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BORON–NITROGEN COMPOUNDS

XCVI *. STUDIES OF THE CHEMICAL BEHAVIOR OF MONOMERIC PYRAZOL-1-YLBORANES

FAZLUL ALAM and KURT NIEDENZU
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506 (U.S.A.)
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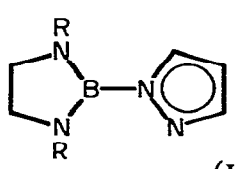
Summary

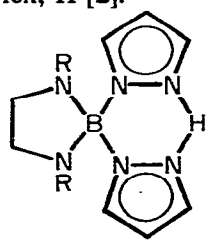
Two 1,3-dimethyl-2-(methylpyrazol-1′-yl)-1,3,2-diazaboracyclopentanes have been prepared. The interaction of such monomeric pyrazol-1-ylboranes containing trigonal boron with pyrazoles has been examined and 1/1 molar addition compounds have been identified and isolated. Labelling experiments support spectroscopic evidence to suggest a mobile bridging hydrogen in the cited adducts at ambient temperature and above. Monomeric 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane reacts with (dimethylamino)dialkylboranes by an exchange of the pyrazolyl with the dimethylamino group. A cyclic transition state involving a B_2N_3 ring system is suggested for this process in which the corresponding 2-dimethylamino-1,3,2-diazaboracyclopentane and *B*-tetraalkylpyrazaboles are the final products. The latter are also found among the reaction products of pyrazole adducts of monomeric pyrazol-1-ylboranes with (dimethylamino)dialkylboranes. The interaction of (dimethylamino)dialkylboranes with pyrazole gives *B*-tetraalkylpyrazaboles in essentially quantitative yield.

Introduction

Although monomeric pyrazol-1-ylboranes such as I are available by two preparative pathways [2,3], very little is yet known about the chemistry of such species. However, it has been shown that the boron atom of I is sufficiently acidic to react with pyrazole to form a 1/1 molar complex, II [2].



(I)



(II)

* For Part XCV, see ref. 1.

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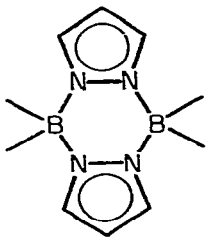
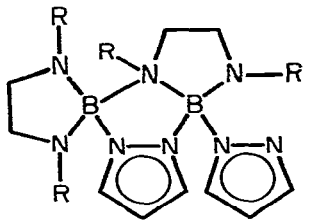
On the other hand, the acidity of boron in I ($R = CH_3$) is insufficient to promote dimerization to yield pyrazaboles of type III. This latter observation also suggests that the pyrazole-N(2) atom of I is less basic than that of free pyrazole. In this context it is worth noting that at low temperatures I dimerizes but in unusual fashion inasmuch as IV is formed rather than a pyrazabole of type III [2].



(III)

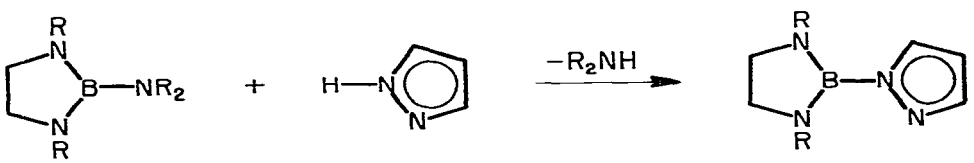


(IV)

The cited observations seem to dispute that the lack of dimerization of I to yield a pyrazabole of type III is due to steric factors; rather it seems to be clearly related to electronic effects. However, this feature has not yet been explored in detail nor are any additional studies on monomeric pyrazol-1-ylboranes known. The present work reports the preparation of two such new species and is a first effort to study their chemical behavior. It is limited to an investigation of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentanes.

Preparation and characterization of 2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentanes

Previous procedures for the preparation of monomeric pyrazol-1-ylboranes involve the condensation of 1,3-dimethyl-1,3,2-diazaboracycloalkanes with pyrazole [2] or the symmetrical cleavage of pyrazabole and C-substituted derivatives thereof by reaction with *N,N*-dimethyl α,ω-diaminoalkanes [3]. As a possible alternate synthesis, the transamination of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane (V) with pyrazoles has now been studied. It was found that, although the reaction proceeds according to eq. 1, the yield of the desired product is exceedingly low and substantial amounts of dimethylamine-tris(pyrazol-1-yl)borane, $(CH_3)_2HN{-}Bpz_3$ (pz = pyrazol-1-yl = $N_2C_3H_3$) [2], and the pyrazole adduct of the desired compound (i.e., II) were obtained as by-products. The interaction of V with 3,5-dimethylpyrazole gave similar results.



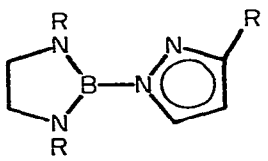
(1)

(V) (I)

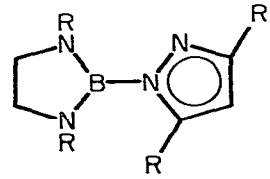
It is reasonable to assume that initial reaction according to eq. 1 does, indeed, occur. However, once formed, I reacts more readily with remaining free pyrazole as compared to the transamination procedure and, thus, II is formed. This interpreta-

tion also suggests that the initial step in a reaction according to eq. 1 may be a Lewis acid–base type interaction of the two reagents and that the Lewis acidity of boron versus pyrazole is greater in I than in V. Moreover, once formed II seems to react quite readily with the system dimethylamine/pyrazole leading to the observed formation of $(CH_3)_2HN{-}Bpz_3$. This event is not surprising in view of the ready formation of the latter species on reaction of tris(dimethylamino)borane with pyrazole [4]. Under these aspects, transamination according to eq. 1 cannot be recommended for the preparation of compounds of type I.

As stated above, the initial step of the transamination according to eq. 1 seems to be the formation of a 1/1 molar adduct of the reactants. This interpretation is supported by the fact that when 1,3-dimethyl-1,3,2-diazaboracyclopentane is mixed with an equimolar quantity of 3-methylpyrazole (solution in $CDCl_3$) at room temperature and a ^{11}B NMR spectrum is recorded of this mixture, only one resonance signal, $\delta(^{11}B)$ 0.9 ppm, indicative of four-coordinate boron, is observed. Only on prolonged heating of the neat mixture of the reagents does the condensation occur with elimination of hydrogen leading to VI (containing trigonal boron). Compound VII is prepared in similar fashion. Hence, although time-consuming, the condensation reaction works well even with C-methylated pyrazoles.



(VI)



(VII)

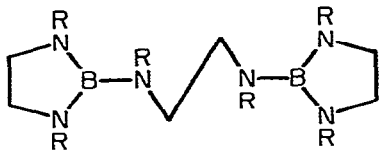
The ambient temperature NMR spectra of VI give no evidence for borotropism (i.e., 1,2-shift of the boryl group) as was observed for other pyrazol-1-ylboranes [2]. Rather, the structure of VI with the pyrazole-bonded methyl group being located at the indicated C(3′) atom can be deduced from the spectral data. The following signals are observed for the annular C and H atoms of the pyrazole ring of VI:

Position	$\delta(^1H)$ (ppm)	$\delta(^{13}C)$ (ppm)
3′	–	150.2
4′	6.06	105.9
5′	7.50	133.8

The foregoing assignments are based on the observation that of the two ^{13}C NMR signals assignable to the 3′ or 5′ position, respectively, the higher field signal is much less affected by changes at the N(2′) site of such monomeric pyrazol-1-ylboranes than is the lower field signal (see below). The sharpness and complete lack of additional lines disputes the presence of an isomer, i.e., with the methyl group in the 5′ position of the pyrazole ring of VI. The ^{13}C NMR signals of VII can be assigned on that same basis.

It has been reported that I undergoes an auto-rearrangement (of yet undetermined nature) on standing at ambient temperature; it can be completely reversed by simple redistillation of the material [2]. An analogous auto-rearrangement (indi-

cated by the appearance of many additional NMR lines) was observed on standing of VI but not for VII. This contrasting behavior may be due to a better steric protection of the boron atom in VII (as compared to I and VI) by the various methyl groups (which may also account for the cited lack of borotropism for VI). This interpretation tends to suggest that the auto-rearrangement is induced by a Lewis acid–base type interaction at the boron site and this feature is under further investigation. However, one of the various products resulting from the auto-rearrangement (prepared by an independent synthesis) was identified as VIII.

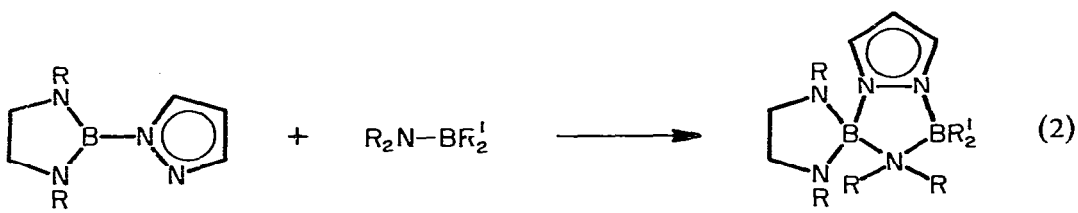


(VIII)

The ^{11}B NMR spectrum of VIII exhibits a signal $\delta(^{11}B)$ 27.4 ppm and ^{13}C NMR signals are observed at $\delta(^{13}C)$ 52.0, 49.6, 36.5 and 35.4 ppm. These same signals are clearly identified in the relevant spectra of the auto-rearranged compounds I and VI.

Reaction of the pyrazol-1-ylborane I with (dimethylamino)dialkylboranes

When equimolar amounts of I and (dimethylamino)diethylborane are mixed at −78°C, the mixture is then warmed to −20°C, and a ^{13}C NMR spectrum is recorded, the data clearly illustrate the exclusive existence of the adduct IX (R = CH_3, R′ = C_2H_5) which is formed according to eq. 2. (It is worth noting that the central B_2N_3 ring of IX has a counterpart in the previously reported dimer IV [2].)

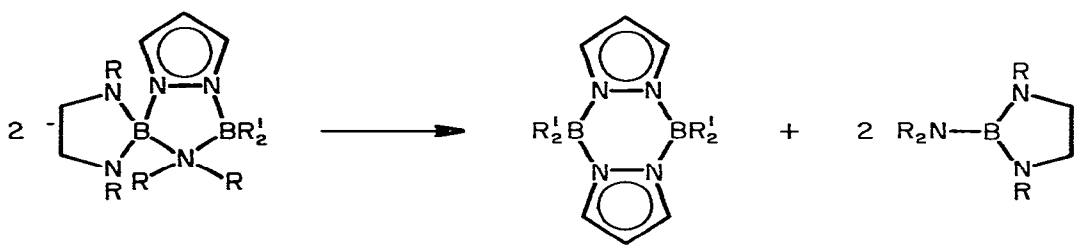


(I) (IX) (2)

The NMR signals of IX with $\delta(^{13}C)$ 134.6 (C(3′)) and 133.5 ppm (C(5′)) as well as 106.3 ppm (C(4′)) are readily assigned to the indicated pyrazole carbon atoms. These assignments are based on the relevant NMR data of I [2]; it is worth noting here that the signal of C(3′) shifts from 141.2 ppm in I to 134.6 ppm in IX whereas that of C(5′) is hardly affected (133.0 ppm in I versus 133.5 ppm in IX). This observation lends credence to the assignment of C(3′) in both I and VI (see above). Additional NMR signals of IX are readily assigned on comparison with the relevant spectra of I, II and $(CH_3)_2NB(C_2H_5)_2$ and the data are summarized as follows:

$\delta(^{13}C)$ (ppm)	Assignment
134.6	C(3') of pyrazole ring
133.5	C(5') of pyrazole ring
106.3	C(4') of pyrazole ring
53.2/51.9	anular C's of ethylenediamine moiety
39.0/38.7	dimethylamino moiety
35.4/34.3	N-bonded CH_3 of ethylenediamine moiety
18.1 8.9/8.7 }	boron-bonded C_2H_5 groups

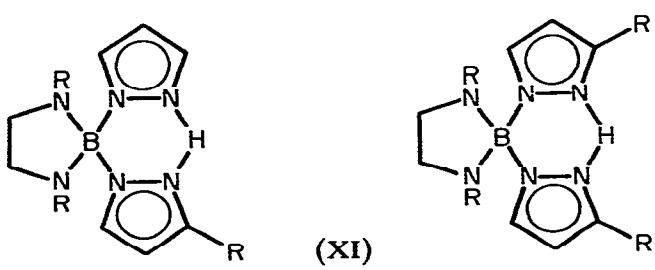
However, near room temperature IX is thermally unstable and decomposes in an exothermic reaction with the formation of *B*-tetraethylpyrazabole (X, $R' = C_2H_5$) and 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane as illustrated in eq. 3. This observation suggests a single type of cleavage of IX in which the NR_2 group exhibits a strong preference for bonding to the boron which is incorporated in the heterocyclic system rather than that of the BR'_2 group.



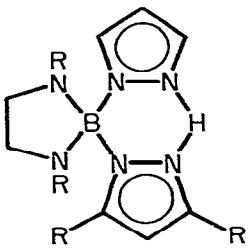
(IX) (X) (3)

Pyrazole adducts of monomeric pyrazol-1-ylboranes

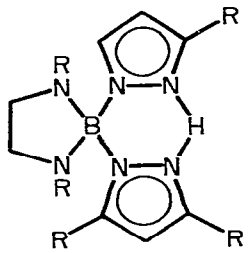
As noted above, the monomeric pyrazol-1-ylborane I reacts readily with free pyrazole to form the 1/1 molar adduct II. NMR spectral data recorded on a solution of II at room temperature indicated the equivalence of both pyrazole moieties of II under these conditions [2]. This is now verified inasmuch as spectral data on the adduct formed between I and 3-methylpyrazole are exactly identical to those of the adduct formed between VI and pyrazole. This observation also localizes the position of the (pyrazole)methyl group as illustrated in XI. Similarly, XII was obtained on interaction of VI with 3-methylpyrazole (XIII) was obtained from I and 3,5-dimethylpyrazole, and XIV was prepared from VI and 3,5-dimethylpyrazole.



(XI) (XII)



(XIII)

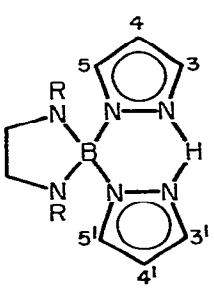


(XIV)

However, the ambient temperature ^{11}B NMR spectra of XII, XIII and XIV also show the presence of some uncomplexed trigonal borane (less than 10% in each case). Moreover, on interaction of VII with 3,5-dimethylpyrazole, only very little adduct formation is observed: The ^{11}B NMR spectrum of the reaction mixture (solution in $CDCl_3$) exhibits only a very minor signal for four-coordinate boron with $\delta(^{11}B)$ 4.1 ppm but a very strong signal for trigonal boron with $\delta(^{11}B)$ 25.4 ppm (half-maximum band width 165 Hz), i.e., essentially that of VII. This observation suggests steric impairment of the adduct formation by the methyl groups. Low-temperature NMR spectra do not provide a conclusive answer, due to the documented localization of the bridging proton in the expected adducts at lower temperatures [2]. Indeed, a ^{13}C NMR spectrum of XIII recorded at $-59°C$ exhibits six signals for the two central annular carbon atoms of the pyrazole rings suggesting random localization of the "bridging" protons as well as the presence of uncomplexed pyrazole moieties.

In any case, assignments of the ambient temperature ^1H and ^{13}C chemical shifts for the pyrazole atoms in XI to XIV can be made and are summarized below using the numbering as shown in XV (an asterisk denotes a broad signal):

Position	XI		XII		XIII		XIV	
	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
3	7.61	140.1	–	148.5*	7.62*	138.5*	–	149*
4	6.28	105.1	6.02	104.6	6.21	105.2	6.02	105.0
5	7.61	133.7	7.42*	134.0*	7.62*	133.4*	7.56*	134.5*
3′	–	148.3*	–	148.5*	–	144*	–	144*
4′	6.04	105.0	6.02	104.6	5.75	104.6	5.79	105.0
5′	7.39	134.3	7.42*	134.0*	–	144*	–	144*



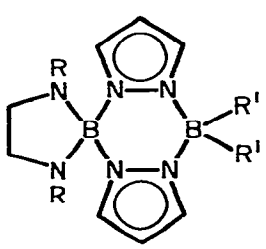
(XV)

A comparison of the ^{13}C NMR data for the methylpyrazole ring in VI versus XI provides additional support for the assignments of C(3′) and C(5′) in VI as presented above, since the former signal is much more affected by complexation (to yield XI) than is the latter. Furthermore, it is of interest to note that the chemical shift of the bridging proton was found to be very sensitive to the concentration and nature of solvent. For example, $\delta(^1H)$ of the bridging proton in XI shifts from 7.35 ppm (saturated solution in $CDCl_3$) to 7.03 ppm (dilute solution in $CDCl_3$) or 8.07 ppm (saturated solution in CCl_4); and for XII that same signal is observed with $\delta(^1H)$ 7.51 ppm (saturated solution in $CDCl_3$) but shifts to 7.00 ppm on tenfold dilution. These latter observations may suggest a weak N–H–N bond and, hence, the various species may be viewed as undissociated acids of a bis(pyrazol-1-yl)borate anion. If this can be verified, e.g., by preparation of salts of such anions (which is now being studied), it offers an interesting new perspective on the coordination chemistry of such poly(pyrazol-1-yl)borate ions. So far, such species are known only with identical pyrazole groups bonded to a given boron atom [5]. However, having two different such moieties at the boron and complexing these then with transition metal derivatives can render the transition metal atom to be a chiral center! The indicated possibility of tailoring poly(pyrazol-1-yl)borate anions exhibiting a range of electronic and steric effects coupled with the great stability of their complexes should considerably enhance their even already wide use in coordination chemistry.

Reaction of pyrazole adducts of monomeric pyrazol-1-ylboranes with (dimethylamino)dialkylboranes

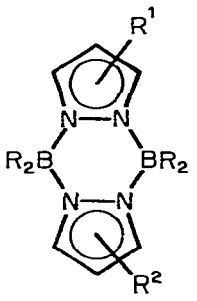
In view of the fact that the bridging hydrogen atom in pyrazole adducts of monomeric pyrazol-1-ylboranes of type II is not localized at a given pyrazole ring (see above) the reaction of such adducts with (dimethylamino)dialkylboranes was also studied. It was thought that the cited hydrogen atom could be displaced to yield, with the release of dimethylamine, unsymmetrical pyrazaboles of type XVI.

However, when the two reagents are mixed at low temperatures, no reaction is observed. Only at elevated temperatures does reaction occur and the pyrazabole X is formed in essentially quantitative yield (based on reacted (dimethylamino)dialkylborane). Major by-products are the aminoborane V and the monomeric pyrazol-1-ylborane I. This makes it appear that I serves merely as pyrazole carrier (since (dimethylamino)dialkylboranes were also found to react readily with pyrazole to form pyrazaboles of type X) which, of course, is not in consonance with the spectroscopic data found for adducts of type II. The simple carrier function, however, can be tested by a preparative experiment. For example, if one of the



(XVI)

pyrazole rings of II is labelled with a methyl group, e.g., XI, only the "coordinated" molecule should be converted to the pyrazabole, unless the bridging hydrogen atom is indeed delocalized. Hence, XI was treated with an equimolar amount of (dimethylamino)dipropylborane. Three pyrazaboles, XVIIa to XVIIc, were obtained as reaction products in approximately 10/5/1 molar ratio (based on mass spectroscopic data).



(XVIIa: $R = C_3H_7$, $R^1 = R^2 = H$;

XVIIb: $R = CH_3$, $R^1 = H$, $R^2 = CH_3$;

XVIIc: $R = CH_3$, $R^1 = R^2 = CH_3$)

This observation suggests prototropism of the bridging hydrogen as indicated in XI but is not completely conclusive. First of all, the mixture of the pyrazaboles could not be separated and the given product distribution is only approximate. Secondly, a scrambling of different pyrazaboles via symmetrical cleavage and recombination of the fragments, though unlikely, cannot be completely excluded. And thirdly, a partial dissociation of XI at the elevated reaction temperature may occur and may be affected by a steric influence of the C-bonded methyl group of XI. Moreover, it is possible that an unsymmetrical pyrazabole of type XIV is indeed formed at the elevated reaction temperatures, but these latter are sufficient to cause symmetrization to yield the cited *B*-tetraalkylpyrazaboles XVII. However, in conjunction with the NMR data on II as well as XI to XV, the preparative findings lend credence to the existence of a delocalized bridging hydrogen in these adducts.

Conclusions

The transamination of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane with pyrazoles is not well suited for the preparation of monomeric 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentanes containing trigonal boron. Rather, the high Lewis acidity of boron incorporated into a 1,3,2-diazaboracyclopentane ring promotes secondary reactions leading to four-coordinate boron derivatives and yields of the desired products are low. However, the latter are readily obtained by condensation of 1,3-dimethyl-1,3,2-diazaboracyclopentane with pyrazoles, a process which proceeds via an intermediate containing four-coordinate boron.

The cited Lewis acidity of boron in a 1,3,2-diazaboracyclopentane ring is further documented by the formation of 1/1 molar adducts of 1,3-dimethyl-2-(pyrazol-1′-

yl)-1,3,2-diazaboracyclopentanes with pyrazoles. Steric crowding at the boron site may impair such adduct formation. NMR spectroscopic and preparative data suggest that the N-bonded proton of the adducts is delocalized and the species may be viewed as the undissociated acids of bis(pyrazol-1-yl)borates.

The monomeric pyrazol-1-ylboranes as well as their pyrazole adducts react with (dimethylamino)dialkylboranes in a ligand exchange process to yield, among other products, *B*-tetraalkylpyrazaboles. The latter can also be prepared directly from (dimethylamino)dialkylboranes and free pyrazole.

Experimental

All reactions and transfers were carried out under a dry argon atmosphere. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorr.) were determined in sealed capillaries on a Mel-Temp block. Infrared spectra were recorded on a Perkin-Elmer Model 621 instrument under standard operating conditions. 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, CFT-20 and/or EM-390 instrument. Boron-11 (reference: $(C_2H_5)_2OBF_3$ capillary) NMR spectra were recorded on a Varian FT-80A spectrometer, carbon-13 NMR data were obtained on a Varian FT-80A instrument and are references to tetramethylsilane. All chemical shift data are reported in ppm with positive values indicating downfield from a given (unless otherwise noted: internal) reference. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = multiplet, sh = shoulder, br = broad.

Pyrazoles were commercial products. They were dried by treatment with a small amount of metallic sodium and subsequent distillation or sublimation. 1,3-Dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane [6], 1,3-dimethyl-1,3,2-diazaboracyclopentane [7], (dimethylamino)diethylborane [8] and (dimethylamino)di-n-propylborane [9] were prepared by the indicated literature procedures.

Reaction of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane with pyrazoles

A mixture of 38.5 g (270 mmol) of 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane and 17.6 g (258 mmol) of pyrazole was heated to gentle reflux for 2 h. A small amount of precipitate was collected and the filtrate was distilled through a 30-cm silver-mantle column to yield 11.5 g (70 mmol, 28% yield) of the desired 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane (I) identical (NMR data) to the previously described material [2]. The solid residue was combined with the solids from the preceding filtration and the material washed several times with n-hexane. The remaining 4.2 g of colorless material were identified by spectroscopic data as dimethylamine-tris(pyrazol-1-yl)borane, $(CH_3)_2HN{-}Bpz_3$ [2]. On concentration of the n-hexane washings 3.9 g of the pyrazole adduct of 1,3-dimethyl-2-(pyrazol-1′-yl)-1,3,2-diazaboracyclopentane (II) were obtained and identified by spectroscopic data [2].

In an analogous reaction employing 3,5-dimethylpyrazole only 17% of the desired

1,3-dimethyl-2-(3',5'-dimethylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VI) were obtained (characterization see below).

1,3-Dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VI)

A mixture of 24.5 g (250 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclopentane and 14.4 g (175 mmol) of 3-methylpyrazole was refluxed for 40 h, during which time the calculated amount of hydrogen was generated. The material was distilled through a 30-cm silver-mantle column to yield 29.5 g (166 mmol, 95%) of VI, b.p. 99°C/4 Torr. Analysis: Found: C, 54.18; H, 8.55; N, 31.20; B, 5.77. $C_8H_{15}N_4B$ calcd.: C, 53.97; H, 8.49; N, 31.47; B, 6.07%.

NMR data: $\delta(^1H)$ (solution in $CDCl_3$) 7.50 (d, 1H), 6.06 (d, 1H), 3.22 (s, 4H), 2.73 (s, 6H). $\delta(^{11}B)$ (neat) 27.2 (half-maximum band width 340 Hz). $\delta(^{13}C)$ (solution in $CDCl_3$) 150.2 (s), 133.8 (d, *J* 182 Hz), 105.9 (d, *J* 173 Hz), 51.0 (t, *J* 139 Hz), 33.7 (q, *J* 134 Hz), 13.1 (q, *J* 126 Hz).

1,3-Dimethyl-2-(3',5'-dimethylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VII)

In a procedure analogous to the preceeding one 19.1 g (195 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclopentane and 17.1 g (178 mmol) of 3.5-dimethylpyrazole were refluxed for 25 h. Distillation yielded 32.3 g (168 mmol, 94%) of VII, b.p. 100–103°C/1 Torr. Analysis: Found: C, 56.37; H, 9.05; N, 29.10; B, 5.16. $C_9H_{17}N_4B$ calcd.: C, 56.28; H, 8.92; N, 29.17; B, 5.63%.

NMR data: $\delta(^1H)$ (solution in $CDCl_3$) 5.83 (s, 1H), 3.29 (s, 4H), 2.54 (s, 6H), 2.24 (s, 6H). $\delta(^{11}B)$ (neat) 28.6 (half-maximum band width 420 Hz). $\delta(^{13}C)$ (solution in $CDCl_3$) 149.9 (s), 142.4 (s), 105.5 (d, *J* 170 Hz), 50.4 (t, *J* 139 Hz), 33.1 (q, *J* 134 Hz), 12.8 (q, *J* 126 Hz), 10.8 (q, *J* 127 Hz).

The mass spectrum shows the parent ion *m/z* 192.

Preparation of pyrazole adducts of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentanes (general procedure)

Equimolar amounts of a (liquid) freshly distilled 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane and a (solid) pyrazole are mixed with stirring. An exothermic reaction occurs leading to a viscous liquid product (if not, slight warming of the reaction vessel will liquefy all material) which crystallizes on cooling to room temperature and standing overnight. The adducts are readily recrystallized from solvents such as n-hexane; yields are essentially quantitative.

3-Methylpyrazole-[1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane] (XI)

Reaction of either 3-methylpyrazole with 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane (I) or of pyrazole with 1,3-dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VI) yielded the same product (XI), m.p. 74°C. Analysis: Found: C, 54.58; H, 8.00; N, 34.14; B, 4.31. $C_{11}H_{19}N_6B$ calcd.: C, 53.68; H, 7.78; N, 34.15; B, 4.39%.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.61 (d, 2H), 7.39 (d, 1H), 7.35br (1H), 6.04 (d, 1H), 3.09 (s, 4H), 2.29 (s, 9H). $\delta(^{11}B)$ 4.1 (half-maximum band width 50 Hz). $\delta(^{13}C)$ (ambient temperature) 148.3br (s), 140.1 (d, *J* 183 Hz), 134.3 (d, *J* 183 Hz), 133.7 (d, *J* 183 Hz), 105.0 (d, *J* 171 Hz), 50.8 (t, *J* 139 Hz), 34.5 (q, *J* 137 Hz), 13.4 (q, *J* 126 Hz); (−44°C, proton-decoupled) 150.4br, 146.9br, 141.7br, 138.2br, 134.2br, 133.0br, 105.0br, 50.5, 34.5, 13.6.

Infrared spectrum (solution in CCl_4, NaCl cell): 3135(sh), 3095ms, 3056(sh), 2955s, 2923s, 2896(sh), 2873s(br), 2851(sh), 2795s, 2712(sh), 2685(sh), 1474(sh), 1466(sh), 1458vs, 1447(sh), 1428w, 1418(sh), 1409s, 1386vs, 1365w, 1350s, 1337(sh), 1311wm, 1296wm, 1260m, 1208vs(br), 1138(sh), 1156m, 1138m, 1114w, 1106(sh), 1081s, 1036vs, 996m(br), 969(sh), 935s, 916m, 873(sh), 858s.

3-Methylpyrazole-[1,3-dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane] (XII)

This compound was prepared from 3-methylpyrazole and 1,3-dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VI); m.p. 92°C. Analysis: Found: C, 55.29; H, 8.02; N, 32.27; B, 4.09. $C_{12}H_{21}N_6B$ calcd.: C, 55.40; H, 8.14; N, 32.30; B, 4.16%.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.51br (1H), 7.42br (2H), 6.02 (d, 2H), 3.04 (s, 4H), 2.27 (s, 12H). $\delta(^{11}B)$ 3.9 (half-maximum band width 90 Hz), 32.7 (very small). $\delta(^{13}C)$ 148.5vbr, 134.0br (d, J 183 Hz), 104.6 (d, J 173 Hz), 50.4 (t, J 141 Hz), 34.1 (q, J 136 Hz), 13.1 (q, J 126 Hz).

3,5-Dimethylpyrazole-[1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane] (XIII)

This compound was prepared from 3,5-dimethylpyrazole and 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane (I); m.p. 75°C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 8.91br (1H), 7.62br (2H), 6.21 (t, 1H), 5.75 (s, 1H), 3.10br (s, 4H), 2.39br (s, 6H), 2.13 (s, 6H). $\delta(^{11}B)$ 3.8 (half-maximum band width 60 Hz), 26.0 (very small). $\delta(^{13}C)$ (30°C, proton-decoupled) 144vbr, 138.5br, 133.4br, 105.2, 104.6, 50.4, 34.1, 12.0; (10°C, proton-decoupled) 153.7, 149.4br, 144.5br, 140.3br, 134.3, 105.0, 51.3, 35.0, 12.4; (−10°C, proton-decoupled) 153.6br, 149.8, 149.4, 144.2, 141.6, 140.2br, 134.2, 104.9, 51.1, 35.2, 34.9, 12.2br; (solution in CD_2Cl_2, −59°C, proton-decoupled) 153.4, 153.1, 151.1, 149.6, 149.1, 148.0, 146.6, 146.0, 143.8, 143.3, 141.7, 139.2, 134.8, 133.9, 107.0, 106.7, 105.1, 104.6, 104.4, 103.5, 53.8, 35.1, 34.7, 13.3, 12.1, 11.3, 11.2.

3,5-Dimethylpyrazole-[1,3-dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane] (XIV)

This compound was prepared from 3,5-dimethylpyrazole and 1,3-dimethyl-2-(3'-methylpyrazol-1'-yl)-1,3,2-diazaboracyclopentane (VI); m.p. 91°C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 9.15br (1H), 7.56br (1H), 6.02 (d, 1H), 5.79 (s, 1H), 3.14br (s, 4H), 2.41br (s, 6H), 2.24 (s, 3H), 2.12 (s, 6H). $\delta(^{11}B)$ 3.5 (half-maximum band width 65 Hz), 24.8 (very small). $\delta(^{13}C)$ (ambient temperature, proton-decoupled) 149vbr, 144br, 134.5br, 105.0, 50.7, 34.1, 13.4, 12.3; (−45°C, proton-decoupled) 153.4, 153.2, 150.9, 150.3, 149.3, 148.8, 148.2, 147.5, 147.1, 146.6, 146.0br, 143.4br, 142.9, 135.4, 135.1, 134.4, 133.6, 107.3, 106.8, 105.3, 104.9, 104.7, 104.3, 103.4, 50.5, 34.9, 34.5, 13.6, 13.4, 12.0, 11.5.

Reaction of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane with (dimethylamino)diethylborane

Addition of 10.2 g (90 mmol) of (dimethylamino)diethylborane to 14.9 g (88 mmol) of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane caused an exothermic reaction. The mixture was then heated to reflux for 30 min. Volatiles (some

unreacted (dimethylamino)diethylborane and traces of tris(dimethylamino)borane) were removed at room temperature under reduced pressure and 1,3-dimethyl-2-dimethylamino-1,3,2-diazaboracyclopentane distilled off at elevated temperatures. The residue was recrystallized from n-hexane and identified (by spectroscopic data) as *B*-tetraethylpyrazabole (92% yield based on reacted (dimethylamino)diethylborane) [10].

In an analogous reaction employing (dimethylamino)di-n-propylborane, *B*-tetra-n-propylpyrazabole (characterization see below) was obtained in essentially quantitative yield (based on (dimethylamino)di-n-propylborane).

Reaction of the pyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane with (dimethylamino)di-n-propylborane

A mixture of 1.4 g (10 mmol) of (dimethylamino)di-n-propylborane and 1.9 g (8.1 mmol) of the pyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane was refluxed for 1 h. Approximately 2 g of *B*-tetra-n-propylpyrazabole were obtained after recrystallization from n-hexane (characterization see below).

Reaction of the 3-methylpyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane with (dimethylamino)di-n-propylborane

A mixture of 2.9 g (12 mmol) of the 3-methylpyrazole adduct of 1,3-dimethyl-2-(pyrazol-1'-yl)-1,3,2-diazaboracyclopentane and 1.7 g (12 mmol) of (dimethylamino)di-n-propylborane was refluxed for 5 h. The product was filtrated and the residue dissolved in methanol; three fractions of 1.0, 0.3 and 0.3 g, respectively, of solids were obtained on concentrating the solution. The first fraction was mainly *B*-tetra-n-propylpyrazabole containing about 15% methylpyrazole groups; the other two fractions contained about 40% methylpyrazole (based on ^{1}H NMR data: integration of $\delta(^1H)$ 6.42 (t) versus 6.15 (d) for the pyrazole-C(4)-bonded protons in the pyrazaboles). 1,3-Dimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane was distilled off the above filtrate and the pyrazabole XVIIc was detected in the residue (by mass spectrometry).

B-Tetra-n-propylpyrazabole (XVIIa)

A mixture of 12.6 g (90 mmol) of (dimethylamino)di-n-propylborane and 6.0 g (88 mmol) of pyrazole was refluxed for 5 h. The product solidified on cooling to room temperature and was recrystallized from ethanol to yield 13.8 g (96%) of the desired compound XVIIa, m.p. 109°C. Analysis: Found: C, 65.96; H, 10.49; N, 17.06; B, 6.47. $C_{18}H_{34}N_4B_2$ calcd.: C, 65.89; H, 10.44; N, 17.08; B, 6.59%.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.56 (d, 4H), 6.42 (t, 2H), 0.79br (s, 28H). $\delta(^{11}B)$ 1.1 (half-maximum band width 320 Hz). $\delta(^{13}C)$ (proton-decoupled) 133.4, 105.7, 29.4br, 18.4, 17.9.

Infrared spectrum (solution in CCl_4, KBr cell): 2946(br), 2916(sh), 2900(sh), 2865m, 2800(sh), 1455m, 1423m, 1349w, 1338w, 1311m, 1236s, 1213(sh), 1131m, 1085vs, 1072(sh), 1048(sh), 1024w, 983w, 929m, 898w, 885w, 853w, 769s, 761s, 630m.

Mass spectrum (10 eV): *m/z* 286 (22), 285 (100), 284 (52), 283 (7), 71 (13).

s-N,N'-Dimethyl-bis(1,3-dimethyl-1,3,2-diazaboracyclopent-2-yl)ethylenediamine (VIII)

A mixture of 19.6 g (200 mmol) of 1,3-dimethyl-1,3,2-diazaboracyclopentane and 8.8 g (100 mmol) of *N,N'*-dimethyl ethylenediamine was refluxed. After one day

hydrogen evolution became increasingly sluggish and even after two weeks only 25% of the calculated amount was evolved. Unreacted starting materials were stripped off and distillation of the residue yielded 6.3 g of VIII, b.p. 115–118°C/1 Torr, m.p. 32–33°C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 3.00 (s, 12H), 2.66 (s, 6H), 2.59 (s, 12H). $\delta(^{11}B)$ 27.4. $\delta(^{13}C)$ 52.0, 39.6, 36.5, 35.4.

References

1 W.J. Layton, K. Niedenzu and S.L. Smith, Z. Anorg. Allgem. Chem., in press; Part XCIV: see ref. 4.
2 W. Weber and K. Niedenzu, J. Organometal. Chem., 205 (1981) 147.
3 T.G. Hodgkins, K. Niedenzu, K.S. Niedenzu and S.S. Seelig, Inorg. Chem., 20 (1981) 2097.
4 K. Niedenzu, S.S. Seelig and W. Weber, Z. Anorg. Allgem. Chem., 483 (1981) 51.
5 Gmelin Handbuch der Anorganischen Chemie, Erg.-Werk (New Supplement Series) Vol. 23, Borverbindungen, Part 5, 1975, pp. 1–38; Boron Compounds 1st Suppl. Vol. 2, 1980, pp. 217–228.
6 K. Niedenzu, P.J. Busse and C.D. Miller, Inorg. Chem., 9 (1970) 977.
7 K. Niedenzu and J.S. Merriam, Inorg. Synth., 17 (1977) 164.
8 G. Abeler, H. Bayrhuber and H. Nöth, Chem. Ber., 102 (1969) 2249.
9 D.P. Emerick, L. Komorowski, J. Lipinski, F.C. Nahm and K. Niedenzu, Z. Anorg. Allgem. Chem., 468 (1980) 44.
10 S. Trofimenko, J. Amer. Chem. Soc., 89 (1967) 3165.