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Efficient Synthesis and NMR Data of *N*- or *B*-Substituted Borazines

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ABSTRACT: *The thermolysis of borane-primary amine complexes $RNH_2.BH_3$ was reexamined. Excellent yields of N-substituted borazines were obtained at 200°C, when R is an alkyl group, and at 120°C for R = Ph. B-alkyl, vinyl, and alkynyl borazines were easily prepared in good to excellent yields by ammonolysis of bis(diisopropylamino)organoboranes at temperatures above 95°C. The ^1H, ^{13}C, and ^{15}N or ^{14}N NMR data for all borazines prepared are reported for the first time.*
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INTRODUCTION

Boron nitride has been widely used in high temperature technology [1]. Many studies have recently been undertaken [2] in order to develop precursors of boron nitride. Sneddon et al. obtained boron nitride by pyrolysis of polyborazylene polymer that had been obtained by thermal polymerization of borazine $B_3N_3H_6$ [2]. *N*- or *B*-substituted borazines are also interesting compounds that may also be polymerized. These polymers, through pyrolysis at high temperature, could lead to ceramic-like boron nitride and boron carbonitride [2,3]. *N*-substituted borazines are accessible by thermolysis of primary amine-borane complexes $RNH_2 \cdot BH_3$, usually prepared by the reaction of lithium borohydride with primary amine salts [4]. Amine-borane complexes were also obtained by the reaction of diborane or borane-THF complex with primary amines [5]. The thermolysis of these species, usually at 120°C, sometimes led to pure borazines. However, in most cases, mixtures of compounds were obtained. B-substituted borazines constitute an interesting class of compounds that may be polymerized under a variety of conditions [6]. In 1964, Niedenzu et al. reported a synthesis of *B*-vinylborazine in 49% yield by ammonolysis of *bis*(diethylamino)vinylborane at 80–100°C [7].

In this article, we report on a simple way to synthesize primary amine-borane complexes from commercially available borane-dimethylsulfide (BMS). Furthermore, we also have reexamined the thermolysis conditions of these complexes in order to have in hand an efficient preparation of N-substituted borazines. We had developed the synthesis of *bis*(diisopropylamino)organoboranes by borylation of the corresponding organometallics (lithium or magnesium derivatives) with chloro-*bis*(diisopropylamino)borane [8]. We also had extended the work of Niedenzu et al. [7] to B-alkyl, -vinyl, and -alkynyl borazines by ammonolysis of the corresponding *bis*(diisopropylamino)boranes. Also, for the first time, a ^{11}B and ^{15}N or ^{14}N NMR data bank about these N- or B-substituted borazines has been established.

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EXPERIMENTAL

All reactions that required an atmosphere of dry nitrogen were performed in flame-dried glassware and were stirred magnetically. NH_3 (Ammonia, 3.6 nv) was purchased from Alphagaz and $BH_3 \cdot SMe_2$ was purchased from Lancaster. Other reagents and solvents were dried by usual techniques and purified by distillation under nitrogen [9]. *Bis*(dialkylamino)organoboranes **5** were obtained according to procedures reported in the literature [8].

Melting points were measured on a Kofler apparatus (uncorrected). NMR spectra were recorded from $CDCl_3$ solutions (except when another solvent is given) on a Bruker ARX 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) or a Bruker WB 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{11}B: 96 MHz, ^{14}N: 21 MHz, ^{15}N: 30 MHz). Chemical shifts, δ, are expressed in ppm downfield from internal TMS (^{1}H, ^{13}C), external $Et_2O \cdot BF_3$ for ^{11}B, and CH_3NO_2 for ^{14}N and ^{15}N. Mass spectra were measured at 70 eV on a Varian MAT 311 spectrometer (CRMPO, University of Rennes I—France). Microanalysis data were obtained from the central laboratory for analysis (CNRS, Lyon, France).

Alkylamine-Borane Complexes: $RNH_2 \cdot BH_3$ **2**

Ammonia-borane complex **2a** was prepared from $(NH_4)_2CO_3$ and KBH_4 according to procedures in the literature [10] in 70% yield. m.p. 120°C; ^{1}H NMR (THF *d*8): δ = 1.47 (q, 3H, $^1J_{HB}$ = 94 Hz, BH_3), 4.07 (t, 3H, $^1J_{H^{14}N}$ = 34 Hz, NH_3). HRMS: calc. for $H_5N^{11}B$, $[M\text{-}H^{\cdot}]^+$, 30.0510; found: 30.0514.

Alkylamine-borane complexes **2** from $Me_2S \cdot BH_3$: A solution of 200 mmol of amine RNH_2 **1** in 100 mL of dried THF was cooled to −80°C. To this reaction mixture was added 200 mmol of $BH_3 \cdot SMe_2$ over a period of 45 minutes. The reaction mixture was allowed to reach room temperature. THF and SMe_2 were removed under vacuum (15 Torr). Complexes $RNH_2 \cdot BH_3$ were collected and dried under high vacuum (0.03 Torr) for 5 hours.

$MeNH_2 \cdot BH_3$ ***2b***: white solid; yield, 97%; m.p.: 58°C. ^{1}H NMR: δ = 1.50 (q, 3H, $^1J_{HB}$ = 94 Hz, BH_3), 2.56 (t, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3), 3.78 (s broad, 2H, NH_2). ^{13}C NMR: δ = 34.5. HRMS: calc. for $CH_8N^{11}B$, $M^{\cdot+}$, 45.0749; found: 45.0742.

$iPrNH_2 \cdot BH_3$ ***2c***: white solid; yield, 97%, m.p.: 66°C. ^{1}H NMR: δ = 0.60–2.30 (m, 3H, BH_3), 1.27 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH_3), 3.02 (sept, 1H, $^3J_{HH}$ = 6.5 Hz, CH), 3.84 (s broad, 2H, NH_2). ^{13}C NMR: δ = 21.7 (CH_3), 50.1 (CH). HRMS: calc. for $C_3H_{12}N^{11}B$, $M^{\cdot+}$, 73.1062; found: 73.1063.

$BuNH_2 \cdot BH_3$ ***2d***: oil; yield, 95% (decomposition on attempts of purification by distillation under vacuum). ^{1}H NMR: δ = 0.60–2.30 (m, 3H, BH_3), 0.93 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.36 (m, 2H, CH_2CH_3), 1.61 (quint, 2H, $^3J_{HH}$ = 7.3 Hz, $CH_2CH_2CH_3$), 2.77 (m, 2H, CH_2N), 4.00 (s broad, 2H, NH_2). ^{13}C NMR: δ = 13.6 (CH_3), 19.8 (CH_2CH_3), 31.0 ($CH_2CH_2CH_3$), 48.5 (CH_2N). Anal.: $C_4H_{14}NB$ (86.97 M); calc.: C, 55.24; H, 16.23; N, 16.10; found: C, 54.61; H, 15.97; N, 16.01.

$HeptNH_2 \cdot BH_3$ ***2e***: oil, yield: 90% (decomposition on attempts of purification by distillation under vacuum). ^{1}H NMR: δ = 0.50–2.30 (m, 3H, BH_3), 0.87 (t, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.28 (s broad, 8H, 4 × CH_2), 1.61 (s broad, 2H, $CH_2CH_2CH_3$), 2.77 (quint, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2N), 3.92 (s broad, 2H, NH_2). ^{13}C NMR: δ = 14.0 (CH_3), 22.5, 26.6, 28.8, 29.1, 31.6 (CH_2), 48.9 (CH_2N). HRMS: calc. for $C_7H_{17}N^{11}B$, $[M\text{-}3H^{\cdot}]^+$, 126.1454; found: 126.1458.

$PhNH_2 \cdot BH_3$ ***2f***: white solid; yield, 99%; m.p.: 98–100°C. ^{1}H NMR: δ = 0.80–2.90 (m, 3H, BH_3), 5.45 (s broad, 2H, NH_2), 6.68–7.43 (m, 5H, C_6H_5).^{13} C NMR: δ = 117.6, 121.2, 129.1 (CH), 143.9 (CN). HRMS: Calc. for $C_6H_8N^{11}B$, $[M\text{-}2H^{\cdot}]^+$, 105.0749; found: 105.0725.

Thermolysis of $RNH_2 \cdot BH_3$ (**2b, 2c, 2d, 2e, 2f**) *at 120°C*

Borazines are moisture sensitive and must be handled under an inert atmosphere. In a 50 mL flask, 35 mmol of each complex $RNH_2 \cdot BH_3$ **2** was introduced under nitrogen and heated in an oil bath from room temperature to 120°C in 30 minutes. This temperature was maintained for an hour, and the reaction mixture was then cooled to room temperature.

From $MeNH_2 \cdot BH_3$ ***2b***: *N*-trimethylcycloborazane $(MeNH\text{-}BH_2)_3$ **3b** was obtained in 95% yield as a 2:3 mixture of *cis* and *trans* isomers: white solid; m.p. > 250°C. *Cis* and *trans* isomers were not separated. ^{1}H NMR of *cis* isomer: δ = 0.80–2.30 (m, 6H, 3 BH_2), 2.26 (s, 9H, 3 CH_3), 3.06 (s broad, 3H, 3 NH). ^{1}H NMR of *trans* isomer: δ = 0.80–2.30 (m, 6H, 3 BH_2), 2.27 (s, 6H, 2 CH_{3e}), 2.32 (s, 3H, CH_{3a}), 3.06 (s broad, 3H, 3 NH) (*e*, equatorial position, *a*, axial position [5b]). ^{13}C NMR of *cis* isomer: δ = 37.4. ^{13}C NMR of *trans* isomer: δ = 35.4, 36.8 (CH_{3a} + CH_{3e}). HRMS: calc. for $C_3H_{17}N_3{}^{11}B_3$, $[M\text{-}H^{\cdot}]^+$, 128.1697; found: 128.1702 (measured on the mixture of isomers).

From $iPrNH_2 \cdot BH_3$ ***2c***: Thermolysis of **2c** yielded a mixture of iPrNH$_2 \cdot$BH$_3$ **2c** (5%), *N*-triisopropylcycloborazane $(i\text{PrNH-BH}_2)_3$ **3c** (20%), *N*-triisopropylborazine $(i\text{PrN-BH})_3$ **4c** (49%), and 26% of a non-identified product (ni). These products could not be separated. ^{11}B NMR: δ = −24.5 (5%) (q, $^1J_{BH}$ = 125 Hz, N$\cdot$BH$_3$ ni), −21.4 (5%) (q, $^1J_{BH}$ = 94 Hz, i-PrNH$_2 \cdot$BH$_3$), −10.3 (20%) (t, $^1J_{BH}$ = 91 Hz, (iPrNH-BH$_2$)$_3$), −6.5, −5.4 (6%) (t, $^1J_{BH}$ = 97 Hz, N$_2$BH$_2$ ni),

22.7 (15%) (s, N_3B ni), 31.6 (49%) (d, $^1J_{BH}$ = 120 Hz, (*i*PrN-BH)$_3$).

*From $BuNH_2 \cdot BH_3$ **2d***: Thermolysis of **2d** yielded a mixture of $BuNH_2 \cdot BH_3$ **2d** (4%), *N*-tributylcycloborazane (BuNH-BH_2)$_3$ **3d** (66%) and *N*-tributylborazine (BuN-BH)$_3$ **4d** (30%). ^{11}B NMR: δ = −20.0 (4%) (q, $^1J_{BH}$ = 90 Hz, $BuNH_2 \cdot BH_3$), −6.4 (66%) (t, $^1J_{BH}$ = 86 Hz, (BuNH-BH_2)$_3$), 30.6 (30%) (d broad, (BuN-BH)$_3$). *N*-tributylcycloborazane **3d** was obtained after kugelrohr distillation of the reaction mixture as a 42:58 mixture of *cis* and *trans* isomers: oil; yield, 60%; b.p. (0.03 Torr), 70°C. ^{1}H NMR of *cis* isomer: δ = 0.90 (t, 9H, $^3J_{HH}$ = 7.3 Hz, 3 CH_3), 1.28 (sext, 6H, $^3J_{HH}$ = 7.0 Hz, 3 CH_2CH_3), 1.58 (quint, 6H, $^3J_{HH}$ = 7.0 Hz, 3 $CH_2CH_2CH_3$), 1.90–2.80 (m, 6H, 3 BH_2), 2.48 (q, 6H, $^3J_{HH}$ = 7.0 Hz, 3 CH_2N), 3.26 (s broad, 3H, 3 NH). ^{1}H NMR of *trans* isomer: δ = 0.92 (t, 6H, $^3J_{HH}$ = 7.3 Hz, 2 CH_{3e}), 0.93 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_{3a}), 1.29 (sext, 4H, $^3J_{HH}$ = 7.0 Hz, 2 $CH_{2e}CH_{3e}$), 1.30 (sext, 2H, $^3J_{HH}$ = 7.0 Hz, $CH_{2a}CH_{3a}$), 1.60 (quint, 4H, $^3J_{HH}$ = 7.0 Hz, 2 $CH_{2e}CH_{2e}CH_{3e}$), 1.61 (quint, 2H, $^3J_{HH}$ = 7.0 Hz, $CH_{2a}CH_{2a}CH_{3a}$), 1.90–2.80 (m, 6H, 3 BH_2), 2.48 (q, 4H, $^3J_{HH}$ = 7.0 Hz, 2 $CH_{2e}N$), 2.50 (q, 2H, $^3J_{HH}$ = 7.0 Hz, $CH_{2a}N$), 3.26 (s broad, 3H, 3 NH) (*e*, equatorial position, *a*, axial position). ^{13}C NMR of *cis* isomer: δ = 13.8 (CH_3), 20.0 (CH_2CH_3), 30.1 ($CH_2CH_2CH_3$), 51.5 (CH_2N). ^{13}C NMR of *trans* isomer: δ = 13.9 (CH_{3e} + CH_{3a}), 20.3, 20.5 ($CH_{2e}CH_{3e}$ + $CH_{2a}CH_{3a}$), 30.1, 30.2 ($CH_{2e}CH_{2e}CH_{3e}$ + $CH_{2a}CH_{2a}CH_{3a}$), 50.1, 50.9 ($CH_{2e}N$ + $CH_{2a}N$). Anal.: $C_{12}H_{36}N_3B_3$ (254.87 M); calc.: C, 56.55; H, 14.23; N, 16.48; found: C, 56.37; H, 14.01; N, 16.61.

*From $HeptNH_2 \cdot BH_3$ **2e***: Thermolysis of **2e** yielded a mixture of $HeptNH_2 \cdot BH_3$ ***2e*** (3%), N-triheptylcycloborazane (HeptNH-BH_2)$_3$ ***3e*** (52%), *N*-triheptylborazine (HeptN-BH)$_3$ ***4e*** (45%). These products could not be separated. ^{11}B NMR: δ = −19.8 (3%) (q broad, $HeptNH_2$-BH_3), −6.3 (52%) (t broad, (HeptNH-BH_2)$_3$), 31.6 (45%) (d broad, (HeptN-BH)$_3$).

*From $PhNH_2 \cdot BH_3$ **2f***: *N*-triphenylborazine (PhN-BH)$_3$ ***4f*** was obtained in 99% yield: white solid; m.p.: 158°C. ^{1}H NMR: δ = 4.00–5.90 (m, 3H, 3 BH), 6.66–7.38 (m, 15H, 3 C_6H_5). ^{13}C NMR: δ = 124.6, 125.2, 128.8 (CH), 147.9 (CN). HRMS: calc. for $C_{18}H_{18}N_3{}^{11}B_3$, $M^{\cdot+}$, 309.1780; found: 309.1790.

Thermolysis of $RNH_2 \cdot BH_3$ (**2b, 2c, 2d, 2e**) *at 200°C*

In a 50 mL flask, 35 mmol of each complex $RNH_2 \cdot BH_3$ **2** were introduced under nitrogen and heated in an oil bath from room temperature to 120°C in 30 minutes. This temperature was maintained for an hour, and the reaction mixture was then heated at 200°C for another hour after having been cooled to room temperature. Borazines were purified by distillation.

N-trimethylborazine (MeN-BH)$_3$ ***4b***: oil; yield, 77%; b.p. (760 Torr), 134°C. ^{1}H NMR: δ = 3.05 (s, 9H, 3 CH_3), 3.50–5.50 (m, 3H, 3 BH). ^{13}C NMR: δ = 38.0. HRMS: calc. for $C_3H_{11}N_3{}^{11}B_3$, $[M\text{-}H^{\cdot}]^+$ = 122.123; found: 122.124.

N-triisopropylborazine (*i*PrN-BH)$_3$ **4c**: oil; yield, 94%; b.p. (0.03 Torr): 50°C. ^{1}H NMR: δ = 1.23 (d, 18H, $^3J_{HH}$ = 6.7 Hz, 6 CH_3), 3.67 (sept, 3H, $^3J_{HH}$ = 6.7 Hz, 3 CH), 3.70–5.70 (m, 3H, 3 BH). ^{13}C NMR: δ = 26.4 (CH_3), 51.7 (CH). HRMS: calc. for $C_9H_{24}N_3{}^{11}B_3$, $M^{\cdot+}$, 207.225; found: 207.225.

N-tributylborazine (BuN-BH)$_3$ ***4d***: oil; yield, 80%; b.p. (0.03 Torr): 80°C. ^{1}H NMR: δ = 0.90 (t, 9H, $^3J_{HH}$ = 7.1 Hz, 3 CH_3), 1.27 (sext, 6H, $^3J_{HH}$ = 7.1 Hz, 3 CH_2CH_3), 1.47 (quint, 6H, $^3J_{HH}$ = 7.0 Hz, 3 $CH_2CH_2CH_3$), 3.27 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 3 CH_2N), 3.40–5.60 (m, 3H, 3 BH). ^{13}C NMR: δ = 13.9 (CH_3), 19.7 (CH_2CH3), 37.5 ($CH_2CH_2CH_3$), 51.0 (CH_2N). HRMS: calc. for $C_{12}H_{30}N_3{}^{11}B_3$, $M^{\cdot+}$, 249.272; found: 249.271.

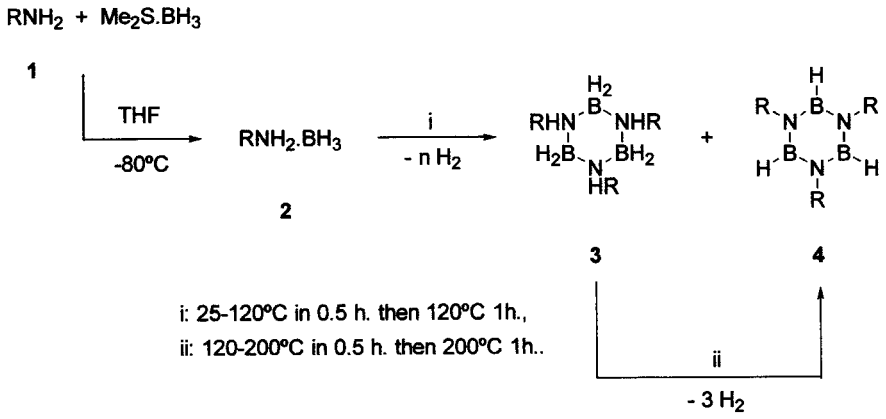
N-triheptylborazine (HeptN-BH)$_3$ ***4e***: oil; yield, 93%; b.p. (0.03 Torr): 95°C. ^{1}H NMR: δ = 0.87 (t, 9H, $^3J_{HH}$ = 6.7 Hz, 3 CH_3), 1.26 (m, 24H, 12 CH_2), 1.47 (m, 6H, 3 CH_2), 3.25 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 3 CH_2N), 3.60–5.20 (m, 3H, 3 BH). ^{13}C NMR: δ = 14.1 (CH_3), 22.7, 26.6, 29.2, 31.9, 35.4 (CH_2), 51.3 (CH_2N). HRMS: calc. for $C_{21}H_{48}N_3{}^{11}B_3$, $M^{\cdot+}$, 375.413; found: 375.412.

Synthesis of Borazine $B_3N_3H_6$ **4a**

Borazine **4a** was prepared by thermolysis of the ammonia-borane complex $NH_3 \cdot BH_3$ **2a** at 160°C in tetraglyme, according to the procedures in the literature [11]. Oil; yield, 67%; b.p. (760 Torr): 55°C. ^{1}H NMR: δ = 4.53 (q, 3H, $^1J_{HB}$ = 133 Hz, 3 BH), 5.54 (t, 3H, $^1J_{H^{14}N}$ = 54 Hz, 3 NH).

Synthesis of B-Trialkylborazines (*HN-BR*)$_3$ **6**

In a 100 mL double-necked flask fitted with a short distillation head (short path), 30 mmol of *bis*(diamino)organoboranes **5** was introduced [with alkynyl-*bis*(diisopropylamino)borane **5b**, 50 mL of toluene was added; with bis(diethylamino)vinylborane **5a**, 0.3 mmol of phenothiazine was also added]. Each reaction mixture was heated at 95°C, except for **5d**, which was heated at 115°C. Ammonia was bubbled through the reaction mixture until the dialkylamine did not distill any more. The B-substituted borazines **6** were purified by distillation or sublimation.



SCHEME 1

TABLE 1 Synthesis of Complexes **2**

Complexes	*$RNH_2.BH_3$*	Yield (%)	*m.p.* (°C)
2b	$MeNH_2 \cdot BH_3$	97	58 (lit. 56 [13])
2c	$iPrNH_2 \cdot BH_3$	97	66 (lit. 65 [13])
2d	$BuNH_2 \cdot BH_3$	95	oil, dec.
2e	$HeptNH_2 \cdot BH_3$	90	oil, dec.
2f	$PhNH_2 \cdot BH_3$	99	98–100

B-trivinylborazine $(H_2C{=}CHB\text{-}NH)_3$ ***6a***: oil; yield, 64%; b.p. (0.10 Torr): 50–52°C. ^{1}H NMR: δ = 4.91 (s broad, 3H, 3 NH), 5.65–5.75 (m, 6H, 3 CH_2), 5.85–6.00 (3, 3H, 3 CH). ^{13}C NMR: δ = 130.3 (CH_2), 137.1 broad (CH). HRMS: calc. for $C_6H_{12}N_3{}^{11}B_3$, $M^{\cdot+}$, 159.131; found: 159.132.

B-trialkynylborazine $(HC{\equiv}CB\text{-}NH)_3$ ***6b***: white solid; yield, 76%; sublimation temp. (0.03 Torr), 103–105°C; m.p.: 142°C. ^{1}H NMR (DMSO *d*6): δ = 2.78 (s, 3H, 3 CH), 5.15 (s broad, 3H, 3 NH). ^{13}C NMR (DMSO *d*6): δ = 75.0 broad (CB), 93.5 (CH). HRMS: calc. for $C_6H_6N_3{}^{11}B_3$, $M^{\cdot+}$, 153.0841; found: 153.0843. Anal.: $C_6H_6N_3B_3$ (152.57 M), calc.: C, 47.24; H, 3.96; N, 27.54; found: C, 47.72; H, 3.80; N, 27.14.

B-trimethylborazine $(MeB\text{-}NH)_3$ ***6c***: oil; yield, 61%; b.p. (760 Torr): 134°C. ^{1}H NMR: δ = 0.26 (s, 9H, 3 CH_3), 4.60 (broad s, 3H, 3 NH). ^{13}C NMR: δ = 2.5 broad. HRMS: calc. for $C_3H_{11}N_3{}^{11}B_3$, $[M\text{-}H^{\cdot}]^+$ = 122.1230; found: 122.1245.

B-tributylborazine $(BuB\text{-}NH)_3$ ***6d***: oil; yield, 65%; b.p. (0.03 Torr): 76°C. ^{1}H NMR: δ = 0.77– 094 (m, 15H, 3 CH_2CH_3), 1.23–1.43 (m, 12H, 3 CH_2CH_2B), 4.69 (s broad, 3H, 3 NH). ^{13}C NMR: δ = 14.1 (CH_3), 17.7 broad (CH_2B), 25.7, 27.6 (CH_2). HRMS: calc. for $C_{12}H_{30}N_3{}^{11}B_3$, $M^{\cdot+}$, 249.2718; found: 249.2716.

B-triphenylborazine $(PhB\text{-}NH)_3$: white solid; yield, 75%; sublimation temp (0.05 Torr): 135–140°C; m.p.: 180°C. ^{1}H NMR: δ = 5.90 (s broad, 3H, 3 NH), 7.46–7.82 (m, 15H, 3 C_6H_5). ^{13}C NMR: δ = 128.2, 130.0, 131.8 (CH), *C*α to boron is not visible at room temperature. HRMS: calc. for $C_{18}H_{18}N_3{}^{11}B_3$, $M^{\cdot+}$, 309.178; found: 309.176.

RESULTS AND DISCUSSION

Synthesis of N-Substituted Borazines

The method described by Brown et al. [5d] did not give good results, and we decided to reinvestigate it. First, we found that alkyl and arylamine-borane complexes were easily accessible by addition of $Me_2S \cdot BH_3$ (instead of the complex $THF \cdot BH_3$ [12] that is more expensive and less stable) to a solution of the amine in THF at low temperature according to Scheme 1. After the mixture had been allowed to warm, THF and SMe_2 were removed under vacuum, and the desired complexes **2** were obtained pure and in excellent yields (Table 1). Complexes **2** are thermally unstable, which prevents the oily derivatives from being purified by distillation.

Thermolysis of compounds **2** was first realized at 120°C, without solvent, under the conditions described by Brown et al. [5d] (Scheme 1). Under these conditions, the complex **2b** led exclusively to **3b** isolated in 95% yield as a 2:3 mixture of *cis* and *trans* diastereomers as evidenced by ^{1}H and ^{13}C NMR. The complex **2f** was the only one that gave exclusively and quantitatively the corresponding borazine **4f** in 99% yield. This result indicates that **2f** is less stable than the other complexes, and the transient cyclotriborazane **3f** as well, as a result of the lower basicity of the aniline nitrogen (Table 2). The other complexes **2b–e** gave variable mixtures of cyclotriborazanes **3,** borazines **4,** and nonidentified species, as described by Brown et al. [5d]. We found that by simply increasing the thermolysis temperature from 120°C to 200°C, we could obtain very easily and in

TABLE 2 Pyrolysis of the Primary Amine-Borane Complexes **2**

			Products (%)			
Pyrolysis of	*R in 2*	*Temp. (°C)*	$RNH_2 \cdot BH_3$ **2**	$(RNH_2 \cdot BH_2)_3$ **3**	$(RN \cdot BH)_3$ **4**	*Undefined*
2b	Me	120	0	95[a]	0	0
		200	0	0	77[a]	0
2c	*i*Pr	120	5[b]	20[b]	49[b]	26[b]
		200	0	0	94[a]	0
2d	Bu	120	4[b]	66[b]	30[b]	0
		200	0	0	80[a]	0
2e	Hept	120	3[b]	52[b]	45[b]	0
		200	0	0	93[a]	0
2f	Ph	120	0	0	99[a]	0

[a]Yields refer to isolated pure products.
[b]Determined on ^{11}B NMR spectra.

TABLE 3 Synthesis of *Bis*(diamino)organoboranes **5**

Compounds	*RM*	*RB* $(NR'_2)_2$	*Yield (%)*[a]
5a	$H_2C=CHMgBr$	$H_2C=CHB(NEt_2)_2$	74
5b	$HC\equiv CLi$	$HC\equiv CB(NiPr_2)_2$	86
5c	MeMgI	$MeB(NiPr_2)_2$	87
5d	BuLi	$BuB(NiPr_2)_2$	92
5e	PhLi	$PhB(NiPr_2)_2$	87

[a]Yields are for isolated pure products.

excellent yield (77–95%) the borazines **4b–e,** as can be seen from Table 2. All these compounds were isolated pure and completely characterized by ^1H, ^{13}C, ^{11}B, and ^{15}N NMR and mass spectrometry. Therefore, this simple modification of the conditions of thermolysis of the primary amine-borane complexes makes that method a very efficient one for the synthesis of N-substituted borazines.

Synthesis of B-Substituted Borazines

B-trivinylborazine **6a** was obtained in a 49% yield from the *bis*(diethylamino)vinylborane **5a** by ammonolysis at 80–100°C according to the report of Niedenzu et al. [7]. We could obtain a 64% yield of **6a** by ammonolysis of the *bis*(diethylamino)vinylborane in the presence of one mole percent of phenothiazine. The interest in this synthesis consists in the easy access to *bis*(diethylamino)vinylborane by borylation of vinylmagnesium bromide, and the increase of the yield of ammonolysis is achieved by addition of a small amount of phenothiazine.

We thought that this access to B-substituted borazines could be of some generality and decided to explore this possibility. Borylation of Grignard and organolithium reagents with chloro-*bis*(diisopropylamino)borane has been reported to give a general access to boronic amides 5 [8]. Aminoboranes **5a–e** (Table 3) were easily prepared and purified. They are moisture sensitive and therefore must be stored under nitrogen. Bubbling of dry ammonia through a toluene solution of **5** at 95°C or through pure **5** at 95 to 115°C produced the B-substituted borazines **6** and dialkylamine, which distilled off as soon as it was formed (Scheme 2). Results are reported in Table 4. As can be seen from this table, borazines **6** were obtained in good yields and, therefore, the ammonolysis of *bis*(dialkylamino)organoboranes **5** at a temperature around 100°C appears to represent a general access to B-substituted borazines **6.** Of special interest is the *B*-trialkynylborazine **6b,** which was shown to polymerize when heated. The pyrolysis of the obtained polymer up to 1800°C led to a boron carbonitride ceramic [14].

NMR Data

^{11}B NMR data for compounds **2, 3, 4, 5,** and **6** are collected in Table 5. For borazines **4a** and **4b,** the observed ^{11}B data are in agreement with the values reported in the literature [15]. ^{11}B NMR spectroscopy is useful to follow the thermal decomposition of complexes **2** because ^{11}B chemical shifts of the three species present in the reaction mixture are very different. This is not the case for the ammonolysis of compounds **5,** in which the $\delta^{11}B$ of **5** and **6** are in the same range. Similarly, it is not possible to use ^{11}B NMR spectroscopy to evaluate the ratios of diastereomeric cyclotriborazanes **3a, 3b, 3c,** and **3d.**

Very little information if any concerning ^{15}N and ^{14}N NMR spectroscopy of these derivatives is available from the literature [16]. We have recorded the ^{15}N or ^{14}N NMR spectra of compounds **2, 4,** and **6** whenever it was possible. The data are collected in Table 6. It is interesting to note that the nitrogen

TABLE 4 Synthesis of B-substituted Borazines **6**

Entry	*R*	*Type of Thermolysis*	*Yield (%)*[a]	*b.p. (mmHg)(°C)*	*m.p. (°C)*
6a	$H_2C=CH$	without solvent, 95°C, 1h[b]	64	50–52(0.10)	–
6b	HC≡C	toluene, 95°C, 6h	76	–	142
6c	Me	without solvent, 95°C, 2h	61	134(760)	–
6d	Bu	without solvent, 115°C, 2h	65	76(0.03)	–
6e	Ph	without solvent, 95°C, 1h	75	–	180
		toluene, 95°C, 6h	70	–	180

[a]Yields are for isolated pure products.
[b]1% Phenothiazine

TABLE 5 ^{11}B NMR Data[a] of Compounds **2, 3, 4, 5,** and **6**[b]

R	$RNH_2 \cdot BH_3$ **2**	$(RNH\text{-}BH_2)_3$ **3**	$(RN\text{-}BH)_3$ **4**	$RB(NR'_2)_2$ **5**	$(HN\text{-}BR)_3$ **6**
H	−22.4, q, 94[c,d]	–	30.4, d, 133[c,e]	–	30.4, d, 133[c,e]
Me	−18.4, q, 94[e]	−4.8, t, 100[e]	32.7, d, 135	39.3, s	35.0, s
*i*Pr	−20.7, q, 92[e]	−10.3, t, 91	32.1, d, 132[e]	–	–
Bu	−19.4, q, 90[e]	−6.4, t, 86	33.0, d[e,f]	39.3, s	35.2 s
Hept	−20.0, q, 90[e]	−6.3, t[f]	33.1 d[f]	34.7, s	–
Ph	−16.2, q, 94[e]	–	32.4, d[e,f]	37.5, s	33.7, s
$H_2C=CH$	–	–	–	31.1, s	31.2, s
HC≡C	–	–	–	25.0, s	24.6, s

[a]Solvent = $CDCl_3$ (if not stated otherwise).
[b]δ, multiplicity; $^1J_{BH}$ in Hz.
[c]These data are given for the sake of comparison.
[d]Solvent = THF d8.
[e]Solvent = C_6D_6.
[f]Broad signal where $^1J_{BH}$ could not be measured.

TABLE 6 ^{15}N or ^{15}N NMR Data[a] of Compounds **2, 4,** and **6**[b]

R	$RNH_2 \cdot BH_3$ **2**	$(RN\text{-}BH)_3$ **4**	$(HN\text{-}BR)_3$ **6**
H	−373.6, q, 70[c,d]	−265.8, d, 67[c,d]	−265.8, d, 67[c,d]
Me	−368.9, t, 71[d]	−268.4[e]	−270.2[f]
iPr	−340.7, t, 69	−231.9[e]	/
nBu	−355.3, t, 70	−248.5[e]	−274.7[f]
Hept	−355.2, t, 70	−253.8[e]	/
Ph	−338.9[f]	−232.3[e]	−281.2[f]
$H_2C=CH$	/	/	not recorded
HC≡C	/	/	−263.2[f,g]

[a]Solvent = $CDCl_3$ (if not stated otherwise).
[b]δ, multiplicity; $^1J_{^{15}NH}$ in Hz.
[c]These data are given for the sake of comparison.
[d]Solvent = C_6D_6.
[e]^{14}N NMR.
[f]^{15}N NMR DEPT sequence.
[g]Solvent = DMSO d6.

chemical shifts vary from −231.9 to −373.6 ppm. That is over a 140 ppm range which is much wider than that for ^{11}B chemical shifts. δ^{15}N in B-substituted borazines **6** appear between −263.2 and −281.2 ppm, and between −231.9 and −268.4 ppm in N-substituted borazines **4,** whereas in complexes **2,** values are from −340.7 to −373.6 ppm. Thus, we clearly observe three different zones, each being characteristic of a type of structure. This means that ^{15}N or ^{14}N chemical shifts may be used to identify the environment of nitrogen atoms in boron nitrogen compounds and eventually in polymers. This point is under active investigation in this group for ^{14}N and ^{15}N NMR spectroscopy in solution, and Babonneau's group [17] is carrying out similar studies for the solid state. Figure 1 summarizes the collected information. To collect these ^{15}N NMR data, we have used two different sequences, one being the normal gated decoupled sequence, which allows the measurement of chemical shift δ and J_{NH} coupling constant, and the second being a DEPT 135 sequence. This last one is much more sensitive but at the expense of losing the coupling constant information. ^{14}N NMR spectra were also recorded in some cases. Broad signals were obtained with a very good sensitivity allowing the determination of nitrogen chemical shifts.

CONCLUSION

In this article, we have generalized on the synthesis of N-substituted borazines $(RN\text{-}BH)_3$ **4** and B-substituted borazines $(HN\text{-}BR)_3$ **6** from primary amine-bo-

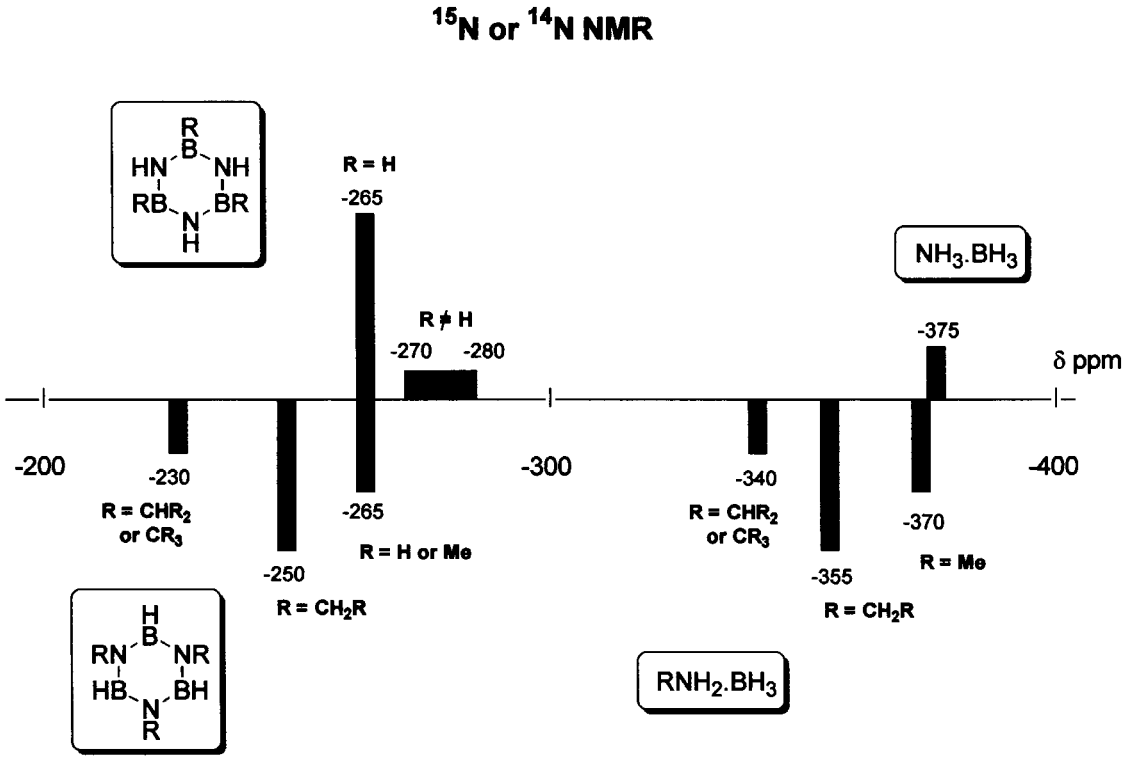
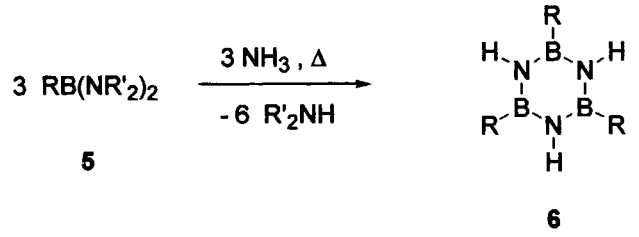


FIGURE 1



SCHEME 2

rane complexes $RNH_2 \cdot BH_3$ **2** and *bis*(dialkylamino)organoboranes $RB(NR'_2)_2$ **5**, respectively. These borazines **4** and **6** were easily obtained in good yields. Under certain conditions, these compounds may be polymerized leading to precursors of boron nitride based ceramics [18]. ^{11}B and ^{15}N or ^{14}N NMR data are reported. ^{15}N or ^{14}N chemical shifts were observed over a 150 ppm range and appeared to be sensitive to the substitution at nitrogen. This could make this NMR technique a very useful one for the structural determination of boron-nitrogen derivatives, including polymers.

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