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BORON—NITROGEN COMPOUNDS

LXXXIX*. NEW BORON DERIVATIVES OF PYRAZOLE AND IMIDAZOLE

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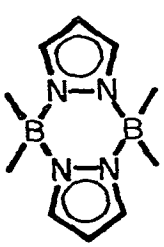
Summary

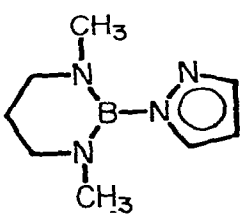
New monomeric *N*-borylated pyrazole and imidazole derivatives have been synthesized and some of their characteristic features have been explored. The suggested structures are supported by spectroscopic data.

Introduction

Pyrazol-1-ylboranes R_2Bpz (pz = pyrazol-1-yl = $C_3H_3N_2$) generally exist in the dimeric pyrazabole structure I [2]. The first monomeric pyrazol-1-ylborane containing trigonal boron has been obtained only recently when 1,3-dimethyl-1,3,2-diazaboracyclohexane and pyrazole were condensed to yield 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclohexane (II) [3].



(I)



(II)

It was concluded that B—N π-bonding within the B—N—C heterocycle of II results in electronic saturation of the boron atom, thus preventing the formation of a pyrazabole structure of type I. Hence, the role of the pyrazolyl group in II seems to be reduced to that of an ordinary heteroaromatic substituent.

* For Part LXXXVIII, see ref. 1.

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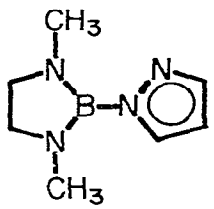
On that basis the synthesis of additional monomeric amino-(pyrazol-1-yl)-boranes should be possible. Furthermore, similar *N*-borylated heteroaromatic nitrogen bases such as imidazole derivatives may exhibit an analogous behavior and corresponding monomeric species may well result from intramolecular electronic saturation of the boron.

Results and discussion

1,3-Dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane

Condensation of 1,3-dimethyl-1,3,2-diazaboracyclopentane with pyrazole was found to occur in a fashion similar to that of the corresponding 1,3,2-diazaboracyclohexane with the same base; the monomeric compound III was obtained readily and in good yield.



(III)

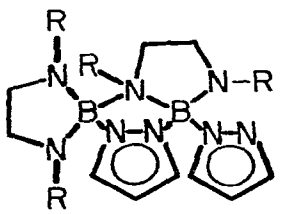
Freshly distilled III is a solid, m.p. 24 to 25° C, the monomeric nature of which is illustrated by NMR spectral data. For example, the observed ^{11}B chemical shift δ 25.1 ppm is indicative of trigonal boron and thus disputes a pyrazabole structure for the species. Also, the ^{13}C NMR spectrum of the compound shows the expected signals for three non-equivalent carbon atoms of the pyrazolyl group with δ (^{13}C) 141.2, 133.0 ($C^{3,5}$) and 105.7 (C^4) ppm, respectively. It is noteworthy that the former two signals are considerably broadened in the spectrum of the neat liquid material. This is similar to the case of II where a sharpening of the corresponding ^{13}C resonance signals is also observed in the solution spectrum. Moreover, on heating of II these cited signals collapse to a single resonance line (see below). This latter process cannot be followed in the ^{13}C NMR spectrum of III due to rearrangement processes that occur in the liquid state (see below).

The ^{14}N NMR spectrum of III exhibits a broad signal with δ (^{14}N) near —376 ppm which is assigned to the NCH_3 atoms of the B—N—C heterocycle of III; a reasonably sharp signal for the N^1 atom of the pyrazole ring, δ (^{14}N) —170 ppm; and a very broad shoulder with δ (^{14}N) near —62 ppm, assigned to the N^2 nitrogen atom of the pyrazole ring. Somewhat surprisingly, the ^1H NMR spectrum of the compound shows only two signals for the protons of the pyrazole ring and it appears that the signals of the hydrogen atoms bonded to C^3 and C^5 accidentally overlap. This interpretation is reasonable inasmuch as the corresponding signals of II are separated by only 0.14 ppm (spectrum in solution [3]) but coincide in the spectrum of the neat liquid (see experimental section).

The monomeric nature of III is further supported by the observation of the molecular ion as the base peak of the mass spectrum. Also, a band at 1517 cm^{-1}

in the infrared spectrum of III is likely to be assigned to an antisymmetric B—N stretching mode involving trigonal boron.

As noted above, III is a low melting solid. Once liquefication of the material starts, the compound liquefies within a few days while standing at ambient temperature. Additional new species are observed in the ^{11}B and ^{13}C NMR spectra of the thus obtained liquid; however, this latter formation is completely reversed by redistillation of the material. The nature of these new species formed on liquefication has not yet been elucidated. The ^{11}B NMR spectrum shows the presence of one additional trigonal and at least three four-coordinate boron atoms. Another unique property of III is the reversible formation of a new species in equilibrium with III at temperatures below —40° C. Based on preliminary ^{1}H and ^{13}C NMR data, this latter new compound may probably be formulated

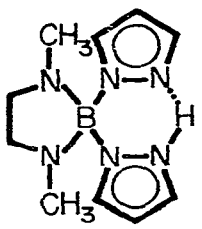


(IV, R = CH_3)

as IV. For example, the low temperature ^{13}C NMR spectrum (solution in CD_2Cl_2) exhibits six additional resonance signals in the pyrazole region of the spectrum with δ 140.4, 135.0, 130.8, 130.4, 109.0 and 104.6 ppm, respectively. (Note: the relevant signals of the original monomer are slightly shifted to 141.7, 133.4 and 105.8 ppm). This finding clearly disputes a pyrazabole structure for the new species. Also, the *N*-methyl resonance signal of III is shifted from 34.0 to 33.1 ppm and, among others, four additional methyl signals are observed at low temperature with δ (^{13}C) 41.7, 36.8, 34.6 and 33.9 ppm, again disputing a pyrazabole structure. These new signals are, however, in good accordance with IV. Similarly, the ^{1}H NMR spectrum (solution in CD_2Cl_2, $CHDCl_2$ as internal reference) shows a slight shift for the hydrogens of the pyrazole group of the monomer to 7.75, 7.73 and 6.40 ppm at low temperature versus 7.78, 7.75 and 6.41 ppm in the room temperature spectrum. The low temperature spectrum, however, features additional pyrazole signals with δ (^{1}H) 7.92 (broadened singlet), 7.55 (broadened singlet), 7.45 (broadened singlet), 6.60 (triplet) and 6.31 (triplet) ppm with a relative area ratio of 1/1/2/1/1. These observations again are most readily interpreted by the proposed structure IV and are definitely not in consonance with a pyrazabole-type dimerization. In this context it is of interest to note that intermolecular adducts similar to IV have been postulated as intermediates in exchange reactions of boron—oxygen [4 to 6] and boron—sulfur [7] heterocycles. However, no intermediates could be identified in these cases. This lack may be due to the fact that presumably an intermediate four-membered ring structure is formulated as a result of a dimeric transition state, which is generally less favored than a five-membered heterocycle as postulated in the present study. However, additional experiments are needed to clarify the present observation.

The successful isolation and characterization of a second example of a monomeric pyrazol-1-ylborane lends credence to the earlier [3] suggestion that electron-rich boron substituents will prevent their dimerization to a pyrazabole structure. Any role of steric factors can be discarded in view of the following observation:

The monomeric pyrazol-1-ylborane (III) interacts readily and exothermally with pyrazole to form a 1/1 molar complex which is formulated as V.



(V)

The ^{11}B NMR spectrum of V exhibits a single resonance line with δ (^{11}B) 4.0 ppm, demonstrating the existence of four-coordinate boron in the species. The suggested structure of V is further substantiated by the observation of three ^{13}C NMR signals in the pyrazole region of the spectrum with δ (^{13}C) 139.8, 133.7 and 104.7 ppm, respectively. At —64° C, all three signals are split and the pair with δ 134.8 and 132.8 ppm is likely to be indicative of the two carbon atoms of the pyrazole ring that are closest to the boron whereas those with δ 141.4 and 138.0 ppm can be assigned to the other N-bonded carbon atoms of the pyrazole rings.

A similar situation is encountered for the ^1H NMR spectrum of the compound. Since the signal for the NH proton falls in the region where the protons of the pyrazole rings are also observed, the N-deuterated species was prepared and its ^1H NMR spectrum was recorded. At room temperature, one signal with δ (^1H) 6.29 ppm is observed for the protons bonded to the two C^4 atoms of the pyrazole rings and another signal, δ (^1H) 7.62 ppm, is found for the four protons bonded to the C^3 and C^5 atoms. At —66° C, the latter signal is split into four distinct resonances with δ (^1H) 8.01, 7.65, 7.57 and 7.36 ppm, respectively. These observations suggest that, at ambient temperature, V is best descriptive of the adduct and the N-bonded hydrogen is rapidly exchanging between the two pyrazole groups. At low temperatures, however, this migration process is frozen and the two pyrazole moieties of V are sufficiently different for two types to be observed. The two signals with δ (^1H) 8.01 (pyrazole group) and 7.36 (pyrazolyl group) ppm are tentatively assigned to the two hydrogen atoms farthest from the boron; and the signals with δ (^1H) 7.65 and 7.57 ppm are assigned to the two hydrogen atoms of the pyrazole rings that are closest to the boron.

Structure V finds some additional support by infrared spectral data. In solutions of pyrazole, hydrogen bonding is evidenced by broad absorptions between 3170 and 2890 cm^{-1} and, in a saturated solution in CCl_4, a weak but sharp band of an uncomplexed NH group appears at 3480 cm^{-1}. On dilution, this latter band increases in intensity accompanied by weakening of the cited broad bands. The broad NH stretching mode of V is centered at 3120 cm^{-1} (identified by

comparison with a spectrum of the N-deuterated material) but no band is observed in the 3480 cm^{-1} region.

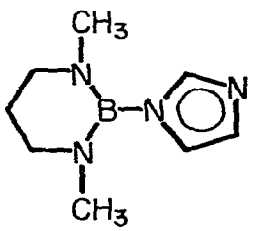
The species V is the first characterized adduct of a 1,3,2-diazaboracycloalkane derivative in which the boron is four-coordinate. The nitrogen atoms of the B—N—C heterocycle should, therefore, be sp^3 hybridized and thus are likely to result in a nonplanar conformation of the BN_2C_2 ring system. Indeed, a considerable broadening of the NCH_2 signals of V is observed in the low temperature ^1H and ^{13}C NMR spectra of the compound, which may be indicative of freezing of conformational isomers.

One may speculate that the ready formation of V (and of the corresponding adduct of II with pyrazole as well as with C-substituted pyrazoles) is a consequence of favorable geometrical factors. Indeed, if one assumes that a bridging boryl group may be similar in some respects to a bridging hydrogen, V can be viewed as a relative of the pyrazaboles, I. In any case, the existence of adducts such as V disputes that steric factors prevent the formation of a pyrazabole structure of II or III, respectively. Therefore, the monomeric nature of the latter species must be due to a stabilization by electronic factors. It is possible that this event is particularly enhanced by endocyclic effects [12].

1,3-Dimethyl-2-(imidazol-1'-yl)-1,3,2-diazaboracycloalkanes

Very limited data on boron derivatives of imidazoles are known and the existence of monomeric as well as oligomeric species has been deduced from the experimental data [8—11]. For example, diethyl(imidazol-1-yl)borane has been reported to be an oligomer [8,11] but structures analogous to the pyrazaboles cannot be formed in this case. (2-Methylimidazol-1-yl)-dimethyl- [9] and -diethylborane [8] have been found to exist as tetramers and a cyclic structure resulting from intermolecular B—N^3 coordination has been deduced [9].

In the present work, the condensation of 1,3-dimethyl-1,3,2-diazaboracyclohexane with imidazole was found to readily yield monomeric 1,3-dimethyl-2-(imidazol-1'-yl)-1,3,2-diazaboracyclohexane (VI).



(VI)

The monomeric nature of VI is readily demonstrated by the ^{11}B NMR datum, since only a single resonance signal, δ 24.4 ppm, is observed which is indicative of trigonal boron. The ^{13}C and ^{14}N NMR data are also in consonance with structure VI. Furthermore, a strong infrared absorption at 1531 cm^{-1} is assigned to B—N stretching involving trigonal boron.

Noteworthy is the broadness of the ^{13}C NMR signals for the C^4 and C^5 atoms of the imidazole ring of VI with δ (^{13}C) 128.6 and 119.7 ppm, respectively. This observation suggests dynamic processes, i.e., a 1,3-shift of the boryl group bon-

ded to the imidazole nitrogen. Such dynamic behavior has been observed for N-bonded silicon [13,14] and germanium [14] derivatives of pyrazoles and was interpreted by an intramolecular 1,2-shift of the N-substituents. No such phenomenon was found for analogous germanium derivatives of imidazoles, not even on heating trimethyl(imidazol-1-yl)germanes to temperatures as high as 185°C [14]. On heating of VI to 80°C, however, the two cited broad ^{13}C NMR signals have merged to a singlet and an analogous merging is observed for the C^3 and C^5 signals of the pyrazole ring of II (see above). The equivalence of the cited carbon atoms at high temperatures indicates rapid 1,3- or 1,2-shifts, respectively, of the N-bonded boryl groups in VI and II. In the former case, significant line narrowing is observed at ambient temperature on dilution of the sample, suggesting that the 1,2-shift is intermolecular (in contrast to the findings on the Si and Ge derivatives cited above [13,14]). Obviously, the described phenomena need further studying and a detailed NMR analysis is in progress.

The existence of monomeric VI is in consonance with the previous conclusion [3], that a pyrazolyl group bonded to an electron-rich boron atom seems to behave as an ordinary heteroaromatic substituent. The same appears to hold true for the imidazolyl group. Therefore, one must assume that, in general, strongly electron-donating substituents will prevent the formation (via intermolecular coordination of pyrazol-1-ylboranes and imidazol-1-ylboranes) of aggregated species and the monomers are thermodynamically stable. It remains to be seen whether or not other substituents such as organyloxy groups will have the same type of effect.

In a procedure similar to that outlined above, condensation of 1,3-dimethyl-1,3,2-diazoboracyclopentane with imidazole yielded 1,3-dimethyl-2-(imidazol-1′-yl)-1,3,2-diazaboracyclopentane, m.p. 108 to 110°C. In solution as well as in the gas phase the compound is definitely monomeric, as is documented by the NMR and mass spectral data (see experimental section). However, in view of the relatively high melting point of the material, some association in the solid state cannot be excluded. It is noteworthy that at ambient temperature only one broad singal is observed for C^4 and C^5 of the imidazolyl moiety of the compound, indicating rapid boryl group exchange between the N^1 and N^3 site. It should also be noted that the preparation and isolation of this particular compound is much more tedious than that of the other 1,3,2-diazaboracycloalkane derivatives described above and is always accompanied by the formation of substantial amounts of unidentified byproducts.

Experimental

All reactions and transfers were carried out under a dry argon atmosphere. Pyrazole and imidazole were commercial products and were treated with a small quantity of metallic sodium and freshly distilled or sublimed before use. 1-Deuteropyrazole was prepared by dissolving pyrazole in an excess of D_2O and drying the material in a vacuum desiccator over KOH. 1,3-Dimethyl-1,3,2-diazaboracycloalkanes were prepared by the literature procedure [15]. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Infrared spectra were recorded on a Perkin—Elmer Model 621 instrument un-

der standard operating procedures. Wavenumbers are given in cm^{-1}, abbreviations of intensities are: s = strong, m = medium, w = weak, (br) = broad, v = very, (sh) = shoulder. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-7 instrument at 70 eV and, unless otherwise noted, at an inlet temperature of 180°C. The data are listed for ions with a relative abundance (in parentheses) of 5% or greater only. Proton NMR spectra were recorded on a Varian T-60 or CFT-20 spectrometer, respectively, and are referenced to tetramethylsilane. Boron-11 (reference: $(C_2H_5)_2OBF_3$) and nitrogen-14 (reference: aqueous NH_4NO_3) NMR spectra were recorded on a Bruker Model WP200 instrument, carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer and are referenced to tetramethylsilane. All chemical shift data are reported in ppm with positive values indicating downfield from the cited (unless otherwise noted: external) references. The spectra were normally recorded at ambient temperature. An asterisk denotes a relatively broad signal; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = multiplet, sh = shoulder.

General procedure for the preparation of 1,3-dimethyl-2-yl-1,3,2-diazaboracycloalkanes

A mixture of the heteroaromatic amine (pyrazole, imidazole) and the 1,3-dimethyl-1,3,2-diazaboracycloalkane in approximately 1/1.2 molar ratio is heated to gentle reflux until hydrogen evolution ceases. The excess of 1,3-dimethyl-1,3,2-diazaboracycloalkane is removed under reduced pressure and the residue is distilled under vacuum.

1,3-Dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane (III)

Prepared from 63.4 g (0.932 mol) pyrazole and 108.0 g (1.10 mol) 1,3-dimethyl-1,3,2-diazaboracyclopentane; reflux time: 4 days. Yield: 129.4 g (85%),, b.p. 108°C/9 Torr, m.p. 24 to 25°C (see text). Analysis: Found: C, 51.21; H, 8.07; N, 33.90; B, 6.86. $C_7H_{13}N_4B$ calcd.: C, 51.26; H, 7.99; N, 34.16; B, 6.59%.

NMR data: δ (^{1}H) (neat) 7.70 (d, 2 H), 6.33 (t, 1 H), 3.25 (s, 4 H), 2.83 (s, 6 H); (solution in CCl_4) 8.00 (d, 2 H), 6.66 (t, 1 H), 3.73 (s, 4 H), 3.24 (s, 6 H); (solution in $CDCl_3$) 8.17 (d?, 2 H), 6.81 (t, 1 H), 3.77 (s, 4 H), 3.24 (s, 6 H). δ (^{11}B) (neat) 24.6; δ (^{13}C) (neat) 141.2 * (d), 133.0 * (d), 105.7 (d of t, ^1J 175 Hz, ^2J 10 Hz), 50.7 (t, ^1J 139 Hz), 33.3 (q, ^1J 134 Hz); (solution in CD_2Cl_2, proton-decoupled) 142.4, 133.9, 106.4, 51.4, 34.0. δ (^{14}N) (neat) —62 * (sh), —170 (N^1 of pyrazole), —376 * (NCH_3).

Infrared spectrum (neat liquid, KBr plates): 3130(sh), 3095w(b), 2858vs(b), 2795wm, 1517vs(br), 1475wm, 1449s, 1410s, 1388m, 1345s, 1296s, 1260(sh), 1245m, 1214m(b), 1173m, 1107m, 1079w(br), 1055w, 1039ms, 985m, 949s, 917wm, 900w, 875vw(br), 858w, 817vw, 705w, 754s, 670wm, 630s, 616(sh), 601vw; (solution in CCl_4, NaCl cell) 3100w, 2975(sh), 2860s, 2793m, 1254vs, 1514(sh), 1476m, 1448s, 1419w, 1409s, 1388ms, 1343s, 1296s, 1245m, 1210w, 1171ms, 1105s, 1074vw, 1052wm, 1046ms, 1005(sh), 984wm, 947s, 914wm, 897w, 877w.

Mass spectral data: *M/z* = 165 (10), 164 (100), 163 (48), 162 (7), 149 (17), 148 (6), 136 (17), 135 (25), 134 (13), 122 (26), 121 (11), 120 (8), 109 (12), 108 (44), 107 (15), 106 (7), 96 (7), 95 (15), 94 (12), 93 (6), 81 (41), 80 (18), 79 (13), 68 (22), 67 (9), 62 (9), 42 (6), 40 (6).

1,3-Dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclohexane (II)

Preparative and physical data see ref. 3. Additional NMR data: δ (^{1}H) (neat) 7.73 (d, 2 H), 6.43 (t, 1 H), 3.13 (t, 4 H), 2.63 (s, 6 H), 2.07 (p, 2 H). δ(^{13}C) (neat) 141.1 *, 132.8 * (d), 105.2 (d of t, ^1J 175 Hz, ^2J 10 Hz), 48.4 (t, ^1J 134 Hz), 37.1 (q, ^1J 135 Hz), 26.1 (t, ^1J 127 Hz); (neat at 80°C, proton-decoupled) 136.1 * (approximate half-height band width 180 Hz), 104.5, 48.1, 36.4, 25.8.

1,3-Dimethyl-2-(imidazol-1'-yl)-1,3,2-diazaboracyclohexane (VI)

Prepared from 7.2 g (0.106 mol) imidazole and 13.0 g (0.116 mol) 1,3-dimeth yl-1,3,2-diazaboracyclohexane; reflux time: 2 days. Yield: 14.6 g (77%), b.p. 128 to 129°C/5 Torr. Analysis: Found C, 54.02; H, 8.63; N, 31.39; B, 5.73. $C_8H_{15}N_4B$ calcd.: C, 53.97; H, 8.49; N, 31.47; B, 6.07%.

NMR data: δ (^{1}H) (neat) 7.70 (s, 1 H), 7.23 (s, 2 H), 3.19 (t, 4 H), 2.65 (s, 6 H), 2.07 (p, 2 H); (solution in $CDCl_3$) 7.98 (s, 1 H), 7.64 (s, 1 H), 7.38 (s, 1 H) 3.94 (t, 4 H), 2.92 (s, 6 H), 2.44 (p, 2 H). δ(^{11}B) (neat) 24.4; δ(^{13}C) (neat) 138.6 (d of t, ^1J 205 Hz, ^2J 10 Hz), 128.6 * (d), 119.7 * (d), 48.1 (t, J 133 Hz), 36.6 (g, J 135 Hz), 25.8 (t, J 126 Hz); (neat at 3°C, proton-decoupled) 138.7, 129.1, 119.4, 48.0, 36.7, 25.8; (neat at 80°C, proton-decoupled) 138.3, 123.5 *, 48.1, 36.5, 25.9; (solution in $CDCl_3$, proton-decoupled) 139.0, 129.2 *, 119.7 *, 48.2, 37.0, 25.9; δ(^{14}N) (neat) ca. —108 * (N^3 of imidazole), —208 (N^1 of imidazole), —325 * (NCH_3).

Infrared spectrum (neat liquid, KBr plates); 3120(sh), 3095w(br), 2985w, 2918m, 2864s, 2836(sh), 2795m, 1650wm(br), 1552(sh), 1531vs, 1496vs, 1470vw, 1446s, 1413vs, 1403ms, 1362vs, 1324vs, 1286m, 1245(sh), 1227s, 1202wm, 1184wm, 1136w, 1104wm, 1090ms, 1061vw, 1048s, 961m, 908m, 877w, 832m(br), 747m(br), 669ms, 646w, 629vw.

Mass spectral data: *M/z* 179 (10), 178 (100), 177 (75), 176 (14), 163 (6), 151 (45), 150 (32), 149 (13), 148 (7), 137 (15), 136 (23), 135 (9), 134 (15), 133 (5), 123 (8), 122 (10), 111 (9), 109 (7), 108 (9), 107 (7), 95 (5), 83 (7), 81 (7), 80 (6), 79 (6).

1,3-Dimethyl-2-(imidazol-1'-yl)-1,3,2-diazaboracyclopentane

Prepared from 20.1 g (0.286 mol) of imidazole and 36.3 g (0.370 mol) of 1,3-dimethyl-1,3,2-diazaboracyclopentane. After 24 h of heating a glassy material had formed and 25 ml of toluene were added and the mixture was stirred at room temperature for two days. Insolubles were collected and extracted with hot benzene. The volume of the benzene solution was reduced to approximately 15 ml and after three days standing at ambient temperature 11.7 g of the desired material had precipitated. Another 9.8 g were obtained from the toluene solution by evaporation to dryness and recrystallization from benzene, resulting in a combined yield of 21.5 g (44%), m.p. 108 to 110°C. The material can be sublimed at 130°C/0.1 Torr. Analysis: Found: C, 51.47; H, 8.15; N, 33.68; B, 7.07. $C_7H_{13}N_4B$ calcd.: C, 51.26; H, 7.99; N, 34.16; B, 6.59%.

NMR data: δ (^{1}H) (solution in $CDCl_3$) 8.06 (s, 1 H), 7.51 (s, 2 H), 3.78 (s, 4 H), 3.10 (s, 6 H) (for internal TMS reference subtract 0.48 ppm). δ (^{11}B) (solution in $CDCl_3$) 25.7. δ (^{13}C) (solution in $CDCl_3$) 139.1 (d of t, ^1J 206 Hz, ^2J 9 Hz), ca. 124 *, 50.4 (t, J 140 Hz), 33.1 (q, J 135 Hz). δ (^{14}N) (solution in $CDCl_3$) shoulder near —100 to —120 (N^3 of imidazole), —168 * (N^1 of imidazole), —328 * (NCH_3).

Infrared spectrum (solution in CCl_4, 4000 to 900 cm^{-1} region): 2895wm, 2925(sh), 2903(sh), 2863vs, 2800s, 1508(sh), 1504vs, 1480m, 1453vs, 1423m, 1415vs, 1362s, 1339w, 1318vs, 1300vs, 1250(sh), 1242s, 1202m, 1129vw, 1101m, 1096s, 1070s, 1020vs, 962m, 908m.

Mass spectral data: *M/z* 165 (10), 164 (93), 163 (100), 162 (22), 148 (16), 147 (8), 136 (10), 121 (13), 120 (10), 119 (8), 109 (5), 108 (5), 107 (7), 106 (5), 95 (11), 94 (15), 93 (7), 92 (6), 81 (6), 80 (6), 79 (5), 78 (11), 77 (7), 68 (5), 67 (18), 66 (9), 65 (6), 54 (7), 53 (8), 52 (6), 51 (15), 50 (8), 43 (10), 42 (5), 41 (10), 40 (11), 39 (8), 38 (7), 26 (5), 25 (5).

Pyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane (V)

Upon mixing of 3.4 g (0.050 mol) of pyrazole and 8.5 g (0.052 mol) of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane (III) an exothermic reaction occurs resulting in the formation of a viscous liquid. On cooling to room temperature, crystallization occurs. The crude material is recrystallized from 50 ml of hexane and is dried under vacuum at room temperature to yield 9.9 g (85%) of the desired product, m.p. 68 to 69°C. Analysis: Found: C, 52.08; H, 7.63; N, 36.02; B, 4.41. $C_{10}H_{17}N_6B$ calcd.: C, 51.75; H, 7.38; N, 36.21; B, 4.66%.

NMR data: δ (^1H) (solution in CD_2Cl_2 internal $CHDCl_2$ as reference) 7.64 * (4 H), 7.48 * (1 H), 6.32 (*t*, 2 H), 3.11 (s, 4 H), 2.21 (s, 6 H); (solution in CD_2Cl_2, internal $CHDCl_2$ as reference, at —62°C) 8.02 (1 H), 7.67 (1 H), 7.58 (1 H), 7.37 (1 H), 6.34 * (2 H), 2.96 * (4 H), 2.09 (6 H). δ (^{11}B) (solution in C_6D_6) 4.0. δ (^{13}C) (solution in CD_2Cl_2, proton-decoupled) 139.8, 133.7, 104.7, 50.8 (CH_2), 34.5 (CH_3); (solution in CD_2Cl_2 at —64°C, proton-decoupled) 141.4, 138.0, 134.5, 132.8, 105.0, 104.3, 50.5 *, 34.6. δ (^{14}N) (solution in C_6D_6) —160 * (half-maximum band width ca. 800 Hz), —390 * (half-maximum band width ca. 1200 Hz).

Infrared spectrum (solution in CCl_4, NaCl cell) 3133(sh), 3120(sh), 3100ms, 2956s, 2920(sh), 2898(sh), 2875s, 2853m, 2795s, 2715w, 1755(sh), 1717w(br), 1526(sh), 1508(sh), 1501vs, 1458s, 1427(sh), 1410s, 1384vs, 1365w, 1338wm, 1313m, 1291vs, 1262m, 1249w, 1219vs, 1200(sh), 1183w, 1176(sh), 1157wm, 1139m, 1114wm, 1081vs, 1037vs, 997wm, 976m, 948w, 932ms, 917s, 874w, 860s, 830m.

N-Deuteriopyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane

The compound was prepared in analogous manner as V, above. NMR data: δ (^1H) (solution in CD_2Cl_2, internal $CHDCl_2$ as reference) 7.62 (s, 4 H), 6.29 (t, 2 H), 3.07 (s, 4 H), 2.17 (s, 6 H); (solution in CD_2Cl_2 at —66°C, internal $CHDCl_2$ as reference) 8.01 (s, 1 H), 7.65 (s, 1 H), 7.57 (s, 1 H), 7.36 (s, 1 H), 6.31 * (s, 2 H), 2.85 * (s, 4 H), 2.07 (s, 6 H).

Infrared spectrum (solution in CCl_4, NaCl cell) 3140vw, 3100w, 3000(sh), 2957ms, 2898(sh), 2878s, 2850m, 2797s, 2308m(br), 1715w(br), 1526(sh), 1503s, 1475(sh), 1457s(br), 1448(sh), 1411s, 1388vs, 1365w, 1341wm, 1295vs, 1279w, 1243wm, 1224s, 1192s, 1167w, 1139vw, 1116(sh), 1093vs, 1075(sh), 1046s, 1039m, 1005wm, 978w, 950m, 925w, 919wm, 899wm, 8[illegible] 858m.

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