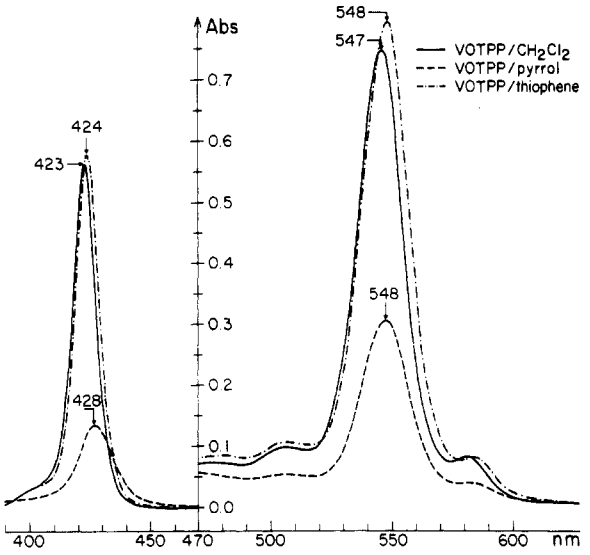

Figure 2. Comparative spectra of 1.5×10^{-5} M solutions of VO(TPP) in (a) dichloromethane, (b) pyrrole and (c) thiophene.

The calculated mean values (μ) and standard deviations (σ) for K_f were found to be the following:

	μ	σ
n-butylamine	1.24	0.060
tert-butylamine	0.07	0.017
aniline	0.186	0.005
piperidine[13]	0.75	0.050
pyridine[14]	0.148	0.015
imidazole	1.33	0.160
Me_2SO[16]	0.051	0.007

Diethylamine, pyrrole, *n*-butanol, and tetrahydrofuran weakly coordinated to VO(TPP). They bring small changes on the visible spectra but not enough to calculate K_f from spectrophotometric data. These K_f values must be smaller than those shown above. Triethylamine, acetonitrile, acetone, thiophene, and *n*-pentanethiol do not coordinate to VO(TPP).

The coordinating ability of the Lewis bases to VO(TPP) was found to follow the sequence in decreasing order nitrogenated > oxygenated $\gtrsim$ sulfurated. It was also observed that axial ligation is sensitive to steric factors in the ligand, i.e. *n*-butylamine > *tert*-butylamine > diethylamine $\gg$ triethylamine. This effect can be understood from the results of X-ray structural studies of VO(TPP).[18] Vanadium is 0.53 Å above the plane formed by the nitrogen group of the porphyrin macrocycle. This means that the ligand has to enter a small cavity in order to effect coordination while hindered nucleophiles cannot reach the metal. Bonnett et al.[19] have qualitatively observed this effect in the interactions of several nitrogenated solvents with vanadyl octaethylporphyrin.

The presence of weakly coordinating aromatic solvents such as pyrrole causes the visible spectra of VO(TPP) to change in a different manner (Figure 2). The Soret band is widened and red-shifted 5 nm. The extintion coefficient of the peak's maxima diminishes considerably: VO(TPP)/CH_2Cl_2, λ = 423 ($\epsilon = 4.07 \times 10^5$) and 547 ($\epsilon = 2.01 \times 10^4$); VO(TPP)/pyrrole: λ = 428 ($\epsilon = 1.12 \times 10^5$) and 548 ($\epsilon = 7.63 \times 10^3$). Probably the VO(TPP)–base interaction is different from the one described above. The spectra changes could be the result of π–π interactions between the aromatic rings of the pyrrole and the porphyrin macrocycle (a tetrapyrrole), rather than an axial coordination of the nitrogen in the pyrrole to the vanadium. This effect was not observed in toluene nor in thiophene.

In general, it can be concluded that axial interactions of Lewis bases with vanadium are small ($K_f < 2$) and sterically affected.

Acknowledgment. The authors thank the Venezuelan Council for Scientific and Technological Research (CONICIT) for its support under Grant S1-1387. We are grateful to Dr. G. Chuchani and R. Sânchez-Delgado for reading this paper. C.R. thanks FundaAyacucho for his scholarship.

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(14) Hambright et al.[15] reported a K_f value of 0.43 ± 15% for VO(TPP)–pyridine in chloroform at 25 °C.
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Boron Derivatives of 3-Methylpyrazole[1]

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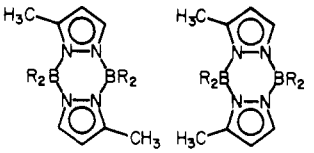
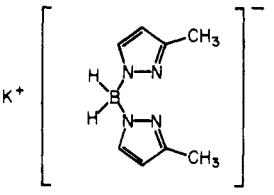
The knowledge of boron derivatives of 3-methylpyrazole, HpzMe, is extremely limited. This lack is likely due to the mobility of the N-bonded proton in 3-methylpyrazole, the replacement of which may yield isomeric products, i.e., derivatives of either 3- or 5-methylpyrazole. Indeed, when trimethylborane was reacted with 3-methylpyrazole, the resultant pyrazabole was found to be a mixture of **1** and **2** (R = CH_3) in approximately 4:3 molar ratio



1 **2**

(based on ^{1}H NMR data) that could not be separated.[2] Stereochemically pure **1** with R = C_2H_5 was obtained from the interaction of (dimethylamino)diethylborane with 1,3-dimethyl-2-(methylpyrazol-1-yl)-1,3,2-diazaboracyclohexane.[3]

The only other known boron derivative of 3-methylpyrazole, i.e., the salt $K[H_2B(pzMe)_2]$, was obtained by condensation of KBH_4 with HpzMe. On the basis of high-resolution ^{1}H NMR data, the product of this latter reaction consisted of only one isomer, **3**, with the methyl group being exclusively in the 3-position of the pyrazole ring.[4]



3

We have now found that the salts $K[HB(pzMe)_3]$ and $K[B(pzMe)_4]$, which are also readily obtained from the interaction of KBH_4 with HpzMe, analogously exist in only one isomeric form corresponding to **3**.

As expected, reaction according to eq 1 yielded the two isomers **1** and **2** (R = H), which were obtained in approximately 3:2 molar ratio. It seems that base displacement is the first step of the reaction. For steric reasons, this should result in the formation

$$2HpzMe + 2(CH_3)_3N{\cdot}BH_3 \rightarrow 2(CH_3)_3N + 2H_2 + H_2B(\mu\text{-}pzMe)_2BH_2 \quad (1)$$

(1) Boron-Nitrogen Compounds. 105. Part 104: see ref 11. Part 103: Bielawski, J.; Niedenzu, K.; Stewart, S. J. *Z. Naturforsch. B Anorg. Chem. Org. Chem.* **1985**, *40*, 389.
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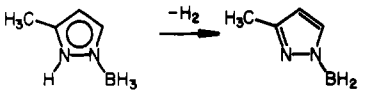
of (5-methylpyrazol-2-yl)borane, which then loses H_2 to yield the (3-methylpyrazol-1-yl)borane (**4**) as illustrated in eq 2. Sub-



(2)

4

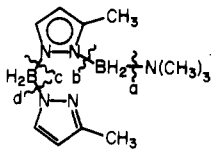
sequently, the dimerization of **4** to yield the pyrazabole **1** (R = H) could compete with a sigmatropic boryl group shift following dimerization of the thus rearranged material to yield **2** (R = H). On the basis of the observed isomer distribution in the reaction product, the former process seems to be slightly preferred.

By fractional crystallization and sublimation it was possible to enrich mixtures of **1** and **2** (R = H) to approximately 85% of an individual species. It was found that **1** is slightly less volatile and less soluble and has the higher melting point (near 90–100 °C). NMR signals for **1** (R = H): $\delta(^1H)$ = 7.49, 6.07, 3.5*, 2.34; $\delta(^{11}B)$ = −10.5. The fraction enriched with **2** (R = H) has a melting point of 72–78 °C. NMR data for **2** (R = H); $\delta(^1H)$ = 7.48, 6.07, 3.5*, 2.36; $\delta(^{11}B)$ = −9.0, −12.2. On the basis of ^{11}B NMR spectral data for $(C_2H_5)_2B(\mu\text{-pzMe}_2)_2BH_2$ ($HpzMe_2$ = 3,5-dimethylpyrazole),[5] the signal $\delta(^{11}B)$ = −12.2 is assigned to B8 of **2**, i.e., the boron atom closest to the (C)CH_3 groups.

On the basis of the structure of **3**, it was hoped that the reaction according to eq 3 would proceed with the formation of only one

$$3 + (CH_3)_3N{\cdot}BH_2I \rightarrow (CH_3)_3N + KI + 2\ (R = H) \quad (3)$$

isomer of the resultant pyrazabole, i.e., **2** (R = H). However, this was not the case, and only a mixture of **1** and **2** (R = H) in approximately 2:1 molar ratio was obtained. This result suggests at least two different pathways for the cited process. It is reasonable to assume that the first step of the overall reaction involves the formation of KI, thus providing for the neutral molecule **5**.



5

There are four donor–acceptor bonds in **5** that can be broken in the transformation process to yield a pyrazabole and free trimethylamine. Cleavage of *b* would give the initial anion $[H_2B(pzMe)_2]^-$ and the (supposedly unstable) cation $(CH_3)_3NBH_2^+$ containing trigonal boron and, thus, seems not very likely to occur; and cleavage of *d* would yield the $pzMe^-$ anion and the cation $(CH_3)_3N(H_2)B(\mu\text{-pzMe})BH_2^+$, the latter also containing trigonal boron. Simple displacement of $(CH_3)_3N$ from **5** by the two-coordinate nitrogen of the terminal methylpyrazolyl group, i.e., cleavage of *a* (the anticipated process), should lead cleanly to **2** (R = H). On the other hand, cleavage of *c* yields the trigonal neutral borane $H_2B(pzme)$, which is likely to dimerize to form **1** (R = H), provided the dimerization is faster than a sigmatropic boryl group shift from one pyrazol-1-ylborane nitrogen site to the other. (Sigmatropic boryl group shifts in monomeric trigonal pyrazol-1-ylboranes have been observed previously.[3,6,7]) The remaining fragment of the cleavage of *c*, i.e., $(CH_3)_3N{\cdot}(H_2)B(pzMe)$, should dimerize under displacement of $(CH_3)_3N$. Since the most likely donor site would appear to be the lone two-coordinate nitrogen of the methylpyrazolyl group, this process should yield **1** (R = H). The observed isomer distribution in the reaction product clearly suggests that simple displacement of $(CH_3)_3N$ in **5** is not the most favored process. Rather, the formation of pyrazol-1-ylboranes plays a significant role in the formation of the pyrazabole.

The formation of an isomer mixture in the reaction according to eq 3 accounts for some earlier observations: The reaction of poly(pyrazol-1-yl)borates with R_2BX species (where X is a ready leaving moiety) has previously[8,9] been used for the preparation of unsymmetrically 4,8-substituted pyrazaboles. However, the yields were generally not very satisfying due to the simultaneous formation of symmetrically substituted species as byproducts. Since these reactions should also involve intermediates similar to **5** and since the present study illustrates that there are at least two reasonably pathways for the conversion of such intermediates to pyrazaboles, the unsatisfactory yields of the desired products are readily explained. Moreover, the present data suggest the transient existence of monomeric pyrazol-1-ylboranes containing trigonal boron, even for reactions carried out at a relatively low temperature. This occurrence had previously[5] been established for high-temperature processes.

A mixture of **1** and **2** (R = H) was reacted with excess HpzMe to yield the *B*-pyrazolylpyrazabole $(pzMe)_2B(\mu\text{-pzMe})_2B(pzMe)_2$. The reaction proceeded smoothly, and on the basis of ^1H NMR data, the terminal pzMe groups of the product are exclusively boron bonded at the same nitrogen site, i.e., most likely forming the 3-methylpyrazol-1-yl derivative. Isomers could not be detected in the ^{11}B NMR spectrum, where only one signal at $\delta(^{11}B)$ = −0.6 ($h_{1/2}$ = 42 Hz) was observed. On the basis of digital resolution, the ^{11}B chemical shifts of the possible isomers cannot differ by more than 0.1–0.2 ppm. (Note: $\delta(^{11}B)$ of the structurally related $(pzMe_2)_2B(\mu\text{-pzMe}_2)_2B(pzMe_2)_2$ is observed at −0.7 ppm.[5]) In contrast to the starting material, the $(pzMe_2)_2B(\mu\text{-pzMe}_2)_2B(pzMe_2)_2$ NMR signal for the CH_3 groups of the bridging pzMe moieties at lower field was found to be the more intensive in the product. Unless the effect of boron substitution would cause a crossover of signals, one must assume that the isomer distribution with respect to the location of the cited groups was changed during the course of the reaction. This can be explained only by an opening of the central B_2N_4 ring during the (high-temperature) process, most likely a complete symmetrical cleavage of the pyrazabole molecule.

Reaction of a mixture of **1** and **2** (R = H) with elemental bromine gave the *B*-tetrabromo species. Surprisingly, the ^1H and ^{11}B NMR data suggest the presence of only one isomer in the product. On the other hand, this observation is disputed by the 8 °C melting range of the material. Presumably, the latter contains a planar B_2N_2 ring;[9-11] this event would seem to be more likely to cause an accidental overlap of the NMR signals of isomers than in species containing the B_2N_2 ring in the (more usual) boat conformation. This interpretation is supported by the fact that the ^1H NMR signals of the brominated pyrazabole $Br_2B(\mu\text{-pzMe})_2BBr_2$ are distinctly broader than those normally observed for stereochemically pure pyrazaboles.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory results. Melting points (uncorrected) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 spectrometer. Chemical shift data are given in ppm, with positive values indicating downfield from the reference (internal Me_4Si for ^1H, external Et_2OBF_3 for ^{11}B); an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer under standard operating conditions (frequencies in cm^{-1}).

Potassium Dihydrobis(3-methylpyrazol-1-yl)borate. The salt was prepared by basically following the earlier[4] procedure. When a mixture of 50 g (609 mmol) of 3-methylpyrazole and 10 g (185 mmol) of potassium tetrahydroborate was heated to 110–120 °C for 3.5 h, an almost clear melt was obtained and hydrogen evolution essentially ceased. A few solid particles were mechanically removed, and the clear melt was poured with stirring into 150 mL of benzene. The insoluble material was collected, washed with benzene and twice with petroleum ether, and dried under vacuum: 38 g (96%); mp 217 °C (lit.[4] mp 204–206 °C).

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NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.29 (1 H, d), 5.75 (1 H, d), 2.16 (3 H, s); $\delta(^{11}B)$ = −6.9 (t, J = 100). Additional ^1H NMR data recorded in various solvents have been reported elsewhere.[4] IR spectrum: ν(BH) = 2400–2300 (s, br).

Potassium Hydrotris(3-methylpyrazol-1-yl)borate. A mixture of 10 g (185 mmol) of potassium tetrahydroborate and 50 g (609 mmol) of 3-methylpyrazole was slowly heated to 180–190 °C and was kept at the latter temperature for approximately 4.5 h. After that time, the essentially clear melt started to solidify. The temperature was maintained for another 45 min, and the reaction was then stopped. After cooling to room temperature, the material was crushed and washed with copious amounts of benzene and then with 50 mL of petroleum ether and was dried under vacuum: 51 g (93%); mp 244–246 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 7.41 (1 H, d, J = 1.9), 5.81 (1 H, d, J = 1.7), 2.19 (3 H, s); $\delta(^{11}B)$ = −1.3 (d, J = 105). The boron-bonded H was not observed.

Potassium Tetrakis(3-methylpyrazol-1-yl)borate. A mixture of 2.7 g (50 mmol) of potassium tetrahydroborate and 20 g (250 mmol) of 3-methylpyrazole was heated to maintain gentle reflux of the excess 3-methylpyrazole for 12 h. After that period of time, the mixture began to turn yellow and the reaction was stopped. The solid but moist material was crushed under benzene cover and washed with copious amounts of benzene. The colorless insoluble product was collected and dried under vacuum; 16.9 g (90%). An analytical sample was prepared by dissolving the crude material in methanol and precipitation with dichloromethane to give an asbestos-like material, mp near 340 °C dec.

NMR data (solution in CD_3OD): $\delta(^1H)$ = 7.21 (1 H, d, J = 1.8), 5.93 (1 H, d, J = 2.1), 2.23 (3 H, s); $\delta(^{11}B)$ = +0.9 (s, $h_{1/2}$ = 20 Hz).

1,5(7)-Dimethylpyrazabole. A mixture of 18.25 g (0.25 mol) of trimethylamine–borane, 20.44 g (0.25 mol) of 3-methylpyrazole, and 250 mL of toluene was heated to gentle reflux for 6 h. After it was cooled to room temperature, a small amount of gelatinous material was filtered off and toluene was removed from the clear filtrate under reduced pressure. The remaining crude material was recrystallized from ethanol: 16.64 g (71% yield); mp 68–88 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.29 (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H; ratio approximately 2:3); $\delta(^{11}B)$ = −9.0 (t, J = 105) + −12.2 (t, J = 105, ca. 2 B), −10.5 (t, J = 105, ca. 3 B).

Alternate Procedure. A mixture of 7.0 g (32.7 mmol) of potassium dihydrobis(3-methylpyrazol-1-yl)borate, 6.5 g (32.7 mmol) of trimethylamine–iodoborane,[12] and 150 mL of toluene was heated with stirring first for 12 h at 70 °C, another 12 h at 85 °C, and finally 4 h to gentle reflux. After cooling to room temperature, the mixture was filtered and toluene was evaporated from the clear filtrate. The residue was recrystallized from ethanol: 4.7 g (61%); mp 74–84 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.28 (1 H, two overlapping unresolved d), 6.07 (1 H, two overlapping unresolved d), ca. 3.5** (2 H), 2.36 (s) + 2.34 (s) (3 H, ratio approximately 1:2); $\delta(^{11}B)$ = −9.0 + −12.2 (ca. 1 B), −10.5 (ca. 2 B). IR: ν(BH) = 2448 (ms), 2395–2340 (s, br).

1,5(7)-Dimethyl-4,4,8,8-tetrabromopyrazabole. A solution of 3.0 mL (59 mmol) of Br_2 in 15 mL of CH_2Br_2 was added dropwise to a saturated solution of 1,5(7)-dimethylpyrazabole in (ca. 15 mL) CH_2Br_2. Subsequently, the mixture was refluxed for 30 min. After the mixture was cooled to room temperature, colorless crystals of the desired compound precipitated and were collected, washed with a small amount of CH_2Br_2 and then petroleum ether, and dried under vacuum: 5.42 g (67%); mp 249–257 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.51* (1 H, unresolved d), 6.60* (1 H, unresolved d), 2.88* (3 H, s); $\delta(^{11}B)$ = −7.4 (s, $h_{1/2}$ = 25 Hz).

1,5(7)-Dimethyl-4,4,8,8-tetrakis(methylpyrazol-1-yl)pyrazabole. A mixture of 9.4 g (50 mmol) of 1,5(7)-dimethylpyrazabole and 20 g (244 mmol) of 3-methylpyrazole was slowly heated in an oil bath. Hydrogen evolution began at a bath temperature near 130 °C. After 6 h, the temperature was slowly increased to reflux (of the excess methylpyrazole), which was maintained for 12 h. After the mixture was cooled to room temperature, 50 mL of petroleum ether was added to the viscous oil and the mixture was stirred for several hours to give a solid precipitate of the desired crude product. The latter was collected, dried, and recrystallized from cyclohexane: 16.2 g (64%); mp 240–242 °C.

^1H NMR data (solution in CDL_3): δ(terminal pyrazolyl groups) = 6.49 (1 H, d, J = 2.4), 5.72 (1 H, d, J = 2.5), 2.19 (3 H, s); δ(bridging pyrazolyl groups) (isomer A) = 7.29 (d, J = 2.4), 6.27 (d, J = 2.5), 1.79 (s); δ(bridging pyrazolyl groups) (isomer B) = 7.42 (d, J = 2.5), 6.55 (unresolved d), 1.72 (s); ratio A:B ca. 2:1. $\delta(^{11}B)$ = −0.6 (s, $h_{1/2}$ = 40 Hz).

Acknowledgment. This work was supported by the Office of Naval Research.

Additions and Corrections

1984, Volume 23

Mary Ellen Foss Sheridan,* Moo-Jin Jun, and Chui Fan Liu*: Synthesis and Stereochemistry of Dichlororhodium(III) Complexes of Ethylenediamine-*N*,*N*′-di-(*S*)-α-propionic Acid.

Page 1485. Work described represents the Dissertation of Mary Ellen Sheridan, University of Illinois at Chicago, 1970. Inquiries may be addressed to Dr. Sheridan at the Office of Sponsored Program Development, State University of New York at Binghamton, Binghamton, NY 13901.—Chui Fan Liu and Mary Ellen Foss Sheridan