the isolation of a material (242 mg) which was shown by GLC analysis (3 ft, 3% TCP, 65 °C) to be composed of a 4:1 mixture of *B*-(CH_2=CH)-$B_3N_3H_5$, I, and *B*-Et-$B_3N_3H_5$ (VIII, Rv = 2.9, Rv = 1 for $B_3N_3H_6$). Also isolated was 1.42 g (17.7 mmol) of unreacted borazine stopping in a −95 °C trap. This corresponds to an 81% yield of B-substituted borazine products and approximately five catalyst turnovers during the reaction period. No noncondensable gases were given off in the reaction; however, GLC analysis ($AgNO_3$ column, 30 °C) of the material passing the −70 °C trap showed the presence of ethane. Exact mass calcd for $^{11}B_3{}^{14}N_3{}^{12}C_2{}^{1}H_{10}$, VIII 109.115, fd 109.116.

$B_3N_3H_6$ and Propene. In an analogous reaction, 30 mmol of borazine and 30 mmol of propene were reacted with 0.148 g (0.56 mmol) of PdBr$_2$ for 6 h. Fractionation of the volatile materials gave a material stopping in the −65 °C trap (0.796 g) which was analyzed by GLC (6 ft, 6% TCP, 120 °C) and found to be composed of a mixture of *B*-propenylborazines (78%) and *B*-propylborazine (IX, 22%). The *B*-propenylborazines were separated by preparative GLC and found to be III (88%) and IV (12%) as identified by their ^1H and ^{11}B NMR spectra.

***N*-Me$_3$-$B_3N_3H_3$ and Ethylene.** In an analogous reaction, 1.345 g (11.0 mmol) of *N*-Me$_3$—$B_3N_3H_3$ and 30 mmol of ethylene were reacted with 0.059 g (0.22 mmol) of PdBr$_2$ at room temperature for 24 h. Fractionation of the volatiles gave unreacted *N*-Me$_3$-$B_3N_3H_3$ (0.978 g, 8.0 mmol) in a −78 °C trap. GLC analysis (3 ft, 3% TCP column, 70 °C) of the material retained in a −25 °C trap (375 mg) showed it to be a mixture of *B*-(CH_2=CH)-N-Me$_3$-$B_3N_3H_2$ (X, Rv = 5.5, 79.7%) and *B*-Et-N-Me$_3$-$B_3N_3H_2$ (Rv = 4.7, 20.3%), (Rv = 1.0 for *N*-Me$_3$-$B_3N_3H_3$). A pure sample of X was obtained by preparative GLC. Exact mass calcd for X, $^{11}B_3{}^{14}N_3{}^{12}C_5{}^{1}H_{16}$, 149.146, fd 149.146.

Preparations of Poly(alkenylborazines). Polymerization of *B*-Vinylborazine I. Insoluble Polymer XI. A 25-mL reaction flask was evacuated and charged with 324 mg (3.0 mmol) of I at −196 °C. The flask was then heated at 120 °C for ~4 h resulting in the production of a clear, rubbery polymer, XI. The polymer was found to be insoluble in acetone, C_6H_6, THF, or DMF. Further heating at 120 °C caused a hardening of the polymer with no noticeable evolution of H_2. Elemental Anal.: C, 23.43; H, 6.98; N, 39.68; B, 29.54; calcd for poly(*B*-vinylborazine) ($C_2B_3N_3H_8$)$_x$: C, 22.55; H, 7.57; N, 39.44; B, 30.44.

Polymerization of *B*-Vinylborazine I. Soluble Polymer XII. In a typical reaction, 551 mg (5.2 mmol) of I and 213 mg (2.7 mmol) of $B_3N_3H_6$ were condensed into a 25-mL reaction flask at −196 °C. The reaction mixture was then stirred in an oil bath at 120 °C. As the reaction progressed, the sample became increasingly viscous until the magnetic stir bar would no longer move (~2 h). At this point the flask was frozen at −196 °C and degassed to remove a small amount of noncondensable gas. The flask was then brought to room temperature, and the volatile materials were removed in vacuo. The remaining polymeric material, 587 mg, was found to be soluble in C_6H_6, Et_2O, or THF. GPC data: Mw = 977, Mn = 812, Mw/Mn = 1.2. Elemental Anal.: B, 32.36; N, 41.46; C, 19.36; H, 6.74.

Polymerization of *B*-Propenylborazines III and IV. Soluble Polymer XIII. In a typical reaction, a 278-mg (2.3 mmol) sample composed of a 4:1 mixture of III and IV and 97 mg (1.20 mmol) of $B_3N_3H_6$ were condensed into a 50-mL reaction flask at −196 °C. The reaction mixture was then stirred in an oil bath at 120 °C until the liquid became so viscous that the magnetic stir bar would no longer move. At this point the mixture was frozen at −196 °C, and the small amount of noncondensable gas was removed. The flask was then brought to room temperature, and the volatile materials were removed in vacuo. The remaining polymeric material XIII, 257 mg, was soluble in C_6H_6, Et_2O, or THF. GPC data: Mw = 1111; Mn = 690; Mw/Mn = 1.61. Elemental Anal.: B, 25.44; N, 28.61; C, 31.00; H, 8.81.

Polymerization of *B*-Butenylborazines V, VI, and VII. Soluble Polymer XIV. A 50-mL flask was charged with 194 mg (1.4 mmol) of *B*-butenylborazine (V, VI, and VII) and 77 mg (0.96 mmol) of $B_3N_3H_6$. The reaction was stirred at 120 °C until the reaction mixture became so viscous that the magnetic stir bar stopped stirring (~2 h). The flask was then frozen at −196 °C, and the small amount of noncondensable gas was removed. The volatile materials were then transferred to the vacuum line leaving 172 mg of polymeric material XIV. The polymer was found to be soluble in C_6H_6, Et_2O, or THF. GPC data: Mw = 1235; Mn = 783; Mw/Mn = 1.58. Elemental Anal.: B, 24.12; N, 30.09; C, 32.71; H, 8.85.

Polymerization of *B*-Propenylborazines III and IV. Insoluble Polymer XV. A neat sample of a 4:1 mixture of III and IV (150 mg, 1.2 mmol) was heated in vacuo for ~4 h at 120 °C resulting in the formation of a clear, rubbery material. The polymer was insoluble in acetone, C_6H_6, THF, or DMF. Elemental Anal.: fd C, 28.94; N, 34.44; B, 26.28; H, 6.94; calcd for poly(propenylborazine): C, 29.89; N, 34.85; B, 26.90; H, 8.36.

Ceramic Conversion Reactions. Polymer XI (Ar). A platinum lined fused silica combustion boat was charged with 260 mg of polymer XI. The boat was placed in a Lindberg tube furnace in a quartz tube, heated under a flow of Ar (~100 mL/min) at a rate of 10 °C/min to 1000 °C, and held at that temperature for 1 h. Upon cooling, 218 mg of a black material was isolated corresponding to a ceramic yield of 83.7%. Elemental Anal.: fd B, 34.10; N, 44.32; C, 16.98; H, 0.84; density 1.71 g/mL. The material was found to be amorphous by X-ray diffraction.

Polymer XI (NH_3). A platinum lined fused silica combustion boat containing 658 mg of polymer XI was placed into a tube furnace in a quartz tube and was slowly heated under a flow of ammonia (~100 mL/min) at a rate of 10 °C/min to 550 °C, where it was held at this temperature for 1 h. The sample was next further heated at a rate of 10 °C/min to 1000 °C and then held at this temperature for an additional 6 h. Upon cooling, 493 mg of a brown/black material remained in the boat corresponding to a 74.9% ceramic yield. Elemental Anal.: fd B, 38.82; N, 49.52; C, 3.71; H, 0.34; density 1.78 g/mL. The material was found to contain turbostratic BN by X-ray diffraction.[27-31]

Polymer XII (NH_3). Polymer XII (734 mg), dissolved in diethyl ether, was placed into a platinum lined fused silica boat, which was placed into a quartz tube in the tube furnace. The diethyl ether was then allowed to evaporate at room temperature under an ammonia flow (~100 mL/min). The sample was then slowly heated (5 °C/min) to 550 °C and held at this temperature for 1 h. The sample was then further heated at a rate of 10 °C/min to 1000 °C and held at this temperature for an additional hour. After cooling to room temperature, a tan material (540.5 mg, 73.6% ceramic yield) was obtained. Elemental Anal.: fd B, 41.67; N, 54.84; C, 1.30; H, 0.40; density, 1.6 g/mL. The X-ray diffraction pattern was characteristic of turbostratic BN.[27-31] The tan material was further heated at higher temperatures (1450 °C, 12 h) to produce white, crystalline h-BN as shown by X-ray diffraction.[27-31] Elemental Anal.: fd B, 42.59; N, 55.62; C, 0.27; H, 0.15; density 2.1 g/mL.

Results

Metal-Catalyzed Reactions with Borazine. Acetylene Reactions. The reactions of borazine with various alkynes, including acetylene,

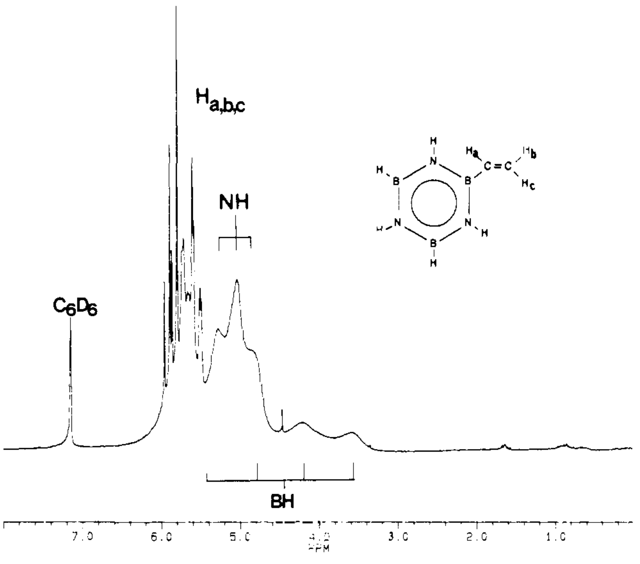
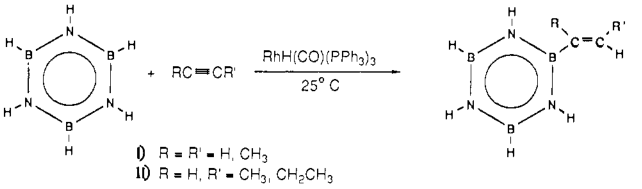


Figure 1. 200 MHz ^{1}H NMR spectrum of *B*-($CH_2{=}CH$)—$B_3N_3H_5$, I.

propyne, and butyne, in the presence of catalytic amounts of $RhH(CO)(PPh_3)_3$ were explored and in all cases were found to be excellent synthetic routes to B-substituted alkenylborazines. Reactions were generally run without solvent with a borazine/alkyne/catalyst ratio of 1:1:0.003. All reactions proceeded at moderate temperatures and were found to give good yields (70–85%) of boron-substituted alkenylborazine products according to eq 2.



(2)

Thus, in a typical reaction $B_3N_3H_6$ and acetylene were stirred in the presence of 0.03 mol % of the catalyst. After an induction period of ~2 min the initial yellow reaction solution changed to a homogeneous dark red, which then remained unchanged for the remainder of the reaction period. The reaction was usually stopped after 4 h, to avoid the formation of divinylborazine, and fractionated through a −70 °C trap. The *B*-vinylborazine was isolated in high purity by simple vacuum line fractionation in 70% yield, with a catalyst turnover rate exceeding 50/h. The acetylene reaction must be carried out at room temperature since higher reaction temperatures result in polymerization of the *B*-vinylborazine.

The ^{11}B NMR spectrum of *B*-($CH_2{=}CH$)-$B_3N_3H_5$ (I) consists of two peaks, a doublet and a singlet, with relative intensities of 2:1, confirming substitution at the boron. The ^{1}H NMR spectrum (Figure 1) exhibits broad resonances for the N–H and B–H protons as well as resonances expected for the vinylic protons centered at 5.85 ppm. The complex pattern observed for the vinyl resonances is similar to that observed[32] for other ABC spin systems such as styrene. The proton decoupled ^{13}C NMR spectrum at 60 °C (Figure 2a) shows a quartet ($J_{^{11}BC}$ = 67 Hz) and a singlet consistent with B-substitution at the borazine ring. Lowering the temperature induces thermal decoupling of the boron bound to the carbon,[33] and, as a result, the proton-decoupled ^{13}C NMR spectrum at −50 °C shows two singlets (Figure 2b). The corresponding proton-coupled ^{13}C NMR spectrum (Figure 2c) shows a doublet for the carbon bound to the boron and a complex pattern of peaks for the CH_2 carbon. The infrared spectrum shows characteristic adsorptions at 3480 cm^{-1} (NH), 3070 cm^{-1} (geminal CH stretching), 2980 and 2970 cm^{-1} (olefinic CH stretching), 2520 cm^{-1} (BH), and 1620 cm^{-1} (carbon–carbon double bond stretch).

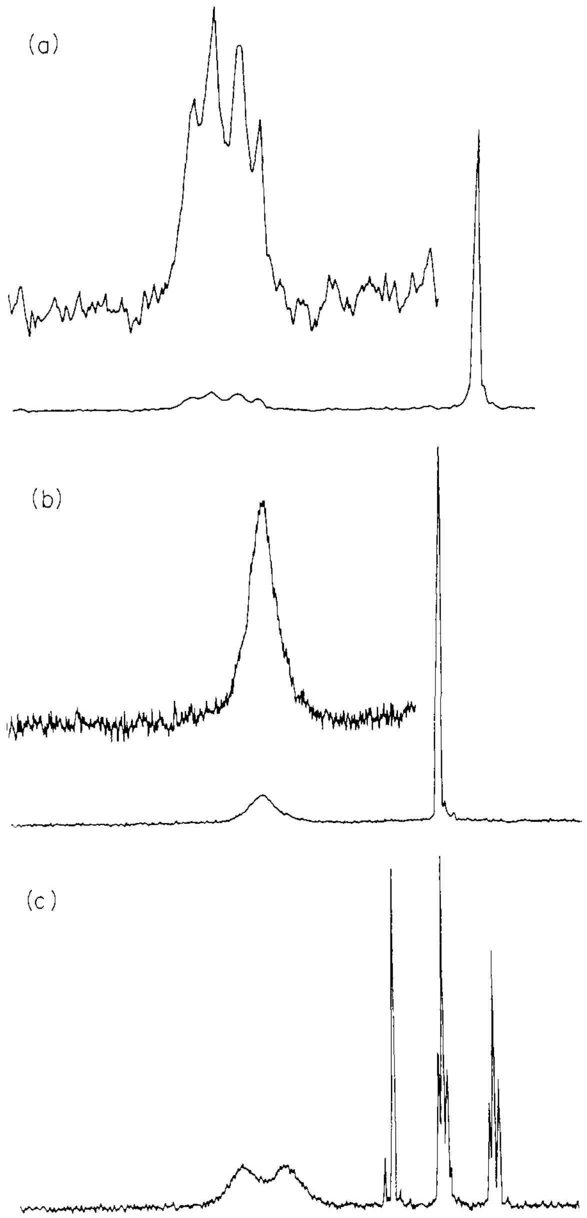


Figure 2. 125.8 MHz ^{13}C NMR spectrum of *B*-($CH_2{=}CH$)—$B_3N_3H_5$, I: (a) proton spin decoupled spectrum at 60 °C, (b) proton spin decoupled spectrum at −50 °C, and (c) proton spin coupled spectrum at −50 °C.

Other terminal and internal alkynes, including propyne and 1- and 2-butyne, were found to undergo similar reactions in the presence of borazine and catalytic amounts of $RhH(CO)(PPh_3)_3$. In these cases, unlike the acetylene reaction, the reaction solution remained yellow throughout the entire reaction period. The corresponding alkenylborazines were again isolated in high purity through simple vacuum line fractionation in ~80% yields with catalyst turnover rates of ~25–30/h.

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(27) Pease, R. S. *Acta. Crystallogr.* **1952**, *5*, 356–361.

(28) Biscoe, J.; Warren, B. E. *J. Appl. Phys.* **1942**, *13*, 364.

(29) Thomas, J.; Weston, N. E.; O'Connor, T. E. *J. Am. Chem. Soc.* **1962**, *84*, 4619–4622.

(30) Economy, J.; Anderson, R. *Inorg. Chem.* **1966**, *5*, 989–992.

(31) Matsuda, T.; Uno, N.; Nakae, H.; Hirai, T. *J. Mat. Sci.* **1986**, *21*, 649.

(32) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969.

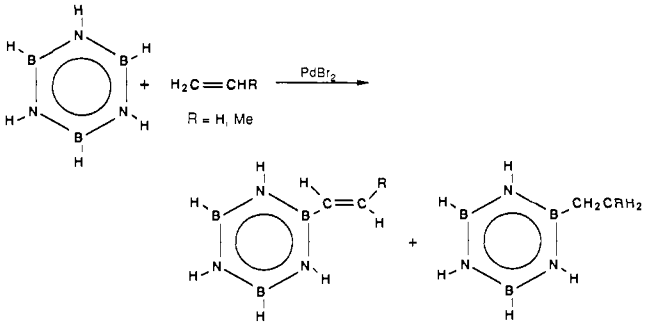
(33) (a) Wrackmeyer, B. In *Progress in NMR Spectroscopy, 12*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon: New York, 1979; 227–259. (b) Gragg, B. R.; Layton, W. J.; Niedenzu, K. *J. Organomet. Chem.* **1977**, *132*, 29–36.

The ^{1}H NMR spectrum of the product of the reaction of $B_3N_3H_6$ with propyne showed two sets of vinylic protons, at 5.44 and 5.95 ppm for IV and 5.27 and 5.43 for V, indicating that it was an isomeric mixture of *trans*-(1-MeCH=CH)-$B_3N_5H_5$ (III) and 2-(CH_2=CMe)-$B_3N_3H_5$ (IV) in a 4:1 ratio. The ^{11}B NMR spectra of both isomers again confirm substitution at the boron, showing two peaks, a singlet and a doublet, in a ratio of 2:1. Similar products, *B*-*trans*-(1-(EtCH=CH))-$B_3N_3H_5$ (V) and *B*-2-(1-(CH_2=CEt))-$B_3N_3H_5$ (VI), were isolated in the reaction of 1-butyne and $B_3N_3H_6$.

The reaction of 2-butyne with $B_3N_3H_6$ produced an isomeric mixture of *trans*-2-(*cis*-2-MeCH=CMe)-$B_3N_3H_5$ (VII) (60%) and *B*-*trans*-1-(EtCH=CH)-$B_3N_3H_5$ (V) (40%). VII is the expected product from a cis addition of B–H to 2-butyne. The formation of V, in which the double bond has migrated to a terminal position, is surprising; however, RhH(CO)(PPh_3)$_3$ has previously been shown to catalyze olefin isomerizations.

The IrCl(CO)(PPh_3)$_2$-catalyzed alkyne-addition reactions were found to produce products similar to those of the analogous rhodium-catalyzed reactions but with lower yields (~50%) and with small (~5%) *B*-alkylborazine impurities. For example, the reaction of propyne and $B_3N_3H_6$ in the presence of IrCl(CO)(PPh_3)$_2$ at 55 °C produced B-substituted products in ~52% yield (14 catalyst turnovers) which GLC analysis showed to be a mixture of III, IV, and *B*-propylborazine.

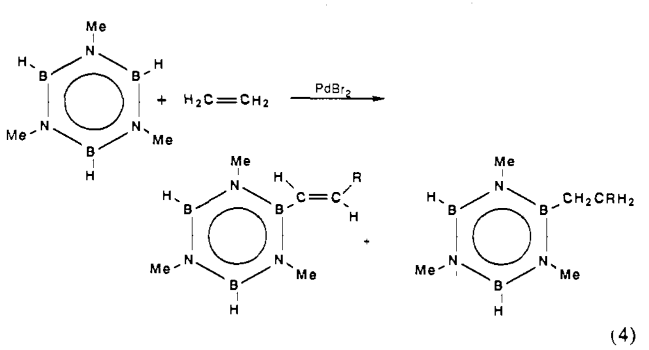
Reactions with Olefins. Alkenylborazines were also synthesized via a $PdBr_2$-catalyzed olefin/borazine coupling reaction with olefins such as ethylene and propene. The reactions were generally run neat, at room temperature, and produced B-substituted products in high yield (~85%). However, the reactions were not selective and also produced (20–25%) the corresponding B-substituted alkylborazines.



(3)

Thus, the reaction of borazine with ethylene produced a 4:1 mixture of *B*-vinylborazine I and *B*-ethylborazine VII, while the borazine-propene coupling reaction produced the *B*-propenylborazines (III and IV) and *B*-propylborazine IX. In both reactions, the product mixtures could be readily separated from unreacted borazine by simple vacuum line fractionation, but pure samples of each compound could only be obtained by preparative GLC.

The reaction of *N*-Me_3-$B_3N_3H_3$ with ethylene in the presence of catalytic amounts of $PdBr_2$ resulted in the formation of *B*-(CH_2=CH)-*N*-Me_3-$B_3N_3H_2$ X and *B*-Et-*N*-Me_3-$B_3N_3H_2$ in ~ 80% yield. The NMR data for X again confirm vinyl substitution at the boron, showing a singlet and a doublet in a 2:1 ratio in the ^{11}B spectrum and two ring-methyl resonances in a 2:1 ratio along with a complex pattern for the vinylic protons centered at 5.8 ppm in the ^{1}H spectrum. The mass spectrum of *B*-Et-*N*-Me_3-$B_3N_3H_2$ showed the expected cutoff at *m*/*e* 151; however, the compound was isolated in insufficient amounts for complete spectral characterization.



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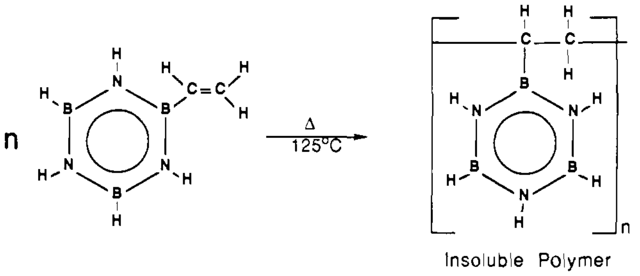
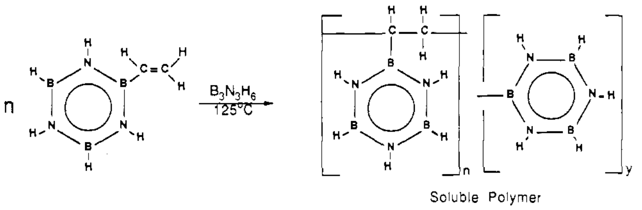
Polymerization of Alkenylborazines. *B*-Alkenylborazines were found to undergo thermally induced polymerizations under mild conditions to produce, depending on reaction conditions, either insoluble or soluble poly(alkenylborazines). For example, *B*-vinylborazine heated neat, at 120 °C, yielded, after 4 h, a clear, rubbery material XI which was found to be insoluble in solvents such as C_6H_6, THF, and DMF.



(5)

Heating the material for longer periods of time caused hardening with no noticeable loss of H_2. Elemental analysis confirmed a $B_3N_3C_2H_8$ composition for the polymer. The infrared spectrum showed B–H, N–H, and B–N stretches but no carbon–carbon double bond stretch, indicating that the polymer has a saturated carbon system. XI is thermally stable for months when stored under vacuum, but upon exposure to air slowly forms a cloudy crust over several hours.

Reactions of 1:2 mol ratios of borazine and *B*-alkenylborazines under the same conditions produced soluble poly(alkenylborazine) materials. For example, when vinylborazine was heated for ~2 h in the presence of a 50 mol % of borazine, a viscous polymeric material, poly(vinylborazine) XII, was produced which was soluble in C_6H_6, Et_2O, or THF. Heating for longer periods of time caused hardening of the polymer, and it became insoluble. Elemental analysis of XII showed the polymer to have an empirical formula of $B_3N_3C_{1.6}H_{7.5}$, suggesting that additional borazine had been incorporated into the polymer framework. The infrared spectrum showed peaks corresponding to N–H, C–H, B–H and B–N stretches, but again no carbon–carbon double bond stretch was observed.



(6)

The ^{11}B NMR spectrum of XII (Figure 3) consists of two broad peaks, a singlet and a doublet, in a 1:2 ratio, with the singlet shifted downfield by ~5 ppm. The singlet shift is consistent with those observed for borazine borons substituted by alkyl groups.[34] The ^{1}H NMR spectrum shows broad resonances centered at 0.8 ppm for aliphatic protons, 4.4 and 4.9 ppm for B–H and N–H protons, respectively, but no peaks are observed in the vinylic proton region. These NMR data strongly support the formulation of polymer XII as a polyethylene carbon backbone with pendant borazines. The GPC data show the material to be composed of low molecular weight oligomers with molecular weights of ~900, corresponding

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(34) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; pp 188–196.

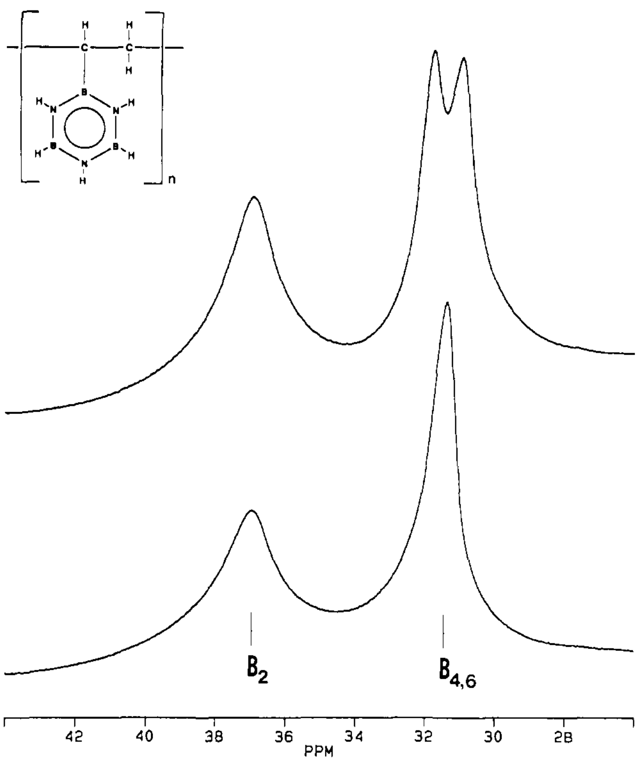

Figure 3. 160.5 MHz ^{11}B NMR spectrum of polymer XII. Bottom spectrum is proton spin decoupled.

Table IV. Summary of Polymer Pyrolysis Reactions

polymer	pyrolysis conditions	color	composition	density (g/mL)	crystallinity
XI	Ar 1000 °C	black	$B_{1.00}N_{1.00}C_{0.45}H_{0.26}$	1.71	amorphous
XI	NH_3 1000 °C	brown	$B_{1.00}N_{0.98}C_{0.09}H_{0.09}$	1.78	turbostratic
XII	NH_3 1000 °C	tan	$B_{1.00}N_{1.01}C_{0.03}H_{0.10}$	1.6	turbostratic
XII	NH_3 1000 °C Ar, 1450 °C	white	$B_{1.00}N_{1.01}C_{0.006}H_{0.04}$	2.1	hexagonal

to a chain length of about seven alkenylborazine units. The elemental analysis is also in agreement with this interpretation.

Soluble polymers were also made from *B*-propenyl- (III and IV) and *B*-butenylborazines (V, VI, and VII), by heating the alkenylborazines in the presence of 50 mol % of borazine. Their ^{1}H NMR spectra again show broad resonances for the C–H, N–H, and B–H protons, but no peaks are observed in the vinylic proton region. The GPC data show both polymers to be low molecular weight, ~1000, corresponding to chain lengths of about eight monomer units. The elemental analyses of the polymers are again in agreement with the incorporation of additional borazine into the polymer.

Ceramic Conversion Reactions. The ceramic conversion reactions of the vinyl polymers XI and XII were studied by heating the polymers in a tube furnace, under a flow of Ar or NH_3, at a heating rate of 5–10 °C and are summarized in Table IV.

The theoretical ceramic yield[2a] for the conversion of a poly(vinylborazine) polymer to pure nitride (eq 7) is 70%.

$$(B_3N_3C_2H_8)_x \rightarrow 3BN + 2CH_4 \qquad (7)$$

Bulk pyrolysis of insoluble polymer XI under Ar produced an amorphous black material XVI in 83.7% ceramic yield indicating, in agreement with the analytical data, the incorporation of substantial carbon (16.98%) in the material. The infrared spectrum of XVI was complex, exhibiting a large, broad peak between 3400 and 3000 cm^{-1}, arising from residual N–H and C–H groups, a broad B–N stretching band at 1440 cm^{-1}, and a number of sharp peaks from 1099 to 698 cm^{-1}.

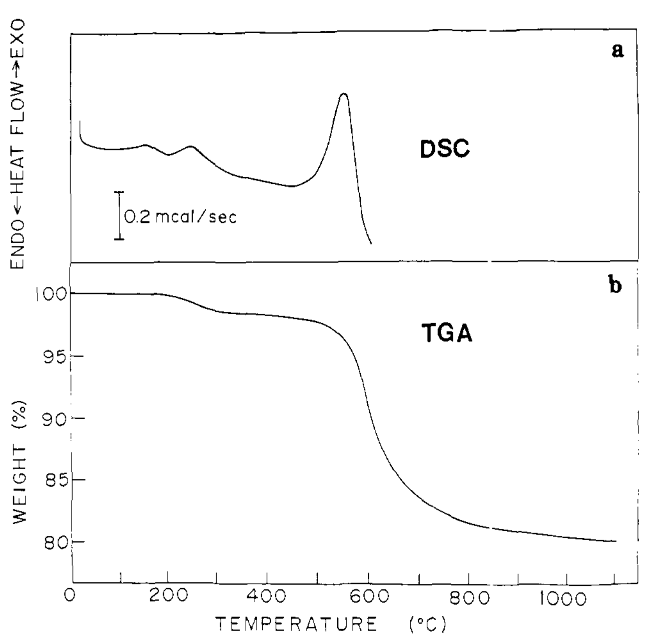

Figure 4. Thermogravimetric (b) and differential calorimetry (a) studies of the decomposition of polymer XI.

The decomposition of XI under nitrogen was also studied by thermogravimetric analysis (Figure 4a). An initial weight loss of 1.5% was observed between 200 and 300 °C, which may result from residual crosslinking via B–B bond formation accompanied by the loss of H_2. This was followed by a large weight decrease (14%) between 500 and 700 °C. A total loss of 20.1% was observed by 900 °C. Since the theoretical weight loss corresponding to the conversion of the polymer to pure boron nitride is 30%, these data indicate, in agreement with the results of the bulk pyrolyses discussed above, that significant carbon from the polymer backbone was retained in the final product.

The ceramic conversion reactions were also studied by DSC experiments (Figure 4b). Two small exotherms at 150 and 250 °C and a large pyrolytic exotherm beginning at 550 °C were observed. These observations are consistent with the TGA experiments which showed weight losses at corresponding temperatures.

Ceramic materials with reduced carbon contents were obtained when the polymer pyrolyses were carried out under ammonia. For example, bulk pyrolysis of XI under ammonia produced a dark brown material XVII with 3.71% carbon in ~75% ceramic yield. The diffuse reflectance IR spectrum of XVII is similar to spectra previously reported for boron nitride,[35-37] containing peaks at 1450 and 820 cm^{-1}; however, also present is a sharp peak at 3450 cm^{-1} suggesting the presence of N–H groups. XVII was found to contain turbostratic BN[27-31] by X-ray diffraction.

The reaction of XI under ammonia was also examined by TGA and gave similar results to the TGA under nitrogen. Again, the major weight loss occurred in the 500–700 °C region. However, the observed overall weight loss (24.5%) was greater than that found under Ar, consistent with the observed reduction of carbon found in the products of the bulk pyrolysis under ammonia.

BN powders with the lowest carbon and hydrogen contaminants were obtained by the pyrolysis of soluble polymer XII under ammonia. Heating at 1000 °C produced a tan material which the analytical data indicated had a B/N ratio of 0.99 and only 1.3% carbon and 0.4% hydrogen. The diffuse reflectance IR spectrum of the material was again similar to spectra previously reported for boron nitride;[35-37] however, a sharp adsorption at 3450 cm^{-1} was still observed suggesting the presence of residual N–H

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(35) Brame, E. G., Jr.; Margrave, J. L.; Meloche, V. W. *J. Inorg. Nucl. Chem.* **1957**, *5*, 48–52.

(36) Rand, M. J.; Roberts, J. F. *J. Elect. Chem. Soc.* **1968**, *115*, 423–429.

(37) Takahashi, T.; Itoh, H.; Takeuchi, A. *J. Cryst. Growth* **1979**, *47*, 245–250.

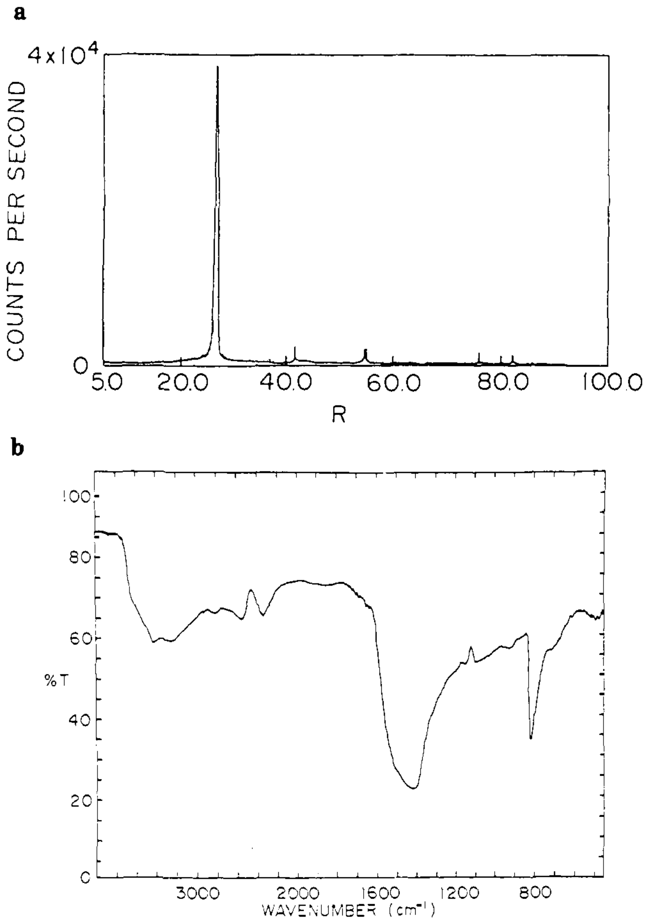

Figure 5. Diffuse reflectance infrared spectrum (b) and X-ray diffraction pattern (a) for h-BN made from the pyrolysis of polymer XII under ammonia at 1000 °C followed by treatment at 1450 °C under argon (see Experimental Section for details).

impurities. The tan material had a density of 1.4–1.6 g/mL and showed an X-ray diffraction pattern consistent with the presence of turbostratic BN.[27-31]

Upon heating the tan material at 1450 °C a white, crystalline powder was produced which was indistinguishable from authentic h-BN. Thus, the material exhibited both an X-ray powder diffraction pattern (Figure 5a) containing a sharp peak at 3.34 Å (002)[27-31] and a density (2.1 g/mL vs 2.2 g/mL[38] for h-BN) characteristic of h-boron nitride. Furthermore, the diffuse reflectance IR spectrum (Figure 5b) showed no hydrogen impurities and was identical with that observed for h-BN.[35-37]

Discussion

We have previously demonstrated that transition-metal reagents may be used to catalyze a wide variety of reactions involving polyhedral boranes and carboranes.[1,3-5,39-41] The work presented herein has now shown that transition-metal catalysts may also be used to activate similar reactions of borazine, including borazine–alkyne addition and borazine–olefin coupling. Both types of reactions produce *B*-alkenylborazines in high yields under mild conditions and are the first synthetic routes to the parent monoalkenylborazines to be developed.

Both $IrCl(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$ were found to catalyze borazine–alkyne additions; however, reactions with $IrCl(CO)(PPh_3)_2$ were slow and produced small amounts (~5%) of alkylborazine products along with significant polymeric residues. In contrast, reactions with $RhH(CO)(PPh_3)_3$ resulted in the formation of a variety of *B*-alkenylborazines in high yields and selectivities, with little product polymerization.

No mechanistic studies were performed; however, the results obtained for the borazine–alkyne addition reactions catalyzed by $RhH(CO)(PPh_3)_3$ appear to be consistent with the mechanisms proposed for the hydrosilylation reactions[42-47] utilizing this catalyst. Thus, steps involving ligand dissociation, alkyne addition, oxidative addition of a B–H to the rhodium, alkyne insertion into the B–Rh bond, reductive elimination, and addition of another equivalent of alkyne lead to the observed *B*-alkenylborazine products and regenerate the catalyst. Oxidative addition at a boron, rather than a nitrogen, site is also consistent with the nucleophilic nature of the catalyst. As in the hydrosilylation reactions,[47] the borazine–alkyne addition reactions produce a mixture of isomers resulting from both Markownikoff (IV and VI) and anti-Markownikoff (III and V) additions.

B-Alkenylborazines were also produced via a $PdBr_2$-catalyzed olefin–borazine coupling reaction. Thus, reactions of borazine with either ethylene or propene in the presence of $PdBr_2$ resulted in the catalytic formation of *B*-alkenylborazines along with smaller amounts of the corresponding *B*-alkyl products. The overall reaction appears at first to be similar to the well-known Pd^{2+}-promoted arene–olefin coupling reaction (eq 8);[48] however, as discussed below, the two reactions probably occur by different pathways.

$$C_6H_6 + H_2C{=}CH_2 \xrightarrow{Pd(OAc)_2} CH_2{=}CH{-}C_6H_5 + Pd^0 + 2HOAc \quad (8)$$

The first step in arene–olefin coupling is thought to involve an electrophilic attack at the arene to generate an arylpalladium intermediate. This intermediate can then coordinate and insert an olefin. A subsequent reductive elimination step produces the observed arene–olefin coupled product.

$$ArH + Pd(OAc)_2 \rightarrow ArPdOAc + HOAc \quad (9)$$

Given the similarities between benzene and borazine, it might be expected that the initial step in the borazine–olefin coupling reaction might also involve an electrophilic attack by palladium bromide. In borazine, the nitrogens are the sites of highest electron density, and such an attack should therefore result in the formation of a nitrogen bound borazinylpalladium intermediate. However, since no N-substituted products were observed in the reaction, initial electrophilic attack seems unlikely. This conclusion is additionally supported by the fact that when the ring nitrogens are blocked, as in N-Me_3-$B_3N_3H_3$, vinylation is still observed.

The mechanism of the $PdBr_2$ borazine/olefin coupling reaction most likely involves the oxidative addition of a BH group. Since small amounts of B-Br-$B_3N_3H_5$ were also isolated from the product mixture, an initial step in the reaction may involve the reduction

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(38) *Gmelin Handbuch der Anorganischen Chemie, Boron Nitride. B–N–C Heterocycles. Polymeric B–N Compounds*; Springer-Verlag: New York, 1974; Vol. 13, Part 1, pp 1–87.

(39) (a) Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837–846. (b) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506–514. (c) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182. (d) Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793–7800. (e) Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446–7450. (e) Mirabelli, M. G. L.; Sneddon, L. G. *Organometallics* **1986**, *5*, 1510–1511.

(40) Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1963–1964.

(41) Corcoran, E. W., Jr.; Sneddon, L. G. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; pp 71–89.

(42) Chalk, A. J. *J. Organomet. Chem.* **1970**, *21*, 207–213.

(43) Rejhon, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3190–3198.

(44) Pukhnarevich, B. V.; Kopylova, L. I.; Tsetlina, E. O.; Pestanovich, V. A.; Chvalovsky, V.; Hetflejs, J.; Voronkov, M. G. *Proc. Acad. Sci. USSR* **1976**, *231*, 764–768.

(45) Pukhnarevich, B.; Kopylova, L. I.; Capka, J.; Hetflajs, J.; Satsuk, E. N.; Sigalov, M. V.; Chvalovsky, V.; Voronkov, M. G. *J. Gen. Chem. USSR* **1981**, *50*, 1259.

(46) Voronkov, M. G.; Pukharevich, V. B.; Tsykhanskaya, I. I.; Varshavskii, Y. S. *Proc. Acad. Sci. USSR* **1981**, *254*, 449–451.

(47) Jardine, F. H. *Polyhedron* **1982**, *1*, 569–605, and references therein.

(48) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; pp 116–117. (b) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518–5526. (c) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166–7169. (d) Shue, R. S. *J. Catal.* **1972**, *26*, 112–117.

of Pd^{+2} to Pd^0 by borazine. Palladium(II) salts are electrophilic reagents and not susceptible to oxidative addition; however, palladium(0) complexes are strong nucleophiles and should readily attack the ring borons.[49] Subsequent steps, as proposed in the rhodium reaction discussed above, could then result in the observed *B*-alkenylborazine products.

It should also be noted that, as in the previously reported pentaborane–olefin coupling reaction[40,41] and in contrast to arene–olefin coupling,[48] the $PdBr_2$-catalyzed borazine–olefin coupling was found to be catalytic without the addition of an oxidizing reagent. The fact that no hydrogen was evolved in these reactions and that the formation of ethane was observed in the ethylene reaction suggests, as was proposed[40,41] for pentaborane(9)–olefin coupling, that the coupling reaction is accompanied by the hydrogenation of a second equivalent of olefin.

Like borazine, the *B*-alkenylborazines are stable to O_2 but are very reactive to H_2O and decompose in moist air. The compounds are stable when stored under vacuum at lower temperatures but upon sitting at room temperature slowly polymerize over several weeks to form an intractable material.

Further studies of the chemical properties of the *B*-alkenylborazines showed that they could be readily polymerized to produce, depending upon reaction conditions, both soluble and insoluble forms of the new polymer systme, poly(*B*-alkenylborazine). For example, heating neat samples in vacuo was found to result in the formation of clear, insoluble polymers, while heating mixtures of a *B*-alkenylborazine and borazine resulted in the formation of soluble polymers. GPC data for the soluble polymers indicated molecular weights of ~1000, suggesting a chain length of about 7–8 monomer units. Although the role of the added borazine in the reactions leading to the formation of the soluble polymers has yet to be identified, it may be simply serving as a chain terminating reagent[50] and thus cap the ends of the carbon backbone of the vinyl polymer. This should then result in the formation of lower molecular weight, soluble oligomers. Elemental analyses of these polymers are also consistent with the incorporation of additional borazine units in the polymer chain.

The spectroscopic data obtained for the soluble polymers are consistent with a structure composed of a polyethylene backbone containing pendant borazine rings. Thus, these new polymers may be considered borazine analogues of both poly(styrene) and the known inorganic polyenes of the general formula $(—CH_2CHX—)_n$ where X is, for example, a pendant boranyl,[5] carboranyl,[51] ferrocenyl,[52] or phosphazenyl[53] group.

As discussed in the introduction, poly(*B*-alkenylborazines) appear to satisfy a number of the criteria previously identified[2a] for successful ceramic syntheses from polymers, and the use of these materials as precursors to boron nitride ceramics were investigated. Of most interest were polymers derived from vinylborazine (XI and XII), since these polymers have the highest BN/C ratio. It was found that, depending upon the polymer and pyrolysis conditions, a variety of ceramic materials can be produced, ranging from black, high carbon content materials to white h-BN. In each case, the polymer/ceramic conversion was found to take place with both high ceramic and chemical yields and give materials with a B/N ratio of ~1.0.

Poly(vinylborazine) pyrolyses under argon always led to the retention of significant carbon in the ceramic material. Previous work by Seyferth and Rees[10] and by Ultrasystems[11,12] has demonstrated that ammonia pyrolyses of certain boron polymers resulted in reduction of the carbon impurities. It was similarly found that when the poly(vinylborazine) pyrolyses were carried out under an ammonia flow, the residual carbon could be significantly reduced. Best results were obtained from the pyrolysis of soluble polymer XII under ammonia, which resulted in the formation of boron nitride with only 0.27% carbon impurity corresponding to an empirical formula of $B_{1.00}N_{1.01}C_{0.006}H_{0.04}$.

TGA studies of the polymer/ceramic conversions under both argon and ammonia were similar and showed that the polymers follow a well-defined decomposition path, with the majority of the expected weight loss occurring at low temperatures in the narrow range between 500 and 700 °C. Thus, according to the TGA the ceramic conversions would appear to be essentially complete by ~700 °C, but, in fact, the nature of the ceramic materials obtained in the bulk pyrolyses were highly dependent on the ultimate pyrolysis temperature. For example, materials that were heated to 1000 °C under ammonia had X-ray power diffraction patterns characteristic of turbostratic boron nitride, thus indicating that the boron nitride layer structure had been formed, but the layers still had random rotational and translational order. These materials also exhibited relatively low densities (1.6–1.8 g/mL) and showed significant N–H stretches in their DRIFT spectra. However, further heating of these materials at 1450 °C under argon produced white ceramics having densities, DRIFT spectra, and X-ray diffraction patterns characteristic of h-boron nitride.

In summary, the development of transition-metal-catalyzed routes to *B*-alkenylborazines has now allowed the first syntheses of poly(alkenylborazine) polymers. These polymers have been shown to be useful precursors to boron nitride ceramics, and the soluble polymers should prove particularly valuable for producing either thin film or coated ceramic materials. We are presently exploring these possibilities. In addition, the results presented herein suggest that borazine may be capable of undergoing a range of transition-metal-promoted reactions and that such reactions may result in the production of a variety of new molecular and polymeric materials previously unattainable by using conventional synthetic techniques.

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Registry No. I, 110272-04-3; I (homopolymer), 121232-08-4; II, 121252-71-9; III, 110272-05-4; (III)(IV) (copolymer), 121232-09-5; IV, 110272-06-5; V, 121232-03-9; (V)(VI)(VII) (copolymer), 121252-72-0; VI, 121232-04-0; VII, 121232-05-1; VIII, 88916-94-3; IX, 121232-06-2; X, 121232-07-3; $B_3N_3H_6$, 6569-51-3; $HC\equiv CH$, 74-86-2; $RhH(CO)(PPh_3)_3$, 17185-29-4; $HC\equiv CCH_3$, 74-99-7; $HC\equiv CCH_2CH_3$, 107-00-6; $H_3CC\equiv CCH_3$, 503-17-3; $IrCl(CO)(PPh_3)_2$, 14871-41-1; $PdBr_2$, 13444-94-5; *N*-Me_3-$B_3N_3H_3$, 1004-35-9; *B*-Et-*N*-Me_3-$B_3N_3H_2$, 89416-96-6; BN, 10043-11-5.

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(49) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113–1226.

(50) Vollmert, B. *Polymer Chemistry*; Springer-Verlag: New York, 1973; pp 58–73.

(51) (a) Ditter, J. F. In *Gmelin Handbuch der Anorganischen Chemie, Ergaenzungswerk, Vol. 27, Borverbindungen, Part 6*; Springer-Verlag: Berlin, 1975; Chapter 4. (b) Heying, T. L. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon Press: New York, 1970; Vol. 2, Chapter 3.

(52) Rausch, M. D.; Macomber, D. W.; Fang, F. G.; Pittman, C. U., Jr.; Jayaraman, T. v.; Priester, R. D., Jr., In *New Monomers and Polymers*; Culbertson, B. M., Pittman, C. U., Jr., Eds.; Plenum Press: New York, 1984; pp 243–267.

(53) (a) Dupont, J. G.; Allen, C. W. *Macromolecules* **1979**, *12*, 169–172. (b) Allen, C. W.; Bright, R. P. *Macromolecules* **1986**, *19*, 571–574.