

Pyrazole Derivatives of Diborane(4)

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Abstract: Tetrakis(dimethylamino)diborane(4), $(\text{Me}_2\text{N})_2\text{B}-\text{B}(\text{NMe}_2)_2$, reacts with 4 mol equiv of pyrazole (=Hpz) to form the corresponding species $(\text{pz})_2\text{B}-\text{B}(\text{pz})_2$ as a dimer with a unique triply bridged pyrazabole structure but in mixture with polymeric product of the same elemental composition and with excess of Hpz to form the adduct tetrakis(1-pyrazolyl)diborane(4)-bis(pyrazole), $(\text{pz})_2\text{B}-\text{B}(\text{pz})_2\cdot 2\text{Hpz}$. This latter compound crystallizes in the triclinic system in space group $P\bar{1}$ (No. 2) with $a = 13.945$ (2) Å, $b = 18.392$ (3) Å, $c = 9.048$ (2) Å, $\alpha = 102.92$ (2)°, $\beta = 94.85$ (1)°, $\gamma = 105.18$ (1)°, and $Z = 4$ at 296 (2) K. The salt $\text{K}_2[(\text{pz})_3\text{B}-\text{B}(\text{pz})_3]$ is obtained on reaction of $(\text{Me}_2\text{N})_2\text{B}-\text{B}(\text{NMe}_2)_2$ with 2 equiv of Kpz and excess Hpz. This potassium salt reacts with π -allylpalladium chloride dimers (allyl = CH_2CHCH_2 or $\text{CH}_2\text{CCH}_3\text{CH}_2$) to give $(\eta^3\text{-allyl})\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B}-\text{B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-allyl})$ complexes, thus establishing the $[(\text{pz})_3\text{B}-\text{B}(\text{pz})_3]^{2-}$ ion as a novel bis(polydentate) ligand. In solution, the $\text{Pd}(\mu\text{-pz})_2\text{B}(\text{pz})$ moieties are fluxional and only one set of ^1H NMR signals is observed for the pz groups, even at low temperatures. The formulation involving two bridging and one terminal pz groups at each boron site is, however, supported by X-ray diffraction data. The complex $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B}-\text{B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$ crystallizes in the monoclinic system in either space group $P2/c$ (No. 13) or Pc (No. 7) with $a = 18.864$ (4) Å, $b = 9.925$ (3) Å, $c = 16.626$ (4) Å, $\beta = 115.11$ (2)°, and $Z = 4$ at 296 (2) K.

N-Bonded borane(3) derivatives of pyrazole (which normally exist in the dimeric pyrazabole structure containing a chemically stable B_2N_4 heterocycle with four-coordinate boron, e.g., $\text{R}_2\text{B}(\mu\text{-pz})_2\text{BR}_2$ where Hpz = pyrazole) and of the tetrahydroborate ion have been known for about 20 years. The pyrazaboles have been studied in limited detail, but poly(1-pyrazolyl)borate anions, $[\text{R}_{4-n}\text{B}(\text{pz})_n]^-$ ($n = 2-4$, R = noncoordinating substituent), have been used extensively as chelating ligands in transition-metal chemistry.¹

The present study was based on the assumption that a neutral $(\text{pz})_2\text{B}-\text{B}(\text{pz})_2$ species would likely exist in a polymeric structure. Therefore, it should contain the bridging $\text{B}(\mu\text{-pz})_2\text{B}$ units typical for pyrazaboles but also terminal B-bonded pz groups and thus would be related to B-poly(1-pyrazolyl)pyrazaboles. Furthermore, a $[(\text{pz})_3\text{B}-\text{B}(\text{pz})_3]^{2-}$ ion should be similar to a $[\text{RB}(\text{pz})_3]^-$ ion but for the fact that the former has two polydentate sites. These possibilities should provide for interesting variations as compared to the chemistry of B-1-pyrazolylpyrazaboles and poly(1-pyrazolyl)borates, respectively.

Experimental Section

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

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given (ppm), with positive values indicating downfield from the reference (internal Me_4Si for ^1H NMR, external $\text{Et}_2\text{O}\cdot\text{BF}_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = heptet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer.

$[(\text{pz})_2\text{B}-\text{B}(\text{pz})_2]_n$. A mixture of 2.97 g (15 mmol) of tetrakis(dimethylamino)diborane(4),² 4.22 g (62 mmol) of pyrazole, and 50 mL of benzene was refluxed with stirring for several hours. (If formed, a very small amount of insoluble material was filtered off. It was identified as $\text{H}_2[(\text{pz})_3\text{B}-\text{B}(\text{pz})_3]$; see below.) When the reaction mixture was cooled to room temperature, a colorless precipitate (2-2.5 g) was formed and collected. Concentration of the filtrate gave additional product for a total yield of about 3.6 g (84%) of dried (for 24 h under vacuum over paraffin wax) crude product. A ^1H NMR spectrum of this material showed traces of methyl signals and a strong benzene signal as impurities. These disappeared on heating of the material in an oil bath (80 °C for 24 h and then 16 h at 200 °C) under high vacuum (10^{-3} Torr). Some pyrazole sublimed off, and the residue was analyzed (C, H, N, B) for the expected composition $\text{C}_6\text{H}_6\text{BN}_4$ but exhibited a complex ^1H NMR spectrum.

$[(\text{pz})_2\text{B}-\text{B}(\text{pz})_2]_2$ (**1a**) was isolated from this mixture by sublimation [24 h at 260 °C bath temperature (10^{-4} Torr)]. The pure dimer (30-50% of the crude product) has a mp 298-300 °C dec.

NMR data (solution in CDCl_3): $\delta(^1\text{H})$ 7.74 (1 H, d, $J = 1.6$), 7.53 (1 H, d, $J = 2.3$), 7.06 (2 H, d, $J = 2.4$), 6.34 (1 H, unsymmetrical t = two overlapping d in high-resolution spectrum), 6.04 (1 H, t, $J = 2.4$); $\delta(^{11}\text{B})$ 2.2 (s, $h_{1/2} = 570$ Hz). Selective decoupling experiments showed that the sets $\delta(^1\text{H})$ 7.06/6.04 and 7.74/7.53/6.34, respectively, belong to individual (bridging and terminal) pz groups.

The 14-eV mass spectrum of the material exhibited only one major ion cluster near m/z 579 (clearly containing four B atoms). In the 70-eV spectrum, major ion clusters were observed in the m/z 579, 301, 289, 223, and 79 regions, and additional clusters were found near m/z 511, 445/444, 435, 377, 368, and 195.

$[(\text{pz})_2\text{B}-\text{B}(\text{pz})_2]_n$ ($n > 2$; **1b**) remained as residue after the above sublimation. This material changed color to a pale brown on heating to about 300 °C and began to decompose, leaving an intractable material, which was not further characterized. Part of the original sublimation residue was readily soluble in chloroform. The ^1H NMR spectrum of this material showed bridging ($\delta(^1\text{H})$ 7.58 (2 H, d, $J = 2.0$)/6.34 (1 H, t, $J = 2.0$) and two different types of terminal [$\delta(^1\text{H})$ 7.60 (1 H, d, $J = 1.6$)/6.96 (1 H, d, $J = 2.2$)/6.31 (1 H, unsymmetrical t = two overlapping d) and 7.52 (1 H, d, $J = 2.4$)/7.19 (1 H, d, $J = 2.4$)/6.10 (1 H, unsymmetrical t = two overlapping d)] pz groups, identified by selective decoupling experiments. The ^{11}B NMR spectrum exhibited an extremely broad ($h_{1/2} \sim 1500$ Hz) and unsymmetrical signal with a maximum near 1.4 ppm. These data suggest a species with $n = 3$. The insoluble part was not further investigated.

$(\text{pz})_2\text{B}-\text{B}(\text{pz})_2\cdot 2\text{Hpz}$. A solution of 2.97 g (15 mmol) of tetrakis(dimethylamino)diborane(4)² in 10 mL of toluene was added dropwise with stirring to a refluxing solution of 6.8 g (0.1 mol) of pyrazole in 50 mL of toluene. The mixture was refluxed for 6 h. After the colorless precipitate was cooled to room temperature, it was collected, washed extensively with ether, and dried under vacuum to yield 4.03 g (63%) of the crude product, mp 216-222 °C dec. A purified sample, mp 220-224 °C, was obtained by dissolving the crude product in methylene chloride and precipitating with hexane. Anal. ($\text{C}_{18}\text{H}_{20}\text{B}_2\text{N}_{12}$) C, H, B, N.

NMR data (solution in CDCl_3): $\delta(^1\text{H})$ 7.59 (1 H, d, $J = 1.9$), 7.07 (1 H, d, $J = 1.6$), 6.18 (1 H, unsymmetrical t = two overlapping d, $J = 1.8$); $\delta(^{11}\text{B})$ 1.8 (s, $h_{1/2} = 450$ Hz).

Crystal and Molecular Structure of $(\text{pz})_2\text{B}-\text{B}(\text{pz})_2\cdot 2\text{Hpz}$. The compound tetrakis(1-pyrazolyl)diborane(4)-bis(pyrazole), $\text{C}_{18}\text{H}_{20}\text{B}_2\text{N}_{12}$, crystallizes as colorless laths in the triclinic system with $a = 13.945$ (2) Å, $b = 18.392$ (3) Å, $c = 9.048$ (2) Å, $\alpha = 102.92$ (2)°, $\beta = 94.85$ (1)°, $\gamma = 105.18$ (1)°, and $Z = 4$ at 296 (2) K. There are 2 full formula units in the asymmetric unit of the space group $P\bar{1}$ (No. 2; centrosymmetric choice confirmed by the successful refinement). All data with $h \geq 0$ and $2\theta \leq 50^\circ$ were measured on an Enraf-Nonius CAD4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator (7582 unique reflections). Data with $50^\circ < 2\theta < 55^\circ$ were measured but were not included in the analysis since only 47 of 2306 reflections had $I > 3\sigma(I)$. No correction was made for decomposition (ca. 1.6% overall), absorption (crystal size $0.16 \times 0.25 \times 0.38$ mm; $\mu = 0.811$ cm^{-1}), or extinction. The

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structure was solved by MULTAN⁷³ after the overall temperature factor originally estimated by NORMAL was increased. Other programs and procedures utilized for crystal structure solution, refinement, and analysis have been described previously.⁴ Refined values of the isotropic displacement parameters were used to distinguish between the N and C atoms in the 2- and 5-positions of the pyrazole rings; most of these assignments were later confirmed (see below). Hydrogen atoms attached to C atoms could be located in a difference Fourier map but were placed in calculated positions [$r(\text{C-H}) = 1.00 \text{ \AA}$; $B_{\text{H}} = 1.0 \text{ \AA}^2$ greater than B_{eq} for the attached C atom]. After refinement of this model to convergence (full-matrix least squares; agreement factors R and R_w on F_o of 0.047 and 0.050), the positions of the four remaining H atoms could be inferred from the N...N distances. Within each fragment two such distances shorter than 2.63 Å were found; all other N...N distances were greater than 2.83 Å. Nitrogen atoms are not found so close together, unless they are linked by a hydrogen bond. A difference map revealed four peaks with heights 0.30–0.32 e Å⁻³; all other peaks had heights <0.20 e Å⁻³. The locations of three of the four peaks were consistent with the formation of H bonds [$r(\text{N-H}) = 1.08\text{--}1.14 \text{ \AA}$; $r(\text{H}\cdots\text{N}) = 1.51\text{--}1.57 \text{ \AA}$; $\angle(\text{N-H}\cdots\text{N}) = 158\text{--}171^\circ$]. The fourth peak was located intermediate between two N atoms [$r(\text{N-H}) = 1.30, 1.31 \text{ \AA}$; $\angle(\text{N-H-N}) = 169^\circ$]. These four H atoms were included as fixed contributions after idealization [$r(\text{N-H}) = 1.00 \text{ \AA}$; $B_{\text{H}} = 1.0 \text{ \AA}^2$ greater than B_{eq} for the attached N atom]. At convergence (maximum shift/error 0.0), the factors R and R_w on F_o dropped to 0.044 and 0.046 for 577 variables and the 3199 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. The error in an observation of unit weight is 2.01. The deepest troughs in a final difference Fourier map have heights ca. -0.24 e \AA^{-3} and are located at the centers of the pyrazole rings. The biggest peak has height 0.20 e Å⁻³ and is located near N(24), which is not involved in any H bond. Several other observations suggested that the C and N atoms in this ring may not have been assigned correctly. The N(24)–C(34) bond length is about 0.03 Å too long and the C(35)–C(36) bond about 0.03 Å too short. The B values for N(24) and C(36) are a little high and low, respectively. The orientation of the N–N bond relative to the B–B bond is reversed in this ring relative to what is found for the other three analogous rings; that is, the torsion angle N(24)–N(23)–B(4)–B(3) is much less than 90° while the torsion angles N(6)–N(5)–B(1)–B(2), N(12)–N(11)–B(2)–B(1), and N(18)–N(17)–B(3)–B(4) are all much greater than 90°. We tried re-refining the structure after reversing the N(24) and C(36) assignments and relocating H(36). The agreement factors at convergence were a little higher than before (0.046 and 0.048; observation in a reflection of unit weight 2.11), and the bond length discrepancies increased from about 0.03 to 0.05 Å. We strongly suspect that this ring adopts two orientations but did not consider further refinement worthwhile. The atomic coordinates given in Table I correspond to the major orientation.

K₂(pz)₃B–B(pz)₃. Freshly prepared Kpz (11.75 g, 120 mmol) was added in portions to a stirred solution of 11.90 g (60 mmol) of (Me₂N)₂B–B(NMe₂)₂ in 75 mL of toluene. Pyrazole (20.4 g, 300 mmol) was then added in portions, and the mixture was refluxed with stirring for 20 h. After the solid material was cooled to room temperature, it was collected and washed with toluene, with copious amounts of ether, and finally with some absolute alcohol. The resultant crude product, mp 366–370 °C dec, was obtained in essentially quantitative yield and was used without further purification (although elemental analysis data suggest the material to be slightly impure; traces of adhering Hpz can be sublimed off under vacuum). NMR data were not obtained due to solubility problems.

(η³-CH₃CCH₃CH₂)Pd(μ-pz)₂(pz)B–B(pz)(μ-pz)₂Pd(η-CH₂CCH₃CH₂). A mixture of 1.34 g (2.67 mmol) of crude K₂[(pz)₃B–B(pz)₃] (see above), 1.05 g (2.67 mmol) of [(η³-CH₃CCH₃CH₂)PdCl]₂, and 50 mL of CH₂Cl₂ was stirred for 30 min to give a colorless solution containing a colorless precipitate. The latter was filtered off (0.40 g of KCl), and the clear filtrate was evaporated under vacuum to give 1.95 g of a faintly yellow solid. The latter was recrystallized from CH₂Cl₂ to yield 0.70 g of colorless product, decomposing near 170 °C. Anal. (C₂₄H₂₈B₂N₁₂Pd₂) C, H, B, N, Pd.

NMR data (solution in CDCl₃): δ(¹H) 7.51 (6 H, d, $J = 1.8$), 6.01 (3 H, unsymmetrical t = 2 overlapping d, $J \sim 2$), 3.44 (2 H, s), 2.49 (2 H, s), 1.86 (3 H, s); δ(¹³C) 2.4 ($h_{1/2} = 600 \text{ Hz}$). In low-temperature spectra, all ¹H NMR signals began to broaden near $-25 \text{ }^\circ\text{C}$ but no signal separation was observed at temperatures as low as $-50 \text{ }^\circ\text{C}$.

(η³-CH₃CHCH₂)Pd(μ-pz)₂(pz)B–B(pz)(μ-pz)₂Pd(η³-CH₃CHCH₂) was prepared as a colorless solid in a manner similar to that of the

Table I. Positional Parameters and Equivalent B Values for the Atoms of the Two Independent Molecules of Tetrakis(1-pyrazolyl)diborane(4)–Bis(pyrazole), (pz)₂B–B(pz)₂·2Hpz^a

atom	x	y	z	$B_{\text{eq}}, \text{ \AA}^2$
N(1)	0.2910 (02)	0.67210 (18)	0.1855 (04)	3.1 (1)
N(2)	0.2186 (03)	0.70808 (20)	0.1748 (04)	4.3 (1)
N(3)	0.4619 (02)	0.65577 (17)	0.1897 (04)	2.8 (1)
N(4)	0.5052 (03)	0.68391 (19)	0.3405 (04)	3.5 (1)
N(5)	0.3708 (02)	0.66313 (18)	-0.0557 (04)	3.0 (1)
N(6)	0.3120 (03)	0.58768 (20)	-0.1186 (04)	4.3 (1)
N(7)	0.3907 (03)	0.84267 (17)	0.0704 (03)	3.0 (1)
N(8)	0.2882 (03)	0.82091 (20)	0.0432 (04)	4.1 (1)
N(9)	0.4300 (02)	0.83938 (17)	0.3389 (04)	3.0 (1)
N(10)	0.4478 (03)	0.80773 (19)	0.4566 (04)	3.9 (1)
N(11)	0.5588 (02)	0.82980 (18)	0.8299 (03)	2.8 (1)
N(12)	0.6116 (03)	0.90668 (18)	0.2211 (04)	3.6 (1)
N(13)	-0.1258 (02)	0.67040 (19)	0.4524 (04)	3.3 (1)
N(14)	-0.1700 (03)	0.70515 (19)	0.3608 (04)	4.0 (1)
N(15)	-0.0417 (03)	0.65693 (20)	0.6947 (04)	3.7 (1)
N(16)	0.0579 (03)	0.68777 (22)	0.6940 (04)	4.8 (1)
N(17)	-0.2225 (03)	0.65320 (18)	0.6670 (03)	3.0 (1)
N(18)	-0.2673 (03)	0.57648 (19)	0.5913 (04)	4.0 (1)
N(19)	-0.1689 (03)	0.83619 (18)	0.6820 (04)	3.4 (1)
N(20)	-0.2251 (03)	0.81750 (20)	0.5400 (04)	4.0 (1)
N(21)	0.0010 (03)	0.84018 (19)	0.6175 (04)	3.6 (1)
N(22)	0.0804 (03)	0.81129 (02)	0.5886 (04)	5.0 (2)
N(23)	-0.0371 (03)	0.82733 (20)	0.8766 (04)	3.3 (1)
N(24)	-0.0546 (03)	0.7827 (02)	0.9788 (04)	5.2 (2)
C(1)	0.1413 (04)	0.6759 (03)	0.2377 (06)	5.6 (2)
C(2)	0.1631 (04)	0.6172 (03)	0.2922 (06)	6.1 (2)
C(3)	0.2577 (04)	0.6167 (03)	0.2574 (05)	4.6 (2)
C(4)	0.5646 (03)	0.6410 (03)	0.3676 (05)	4.2 (2)
C(5)	0.5606 (04)	0.5844 (02)	0.2351 (05)	4.2 (2)
C(6)	0.4946 (03)	0.5956 (02)	0.1268 (05)	3.3 (1)
C(7)	0.3157 (04)	0.5756 (03)	-0.2691 (05)	4.3 (2)
C(8)	0.3751 (04)	0.6411 (03)	-0.3028 (05)	4.7 (2)
C(9)	0.4089 (03)	0.6952 (02)	-0.1659 (05)	3.4 (1)
C(10)	0.2625 (04)	0.8670 (03)	-0.0376 (06)	4.9 (2)
C(11)	0.3462 (04)	0.9190 (03)	-0.0623 (05)	4.7 (2)
C(12)	0.4262 (03)	0.9021 (02)	0.0064 (05)	3.8 (2)
C(13)	0.4375 (04)	0.8542 (03)	0.5866 (05)	4.7 (2)
C(14)	0.4128 (03)	0.9169 (02)	0.5540 (05)	4.3 (2)
C(15)	0.4086 (03)	0.90642 (22)	0.3986 (05)	3.5 (1)
C(16)	0.7056 (03)	0.9111 (02)	0.1985 (05)	3.9 (2)
C(17)	0.7166 (03)	0.8391 (03)	0.1298 (05)	4.1 (2)
C(18)	0.6227 (03)	0.7894 (02)	0.1089 (05)	3.8 (2)
C(19)	-0.1766 (04)	0.6677 (03)	0.2151 (05)	4.8 (2)
C(20)	-0.1361 (04)	0.6067 (03)	0.2091 (05)	5.2 (2)
C(21)	-0.1057 (03)	0.6096 (02)	0.3594 (05)	4.2 (2)
C(22)	0.1075 (04)	0.6481 (04)	0.7623 (07)	6.6 (2)
C(23)	0.0401 (05)	0.5918 (03)	0.8082 (07)	6.7 (2)
C(24)	-0.0538 (04)	0.5986 (03)	0.7645 (06)	5.1 (2)
C(25)	-0.3503 (04)	0.5556 (02)	0.6515 (05)	4.1 (2)
C(26)	-0.3619 (04)	0.6163 (03)	0.7635 (05)	4.9 (2)
C(27)	-0.2798 (03)	0.6774 (02)	0.7700 (05)	4.0 (2)
C(28)	-0.2911 (04)	0.8580 (03)	0.5525 (06)	5.2 (2)
C(29)	-0.2793 (04)	0.9034 (03)	0.7015 (06)	5.2 (2)
C(30)	-0.2010 (04)	0.8881 (02)	0.7796 (05)	4.1 (2)
C(31)	0.1422 (04)	0.8627 (04)	0.5280 (06)	6.0 (2)
C(32)	0.1047 (04)	0.9225 (03)	0.5163 (06)	5.8 (2)
C(33)	0.0153 (04)	0.9069 (03)	0.5726 (05)	5.0 (2)
C(34)	-0.0077 (04)	0.8305 (03)	1.1181 (05)	4.7 (2)
C(35)	0.0358 (04)	0.9030 (03)	1.0998 (06)	5.2 (2)
C(36)	0.0171 (04)	0.9002 (02)	0.9499 (05)	3.9 (2)
B(1)	0.3926 (04)	0.6988 (03)	0.1194 (05)	2.7 (2)
B(2)	0.4448 (04)	0.8010 (03)	0.1691 (05)	2.7 (2)
B(3)	-0.1198 (04)	0.6961 (03)	0.6325 (05)	3.0 (2)
B(4)	-0.0817 (04)	0.7986 (03)	0.7041 (06)	3.4 (2)

^aThe equivalent displacement parameter is defined as $^{4/3}Tr(\beta \cdot G)$, where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

preceding compound, decomposing near 170 °C (86% yield). Anal. (C₂₄H₂₈B₂N₁₂Pd₂) C, H, B, N, Pd.

NMR data (solution in CDCl₃): δ(¹H) 7.49 (6 H, d, $J = 1.8$, of d, $J = 0.6$), 6.04 (3 H, unsymmetrical t; resolution enhanced: 2 overlapping d, $J = 2.3$ each), 5.25 (1 H, h), 3.66 (2 H, d, $J = 6.8$), 2.46 (2 H, d, $J = 12.4$); δ(¹³C) 2.0 (s, $h_{1/2} = 600 \text{ Hz}$). The ¹H NMR signals broaden on lowering of the temperature, but no separation of signals was observed

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at -50 °C.

The mass spectrum of the compound exhibits a very weak parent ion cluster in the *m/z* 718 region; ready loss of one allyl or one pz group from the parent was also observed.

Crystal and Molecular Structure of $(\eta^3\text{-CH}_2\text{CHCH}_2)_2\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)_2$. The compound crystallizes as colorless chunks and prisms in the monoclinic system with *a* = 18.864 (4) Å, *b* = 9.925 (3) Å, *c* = 16.626 (4) Å, β = 115.11 (2)°, and *Z* = 4 at 296 (2) K. The systematic absences *h*0*l*, *l* = 2*n* + 1, correspond to either the centrosymmetric space group *P2/c* (No. 13) or the noncentrosymmetric space group *Pc* (No. 7). All data with *h*, *k* ≥ 0 and 2θ ≤ 55° were measured on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation and a graphite monochromator (6449 unique reflections). No correction was made for change of intensity with X-ray exposure (ca. +0.5% overall). An empirical correction was made for absorption (crystal size 0.15 × 0.20 × 0.38 mm; μ = 12.96 cm⁻¹); correction factors ranged from 1.20 to 1.49 and averaged 1.37. The structure was solved easily in the space group *P2/c*; the Pd atoms were located from a Patterson map, and the program DIRDIF⁵ revealed the positions of all the other atoms. Peak heights and refined values of the isotropic displacement parameters were used to distinguish between the N and C atoms in the 2 and 5 positions of the two pyrazole rings that are not coordinated to Pd atoms.

Problems with the structure became apparent during anisotropic refinement. Atomic U tensors for the allyl C atoms attached to the Pd(2) atom are just barely positive definite. Bond lengths in the ring composed of atoms N(5), N(6), C(7), C(8), and C(9) and in the allyl group composed of atoms C(22), C(23), and C(24) deviate markedly from standard values. Estimated standard deviations on all bond lengths and angles are larger than expected. The weighted agreement factors for reflections having *h* = 0 or *k* = 0 are significantly higher than average; the agreement is especially poor for reflections having *h* = 0 and either *k* = 2*n* or *l* = 2*n* + 1. In a "final" difference Fourier map there is a rather large peak (1.5 e Å⁻³) within 2.1 Å of C(14) and 1.5 Å from the calculated position of H(14). There were, however, no unreasonable intermolecular contacts.

We considered the possibility that this structure could be described better in the noncentrosymmetric group *Pc*. The morphology of many of the crystals can be imagined to lack an inversion center. According to the programmers who wrote DIRDIF, the distribution of reflection intensities may correspond to a noncentrosymmetric atomic distribution. We have the impression that *Pc* is a more common space group than *P2/c*. An initial structure solution in the group *Pc* was obtained from DIRDIF; isotropic refinements, however, yielded unreasonable bond lengths and angles, even when the C₃N₂ rings and C₃ allyl groups were treated as rigid bodies. Most of the structure probably conforms well to the symmetry of the group *P2/c*, but the allyl groups at the ends of the molecules probably do not. The C₃N₂ ring containing the atoms N(5) and N(6), which is not coordinated to any Pd atom, may also adopt two slightly different positions. It should be noted that all 57 reflections included in the final refinement that have |(F_o - F_c)| > 10σ(F_o) also have F_o > F_c, often by a substantial amount. This pattern suggests that significant localized electron density is missing from the model. In any event, any deviations of the structure from inversion symmetry are not large enough to allow successful refinement in the lower symmetry group. The distances between superimposed atoms range from about 0.1 to 0.4 Å if an inversion center is added to the *Pc* model.

In the final refinement the H atoms of the C₃N₂ rings were placed in calculated positions [*r*(C-H) = 1.00 Å; B_H = 1.0 Å² greater than B_{eq} for the attached C atom]; the H atoms of the allyl groups were not included in the model. At convergence (maximum shift/error 0.09) the agreement factors *R* and *R_w* on F_o are 0.056 and 0.077 for 361 variables and the 3693 reflections having F_o² ≥ 3σ(F_o²). The values of *R* and *R_w* on *I* for all 6449 reflections are 0.109 and 0.138 (negative intensities set to zero). None of the 2756 reflections omitted from the refinement cycles has |I_o - I_c| > 3σ(I). The error in an observation of unit weight is 3.48. A final difference Fourier map has the peak described above and a set of peaks (ca. 0.7 e Å⁻³) and troughs (ca. -1.1 e Å⁻³) in the regions of the Pd atoms and allyl groups.

Positional parameters for the atoms of $(\eta^3\text{-CH}_2\text{CHCH}_2)_2\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)_2$ are given in Table II.

Results

(pz)₂B-B(pz)₂. Reaction of 4 mol equiv of pyrazole (=Hpz) with tetrakis(dimethylamino)diborane(4), (Me₂N)₂B-B(NMe₂)₂,

(5) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins-Slot, H. J.; Haltiwanger, R. C.; Strumpel, M. K.; Smits, J. M. *DIRDIF*, Technical Report 1984/1; Crystallography Laboratory, Toernooiveld: 6525 ED Nijmegen, The Netherlands; 1984.

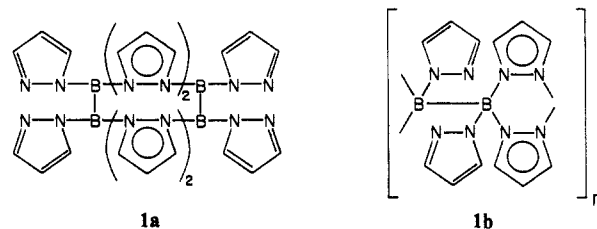
Table II. Positional Parameters and Equivalent *B* Values for the Atoms of $(\eta^3\text{-CH}_2\text{CHCH}_2)_2\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> , Å ²
Pd(1)	0.16572 (05)	0.13513 (09)	0.21441 (05)	3.10 (3)
Pd(2)	0.38045 (05)	-0.57653 (09)	0.49023 (06)	3.58 (3)
N(1)	0.2168 (04)	-0.0565 (08)	0.3718 (05)	2.6 (3)
N(2)	0.1870 (05)	0.0719 (09)	0.3399 (05)	3.4 (3)
N(3)	0.2916 (04)	-0.0769 (08)	0.2752 (05)	2.7 (3)
N(4)	0.2674 (05)	0.0364 (08)	0.2262 (05)	2.7 (3)
N(5)	0.1591 (04)	-0.1810 (09)	0.2277 (05)	2.9 (3)
N(6)	0.1565 (05)	-0.2129 (10)	0.1508 (05)	3.7 (3)
N(7)	0.3581 (05)	-0.2753 (09)	0.4598 (05)	3.1 (3)
N(8)	0.4008 (05)	-0.3727 (09)	0.5160 (06)	3.8 (3)
N(9)	0.3064 (05)	-0.4120 (09)	0.3184 (05)	3.1 (3)
N(10)	0.3359 (05)	-0.5350 (09)	0.3566 (06)	3.4 (3)
N(11)	0.2246 (05)	-0.3843 (08)	0.4006 (05)	2.8 (3)
N(12)	0.2316 (06)	-0.4007 (10)	0.4827 (06)	4.1 (3)
C(1)	0.1732 (07)	0.1320 (12)	0.4058 (08)	4.5 (5)
C(2)	0.1892 (06)	0.0445 (12)	0.4745 (07)	3.8 (4)
C(3)	0.2169 (06)	-0.0717 (11)	0.4516 (06)	3.3 (3)
C(4)	0.3198 (06)	0.0683 (11)	0.1978 (06)	3.0 (3)
C(5)	0.3821 (06)	-0.0216 (12)	0.2302 (07)	4.1 (4)
C(6)	0.3612 (06)	0.1125 (12)	0.2792 (07)	3.6 (4)
C(7)	0.0843 (07)	-0.2330 (14)	0.0978 (08)	4.8 (5)
C(8)	0.0350 (06)	-0.2121 (16)	0.1438 (08)	5.7 (5)
C(9)	0.0828 (06)	-0.1783 (14)	0.2229 (08)	4.7 (5)
C(10)	0.4592 (07)	-0.3116 (15)	0.5862 (08)	5.1 (5)
C(11)	0.4552 (07)	-0.1720 (12)	0.5746 (07)	4.2 (4)
C(12)	0.3916 (06)	-0.1559 (11)	0.4955 (07)	3.7 (4)
C(13)	0.3412 (06)	-0.6122 (11)	0.2913 (08)	4.0 (4)
C(14)	0.3112 (07)	-0.5455 (12)	0.2119 (08)	4.2 (4)
C(15)	0.2910 (06)	-0.4155 (12)	0.2312 (06)	3.5 (4)
C(16)	0.1692 (07)	-0.4737 (13)	0.4760 (08)	4.3 (5)
C(17)	0.1218 (07)	-0.5003 (12)	0.3922 (10)	5.0 (6)
C(18)	0.1571 (07)	-0.4443 (12)	0.3437 (08)	4.8 (5)
C(19)	0.0562 (07)	0.2327 (17)	0.1819 (08)	6.4 (6)
C(20)	0.0966 (08)	0.2950 (17)	0.1337 (09)	6.8 (6)
C(21)	0.1173 (07)	0.2013 (13)	0.0799 (08)	4.6 (4)
C(22)	0.4405 (12)	-0.6551 (19)	0.6224 (10)	8.4 (8)
C(23)	0.3791 (12)	-0.7391 (17)	0.5715 (13)	8.3 (9)
C(24)	0.3805 (10)	-0.7907 (13)	0.4871 (12)	7.9 (8)
B(1)	0.2393 (06)	-0.1555 (11)	0.3135 (07)	2.2 (3)
B(2)	0.2825 (06)	-0.3082 (13)	0.3734 (07)	2.7 (4)

^aThe equivalent displacement parameter is defined as $\frac{1}{3}\text{Tr}(\beta\cdot G)$, where β_{ij} = 2π²*a_ia_j*U_{ij}.

proceeds in a simple transamination reaction. However, solvent (benzene) adheres strongly to the product and can only be removed by prolonged heating of the material under vacuum. After such treatment, the product analyzes as (pz)₂B-B(pz)₂ and the ¹H NMR spectrum of the crude product exhibits only signals for pz groups and in the correct ratio of 2:1 for H(3,5) (7.8–7.0 ppm region) and H(4) (6.4–6.0 ppm region) of pz groups. The spectrum is, however, quite complex although it is dominated by two equally abundant sets for a bridging [δ(¹H) 7.06 (2 H)/6.04 (1 H)] and a terminal [δ(¹H) 7.74 (1 H)/7.53 (1 H)/6.34 (1 H)] pz group. The abundance of these signals varied somewhat (30–50% of the total) in accordance with the mode of combining the reactants, the duration of the reflux period, and the temperature control during solvent removal.

The cited sets of ¹H NMR signals belong to a dimeric species [(pz)₂B-B(pz)₂]₂ (**1a**), which was isolated from the crude product by sublimation. The additional ¹H NMR signals are due to polymeric species of the general structure **1b**.



The sublimation residue (**1b**) contained a fraction that was

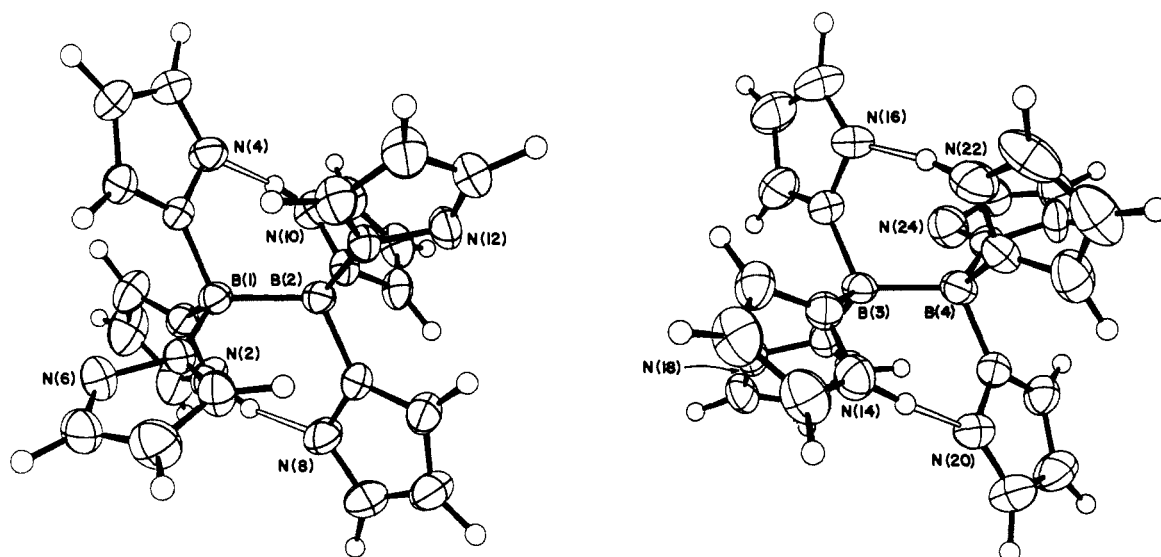


Figure 1. Perspective view of the two independent molecules of $(pz)_2B-B(pz)_2 \cdot 2Hpz$. In this and the other figures, the shapes of the ellipsoids for the non-hydrogen atoms correspond to 50% probability contours of atomic displacement. The atom numbering in this compound and in $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-CH_2CHCH_2)$ is defined by the numbers shown on the drawings and by the information that the atoms within the pz rings are numbered sequentially $N(2n-1)$, $N(2n)$, $C(3n-2)$, $C(3n-1)$, $C(3n)$; the atoms $N(2n-1)$ participate in B-N bonds.

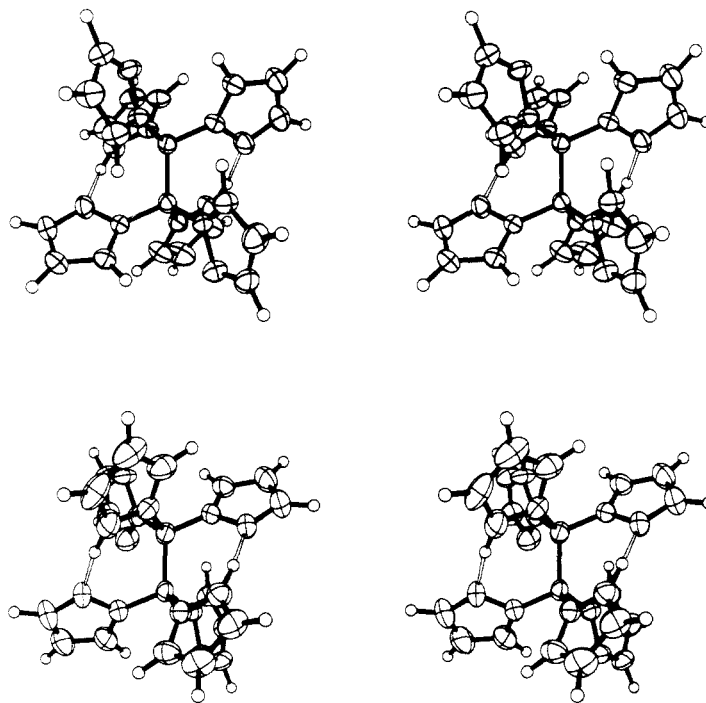


Figure 2. Stereoscopic view of the two independent molecules of $(pz)_2B-B(pz)_2 \cdot 2Hpz$.

soluble in chloroform. The 1H NMR spectrum of this portion showed only one type of bridging but two different but equally abundant types of terminal pz groups in 1:1 ratio (terminal to bridging). This would seem to be in best agreement with **1b** and $n = 3$, likely to be a linear polymer $(pz)_2B-B(pz)(\mu-pz)_2B-(pz)-B(pz)(\mu-pz)_2B(pz)-B(pz)_2$. The chloroform-insoluble part (which is partially soluble in benzene) is then a mixture of **1b**, with n being variable but >3 .

$(pz)_2B-B(pz)_2 \cdot 2Hpz$. Reaction of $(Me_2N)_2B-B(NMe_2)_2$ with excess Hpz leads to the formation of the complex $(pz)_2B-B(pz)_2 \cdot 2Hpz$. The two acidic protons are generally not observed in the 1H NMR spectrum but were identified in an X-ray structure determination of the compound; they are also clearly evident in the IR spectrum of the compound ($\nu(NH) = 3125\text{ cm}^{-1}$).

The crystal and molecular structures of the species were determined by single-crystal X-ray diffraction. Selected bond length and bond angle data are given in Table III together with data for $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-$

$CH_2CHCH_2)$ (see below). ORTEP plots of the two independent molecules of the asymmetric unit of $(pz)_2B-B(pz)_2 \cdot 2Hpz$ are shown in Figure 1; a stereoscopic view is given in Figure 2.

In the solid state, the two acidic protons of $(pz)_2B-B(pz)_2 \cdot 2Hpz$ are localized between two pz groups bonded to two adjacent boron atoms. The B-N bonds of those pz groups (average $1.579(10)\text{ \AA}$) are a little longer than are those for the pz groups, which are not involved in hydrogen bonding (average $1.544(5)\text{ \AA}$). All B-N bonds are considerably longer than those reported for *B,B'*-bis-(1,2-dimethyl-1,3,2-diazaborilidin-2-yl), a diborane(4) derivative containing B-N bonds but trigonal boron.⁶ The B-B bond distances (with an average value of $1.767(3)\text{ \AA}$) are similar to, but much more precise than, those of the two other diborane(4) derivatives containing four-coordinate boron that are listed in the January 1987 Cambridge Structural Database,⁷ i.e., B_2H_4 .

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Table III. Selected Bond Lengths (Å) and Angles (deg) Including Average Values^a

(pz) ₂ B-B(pz) ₂ ·2Hpz			[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂			(pz) ₂ B-B(pz) ₂ ·2Hpz			[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂		
atoms		distance	atoms		distance	atoms		distance	atoms		distance
B(1)	B(2)	1.765 (6)	B(1)	B(2)	1.807 (16)	N(3)	N(4)	1.370 (4)	N(5)	N(6)	1.298 (10)
B(3)	B(4)	1.769 (6)				N(5)	N(6)	1.376 (4)	N(11)	N(12)	1.326 (10)
B(1)	N(1)	1.586 (5)	B(1)	N(1)	1.560 (12)	N(7)	N(8)	1.365 (4)			
B(1)	N(3)	1.576 (5)	B(1)	N(3)	1.587 (12)	N(11)	N(12)	1.368 (4)			
B(2)	N(7)	1.565 (5)	B(2)	N(7)	1.570 (13)	N(15)	N(16)	1.358 (5)			
B(2)	N(9)	1.596 (5)	B(2)	N(9)	1.566 (14)	N(17)	N(18)	1.373 (4)			
B(3)	N(13)	1.580 (5)				N(19)	N(20)	1.370 (4)			
B(3)	N(15)	1.584 (5)				N(23)	N(24)	1.364 (4)			
B(4)	N(19)	1.568 (6)							Pd(1)	N(2)	2.049 (8)
B(4)	N(21)	1.577 (6)							Pd(1)	N(4)	2.088 (8)
B(1)	N(5)	1.543 (5)	B(1)	N(5)	1.598 (12)				Pd(2)	N(8)	2.070 (10)
B(2)	N(11)	1.546 (5)	B(2)	N(11)	1.545 (13)				Pd(2)	N(10)	2.056 (9)
B(3)	N(17)	1.537 (6)							Pd(1)	C(19)	2.133 (10)
B(4)	N(23)	1.548 (5)							Pd(1)	C(20)	2.130 (12)
N(1)	N(2)	1.352 (4)	N(1)	N(2)	1.403 (11)				Pd(1)	C(21)	2.130 (11)
N(9)	N(10)	1.357 (4)	N(3)	N(4)	1.350 (10)				Pd(2)	C(22)	2.147 (13)
N(13)	N(14)	1.354 (4)	N(7)	N(8)	1.348 (11)				Pd(2)	C(23)	2.112 (14)
N(21)	N(22)	1.351 (4)	N(9)	N(10)	1.380 (11)				Pd(2)	C(24)	2.126 (14)
									C(19)	C(20)	1.457 (18)
									C(20)	C(21)	1.454 (17)
									C(22)	C(23)	1.386 (24)
									C(23)	C(24)	1.506 (22)

(pz) ₂ B-B(pz) ₂ ·2Hpz				[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂				(pz) ₂ B-B(pz) ₂ ·2Hpz				[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂			
atoms		angle		atoms		angle		atoms		angle		atoms		angle	
B(2)	B(1)	N(1)	112.6 (3)	B(2)	B(1)	N(1)	111.3 (7)	N(1)	B(1)	N(3)	103.1 (3)	N(1)	B(1)	N(3)	108.5 (8)
B(2)	B(1)	N(3)	113.0 (3)	B(2)	B(1)	N(3)	114.9 (7)	N(1)	B(1)	N(5)	107.5 (3)	N(1)	B(1)	N(5)	104.5 (7)
B(1)	B(2)	N(7)	113.4 (3)	B(1)	B(2)	N(7)	110.6 (8)	N(3)	B(1)	N(5)	107.3 (3)	N(3)	B(1)	N(5)	103.6 (7)
B(1)	B(2)	N(9)	111.5 (3)	B(1)	B(2)	N(9)	113.8 (8)	N(7)	B(2)	N(9)	102.3 (3)	N(7)	B(2)	N(9)	107.2 (8)
B(4)	B(3)	N(13)	112.1 (3)					N(7)	B(2)	N(11)	107.6 (3)	N(7)	B(2)	N(11)	108.3 (8)
B(4)	B(3)	N(15)	112.4 (3)					N(9)	B(2)	N(11)	105.8 (3)	N(9)	B(2)	N(11)	105.3 (9)
B(3)	B(4)	N(19)	113.2 (4)					N(13)	B(3)	N(15)	103.8 (3)				
B(3)	B(4)	N(21)	112.4 (3)					N(13)	B(3)	N(17)	105.8 (3)				
B(2)	B(1)	N(5)	112.7 (3)	B(2)	B(1)	N(5)	113.2 (8)	N(15)	B(3)	N(17)	106.0 (3)				
B(1)	B(2)	N(11)	115.1 (3)	B(1)	B(2)	N(11)	111.2 (8)	N(19)	B(4)	N(21)	103.7 (3)				
B(4)	B(3)	N(17)	115.8 (3)					N(19)	B(4)	N(23)	106.6 (3)				
B(3)	B(4)	N(23)	114.1 (3)					N(21)	B(4)	N(23)	106.0 (3)				
												N(2)	Pd(1)	N(4)	89.2 (3)
												N(8)	Pd(2)	N(10)	89.0 (3)
												C(19)	C(20)	C(21)	114.0 (14)
												C(22)	C(23)	C(24)	115.6 (18)

average values		average values		
(pz) ₂ B-B(pz) ₂ ·2Hpz	[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂	(pz) ₂ B-B(pz) ₂ ·2Hpz	[(η ³ -CH ₂ CHCH ₂)-Pd(μ-pz) ₂ (pz)B] ₂	
r(B-B)	1.767 (3)	1.807 (16)	Δ(B-B-N)	113.2 (13)
r(B-N)	1.567 (19)	1.571 (19)	Δ(N-B-N)	105.5 (18)
r(N-N)	1.363 (9)	1.351 (37)	Δ(N-N-C)	107.9 (16)
r(N-C)	1.339 (11)	1.348 (31)	Δ(N-C-C)	109.4 (12)
r(C-C)	1.372 (11)	1.373 (42)	Δ(C-C-C)	105.4 (10)
r(Pd-N)		2.066 (17)	Δ(N-Pd-N)	
r(Pd-C)		2.130 (11)	Δ(C-C-C) _{allyl}	114.8 (11)
r(C-C) _{allyl}		1.451 (49)		

^aNumbers in parentheses are estimated standard deviations. For the averages, the numbers in parentheses are the esd's of the means.

2P(C₆H₅)₃⁸ (1.76 (2) Å) and B₂Cl₄·2N(CH₃)₃⁹ (1.72 Å; no esd available). The B-B distance in (pz)₂B-B(pz)₂·2Hpz appears to be longer than those of diborane(4) derivatives containing trigonal boron, which average 1.70 Å.^{6,10,11} Bond distances within the pz skeletons fall in the normal range observed in similar molecules, e.g., (pz)₂B(μ-pz)₂B(pz)₂.¹²

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(η³-Allyl)Pd(μ-pz)₂(pz)B-B(pz)(μ-pz)₂Pd(η³-allyl). The salt K₂[(pz)₃B-B(pz)₃] was obtained on reaction of (Me₂N)₂B-B(NMe₂)₂ with 2 mol equiv of Kpz and an excess of Hpz. No NMR data were obtained for the salt (due to solubility problems), and analytical data suggested the material to be slightly impure. Nevertheless, the crude material can be used for reactions with metal complexes such as (η³-allyl)palladium chloride dimers to yield species of the type (η³-allyl)Pd(μ-pz)₂(pz)B-B(pz)(μ-pz)₂Pd(η³-allyl) (allyl = CH₂CHCH₂ or CH₂CCH₃CH₂).

Even at low temperatures only one set of (two) pz signals is observed in the ¹H NMR spectra of these latter complexes, thus implying spectroscopic identity for the pz groups. This observation is common for some poly(1-pyrazolyl)borate complexes and has been ascribed to exchange processes of bridging and terminal pz

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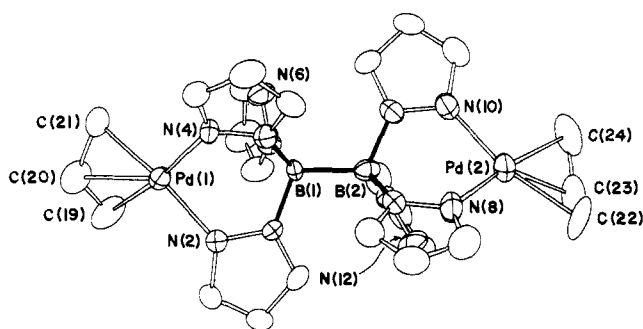


Figure 3. Perspective view of a molecule of $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$ (see also caption to Figure 1).

groups that is fast on the NMR time scale. Frequently, this fluxional behavior is slowed down on lowering of the temperature, but this was not the case for the present Pd complexes. However, the above formulation of the complexes is clearly supported by a single-crystal X-ray structure determination.

Bond distances and angles for $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$ have been given in Table III. An ORTEP plot of the molecule is shown in Figure 3. Although the precision of the structure determination was limited by space group problems, the data clearly establish that, in the solid state, only two of the three pz groups attached to each B atom bond to the Pd atom. In general, bond distances are quite similar to those found for $\text{H}_2[(\text{pz})_3\text{B-B}(\text{pz})_3]$ (see above).

Discussion

When tris(dimethylamino)borane, $(\text{Me}_2\text{N})_3\text{B}$, and pyrazole, Hpz, are combined in solution, the primary product is the complex $\text{Me}_2\text{HN}\cdot\text{B}(\text{pz})_3$. The reaction is reasonably independent of the stoichiometry of the reagents and the temperature. At room temperature, the (N)H proton is not localized and the species is best formulated as $\text{H}[\text{Me}_2\text{NB}(\text{pz})_3]$. Even in the presence of a large excess of Hpz, the remaining dimethylamine is not displaced to form $\text{Hpz}\cdot\text{B}(\text{pz})_3 = \text{H}[\text{B}(\text{pz})_4]$. Rather, under thermolytic conditions and in the presence of excess Hpz, the pyrazabole $(\text{pz})_2\text{B}(\mu\text{-pz})_2\text{B}(\text{pz})_2$ is the ultimate product.¹³

The reaction of Hpz with tetrakis(dimethylamino)diborane(4), $(\text{Me}_2\text{N})_2\text{B-B}(\text{NMe}_2)_2$, with Hpz is distinctly different. Even under mild conditions and employing a 4:1 stoichiometry of reactants, all four dimethylamino groups are readily displaced to form the pyrazabole $[(\text{pz})_2\text{B-B}(\text{pz})_2]_2$ (**1a**) and a polymeric species (**1b**) of the same composition; and in the presence of excess Hpz, the species $(\text{pz})_2\text{B-B}(\text{pz})_2\cdot 2\text{Hpz}$ is formed. These differences in chemical behavior clearly reflect an effect of the replacement of one Me_2N group of the borane(3) derivative $(\text{Me}_2\text{N})_3\text{B}$ by $(\text{Me}_2\text{N})_2\text{B}$ in the diborane(4) derivative $(\text{Me}_2\text{N})_2\text{B-B}(\text{NMe}_2)_2$.

The species $[(\text{pz})_2\text{B-B}(\text{pz})_2]_2$ is an unusual pyrazabole. Its cage-like central $\text{B}_2(\mu\text{-pz})_2\text{B}_2$ unit seems to be responsible for the fact that benzene (and other solvents) adheres strongly to the molecule. This feature may have some practical implications and needs to be explored in more detail. Furthermore, the compound may be viewed as a triply bridged pyrazabole, i.e., as a species of the type $\text{RB}(\mu\text{-pz})_2(\mu\text{-X})\text{BR}$ where the two boron atoms of a pyrazabole skeleton $\text{B}(\mu\text{-pz})_2\text{B}$ are linked by an additional moiety, i.e., $\text{X} = \text{BR}(\mu\text{-pz})_2\text{BR}$ and $\text{R} = \text{pz}$. Only two other such species have previously been described, namely $\text{RB}(\mu\text{-pz})_2(\mu\text{-X})\text{BR}$ with $\text{X} = \text{OBRO}$ and $\text{R} = \text{C}_2\text{H}_5$ or C_6H_5 .¹⁴ It may well be that other such triply bridged pyrazaboles exist, and a search for the synthesis of such additional species with various X bridges is currently underway.

Similarly, the ion $[(\text{pz})_3\text{B-B}(\text{pz})_3]^{2-}$ acts like a typical poly-(1-pyrazolyl)borate and may best be compared to the $[\text{RB}(\text{pz})_3]^-$ ion ($\text{R} = \text{noncoordinating substituent}$) but for the fact that the former is bis(polydentate) and a dianion. Hence, whereas $[\text{RB}(\text{pz})_3]^-$ forms monometallic complexes such as $\text{RB}(\text{pz})_3\text{ML}$ ($\text{M} = \text{metal}$, $\text{L} = \text{other ligand(s)}$), the ion $[(\text{pz})_3\text{B-B}(\text{pz})_3]^{2-}$ forms bimetallic analogues, i.e., $\text{LM}(\text{pz})_3\text{B-B}(\text{pz})_3\text{ML}$. This event opens additional opportunities for the syntheses of novel polynuclear chain-type species containing boron and metal centers similar to those described recently.¹⁵ Moreover, since the $[\text{RB}(\text{pz})_3]^-$ ion can also act as tridentate ligand,¹ the $[(\text{pz})_3\text{B-B}(\text{pz})_3]^{2-}$ should behave in analogous fashion to give compact bimetallic complexes, possibly even containing two different metals in the same molecule, or macromolecular materials of the general composition $[(\text{pz})_3\text{B-B}(\text{pz})_3\text{M}]_n$.

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Registry No. **1a**, 112069-08-6; $[(\text{PZ})_2\text{B-B}(\text{pz})_2]_n$, 112112-41-1; $(\text{Me}_2\text{N})_2\text{B-B}(\text{NMe}_2)_2$, 1630-79-1; $(\text{pz})_2\text{B-B}(\text{pz})_2\cdot 2\text{Hpz}$, 112069-09-7; Kpz, 40802-36-6; $\text{K}_2[(\text{pz})_3\text{B-B}(\text{pz})_3]$, 112087-33-9; $[(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)\text{PdCl}]_2$, 12081-18-4; $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$, 112112-43-3; $(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CCH}_3\text{CH}_2)$, 112112-42-2; $[(\eta^3\text{-CH}_2\text{CHCH}_2)\text{PdCl}]_2$, 12012-95-2; pyrazole, 288-13-1.

Supplementary Material Available: Complete listing of bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for $(\text{pz})_2\text{B-B}(\text{pz})_2\cdot 2\text{Hpz}$ and $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$ (11 pages); tables of final observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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