Table III. Ideal and Observed Dihedral Angles (deg) for Compound **6**

structure	δ at b_1	δ at b_2	remaining δ
ideal octahedron	70.5, 70.5 70.5	70.5, 70.5 70.5	70.5, 70.5, 70.5 70.5, 70.5, 70.5
ideal trigonal prism	0, 0, 0	120, 120 120	90, 90, 90 90, 90, 90
iron complex-1[a]	45.8, 46.2 45.8	88.5, 88.6 89.0	67.7, 67.9, 68.0 80.2, 80.9, 81.8
iron complex-2[a]	47.8, 48.3 48.9	86.6, 87.2 87.6	66.4, 67.4, 68.1 80.4, 80.7, 81.1

[a] See Figure 4 in this paper and ref 39.

between trigonal faces sharing common edges of the polyhedron.[38,39] The idealized-octahedral and trigonal-prismatic versus observed dihedral angles for the two iron complex molecules are given in Table III and are graphically presented in Figure 4. It is clear from both presentations that the twist angle and dihedral angle treatments are in good agreement in defining the coordination polyhedra of the ferric complex molecules as intermediate in the D_{3d}-D_{3h} reaction path.

In conclusion, hexadentate amide ligands derived from 2-mercaptopyridine-6-carboxylic acid 1-oxide and triamines have been prepared and characterized. The ferric complexes of these ligands also have been isolated and characterized. The structure of the ferric complex of the *N,N′,N″*-trris((1,2-didehydro-1-hydroxy-2-thioxopyrid-6-yl)carbonyl)-2,2′,2″-triaminotriethylamine shows a coordination polyhedron similar to that of the ferric complex of 1-hydroxy-2(1*H*)-pyridinone. This establishes that there is no significant strain in the complex structure caused by the amine backbone, which make this ligand geometry suitable for iron binding.

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Supplementary Material Available: Listings of positional and thermal parameters of hydrogen atoms (Table S1), general temperature factor expressions (*B*'s) (Table S2), root-mean-square amplitudes of vibration (Table S3), and complete bond lengths and angles (Table S5) (13 pages); a table of observed and calculated structure factors (Table S4) (45 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506,
and du Pont Electronics Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Boron Derivatives of 3-Ferrocenylpyrazole

K. Niedenzu,*[,†] J. Serwatowski,[†] and S. Trofimenko*[,‡]

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3-Ferrocenylpyrazole (=Hpz*) has been prepared and was converted to the salt Kpz* and the complex $[(\pi\text{-}CH_2CCH_3CH_2)Pd(pz^*)]_2$. In many respects Hpz* reacts with boron compounds in a manner similar to the unsubstituted parent pyrazole. Thus, the pyrazaboles $R_2B(\mu\text{-}pz^*)_2BR_2$ (R = H, C_2H_5); the adducts $(CH_3)_2HN\cdot B(pz^*)(C_2H_5)_2$, $(CH_3)_2HN\cdot B(pz^*)(C_8H_{14})$ (where $C_8H_{14}BH$ = 9-borabicyclo[3.3.1]nonane), $Hpz^*\cdot B(pz^*)(C_8H_{14})$, and $(CH_3)_2HN\cdot B(pz^*)_3$; the salts $Tl[(pz^*)_2BH_2]$, $K[(pz^*)_2B(C_2H_5)_2]$, and $M[(pz^*)_2B(C_8H_{14})]$ (M = Na, K); and the complexes $(C_2H_5)_2(\mu\text{-}pz^*)_2Pd(\pi\text{-}CH_2CHCH_2)$ and $(C_8H_{14})B(\mu\text{-}pz^*)_2Pd(\pi\text{-}CH_2CHCH_2)$ have been prepared and characterized. On the other hand, the relative lability of the ferrocenyl unit of Hpz* prevents some reactions that are possible with other pyrazoles, e.g., formation of $K[HB(pz^*)_3]$ or $K[B(pz^*)_4]$ from Hpz* and KBH_4 or the halogenation at the boron sites of $H_2B(\mu\text{-}pz^*)_2BH_2$.

Introduction

There are many compounds known in which the two adjacent nitrogen atoms of pyrazolyl moieties bridge a boron and a metal atom (M) to give the structural arrangement $B(\mu\text{-}pz)_nM$ (Hpz = pyrazole; n = 1–3).[1] In contrast, no materials are known in which a boron atom is bonded to a metal via the dinitrogen unit and simultaneously to a different metal via one nitrogen and the carbon framework of the same pyrazolyl group. The synthesis and characterization of such species derived from 3-ferrocenylpyrazole were the ultimate goal of the present study.

Experimental Section

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

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (^{11}B and high resolution) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR spectroscopy, external $(C_2H_5)_2O\cdot BF_3$ for ^{11}B NMR spectroscopy); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = septet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. ^{13}C NMR spectra were generally recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received.

3-Ferrocenylpyrazole (=Hpz*). To 54 g (1 mol) of dry sodium methoxide slurried in 1 L of toluene was added with stirring a solution of 228 g (1 mol) of acetylferrocene and a large excess of ethyl formate in toluene. An exothermic controlled reaction occurred, a red solution formed, and finally an orange-brown precipitate was obtained. The latter was collected and dissolved in methanol, and the resulting mixture was reacted with an aqueous solution of 68.5 g (1 mol) of hydrazine monohydrochloride. The product was extracted with methylene chloride, and the latter solvent was evaporated to leave a red tar. This material was refluxed for 1 h with 25 g (0.5 mol) of hydrazine hydrate in methanol (or ethanol). The dark reddish solution was poured slowly and with stirring into about 1 L of cold water. An oil formed, which soon solidified. The solid was collected, washed with water, and then dissolved in ca. 200 mL of methylene chloride. The solution was filtered through a short alumina column, and the orange filtrate was concentrated until crystals started appearing. After transfer to a smaller vessel, methylene chloride was driven off and, on cooling, 130 g (61%) of crystalline orange product, mp 148–149 °C, was obtained. Anal. Calcd for $C_{13}H_{12}FeN_2$

[†] University of Kentucky.

[‡] E. I. du Pont de Nemours & Co.

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(M_r = 252.10): C, 61.94; H, 4.80; Fe, 22.15; N, 11.11. Found: C, 61.26; H, 5.09; Fe, 22.09; N, 11.80.

NMR data: $\delta(^1H)$ 11.1* (1 H, s), 7.57 (1 H, d, J = 1.5), 6.37 (1 H, unresolved d), 4.66 (2 H, unresolved t), 4.30 (2 H, t, J = 1.7), 4.08 (5 H, s); $\delta(^{13}C)$ 147.4*, 135.5*, 103.5, 76.8, 69.8, 69.0, 67.0; (solution in THF-d_8) $\delta(^1H)$ 7.42* (1 H, s), 6.27* (1 H, s), 4.63* (2 H, s), 4.21* (2 H, s), 4.00* (5 H, s). The (14 eV) mass spectrum of the compound exhibited a parent ion cluster with the base peak at m/z 252.

Kpz*. A stirred mixture of 6.6 g (26 mmol) of Hpz*, 120 mL of benzene, and 1.1 g (28 mmol) of small chunks of metallic potassium was heated to 50–60 °C for 4 h. After that time the evolution of hydrogen had stopped. The orange-gray precipitate was collected, washed with benzene, and dried to give an essentially quantitative yield (7.6 g) of Kpz*, which sintered at 170 °C and decomposed at 180 °C. Anal. Calcd for $C_{13}H_{11}FeKN_2$ (M_r = 290.05): C, 53.79; H, 3.82; Fe, 19.26; K, 13.48; N, 9.65. Found: C, 53.65; H, 4.02; Fe, 19.12; K, 12.98; N, 9.25.

NMR data: (solution in THF-d_8) $\delta(^1H)$ 7.51* (1 H, s), 6.16* (1 H, s), 4.61* (2 H, s), 4.06* (2 H, s), 3.92* (5 H, s); $\delta(^{13}C)$ 149.0, 139.6, 101.0, 85.6, 70.0, 67.8, 66.9.

$[(\pi\text{-}CH_2CCH_3CH_2)Pd(pz^*)]_2$. A mixture of equimolar amounts (10 mmol) of Hpz* (2.5 g), (π-$CH_2CCH_3CH_2$)PdCl (as the dimer, 1.3 g), and $(C_2H_5)_3N$ (1.0 g) was stirred for 30 min in 100 mL of methylene chloride to which 50 mL of water has been added. The yellow-orange organic layer was filtered through Celite and evaporated to leave an essentially quantitative yield of the compound as yellow solid, sintering from 222 °C and decomposing at 239–241 °C. Anal. Calcd for $C_{17}H_{18}FeN_2Pd$ (M_r = 412.6): C, 49.49; H, 4.39; Fe, 13.55; N, 6.79; Pd, 25.79. Found: C, 49.14; H, 4.31; Fe, 13.32; N, 6.68; Pd, 25.83. Both ^1H and ^{13}C NMR spectra were complex, showing the presence of rotamers.

$Zn(pz^*)_2$. To a solution of 2.1 g (8.3 mmol) of Hpz* and 0.84 g (8.3 mmol) of triethylamine in 50 mL of methylene chloride was added 4.15 mL of a 1 M solution of zinc chloride in diethyl ether. The mixture was stirred for 3 h at ambient temperature, and the precipitate (2.2 g, 94%) was filtered off, washed with methylene chloride, and dried under vacuum. The product decomposed near 340 °C. Anal. Calcd for $C_{26}H_{22}Fe_2N_4Zn$ (M_r = 567.26): C, 55.00; H, 3.92; Fe, 19.69; N, 9.60; Zn, 11.53. Found: C, 54.88; H, 4.15; Fe, 19.74; N, 9.60; Zn, 11.50. The material was insoluble in common organic solvents, and no NMR data could be recorded.

$H_2B(\mu\text{-}pz^*)_2BH_2$. A mixture of 12.6 g (0.05 mol) of Hpz* and 3.7 g (0.05 mol) of trimethylamine–borane, $(CH_3)_3N\cdot BH_3$, was refluxed in 250 mL of toluene until gas evolution ceased (ca. 1 h). The solvent was evaporated, and the residue was dissolved in methylene chloride and chromatographed on alumina. The eluate was dropped into refluxing heptane so that the methylene chloride slowly distilled out. This procedure gave slow formation of orange crystals of the compound; it begins to sinter near 230 °C, mp 245–246 °C dec. Anal. Calcd for $C_{26}H_{26}B_2Fe_2N_4$ (M_r = 527.51): C, 59.39; H, 4.60; B, 4.11; Fe, 21.24; N, 10.65. Found: C, 59.21; H, 4.61; B, 4.09; Fe, 21.08; N, 10.58.

NMR data: $\delta(^1H)$ 7.51 (1 H, d, J = 2.3), 6.34 (1 H, d, J = 2.3), 4.71 (2 H, unresolved), 4.36 (2 H, unresolved), 4.14 (5 H, s), 3.6* (2 H, s); $\delta(^{11}B)$ −9.2 (s, $h_{1/2}$ = 400 Hz); $\delta(^{13}C)$ 148.2, 135.6, 105.6, 74.8, 70.2, 69.9, 69.3; (solution in CD_2Cl_2) $\delta(^{13}C)$ 148.1, 135.4, 105.6, 74.7, 70.2, 70.0, 69.4. EI mass spectrum (14 eV): m/z 529 (5), 528 (31), 527 (100), 526 (53), 525 (21), 524 (8), 459 (7), 264 (23), 263 (5), 252 (9).

$(C_2H_5)_2B(\mu\text{-}pz^*)_2B(C_2H_5)_2$. To a solution of 0.50 g (2 mmol) of Hpz* in 25 mL of toluene was added 0.22 g (2 mmol) of (dimethylamino)diethylborane, $(CH_3)_2NB(C_2H_5)_2$,[2] and the mixture was heated to reflux for 8 h. Volatiles were removed under reduced pressure to leave a dark gummy material. The latter was boiled with cyclohexane, and the hot mixture was filtered to give a clear bright orange solution of the desired product and some unreacted Hpz*. Cyclohexane was removed under vacuum, and the residue was treated with ethanol to leave 0.22 g (35%) of the compound. It was purified by dissolving it in a minimum amount of toluene, adding a 5-fold volume of ethanol, and placing the mixture in an ice bath. The resultant bright orange precipitate had a melting point of 182–185 °C. Anal. Calcd for $C_{34}H_{42}B_2Fe_2N_4$ (M_r = 639.64): C, 63.80; H, 6.61; B, 3.39; Fe, 17.45; N, 8.75. Found: C, 63.15; H, 6.53; B, 3.43; Fe, 17.39; N, 8.76.

NMR data: $\delta(^1H)$ 7.50 (1 H, d, J = 2.5), 6.56 (1 H, d, J = 2.4), 4.54 (2 H, t, J = 1.8), 4.29 (2 H, t, J = 1.8), 4.19 (5 H, s), 0.48 (4 H, q, J = 7), 0.29 (6 H, t, J = 7); $\delta(^{11}B)$ 3.0 (s, $h_{1/2}$ = 500 Hz); $\delta(^{13}C)$ 147.6, 133.8, 109.7, 78.9, 71.9, 69.9, 68.4, 16.2*, 9.0. The EI mass spectrum exhibited a weak parent ion at m/z 640.

$(CH_3)_2HN\cdot B(pz^*)(C_8H_{14})$. To a stirred mixture of 1.1 g (4.4 mmol) of Hpz* and 40 mL of ether was added 0.72 g (4.4 mmol) of 9-(dimethylamino)-9-borabicyclo[3.3.1]nonane, $(CH_3)_2NB(C_8H_{14})$.[3] The pyrazole dissolved completely, and a new precipitate developed rapidly. The mixture was stirred for 15 min at room temperature and was filtered to give 1.35 g (74%) of the desired orange compound. (Some additional material can be obtained by concentration of the filtrate.) The product sinters at 130–140 °C and melts at 170–180 °C dec. Anal. Calcd for $C_{23}H_{32}BFeN_3$ (M_r = 417.19): C, 66.22; H, 7.73; B, 2.59; Fe, 13.39; N, 10.07. Found: C, 65.59; H, 7.74; B, 2.87; Fe, 13.47; N, 9.91.

NMR data: $\delta(^1H)$ 7.49 (1 H, d, J = 1.8), 6.27 (1 H, d, J = 2.1), 4.71 (2 H, s), 4.19 (2 H, s), 3.99 (5 H, s), 3.9* (ca. 1 H, s), 2.41 (6 H, d, J = 6.0), 2.05–1.15 (14 H, m); $\delta(^{11}B)$ 1.2 (s, h_{12} = 225 Hz); $\delta(^{13}C)$ 149.6, 133.6, 101.2, 81.3, 69.2, 67.7, 66.5, 36.3, 31.1, 30.9, 24.0, 23.3, 20.6*.

$Hpz^*\cdot B(pz^*)(C_8H_{14})$. A stirred slurry of 1.5 g (3.6 mmol) of $(CH_3)_2HN\cdot B(pz^*)(C_8H_{14})$ (see above) and 0.91 g (3.6 mmol) of Hpz* in 20 mL of toluene was heated to reflux for 3 h. The mixture was filtered, and the clear filtrate was evaporated to leave 1.95 g (87%) of brown solid, which began to sinter at ca. 160 °C and decomposed near 220 °C. Anal. Calcd for $C_{34}H_{37}BFe_2N_4$ (M_r = 624.20): C, 65.42; H, 5.98; B, 1.73; Fe, 17.89; N, 8.98. Found: C, 64.86; H, 5.56; B, 1.58; Fe, 17.61; N, 9.05.

NMR data: $\delta(^1H)$ 7.68* (2 H), 6.29* (2 H), 4.65* (4 H), 4.22* (4 H), 3.9* (10 H), 2.43* (2 H), 2.1–1.2 (12 H, m) (note: all signals have satellites or shoulders); $\delta(^{11}B)$ 32.8 (s, $h_{1/2}$ = 550 Hz) and 1.2 (s, $h_{1/2}$ = 400 Hz) in a ca. 1:10 ratio (but varying considerably with the concentration, the signal at 1.2 ppm increasing with increasing concentration).

$Na[(pz^*)_2B(C_8H_{14})]$. To a stirred solution of 1.60 g (2.56 mmol) of $Hpz^*\cdot B(pz^*)(C_8H_{14})$ (see above) in 30 mL of benzene was added 0.15 g (5.3 mmol) of sodium hydride. The mixture was stirred for 2 h at room temperature, and hydrogen evolution ceased. The mixture was filtered, and solvent was evaporated from the clear filtrate to leave an essentially quantitative yield of the soidum salt. It began to sinter at 40–50 °C and decomposed near 100 °C.

NMR data: (solution in CD_2Cl_2) $\delta(^1H)$ 7.62 (1 H, d, J = 2.0), 7.44* (1 H, s), 6.33* (1 H, s), 6.24 (1 H, d, J = 2.1), 4.58* (2 H, s), 4.49 (2 H, t, J = 1.9), 4.29* (2 H, s), 4.16 (2 H, t, J = 1.9), 4.09 (5 H, s), 4.05 (5 H, s), 1.95–1.25 (14 H, m); $\delta(^{11}B)$ −1.5 (shoulder at 1.4).

$K[(pz^*)_2B(C_8H_{14})]$. To a stirred slurry of 1.7 g (4.1 mmol) of $(CH_3)_2HN\cdot B(pz^*)(C_8H_{14})$ (see above) and 30 mL of benzene was added 1.15 g (3.96 mmol) of Kpz*. The mixture was heated to reflux for 3 h, and the orange insoluble material was collected, washed with benzene, and dried to give 2.2 g (81.5% yield) of product, mp 280 °C dec. (Some additional material can be obtained from concentration of the solution.) Anal. Calcd for $C_{34}H_{36}BFe_2KN_4$ (M_r = 662.29): C, 61.66; H, 5.48; B, 1.63; Fe, 16.86; K, 5.90; N, 8.46. Found: C, 61.07; H, 5.14; B, 1.84; Fe, 17.01; K, 5.68; N, 8.09.

NMR data: (solution in $(CD_3)_2CO$) $\delta(^1H)$ 7.53 (1 H, d, J = 2), 6.12 (1 H, d, J = 1.9), 4.60 (2 H, t, J = 1.8), 4.09 (2 H, t, J = 1.9), 3.93 (5 H, s), 2–1.1 (14 H, m); $\delta(^{11}B)$ −1.0 (s, $h_{1/2}$ = 230 Hz); $\delta(^{13}C)$ 148.7, 133.1, 101.6, 83.8, 70.1, 68.2, 66.9, 32.6, 25.6, 25.0*.

$(C_8H_{14})B(\mu\text{-}pz^*)_2Pd(\pi\text{-}CH_2CHCH_2)$. To a stirred slurry of 1.40 g (2.11 mmol) of $K[(pz^*)_2B(C_8H_{14})]$ and 30 mL of methylene chloride was added 0.40 g (1.09 mmol) of $[(\pi\text{-}CH_2CHCH_2)PdCl]_2$. Most of the material dissolved, and the mixture was stirred for 2 h at ambient temperature. It was filtered, and solvent was evaporated from the clear filtrate to give 1.2 g (74%) of orange solid, which decomposed at 230–240 °C. The compound can be recrystallized from benzene or toluene (with considerable losses). Anal. Calcd for $C_{37}H_{41}BFeN_4Pd$ (M_r = 770.2): C, 57.65; H, 5.37; B, 1.40; Fe, 14.50; N, 7.27; Pd, 13.81. Found: C, 57.46; H, 5.03; B, 1.28; Fe, 14.51; N, 6.91; Pd, 14.01.

NMR data: (solution in CD_2Cl_2) $\delta(^1H)$ 7.76 (2 H, d, J = 2.3), 6.41 (2 H, d, J = 2.3), 5.19 (1 H, h), 4.76 (2 H, m), 4.44 (2 H, m), 4.3 (4 H, m), 4.20 (10 H, s), 3.08 (2 H, d, J = 6.8), 2.47 (2 H, d, J = 12.3), 2.4–1.1 (14 H, m); $\delta(^{11}B)$ 0.1 (s, $h_{1/2}$ = 275 Hz); $\delta(^{13}C)$ 151.2, 135.3, 112.8, 105.2, 81.8, 70.7, 70.1, 69.5, 68.7, 68.4, 57.9, 33.2, 30.9, 28.0*, 24.5, 21.5*. The mass spectrum exhibited a parent ion cluster at m/z 770.

$K[(pz^*)_2B(C_2H_5)_2]$. To a stirred slurry of 1.6 g (6.3 mmol) of Hpz* in 80 mL of ether was added 0.70 g (6.2 mmol) of $(CH_3)_2NB(C_2H_5)_2$. The mixture was stirred for 15 min, and a very small amount of insoluble material was filtered off. Solvent was removed from the filtrate. The residue, mp = ca. 50 °C, assumed to be $(CH_3)_2HN\cdot B(pz^*)(C_2H_5)_2$ [NMR data: $\delta(^1H)$ 7.40 (1 H, d, J = 2.2), 6.20 (1 H, d, J = 2), 5.5* (1 H), 4.67 (2 H, t, J = 1.8), 4.20 (2 H, t, J = 1.7), 4.00 (5 H, s), 2.37 (6 H, d, J = 5.9), 0.9–0.5 (10 H, m)], was dissolved in benzene, and 1.86 g (6.4 mmol) of Kpz* was added to the brown solution. The stirred slurry was heated to reflux for 90 min until no more amine evolved. The

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mixture was filtered, and the collected solid was washed with benzene and dried under vacuum to give 2.7 g of material, which sintered near 160 °C and decomposed at 178 °C.

NMR data: (solution in C_2D_5OD) $\delta(^1H)$ 7.46* (1 H, s), 6.28* (1 H, s), 4.73* (2 H, s), 4.28* (2 H, s), 3.98* (5 H, s), 1.0–0.1 (5 H, m); $\delta(^{11}B)$ 6.5 (s, $h_{1/2}$ = 950 Hz).

$(C_2H_5)_2B(\mu\text{-pz}^*)_2Pd(\pi\text{-}CH_2CHCH_2)$. To a stirred slurry of 2.05 g (3.36 mmol) of $K[(pz^*)_2B(C_2H_5)_2]$ (see above) in 30 mL of benzene was added 0.61 g (1.18 mmol) of $[(\pi\text{-}CH_2CHCH_2)PdCl]_2$. The mixture was stirred at room temperature overnight and filtered, and solvent was evaporated from the clear filtrate to leave 2.35 g (97%) of crude solid product, which sintered at 170 °C and decomposed at 190–200 °C. The compound can be recrystallized from cyclohexane, but the resultant product is then obtained as the solvate with one molecule of cyclohexane, which could not be removed under vacuum at room temperature. Anal. Calcd for $(C_2H_5)_2B(\mu\text{-pz}^*)_2Pd(\pi\text{-}CH_2CHCH_2)\cdot C_6H_{12} = C_{39}H_{49}BFe_2N_4Pd$ (M_r = 802.3): C, 58.33; H, 6.16; B, 1.35; Fe, 13.92; N, 6.98; Pd, 13.26. Found: C, 58.36; H, 5.94; B, 1.49; Fe, 13.99; N, 6.62; Pd, 13.98.

NMR data: (solution in CD_2Cl_2) $\delta(^1H)$ 7.69 (2 H, d, J = 2.2), 6.45 (2 H, d, J = 1.7), 5.08 (1 H, h), 4.68* (2 H, s), 4.50* (2 H, s), 4.30 (4 H, t, J = 1.7), 4.17 (10 H, two overlapping s), 2.84 (2 H, ill-resolved d, J = ca. 6–7), 2.31 (2 H, d, J = 11.5), 1.43 (12 H, s, cyclohexane), 1.3–1.06 (10 H, m); $\delta(^{11}B)$ 1.0 (s, $h_{1/2}$ = 225 Hz); $\delta(^{13}C)$ 152.5, 135.2, 113.6, 105.2, 81.8, 70.5, 70.2, 69.8, 68.8, 68.5, 58.8, 27.4 (cyclohexane), 18*, 12*, 10.0, 9.6. The mass spectrum exhibited the highest peak cluster at m/z 689 for $[M-C_2H_5]$.

$Tl[(pz^*)_2BH_2]$. A stirred mixture of 2.7 g (50 mmol) of KBH_4, 28 g (0.11 mol) of Hpz*, and 300 mL of dimethylacetamide was heated until 2.5 L of hydrogen had evolved. Volatile material was removed under vacuum at 130–140 °C. The solid residue was dissolved in a mixture of 400 mL of tetrahydrofuran and 50 mL of acetone and filtered through Celite. An aqueous solution of 0.2 mol of $TlNO_3$ was added to the filtrate, and the mixture was stirred. The resultant precipitate was collected, washed with methanol, and dried to give 13 g (36%) of the desired orange complex, decomposing at 203–206 °C. (Unreacted Hpz* can be recovered from the filtrate by stirring with water and methylene chloride. The organic phase is then filtered through alumina and evaporated to dryness.) Anal. Calcd for $C_{26}H_{24}BFe_2N_4Tl$ (M_r = 719.38): C, 43.39; H, 3.36; B, 1.50; Fe, 15.53; N, 7.79; Tl, 28.43. Found: C, 43.67; H, 3.94; B, 1.19; Fe, 15.17; N, 7.54.

NMR data: (solution in CD_2Cl_2) $\delta(^1H)$ 7.44 (1 H, d, J = 2.2), 6.25 (1 H, d, J = 2.0), 4.53 (2 H, t, J = 1.9), 4.26 (2 H, t, J = 1.8), 4.05 (5 H, s), 1.5* (1 H); $\delta(^{11}B)$ −8.8 (ill-resolved t, J = ca. 90); $\delta(^{13}C)$ 152.1, 137.9, 103.7, 79.6, 70.1, 69.1, 67.8. The mass spectrum exhibited a parent ion cluster at m/z 719 with the correct calculated isotopic distribution.

$(CH_3)_2HN\cdot B(pz^*)_3$. A mixture of 3.6 g (14 mmol) of Hpz*, 0.68 g (4.8 mmol) of tris(dimethylamino)borane, $[(CH_3)_2N]_3B$,[4] and 50 mL of benzene was refluxed with stirring for 2 h. The mixture was cooled to room temperature and filtered, and benzene was stripped of the clear filtrate to leave an essentially quantitative yield of the desired material as a dark orange solid, mp 170–175 °C dec. Anal. Calcd for $C_{41}H_{40}BFe_3N_7$ (M_r = 809.17): C, 80.86; H, 5.02; B, 1.34; Fe, 20.70; N, 12.12. Found: C, 60.70; H, 5.08; B, 1.39; Fe, 19.86; N, 11.69.

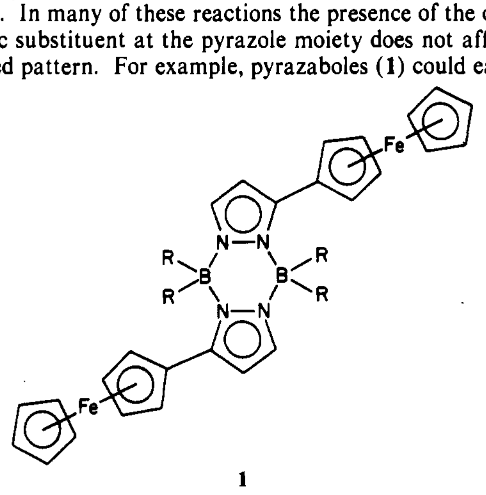
NMR data: $\delta(^1H)$ 7.13 (3 H, d, J = 1.7), 6.30 (3 H, d, J = 1.9), 4.71* (6 H, s), 4.25* (6 H, s), 4.04* (15 H, s), 2.98* (6 H, s); $\delta(^{11}B)$ 0.8 ($h_{1/2}$ = 50 Hz); $\delta(^{13}C)$ 152.6, 135.9, 103.0, 79.6, 69.3, 68.2, 66.6, 39.5; (solution in CD_2Cl_2) $\delta(^1H)$ 7.12 (3 H, d, J = 2.4), 6.33 (3 H, d, J = 2.3), 4.71 (6 H, t, J = 1.8), 4.6* (1 H, s), 4.26 (6 H, t, J = 1.8), 4.04 (15 H, s), 2.94 (6 H, s).

Results and Discussion

3-Ferrocenylpyrazole (=Hpz*) has been prepared in a manner analogous to that used for the synthesis of 3-*tert*-butylpyrazole and 3-phenylpyrazole.[5] A substantial amount of $[(Fc)COCH_2CH{=}N-]_2$ (Fc = ferrocenyl) was coproduced along with Hpz* during this reaction, but this byproduct could be reacted with additional hydrazine to give a reasonable yield of the desired product. (Note: This latter complication is not encountered when simpler substituted pyrazoles are synthesized.) The compound is an orange crystalline material that is stable in air.

3-Ferrocenylpyrazole was reacted with metallic potassium to form the salt Kpz* and with $[(\pi\text{-}CH_2CCH_3CH_2)PdCl]_2$ to yield the complex $[(\pi\text{-}CH_2CCH_3CH_2)Pd(pz^*)]_2$. The former was characterized by NMR data. The species $Zn(pz^*)_2$ was also prepared from Hpz* and $ZnCl_2$ in the presence of triethylamine as HCl acceptor, but was found to be an insoluble material that could not be studied by solution NMR spectroscopy.

Reactions of Hpz*—analogous to those of the unsubstituted parent pyrazole (=Hpz)—with various boron species have been studied. In many of these reactions the presence of the organometallic substituent at the pyrazole moiety does not affect the expected pattern. For example, pyrazaboles (**1**) could easily be obtained; i.e., the reaction of Hpz* with $(CH_3)_2N\cdot BH_3$ readily gave the pyrazabole $H_2B(\mu\text{-pz}^*)_2BH_2$, analogous to the corresponding reaction of Hpz,[6] and the pyrazabole $(C_2H_5)_2B(\mu\text{-pz}^*)_2B(C_2H_5)_2$ was prepared from $(CH_3)_2NB(C_2H_5)_2$ in the same manner as described for the reaction of the latter aminoborane with Hpz.[7] However, in both cases the resultant pyrazabole was the symmetrical species with the ferrocenyl substituents in the 1,5-positions of the pyrazabole skeleton, as evidenced by the NMR data. This is in agreement with analogous reactions of 3-substituted pyrazoles containing a bulky substituent (C_6H_5, $C(CH_3)_3$)[8] but in contrast to the reaction of 3-methylpyrazole with, for example, $(CH_3)_3N\cdot BH_3$.[9] In this latter case, a mixture of both 1,5- and 1,7-dimethylpyrazabole was obtained. Hence, the ferrocenyl substituent exhibits a distinct directive effect in the formation of the pyrazaboles.



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The reaction of Hpz* with aminoboranes proceeded in the same stepwise fashion that has been observed for the reaction of Hpz with the same boranes. Thus, the complexes $(CH_3)_2NH\cdot B(C_8H_{14})(pz^*)$ and $Hpz^*\cdot B(pz^*)(C_8H_{14})$ (where $(C_8H_{14})BH$ = 9-borabicyclo[3.3.1]nonane) were obtained by paralleling corresponding reactions of Hpz.[3] Only very broad and featureless signals (of appropriate intensities) were observed in the ^1H NMR spectrum of the material. In addition, the ^{11}B NMR spectrum exhibited two signals, i.e., for three- and four-coordinate boron. These observations suggest an equilibrium between the individual donor and acceptor and the complex. This same feature has been observed for other complexes of the type $Hpz\cdot B(pz)R_2$, where R is a bulky substituent.[10] The NMR data gave no evidence for the presence of isomeric species, and the ferrocenyl substituent is presumably always in the 3-position of the pyrazole ring.

The complex $Hpz^*\cdot B(pz^*)(C_8H_{14})$ was reacted with NaH to give the salt $Na[(pz^*)_2B(C_8H_{14})]$, and the corresponding potassium salt was obtained from the reaction of Kpz* with $(CH_3)_2HN\cdot B(pz^*)(C_8H_{14})$.

Finally, the reaction of tris(dimethylamino)borane with Hpz* gave access to $(CH_3)_2HN\cdot B(pz^*)_3$ in a fashion analogous to the corresponding reaction of the cited borane with Hpz.[11]

On the other hand, the ferrocenyl substituent can render the pyrazole–boron derivatives sensitive to chemical attack. For

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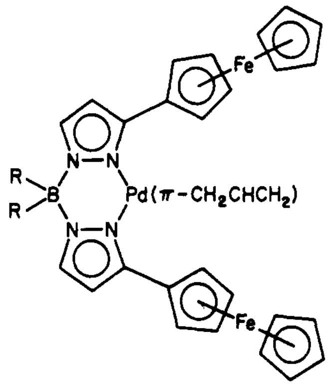
example, although the parent pyrazabole $H_2B(\mu\text{-pz})_2BH_2$ is readily halogenated with elemental halogen to give $X_2B(\mu\text{-pz})_2BX_2$ (X = Cl, Br),[8] the pyrazabole $H_2B(\mu\text{-pz*})_2BH_2$ decomposed on reaction with elemental halogen under identical reaction conditions. Furthermore, extensive decomposition was observed on treatment of $H_2B(\mu\text{-pz*})_2BH_2$ with $(C_2H_5)_2O\cdot BF_3$, although in the case of $H_2B(\mu\text{-pz})_2BH_2$ the reaction has been used for the preparation of both $F_2B(\mu\text{-pz})_2BH_2$ and $F_2B(\mu\text{-pz})_2BF_2$.[8]

The ion $[H_2B(pz^*)_2]^-$ was obtained by the reaction of KBH_4 with Hpz* and was isolated as the Tl(I) salt. The formation of the anion is analogous to the reaction of Hpz with KBH_4.[12] However, in the case of Hpz*, at the temperatures required to make tris(1-pyrazolyl)borates,[12] the generation of hydrogen stopped after about half of the theoretical amount had been generated and, subsequently, extensive decomposition occurred and the formation of cyclopentadiene was observed.

Representative transition-metal complexes were prepared from the bis(3-ferrocenylpyrazol-1-yl)borate anions, e.g., $(C_2H_5)_2B(\mu\text{-pz*})_2Pd(\pi\text{-}CH_2CHCH_2)$ and $(C_8H_{14})B(\mu\text{-pz*})_2Pd(\pi\text{-}CH_2CHCH_2)$ (**2**). These species are interesting since they are the first poly(1-pyrazolyl)borate complexes in which the boron is bonded to a transition metal via the dinitrogen group of a pyrazole and is simultaneously bonded to another transition metal via one nitrogen and the carbon framework of the same pyrazole moiety.



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It is of interest to note that for both of the complexes $R_2B(\mu\text{-pz*})_2Pd(\pi\text{-}CH_2CHCH_2)$ the room-temperature ^1H and ^{13}C NMR signals of the C_5H_4 ring of the ferrocenyl moiety (i.e., the ring directly bonded to the pyrazole framework) are complex. Nevertheless, the assignments of the observed signals can be made on the basis of their relative intensities and in conjunction with relevant data of related species.[3,13] For example, the ^1H (^{13}C) signals (all in ppm) of $(C_2H_5)_2B(\mu\text{-pz*})_2Pd(\pi\text{-}CH_2CHCH_2)$ for the allyl group are assigned at 5.08 (113.6) for the CH moiety and at 2.84/2.31 (58.8) for the two CH_2 groups. Relevant signal sets of the pyrazolyl ring are – (152.5) for the 3-position, 6.45 (105.2) for the 4-position, and 7.69 (135.2) for the 5-position. The lone C atom of the pz-bonded C_5H_4 ring of the ferrocenyl moiety is at 85.6, and the $^1H(^{13}C)$ signals for the C_5H_5 ring are at 4.17 (70.2). The two ^1H signals at 4.68 (1 H) and 4.50 (1 H) correlate with the ^{13}C signals at 70.5 and 69.8, and the ^1H signal at 4.30 (2 H) has two ^{13}C counterparts at 68.8 and 68.5, thus completing the assignments of the ferrocenyl moiety. All ^1H NMR signals sharpen on lowering of the temperature, and at –70 °C the signals of the C_2H_5 group are sufficiently resolved to clearly show the presence of two magnetically nonequivalent ethyl groups.

The cited assignments do not give an answer, however, as to why essentially four different signals are observed for the four CH units of the C_5H_4 ring. This feature may be explained by interaction of this ring with the allyl group. Indeed, the ^1H NMR signals of the latter are not as well resolved as is the case for similar derivatives obtained from (C-)unsubstituted pyrazole. On the other hand, such latter complexes gave clear evidence for the presence of allyl group rotamers, which also may be reflected in the signals of the (neighboring) C_5H_4 ring of the ferrocenyl groups in the present case.

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