resemble the pattern observed for $[Mn(CO)_5]^-$ and $[Mn(CO)_4PPh_3]^-$, the deviations from C_{3v} symmetry for $Fe(CO)_4PPh_3$ are less severe, i.e., the axial–Fe–equatorial bond angles are close to 90° (88.2–92.3°) and the C(1)–Fe–P angle is essentially linear (178.3°). As shown in Table VI, Fe lies out of the plane of the equatorial carbon atoms and away from the PPh_3 ligand, a feature which is common in trigonal-bipyramidal ML_4L' structures and which was discussed in the preceding section.

Figure 3 illustrates the packing arrangement of the $[Ph_4P]^+$ and $[Mn(CO)_4PPh_3]^-$ ions. Each $[Mn(CO)_4PPh_3]^-$ ion is surrounded by two cations and two anions at distances of ca. 3.25 Å and by an additional two cations and two anions at distances of ca. 3.5 Å. As shown in Figure 4, each $Fe(CO)_4PPh_3$ molecule is surrounded by eight other molecules at distances of ca. 3.5 Å. Neither arrangement corresponds to an easily recognizable type of molecular packing.

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Registry No. $[Ph_4P][Mn(CO)_4PPh_3]$, 71927-68-9; $Fe(CO)_4PPh_3$, 35679-07-3.

Supplementary Material Available: Listings of structure factor amplitudes and fractional coordinates (58 pages). Ordering information is given on any current masthead page.

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Iron–Nitrogen Bond Lengths in Low-Spin and High-Spin Iron(II) Complexes with Poly(pyrazolyl)borate Ligands

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The structures of bis[hydrotris(1-pyrazolyl)borato]iron(II) (**1**), $C_{18}H_{20}N_{12}B_2Fe$, and bis[hydrotris(3,5-dimethylpyrazolyl)borato]iron(II) (**2**), $C_{30}H_{44}N_{12}B_2Fe$, have been elucidated by single-crystal X-ray diffraction techniques. The iron atom in **1** is in the low-spin state at room temperature, whereas in **2** the iron atom is in the high-spin state at room temperature. Both molecules possess virtual D_{3d} symmetry in the solid state. The average metal–ligand bond distances, $\langle$Fe–N$\rangle$, are 1.973 (7) Å for **1** and 2.172 (22) Å for **2**. The $\langle$Fe–N$\rangle$ value for the high-spin complex is thus 0.199 Å longer than the similar value for the low-spin complex. This is one of the largest values observed for the bond length expansion between the low-spin and high-spin states. The averages of the independent N–Fe–N bond angles are 88.3 (2)° for **1** and 86.6 (5)° for **2**. Crystal data for **1** are as follows: space group $P2_1/c$; $Z = 4$; $a = 12.258$ (3), $b = 11.606$ (2), $c = 16.518$ (3) Å; $\beta = 107.56$ (2)°; $V = 2240$ Å^3; $R = 5.2\%$ for 1890 reflections. Crystal data for **2** are as follows: space group $P1$; $Z = 1$; $a = 8.824$ (3), $b = 10.216$ (4), $c = 10.787$ (4) Å; $\alpha = 116.36$ (3), $\beta = 85.24$ (3), $\gamma = 100.09$ (3)°; $V = 858$ Å^3; $R = 3.9\%$ for 1819 reflections.

Introduction

Beginning in 1966[2] the coordination chemistry of poly(1-pyrazolyl)borate ligands has been the center of exhaustive research. One of the earlier types of complexes studied was of the form $(HBPz_3)_2M$, where M is a divalent metal ion. A crystal structure of one such complex, $(HBPz_3)_2Co$,[3] has appeared. The temperature dependence of the magnetic moment of the complex $(HBPz_3)_2Fe$ (**1**) in chloroform indicated a "spin equilibrium" between the low- and high-spin forms.[4] Spin crossover in the solid state was first implied by the observation of a color change from purple to white upon heating.[5] Magnetic susceptibility and Mössbauer and infrared spectroscopic studies have confirmed this spin crossover at 393 K.[6] Although several Fe(II) compounds are known which exhibit spin-equilibrium characteristics, this Fe(II) complex is unique in that the crossover is from low to high spin and occurs above room temperature. The magnetic properties of a very similar complex, $[HB(C_5H_7N_2)_3]_2Fe$ (**2**), indicated that it is a high-spin complex at room temperature.

Since a change from $t_{2g}{}^6$ low-spin state to a $t_{2g}{}^4e_g{}^2$ high-spin state is predicted to be accompanied by an expansion of the metal–ligand bond length, accurate X-ray crystal analyses are important to obtain the magnitude and pattern of such changes. An approximate value for the bond-length difference, δ, of 0.12 Å resulted from a structure study[7] of $[Fe(phen)_2(NCS)_2]$ at 295 and 100 K; however, the accuracy of these determinations was poor. The room-temperature structural study[8] of two solvated forms of the α-picolyamine (α-P) complex, $[Fe(\alpha\text{-}P)_3]Cl_2$, have yielded a more accurate value of 0.192 Å for δ. In addition to the spin-state difference, a major stereochemical change resulted from a difference in solvation. For the aquated form, the three amine nitrogen atoms occupy a triangular face of the coordination octahedron. In the methanol solvated form, two amine nitrogen atoms and one pyridine nitrogen atom occupy this triangular face. The possibility thus exists that the spin-state difference as well as the stereochemical difference might both contribute to δ. With this in mind we have completed the structural analysis of the complexes **1** and **2** in order to obtain an accurate value for δ in the absence of a stereochemical change.

Experimental Section

Syntheses of **1** and **2** were accomplished by a previously published method.[9] All X-ray measurements were made on a four-circle

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(1) (a) On Sabbatical leave from Department of Chemistry, West Texas State University, Canyon, Texas. (b) Baylor University. (c) Abilene Christian University.

(2) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

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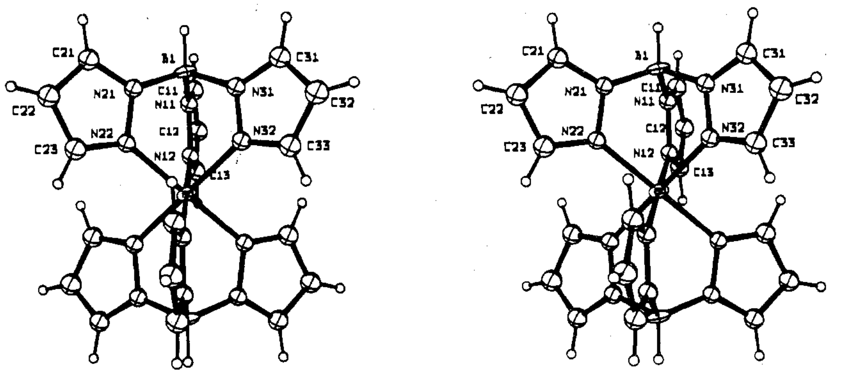

Figure 1. Stereoview of $(HBPz_3)_2Fe$. Thermal motion ellipsoids enclosing 30% probability are represented, except for the hydrogen atoms which are drawn artifically small.

Table I

Summary of Crystal Data		
compd	1	2
formula	$C_{18}H_{20}N_{12}B_2Fe$	$C_{30}H_{44}N_{12}B_2Fe$
fw	481.9	650.3
a, Å	12.258 (3)	8.824 (3)
b, Å	11.606 (2)	10.216 (4)
c, Å	16.518 (3)	10.787 (4)
α, deg		116.36 (3)
β, deg	107.56 (2)	85.24 (3)
γ, deg		100.09 (3)
Z	4	1
vol, Å^3	2240.3	857.8
space group	$P2_1/c$	$P\bar{1}$
d, g cm^{-3} (found)	1.43 (1.45)	1.26 (1.26)
$F(000)$	992	344
T, °C	16	16
Data Collection		
cryst dimens, mm	0.25 × 0.31 × 0.36	0.32 × 0.32 × 0.35
μ(Mo K$\bar{\alpha}$), cm^{-1}	7.03	4.76
limiting sphere	4° < 2θ < 52°	2.6° < 2θ < 50°
λ(Mo K$\bar{\alpha}$), Å	0.710 69	0.710 69
total data	4408	2998
used data	1890	1819
signif criterion, $I > n \times \sigma(I)$	$n = 3$	$n = 2$

Enraf-Nonius CAD-4 autodiffractometer equipped with a Si(Li) energy-dispersive detector.

The cell parameters for each crystal listed in Table I were obtained from a least-squares refinement of 25 carefully centered reflections. Intensity data were collected by the θ–2θ scan method at a variable scan rate determined by a fast (3.3° min^{-1}) prescan. For each crystal the intensities of two check reflections were monitored every 2 h of data collection. Examination of these intensities revealed only random variations (<6% deviation from mean intensity) that did not constitute any trend. Stability of the crystals and instrument was thus ensured.

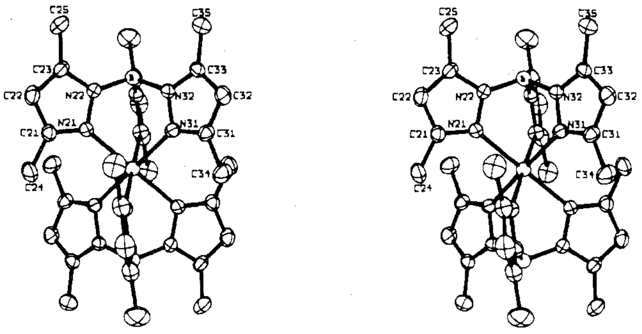

Figure 2. Stereoview of $[HB(C_5H_7N_2)_3]_2Fe$. Thermal motion ellipsoids enclosing 30% probability are represented.

The data were corrected for Lorentz and polarization effects. Due to the small values for μ and the isometric shape of each crystal, analytical corrections for absorption were deemed unnecessary. Standard deviations of the structure factors were calculated according to

$$\sigma(|F_o|) = 0.5(\mathrm{VLP})^{1/2}[(\mathrm{Pk} + \mathrm{Bg} + p^2 I_{\mathrm{rel}}^2)/I_{\mathrm{rel}}]^{1/2}$$

where VLP is the standard Lorentz–polarization term, Pk is the peak intensity, Bg is the sum of the background counts taken on both sides of the peak, p is the ignorance factor (0.02 for both compounds), and I_{rel} is Pk − Bg.

Structure Solution and Refinement

A C-centered arrangement of the Fe atoms for **1** was suspected due to the strong reflections being dominated by the *uuu* and *ggg* parity groups. Attempts to solve the structure by conventional heavy-atom

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $(HBPz_3)_2Fe$

ATOM	X[A]	Y	Z	U11 OR B[B]	U22	U33	U12	U13	U23
FE(1)	5000	5000	5000	293(7)	382(9)	277(7)	-81(8)	13(5)	19(8)
FE(2)	0	10000	5000	401(8)	408(9)	307(7)	-127(9)	71(5)	25(8)
B(1)	3358(6)	3559(7)	3579(4)	342(44)	401(51)	265(45)	-137(39)	-74(34)	9(38)
B(2)	73(7)	7807(7)	6061(5)	487(53)	432(54)	414(48)	-155(44)	65(40)	161(42)
HB(1)[C]	280	307	310	5.0					
HB(2)	9	706	642	5.0					

[A] NUMBERS IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES REFER TO THE ESTIMATED STANDARD DEVIATIONS IN THE UNITS OF THE LEAST SIGNIFICANT DIGITS. POSITIONAL AND THERMAL PARAMETERS ARE PRESENTED X10^4. [B] THE FORM OF THE ANISOTROPIC THERMAL EQUATION IS: $\mathrm{EXP}[-19.74(U11H^2A^{*2} + U22K^2B^{*2} + U33L^2C^{*2} + 2U12HKA^*B^* + 2U13HLA^*C^* + 2U23KLB^*C^*)]$. [C] POSITIONAL PARAMETERS FOR THE REMAINING ATOMS ARE PRESENTED X10^3.

Table III. Rigid Group Parameters for $(HBPz_3)_2Fe$

RIGID GROUP PARAMETERS

GROUP	X_C^A	Y_C	Z_C	$DELTA^B$	EPSILON	ETA
PH(1)	0.4664(3)	0.3344(3)	0.5055(2)	0.190(3)	2.673(3)	-2.376(3)
PH(2)	0.3341(2)	0.5266(3)	0.4475(2)	-2.174(3)	2.998(3)	-0.679(3)
PH(3)	0.5125(3)	0.4729(3)	0.3853(2)	1.862(6)	-2.099(3)	-1.945(6)
PH(4)	-0.0586(3)	0.9833(4)	0.5986(2)	-2.300(5)	2.191(3)	0.938(5)
PH(5)	-0.0724(3)	0.8521(3)	0.4584(3)	-0.790(4)	-2.485(3)	0.910(4)
PH(6)	0.1381(3)	0.9148(3)	0.5642(2)	1.473(3)	-3.152(3)	2.540(3)

DERIVED ATOMIC PARAMETERS

ATOM	X^C	Y	Z	B, A^2	ATOM	X^C	Y	Z	B, A^2
N(11)	3909(3)	2825(3)	4376(2)	3.0(1)	N(41)	-475(3)	8803(3)	6397(3)	3.5(1)
N(12)	4664(3)	3344(3)	5055(2)	2.9(1)	N(42)	-585(3)	9833(4)	5986(2)	3.4(1)
C(11)	3841(3)	1700(3)	4538(2)	3.9(2)	C(41)	-906(4)	8884(3)	7050(2)	3.8(2)
C(12)	4561(4)	1467(3)	5336(3)	4.0(2)	C(42)	-1310(4)	9984(4)	7074(2)	4.1(1)
C(13)	5060(3)	2519(4)	5638(2)	3.6(1)	C(43)	-1093(4)	10550(3)	6398(3)	3.8(2)
H(11)	3376(5)	1144(4)	4169(4)	5.0	H(41)	-935(6)	8289(5)	7437(3)	5.0
H(12)	4681(6)	740(4)	5611(4)	5.0	H(42)	-1659(5)	10277(6)	7472(3)	5.0
H(13)	5603(4)	2627(6)	6180(2)	5.0	H(43)	-1281(6)	11333(3)	6254(4)	5.0
N(21)	2741(3)	4575(3)	3829(2)	2.9(1)	N(51)	-619(3)	7613(4)	5122(2)	3.4(1)
N(22)	3341(2)	5266(3)	4475(2)	2.8(1)	N(52)	-723(3)	8521(3)	4584(3)	3.3(1)
C(21)	1662(3)	4958(4)	3527(2)	3.6(1)	C(51)	-1192(4)	6706(3)	4697(3)	4.0(2)
C(22)	1542(3)	5918(4)	3979(3)	3.9(2)	C(52)	-1686(3)	7015(4)	3864(2)	4.2(2)
C(23)	2613(3)	6082(3)	4566(2)	3.7(1)	C(53)	-1371(3)	8158(4)	3819(2)	3.5(2)
H(21)	1068(4)	4630(5)	3076(3)	5.0	H(51)	-1255(6)	5966(3)	4925(4)	5.0
H(22)	868(4)	6362(5)	3899(4)	5.0	H(52)	-2140(5)	6540(5)	3423(3)	5.0
H(23)	2792(5)	6689(4)	4971(3)	5.0	H(53)	-1590(5)	8608(5)	3316(3)	5.0
N(31)	4351(3)	4047(3)	3294(2)	3.0(1)	N(61)	1279(3)	8188(3)	6085(3)	3.5(1)
N(32)	5125(3)	4729(3)	3853(2)	3.0(1)	N(62)	1381(3)	9148(3)	5642(2)	3.4(1)
C(31)	4616(4)	3979(3)	2565(2)	3.6(1)	C(61)	2321(4)	7763(3)	6481(3)	4.7(2)
C(32)	5581(4)	4625(4)	2640(2)	4.2(2)	C(62)	3128(3)	8452(4)	6298(3)	5.4(2)
C(33)	5872(3)	5080(3)	3456(2)	3.7(1)	C(63)	2504(4)	9309(4)	5771(3)	4.5(2)
H(31)	4213(5)	3558(5)	2072(3)	5.0	H(61)	2489(6)	7098(4)	6831(4)	5.0
H(32)	5955(5)	4728(6)	2220(3)	5.0	H(62)	3933(3)	8351(7)	6495(5)	5.0
H(33)	6511(4)	5568(5)	3690(4)	5.0	H(63)	2836(5)	9917(5)	5540(4)	5.0

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN PREVIOUSLY DEFINED: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511,(1965). [C] POSITIONAL PARAMETERS ARE PRESENTED X10^4.

techniques produced ambiguous results. Both structures were eventually solved by direct methods using the MULTAN[10] package. Each structure was refined by full-matrix least-squares techniques. For **1** the six pyrazolyl rings were treated as rigid groups of idealized geometry.[11] The hydrogen atoms were included at their idealized positions and were not refined. Variable, isotropic extinction parameters,[12] 2.0 (1) × 10^{-6} for **1** and 4.8 (2) × 10^{-6} for **2**, were also utilized. The final values for $R_F = \sum\Delta F/\sum|F_o|$, where $\Delta F = ||F_o| - |F_c||$, are 0.052 for **1** and 0.039 for **2**. The final values for $R_{wF} = [\sum w(\Delta F)^2/\sum w(|F_o|)^2]^{1/2}$, where $w = \sigma^{-2}(|F_o|)$, are 0.052 and 0.035 for **1** and **2**, respectively. In the final least-squares cycles the largest shift:σ ratio for any parameter was 0.4 and the standard deviations of an observation of unit weight were 1.27 for **1** and 0.78 for **2**. Final difference electron density maps revealed a randomly fluctuating background below 0.4 e $Å^{-3}$. Additional peaks of density +0.6 e $Å^{-3}$ along the C21–C22 and C41–C42 bonds were observed for **1**. Atomic

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Table IV. Positional and Thermal Parameters for $[HB(C_5H_7N_2)_3]_2Fe$

ATOM	X[A]	Y	Z	U11 OR B[B]	U22	U33	U12	U13	U23
FE	5000	5000	5000	47(1)	45(1)	44(1)	7(1)	0(1)	20(1)
N(11)	3577(4)	5737(4)	3938(4)	58(3)	45(3)	52(3)	13(2)	-1(2)	21(2)
N(12)	3114(4)	4718(4)	2626(4)	45(3)	58(3)	55(3)	9(2)	0(2)	31(2)
N(21)	6052(4)	3804(4)	2996(4)	42(2)	52(2)	45(2)	7(2)	0(2)	15(2)
N(22)	5082(4)	3017(4)	1886(4)	46(2)	50(2)	42(3)	7(2)	4(2)	18(2)
N(31)	3272(4)	3074(4)	4439(4)	54(3)	48(2)	40(2)	1(2)	-1(2)	19(2)
N(32)	2664(4)	2471(4)	3127(4)	44(2)	43(2)	44(3)	4(2)	0(2)	15(2)
C(11)	3205(5)	7021(5)	4104(6)	59(4)	54(4)	80(4)	18(3)	6(3)	33(3)
C(12)	2529(6)	6842(6)	2912(7)	74(4)	78(4)	109(5)	30(3)	9(4)	66(4)
C(13)	2499(5)	5393(6)	1999(6)	52(3)	85(4)	78(4)	15(3)	2(3)	56(4)
C(14)	3510(6)	8389(5)	5423(6)	105(5)	53(4)	103(5)	27(3)	9(4)	33(4)
C(15)	1937(7)	4588(7)	550(6)	112(5)	125(5)	94(5)	17(4)	-31(4)	70(4)
C(21)	7481(5)	3595(5)	2506(5)	47(3)	51(3)	57(3)	10(3)	5(3)	20(3)
C(22)	7431(6)	2693(5)	1087(5)	54(4)	67(4)	67(4)	19(3)	18(3)	24(3)
C(23)	5915(6)	2354(5)	719(5)	65(4)	56(3)	40(3)	11(3)	10(3)	17(3)
C(24)	8851(5)	4255(5)	3426(5)	43(3)	85(4)	83(4)	13(3)	5(3)	24(3)
C(25)	5197(6)	1425(6)	-676(5)	90(4)	88(4)	45(3)	11(3)	11(3)	17(3)
C(31)	2453(5)	2277(5)	5052(5)	65(3)	48(3)	47(3)	4(3)	4(3)	22(3)
C(32)	1358(6)	1204(5)	4161(6)	70(4)	54(3)	70(4)	-9(3)	6(3)	31(3)
C(33)	1510(5)	1355(5)	2957(5)	46(3)	41(3)	53(3)	-2(2)	0(3)	12(3)
C(34)	2759(6)	2611(5)	6524(5)	100(4)	75(4)	60(4)	-2(3)	3(3)	41(3)
C(35)	589(6)	507(5)	1672(5)	71(4)	65(4)	67(4)	-8(3)	-8(3)	16(3)
B	3347(6)	3101(6)	2093(5)	48(4)	57(4)	48(4)	5(3)	-1(3)	22(3)
H(1A)[C]	261	861	603	6.0					
H(1B)	428	832	600	6.0					
H(1C)	390	929	533	6.0					
H(2)	216	762	276	6.0					
H(3A)	202	519	4	6.0					
H(3B)	249	376	-3	6.0					
H(3C)	85	413	46	6.0					
H(4A)	858	485	437	6.0					
H(4B)	942	354	342	6.0					
H(4C)	959	492	315	6.0					
H(5)	832	236	48	6.0					
H(6A)	593	103	-139	6.0					
H(6B)	446	59	-68	6.0					
H(6C)	462	198	-95	6.0					
H(7A)	209	195	683	6.0					
H(7B)	380	251	666	6.0					
H(7C)	262	360	718	6.0					
H(8)	61	47	434	6.0					
H(9A)	-19	-25	172	6.0					
H(9B)	5	113	144	6.0					
H(9C)	121	1	86	6.0					
HB	275	244	108	6.0					

[A] NUMBERS IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES REFER TO THE ESTIMATED STANDARD DEVIATIONS IN THE UNITS OF THE LEAST SIGNIFICANT DIGITS. POSITIONAL($X10^4$) AND THERMAL($X10^3$) PARAMETERS ARE PRESENTED.[B] THE FORM OF THE ANISOTROPIC THERMAL EQUATION IS: $EXP[-19.74(U11H^2A^{*2}+U22K^2B^{*2}+U33L^2C^{*2}+2U12HKA^*B^*+2U13HLA^*C^*+2U23KLB^*C^*)]$. POSITIONAL PARAMETERS[C] FOR THE REMAINING ATOMS ARE PRESENTED $X10^3$.

scattering factors for all atoms and the anomalous dispersion terms for Fe were taken from the usual source.[13] Final atomic parameters are given in Tables II, III, and IV. For a description of the major computer programs used in this work, see ref 11.

Discussion of Results

The molecular geometries of **1** and **2** are displayed in Figures 1 and 2, respectively. Since the two crystallographically independent molecules of **1** are virtually identical in every detail, only the molecule containing Fe(1) is shown. The

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Table V. Selected Bond Distances (Å) for $(HBPz_3)_2Fe$

Fe(1)–N(12)	1.973 (3)	B(1)–N(11)	1.543 (8)
Fe(1)–N(22)	1.980 (3)	B(1)–N(21)	1.523 (8)
Fe(1)–N(32)	1.972 (3)	B(1)–N(31)	1.541 (8)
Fe(2)–N(42)	1.979 (3)	B(2)–N(41)	1.524 (9)
Fe(2)–N(52)	1.960 (3)	B(2)–N(51)	1.544 (8)
Fe(2)–N(62)	1.971 (4)	B(2)–N(61)	1.533 (9)
Fe(1)–B(1)	3.083 (5)		
Fe(2)-B(2)	3.076 (5)		

Table VI. Selected Bond Distances (Å) for $[HB(C_5H_7N_2)_3]_2Fe$

Fe–N(11)	2.190 (4)	C(11)–C(12)	1.387 (9)
Fe–N(21)	2.179 (4)	C(11)–C(14)	1.489 (9)
Fe–N(31)	2.147 (4)	C(21)–C(22)	1.393 (8)
N(11)–N(12)	1.377 (6)	C(21)–C(24)	1.491 (7)
N(11)–C(11)	1.340 (7)	C(31)–C(32)	1.381 (7)
N(21)–N(22)	1.373 (5)	C(31)–C(34)	1.506 (7)
N(21)–C(21)	1.341 (6)	C(13)–C(12)	1.363 (9)
N(31)–N(32)	1.381 (5)	C(13)–C(15)	1.487 (9)
N(31)–C(31)	1.348 (6)	C(23)–C(22)	1.368 (7)
N(12)–C(13)	1.355 (7)	C(23)–C(25)	1.500 (7)
N(22)–C(23)	1.360 (6)	C(33)–C(32)	1.369 (8)
N(32)–C(33)	1.345 (6)	C(33)–C(35)	1.486 (7)
N(12)–B	1.536 (7)	N(22)–B	1.542 (6)
		N(32)–B	1.553 (7)

Table VII. Selected Bond Angles (deg) for $(HBPz_3)_2Fe$

Fe(1)–N(12)–N(11)	119.6 (3)	Fe(2)–N(42)–N(41)	119.4 (3)
Fe(1)–N(22)–N(21)	119.5 (3)	Fe(2)–N(52)–N(51)	120.4 (3)
Fe(1)–N(32)–N(31)	120.3 (3)	Fe(2)–N(62)–N(61)	119.9 (3)
Fe(1)–N(12)–C(13)	133.9 (3)	Fe(2)–N(42)–C(43)	134.1 (3)
Fe(1)–N(22)–C(23)	133.8 (3)	Fe(2)–N(52)–C(53)	133.1 (3)
Fe(1)–N(32)–C(33)	133.2 (3)	Fe(2)–N(62)–N(63)	133.6 (3)
N(12)–Fe(1)–N(22)	88.3 (2)	N(42)–Fe(2)–N(52)	88.0 (2)
N(12)–Fe(1)–N(32)	88.1 (2)	N(42)–Fe(2)–N(62)	88.5 (2)
N(22)–Fe(1)–N(32)	88.3 (1)	N(52)–Fe(2)–N(62)	88.5 (2)
B(1)–N(11)–N(12)	118.2 (4)	B(2)–N(41)–N(42)	118.3 (4)
B(1)–N(21)–N(22)	118.3 (4)	B(2)–N(51)–N(52)	117.3 (4)
B(1)–N(31)–N(32)	117.4 (4)	B(2)–N(61)–N(62)	117.8 (4)
B(1)–N(11)–C(11)	132.1 (4)	B(2)–N(41)–C(41)	132.1 (4)
B(1)–N(21)–C(21)	132.1 (4)	B(2)–N(51)–C(51)	133.1 (4)
B(1)–N(31)–C(31)	133.0 (4)	B(2)–N(61)–C(61)	132.6 (5)
N(11)–B(1)–N(21)	108.8 (5)	N(41)–B(2)–N(51)	107.9 (5)
N(11)–B(1)–N(31)	106.3 (5)	N(41)–B(2)–N(61)	107.5 (5)
N(21)–B(1)–N(31)	107.5 (5)	N(51)–B(2)–N(61)	107.6 (5)

Table VIII. Selected Bond Angles (deg) for $[HB(C_5H_7N_2)_3]_2Fe$

N(11)–Fe–N(21)	87.1 (1)	B–N(32)–C(33)	129.7 (4)
N(11)–Fe–N(31)	86.3 (1)	N(11)–C(11)–C(12)	110.2 (5)
N(21)–Fe–N(31)	86.3 (1)	N(11)–C(11)–C(14)	121.5 (5)
N(12)–B–N(22)	108.9 (4)	C(12)–C(11)–C(14)	128.2 (5)
N(12)–B–N(32)	110.8 (4)	N(21)–C(21)–C(22)	109.8 (4)
N(22)–B–N(32)	110.1 (4)	N(21)–C(21)–C(24)	121.9 (5)
Fe–N(11)–N(12)	115.7 (3)	C(22)–C(21)–C(24)	128.3 (4)
Fe–N(21)–N(22)	117.1 (3)	N(31)–C(31)–C(32)	110.7 (5)
Fe–N(31)–N(32)	116.9 (3)	N(31)–C(31)–C(34)	121.2 (4)
Fe–N(11)–C(11)	137.1 (4)	C(32)–C(31)–C(34)	128.1 (5)
Fe–N(21)–C(21)	136.5 (3)	C(11)–C(12)–C(13)	106.1 (5)
Fe–N(31)–C(31)	138.0 (3)	C(21)–C(22)–C(23)	106.5 (5)
N(12)–N(11)–C(11)	106.1 (4)	C(31)–C(32)–C(33)	106.2 (5)
N(22)–N(21)–C(21)	106.4 (4)	N(12)–C(13)–C(12)	108.2 (5)
N(32)–N(31)–C(31)	104.9 (4)	N(12)–C(13)–C(15)	122.1 (5)
B–N(12)–N(11)	120.1 (4)	C(12)–C(13)–C(15)	129.7 (6)
B–N(22)–N(21)	119.2 (4)	N(22)–C(23)–C(22)	107.5 (4)
B–N(32)–N(31)	119.7 (4)	N(22)–C(23)–C(25)	123.0 (4)
N(11)–N(12)–C(13)	109.4 (4)	C(22)–C(23)–C(25)	129.4 (5)
N(21)–N(22)–C(23)	109.8 (4)	N(32)–C(33)–C(32)	107.6 (4)
N(31)–N(32)–C(33)	110.6 (4)	N(32)–C(33)–C(35)	123.8 (4)
B–N(12)–C(13)	130.5 (4)	C(32)–C(33)–C(35)	128.6 (5)
B–N(22)–C(23)	130.8 (4)		

dramatic stereochemical similarity for **1**, **2**, and $(HBPz_3)_2Co^3$ is immediately obvious. Tables V, VI, VII, and VIII present the chemically important bond lengths and bond angles for **1** and **2**.

For **1** the planes defined by the pyrazolyl rings associated with Fe(1) intersect to form angles of 126° [PZ(1) with PZ(2)], 117° [PZ(1) with PZ(3)], and 117° [PZ(2) with PZ(3)]; while those associated with Fe(2) intersect to form angles of 119° [PZ(4) with PZ(5)], 119° [PZ(4) with PZ(6), and 122° [PZ(5) with PZ(6)]. For **2** the planes defined by the pyrazolyl rings intersect to form angles of 113° (ring 1 with ring 2), 122° (ring 1 with ring 3), and 123° (ring 2 with ring 3). The virtual D_{3d} symmetry observed for $(HBPz_3)_2Co^3$ is thus also possessed by these molecules.

The predominant interest in these structures involves the variations in the Fe–N bond lengths. A predicted value for the change in ionic radius for Fe(II) upon going from the low-spin to high-spin electronic configuration is 0.17 Å.[14] The largest Fe–N bond length difference, δ, previously observed for the spin transition was 0.192 Å,[8] with the ⟨Fe–N⟩ bond lengths being 2.006 (22) and 2.198 (18) Å for the low-spin and high-spin forms, respectively. This value for δ is thus 4.8 times the sum of the standard deviations of these average values. The ⟨Fe–N⟩ bond lengths are 1.973 (7) and 2.172 (22) Å for **1** and **2**, respectively. The difference in ⟨Fe–N⟩ bond lengths, δ, in the current work, 0.199 Å, is in excellent agreement with the value of Greenaway and Sinn;[8] however, this value of δ is 6.9 times the sum of the standard errors for the average bond lengths. Such agreement for the value of δ thus indicates the stereochemical change observed for the $[Fe(\alpha\text{-}P)_3]^{2+}$ cation did not make a significant contribution to δ.

Although **1** and $(HBPz_3)_2Co^3$ are isostructural on the molecular level, their molecular packing schemes, and thereby their lattice constants, are entirely different. Several crystals were mounted in an attempt to find a crystal that was isomorphous to the Co analogue, but to no avail. The solvent from which the crystals of $(HBPz_3)_2Co$ were grown was not known; thus the extent to which the solvent influenced the crystal morphology could not be ascertained.

The molecules within both crystals are separated by normal van der Waals contact distances. For **2** no intramolecular contact distances involving nonbonded atoms are shorter than the sum of their respective van der Waals radii.

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Supplementary Material Available: Listings of the structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(14) J. E. Huheey, "Inorganic Chemistry", 2nd ed., Harper and Row, New York, 1978, pp 367–368.