Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and Polymer Products Department, E. I. du Pont de Nemours and Company, Inc., Parkersburg, West Virginia 26101

Polyboron Spiro Cations Based on Bridging Dipyrazolylboryl Units[1]

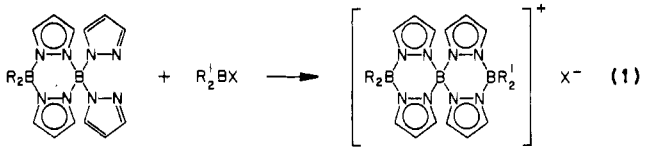
C. M. CLARKE,[†] K. NIEDENZU,*[†] P. M. NIEDENZU,[†] and S. TROFIMENKO[‡]

Received November 27, 1984

Syntheses are described for polyboron spiro cations of the types $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BR'_2]^+$ (pz = pyrazolyl = $N_2C_3H_3$; R = R' = H, R = H and R' = C_2H_5, or R = R' = C_2H_5) and $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BR_2]^{2+}$ (R = H, C_2H_5), which were obtained by reaction of *B*-pyrazol-1'-ylpyrazaboles with $(CH_3)_3NBH_2I$ or $(C_2H_5)_2BOts$ (ts = tosyl), respectively. In addition, an intermediate species containing both terminal and bridging pyrazolyl groups, i.e. $[(CH_3)_3NBH_2(\mu\text{-pz})B(pz)(\mu\text{-pz})_2B(pz)(\mu\text{-pz})BH_2N(CH_3)_3]^{2+}$, was identified and characterized. NMR data of the various species are reported; specific assignments of ^1H and ^{13}C NMR signals to individual pyrazolyl groups were made on the basis of HOMCOR and HETCOR 2D NMR studies.

Introduction

The ability of polypyrazol-1-ylborate ions, $[B(pz)_{4-n}R_n]^-$ (pz = pyrazolyl = $N_2C_3H_3$; R = noncoordinating ligand; n = 0–2), to act as uninegative polydentate ligands has been well established, and numerous metal complexes employing polypyrazol-1-ylborate groups have been described.[2] The terminal pyrazolyl groups of (the neutral) *B*-pyrazol-1'-ylpyrazaboles should also exhibit coordinating ability. Indeed, a brief note reports the interaction of 4,4-diethyl-8,8-dipyrazol-1'-ylpyrazabole, $(C_2H_5)_2B(\mu\text{-pz})_2B(pz)_2$, and 4,4,8,8-tetrapyrazol-1'-ylpyrazabole, $(pz)_2B(\mu\text{-pz})_2B(pz)_2$, with $(C_2H_5)_2BOts$ (ts = tosyl) or π-allylpalladium chloride dimer, but few experimental details were given.[3] The present study describes the interaction of *B*-pyrazol-1'-ylpyrazaboles with boranes containing a ready leaving group according to the general eq 1. Thus,



(1)

the basic reaction involves the conversion of two boron-bonded terminal pyrazolyl groups into units that bridge to an additional boron atom; the latter then carries a formal 1+ charge.

Experimental Section

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

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal Me_4Si for ^1H and ^{13}C NMR, external $Et_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, and m = unresolved multiplet and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Details for HOMCOR and HETCOR 2D NMR experiments have been described elsewhere.[4]

$[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^+PF_6^-$. A solution of 1.99 g (10 mmol) of trimethylamine–iodoborane[5] in 150 mL of mesitylene was added to a solution of 2.92 g (10 mmol) of 4,4-dipyrazol-1'-ylpyrazabole[6] in 25 mL of toluene. The stirred mixture was slowly warmed to reflux over a period of 6 h, and reflux was then maintained for 25 h. After the mixture was cooled to room temperature, the precipitate was collected, washed with toluene and then with petroleum ether, and dried in vacuum. The crude product (3.6 g) was dissolved in 30 mL of water, and a small amount of insoluble material was filtered off. A concentrated aqueous solution of ammonium hexafluorophosphate was added to the clear filtrate until no further precipitate formed. The precipitate was collected, washed with water, and dried to give 2.4 g (53%) of the desired material, which starts shrinking near 150 °C and melts (with decomposition) at 165–168 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ 8.18 (1 H, unresolved d), 7.73 (1 H, d, J = 2.4), 6.72 (1 H, t, J = 2.2), ca. 3.5* (1 H); $\delta(^{11}B)$ −1.3 (1 B), −7.7* (2 B, sharpens in proton-decoupled spectrum); $\delta(^{13}C)$ (proton decoupled) = 141.1, 139.3, 110.3.

$[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+PF_6^-$. To a solution of 2.92 g (10 mmol) of 4,4-dipyrazol-1'-ylpyrazabole[6] in 100 mL of toluene was added slightly more than 2 molar equiv of a standard solution of diethylboryl tosylate[7] in toluene. The mixture was refluxed for 2 h. On cooling, a viscous oil settled and the toluene was decanted. The oil was shaken briefly with three 25-mL portions of toluene and then dissolved in 25 mL of water. After filtration, a concentrated aqueous solution of ammonium hexafluorophosphate was added to the clear filtrate until no further precipitate was formed. The precipitate was collected, washed with water, and dried to give 2.2 g (43.5%) of the title compound, mp 168–171 °C dec.

NMR data (solution in CD_3CN): $\delta(^1H)$ 8.23 (1 H, unresolved d), 8.18 (1 H, unresolved d), 7.94 (1 H, unresolved d), 7.41 (1 H, unresolved d), 6.84 (1 H, ill-resolved t, $J \simeq 2.2$), 6.70 (1 H, ill-resolved t, $J \simeq 2.6$), ca. 3.4* (1 H), 0.86 (2 H, q, $J \simeq 7.3$), 0.59 (3 H, t, $J \simeq 7.5$); $\delta(^{11}B)$ + 5.2* (1 B), −1.5 (1 B), −7.5* (1 B, sharpens in proton-decoupled spectrum).

$[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+PF_6^-$. To a solution of 3.48 g (10 mmol) of 4,4-diethyl-8,8-dipyrazol-1'-ylpyrazabole[7] in 100 mL of toluene was added, with stirring, 10 mL of a 1.0 M solution of diethylboryl tosylate[7] in toluene. The resultant precipitate was collected and dissolved in a minimum quantity of hot water. The title compound was precipitated by adding an excess of aqueous ammonium hexafluorophosphate solution. The crude product was collected and was purified by dissolving the product in a minimum quantity of hot acetonitrile, filtering the hot solution and adding ethyl acetate to a cloud point. On cooling, 3.5 g (62%) of the crystalline salt, mp 220–223 °C, were obtained.

Alternate Procedure. A mixture of 3.2 g of potassium tetrapyrazol-1'-ylborate and 200 mL of a 0.4 M solution of diethylboryl tosylate in toluene was refluxed with stirring for 3 h. After the mixture was cooled to room temperature, the clear toluene solution was decanted to leave an oily residue, which crystallized after being covered and shaken with 30 mL of water. The solid material was collected, washed with ether, and dried to give 2.95 g (50.2%) of the tosylate salt of the title cation. It was purified by dissolving the product in acetonitrile and precipitating with ether; mp 212–215 °C.

NMR data (solution in Me_2SO-d_6): $\delta(^1H)$ 8.63 (4 H, d, J = 2.2), 7.64 (4 H, d, J = 2.6), 7.52 (2 H, d, J = 8), 7.12 (2 H, d, J = 8), 7.01 (4 H, t, J = 2.5), 2.29 (3 H, s), 0.87 (8 H, q, J = 7), 0.61 (10 H, t, J = 7); $\delta(^{11}B)$ +4.7* (2 B), −2.2 (1 B, $h_{1/2}$ = 25 Hz).

The tosylate salt was converted to the hexafluorophosphate salt by suspending the former in an aqueous solution of 2.5 g of ammonium hexafluorophosphate and stirring the mixture for 3 h at room temperature. The solid material was collected, dissolved in acetonitrile, and precipitated with water to give a pure material, mp 217–221 °C. An analytical sample had a melting point of 225–226 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ 8.24 (1 H, unresolved d), 7.52 (1 H, unresolved d), 6.81 (1 H, ill-resolved t, $J \simeq 2.5$), 0.89 (2 H, q, $J \simeq 7.6$), 0.65 (3 H, t, $J \simeq 7.5$); $\delta(^{11}B)$ + 5.1* (2 B), −1.8 (1 B); $\delta(^{13}C)$ (proton decoupled) 140.9, 138.4, 112.1, ca. 18*, 9.4.

$[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^{2+}[PF_6^-]_2$. A mixture of 6.4 g (15 mmol) of 4,4,8,8-tetrapyrazol-1'-ylpyrazabole,[8] 6.5 g (33 mmol) of tri-

[†] University of Kentucky.
[‡] E. I. du Pont de Nemours and Co., Inc.

(1) Boron–Nitrogen Compounds. 106 (K.N.). Part 105: Niedenzu, K.; Niedenzu, P. M.; Warner, K. R. *Inorg. Chem.* **1985**, *24*, 1604.
(2) "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement Boron Compounds 5, pp 10–38.
(3) Trofimenko, S. *J. Coord. Chem.* **1972**, *2*, 75.
(4) Layton, W. J.; Niedenzu, K.; Smith, S. L. *Z. Anorg. Allg. Chem.* **1982**, *495*, 52.
(5) Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Synth.* **1972**, *12*, 116.
(6) Niedenzu, K.; Niedenzu, P. M. *Inorg. Chem.* **1984**, *23*, 3713.
(7) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 1714.
(8) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948.

0020-1669/85/1324-2648$01.50/0

methylamine–iodoborane[5] and 125 mL of mesitylene was heated with stirring for 6 h in an oil bath at 60 °C, another 8 h at 90 °C, and finally at reflux for 6 h. After the mixture was cooled to room temperature, the insoluble material was collected, washed with benzene, and dried. It was dissolved in water, and a small amount of insoluble material was filtered off. A solution of 6 g of ammonium hexafluorophosphate in water was added, and the mixture was stirred for 15 min. The precipitate was collected, washed with water (and dried to give 9.5 g (86%) of crude product, mp 210–212 °C dec. It was purified by dissolving the product in a minimum quantity of acetonitrile and adding a large excess of ethyl acetate. The resultant precipitate was collected, washed with ethyl acetate, and dried under vacuum to give 6.9 g (62%) of a material mp 220–224 °C dec. An analytical sample had a melting point of 224–228 °C dec.

NMR data (solution in CD_3CN): $\delta(^1H)$ 8.37 (2 H, d, J = 2.9), 8.28 (2 H, d, J = 2.2), 7.64 (2 H, d, J = 2.9), 7.04 (1 H, t, J = 2.8), 6.75 (2 H, t, J = 2.6), ca. 3.4* (2 H); $\delta(^{11}B)$ −1.5 (1 B), −7.5* (1 B, sharpens in proton-decoupled spectrum); $\delta(^{13}C)$ (proton decoupled) 145.2, 142.5, 139.2, 114.6, 111.2.

$[(C_2H_2)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^{2+}[PF_6^-]_2$. Twenty milliliters of a 1.0 M solution of diethylboryl tosylate in toluene was added with stirring to a solution of 4.24 g (10 mmol) of 4,4,8,8-tetrapyrazol-1′-ylpyrazabole[8] in 250 mL of hot toluene, and the mixture was refluxed for 30 min. After the mixture was cooled to room temperature, 8.3 g (90%) of colorless crystals of the tosylate salt were collected. They were converted to the corresponding hexafluorophosphate salt by dissolving the tosylate in dimethylformamide/water (10:1 by volume) and adding excess aqueous ammonium hexafluorophosphate solution. The resultant precipitate was purified by dissolving it in hot acetonitrile, filtering while hot, and adding ethyl acetate to a cloud point. On cooling, 5.8 g (68%) of crystalline material, decomposing at 332–334 °C (by DSC), was obtained.

NMR data (solution in CD_3CN): $\delta(^1H)$ 8.35 (2 H, d, J = 2.2), 7.99 (2 H, d, J = 2.5), 7.71 (2 H, d, J = 2.9), 7.00 (1 H, t, J = 2.7), 6.94 (2 H, t, J = 2.7), 0.9 (4 H, unresolved m), 0.7 (6 H, unresolved m); $\delta(^{11}B)$ +6.5 (1 B, $h_{1/2}$ = 300 Hz), −1.5 (1 B, $h_{1/2}$ = 20 Hz); $\delta(^{13}C)$ (proton decoupled) 144.7, 144.4, 142.3, 142.1, 139.3, 139.0, 115.3, 112.4, 18.1*, 9.1. NMR data (solution in Me_2SO-d_6): $\delta(^1H)$ 8.70 (2 H, d, J = 2.2), 8.20 (2 H, d, J = 2.7), 8.17 (2 H, d, J = 2.9), 7.18 (1 H, t, J = 2.7), 7.08 (2 H, t, J = 2.6), 0.9 (4 H, m), 0.65 (6 H, m); $\delta(^{11}B)$ ca. +6*, −2.0 ($h_{1/2}$ = 50 Hz); $\delta(^{13}C)$ (proton decoupled) 143.3, 141.1, 138.6, 114.2, 111.0, 16.7*, 8.6.

Results and Discussion

The interaction of nitrogen bases with trimethylamine–iodoborane can lead to both iodide ion and base displacement according to eq 2.[9]

$$(CH_3)_3N{\cdot}BH_2I + 2L \rightarrow (CH_3)_3N + [L_2BH_2]^+I^- \quad (2)$$

On that basis, the reaction of 4,4-dipyrazol-1′-ylpyrazabole with trimethylamine–monoiodoborane could proceed as follows:

$$(CH_3)_3N{\cdot}BH_2I + (pz)_2B(\mu\text{-}pz)_2BH_2 \rightarrow (CH_3)_3N + [H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+I^- \quad (3)$$

Indeed, reaction according to eq 3 can be realized, and the cation $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+$ was isolated as its hexafluorophosphate salt. However, the reaction requires extreme care if somewhat reasonable yields of product are desired. First, the reaction temperature should only gradually be increased, apparently in order to avoid decomposition of yet unreacted $(CH_3)_3N{\cdot}BH_2I$. Second, sufficiently long reaction times at fairly high temperatures are required to remove at least most of the trimethylamine from an intermediate product.

The overall process seems to involve at least two steps. Initially, iodide ion displacement occurs to give the intermediate $[H_2B(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2{\cdot}N(CH_3)_3]^+I^-$. This process is fairly slow at room temperature but proceeds more readily at 50–70 °C. In the second phase of the reaction trimethylamine is displaced by the N2 atom of the lone terminal (i.e., nonbridging) pyrazolyl group to give the desired cation $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+$. This second step is much more sluggish and requires prolonged heating at relatively high temperatures. (Note: A similar two-step mechanism has been postulated for the hydrolysis of $(CH_3)_3N{\cdot}BH_2I$.[10])

(9) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1968**, *7*, 106.

Table I. Survey of Selected Chemical Shift Data of Spiro Cations of Type **1**

compd	$\delta(^1H)$ of position 1 (6)	2 (5)	3 (4)
R = R′ = H	7.73	6.72	8.18
R = H, R′ = C_2H_5	7.94 (7.52)	6.81 (6.84)	8.18 (8.23)
R = R′ = C_2H_5	7.52	6.81	8.24

compd	$\delta(^{11}B)$ of B(a)	B(b)	B(c)
R = R′ = H	−7.7	−1.3	−7.7
R = H, R′ = C_2H_5	−7.5	−1.5	+5.2
R = R′ = C_2H_5	+5.1	−1.8	+5.1

The pure salt $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+PF_6^-$ was isolated from aqueous solution. A HETCOR 2D NMR experiment showed that the $\delta(^1H)/\delta(^{13}C)$ signal pairs 8.18/141.1, 7.73/139.2, and 6.72/110.3 belong to the individual CH groups of the bridging pyrazolyl moieties.

In order to test the above mechanistic assumptions, the interaction of 4,4,8,8-tetrapyrazol-1′-ylpyrazabole, $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$, with 2 molar equiv of $(CH_3)_3N{\cdot}BH_2I$ was studied in more detail. The stepwise progress of the reaction could be observed by ^{11}B NMR spectroscopy. When a solution of the two cited reagents was stirred at room temperature for several hours, the ^{11}B NMR signals (solution in $CDCl_3$) of $(CH_3)_3N{\cdot}BH_2I$ ($\delta(^{11}B)$ −9.6) and of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ ($\delta(^{11}B)$ −0.1) still dominated the spectrum. However, two minor signals, $\delta(^{11}B)$ −1.9 and +4.0, respectively, were also apparent. These latter became the major signals (and were in a 1:1 area ratio) after the reaction mixture was refluxed in benzene for 10 h. At this time, the signal for $(CH_3)_3N{\cdot}BH_2I$ was no longer observed and only a minor signal ($\delta(^{11}B)$ −0.1) was still present.

On the basis of ^1H and ^{13}C NMR data (solution in Me_2SO-d_6), the primary product at this stage was identified as the salt $[(CH_3)_3N{\cdot}BH_2(\mu\text{-}pz)B(pz)(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2{\cdot}N(CH_3)_3]^{2+}[I^-]_2$. The following $\delta(^1H)/\delta(^{13}C)$ signals were observed and were assigned on the basis of fine structure as well as HOMCOR and HETCOR 2D NMR experiments: 7.76(1 H, d)/142.6, 7.37(1 H, d)/137.2 and 6.42(1 H, 2 overlapping d)/107.0 for the two terminal (nonbridging) pyrazolyl groups and the sets 8.55(1 H, d)/140.6, 7.24(1 H, d)/134.0, and 6.74(1 H, t)/109.5 as well as 8.41(1 H, d)/141.2, 8.18(1 H, d)/142.4, and 7.04(1 H, t)/110.9 for the two different types of bridging (μ-pz) pyrazolyl groups. The boron-bonded hydrogen was evidenced by a very broad signal near 3.4 ppm; the CH_3 groups exhibited a signal at $\delta(^1H)$ 2.80; $\delta(^{13}C)$ 51.9.

The ion $[(CH_3)_3N{\cdot}BH_2(\mu\text{-}pz)B(pz)(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2{\cdot}N(CH_3)_3]^{2+}$ loses trimethylamine only on prolonged heating in a mixture with toluene or, even better, mesitylene. The process of the reaction can be seen by a continuous decrease in the intensity of the ^1H NMR signal of the trimethylamine. However, some residual trimethylamine always remains in the crude product though, ultimately, the salt $[H_2B(\mu\text{-}pz)_2(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^{2+}[I^-]_2$ is formed. A HOMCOR 2D NMR experiment (in Me_2SO-d_6) showed that the observed signals $\delta(^1H)$ 8.67 (2 H, d) and 7.20 (1 H, t), belong together and must be assigned to the central bridging pyrazolyl groups, and the set $\delta(^1H)$ 8.21 (2 H, d), 8.20 (2 H, d), and 6.87 (2 H, t) is then readily assigned to the remaining pyrazolyl groups of the ion. The boron-bonded protons were observed as a very broad signal near $\delta(^1H)$ 3.9. In addition, various minor impurity signals and a reasonably strong signal for trimethylamine groups were observed. However, a pure material could be obtained by precipitation of the cation from aqueous solution as the hexafluorophosphate salt, which was further characterized.

On the basis of HOMCOR and HETCOR 2D NMR experiments, the $\delta(^1H)/\delta(^{13}C)$ signal pairs of $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B$-

(10) Lowe, J. R.; Uppal, S. S.; Weidig, C.; Kelly, H. C. *Inorg. Chem.* **1970**, *9*, 1423.

Table II. Survey of Selected Chemical Shift Data of Spiro Cations of Type **2**

compd	$\delta(^1H)/\delta(^{13}C)$ of position				
	1	2	3	4	5
R = H	7.64/139.2	6.75/111.2	8.28/142.5	8.37/145.2	7.04/114.6
R = C_2H_5	7.71/139.1	6.94/112.4	8.35/142.2	7.99/144.4	7.00/115.3

compd	$\delta(^{11}B)$ of	
	B(a)	B(b)
R = H	−7.5	−1.5
R = C_2H_5	+6.5	−1.5

$(\mu\text{-pz})_2BH_2]^{2+}$ (solution in CD_3CN) at 8.37/145.2 and 7.04/114.6 were assigned to the central pyrazolyl groups and the sets 8.28/142.5, 7.64/139.2, and 6.75/111.2 to the second type of bridging pyrazolyl groups.

Whereas the reaction of terminal $B(pz)_2$ groups of *B*-pyrazol-1′-ylpyrazaboles with $(CH_3)_3N{\cdot}BH_2I$ progressed in stepwise fashion, the interaction of the former with $(C_2H_5)_2BOts$ (ts = tosyl) was straightforward and rapid.[3] Of course, the boron atom in the latter reagent is only in a trigonal environment and, hence, coordinates readily with the N(2) atom of a terminal boron-bonded pyrazolyl group. In addition, the tosylate group appears to be an even better leaving moiety than the iodide ion. Finally, the tedious trimethylamine displacement is not required in this case. Thus, the reaction of $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ with $(C_2H_5)_2BOts$ proceeded readily to yield the desired cation $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^{2+}$, which was previously isolated as the hexafluorophosphate salt[3] and was now characterized by NMR data.

The NMR data of the latter species were again assigned on the basis of fine structure as well as HOMCOR and HETCOR 2D NMR experiments (solution in $Me_2SO\text{-}d_6$) as follows: $\delta(^1H)/\delta(^{13}C)$ 8.20/143.3 and 7.18/114.2 sets to the central bridging pyrazolyl groups and the signals 8.70/141.1, 8.17/138.6, and 7.08/111.0 to the pyrazolyl groups bridging the unsymmetrically substituted boron atoms to the central unit. In CD_3CN (but not in $Me_2SO\text{-}d_6$) the two types of boron atoms in different environments are not only clearly seen with $\delta(^{11}B)$ +6.5 and −1.5, respectively, but the line shape clearly mandates assignment of the latter signal to the boron atoms in the symmetrical environment, i.e. the central ones. In $Me_2SO\text{-}d_6$, however, the NMR signal of the boron atoms in the unsymmetrical environment can hardly be recognized.

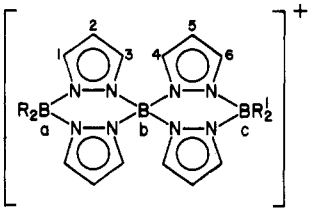
In this connection it is of interest to note that the ^{13}C NMR signals of the N-bonded CH units of the pyrazolyl groups in $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^{2+}$ are split in CD_3CN solution (at 22 °C) but not in $Me_2SO\text{-}d_6$. The signals merge rapidly, however, with even minor increases in temperature. This observation suggests the existence of conformational isomers. The formation of such polyboron spiro species would ideally give cause to a linear structure with planar B_2N_4 rings. On the other hand, angle considerations for the bonds about boron would tend to favor a boat conformation for the B_2N_4 rings. An evaluation of the molecular structures of a series of pyrazaboles as determined by X-ray diffraction has shown that the B_2N_4 ring of these compounds can exist in planar, chair, or boat conformation, of which the latter predominates.[11] However, energy differences between the various conformations are very small, and packing effects seem to be the major factor governing the conformation of a specific species in the solid state.

In analogy to the above reaction, interaction of $(C_2H_5)_2B(\mu\text{-pz})_2B(pz)_2$ with 1 molar equiv of $(C_2H_5)_2BOts$ gave the expected monocation $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+$, which again was isolated as the hexafluorophosphate salt.[3] This latter species has now also been characterized by NMR data (see Experimental Section). On the basis of a HETCOR 2D NMR experiment, the signal pairs $\delta(^1H)/\delta(^{13}C)$ 8.24/140.9, 7.52/138.4, and 6.81/112.1 belong to individual CH units of the pyrazolyl rings.

The same ion, $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+$, was also obtained in a one-step procedure originating from $K[B(pz)_4]$ and 2 molar equiv of $(C_2H_5)_2BOts$. However, the yield of this latter reaction was noticeably lower than in the case when a pyrazabole was used as starting material.

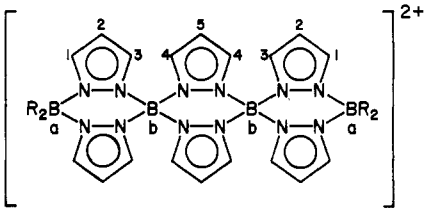
Furthermore, the reaction of $(pz)_2B(\mu\text{-pz})_2BH_2$ with $(C_2H_5)_2BOts$ was employed to form the unsymmetrical cation $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^+$, in which the two terminal boron atoms are in a nonequivalent environment. This is readily apparent from the ^{11}B NMR spectral data (see Experimental Section).

The NMR spectral data of the various cations show some noteworthy trends. Individual positions of the three monocations are labeled in **1**, and relevant ^1H and ^{11}B NMR data are summarized in Table I. The suggested assignments of H^3 (H^4) vs. H^1 (H^6) are based on the assumption that chemical shift data for the former should be much less affected by the nature of R and R′ than the latter.



1

Similarly, individual positions of the two dications are labeled in **2**, and relevant $\delta(^1H)/\delta(^{13}C)$ and $\delta(^{11}B)$ data are listed in Table II. ($\delta(^{13}C)$ signals for positions 1, 3, and 4 for R = C_2H_5 are averaged for the two distinct signals that are observed for each in CD_3CN solution.)



2

The ^1H and ^{11}B NMR chemical shift data for the two sets of cations appear to correlate well. The one surprising feature is the fact that, for **2** with R = C_2H_5, the most downfield ^{13}C NMR signal does not go with the most downfield ^1H NMR signal.

The yields of the various salts as described in the preceding section are not always satisfactory. Admittedly, no serious effort has yet been made to improve on yields. However, in view of recent findings that—in contrast to earlier assumptions[12] —the pyrazabole ring can indeed open during chemical manipulations,[13] more basic studies on the chemistry of pyrazaboles are needed in order to influence the progress of desired processes and limit side reactions.

(11) Brock, C. P.; Niedenzu, K.; Hanecker, E.; Nöth, H. *Acta Crystallogr.*, in press.

(12) Niedenzu, K.; Nöth, H. *Chem. Ber.* **1983**, *116*, 1132.

(13) Layton, W. J.; Niedenzu, K.; Niedenzu, P. M.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 1454.

In any case, the present data clearly suggest that even larger cations of this same type with the general formula $[R_2B(\mu\text{-}pz)_2\{B(\mu\text{-}pz)_2\}_nBR_2]^{n+}$ should be accessible; terminal R substituents of a structural unit $(\mu\text{-}pz)_2BR_2$ have been replaced by halogen,[12,14] which, in turn, was replaced by pyrazolyl groups,[13] thus providing a site for further chain elongation.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.). Dr. J. Bielawski developed the synthesis of $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^+PF_6^-$ originating from $K[B(pz)_4]$; W. J. Layton recorded the NMR spectra.

Registry No. $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+PF_6^-$, 97073-75-1; $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^+PF_6^-$, 97073-77-3; $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^+PF_6^-$, 40249-67-0; $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^{2+}[PF_6^-]_2$, 97102-13-1; $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^{2+}[PF_6^-]_2$, 40249-68-1; $(CH_3)_3N{\cdot}BH_2I$, 25741-81-5; $(pz)_2B(\mu\text{-}pz)_2BH_2$, 92242-00-7; $(C_2H_5)_2BOts$, 97073-78-4; $(C_2H_5)_2B(\mu\text{-}pz)_2B(pz)_2$, 86050-17-1; $[(pz)_4B]^-K^+$, 14782-58-2; $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$, 16243-58-6.

(14) Hanecker, E.; Hodgkins, T. G.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1985**, *24*, 459.

Contribution from the Department of Chemistry, University of California, Davis, California 95616

Proton Nuclear Magnetic Resonance Studies of Iron Porphyrin Complexes with a Vinyl Carbene Inserted between Iron and a Pyrrole Nitrogen

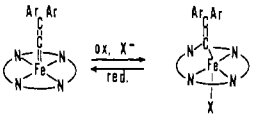
ALAN L. BALCH,* RU-JEN CHENG, GERD N. LA MAR,* and LECHOSLAW LATOS-GRAZYNSKI

Received February 15, 1985

Proton NMR spectra have been obtained for the paramagnetic ($S = {}^3/_2$) iron(III) complexes P[C=C(*p*-$C_6H_4Cl)_2$]FeX (X = Cl, Br, I; P = porphyrin dianion from *meso*-tetraarylporphyrin, or protoporphyrin IX dimethyl ester). Functional group assignments have been made with use of selective deuterium and methyl labeling. More detailed assignments have been made on the basis of the temperature dependence of the spectra and analysis of the line widths, which are dominated by dipolar relaxation. The spectra are indicative of C_s symmetry for these complexes in solution. This result is in accord with the solid-state structure of these complexes but requires some oscillatory motion of one of the *p*-ClC_6H_4 groups. The dominant π-spin transfer to the pyrroles indicates that, of the alternate ground states $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_{x^2-y^2})^1$ and $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_{z^2})^1$, the latter is present. The complexes exhibit axial magnetic anisotropy dominated by negative zero-field splitting. For the protoporphyrin IX derivative, the spectrum indicates that the four isomers resulting from carbene insertion into each of the four distinct Fe–N bonds are present.

Introduction

Recently several remarkable reactions of metalloporphyrins that involve the transfer of substituents from metal to pyrrole nitrogen have been discovered.[1-10] The carbene migration shown in eq 1 is an example in which the migration is coupled with a redox reaction.[3-5] The process is reversible.



1 2 (1)

The formation of **2** via reaction 1 has produced several suggestions regarding the nature of highly oxidized forms of heme proteins which are involved in the mechanism of action of the peroxidases and cytochromes P450. Thus a species analogous to **2** but with an oxygen atom replacing the carbene moiety has been considered as a structural alternative to the more conventional iron oxo unit in highly oxidized heme proteins.[3,4] Spectroscopic similarities between **2** and the enzymic intermediate, catalase compound I, have produced the proposal that similar structures are involved.[3] It has been suggested that an oxygen atom migration analogous to reaction 1 might be involved in heme degradation that is produced by heme oxygenase.[4,9]

The insertion product **2** has been characterized by two independent X-ray diffraction studies.[3,9] Magnetic susceptibility, electron spin resonance, and Mössbauer spectroscopic studies indicate that this complex is best described as an iron(III) complex with an $S = {}^3/_2$ ground state.[5]

Proton NMR spectroscopy provides a uniquely useful probe for studying the structure of iron porphyrins in solution.[11] For paramagnetic complexes the hyperfine shift patterns are particularly sensitive to the spin, ligation, and oxidation state of the metal. For complexes derived from synthetic, symmetric porphyrins, the presence of a substituent on one nitrogen reduces the symmetry to at most C_s and thereby introduces a greater inherent complexity to their NMR spectra. Here we report a detailed examination of the ^1H NMR spectra of a variety of substituted forms of **2**.

Results and Discussion

Assignment of ^1H NMR Resonances to Functional Groups through Labeling Studies. Our analysis of the complex spectra of **2** and variously substituted derivatives relates directly to the geometric information available from the X-ray studies. The structure of **2** as determined by X-ray diffraction[9] is shown in Figure 1. While the molecule has no symmetry in the solid state, it appears to have C_s symmetry in solution, with the mirror plane passing through the iron atom, the axial chloride ligand, and the carbene carbon. Accordingly, labels have been affixed to the four pyrrole (pyrr) positions and to the four phenyl rings.

The full ^1H NMR spectrum of **2** (X = I; C, D = *p*-C_6H_5) in chloroform-*d* solution is shown in Figure 2. Four resonances, three upfield and one downfield, are particularly evident. On the

(1) Ogoshi, H.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1973**, *95*, 1666.
(2) Ogoshi, H.; Watanabe, E.; Koketzu, N.; Yoshida, A. *J. Chem. Soc., Chem. Commun.* **1974**, 943.
(3) Chevrier, B.; Weiss, R.; Lauge, M.; Mansuey, D.; Chottard, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2899.
(4) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.
(5) Mansuy, D.; Morgenstern-Badarau, I.; Lange, M.; Gaus, P. *Inorg. Chem.* **1982**, *21*, 1427.
(6) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348.
(7) Mansuy, D.; Battioni, J.-P.; Dupré, D.; Satori, E.; Chottard, G. *J. Am. Chem. Soc.* **1982**, *104*, 6159.
(8) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, O. *J. Am. Chem. Soc.* **1982**, *104*, 3545.
(9) Olmstead, M. M.; Cheng, R.-J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143.
(10) Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472.
(11) La Mar, G. N.; Walker (Jensen), F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, p 61.

0020-1669/85/1324-2651$01.50/0