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Transition Metal-Promoted Reactions of Boron Hydrides. 14.[1] A New Synthetic Route to B-Substituted Mono-, Di-, and Trialkylborazines, *B*-Vinyl-*B*,*B*-dialkylborazines, and *B*-Alkylpolyborazylenes via Rhodium-Catalyzed Borazine/Olefin Hydroboration Reactions

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The $RhH(CO)(PPh_3)_3$-catalyzed reactions of borazine with a variety of olefins, including ethylene, propene, 1-butene, *cis*- and *trans*-2-butene, 3,3,3-trifluoropropene, styrene, α-methylstyrene, and 4-allylanisole, have been found to give the mono-, di-, and tri-*B*-alkylborazines in excellent yields. The reactions proceed at room temperature, with low catalyst concentrations, and the degree of substitution is controlled by altering the reactant ratios and reaction times. Unsymmetrically substituted tri-*B*-alkylborazines are produced by the catalyzed reaction of mono- or di-B-substituted borazines with a different olefin. *B*-Vinyl-*B*,*B*-dialkylborazines are prepared by the reaction of di-*B*-alkylborazines with acetylene in the presence of catalyst. The catalyzed reaction of borazine with 1,3-butadiene gives a mixture of monohydroboration products, but reaction with 1,5-hexadiene yields mono- and dihydroboration products and a $(B_3N_3H_4)[(CH_2)_6]_{1.22}$ polymer. The catalyzed reaction of di-*B*-propylborazine with 1,5-hexadiene gives only the dihydroboration product 1,6-bis(2,4-dipropyl-6-borazinyl)hexane. $RhH(CO)(PPh_3)_3$ is also used to catalyze direct alkylation of borazine-based polymers. Thus, the catalyzed addition of either ethylene or propene with polyborazylene, $(B_3N_3H_{\sim 4})_x$, yields the B-alkylated polymers $(C_2H_5)_y(B_3N_3H_{\sim 4-y})$ and $(C_3H_7)_y(B_3N_3H_{\sim 4-y})$, respectively.

Introduction

The recent design of new borazine-based polymers for use as processable precursors to boron nitride[2] has stimulated new studies of the development of high yield selective routes for borazine derivatization. The substitution of the reactive hydrogens present in the parent borazine, $B_3N_3H_6$, can significantly alter both molecular and polymeric properties, including chemical and thermal stabilities, viscosities, and polymer cross-linking pathways. The control and systematic variation of these properties are key to the development of processable polymers that yield ceramic materials in desired compositions and forms.[2,3] In this paper we report a new transition metal-catalyzed synthetic route by which B-substituted mono-, di-, and trialkylborazines, as well as *B*-vinyl-*B*-dialkylborazines and B-alkylated polyborazylene polymers, are produced selectively in excellent yields.[4]

The introduction of organic groups at both the boron and nitrogen sites in borazine has been previously reported. *N*-Alkyl- and *N*-arylborazines have been synthesized in excellent yields from the reaction of alkyl or arylamines and ammonium salts with borane reagents, such as boron trichloride[5] and metal borohydrides.[6] The degree of substitution is varied by using a mixture of ammonium salts.[6c,7] Nitriles are also used to produce *N*-alkylborazines by reaction with diborane in 35–40% yields.[8]

Tri-*B*-alkylborazines have been synthesized by a number of methods. For example, both the reaction of amine–borane adducts with ammonia at 100–450 °C[9] and the reaction of alkyldihalo- or alkyldimercaptoboranes[10e,f] with ammonia or amines at room temperature produce tri-*B*-alkylborazines in 60–90% yields. Substitution reactions at the borazine ring are also used to produce tri-*B*-

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[1] For part 13, see: Mazighi, K.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1993**, *32*, 1963–1969.

[2] (a) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73–91. (b) Paine, R. T.; Sneddon, L. G. in *Inorganic and Organometallic Polymers*; Allcock, H., Wynne, K. J., Wisian-Neilson, P., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1994.

[3] (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.

[4] The boron positions in the borazine ring are numbered 2, 4, and 6 and the nitrogen positions are numbered 1, 3, and 5.

[5] (a) Brown, C. A.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 3699–3700. (b) Emeléus, H. J.; Videla, G. J. *J. Chem. Soc.* **1959**, 1306–1307. (c) Hohnstedt, L. F.; Haworth, D. T. *J. Am. Chem. Soc.* **1960**, *82*, 89–92. (d) Turner, H. S.; Warne, R. J. *J. Chem. Soc.* **1965**, 6421–6450. (e) Butcher, I. M.; Gerrard, W. *J. Inorg. Nucl. Chem.* **1965**, *27*, 823–829.

[6] (a) Schaeffer, G. W.; Anderson, E. R. *J. Am. Chem. Soc.* **1949**, *71*, 2143–2145. (b) Hough, W. V.; Schaeffer, G. W.; Dzurus, M.; Stewart, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 864–865. (c) Beachley, O. T., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4223–4227.

[7] (a) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 93–98. (b) Beachley, O. T., Jr. *Inorg. Chem.* **1969**, *8*, 981–985.

[8] (a) Emeléus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614–2617. (b) Jennings, J. R.; Wade, K. *J. Chem. Soc.* (*A*) **1968**, 1946–1950.

[9] (a) Zhigach, A. F.; Kazakova, E. B.; Krongauz, E. S. *Doklady Akad. Nauk SSSR* **1956**, *111*, 1029–1030. (b) Köster, R. *Angew. Chem.* **1958**, *70*, 413–414. (c) Hawthorne, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 5836–5837. (d) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 833–834. (e) Henle, W.; Schaeffer, R.; Murib, J.; Urry, G.; Schlesinger, H. I. *Abstracts of Papers*, 127th National Meeting of the American Chemical Society, Cincinnati, OH, 1955; American Chemical Society: Washington, DC; S. 26 Q, paper 60.

[10] (a) Nöth, H. *Z. Naturforsch.* **1961**, *16b*, 618–620. (b) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1986**, *25*, 4623–4628. (c) Ruigh, W. L. *Angew. Chem.* **1957**, *69*, 688. (d) Ruigh, W. L.; Gunderloy, F. C. *Abstracts of Papers*, 129th National Meeting of the American Chemical Society, Dallas, TX, 1956; American Chemical Society: Washington, DC; S. 40N/41N, paper 64. (e) Mikhailov, B. M.; Kozminskaya, T. K. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1960**, 2084–2085. (f) Mikhailov, B. M.; Kozminskaya, T. K.; Fedotov, N. S.; Dorokhov, V. A. *Doklady Akad. Nauk SSSR* **1959**, *127*, 1023.

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alkylborazines. Thus, tri-*B*-chloroborazine[11f] and tri-*N*-organo-tri-*B*-haloborazines[7a,11b,f] react with Grignard reagents to give tri-*B*-alkyl, tri-*B*-arylborazines, and tri-*N*-organo-tri-*B*-alkylborazines, respectively, in high yields, but alkyldiborazines and fused polycyclics are also produced in the reactions with the tri-*B*-chloroborazine.[11g-k] Reactions of tri-*N*-aryl- or tri-*N*-alkylborazines with Grignard reagents produce tri-*N*-aryl(alkyl)-tri-*B*-alkylborazines;[11a] however, comparable reactions of the parent borazine with Grignard reagents[11c,12a] or alkyllithiums[12] do not produce tri-B-substituted borazines in good yields.

Mono- and di-*B*-alkylborazines have been synthesized with varying degrees of success. The reaction of tri-*N*-arylborazines with deficient amounts of methyl or phenyl Grignards or lithium reagents selectively produce mono- and di-*B*-substituted borazines in high yields,[11a] but similar reactions with tri-*N*-alkylborazines are less selective, producing mixtures of mono-, di- and tri-*B*-alkylborazines.[7a,11a,e] Tri-*N*-alkyl-tri-*B*-haloborazines react with deficient amounts of Grignard reagents to give complex mixtures of tri-*N*-monoalkyldihalo-, dialkylmonohalo-, and trialkylborazines.[11b] Synthesis of mono-*B*-alkyl and di-*B*-alkylborazines from the parent borazine has been accomplished by direct reaction with Grignard reagents and alkyllithiums, but these reactions are not selective and generally give poor yields. For example, the addition of deficient amounts of alkyllithiums to ethereal solutions of borazine produced mixtures of mono- and di-*B*-alkylborazines, but these mixtures were not separated and the compounds were identified only by gas chromatography.[12a] Borazine is also reported to react with deficient amounts of methyl Grignard to produce a mixture of *B*-methylborazine and di-*B*-methylborazine in low yields.[7b] Again, separation and purification was difficult. *B*-Chloroborazine reacts with methyl Grignard to give *B*-methylborazine in low yields (28%).[11d] Mono-*B*-ethyl and *B*-propylborazine were also found as side-products, in 20–25% yields, from transition metal-catalyzed borazine/olefin coupling reactions.[13]

Our previous work has demonstrated that transition metal catalysts are effective at promoting the reaction of acetylenes with either polyhedral boranes[14] or borazine[13] to yield the corresponding *B*-vinyl derivatives. Likewise, we have also recently reported that platinum catalysts can be used to promote the reactions of decaborane[14] with olefins to yield 6,9-$R_2B_{10}H_{12}$ compounds.[1] Others have employed metal catalysts to effect high-yield, selective olefin/catechol-borane hydroboration reactions.[15] These earlier studies suggested the work described below that has resulted in the development of a systematic metal-catalyzed route for the selective formation of *B*-alkylborazines.

Experimental Section

All manipulations were carried out using standard high vacuum or inert atmosphere techniques as described by Shriver.[16]

Materials. Borazine was purchased from Callery Chemical Co. and purified by vacuum line fractionation through a −45, −78, and −196 °C trap series. The borazine retained in the −78 °C trap was used without further purification. Polyborazylene was made by the thermal polymerization of borazine as reported previously.[17] Propene (99+%), 3,3,3-trifluoropropene, 1-butene, styrene, α-methylstyrene, 4-allylanisole, 1,5-hexadiene, pentane (anhydrous, 99+%), and THF were purchased from Aldrich Chemical Co. and used as received. *cis*-2-Butene, *trans*-2-butene (tech), and 1,3-butadiene were purchased from Matheson and used without further purification. Ethylene (grade 2.5) and acetylene were purchased from Airco. Acetylene was purified by repeated fractionation through several −78 °C traps into a −196 °C trap. Deuterated solvents were purchased from Aldrich Chemical Co. and Cambridge Isotope Labs. The RhH(CO)(PPh_3)$_3$ was prepared by the literature method.[18]

Physical Measurements. ^1H NMR spectra at 200.1 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 Fourier transform spectrometer. ^1H NMR spectra at 500 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. ^{19}F NMR spectra at 188.3 MHz were obtained on a Bruker AC-200 Fourier transform spectrometer. The ^{11}B NMR chemical shifts are relative to external $BF_3 \cdot O(C_2H_5)_2$ (0.00 ppm) with a negative sign indicating an upfield shift. Chemical shifts for ^1H NMR spectra (ppm) are based on 7.15 ppm for C_6D_6 (relative to Me_4Si at 0.00 ppm). The ^{19}F NMR chemical shifts are relative to external CCl_3F (0.00 ppm).

Unit and high-resolution mass spectra were obtained on a VG-Fisons ZAB-E high-resolution mass spectrometer interfaced to a VG 11–250J data system. High-resolution mass spectra were obtained by chemical ionization using either positive or negative ion detection as indicated.[19] Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5890A gas chromatograph (equipped with a cross-linked methylsilicone column) interfaced to a Hewlett-Packard 5970 mass-selective detector. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. Diffuse reflectance IR spectra (DRIFT) were obtained on a Perkin-Elmer 7770 Fourier transform spectrophotometer equipped with the appropriate diffuse reflectance attachment. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., Madison, NJ.

The reaction conditions, observed product yields, and catalyst turnovers for each reaction are summarized in Table 1. The ^1H and ^{11}B NMR spectra for each new compound are presented in Table 2. General reaction procedures and product isolations are discussed in the following sections.

Borazine and Ethylene. In a typical reaction, 5.3 mg of RhH(CO)(PPh_3)$_3$ (5.8 × 10^{-3} mmol) was placed in a 50-mL one-piece glass flask equipped with a vacuum stopcock which was

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(11) (a) Smalley, J. H.; Stafiej, S. F. *J. Am. Chem. Soc.* **1959**, *81*, 582–586. (b) Ryschkewitsch, G. E.; Harris, J. J.; Sisler, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 4515–4517. (c) Moews, P. C., Jr.; Laubengayer, A. W. *Inorg. Chem.* **1963**, *2*, 1072–1073. (d) Beachley, O. T., Jr. *Inorg. Chem.* **1969**, *8*, 2665–2667. (e) Powell, P. *Inorg. Chem.* **1973**, *12*, 913–915. (f) Haworth, D. T.; Hohnstedt, L. F. *J. Am. Chem. Soc.* **1960**, *82*, 3860–3862. (g) Harris, J. J. *J. Org. Chem.* **1961**, *26*, 2155-2156. (h) Meller, A.; Egger, H. *Monatsh. Chem.* **1966**, *97*, 790–791. (i) Meller, A.; Schlegel, R. *Monatsh. Chem.* **1965**, *96*, 1209–1213. (j) Boone, J. L. *U.S.P. 3,317,596*, 1967; *Chem. Abstr.* **1967**, *67*, 64514m. (k) Boone, J. L.; Willcockson, G. W. *Inorg. Chem.* **1966**, *5*, 311–313.

(12) (a) Powell, P.; Semlyen, J. A.; Blofeld, R. E.; Phillips, C. S. G. *J. Chem. Soc.* **1964**, 280–283. (b) Gutmann, V.; Meller, A.; Schaschel, E. *J. Organomet. Chem.* **1964**, *2*, 287–288.

(13) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201–6209.

(14) (a) Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837–846. (b) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 592–597.

(15) (a) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878–879. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179–1191 and references therein. For more recent papers see (c) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670–1672. (d) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671–6679. (e) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679–6685. (f) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863–8869. (g) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350–9359. (h) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367–4368. (i) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220–9221. (j) Burgess, K.; Jaspars, M. *Organometallics* **1993**, *12*, 4197-4200. (k) Brown, M. B.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866–878.

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

(17) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, 2, 96–97.

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

(19) (a) Positive ionization detection. (b) Negative ionization detection.

Table 1. Reaction Summary

olefin	borazine/ olefin ratio	catalyst, mol [a]	reaction time, h	product, rel % yield	total yield, %	total turnovers
ethylene	7.9:1	1.9×10^{-2}	1	2-ethylborazine, **1**, 100%	100	623
ethylene	1:3	0.14	2	2,4,6-triethylborazine, **2**, 100%	92	2000
ethylene	1:3.5	1.5×10^{-4}	26	2-ethylborazine, **1**, 71% 2,4-diethylborazine, 24% 2,4,6-triethylborazine, **2**, 5%	90	3.6×10^5
propene[b]	8.5:1	1.5×10^{-2}	2	2-propylborazine, **3**, 100%	98	700
propene[b]	7.5:1	1.7×10^{-2}	0.75	2-propylborazine, **3**, 100%	99	750
propene[b]	8:1	2.0×10^{-2}	2	2-propylborazine, **3**, 100%	98	680
propene	1:3.3	7.2×10^{-2}	1	2,4-dipropylborazine, **4**, 44% 2,4,6-tripropylborazine, **5**, 56%	98	3480
1-butene	5.8:1	3.4×10^{-2}	3	2-butylborazine, **6**, 100%	91	440
cis-2-butene	5:1	5.1×10^{-2}	47	2-butylborazine, **6**, 97% 2,4-dibutylborazine, 3%	93	190
trans-2-butene	6:1	5.0×10^{-2}	185	2-butylborazine, **6**, 100%	72	89
3,3,3-trifluoropropene	8.4:1	2.1×10^{-2}	1	2-(trifluoropropyl)borazine, **7**, 100%	98	172
3,3,3-trifluoropropene	1:2.9	0.18	14	2-(trifluoropropyl)borazine, **7**, 2.5% 2,4-bis-(trifluoropropyl)borazine, **8**, 9.7% 2,4,6-tris-(trifluoropropyl)borazine, **9**, 70%	82	1242
styrene	7:1	5.0×10^{-2}	2.5	1-phenyl-2-(2-borazinyl)ethane, **10**, 95%	88	230
α-methylstyrene	4:1	0.12	76	2-phenyl-3-(2-borazinyl)propane, **11**, 100%	74	73
4-allylanisole	10.5:1	6.4×10^{-2}	96.5	1-(4-methoxyphenyl)-3-(2-borazinyl)propane, **12**, 100%	57	90
ethylene/2-propylborazine	1:2.2	0.36	2	2,4-diethyl-6-propylborazine, **13**, 100%	97	270
ethylene/2,4-dipropylborazine	1:3.4	0.52	2	2-ethyl-4,6-dipropylborazine, **14**, 100%	97	185
acetylene/2,4-dipropylborazine	1:3.9	4.4	120	2-vinyl-4,6-dipropylborazine, **15**, 100%	54	9.8
1,3-butadiene/borazine	1:1.6	0.55	20	four products (see text)	*c*	–
1,5-hexadiene/borazine	1.4:1	8.5×10^{-2}	2	2-(5-hexenyl)borazine, **16**	*c*	33
1,5-hexadiene/borazine	1:1	0.15	118	2-(5-hexenyl)borazine, **16** polymer, **17**	*c* –	– –
1,5-hexadiene/2,4-dipropylborazine	9:1	0.15	120	1,6-bis-(2,4-dipropylborazinyl)hexane, **18**	63	93
ethylene/polyborazylene	–	0.3	25	$(C_2H_5)_{0.7}(B_3N_{3.0}H_{2.5})_{1.0}$, **19**	78	178
ethylene/polyborazylene	1:1.8	0.22	24	$(C_2H_5)_{1.0}(B_3N_{3.1}H_{2.0})_{1.0}$, **20**	–	444
propylene/polyborazylene	1:1.1	0.15	48	$(C_3H_7)_{0.4}(B_3N_{2.9}H_{2.5})_{1.0}$, **21**	–	260

[a] With respect to borazine. [b] The same catalyst sample was used in all three reactions. [c] Yields could not be determined since the unreacted borazine/olefin mixtures could not be separated.

then evacuated. Borazine (2.409 g, 29.93 mmol) and 3.8 mmol of ethylene (measured by expansion into a known volume) were condensed into the flask at −196 °C. The reaction mixture was allowed to warm to room temperature, and within minutes the initial yellow solution turned a reddish brown and became completely homogeneous. After 1 h, the flask was attached to a vacuum line, frozen at −196 °C, and degassed to remove a small amount of noncondensable gas. The volatile material was then fractionated through a −78, −110, and −196 °C trap series. Stopping in the −78 °C trap was 0.406 g (3.74 mmol) of 2-C_2H_5-$B_3N_3H_5$. In the −110 °C trap was 2.111 g (26.23 mmol) of unreacted borazine. Analysis by GC/MS and a comparison of its ^{11}B and ^1H NMR and infrared spectra with literature values[14] showed the product to be pure 2-C_2H_5-$B_3N_3H_5$ (**1**).

Borazine and Excess Ethylene. A 3×10^{-5} M solution of $RhH(CO)(PPh_3)_3$ was prepared by dissolving 2.8 mg (3.0×10^{-3} mmol) of $RhH(CO)(PPh_3)_3$ in 100 mL of CH_2Cl_2 in a volumetric flask. A 0.5-mL (2×10^{-5} mmol) aliquot of this solution was then added to a Fischer–Porter glass pressure reaction vessel (part no. 100-205-0003) and the solvent vacuum-evaporated. Borazine (0.778 g, 9.66 mmol) and 34 mmol of ethylene were condensed into the reaction vessel at −196 °C. The reaction mixture was allowed to warm to room temperature and within minutes the reaction mixture turned red-brown. The reaction was allowed to continue for 26 h. Vacuum line fractionation through a −78, −110, and −196 °C trap series then gave 0.482 g of product in the −78 °C trap and 0.41 g of borazine in the −110 °C trap. Analysis by GC/MS showed the product to be 65% 2-(C_2H_5)-$B_3N_3H_5$ (~2.9 mmol), 29.5% 2,4-$(C_2H_5)_2$-$B_3N_3H_4$ (~1.0 mmol), and 5.5% 2,4,6-$(C_2H_5)_3$-$B_3N_3H_3$ (**2**) (~0.20 mmol).

In a separate experiment, borazine (0.636 g, 7.90 mmol) and ethylene (24 mmol) were reacted in the presence of 9.8 mg (1.1×10^{-2} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 2 h. Vacuum line fractionation through −63 and −196 °C traps gave 1.195 g (7.26 mmol) of 2,4,6-$(C_2H_5)_3B_3N_3H_3$ (**2**) in the −63 °C trap. No unreacted borazine was found. The product was pure according to GC/MS, ^{11}B[20] and ^1H[21] NMR and IR spectroscopy.

2,4,6-$(C_2H_5)_3$-$B_3N_3H_3$ (**2**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (vs), 2955 (vs), 2915 (vs), 2875 (vs), 2345 (vw), 1885 (vw), 1480 (vs), 1410 (vs), 1350 (vs), 1310 (m), 1265 (m), 1240 (w), 1165 (vw), 1080 (m), 1015 (m), 990 (w), 810 (m), 770 (vs), 715 (vs).

Borazine and Propene. In an analogous reaction, borazine (3.398 g, 42.21 mmol) and 5 mmol of propene were reacted in the presence of 5.9 mg (6.4×10^{-3} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 2 h. Vacuum line fractionation of the reaction mixture through a −63, −110, and −196 °C trap series gave 0.551 g (4.50 mmol) of 2-(n-C_3H_7)-$B_3N_3H_5$ (**3**) in the −63 °C trap and 3.027 g of unreacted borazine in the −110 °C trap. Analysis of the product by GC/MS and a comparison of its ^{11}B and ^1H NMR and IR spectra with literature values[14] showed it to be pure 2-(n-C_3H_7)-$B_3N_3H_5$.

The unreacted borazine was recondensed onto the original catalyst and reacted with 5 mmol of propene for 45 min. Vacuum line fractionation gave 0.591 g (4.82 mmol) of 2-(n-C_3H_7)-$B_3N_3H_5$ and 2.635 g of unreacted borazine. The unreacted borazine was again recondensed onto the original catalyst and allowed to react with 4 mmol of propene for an additional 2 h. Vacuum line fractionation then gave 0.530 g (4.33 mmol) of 2-(n-C_3H_7)-$B_3N_3H_5$ and 2.278 g of unreacted borazine.

Borazine and Excess Propene. Borazine (0.888 g, 11.0 mmol) and 36 mmol of propene were reacted in the presence of 7.3 mg (7.9×10^{-3} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 1 h. Vacuum line fractionation through a -63, −110, and −196 °C trap series gave 2.034 g of product in the −63 °C trap. No unreacted borazine was recovered in the −110 °C trap. Analysis by GC/MS indicated the product was 39.5% 2,4-(n-C_3H_7)$_2$-$B_3N_3H_4$ (**4**) (~4.8 mmol) and 60.5% 2,4,6-(n-C_3H_7)$_3$-$B_3N_3H_3$ (**5**)

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(20) Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1976**, *109*, 3480–3485.
(21) Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *12*, 23–36.

Table 2. NMR Data

compound	nucleus	δ^{a} ppm (m, assignment, J, Hz)
2,4-(n-C_3H_7)$_2$-$B_3N_3H_4$ (**4**)	$^{11}B^{b}$	30.6 (d, B6, J_{BH} 130), 35.5 (s, B2,4)
	$^{1}H\{^{11}B\}^{b}$	0.72 (t, CH_2, 8), 0.92 (t, CH_3, 7), 1.31 (m, CH_2, 7), 4.62 (s, BH), 4.85 (br, NH)
2,4,6-(n-C_3H_7)$_3$-$B_3N_3H_3$ (**5**)	$^{11}B^{b}$	35.5 (s, B2,4,6)
	$^{1}H^{b}$	0.79 (t, CH_2, 8), 0.92 (t, CH_3, 7), 1.40 (m, CH_2, 7), 4.7 (br, NH)
2-(n-C_4H_9)-$B_3N_3H_5$ (**6**)	$^{11}B^{b}$	30.0 (d, B4,6, J_{BH} 135), 35.1 (s, B2)
	$^{1}H\{^{11}B\}^{b}$	0.64 (t, CH_2, 7), 0.87 (t, CH_3, 7), 1.19 (m of m, CH_2CH_2), 4.6 (s, BH), 4.9 (NH), 5.1 (NH)
2-(n-$CF_3CH_2CH_2$)-$B_3N_3H_5$ (**7**)	$^{11}B^{b}$	30.3 (d, B4,6, J_{BH} 140), 34.2 (s, B2)
	$^{1}H\{^{11}B\}^{b,e}$	0.61 (m, CH_2, 9), 1.46 (m of m, CH_2), 4.45 (s, BH), 4.75 (br, NH), 5.0 (br, NH)
	$^{19}F^{b}$	–68.0 (t, CF_3, $J_{CF_3CH_2}$ 11)
2,4-(n-$CF_3CH_2CH_2$)$_2$-$B_3N_3H_4$ (**8**)	$^{11}B^{b,f}$	30.5 (d, B6, J_{BH} ~120), 34.4 (s, B2,4)
	$^{1}H\{^{11}B\}^{b}$	0.67 (m, CH_2, 8), 1.57 (m, CH_2), 4.1 (br, NH), 4.4 (s, BH)
	$^{19}F^{b}$	–68.4 (t, CF_3, $J_{CF_3CH_2}$ 11)
2,4,6-(n-$CF_3CH_2CH_2$)$_3$-$B_3N_3H_3$ (**9**)	$^{11}B^{d}$	33.8 (s, br, B2,4,6)
	$^{1}H^{d}$	0.72 (m, CH_2, 8), 1.60 (m, CH_2), 4.0 (s, br, NH)
	$^{19}F^{d}$	–68.6 (t, CF_3, $J_{CF_3CH_2}$ 11)
1-C_6H_5-2-(2-$B_3N_3H_5$)-C_2H_4 (**10a**)	$^{11}B^{b}$	30.5 (d, B4,6, J_{BH} 130), 35.3 (s, B2)
	$^{1}H\{^{11}B\}^{c}$	1.21 (t, CH_2, 8), 2.75 (t, CH_2, 8), 4.4 (s, BH), 6.0 (m, br, NH), 7.1 (m, phenyl)
2-C_6H_5-3-(2-$B_3N_3H_5$)-C_3H_6 (**11**)	$^{11}B^{b}$	30.6 (d, B4,6, J_{BH} 140), 35.3 (s, B2)
	$^{1}H\{^{11}B\}^{c}$	1.25 (d, CH_2, 7), ~1.2 (m, CH_3, 7), 3.0 (sextet, CH, 7), 4.4 (s, BH), 5.85 (br, NH), 6.05 (br, NH) 7.15 (m, Ph)
1-(4′-OCH_3-C_6H_4)-3-(2-$B_3N_3H_5$)-C_3H_6 (**12**)	$^{11}B^{b}$	30.5 (d, B4,6, J_{BH} 130), 35.5 (s, B2)
	$^{1}H\{^{11}B\}^{b}$	0.67 (t, CH_2, 8), 1.48 (m, CH_2, 8), 2.46 (t, CH_2, 7), 3.39 (s, OCH_3), 4.5 (s, BH), 4.85 (br, NH), 5.05 (br, NH), 6.9 (m, Ph)
2,4-(C_2H_5)$_2$-6-(n-C_3H_7)-$B_3N_3H_3$ (**13**)	$^{11}B^{b}$	35.8 (s, B2,4,6)
	$^{1}H^{b,e}$	0.78 (t, Pr-CH_2, 8), 0.79 (q, Et-CH_2, 8), 0.95 (t, Et-CH_3, 8), 0.97 (t, Pr-CH_3, 7), 1.37 (m, Pr-CH_2), 4.6 (br, NH)
2-(C_2H_5)-4,6-(n-C_3H_7)$_2$-$B_3N_3H_3$ (**14**)	$^{11}B^{b}$	35.9 (s, B2,4,6)
	$^{1}H^{b,e}$	0.79 (t, Pr-CH_2, 8), 0.80 (q, Et-CH_2, 8), 0.96 (t, Et-CH_3, 8), 0.98 (t, Pr-CH_3, 7), 1.38 (m, Pr-CH_2), 4.6 (br, NH)
2-($CH_2{=}CH$)-4,6-(C_3H_7)$_2$-$B_3N_3H_3$ (**15**)	$^{11}B^{b}$	31.2 (s, B2), 35.9 (s, B2,4)
	$^{1}H^{b}$	0.77 (t, CH_2, 8), 0.96 (t, CH_3, 7), 1.36 (m, CH_2, 7), 4.8 (br, NH), 5.9 (m, $CH_2{=}CH$)
2-($CH_2{=}CH(CH_2)_4$)-$B_3N_3H_5$ (**16**)	$^{11}B^{b}$	30.6 (d, B4,6, J_{BH} 145), 35.6 (s, B2)
	$^{11}H^{b,e}$	0.68 (m, CH_2), 1.18 (m, CH_2), 1.30 (m, CH_2), 1.97 (m, CH_2), 4.6 (q, BH), 4.8 (t, NH, J_{NH} 23), 5.03 (m, 2CH), 5.78 (m, CH)
1,6-(2,4-(n-C_3H_7)$_2$-6-$B_3N_3H_3$)$_2$-C_6H_{12} (**18**)	$^{11}B^{b}$	35.8 (s, B2,4,6)
	$^{1}H^{b}$	0.80 (m, CH_2), 0.98 (t, CH_3), 1.37 (m, CH_2), 4.6 (br, NH)
$(C_2H_5)_{0.7}(B_3N_{3.0}H_{2.5})_{1.0}$ (**19**)	$^{1}H\{^{11}B\}^{c}$	0.97 (br, CH_2CH_3), 5.1 (vbr, NH and BH)
$(C_2H_5)_{1.0}(B_3N_{3.1}H_{2.0})_{1.0}$ (**20**)	$^{1}H\{^{11}B\}^{c}$	0.96 (br, CH_2CH_3), 5.1 (vbr, NH and BH)
$(C_3H_7)_{0.4}(B_3N_{2.9}H_{2.5})_{1.0}$ (**21**)	$^{1}H\{^{11}B\}^{c}$	0.95 (br, CH_3 and CH_2), 1.46 (br, CH_2), 4.6 (br), 4.9 (br), 5.05 (br)

[a] Key: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All spectra recorded at the following except where noted: ^{11}B NMR at 64.2 MHz, ^{1}H NMR at 200.1 MHz, and ^{19}F NMR at 188.3 MHz. [b] C_6D_6. [c] THF-d_8. [d] $CDCl_3$. [e] ^{1}H recorded at 500 MHz. [f] ^{11}B recorded at 160.5 MHz.

(~6.6 mmol). The 2,4-(n-C_3H_7)$_2$-$B_3N_3H_4$ and 2,4,6-(n-C_3H_7)$_3$-$B_3N_3H_3$ were then separated by vacuum line fractionation with condensation in −30 and 0 °C traps, respectively.

2,4-(n-C_3H_7)$_2$-$B_3N_3H_4$ (**4**): liquid; IR (film, NaCl plates, cm^{-1}) 3455 (m), 2965 (m), 2940 (m), 2920 (m), 2885 (m), 2525 (m), 1475 (s), 1470 (s), 1460 (s), 1415 (m), 1380 (m), 1200 (w), 1140 (w), 1095 (w), 1025 (w), 930 (w), 915 (m), 725 (m); exact mass calcd for (P − H) $^{12}C_6{}^{1}H_{17}{}^{11}B_3{}^{14}N_3$ 164.1702, found 164.1707.[19b]

2,4,6-(n-C_3H_7)$_3$-$B_3N_3H_3$ (**5**): liquid; IR (film, NaCl plates, cm^{-1}) 3430 (s), 2960 (s), 2940 (vs), 2915 (vs), 2880 (vs), 1500 (vs), 1490 (vs), 1485 (vs), 1465 (vs), 1450 (vs), 1410 (m), 1360 (s), 1330 (m), 1240 (w), 1200 (w), 1090 (m), 1060 (sh, w), 1030 (sh, w), 1020 (m), 910 (w), 840 (m), 820 (m), 735 (s), 715 (s); exact mass calcd for $^{12}C_9{}^{1}H_{24}{}^{11}B_3{}^{14}N_3$ 207.2249, found 207.2256.[19a]

Borazine and 1-Butene. Borazine (2.349 g, 29.18 mmol) and 5.0 mmol of 1-butene were reacted in the presence of 9.3 mg (1.0 × 10^{-2} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 3 h. Vacuum line fractionation of the reaction mixture through a −45, −110, and −196 °C trap series gave 0.595 g of product stopping in the −45 °C trap and 1.962 g of unreacted borazine in the −110 °C trap. The product was pure 2-(n-C_4H_9)-$B_3N_3H_5$ (**6**) (4.4 mmol), according to chemical analysis and its GC/MS and ^{1}H and ^{11}B NMR and IR spectra.

2-(n-C_4H_9)-$B_3N_3H_5$ (**6**): liquid; IR (gas cell, NaCl windows, 10 cm path, cm^{-1}) 3470 (m), 3460 (sh,m), 2960 (m), 2920 (m), 2880 (m), 2520 (s), 1480 (vs), 1470 (vs), 1450 (s), 1390 (m), 920 (m), 720 (m); exact mass calcd for (P + H) $^{12}C_4{}^{1}H_{15}{}^{11}B_3{}^{14}N_3$ 138.1545, found 138.1542.[19a] Anal. Calcd for $C_4H_{14}B_3N_3$, C, 35.17; H, 10.33; N, 30.76. Found: C, 35.40; H, 10.87; N, 30.40.

Borazine and *cis*-2-Butene. Borazine (1.584 g, 19.68 mmol) and 4.0 mmol of *cis*-2-butene were reacted in the presence of 9.4 mg (1.0 × 10^{-2} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 4 h. Vacuum line fractionation through a −45, −110, and −196 °C trap series gave 0.065 g of product in the −45 °C trap. The product was shown to be pure 2-(n-C_4H_9)-$B_3N_3H_5$ by its GC/MS and ^{11}B and ^{1}H NMR spectra. All material passing the −45 °C trap was recondensed over the original catalyst and allowed to react for an additional 43 h. Fractionation through the same trap series gave 0.188 g of product in the −45 °C trap and 1.425 g of unreacted borazine in the −110 °C trap. Analysis by GC/MS indicated the product was 95% 2-(n-C_4H_9)-$B_3N_3H_5$ (~1.3 mmol) and 5% 2,4-(C_4H_9)$_2$-$B_3N_3H_4$ (~0.05 mmol).

Borazine and *trans*-2-Butene. Borazine (2.369 g, 29.43 mmol) and 5.0 mmol of *trans*-2-butene were reacted in the presence of 13.5 mg (14.7 × 10^{-3} mmol) of $RhH(CO)(PPh_3)_3$ at room temperature for 185 h. Vacuum line fractionation through a −45, −110, and −196 °C trap series gave 0.178 g (1.3 mmol) of 2-(n-C_4H_9)-$B_3N_3H_5$ stopping in the −45 °C trap and 2.224 g (27.63 mmol) of unreacted borazine in the −110 °C trap.

Borazine and 3,3,3-Trifluoropropene. Borazine (2.720 g, 33.79 mmol) and 3,3,3-trifluoropropene (4.0 mmol) were reacted in the presence of 6.7 mg (7.3 × 10^{-3} mmol) of $RhH(CO)(PPh_3)_3$ for 1 h. Vacuum line fractionation through a 0, −45, −110, and −196 °C trap series gave 0.222 g (1.26 mmol) of 2-(n-$CF_3CH_2CH_2$)-$B_3N_3H_5$ (**7**) in the −45 °C trap and 2.617 g of unreacted borazine in the −110 °C trap. The 2-(n-$CF_3CH_2CH_2$)-$B_3N_3H_5$ was pure according to chemical analysis and its GC/MS and ^{11}B, ^{1}H, and ^{19}F NMR spectra.

2-(*n*-$CF_3CH_2CH_2$)-$B_3N_3H_5$ (**7**): liquid; IR (gas cell, NaCl windows, 10-cm path, cm^{-1}) 3485 (m), 2980 (w), 2610 (w), 2535 (s), 2450 (w), 1485 (vs), 1470 (vs), 1455 (vs), 1430 (w, sh), 1390 (s), 1375 (m, sh), 1360 (w, sh), 1330 (w), 1275 (s), 1235 (w), 1155 (s), 1095 (m), 925 (s), 855 (w), 725 (m); exact mass calcd for (P − H) $^{12}C_3{}^{11}B_3{}^{14}N_3{}^{1}H_8{}^{19}F_3$ 176.0950, found 176.0942.[19b] Anal. Calcd for $C_3H_9B_3N_3F_3$, C, 20.41; H, 5.14; N, 23.80. Found: C, 20.61; H, 5.60; N, 23.45.

Borazine and Excess 3,3,3-Trifluoropropene. Borazine (0.242 g, 3.01 mmol) and 3,3,3-trifluoropropene (8.8 mmol) were reacted in the presence of 5.1 mg (5.6 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ for 16 h. The resulting product was solid with a moist appearance. Vacuum line fractionation through −78 and −196 °C traps gave 0.093 g of product in the −78 °C trap which was shown by GC/MS to be 14% (~0.07 mmol) 2-(*n*-$CF_3CH_2CH_2$)-$B_3N_3H_5$ and 84% (~0.30 mmol) 2,4-(*n*-$CF_3CH_2CH_2$)$_2$-$B_3N_3H_4$. The mixture was then separated by vacuum line fractionation though 0 and −196 °C traps with 2,4-(*n*-$CF_3CH_2CH_2$)$_2$-$B_3N_3H_4$ remaining in the 0 °C trap. The solid residue remaining in the reaction flask after removal of the volatile materials was extracted with methylene chloride, the solvent vacuum-evaporated, and the resulting solid sublimed at 80 °C. The sublimed white solid (0.774 g, 2.10 mmol) was shown to be 2,4,6-(*n*-$CF_3CH_2CH_2$)$_3$-$B_3N_3H_3$ on the basis of chemical analysis and its GC/MS and ^{11}B, ^{1}H, and ^{19}F NMR spectra.

2,4-(*n*-$CF_3CH_2CH_2$)$_2$-$B_3N_3H_4$ (**8**): liquid; IR (film, NaCl plates, cm^{-1}), 3450 (s), 2975 (m, sh), 2960 (m), 2920 (m, sh), 2530 (s), 1470 (vs, br), 1420 (s), 1380 (s), 1315 (s), 1290 (s, sh), 1270 (vs), 1220 (s), 1130 (vs), 1075 (vs), 1025 (m), 930 (s), 915 (s), 870 (m), 850 (m), 765 (m), 725 (s), 665 (m); exact mass calcd for (P − H) $^{12}C_6{}^{11}B_3{}^{14}N_3{}^{1}H_{11}{}^{19}F_6$ 272.1136, found 272.1131.[19b]

2,4,6-(*n*-$CF_3CH_2CH_2$)$_3$-$B_3N_3H_3$ (**9**): solid, mp 112–114° C; IR (KBr pellet, cm^{-1}) 3440 (m), 2990 (w), 2960 (w), 1515 (m), 1505 (s), 1485 (vs), 1450 (m), 1415 (w), 1375 (m), 1315 (m), 1270 (s), 1225 (m), 1125 (s), 1090 (m), 1070 (s), 1025 (w, sh), 930 (m), 865 (w), 850 (w), 835 (w), 765 (m), 725 (m), 660 (m), 640 (w, sh), 610 (w, sh), 550 (w), 480 (w); exact mass calcd for (P + H) $^{12}C_9{}^{11}B_3{}^{14}N_3{}^{1}H_{16}{}^{19}F_9$ 370.1479, found 370.1483.[19a] Anal. Calcd for $C_9H_{15}B_3N_3F_9$: C, 29.32; H, 4.10; N, 11.40. Found: C, 29.09; H, 4.03; N, 10.40.

Borazine and Styrene. Borazine (1.430 g, 17.76 mmol) and styrene (0.261 g, 2.51 mmol) were reacted in the presence of 8.1 mg (8.8 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ for 2.5 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.391 g (2.12 mmol) of 1-C_6H_5-2-(2-$B_3N_3H_5$)-C_2H_4 (**10a**) in the 0 °C trap and 1.239 g of unreacted borazine in the −196 °C trap. The 1-C_6H_5-2-(2-$B_3N_3H_5$)-C_2H_4 was found to be >90% pure according to its GC/MS and ^{11}B and ^{1}H NMR spectra; however, according to the GC/MS spectrum, a second isomer (<7%) was also produced. This isomer was not characterized, but may be the internal isomer 1-C_6H_5-1-(2-$B_3N_3H_5$)-C_2H_4 (**10b**).

1-C_6H_5-2-(2-$B_3N_3H_5$)-C_2H_4 (**10a**): liquid; IR (film, NaCl plates, cm^{-1}) 3450 (vs), 3100 (m), 3080 (m), 3040 (s), 2940 (s), 2880 (m), 2600 (m), 2520 (vs), 2460 (m, sh), 2440 (m), 2370 (w, sh), 2350 (w, sh), 2230 (w), 1950 (w), 1910 (w), 1875 (w), 1815 (w), 1610 (m), 1590 (w), 1500 (vs, sh), 1475 (vs, br), 1425 (vs, sh), 1385 (vs), 1360 (vs), 1295 (w), 1245 (w), 1215 (w), 1190 (w), 1165 (w), 1140 (w, sh), 1110 (m), 1080 (w), 1040 (m), 1010 (w), 990 (w), 975 (w), 930 (vs, sh), 915 (vs), 870 (w), 830 (w), 765 (s), 725 (vs), 710 (vs); exact mass calcd for $^{12}C_8{}^{11}B_3{}^{14}N_3{}^{1}H_{14}$ 185.1467, found 185.1473.[19a] Anal. Calcd for $C_8H_{14}B_3N_3$: C, 52.04; H, 7.64; N, 22.76. Found: C, 51.78; H, 7.97; N, 22.43.

Borazine and α-Methylstyrene. Borazine (0.762 g, 9.47 mmol) and α-methylstyrene (0.3 mL, 2.3 mmol) were reacted in the presence of 10.0 mg (1.09 × 10^{-2} mmol) of RhH(CO)$(PPh_3)_3$ for 76 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.163 g (0.82 mmol) of 2-C_6H_5-3-(2-$B_3N_3H_5$)-C_3H_6 (**11**) in the 0 °C trap and 0.680 g of unreacted borazine in the −196 °C trap. The 2-C_6H_5-3-(2-$B_3N_3H_5$)-C_3H_6 was pure according to its GC/MS and ^{11}B and ^{1}H NMR spectra.

2-C_6H_5-3-(2-$B_3N_3H_5$)-C_3H_6 (**11**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (s), 3090 (w), 3070 (w), 3030 (w), 2960 (m), 2900 (m), 2880 (w), 2600 (w), 2510 (s), 2430 (w), 1610 (w), 1465 (vs, br), 1380 (s), 1350 (m), 1285 (w), 1265 (w), 1235 (w), 1200 (w), 1140 (w), 1110 (m), 1095 (w), 1075 (w), 1030 (w), 925 (m, sh), 910 (s), 850 (w), 825 (w), 770 (m), 725 (m), 705 (s); exact mass calcd for $^{12}C_9{}^{11}B_3{}^{14}N_3{}^{1}H_{16}$ 199.1623, found 199.1625.[19a]

Borazine and 4-Allylanisole. Borazine (1.108 g, 13.76 mmol) and 4-allylanisole (0.2 mL, 1.3 mmol) were reacted in the presence of 8.1 mg (8.8 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ for 96.5 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.189 g (0.83 mmol) of 1-(4′-CH_3O-C_6H_4)-3-(2-$B_3N_3H_5$)-C_3H_6 (**12**) in the 0 °C trap and 0.993 g of unreacted borazine in the −196 °C trap. The product was obtained in pure form according to its GC/MS and ^{11}B and ^{1}H NMR spectra.

1-(4′-CH_3O-C_6H_4)-3-(2-$B_3N_3H_5$)-C_3H_6 (**12**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (s), 3030 (w), 3000 (w), 2970 (w, sh), 2920 (m), 2860 (m), 2840 (m, sh), 2590 (w), 2505 (s), 2430 (w), 1615 (m), 1585 (w), 1510 (s), 1480 (vs), 1465 (vs), 1460 (vs, sh), 1450 (vs), 1445 (vs), 1380 (m), 1360 (m), 1300 (m), 1245 (s), 1180 (m), 1125 (w), 1100 (w), 1040 (m), 910 (s), 825 (m), 810 (m), 765 (w), 725 (m); exact mass calcd for $^{12}C_{10}{}^{11}B_3{}^{14}N_3{}^{1}H_{18}{}^{16}O$, 229.1729, found 229.1737.[19a]

2-Propylborazine and Excess Ethylene. 2-(*n*-C_3H_7)-$B_3N_3H_5$ (0.340 g, 2.77 mmol) and ethylene (~6 mmol) were reacted in the presence of 8.8 mg (9.6 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ at room temperature for 2 h. Vacuum line fractionation of the reaction mixture through −45 and −196 °C traps gave 0.478 g (2.68 mmol) of pure 2,4-$(C_2H_5)_2$-6-(*n*-C_3H_7)-$B_3N_3H_3$ (**13**) as determined by its GC/MS and ^{1}H and ^{11}B NMR and IR spectra.

2,4-$(C_2H_5)_2$-6-(*n*-C_3H_7)-$B_3N_3H_3$ (**13**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (m), 2955 (s), 2930 (m), 2915 (m), 2880 (m), 1475 (vs), 1415 (w), 1355 (m), 1275 (w), 1245 (vw), 1165 (vw), 1090 (w), 1025 (w), 1000 (w), 845 (w), 835 (w), 820 (w), 775 (m), 720 (m); exact mass calcd for (M − H) $^{12}C_7{}^{1}H_{19}{}^{11}B_3{}^{14}N_3$ 178.1858, found 178.1850.[19b]

2,4-Dipropylborazine and Excess Ethylene. 2,4-(*n*-C_3H_7)$_2$-$B_3N_3H_4$ (0.148 g, 0.899 mmol) and ethylene (3.1 mmol) were reacted in the presence of 4.3 mg (4.7 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ at room temperature for 2 h. Vacuum line fractionation of the reaction mixture through 0 and −196 °C traps gave 0.167 g (0.87 mmol) of pure 2-(C_2H_5)-4,6-(*n*-C_3H_7)$_2$-$B_3N_3H_3$ (**14**) as determined by chemical analysis and its GC/MS and ^{1}H and ^{11}B NMR and IR spectra. No unreacted 2,4-(*n*-C_3H_7)$_2$-$B_3N_3H_4$ was recovered.

2-(C_2H_5)-4,6-(*n*-C_3H_7)$_2$-$B_3N_3H_3$ (**14**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (m), 2960 (s), 2930 (m), 2910 (m), 2880 (m), 1470 (vs, br), 1415 (m), 1360 (m), 1335 (m, sh), 1240 (w), 1085 (w), 1020 (w), 845 (w), 820 (w), 770 (w), 735 (w, sh), 715 (m); exact mass calcd for (P + H) $^{12}C_8{}^{1}H_{23}{}^{11}B_3{}^{14}N_3$ 194.2171, found 194.2170.[19a] Anal. Calcd for $C_8H_{22}B_3N_3$ C, 49.86; H, 11.51; N, 21.80. Found: C, 50.08; H, 11.46; N, 21.94.

2,4-Dipropylborazine and Excess Acetylene. 2,4-(*n*-C_3H_7)$_2$-$B_3N_3H_4$ (0.131 g, 0.796 mmol) and acetylene (3.1 mmol) were reacted in the presence of 32.0 mg (34.8 × 10^{-3} mmol) of RhH(CO)$(PPh_3)_3$ at room temperature for 5 days. Vacuum line fractionation of the reaction mixture through 0 and −196 °C traps gave 0.064 g (0.34 mmol) of 2-(C_2H_3)-4,6-(*n*-C_3H_7)$_2$-$B_3N_3H_3$ (**15**) as determined by its GC/MS and ^{1}H and ^{11}B NMR spectra.

2-(C_2H_3)-4,6-(*n*-C_3H_7)$_2$-$B_3N_3H_3$ (**15**): liquid; IR (film, NaCl plates, cm^{-1}) 3440 (s), 3060 (w), 2965 (s), 2930 (s), 2910 (s), 2875 (s), 1635 (m), 1615 (m), 1470 (vs), 1415 (m), 1380 (m, sh), 1355 (m), 1335 (m, sh), 1265 (w), 1240 (w), 1195 (w), 1090 (m), 1015 (m), 990 (w), 950 (m), 840 (m), 820 (w, sh), 740 (m, sh), 715 (m); exact mass calcd for $^{12}C_8{}^{1}H_{20}{}^{11}B_3{}^{14}N_3$ 191.1936, found 191.1948.[19a]

Borazine and Excess Butadiene. Borazine (0.300 g, 3.73 mmol) and 1,3-butadiene (6.0 mmol) were reacted in the presence of 18.9 mg (2.06 × 10^{-2} mmol) of RhH(CO)$(PPh_3)_3$ for 20 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.009 g in the 0 °C trap and 0.015 g of product in the −45 °C trap. Analysis by GC/MS showed four compounds, three with parent *m*/*e* of 135, consistent with a formula of C_4H_7-$B_3N_3H_5$, and a fourth with a parent *m*/*e* of 133 consistent with a formula of C_4H_5-$B_3N_3H_5$.

Borazine and 1,5-Hexadiene. Borazine (0.508 g, 6.32 mmol) and 1,5-hexadiene (0.384 g, 4.67 mmol) were reacted in the presence of $RhH(CO)(PPh_3)_3$ (5.0 mg, 5.4 × 10^{-3} mmol) for 2 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.029 g (0.18 mmol) of product in the −45 °C trap which was shown to be $2\text{-}(CH_2{=}CH(CH_2)_4)\text{-}B_3N_3H_5$ (**16**) on the basis of chemical analysis and its ^{11}B and ^{1}H NMR and IR spectra.

$2\text{-}(CH_2{=}CH(CH_2)_4)\text{-}B_3N_3H_5$ (**16**): liquid; IR (film, NaCl plates, cm^{-1}) 3445 (s), 3080 (w), 2920 (s), 2860 (m), 2690 (w), 2510 (s), 2425 (w), 1645 (w), 1470 (vs, br), 1385 (m), 1350 (m), 1105 (w), 970 (w), 910 (s), 720 (s); exact mass calcd for $^{12}C_6{}^{1}H_{16}{}^{11}B_3{}^{14}N_3$, 163.1623, found 163.1631.[19a] Anal. Calcd for $C_6H_{16}B_3N_3$: C, 44.31; H, 9.92; N, 25.84. Found: C, 44.26; H, 10.49; N, 24.82.

In another experiment, borazine (0.458 g, 5.69 mmol) and 1,5-hexadiene (0.479 g, 5.83 mmol) were reacted in the presence of $RhH(CO)(PPh_3)_3$ (7.8 mg, 8.5 × 10^{-3} mmol) for 118 h. Vacuum line fractionation through a 0, −45, and −196 °C trap series gave 0.190 g (1.17 mmol) of product in the −45 °C trap which was shown to be $2\text{-}(CH_2{=}CH(CH_2)_4)\text{-}B_3N_3H_5$ (**16**). The remaining polymeric residue (0.323 g, **17**) was insoluble in benzene, chloroform, THF, and acetonitrile.

Polymer **17**: solid, DRIFT (KBr powder, cm^{-1}) 3440 (s), 2920 (s), 2850 (s), 2510 (s), 2230 (m), 1640 (w), 1460 (vs, br), 1360 (vs), 1080 (s), 910 (vs), 815 (s), 720 (s), 540 (s). Anal. Found: C, 48.93; H, 10.48; N, 23.97; B, 17.79, corresponding to a formula of $B_3N_{3.1}C_{7.4}H_{18.9}$.

1,5-Hexadiene and Excess 2,4-Dipropylborazine. 1,5-Hexadiene (0.072 g, 0.87 mmol) and $2,4\text{-}(n\text{-}C_3H_7)_2\text{-}B_3N_3H_4$ (1.322 g, 8.027 mmol) were reacted in the presence of $RhH(CO)(PPh_3)_3$ (10.8 mg, 11.8 × 10^{-3} mmol) for 5 days. At the end of this time the volatile materials were vacuum-evaporated. The remaining liquid, 0.225 g (0.547 mmol), was shown to be $1,6\text{-}(2,4\text{-}(n\text{-}C_3H_7)_2\text{-}6\text{-}B_3N_3H_3)_2\text{-}C_6H_{12}$ (**18**) by its ^{11}B and ^{1}H NMR, IR, and high resolution mass spectra.

$1,6\text{-}(2,4\text{-}(n\text{-}C_3H_7)_2\text{-}6\text{-}B_3N_3H_3)_2(CH_2)_6$ (**18**): liquid; IR (film, NaCl plates, cm^{-1}) 3450 (m), 2960 (s), 2915 (s), 2880 (s), 1475 (br, vs), 1385 (m), 1365 (m), 1345 (m), 1250 (w), 1210 (w), 1130 (w), 1100 (w), 1030 (w), 855 (w), 830 (w), 745 (m), 725 (s); exact mass calcd for (M + H) $^{12}C_{18}{}^{1}H_{47}{}^{11}B_6{}^{14}N_6$ 413.4420, found 413.4453.[19a]

Polyborazylene and Olefins. Ethylene. A two-necked 100-mL round bottomed flask fitted with a vacuum stopcock and a magnetic stirring bar was charged with polyborazylene[17] (0.478 g) and $RhH(CO)(PPh_3)_3$ (17.4 mg, 18.9 × 10^{-3} mmol). The flask was evacuated and 3 mL of dry THF was vacuum distilled into the flask at −196 °C. The flask was allowed to warm to room temperature and then backflushed with dry nitrogen. Ethylene was slowly bubbled into the solution by a needle introduced through a rubber septum. The reaction was continued for 5 h and then the ethylene flow was stopped. The reaction mixture was then allowed to stir for an additional 20 h. Solvent was removed under vacuum until the solution became viscous. The polymer was then precipitated by slowly dropping the solution into 150 mL of dry pentane. The precipitate was filtered and washed several times with pentane. Residual solvent was removed under vacuum for 28 h to give 0.469 g of light tan solid. The polymer was soluble in dry THF and glyme.

Polymer **19**: solid; DRIFT (KBr powder, cm^{-1}) 3440 (s), 2950 (s), 2915 (m), 2875 (s), 2490 (s), 1455 (vs, br), 1015 (m), 990 (m), 900 (s), 765 (s), 695 (s). Anal. Found: C, 16.50; H, 5.81; N, 40.81; B, 31.41, corresponding to a formula of $B_3N_{3.0}H_{5.9}C_{1.4}$.

In a separate experiment, a one-necked 50-mL round bottomed flask fitted with a vacuum stopcock and a magnetic stirring bar was charged with polyborazylene (0.654 g) and $RhH(CO)(PPh_3)_3$ (17.5 mg, 19.0 × 10^{-3} mmol). The flask was evacuated and ethylene (15 mmol) and 3 mL of dry THF were condensed into the flask at −196 °C. The flask was allowed to warm to room temperature and the reaction was continued for 24 h. Solvent was removed under vacuum until the solution became viscous. The polymer was then precipitated by slowly dropping the solution into 150 mL of dry pentane. The precipitate was filtered and washed several times with pentane. Residual solvent was vacuum evaporated for 28 h. The product was soluble in THF and glyme.

Polymer **20**: Anal. Found: C, 21.05; H, 6.29; N, 39.93; B, 29.06, corresponding to a formula of $B_3N_{3.1}H_{7.0}C_{2.0}$. The IR spectrum was essentially identical to that of **19**.

Propylene. In a similar experiment, a one-necked 50-mL round-bottomed flask fitted with a vacuum stopcock and a magnetic stirring bar was charged with polyborazylene (0.680 g) and $RhH(CO)(PPh_3)_3$ (12.4 mg, 13.5 × 10^{-3} mmol). The flask was evacuated and propylene (5 mmol) and 3 mL of dry THF were condensed into the flask at −196 °C. The flask was allowed to warm to room temperature and the reaction was continued for 24 h. At this time an additional 5 mmol of propylene was condensed into the flask and allowed to react for an additional 24 h. The product was worked up as above. The product was soluble in THF and glyme.

Polymer **21**: solid; DRIFT (KBr powder, cm^{-1}) 3440 (s), 2950 (m), 2930 (m), 2875 (m), 2500 (s), 1460 (vs, br), 1110 (m, sh), 900 (s), 775 (s, sh), 700 (s). Anal. Found: C, 15.60; H, 5.69; N, 42.07; B, 33.50, corresponding to a formula of $B_3N_{2.9}H_{5.5}C_{1.2}$.

Control Experiments. Control experiments were conducted in which borazine was reacted with ethylene, 3,3,3-trifluoropropene, and styrene using conditions identical to those described above, with the exception that no catalyst was present. Analysis of the reaction mixtures showed no alkylborazine product formation in any of the reactions.

Results and Discussion

$RhH(CO)(PPh_3)_3$ is a well-known catalyst for reactions involving olefins including hydrogenations, hydroformylations, isomerizations, and hydrosilations.[22] The results discussed below now clearly demonstrate that $RhH(CO)(PPh_3)_3$ is also a highly active catalyst for the reaction of borazine with a variety of olefins, including ethylene, propene, 1-butene, *cis*- and *trans*-2-butene, 3,3,3-trifluoropropene, styrene, α-methylstyrene, 4-allylanisole, 1,3-butadiene, and 1,5-hexadiene to give, depending upon the reaction conditions, mono- and polysubstituted *B*-alkylborazines.

A typical reaction involved simply stirring a mixture of liquid borazine and olefin in the presence of small amounts (~10^{-2} to 10^{-1} mol %) of $RhH(CO)(PPh_3)_3$ for several hours. Since most reactions did not require a solvent, separation and recovery of products and unreacted borazine was easily accomplished by vacuum line fractionation. The reactions proceeded at room temperature and the degree of substitution was manipulated by controlling the reactant ratios, catalyst concentrations and/or reaction times to give predominately mono-*B*-alkylborazines or tri-*B*-alkylborazines, or mixtures of mono-, di, and tri-*B*-substituted products.

Although no detailed mechanistic studies of the Rh-catalyzed borazine/olefin reactions were undertaken, the results discussed below appear consistent with a reaction sequence similar to those previously proposed for olefin hydrogenation reactions using this catalyst.[22] Such a reaction sequence is depicted in Figure 1. Thus, key steps in this sequence would be (A) dissociation of a phosphine, (B) coordination of the olefin, (C) hydride addition to the olefin, (D) oxidative addition of the borazine BH group, and (E) reductive elimination of the alkylborazine. The observation of exclusively *B*-alkylborazines in these reactions is consistent with the nucleophilic nature of the rhodium catalyst, resulting in oxidative addition of BH rather than NH. In many metal-catalyzed olefin/catecholborane hydroborations initial oxidative addition of the B–H bond has been proposed, followed by coordination

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

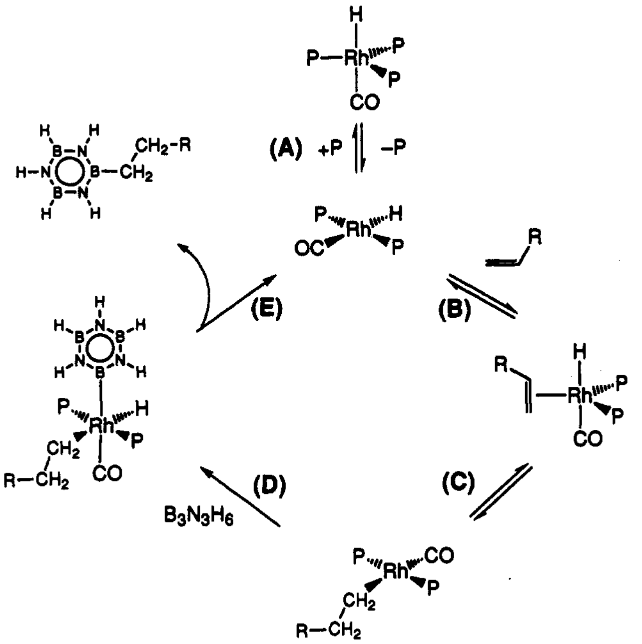


Figure 1. Possible reaction sequence for the rhodium-catalyzed borazine-olefin reactions.

of the olefin. As a result, insertion of the olefin into the metal–boron bond can occur to produce a metalloalkylborane species which may then further react to produce alkylboranes (by hydride addition) or alkenylboranes (by β-hydride elimination).[13b,15h] The absence of any alkenylborazine products in the reactions reported herein suggests that in these systems insertion of the olefin into a metal hydride bond occurs (step C in Figure 1).

Under the conditions employed, no solvent and catalyst concentrations of 10^{-2} to 10^{-1} mol %, a high selectivity for anti-Markovnikov additions, i.e. *n*-*B*-alkylborazine products, was observed. In fact, only in the case of styrene was there any evidence of the formation of an internal product. However, previous studies of the metal-catalyzed reactions of catechol–borane with olefins have shown that the regiochemistry is highly dependent on the reaction conditions, including the catalyst concentrations, the history of the catalyst, the steric properties of the metal-coordinated phosphines, and the presence of additional phosphine.[15c,e,g] These results suggest that with appropriate manipulation of the reaction parameters both Markovnikov, as well as anti-Markovnikov products could be produced.

As indicated in Table 1, terminal olefins exhibited the fastest rates. Reactions with ethylene were extremely fast. For example, borazine was converted to tri-*B*-ethylborazine with excess ethylene during a 30-min reaction period with a catalyst concentration of only 3×10^{-2} mol %, which corresponds to ~2000 catalyst turnovers during the reaction period. When the catalyst concentration was reduced to 1.5×10^{-4} mol %, 360 000 catalyst turnovers were observed during a 26-h period, corresponding to 14 000 turnovers h^{-1} or approximately 4 turnovers s^{-1}. Reactions with excess propene showed 3480 catalyst turnovers during the 1 h reaction period. The presence of electron-withdrawing groups on the olefin reduced the reaction rates as evidenced by reactions with trifluoropropene and vinyl arenes. The rates for the reactions with ethylene and propylene are the highest that have been observed for any metal-catalyzed reaction involving borazine or a polyhedral borane.

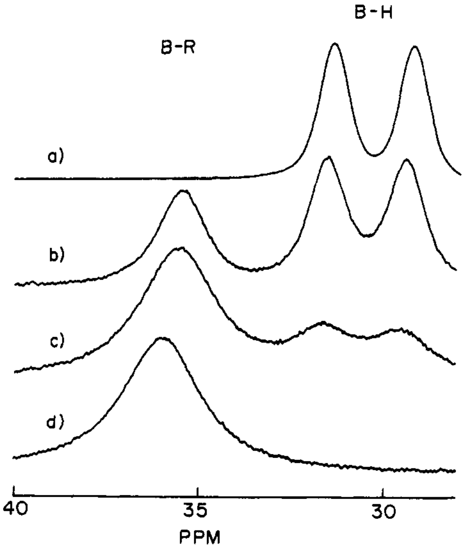
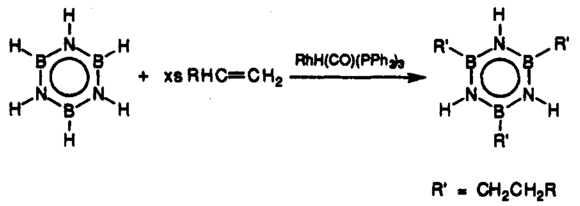


Figure 2. ^{11}B NMR spectrum of (a) $B_3N_3H_6$; (b) 2-C_3H_7-$B_3N_3H_5$ (**3**); (c) 2,4-$(C_3H_7)_2$-$B_3N_3H_4$ (**4**); (d) 2,4,6-$(C_3H_7)_3$-$B_3N_3H_3$ (**5**).

The catalyst was still active upon removal of borazine and product, and the catalyst could be used repeatedly. For example, as indicated in the table, the same catalyst was used for three reactions of borazine with propene with no signs of decreased yields or turnover rates.

Good yields with both terminal aliphatic olefins (>90%) and internal olefins (72–93%) were observed. The lowest yield was observed for the reaction with *trans*-2-butene, which because of its slow rate was carried out for 185 h. Because of the extended reaction period, either decomposition of the starting borazine[23,24] or the *n*-butylborazine product may have been responsible for the lower yields.

To produce tri-*B*-alkylborazines, an excess of olefin was employed and the reaction was continued for sufficient time to allow complete reaction. Workup then required just vacuum distillation of the *B*-trialkylborazine from the reaction flask. The 2,4,6-$(CF_3CH_2CH_2)_3B_3N_3H_3$ (**9**) is a solid, but the remaining tri-*B*-alkylborazines are colorless liquids at room temperature. The properties of many tri-*B*-alkylborazines have previously been reported.[25]



(1)

The tri-*B*-alkylborazines have simple NMR spectra with broad singlets near 36 ppm in their ^{11}B NMR spectra (as shown in Figure 2d for 2,4,6-$(C_3H_7)_3B_3N_3H_3$) and, in addition to the resonances arising from the protons on the alkyl substituents, only a single broad NH resonance near 4.6 ppm is observed in their ^1H NMR spectra. The resonances arising from the alkyl-substituents may be assigned in a straightforward manner as indicated in Table 2. Likewise, their IR spectra (Figure 3d) exhibit char-

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[23] Manatov, G.; Margrave, J. L. *J. Inorg. Nucl. Chem.* 1961, *20*, 348–351.

[24] Fazen, P. J.; Sneddon, L. G. Unpublished results.

[25] *Gmelin Handbush der Anorganishen Chemie, Borazine and Its Derivatives*; Springer-Verlag: New York, 1978; Vol. 17.

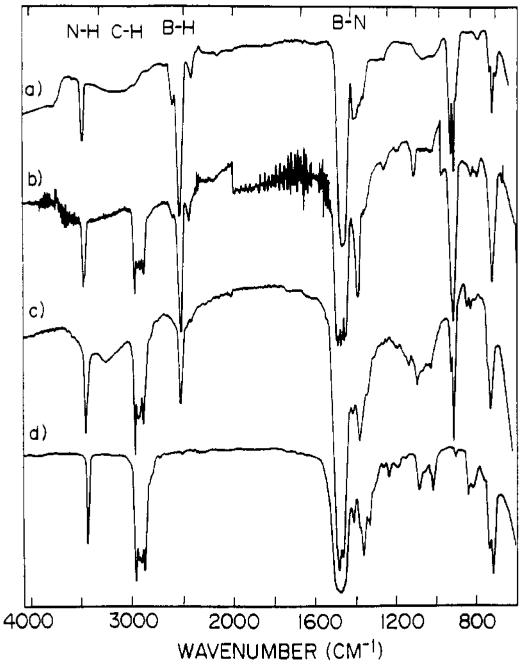
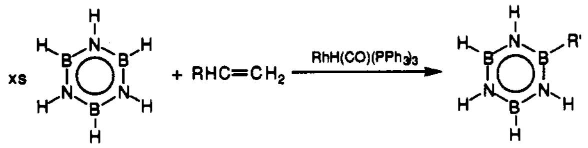


Figure 3. Infrared spectra of (a) $B_3N_3H_6$; (b) 2-C_3H_7-$B_3N_3H_5$ (**3**); (c) 2,4-$(C_3H_7)_2$-$B_3N_3H_4$ (**4**); (d) 2,4,6-$(C_3H_7)_3$-$B_3N_3H_3$ (**5**).

acteristic NH (3470–3485 cm^{-1}), CH (2965–2870 cm^{-1},) and BN (1490–1425 cm^{-1}) absorptions, but the typical borazine (Figure 3a) BH stretching band in the 2505–2535 cm^{-1} range is absent.

In order to produce mono-*B*-alkylborazines, a large excess (≥4×) of borazine to olefin was employed in the reactions. Under these conditions, it was found that mono-*B*-alkylborazines could be obtained selectively in high yields with a variety of olefins.

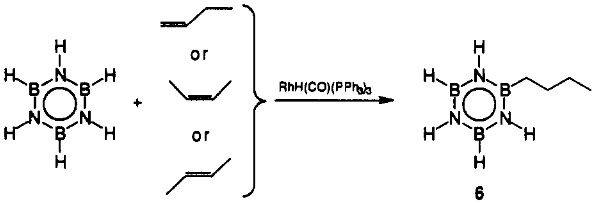


(2)

R' = CH_2CH_2R

As shown in Figure 2b for 2-C_3H_7-$B_3N_3H_5$, the mono-*B*-alkylborazines have characteristic ^{11}B NMR spectra consisting of a doublet of area 2 near 30 ppm and a singlet of area 1 near 36 ppm. In their $^1H\{^{11}B\}$ NMR spectra, the BH resonance appears between 4.4 and 4.6 ppm. The NH resonances appear as overlapping triplets between 4.8 and 5.1 ppm when recorded in benzene, but shift downfield to between 5.8 and 6.1 when recorded in THF. Their infrared spectra (Figure 3b) show the characteristic absorptions in the NH, CH, and BN regions observed for the *B*-trialkyborazines, along with an additional band between 2505–2535 cm^{-1} arising from the BH stretching. Again, all mono-B-alkyl products were isolated as colorless liquids and their purification was readily achieved by vacuum line fractionation.

The reactions of borazine with 1-butene, *cis*-2-butene, and *trans*-2-butene gave the same product, 2-(n-C_4H_9)-$B_3N_3H_5$. The terminal butene reacted fastest, and the *cis*-isomer reacted faster than the *trans*-isomer.



(3)

6

The formation of only the terminally-substituted *n*-*B*-butylborazine from the *internal* olefins, *cis*-2-butene and *trans*-2-butene, is similar to the finding that *n*-pentylsilane is the only product of the reaction of phenyldimethylsilane with *cis*-2-pentene in the presence of a rhodium catalyst.[26] Since $RhH(CO)(PPh_3)_3$ is an olefin isomerization catalyst,[27] olefin isomerization could, in principle, play a part in the observed selectively; however, no isomerized olefins were found in either the above reactions or in the previously reported hydrosilations. The selectivity of this catalyst for terminal products has also been found in olefin hydrogenation[28] and hydroformylation[29] and has generally been attributed to the greater stability of the primary metalloalkyl compared to that of a secondary metalloalkyl.[30] Indeed, in the hydroformylation reaction, addition of phosphine increases the selectivity toward terminal products,[29c] strongly indicating that steric interactions with the phosphine ligands destabilize the secondary metalloalkyl. The formation of *n*-alkyl products from internal olefins in olefin hydrozirconation has been proposed to arise for similar reasons.[31]

Catalyzed styrene/catechol–borane hydroborations using other Rh catalysts report primarily Markovnikov addition products when the catalyst is prepared under anaerobic conditions or when additional phosphine is added to the reaction.[15c,e,g] Catalyzed reactions of borazine with vinyl arenes gave predominantly terminal products. This trend was also observed for the hydrosilation of styrene with triethoxysilane using this catalyst.[32] Thus, borazine reacted with α-methylstyrene and 4-allylanisole (eq 4) to give **11** and **12**. Styrene gave predominately the terminal product (**10a**),[33] but analysis of the product by GC/MS showed evidence for the presence of a second isomer (<7%) which could be the internal isomer **10b**. The spectral data in Table 2 are again in agreement with the proposed structures for **10a**, **11**, **12**.

When an intermediate ratio of borazine to olefin (1:1 ≤ X ≤ 3) was used, a mixture of mono-, di-, and tri-*B*-alkylborazines was produced. The di-*B*-alkylborazines have volatilities intermediate those of the mono- and tri-B-substituted products, therefore they can generally be readily separated, as demonstrated for 2,4-$(C_3H_7)_2$-$B_3N_3H_4$

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

(27) (a) Schunn, R. A. *Inorg. Chem.* **1970**, *9*, 2567–2572. (b) Yagupsky, M.; Wilkinson, G. *J. Chem. Soc. (A)* **1970**, 941–944. (c) Strohmeier, W.; Rehder-Stirnweiss, W. *J. Organomet. Chem.* **1970**, *22*, C27–C28. (d) Strohmeier, W.; Fleischmann, R.; Rehder-Stirnweiss, W. *J. Organomet. Chem.* **1973**, *47*, C37–C40. (e) McQuillin, F. J.; Parker, D. G. *J. Chem. Soc. Perkin Trans. I* **1975**, 2092–2096.

(28) (a) O'Connor, C.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 2665–2671. (b) Ueda, T. *Proc. 5th Int. Cong. Catal.* **1973**, *1*, 431–443.

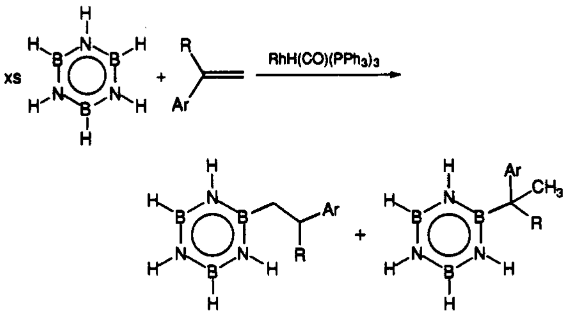
(29) (a) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 3133–3142. (b) Brown, C. K.; Wilkinson, G. *Tetrahedron Lett.* **1969**, *22*, 1725–1726. (c) Brown, C. K.; Wilkinson, G. *J. Chem. Soc. (A)* **1970**, 2753–2764. (d) Wilkinson, G. *Bull. Soc. Chim. Fr.* **1968**, *12*, 5055–5058.

(30) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 5th ed.; Wiley: New York, 1988; pp 1248–1249.

(31) (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115–8116. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.

(32) Rejhon, J.; Hetflejš, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3680–3687.

(33) The terminal structure of **10a** has been confirmed by a single crystal X-ray structure determination of its cyclotriborazane derivative, 2-(1-$CH_2CH_2C_6H_5$)-$B_3N_3H_{11}$: Wille, A. E.; Carroll, P. J.; Sneddon, L. G. Unpublished.



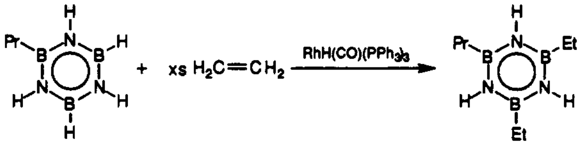
(4)

10a, 11, 12 **10b**

(4) and 2,4-$(CF_3CH_2CH_2)_2$-$B_3N_3H_4$ (8), from these mixtures by simple vacuum line fractionation.

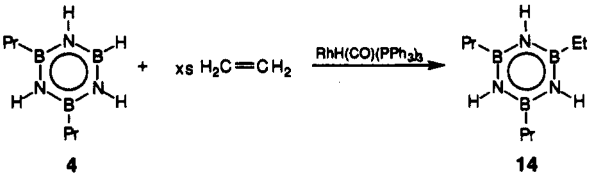
The ^{11}B NMR spectrum of 2,4-$(C_3H_7)_2$-$B_3N_3H_4$, given in Figure 2c, is typical of those of the other di-*B*-alkylborazines, consisting of a doublet near 30 ppm and a singlet at lower field (~35–36 ppm) with relative intensities of 1 to 2, respectively. Their $^1H\{^{11}B\}$ NMR spectra show resonances in the same regions as the mono-*B*-alkylborazines, but with the BH resonance of intensity 1. Likewise, their IR spectra (Figure 3c) are similar to those of the mono-*B*-alkylborazines except that the BH stretching band is less prominent.

Further extension of the reactions above has resulted in the first systematic method for obtaining unsymmetrically substituted tri-*B*-alkylborazines. Previously, complex mixtures containing a variety of such compounds had only been obtained by adding a combination of alkyllithium reagents to borazine in ether solutions, but the unseparated products were identified only by GC.[12a,34] In our work it was found that the selective formation of an unsymmetrically substituted tri-*B*-alkylborazine is readily obtained by the catalyzed reaction of an excess of a suitable olefin with either a mono-*B*-alkylborazine or a di-*B*-alkylborazine, as in the examples given below:



(5)

3 **13**

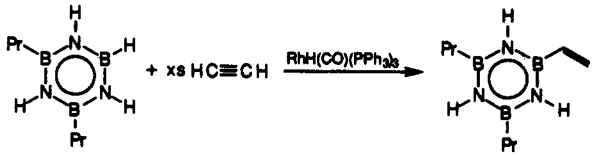


(6)

4 **14**

Both 13 and 14 show only a single broad resonance centered at ~36 ppm in their ^{11}B NMR spectra and a single broad NH resonance near 4.6 ppm in their ^1H NMR spectra. The ^1H NMR spectra also show the resonances arising from the ethyl and propyl groups as assigned in the Table 2. In their IR spectra, the BH stretching band is absent.

Disubstituted borazines were also found to react with acetylene to give the di-*B*-alkyl-*B*-vinylborazine 15 (eq 7), but the reaction was relatively slow (~2 turnovers day^{-1}) compared to that of the metal-catalyzed reaction of the parent borazine with acetylene (~73 turnovers h^{-1}).[14] The ^{11}B NMR spectrum of 15 shows two singlet resonances at 36 and 31 ppm with relative areas of 2:1. The latter resonance occurs at a chemical shift similar to that observed for the vinyl-substituted boron in 2-$(CH_2{=}CH)$-$B_3N_3H_5$ (31.2 ppm).[14] The ^1H NMR spectrum shows, in addition to the propyl resonances, vinyl resonances between 5.5–6.5 ppm. The IR spectrum exhibits NH (3440 cm^{-1}), CH (2965–2875 cm^{-1}), and BN (1470 cm^{-1}) stretches, but the BH stretching absorption is absent. The presence of the vinyl group is consistent with the absorptions at 3060 (CH stretch) and 1635 and 1615 cm^{-1} (C=C stretches).

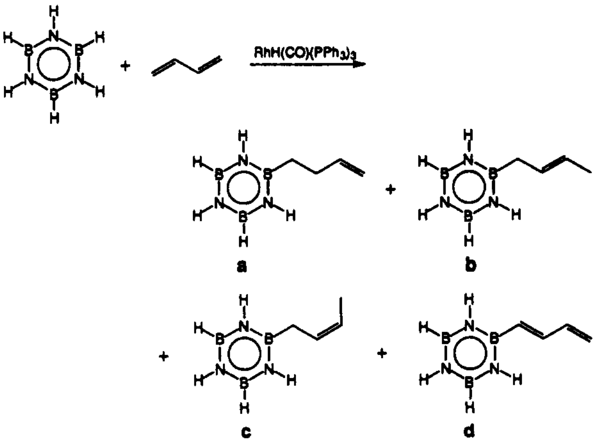


(7)

4 **15**

We have previously shown that the parent *B*-vinylborazine, 2-$(CH_2{=}CH)$-$B_3N_3H_5$, is polymerized upon free radical initiation to give a poly-*B*-vinylborazine homopolymer analogous to polystyrene.[14] The poly-*B*-vinylborazine was also shown to function upon pyrolysis as an excellent preceramic polymer for BN and BNC_x ceramics. New di-B-alkylated *B*-vinylborazines, such as 15, may now prove to be useful monomers for the construction of a range of new B-alkylated *B*-vinylborazine polymers which, because of the absence of reactive BH groups on the ring, have more controllable cross-linking properties. We are currently exploring these possibilities.

The catalyzed reaction of borazine with dienes was of special interest since dihydroboration and/or polymeric products could perhaps be achieved. It was found that borazine reacts slowly at room temperature with butadiene in the presence of catalytic amounts of $RhH(CO)(PPh_3)_3$ to form a mixture of products.



(8)

The ^{11}B NMR spectrum of the mixture was similar to that found for the monoalkylborazines, consisting of a doublet near 30 ppm and a singlet near 36 ppm. These compounds were not isolated, but the GC/MS spectrum of the mixture showed it to be composed of four compounds, three of which exhibited parent ions of *m/z* 135 which would be expected for simple monohydroboration

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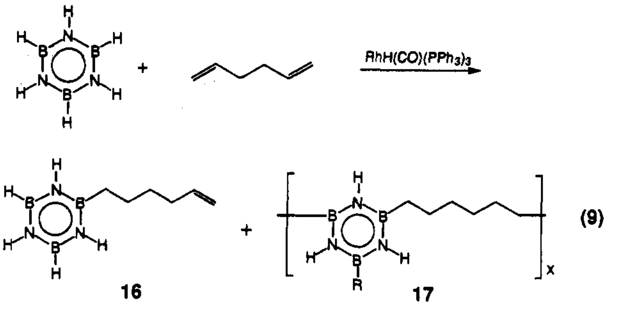
[34] Recently, Niedenzu synthesized amino or thio-substituted alkylborazines from the reaction of dialkylhalo- and alkyldihaloborazines (obtained by the reaction of tri-*B*-alkylborazines with boron trihalides). Although no unsymmetrical tri-*B*-alkylborazines were reported, the dialkylhalo- and alkyldihaloborazines might also serve as precursors to such compounds. See Bai, J.; Niedenzu, K. *Inorg. Chem.* 1991, *30*, 2955–2956.

products, 2-C_4H_7-$B_3N_3H_5$ (**a–c** in eq 8), and one which exhibited a parent ion of *m/z* 133 which could be a dehydrogenative addition product, 2-C_4H_5-$B_3N_3H_5$ (**d**). A similar product distribution was previously found for the RhH(CO)(PPh_3)$_3$-catalyzed reaction of butadiene and trimethylsilane.[35]

Borazine was found to react more selectivity with 1,5-hexadiene in the presence of catalyst to give 2-(5-hexenyl)-borazine (**16**), along with an insoluble polymer **17**. The spectral data for **16** are consistent with the proposed monohydroborated structure. The ^{11}B NMR spectrum of **16** consists of a doublet at 30.6 ppm and a singlet at 35.6 ppm. Its ^{1}H NMR spectrum consists of four multiplets between 0.6 and 2.0 ppm, arising from four different sets of methylene protons, broad BH resonances centered at 4.6 ppm, an NH triplet at 4.8 ppm, a complex multiplet between 4.9 and 5.0 ppm, and a multiplet centered at 5.78 ppm. The latter two multiplets arise from the protons on the terminal vinyl group. The IR spectrum exhibits NH (3445 cm^{-1}), CH (2920–2860 cm^{-1}), BH (2510 cm^{-1}), and BN (1470 cm^{-1}) absorptions characteristic of *B*-monoalkylborazines, in addition to CH (3080 cm^{-1}) and C=C (1645 cm^{-1}) absorptions characteristic of a vinyl group.



R = –H, or –(CH$_2$)$_6$–, or–(CH$_2$)$_4$CH=CH$_2$

The polymeric solid **17** has, according to the elemental analysis, an empirical formula corresponding to an oligomer with a repeat structure of $(B_3N_3H_4)_{1.0}[(CH_2)_6]_{1.22}$. This composition is consistent with the presence of an additional hexenyl group for approximately every 4 to 5 hexenylborazine repeat units. The DRIFT spectrum of **17** shows NH (3439 cm^{-1}), CH (2921 and 2850 cm^{-1}), BH (2510 cm^{-1}), C=C (1638 cm^{-1}), and BN (1460 cm^{-1}) stretches. The observation of a C=C stretch is consistent with the presence of unreacted hexenyl groups in the polymer, suggesting that the polymer probably has a complex cross-linked structure containing both dihydroborated and monohydroborated C$_6$-chains.

The reaction of 2,4-$(C_3H_7)_2$-$B_3N_3H_4$ (**4**) with 1,5-hexadiene was more selective giving only the dihydroboration product, 1,6-(2,4-(*n*-C_3H_7)$_2$-6-$B_3N_3H_3$)$_2$-C_6H_{12} (**18**).

The NMR spectra of **18** are similar to those of the other trisubstituted derivatives showing only a single broad boron resonance and a single NH resonance in its ^{11}B and ^{1}H NMR spectra, respectively. Naturally, the ^{1}H spectra are more complex owing to the overlapping resonances arising from the propyl and hexyl groups, but the observation of only a single triplet resonance of intensity 12, which may be assigned to the four propyl methyl groups, supports the 1,6-substituted configuration.

The fact that the RhH(CO)(PPh_3)$_3$ catalyst is quite active for borazine alkylation suggested that it might also prove effective for the direct alkylation of borazine derived polymers. As discussed in the introduction, a number of new borazine based polymers have recently been synthesized and shown to function as efficient processable precursors to boron nitride ceramics.[2] One borazine polymer of particular importance is polyborazylene, $(B_3N_3H_{\sim 4})_x$, which we have previously shown is the product of thermally induced dehydrocoupling of borazine. This polymer is soluble and processable and upon pyrolysis gives boron nitride in high ceramic and chemical yields.[17] The polymer has been shown to have a complex structure containing linear, branched-chain, and fused-cyclic segments and to contain reactive NH and BH groups, which upon moderate heating undergo inter- and intrachain dehydrocoupling reactions. The substitution of alkyl groups at the ring boron sites in polyborazylene might, in fact, retard such reactions and allow the systematic control of polymer cross-linking properties. For these reasons the metal-catalyzed olefin-hydroboration reactions of polyborazylene were investigated.

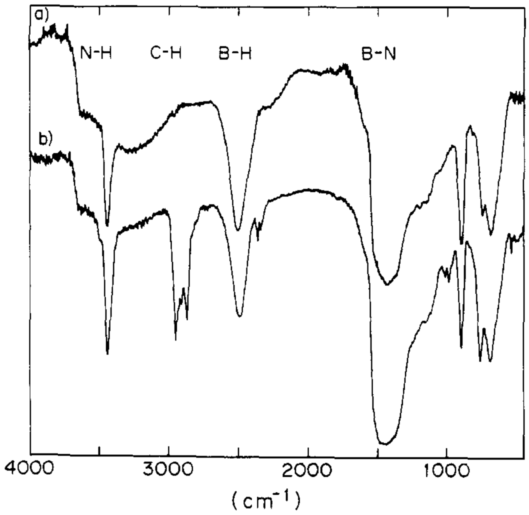
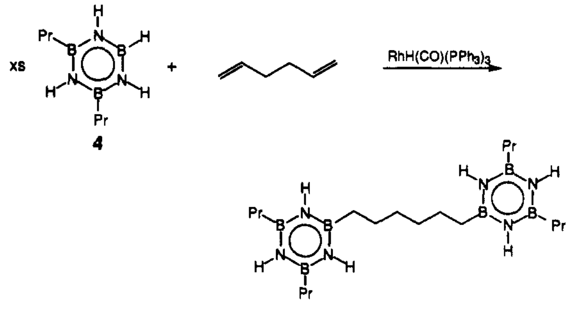


Figure 4. DRIFT spectra of (a) polyborazylene, $(B_3N_3H_{\sim 4})_x$; (b) B-ethylated polyborazylene, $(C_2H_5)_{0.7}(B_3N_{3.0}H_{2.5})$ (**19**).



RhH(CO)(PPh_3)$_3$ was found to catalyze the reaction of either ethylene or propene with polyborazylene in THF solution.

$$[B_3N_3H_{\sim 4}]_x + RHC{=}CH_2 \xrightarrow[\text{THF}]{RhH(CO)(PPh_3)_3} [R'_yB_3N_3H_{\sim 4-y}]_x \quad (11)$$

R = H or CH$_3$ R' = CH$_2$CH$_2$R

Chemical analysis of the products of two different experiments with ethylene gave elemental compositions of $(C_2H_5)_{0.7}(B_3N_{3.0}H_{2.5})$ (**19**) and $(C_2H_5)_{1.0}(B_3N_{3.1}H_{2.0})$ (**20**),

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

while an analogous reaction with propene gave a polymer of composition $(C_3H_7)_{0.4}(B_3N_{2.9}H_{2.5})$ (21). The spectral data for these polymers are again consistent with the formation of B-alkylated materials. Thus, as can be seen in Figure 4, in the DRIFT spectra the B–H stretching band at 2493 cm^{-1} in polymer 19 is decreased relative to the N–H and B–N bands in polyborazylene. The spectra also show new bands at 2953, 2914, and 2874 cm^{-1} which may be assigned to the C–H stretching bands in the ethyl substituents. As in the parent polymer, their ^{11}B NMR spectra show only very broad signals near 30 ppm. The ^{1}H NMR spectra showed broad resonances at 0.97 ppm in the ethyl-substituted polymer and at 0.95 and 1.46 ppm in the propyl-substituted polymer, which are attributed to alkyl groups attached to the polymer. All polymers were soluble in THF. Studies of the molecular weights and ceramic conversion reactions of these polymers will be reported separately,[36] but preliminary thermogravimetric studies of the ceramic conversion reactions of these new B-alkylated polyborazylenes have indeed demonstrated that their thermally-induced cross-linking reactions differ significantly from those of the parent polyborazylene polymer. These observations strongly suggest that further chemical modification of the polyborazylene polymer (or other borazine derived polymers) using metal catalysis may allow the construction of a range of new "second-generation" preceramic polymers in which much finer control of both polymer and ceramic properties may be achieved. We are presently exploring these possibilities.

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(36) Fazen, P. J.; Remsen, E. E.; Sneddon, L. G., manuscript in preparation.