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TECHNICAL REPORT NO. UK/DC/TR-27

Pyrazole Derivatives of 9-Borabicyclo[3.3.1]nonane

by

L. Komorowski, A. Meller, and K. Niedenzu

Prepared for publication in

INORGANIC CHEMISTRY

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October 1989

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

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GSA No. 0704-0128

1a. REPORT SECURITY CLASSIFICATION unclassified			1b. RESTRICTIVE MARKINGS						
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT prepared for publication in INORGANIC CHEMISTRY						
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)						
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UK/DC/TR-27			7a. NAME OF MONITORING ORGANIZATION Office of Naval Research						
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Kentucky		6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000						
6c. ADDRESS (City, State, and ZIP Code) Lexington, KY 40506-0055		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER							
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS						
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		<table border="1"> <tr> <td>PROGRAM ELEMENT NO.</td> <td>PROJECT NO.</td> <td>WORK UNIT R & T Code 4135003-1</td> <td>WORK UNIT ACCESSION NO.</td> </tr> </table>				PROGRAM ELEMENT NO.	PROJECT NO.	WORK UNIT R & T Code 4135003-1	WORK UNIT ACCESSION NO.
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11. TITLE (Include Security Classification) PYRAZOLE DERIVATIVES OF 9-BORABICYCLO[3.3.1]NONANE.. (unclassified)									
12. PERSONAL AUTHOR(S) L. Komorowski, A. Meller, K. Niedenzu									
13a. TYPE OF REPORT interim technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 89/10					
15. PAGE COUNT 16									
16. SUPPLEMENTARY NOTATION									
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)						
FIELD	GROUP	SUB-GROUP	pyrazaboles						
			9-borabicyclo[3.3.1]nonane derivatives						
			pyrazolylborates, 9 -amido- 9 -pyrazolatodiboranes. (AW)K						
			palladium complexes						
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <u>Sodium Fluoride</u> <u>Palladium Chloride</u> (PI) <u>mu</u> 9-Dimethylamino-9-borabicyclo[3.3.1]nonane, (C₈H₁₄)BN(CH₃)₂, reacts with one molar equivalent of pyrazole (= Hpz) to form the complex (C₈H₁₄)B(pz)•(CH₃)₂NH, and with additional Hpz to yield (C₈H₁₄)B(pz)•Hpz. The latter complex is also obtained by the reaction of 9-borabicyclo[3.3.1]nonane dimer, [(C₈H₁₄)BH]₂ (= 9-BBN), with Hpz. The adduct can be deprotonated to form [(C₈H₁₄)B(pz)]₂, which reacts with PdCl₂ to yield Pd[(pz)₂B(C₈H₁₄)]₂. This same Pd complex is obtained when (C₈H₁₄)B(pz)•(CH₃)₂NH is reacted with NaH, and then with [ClPd(η-CH₂CHCH₃)₂] in boiling benzene, whereas at room temperature the latter reaction yields the complex [(pz)Pd(η-CH₂CHCH₃)₂]. Reaction of [(C₈H₁₄)B(pz)]₂ with [ClPd(η-CH₂CHCH₃)₂] yields the complex (C₈H₁₄)B(η-pz)₂Pd(η-CH₂CHCH₃)₂. The pyrazabole (C₈H₁₄)B(η-pz)₂B(C₈H₁₄) is obtained by the reaction of (C₈H₁₄)B(pz)•Hpz with 9-BBN, the direct interaction of 9-BBN with Hpz, or the thermal decomposition of (C₈H₁₄)B(pz)•(CH₃)₂NH in molten Hpz. A relative of this pyrazabole, i.e., (C₈H₁₄)B(η-pz)(η-NHCH₃)B(C₈H₁₄) is obtained by the reaction of (C₈H₁₄)B(pz)•CH₃NH₂ with 9-BBN.									
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ OTC USERS			21. ABSTRACT SECURITY CLASSIFICATION unclassified						
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kurt Niedenzu			22b. TELEPHONE (Include Area Code) (606) 257-7073		22c. OFFICE SYMBOL				

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506-0055,

and Institute for Inorganic Chemistry,

Georg August University, Göttingen, Federal Republic of Germany

Pyrazole Derivatives of 9-Borabicyclo[3.3.1]nonane¹

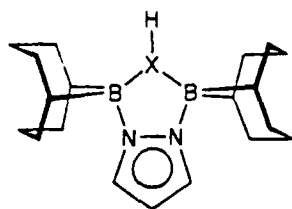
L. Komorowski,^{†§} A. Meller,[‡] and K. Niedenzu^{†*}

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9-Dimethylamino-9-borabicyclo[3.3.1]nonane, $(C_8H_{14})BN(CH_3)_2$, reacts with one molar equivalent of pyrazole (= Hpz) to form the complex $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$, and with additional Hpz to yield $(C_8H_{14})B(pz) \cdot Hpz$. The latter complex is also obtained by the reaction of 9-borabicyclo[3.3.1]nonane dimer, $[(C_8H_{14})BH]_2$ (= 9-BBN), with Hpz. The adduct can be deprotonated to form $[(C_8H_{14})B(pz)_2]^-$, which reacts with $PdCl_2$ to yield $Pd[(\mu-pz)_2B(C_8H_{14})]_2$. This same Pd complex is obtained when $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ is reacted with NaH and then with $[ClPd(\pi-CH_2CHCH_2)]_2$ in boiling benzene, whereas at room temperature the latter reaction yields the complex $[(pz)Pd(\pi-CH_2CHCH_2)]_2$. Reaction of $[(C_8H_{14})B(pz)_2]^-$ with $[ClPd(\pi-CH_2CHCH_2)]_2$ yields the complex $(C_8H_{14})B(\mu-pz)_2Pd(\pi-CH_2CHCH_2)$. The pyrazabole $(C_8H_{14})B(\mu-pz)_2B(C_8H_{14})$ is obtained by the reaction of $(C_8H_{14})B(pz) \cdot Hpz$ with 9-BBN, the direct interaction of 9-BBN with Hpz, or the thermal decomposition of $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ in molten Hpz. A relative of this pyrazabole, *i.e.*, $(C_8H_{14})B(\mu-pz)(\mu-NHCH_3)B(C_8H_{14})$ is obtained by the reaction of $(C_8H_{14})B(pz) \cdot CH_3NH_2$ with 9-BBN.

Introduction

The first pyrazole derivatives of 9-borabicyclo[3.3.1]nonane, $[(C_8H_{14})BH]_2$ (= 9-BBN), have recently been obtained from the reaction of $[(C_8H_{14})B]_2X$ ($X = O, S, Se$) with pyrazole (= Hpz).² The resultant species of type 1 are relatives of the pyrazaboles, $R_2B(\mu-pz)_2BR_2$, but in which one of the bridging pz groups has been replaced by another moiety, *i.e.*, XH.



1

(Similar compounds of the type $R(pz)B(\mu-pz)(\mu-NHR')BR(pz)$ were previously prepared by the reaction of borazines, $(RBNR')_3$, with Hpz.³) The reaction of 1 ($X = O$) with $[(C_8H_{14})BH]_2$ gave the pyrazabole $(C_8H_{14})B(\mu-pz)_2B(C_8H_{14})$,² and the complex $Co[(pz)_2B(C_8H_{14})]_2$ has recently been described and was found to contain two agostic hydrogen bonds.⁴ The present work is concerned with a general study of pyrazole derivatives of 9-BBN.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (high resolution spectra), XL-200 (^{11}B), or GEMINI-200 (1H , ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for 1H and ^{13}C NMR, external $(C_2H_5)_2O \cdot BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = septet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. Unless otherwise noted, ^{13}C NMR spectra were recorded in the proton

decoupled mode. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument.

All non-referenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI and used as received. Pyrazole (= Hpz) was distilled over a small amount of metallic sodium and stored under anhydrous conditions. All syntheses were performed under argon cover.

$(C_8H_{14})BN(CH_3)_2$. A stirred solution of 9-borabicyclo[3.3.1]nonane (= 9-BBN, 100 mL of 0.5 M solution in hexanes) was saturated with anhydrous dimethylamine. A milky mixture formed that was slowly heated to reflux while a slow flow of dimethylamine was maintained. Rapid gas evolution began at about 60 °C; after about 15 min the solution was clear and gas evolution ceased. The mixture was refluxed for an additional 30 min and the solvent was distilled off under atmospheric pressure. The residue was distilled under reduced pressure to give a 90% yield of the desired compound, bp 70 °C (1 Torr).

NMR data: $\delta(^1H)$ 2.78 (6 H, s), 1.9–1.3 (14 H, m); $\delta(^{11}B)$ 47.2 (s, $h_{1/2}$ = 125 Hz); $\delta(^{13}C)$ 38.4, 32.9, 23.2, 21*.

The compound has previously been prepared by the reaction of lithium dimethylamide with 9-methoxy-9-BBN; bp 88 °C (2 Torr); $\delta(^1H)$ 2.74 (6 H, s), 2.0–1.3 (14 H, m).⁵

$(C_8H_{14})B(pz) \cdot (CH_3)_2NH$. A solution of 2.7 g (40 mmol) of Hpz in 30 mL of ether was added slowly with stirring to a solution of 6.4 g (39 mmol) of $(C_8H_{14})BN(CH_3)_2$ in 25 mL of ether. A precipitate formed immediately in a slightly exothermic reaction and the mixture was stirred at ambient temperature for 15 min. The precipitate was collected, washed with ether, and dried under vacuum to give 8.5 g (93%) of (slightly hygroscopic) product. The colorless microcrystalline material decomposed with the release of dimethylamine on heating to 130–140 °C (with some sublimation) and finally melted at 230–240 °C. Anal. Calcd for $C_{13}H_{24}BN_3$ (M_r = 233.17): C, 66.97; H, 10.37; B, 4.64; N, 18.02. Found: C, 66.86; H, 10.41; N, 17.65.

NMR data: $\delta(^1\text{H})$ 7.68 (1 H, d, $J = 1.2$), 7.58 (1 H, d, $J = 2.2$), 6.26 (1 H, unsym t = two overlapping d), 3.9* (1 H, s), 2.36 (6 H, d, $J = 6$), 2.0–1.2 (14 H, m); $\delta(^{11}\text{B})$ 1.1 (s, $h_{1/2} = 150$ Hz); $\delta(^{13}\text{C})$ 139.7, 133.2, 103.5, 36.1 (CH_3), 30.9, 30.6, 23.8, 23.2, 20.6*. Mass spectral data, see text.

$(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$. A mixture of 1.0 g (4.3 mmol) of $(\text{C}_8\text{H}_{14}\text{B}(\text{pz})\cdot(\text{CH}_3)_2\text{NH})$ (see above), 1.5 g (22 mmol) of Hpz, and 30 mL of toluene was refluxed with stirring for 2 h and toluene was removed under reduced pressure. Excess of Hpz was carefully sublimed off the residue under vacuum to leave 1.0 g of material, mp 254–256 °C decomp (after recrystallization from toluene or sublimation under vacuum). Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{BN}_4$ ($M_r = 256.16$): C, 65.64; H, 8.26; B, 4.12; N, 21.87. Found: C, 65.04; H, 8.18; N, 21.36. NMR and mass spectral data, see text.

Alternate Procedure. To a stirred slurry of 1.5 g (6.1 mmol) of $[(\text{C}_8\text{H}_{14})\text{BH}]_2$ in 30 mL of toluene was added 2.0 g (29 mmol) of Hpz. Immediate gas evolution occurred and after about 10 min a clear solution was obtained. The mixture was heated to reflux for 1 h and the precipitate was collected, washed with toluene, and dried under vacuum to give 3.2 g (89%) of the desired product, identical (NMR data) with the above material.

$\text{Na}[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]$. To a mixture of 2.5 g (9.8 mmol) of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ (see above) and 30 mL of benzene was added with stirring 0.40 g (17 mmol) of sodium hydride. Immediate gas evolution occurred; once that subsided the mixture was heated to reflux for 1 h, filtered, and the filtrate evaporated to leave 2.8 g of pale orange material. The latter was dissolved in toluene and the product was precipitated with hexane as a colorless product; on heating to 140–150 °C it turned glassy and began to melt near 210 °C.

NMR data (solution in C_6D_6): $\delta(^1\text{H})$ 7.80 (1 H, d, $J = 1.9$), 7.40 (1 H, unresolved d), 6.18 (1 H, unsym t = two overlapping d, J ca. 2.9), 2.3–1.2 (7 H, m, with distinct spike at 1.29); $\delta(^{11}\text{B})$ –0.7 (s, $h_{1/2} = 700$ Hz); $\delta(^{13}\text{C})$ 139.1, 133.0, 103.9, 31.9, 25.0, 24.3*.

$\text{Pd}[(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})]_2$. To a solution of 1.0 g (8.2 mmol) of $[(\text{C}_8\text{H}_{14})\text{BH}]_2$ in toluene was added 0.85 g (8.0 mmol) of Kpz and the mixture was briefly heated to boiling. It was cooled to room temperature and 0.55 g (8.1 mmol) of Hpz was added. After the vigorous gas evolution had subsided the

mixture was refluxed for 30 min. The precipitate was collected, washed with toluene, and dried under vacuum to give 2.0 g (85%) of $[(C_8H_{14})B(pz)_2]K$. A mixture of 1.7 g (5.8 mmol) of this salt, 0.50 g (2.8 mmol) of $PdCl_2$, and 30 mL of acetonitrile was stirred at ambient temperature for 12 h. The precipitate was collected, washed with water, and dried under vacuum to give 1.2 g (68%) of product. It was recrystallized from benzene, and thus obtained as a pale green material, mp 350 °C decomp. Anal. Calcd for $C_{28}H_{40}BN_4Pd$ ($M_r = 616.70$): C, 54.53; H, 6.54; B, 3.50; N, 18.17; Pd, 17.25. Found: C, 53.76; H, 6.19; B, 3.11; N, 17.44; Pd, 16.81.

NMR data: $\delta(^1H)$ 7.73 (2 H, d, $J = 2.4$), 7.16 (2 H, d, $J = 2.1$), 6.15 (2 H, unsym t = two overlapping d, J ca. 2.3), 4.35* (1 H, s), 2.4–1.95 + 1.6–1.4 (13 H, m); $\delta(^{11}B)$ 1.9 (s, $h_{1/2} = 350$ Hz); $\delta(^{13}C)$ 140.6 (d of d, $^1J = 190$, $^2J = 6.9$), 134.6 (d of d, $^1J = 187$, $^2J = 7.8$), 105.1 (two overlapping d of d, $^1J = 183$, $^2J = 9.2$), 32.5 (t, $J = 123$), 30.6 (t, $J = 125$), 27.4* (d, J ca. 124), 24.2 (t, $J = 124$), 20.6* (d, J ca. 122). The FD mass spectrum exhibited only an ion cluster at m/z 616.

Alternate Procedure. To a stirred mixture of 1.7 g (7.3 mmol) of $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ (see above) and 50 mL of benzene was added 0.25 g (10 mmol) of solid NaH. The mixture was stirred for 3 h at room temperature and a small amount of insoluble material was filtered off. A quantity, 1.4 g (3.8 mmol), of $[ClPd(\pi-CH_2CHCH_2)]_2$ was added and the mixture was refluxed for 18 h, filtered, and the solvent was evaporated to leave 0.85 g of a pasty material. It was washed with pentane and then recrystallized from benzene to give 0.36 g of pale green crystals, mp 350 °C decomp, identical (NMR data) with the above material.

$(C_8H_{14})B(\mu-pz)_2Pd(\pi-CH_2CHCH_2)$. To a stirred slurry of 1.0 g (3.9 mmol) of $(C_8H_{14})B(pz) \cdot Hpz$ (see above) in 20 mL of benzene was added 0.3 g (13 mmol) of solid NaH. Vigorous gas evolution occurred and the $(C_8H_{14})B(pz) \cdot Hpz$ dissolved. The mixture was refluxed for 30 min, filtered, and 0.75 g (2.0 mmol) of $[ClPd(\pi-CH_2CHCH_2)]_2$ was added to the clear filtrate. The mixture was refluxed overnight, filtered, and solvent was evaporated to leave 1.3 g (82%) of a gray-green solid. The latter was recrystallized from heptane to give 0.95 g of pale yellow product, mp 190 °C decomp. Anal. Calcd for $C_{17}H_{25}BN_4Pd$ ($M_r = 402.62$): C, 50.17; H, 6.26; B, 2.68; N, 13.91; Pd, 26.43. Found: C, 50.55; H, 6.16; B, 2.51; N, 14.07; Pd, 26.52.

NMR data: $\delta(^1\text{H})$ 7.68 (d, $J = 2.4$), 7.67 (1 H, d, $J = 2.2$), 7.48 (1 H, d, $J = 2.0$), 7.29 (1 H, d, $J = 1.9$), 6.15 (1 H, t, $J = 2.2$), 6.12 (1 H, t, $J = 2.1$), 5.64 (A) + 5.60 (B) (1 H, two overlapping sets of t of t; A, $^1J = 12.2$, $^2J = 6.9$; B, $^1J = 12.2$, $^2J = 7.0$), 3.97 (1 H, d, $J = 7.0$), 3.87 (1 H, d, $J = 7.0$), 3.07 (1 H, d, $J = 12.2$), 3.01 (1 H, d, $J = 12.2$), 2.95* (1 H, s), 2.35* (1 H, s), 2.2–1.0 (12 H, m) (as is based on selective decoupling experiments (Varian VXR-400 instrument), the sets 7.68/7.48/6.15 and 7.67/7.29/6.12 ppm, respectively, belong to different pz groups of equal abundances; and the signals at 5.6 ppm are coupled with the sets 3.97/3.87 and 3.07/3.01 ppm to account for two different allyl groups of equal abundances); $\delta(^1\text{B})$ -0.3 (s, $h_{1/2} = 165$ Hz); $\delta(^{13}\text{C})$ 141.3 (d of d, $^1J = 185$, $^2J = 7$), 141.2 (d of d, $^1J = 185$, $^2J = 7$), 133.7 (d of d, $^1J = 185$, $^2J = 5.5$), 133.5 (d of d, $^1J = 185$, $^2J = 5.5$), 114.3 (d, $J = 163$), 133.6 (d, $J = 162$), 103.8 (d of d of d, $^1J = 176$, $^2J = 9$), 103.7 (d of d, $^1J = 176$, $^2J = 9$), 56.6 (t, $J = 158$), 32.4 (t, $J = 122$), 32.4 (t, $J = 122$), 32.3 (t, $J = 123$), 30.41 (t, $J = 123$), 30.37 (t, $J = 123$), 27.5* (t = two overlapping d?, J ca. 100), 24.2 (t, $J = 123$), 24.1 (t, $J = 123$), 20.9* (d, $J = 110$). The FD mass spectrum exhibited only an ion cluster at m/z 402.

$[(\text{pz})\text{Pd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$. A mixture of 1.0 g (2.7 mmol) of $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$, 0.6 g (5.6 mmol) of Kpz, and 30 mL of methylene chloride was stirred for 2 h at room temperature. The milky precipitate was filtered off (KCl, 96% recovery) and the clear solution was evaporated to give 1.0 g (85%) of crude product. This latter was recrystallized from benzene to give 0.8 g of off-white material; it does not melt at temperatures up to 420 °C. Anal. Calcd for $[(\text{pz})\text{Pd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ ($M_r = 429.08$): C, 33.59; H, 3.76; N, 13.06; Pd, 49.59. Found: C, 33.73; H, 3.80; N, 13.32; Pd, 49.48.

NMR data: $\delta(^1\text{H})$ 7.53 (d, $J = 2.0$) + 7.49 (d, $J = 2.0$) (2 H), 6.24 (1 H, two overlapping t, $J = 2.0$), 5.65 (t of t, $^1J = 12.3$, $^2J = 7.0$) + 5.54 (t of t, $^1J = 12.2$, $^2J = 7.0$) (1 H), 3.74 (d, $J = 6.9$) + 3.72 (d, $J = 6.9$) (2H), 3.02 (d, $J = 12.3$) + 3.00 (d, $J = 12.4$) (2 H); $\delta(^{13}\text{C})$ 142.1, 141.7, 116.1, 115.9, 104.3, 104.2, 58.3, 58.1. The FD mass spectrum of the material showed a molecular ion cluster at m/z 429.

A material of mp ca. 190 °C decomp (NMR data: $\delta(^1\text{H})$ 7.56 (2 H, two overlapping d), 6.28 (1 H, t, $J = 2.0$), 6.0–5.2 (1 H, m), 3.75 (2 H, d, $J = 7.0$), 3.02 (2 H, d, $J = 12.2$)) has previously been described.⁶

Alternate Procedure. A mixture of 0.8 g (3 mmol) of $[(C_8H_{14})B(pz)N(CH_3)_2]K$ (prepared by dissolving $(C_8H_{14})BN(CH_3)_2$ in benzene and addition of an equimolar amount of Kpz, stirring over night, evaporating the solvent and drying the product under vacuum), 0.55 g (1.5 mmol) of $[ClPd(\pi-CH_2CHCH_2)]_2$, and 30 mL of benzene was stirred for 3 days at ambient temperature. The mixture was filtered and the clear filtrate was evaporated to leave 0.65 g of solid. This was dissolved in benzene and precipitated with hexane to give a material identical (NMR spectra) with the above compound.

$(pz)_2B(\mu-pz)_2Pd(\pi-CH_2CHCH_2)$. A slurry of 0.95 g (3.0 mmol) of $K[B(pz)_4]^7$ and 0.55 g (1.5 mmol) of $[ClPd(\pi-CH_2CHCH_2)]_2$ in 30 mL of methylene chloride was stirred at room temperature for 12 h, and most of the reagents dissolved. The mixture was filtered and solvent was evaporated from the clear filtrate to yield 1.1 g (87%) of a pale yellow product, mp 360 °C decomp (after recrystallization from toluene). Anal. Calcd for $C_{15}H_{17}BN_8Pd$ ($M_r = 426.56$): C, 42.24; H, 4.02; B, 2.53; N, 26.27; Pd, 24.94. Found: C, 42.43; H, 3.82; B, 1.87; N, 24.49; Pd, 25.97.

NMR data: $\delta(^1H)$ 7.66 (4 H, d, $J = 1.2$), 7.04 (4 H, d, $J = 1.9$), 6.27 (2 H, unsym t = two overlapping d, J ca. 1.9), 5.39 (1 H, t of t, $^1J = 12.2$, $^2J = 7.0$), 3.83 (2 H, d, $J = 6.8$), 2.86 (2 H, d, $J = 12.4$); $\delta(^{11}B)$ 0.6 (s, $h_{1/2} = 23$ Hz); $\delta(^{13}C)$ 143.1 (d, $J = 183$), 135.1 (d, $J = 187$), 116.0 (d, $J = 162$), 105.2 (d, $J = 177$), 58.7 (t, $J = 177$). EI mass spectrum (14 eV): m/z 430 (7), 429 (42), 428 (26), 427 (89), 426 (38), 425 (99), 424 (100), 423 (52), 422 (9), 362 (19), 361 (12), 360 (47), 359 (23), 358 (53), 357 (55), 356 (32), 355 (7).

A material of mp 246–248 °C but exhibiting essentially the same 1H NMR spectrum as reported here has been described previously.⁸

$(C_8H_{14})B(\mu-pz)_2B(C_8H_{14})$. A mixture of 2.5 g (9.8 mmol) of $(C_8H_{14})B(pz) \cdot Hpz$ (see above), 1.5 g (6.1 mmol) of $[(C_8H_{14})BH]_2$, and 50 mL of toluene was heated to reflux for 2 h. The volume of the solution was reduced to about 20 mL and, after cooling to room temperature, 1.9 g (82%) of the desired compound was obtained as a precipitate. The latter was recrystallized from toluene to give 1.0 g of pure product, mp 255–256 °C. Anal. Calcd for $C_{22}H_{34}B_2N_4$ ($M_r = 376.16$): C, 70.25; H, 9.11; B, 5.75; N, 14.89. Found: C, 69.99; H, 9.01; N, 15.07.

NMR data: $\delta(^1\text{H})$ 8.08 (2 H, d, $J = 2.5$), 6.20 (1 H, t, $J = 2.5$), 1.93–1.46 (14 H, m); $\delta(^{11}\text{B})$ 3.2 (s, $h_{1/2} = 150$ Hz); $\delta(^{13}\text{C})$ 136.9, 103.8, 32.6, 24.5*, 21.6. The EI mass spectrum exhibited a small parent ion cluster at m/z 376; the base peak was observed at m/z 187. The FD mass spectrum exhibited a strong ion cluster at m/z 376 (base peak) and a weak one near m/z 188 (18% relative abundance), both exhibiting the correct isotopic distribution calculated for the dimer (= pyrazabole) and the monomer, $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})$, respectively.

The same compound has recently been obtained by the reaction of $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})(\mu\text{-OH})\text{B}(\text{C}_8\text{H}_{14})$ with $[(\text{C}_8\text{H}_{14})\text{BH}]_2$.²

Alternate Procedure. A mixture of 2.3 g (10 mmol) of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot(\text{CH}_3)_2\text{NH}$ (see above) and 4–5 g of Hpz was heated with stirring to 180 °C for 2 h. After cooling to room temperature the excess of Hpz washed off with ether (from which it can be recovered) to leave an essentially quantitative yield (1.7 g) of the desired product as colorless crystals of mp 251–252 °C (mp 254–255 °C after recrystallization from toluene). The product was identical (NMR and mass spectral data) with the above material.

Alternate Procedure. A solution of 1.0 g (15 mmol) of Hpz in 50 mL of toluene was dropped into a boiling solution of 1.3 g (7.8 mmol) of $[(\text{C}_8\text{H}_{14})\text{BH}]_2$ in 30 mL of toluene over a period of 2 h. The solution was refluxed for an additional 30 min and then concentrated to a volume of about 20 mL. The crystalline precipitate (1.0 g, 53%) was identical (NMR and mass spectral data) with the pyrazabole derivative described above. A second crop of slightly less pure material was obtained on further concentration of the toluene solution to provide for an overall yield of approximately 90%.

$(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})(\mu\text{-NHCH}_3)\text{B}(\text{C}_8\text{H}_{14})$. Anhydrous methylamine was slowly bubbled through a stirred slurry of 2.0 g (8.2 mmol) of $[(\text{C}_8\text{H}_{14})\text{BH}]_2$ in 100 mL of toluene for 1 h. The solution was then briefly refluxed to remove excess of methylamine and to form $(\text{C}_8\text{H}_{14})\text{BNHCH}_3$ *in situ*. Solid Hpz, 1.1 g (16 mmol), was added and a colorless precipitate developed quickly. The mixture was stirred for 3 h at room temperature and 3.3 g (87%) of crude $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{CH}_3\text{NH}_2$, mp 195–197 °C decomp, was collected. A stirred mixture of 2.0 g (9.1 mmol) of the crude $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{CH}_3\text{NH}_2$, 1.1 g (4.5 mmol) of $[(\text{C}_8\text{H}_{14})\text{BH}]_2$, and 60 mL of toluene was slowly warmed to reflux. The $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{CH}_3\text{NH}_2$ quickly

dissolved with hydrogen evolution. The mixture was refluxed for 30 min and then cooled to room temperature. Toluene was evaporated and the residual oily material crystallized on standing overnight. The product was washed with hexane and 2.2 g (71%) of crude pale yellow material, mp 145–150 °C, was obtained. It was recrystallized from heptane to give a colorless product, mp 158–150 °C. Anal. Calcd for $C_{20}H_{35}B_2N_3$ ($M_r = 339.14$): C, 70.83; H, 10.40; B, 6.38; N, 12.39. Found: C, 70.42; H, 10.80; B, 6.39; N, 12.41.

NMR data: $\delta(^1H)$ 7.77 (2 H, d, $J = 2.3$), 6.34 (1 H, t, $J = 2.3$), 2.85* (1 H, s), 2.24 (3 H, d, $J = 6.2$), 2.2–1.4 (24 H, m), 0.90* (4 H, s); $\delta(^1B)$ 3.5 (s, $h_{1/2} = 175$ Hz); $\delta(^{13}C)$ 132.9, 106.4, 32.8, 32.6, 31.5, 30.7, 28.9, 24.1*, 23.9, 23.2, 21.2*. The EI mass spectrum exhibited a parent ion cluster at m/z 339; the base peak was observed at m/z 187.

Results and Discussion

9-Borabicyclo[3.3.1]nonane dimer, $[(C_8H_{14})BH]_2$ (= 9-BBN), as well as the 9-dimethylamino derivative $(CH_3)_2NB(C_8H_{14})$ (which was prepared from 9-BBN and anhydrous dimethylamine) reacted readily with pyrazole (= Hpz). The former reacted even at room temperature with excess Hpz to give $(C_8H_{14})B(pz) \cdot Hpz$ in essentially quantitative yield. Under similar conditions, $(C_8H_{14})BN(CH_3)_2$ reacted with one molar equivalent of Hpz to form the adduct $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ via complexation and subsequent proton migration (as shown by 1H NMR data). The latter adduct interacted with additional Hpz in refluxing toluene to also give the species $(C_8H_{14})B(pz) \cdot Hpz$.

The EI mass spectra of the adducts $(C_8H_{14})B(pz) \cdot Hpz$ and $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ were essentially identical and exhibited an ion cluster at m/z 188 for $[(C_8H_{14})B(pz)]^+$ as well as its fragmentation and besides peaks for pyrazole or dimethylamine, respectively. Both species were thermally unstable and decomposed (at least partially) below or at their melting point to yield the pyrazabole $(C_8H_{14})B(\mu\text{-}pz)_2B(C_8H_{14})$.

The splitting of the CH_3 signal in the 1H NMR spectrum of the complex $(C_8H_{14})B(pz) \cdot (CH_3)_2NH$ clearly established the location of the N-bonded proton at the dimethylamine–nitrogen. Only one ^{11}B NMR signal was observed for the complex and was located in the region normally associated with four–

coordinate boron;⁹ and the ^{13}C NMR spectrum exhibited one (broad) signal for C_α and two each for C_β and C_γ of the C_8H_{14} moiety.

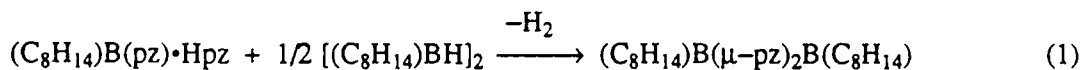
The NMR spectra of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ were dependent on solvent, temperature, and concentration. For example, the ^1H NMR spectrum of a clear solution in CDCl_3 exhibited two signal sets for the pz group, the ratio of which was strongly temperature dependent. A saturated solution (over solid material) exhibited an additional pz signal set. Spectral changes in the pz region were always accompanied by significant changes in the aliphatic region. A solution of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ in CD_3OD exhibited only one set of ^1H NMR signals in the pz region at δ 7.66(2 H)/6.38(1 H). In $(\text{CD}_3)_2\text{CO}$ solution, however, two sets in about 2:3 ratio were observed at δ 7.96(2 H)/6.54(1 H) and 7.62(2 H)/6.29(1 H), respectively. Solution in CD_3CN , $\text{C}_6\text{H}_5\text{CD}_3$, or $(\text{CD}_3)_2\text{SO}$ exhibited similar spectra. The room temperature ^{11}B NMR spectrum in CDCl_3 exhibited three signals at 33.0, 8.7, and 1.0 ppm, the intensity ratio of which was concentration-dependent although the peak at 8.7 ppm was consistently the most intense signal (ca. 80% of the total intensity). At -38°C , only two signals at δ 33.1 and 1.2* (very broad) were observed; a shoulder at 8.2 ppm emerged off the high-field signal at -10°C , and it became the most intense signal at room temperature. These observations may be explained by concentration-dependent equilibria processes, *e.g.*, $(\text{C}_8\text{H}_{14})\text{B}(\text{pz}) + \text{Hpz}$ (a) $\rightleftharpoons (\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ (b) $\rightleftharpoons \text{H}[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]$ (c), which would account for the observation of three ^{11}B NMR signals (a, 33.0; b, 8.7; c, 1.0 ppm). The elemental analysis data supports the composition $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$. Even more important, reaction of the adduct with NaH gave the salt $[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]\text{Na}$, the NMR spectra of which were uncomplicated (including only one ^{11}B signal!) and readily interpreted to further support the given formulation of the adduct. Finally, the reaction of 9-BBN with $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ (see below) is also clearly in consonance with the assigned structure of the latter.

The ion $[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]^-$ was reacted with PdCl_2 to give the complex $\text{Pd}[(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})]_2$. The latter also exhibited a simple ^1H NMR spectrum. Only one set of signals was observed for the pz groups at δ 7.73(2 H)/6.15(1 H). However, the two (BC)H protons of the C_8H_{14} moiety were not equivalent, with one signal being observed at 4.35 ppm, the other one falling within the range of the aliphatic signals in the 2.4–1.5 ppm region. This may suggest that the cited (BC)H is interacting with the Pd.

Interestingly, the complex $\text{Pd}[(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})]_2$ was also obtained when $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot(\text{CH}_3)_2\text{NH}$ was reacted with NaH and then with $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ in boiling benzene. On the other hand, when this same reaction was performed at room temperature, the complex $[(\text{pz})\text{Pd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ was formed as the only Pd-containing product. This latter species has previously been described as the product of the reaction of $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ with Hpz in the presence of diisopropylethylamine as hydrogen chloride acceptor. In the present work, it was also obtained from the reaction of $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ with Kpz. The NMR spectra of the species indicated the presence of rotamers, whereas only one signal set for the allyl group was observed in the spectra of $(\text{pz})_2\text{B}(\mu\text{-pz})_2\text{Pd}(\pi\text{-CH}_2\text{CHCH}_2)$. This latter complex was obtained from the reaction of $\text{K}[\text{B}(\text{pz})_4]$ with $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$.

Reaction of $[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]\text{Na}$ with $[\text{ClPd}(\pi\text{-CH}_2\text{CHCH}_2)]_2$ gave the expected complex $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{Pd}(\pi\text{-CH}_2\text{CHCH}_2)$. The NMR spectra of the species revealed the presence of two isomers (rotamers) in equal abundances, *i.e.*, two nonequivalent pz and allyl groups, but also the nonequivalence of all C atoms of the 9-BBN moiety. As is based on $^1\text{H}/^{13}\text{C}$ HETCOR NMR experiments, the lowest field ^{13}C NMR signal at 141 ppm correlated with the two pz group ^1H NMR signals at 7.48 and 7.29 ppm, and the pairs $\delta(^1\text{H})/\delta(^{13}\text{C})$ 7.7/134 and 6.1/104 completed the assignment of the pz groups. Also, $\delta(^{13}\text{C})$ 114.3 correlated with $\delta(^1\text{H})$ 5.60, $\delta(^{13}\text{C})$ 113.3 correlated with $\delta(^1\text{H})$ 5.64, and $\delta(^{13}\text{C})$ 56.6 correlated with the sets $\delta(^1\text{H})$ 3.9 and 3.0 to characterize the Pd-bonded allyl group. No collapse of ^1H NMR signals was observed at temperatures as high as 90 °C. It is possible that one of the (BC)H hydrogens of the 9-BBN moiety interacts with the Pd.⁴

The pyrazabole $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})$ was most readily obtained from the reaction according to eq 1.

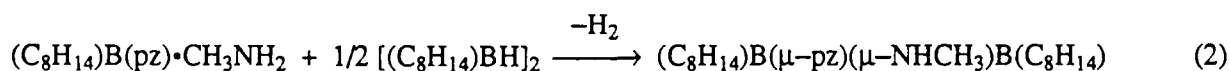


The same pyrazabole was also obtained by the direct interaction of 9-BBN with Hpz, and the thermal decomposition of the adduct $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot(\text{CH}_3)_2\text{NH}$. Furthermore, it has recently been prepared by the reaction of 9-BBN with $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})(\mu\text{-OH})\text{B}(\text{C}_8\text{H}_{14})$.² It is known that $\text{H}^+[\text{B}(\text{pz})_4]^-$ thermally

decomposes with the formation of the pyrazabole $(\text{pz})_2\text{B}(\mu\text{-pz})_2\text{B}(\text{pz})_2$.¹⁰ However, the thermal decomposition of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ ($= \text{H}^+[(\text{C}_8\text{H}_{14})\text{B}(\text{pz})_2]^-$) is possible but is not very suitable for the preparation of the pyrazabole $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})$, since the adduct sublimes even under atmospheric pressure.

The FD mass spectrum of $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})$ exhibited not only the molecular ion cluster at m/z 376 but also one at m/z 188. This observation suggests that the B_2N_4 ring of the pyrazabole readily undergoes symmetrical cleavage to yield the monomer. This same feature has previously been observed for some B-aminosubstituted pyrazaboles,¹¹ and trigonal 1-pyrazolylboranes have been found to exist under normal conditions only when the boron is also bonded to two additional nitrogen atoms and is incorporated into a cyclic structure. This latter feature is likely to be a consequence of electronic saturation of the boron atom, although the boron atom of trigonal 1-pyrazolylboranes shows Lewis acidity.¹²⁻¹⁴ On the other hand, the suggested ease of the symmetrical cleavage of the pyrazabole $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})$ and the unusual NMR observations on $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{Hpz}$ (see above) may well be due to steric rather than electronic factors.

The reaction of $(\text{C}_8\text{H}_{14})\text{B}(\text{pz})\cdot\text{CH}_3\text{NH}_2$ with 9-BBN proceeded according to eq 2.



The resulting $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})(\mu\text{-NHCH}_3)\text{B}(\text{C}_8\text{H}_{14})$ (1, $\text{X} = \text{NCH}_3$) is a relative of the pyrazabole $(\text{C}_8\text{H}_{14})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_8\text{H}_{14})$, where one of the two bridging pz groups is replaced by a bridging NHCH_3 moiety. Analogous pyrazabole relatives have previously been obtained from the reaction of borazines, $(\text{RBNR})_3$, with Hpz ,³ and similar species (1, $\text{X} = \text{O}, \text{S}, \text{Se}$) were recently prepared from the reaction of $(\text{C}_8\text{H}_{14})\text{BXB}(\text{C}_8\text{H}_{14})$ with Hpz .²

Acknowledgment. This work was supported by the Office of Naval Research, and travel funds by the Alexander von Humboldt Foundation are also gratefully acknowledged (K.N.).

Footnotes and References

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