Anionic Poly(pyrazolyl)borate Ligands Obtained from 3,5-Dimethylpyrazole and 3,5-Diphenylpyrazole and Their Cobalt(II) Complexes − X-ray Crystallographic and ^{1}H NMR Studies[‡]

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Synthesis of poly(pyrazolyl)borate anionic ligands composed of 3,5-dimethyl- and 3,5-diphenylpyrazoles and their bis(ligand) high-spin cobalt(II) complexes are described. The molecular structures of [dihydrobis(3,5-diphenylpyrazolyl)borato][hydrobis(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borato]cobalt(II) and bis[dihydro(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borato]cobalt(II) complexes were established by X-ray crystallography. The cobalt center is hexacoordinate in the former with five Co–N$_2$(pyrazolyl) bonds and short Co–H [attached to the boron atom of bis(pyrazolyl)borate] bond (2.03 Å), whereas a distorted tetrahedral geometry was found for the latter due to four Co–N$_2$(pyrazolyl) bonds. Additionally, the pentacoordinate homoscorpionate [tris(3,5-diphenylpyrazolyl)borato]cobalt(II) nitrate side product was obtained from the reaction and characterized structurally. It contains a κ^3-coordinated Tp′ ligand and a κ^2-bound nitrate anion.

Introduction

Heteroscorpionate tris(pyrazolyl)borate anions (Tp′) − tripodal ligands containing two or more substituted pyrazol-1-yl moieties − provide a unique opportunity to construct transition metal complexes of low symmetry. Early work by Trofimenko demonstrated that some homoscorpionate Tp′ ligands undergo intramolecular rearrangement into heteroscorpionate ones in their transition metal complexes by borotropic rearrangement of the 3-R-pyrazolyl residue of Tp′ into the 5-R-pyrazolyl one (R = isopropyl or neopentyl).[1,2] Recently, we reported that 3(5)-methyl-5(3)-phenylpyrazole (Ph,MepzH) gave two Tp′ ligands upon condensation of Ph,MepzH with borohydride anion: the homoscorpionate [hydrotris(5-methyl-3-phenylpyrazolyl)borate]$^-$ and the heteroscorpionate [hydrobis(5-methyl-3-phenylpyrazolyl)(3-methyl-5-phenylpyrazolyl)borate]$^-$, which were characterized structurally in the solid state by X-ray crystallography and in solution by ^{1}H NMR spectroscopy as high-spin cobalt(II) complexes of the general formula Tp′Co(NCS).[3,4]

Continuing our efforts to synthesize a chiral Tp′ ligand with boron-centered chirality we have applied two independent routes to reach the target: a stepwise synthetic approach, in which dihydro(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borate was synthesized in the first step, dihydrobis(pyrazolyl)borate (Bp′) being a convenient substrate for conversion into chiral Tp′ by condensation of NaBp′ with another substituted pyrazole, and a more promising and less laborious method based on a one-step condensation of 2 equiv. of Ph,MepzH and 1 equiv. of 3,5-diMepzH with sodium borohydride.[4] This first-step condensation led to the isolation of a mixture of Tp′ and Bp′ products, some of which were converted into high-spin cobalt(II) complexes, characterized structurally by X-ray crystallography in the solid state and ^{1}H NMR spectroscopy in solution.

Chiral Tp ligands of C_3 symmetry based on pyrazoles derived from camphor and menthone[5] and potentially hexacoordinate hydrotris[3-{2-(pinene[4,5]pyridyl)}pyrazolyl]borate[6] were synthesized recently and used to construct metal complexes of catalytic activity.

Results and Discussion

Synthetic Procedures and Distribution of Products

The synthesis of poly(pyrazolyl)borate anions by condensation of sodium (or potassium) borohydride with pyrazoles in the melt can be controlled exclusively by the appropriate choice of stoichiometry of substrates and often leads to a nonstatistical distribution of products due to inhomogeneity of the reaction mixture. A typical example of this phenomenon is represented by synthetic route (1) (see Exp. Sect.), in which the condensation of KBH$_4$ (or NaBH$_4$)

[‡] Complexes of Heteroscorpionate Tris(pyrazolyl)borate Anionic Ligands, IV. − Part III: Ref.[4]

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with 1 equiv. of 3,5-diphenylpyrazole and 1 equiv. of 3,5-dimethylpyrazole led to the formation of a mixture of potassium (or sodium) dihydrobis(pyrazolyl)borates (Bp′) and hydrotris(pyrazolyl)borates (Tp′), i.e. dihydro(3,5-diphenylpyrazolyl)(3,5-dimethylpyrazolyl)borate, dihydrobis(3,5-diphenylpyrazolyl)borate, dihydrobis(3,5-dimethylpyrazolyl)borate, hydrobis(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borate, hydrobis(3,5-diphenylpyrazolyl)-(3,5-dimethylpyrazolyl)borate, and hydrotris(3,5-diphenylpyrazolyl)borate. The anionic products were identified as their high-spin cobalt(II) complexes. This method was proven to be particularly useful[1−4,7] because it allows for both the isolation of the anionic poly(pyrazolyl)borate ligands and their identification by ^1H NMR spectroscopy. This method is effective in the case of tris(pyrazolyl)borate ligands (Tp′) with large or intermediate steric hindrance imposed by substituents placed at the 3- and/or 5-positions on the pyrazolyl moiety, which can be isolated as Tp′Co(X) complexes, where X = NCS^-, Cl^-, or CO_2^-. The Bp′ and Tp′ ligands obtained in the synthesis described here gave bis(ligand) complexes of the type Bp'_2Co, Bp′CoTp′, and Tp'_2Co along with Tp′Co(X). We have isolated three complexes, containing different Bp′ and Tp′ ligands and found other ligands coordinated to the cobalt(II) ion in the mixture of products. The pyrazoles used for the construction of the Bp′ and Tp′ ligands have small (3,5-dimethylpyrazole) and intermediate (3,5-diphenylpyrazole) steric hindrance. The isolation procedure applied for the separation of cobalt(II) complexes was based on fractional crystallization from THF/hexane solvent mixtures: the least soluble product, the hydrotris(3,5-diphenylpyrazolyl)boratocobalt(II) nitrate complex [$Tp^{Ph_2}Co(NO_3)$, **1**], was isolated as a pure crystalline product in the first instance, although the synthetic yield of the ligand was only 1%. Deliberate synthesis of this ligand and conversion into the $Tp^{Ph_2}Co(NCS)$ complex **1**′ gave the analytically pure product, which was completely insoluble in all common organic solvents, analogously to **1**. Similar $Tp^{Ph_2}Zn(OOCCH_3)$ and $Tp^{Ph_2}NiCl$ complexes have been synthesized before and characterized crystallographically.[8] The purple $Tp^{Ph_2}NiCl$ complex with the ligand κ^3-bound in the solid state was found to be diamagnetic in [D$_6$]DMSO solution as was concluded from its ^1H NMR spectrum.

Even though we observed the formation of only two of the three expected Bp′ ligands in the synthetic route (1) (Exp. Sect.), the conversion of the mixture of anionic ligands into cobalt(II) complexes gave the pink crystalline product Bp′CoTp′ (**2**) in 12% yield. Surprisingly, the Tp′ ligand trapped in this heteroleptic complex is the hydrobis(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borate {$[HB(3,5\text{-diMepz})_2(3,5\text{-diPhpz})]^-$} with intermediate steric hindrance, while the Bp′ ligand turned out to be the symmetrical dihydrobis(3,5-diphenylpyrazolyl)borate {$[H_2B(3,5\text{-diPhpz})_2]^-$} instead of the statistically more probable $[H_2B(3,5\text{-diMepz})(3,5\text{-diPhpz})]^-$ ligand. Although the new heteroscorpionate Tp′ ligand was itself interesting for us from a structural point of view, the synthetic procedure, which was designed to synthesize $[H_2B(3,5\text{-diMepz})(3,5\text{-diPhpz})]^-$, had to be modified. We therefore performed the condensation of $NaBH_4$ with one equivalent each of 3,5-diMepzH and 3,5-diPhpzH in refluxing tetradecane. The reaction at 254° C allowed for better control and thus optimization of the reaction conditions for the desired unsymmetrical Bp′ ligand. The $[H_2B(3,5\text{-diMepz})(3,5\text{-diPhpz})]^-$ ligand was thus isolated as the complex Bp'_2Co (**3**) and characterized structurally in the solid state by single-crystal X-ray diffraction measurements. The isolated yields of **2** and **3** are rather low, although we observed the formation of other $Tp'Co(NO_3)$ and Bp′CoTp′ complexes containing other heteroscorpionate Tp′ and unsymmetrical Bp′ ligands, which were later identified. We were therefore able to determine the composition of the crude reaction mixture obtained in the synthesis of KBp′ (NaBp′) and KTp′ (NaTp′) salts on the basis of the integration of the corresponding resonances in the ^1H NMR spectrum of a mixture composed of $Tp'Co(NO_3)$, Bp′CoTp′, and Bp′CoBp′′ complexes.

X-ray Crystallographic Studies of the Co Complexes

Structure of $Tp^{Ph_2}Co(NO_3)$ (1)

A view of the molecule of **1** is presented in Figure 1, along with selected bond lengths and angles. The cobalt-centered bite angle is 133.1°, which is much lower than those found in tetracoordinate $Tp^{Ph_2}Cu(CO)$ (145.5°)[9] and pentacoordinate $Tp^{Ph_2}Fe(OOCC(O)Ph)$ (139.6°).[10] It is noteworthy that an increasing steric hindrance at *C*-5(pyrazole) in the order H < CH_3 < Ph causes a tightening of the bite angle from 142.0° [5-H in $Tp^{Ph}Co(NCS)(pzH)$],[7] through 140.3° [5-CH_3 in $Tp^{PhMe}Co(NCS)(THF)$][4] to

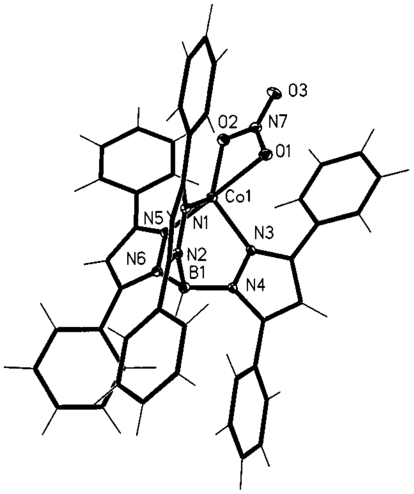

Figure 1. Molecular structure of **1** with crystallographic numbering; selected bond lengths (Å) and angles (°): Co(1)−N(1) 2.038(2), Co(1)−N(3) 2.030(2), Co(1)−N(5) 2.059(2), Co(1)−O(1) 2.230(2), Co(1)−O(2) 2.008(2); N(1)−Co(1)−N(3) 96.18(7), N(1)−Co(1)−N(5) 93.23(7), N(3)−Co(1)−N(5) 89.83(8), O(2)−Co(1)−O(1) 60.67(6), O(1)−N(7)−O(2) 114.15(17), O(1)−N(7)−O(3) 124.2(2), O(2)−N(7)−O(3) 121.68(19)

133.1° [5-Ph in $Tp^{Ph_2}Co(NO_3)$] in pentacoordinate Tp′Co(XY) complexes.

Structure of [Dihydrobis(3,5-diphenylpyrazolyl)borato]-[hydrobis(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)-borato]cobalt(II) (2)

The cobalt(II) center in **2** is surrounded by five nitrogen donors from the pyrazolyl moieties of the Tp′ and Bp′ ligands (Figure 2). The sixth coordination site is occupied by the boron-bonded hydrogen of the Bp′ ligand. The two shortest Co−N(pz) bonds were found for the 3,5-diMepz(Tp′) moieties, whereas the longest Co−N(Tp′) bond was observed for the 3,5-diPhpz moiety, presumably because of steric clashes between 3,5-diPhpz(Tp′) and one of the 3,5-diPhpz(Bp′) ligands. The distance between the cobalt center and hydrogen (Bp′) (2.03 Å) is the shortest amongst this type of complexes. This distance was found to be equal to 2.26 Å in $[H_2B(3\text{-}Phpz)_2]Co[HB(3\text{-}i\text{Pr},4\text{-}Brpz)_3]$,[1] 2.69 Å in $[H_2B(3,5\text{-}diMepz)_2]Cd[HB(3\text{-}Phpz)_3]$,[11] 2.84 Å in BpSmTp,[12] and 2.26 Å and 2.17 Å in hexacoordinate [κ^3-*H*,*N*,*N*(Tp′)] [(κ^3-*N*,*N*,*N*(Tp′′)]Co^{II} complexes, where Tp′ = Tp^{Ph}, $Tp^{iPr,4Br}$ [1] and Tp′ = Tp′′ = Tp^{Ph}.[13]

Structure of $[H_2B(3,5\text{-}diMepz)(3,5\text{-}diPhpz)]_2Co$ (3)

A view of the molecule of **3** is presented in Figure 3 with selected bond lengths and angles. An almost isostructural complex (Bp'_2Zn) has been synthesized previously.[14] In both complexes the M−N(3,5-diMepz) distances are shorter (1.98−1.99 Å) than the M−N(3,5-diPhpz) ones (2.01−2.02 Å). The Co−N(pz) distances are slightly shorter in the Bp_2Co complex (1.93−1.98 Å).[15] In all cases there is no Co−H(Bp′) contact; the Co−H distances increase from 2.93 Å (2.96 Å) for **3** through 3.00 Å (3.06 Å) for Bp_2Co up to 3.26 Å (3.28 Å) for Bp'_2Zn. The closest distance between the metal ion and the boron-bound hydrogen in tetracoordinate complexes with Bp′ ligands was found in the complex $Bp^{tBu}Zn(t\text{Bu})$ (2.47 Å)[16] whereas in other cases it falls in the range 2.9−3.1 Å.[17−23]

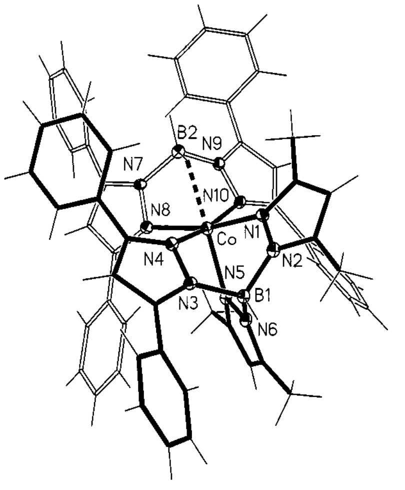

Figure 2. Molecular structure of **2** with crystallographic numbering; selected bond lengths (Å) and angles (°): Co(1)−N(1) 2.091(3), Co−N(4) 2.153(3), Co−N(5) 2.103(3), Co−N(8) 2.113(3), Co−N(10) 2.140(3); N(1)−Co−N(5) 91.00(13), N(1)−Co−N(4) 81.91(12), N(5)−Co−N(4) 90.03(12), N(8)−Co−N(10) 89.91(12)

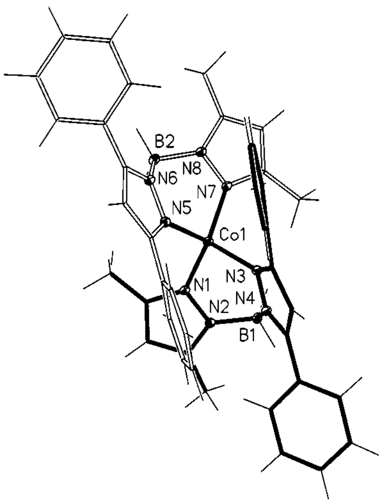

Figure 3. Molecular structure of **3** with crystallographic numbering; selected bond lengths (Å) and angles (°): Co(1)−N(1) 1.985(2), Co(1)−N(3) 2.008(2), Co(1)−N(5) 2.015(2), Co(1)−N(7) 1.987(2), N(1)−Co(1)−N(3) 100.72(7), N(5)−Co(1)−N(7) 101.05(7), N(1)−Co(1)−N(5) 109.11(7), N(1)−Co(1)−N(7) 128.10(7), N(3)−Co(1)−N(5) 106.65(7), N(3)−Co(1)−N(7) 109.89(7)

Spectral Studies

The pink color of **2** is characteristic of pentacoordinate complexes of Tp′Co(XY), which can be produced either by coordination of a neutral ligand, such as a methanol solvent molecule, to Tp′CoX (X = NCS^-, N_3^-, Cl^-), or by chelation of an anionic carboxylate with an additional donor atom (lactate). The most characteristic feature of the ^1H NMR spectra of the high-spin Tp′Co(XY) complexes is the chemical shift of the B−H proton, which depends on the coordination number of the cobalt ion center. Thus, the B−*H* resonances can be found between δ = 0 and −20 for tetracoordinate Tp′Co(X) complexes,[1−3,7,24] between δ = 83 and 130 for hexacoordinate complexes,[1,3,7,24−28] and between δ = 40 and 90 for pentacoordinate complexes, the latter depending on the nature of the fifth donor.[3,7]

There are two interesting features in the ^1H NMR spectrum of **2**: i) the low symmetry of the complex found in the solid state is preserved in solution at room temperature; consequently all the pyrazole proton resonances can be distinguished, and ii) the chemical shift of B−*H* from the Tp′ ligand (δ = 61.3) is rather low in comparison with other typical pentacoordinate Tp′Co(XY) complexes (XY = lactate).[3,7] This low symmetry is even preserved at 383 K (in $[D_8]$toluene) indicating that the mutual rotation of the Tp′ and Bp′ ligands at this temperature is still slow on the timescale of this method. The 2-D ^1H COSY spectrum of **2** taken at 372 K (Figure 4) allowed us to unambiguously identify the *o*-, *m*-, and *p*-H resonances from the three 5-Ph substituents of the Bp′ and Tp′ ligands due to the presence of scalar cross-peaks (lower left inset at Figure 4). These resonances are paramagnetically shifted downfield, as was observed previously for [HB(3-Ph,5-Mepz)2(3-Me,5-Phpz)]Co(NCS)(CD_3OD) and [HB(3-Ph,5-Mepz)(3-Me,5-Phpz)2]Co(NCS)(CD_3OD) complexes.[4,7] Three cross-peaks between the *m*- and *p*-H of the 3-Ph substituents of the Tp′ and Bp′ ligands were also observed, although the scalar connectivity pattern within the 3-Ph substituents was broken due to the short relaxation times of the *ortho* hydrogens (right inset of Figure 4). We were also unable to observe the appropriate NOE cross-peaks between 3-CH_3(Tp′) and *o*-H(Bp′) which would have allowed us to assign all the resonances. Nevertheless, the resonances for *o*-H(3-Ph,Bp′) are shifted upfield considerably less than those of *o*-H(3-Ph,Tp′) which is consistent with the static geometry of the molecule (see above). Very broad resonances at $\delta = 9$ and 10, which can be tentatively assigned to the H-B(Bp′) protons, were observed in the spectrum. One of the resonances for 5-CH_3 (Tp′) is also extremely broad and is placed within the diamagnetic envelope.

The UV/Vis spectra of **2** and **3** are characteristic of high-spin cobalt(II) in octahedral and tetrahedral environments, respectively.[29] Two bands centered at 498 and 538 nm for **2**, which can be assigned to a $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition, have extinction coefficients near 60 $mol^{-1}\ dm^3\ cm^{-1}$. This slightly higher than the corresponding band observed for Tp_2Co,[30] and is probably due to the higher coordination geometry in **2**. In the case of **3** the position and extinction coefficient of the three observed bands are close to those found for Bp_2Co,[30] and can be assigned to a $^4T_1(P) \leftarrow {}^4A_2$ transition.[29]

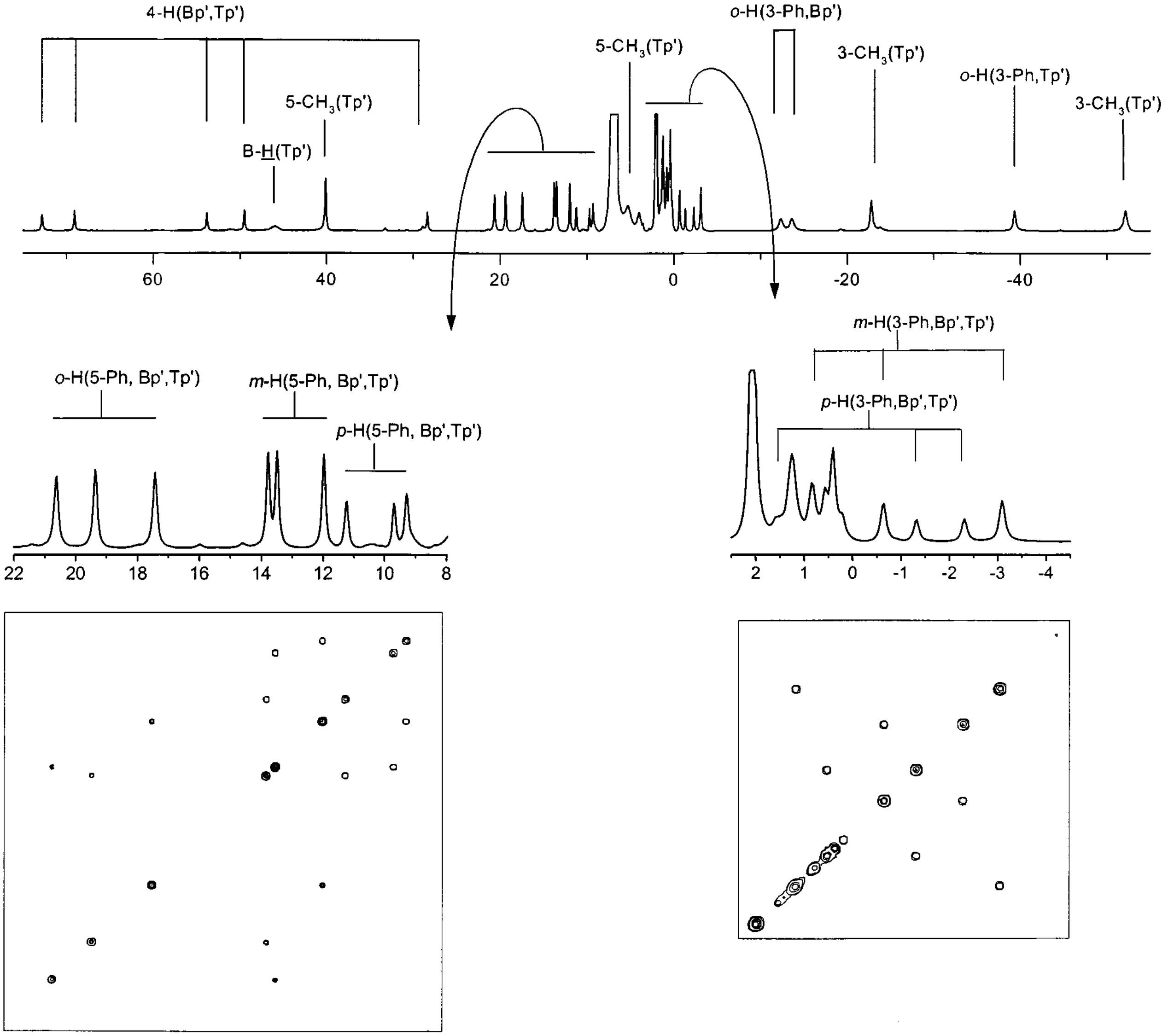

Figure 4. The ^1H NMR spectrum of **2** in [D$_8$]toluene at 373 K; the two lower insets demonstrate the relevant fragments of the COSY map

Experimental Section

Methods: ^{1}H NMR spectra were obtained with a Bruker AMX300 spectrometer operating in the quadrature mode at 300 MHz. The residual peaks of the deuterated solvents were used as internal standards. The 2-D ^{1}H COSY spectrum was obtained with a repetition time of 0.2 s. The magnetic moments of **2** and **3** were measured on the same instrument in $CDCl_3$ at 298 K. The IR and UV/Vis spectra were recorded on a Perkin−Elmer 1725X and a HP 8453 diode-array spectrophotometer, respectively. Elemental analyses were performed with an EA 1108 apparatus (Carbo Erba) at Department of Organic Chemistry, Faculty of Chemistry, Rzeszów University of Technology.

Crystal data for **1−3** are given in Table 1, together with refinement details. All measurements were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were positioned 65 mm from the KM4CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 20 sec. The data were corrected for Lorentz and polarization effects. An absorption correction based on least-squares fitted against $|F_c| - |F_o|$ differences was also applied for **1**.[31] No absorption corrections were applied for **2** and **3**. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs. Structures were solved by direct methods (program SHELXS-97)[32] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97[33] program suite. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the geometry of the molecules and Δρ maps, and refined with isotropic thermal parameters for **1** only.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160912 (**1**), CCDC-160913 (**2**), and CCDC-160914 (**3**). Copies of the data can be obtained free of charge on applicaton to The Director, CCDC, 12 Union Road,m Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Condensation of 3,5-Dimethylpyrazole and 3,5-Diphenylpyrazole with Potassium Borohydride. Route (1): The one-step condensation of KBH_4 (0.818 g, 15.2 mmol) with 3,5-diphenylpyrazole (3.304 g, 15.0 mmol) and 3,5-dimethylpyrazole (1.35 g, 14.1 mmol) was done by heating the reagents in melted pyrazoles at 165−225° C until 725 cm^3 hydrogen had been evolved. The crude reaction mixture was washed with hot heptane (100 cm^3), then petroleum ether (50 cm^3) and dried in air to give 3.131 g of crude product [as a mixture of potassium poly(pyrazolyl)borate salts] in approximately 56% yield.

Route (2): The one-step condensation of $NaBH_4$ (0.352 g, 9.31 mmol) with 3,5-diphenylpyrazole (1.640 g, 7.45 mmol) and 3,5-dimethylpyrazole (0.716 g, 7.45 mmol) was performed by heating the mixture in tetradecane 50 (cm^3) under reflux (254 °C) until 340 cm^3 hydrogen had been evolved. The crude reaction mixture was cooled to about 80° C, filtered to remove unchanged pyrazoles, washed with hot heptane (100 cm^3) and petroleum ether (50 cm^3). The solid residue was dried, crushed into pieces, suspended in 50 cm^3 heptane, boiled, filtered and washed with petroleum ether. A dry mixture of sodium salts of anionic poly(pyrazolyl)borates (1.85 g) was obtained (approximately 57% yield).

Synthesis of Cobalt(II) Complexes with Poly(pyrazolyl)borate Ligands: 1.21 g of potassium salts [approx. 3.3 mmol of crude reac-

Table 1. Crystal data and structure refinement

Compound	1	2	3
Empirical formula	$C_{45}H_{34}BN_7O_3Co$	$C_{58}H_{57}B_2N_{10}Co$	$C_{40}H_{40}B_2N_8Co$
Formula mass	790.53	974.69	713.35
T /K	100(1)	100(2)	100(2)
λ /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a /Å	13.6260(10)	13.326(2)	9.907(2)
b /Å	16.4753(13)	13.713(2)	18.300(4)
c /Å	17.4850(13)	14.721(2)	19.869(4)
α /°	−	85.00(2)	−
β /°	109.086(7)	81.38(2)	99.20(3)
γ /°	−	71.76(2)	−
V /Å^3	3709.5(5)	2523.8(6)	3555.9(13)
Z	4	2	4
D_c /Mg·m^{-3}	1.416	1.283	1.332
μ /mm^{-1}	0.517	0.390	0.525
F(000)	1636	1024	1492
Crystal size /mm	0.23 × 0.17 × 0.15	0.18 × 0.15 × 0.15	0.15 × 0.10 × 0.10
Diffractometer	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD
θ range for data collection, °	3.24−30.00	3.24−25.00	3.33−28.81
Ranges of h,k,l	−12→19, −22→22, −13→13	−14→15, −15→16, −17→15	−13→9, −24→23, −25→26
Reflections collected	41509	14645	25246
Independent reflections (R_{int})	7894 (0.0518)	8665 (0.0493)	8564 (0.0450)
Data/parameters	7894/650	8665/652	8564/460
Absorption coefficients min./max.	0.78279−1.09435	−	−
Goodness-of-fit (F^2)	1.100	1.079	1.112
Final R_1/wR_2 indices ($I > 2\sigma_I$)	0.0516/0.0958	0.0786/0.1913	0.0539/0.0947
Largest diff. peak/hole /e·Å^{-3}	0.309/−0.291	0.850/−0.601	0.306/−0.426

tion mixture obtained in route (1), vide supra] was dissolved in tetrahydrofuran (THF, 150 cm^3) and into this solution a stock solution of cobalt(II) nitrate in THF [1.5 equivalents of cobalt(II) calculated for potassium dihydro(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borate] was added dropwise, with vigorous stirring. The resulting pink-violet solution was concentrated to a volume of 30 cm^3, then 150 cm^3 of methylene dichloride was added and the organic phase was twice extracted rapidly with 150 cm^3 of water. The organic phase was separated and the solvents removed on a rotary evaporator. The solid obtained was dissolved in THF, passed through a short bed of celite and the solution layered with heptane. After two days, 25 mg of deep-violet crystals deposited from the mixture. These crystals were separated and their composition was determined by elemental analysis and X-ray diffraction as hydrotris(3,5-diphenylpyrazolyl)boratocobalt(II) nitrate [Tp^{Ph_2}-$Co(NO_3)$ (**1**)]. The complex was totally insoluble in most organic solvents and water. Yield: approx. 1%.

For comparison we also synthesized potassium hydrotris(3,5-diphenylpyrazolyl)borate KTp^{Ph_2} by the standard procedure[8] and $Tp^{Ph_2}Co(NCS)$ complex (**1′**) by addition of KTp^{Ph_2} in THF to an excess of cobalt(II) thiocyanate, as described previously.[7]

After separation of **1**, crystallization of the cobalt(II) complexes was continued and the mixture of products was examined by ^1H NMR spectroscopy. The major product in the mixture was finally separated after four recrystallizations from THF/heptane as pink crystals (160 mg) and identified by elemental analysis, ^1H NMR spectroscopy, and X-ray crystallography as [dihydrobis(3,5-diphenylpyrazolyl)borato][hydrobis(3,5-dimethylpyrazolyl)(3,5-diphenylpyrazolyl)borato]cobalt(II) (**2**). Yield: approx. 12%.

In a separate synthesis, 1.85 g (approx. 5.3 mmol) of the mixture of poly(pyrazolyl)borate sodium salts obtained from route (2) (vide supra) was converted into a mixture of bis(ligand) cobalt(II) complexes as described above. Fractional crystallization of the complexes from THF/hexane mixture gave pink crystals of a mixture of Bp′CoTp′ compounds and another $Tp'Co(NO_3)$ complex in the first instance (220 mg), whereas the desired Bp′CoBp′′ complexes remained in solution. The complex $[H_2B(3,5\text{-diMepz})(3,5\text{-diPhpz})]_2Co$ (**3**; 385 mg, 0.54 mmol, yield approx. 18%) was obtained from the filtrate as burgundy red crystals and identified by means of an X-ray crystallographic analysis.

1: $C_{45}H_{34}BCoN_7O_3$ (790.53): calcd. C 68.37, H 4.35, N 12.40; found C 68.43, H 4.41, N 12.32.

1′: $C_{46}H_{34}BCoN_7S$ (786.63): calcd. C 70.24, H 4.36, N 12.46; found C 69.99, H 4.51, N 12.24. IR (KBr): $\tilde{\nu}$ = 2065 ν(NCS), 2495 cm^{-1} ν(BH).

2: $C_{58}H_{57}B_2CoN_{10}$ (974.69): C 71.47, H 5.89, N 14.37; found C 71.29, H 5.71, N 14.42. ^1H NMR ($CDCl_3$, 293 K): δ = −68.3 [3 H, CH_3 (*3*,5-diMepzTp′)], −55.1 [2 H, *o*-H (*3*,5-diPhpzTp′)], −32.0 [3 H, CH_3 (*3*,5-diMepzTp′)], −20.9 [2 H, *o*-H (*3*,5-diPhpzBp^{Ph_2})], −19.3 [2 H, *o*-H (*3*,5-diPhpzBp^{Ph_2})], −6.2 [2 H, *m*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph_2})], −5.2 [1 H, *p*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph_2})], −3.9 [1 H, *p*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph_2})], −3.2 [2 H, *m*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph_2})], −1.7 [2 H, *m*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph2})], −0.2 [1 H, *p*-H (*3*,5-diPhpz of Tp′ or Bp^{Ph_2})], 7.9 [3 H, CH_3 (3,*5*-diMepz2Tp′)], 10.2 [1 H, *p*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 10.8 [1 H, *p*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 12.8 [1 H, *p*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 13.6 [2 H, *m*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 15.6 [2 H, *m*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 16.0 [2 H, *m*-H (3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 20.9 [2 H, *o*-H(3,*5*-diPhpz3 of Tp′ or Bp^{Ph_2})], 23.1 [2 H, *o*-H(3,*5*-diPhpz3 of Tp′ or Bp^{Ph_2})], 25.3 [2 H, *o*-H(3,*5*-diPhpz of Tp′ or Bp^{Ph_2})], 31.5 [1 H, 4-H (pz of Tp′ or Bp^{Ph_2})], 51.3 [3 H, CH_3 (3,*5*-diMepzTp′)], 59.3 [1 H, 4-H (pz of Tp′ or Bp^{Ph_2})], 61.3 [1 H (broad), B-*H* of Tp′], 65.2 [1 H, 4-H (pz of Tp′ or Bp^{Ph_2})], 83.3 [1 H, 4-H (pz of Tp′ or Bp^{Ph_2})], 88.2 [1 H, 4-H (pz of Tp′ or Bp^{Ph_2})]. IR (KBr): $\tilde{\nu}$ = 2501 (m) ν[BH (Tp′)], 2275 (w) ν[BH (Bp′)], 2190 cm^{-1} (m). Magnetic moment (Evans method): μ = 4.53 B.M. UV/Vis (CH_2Cl_2): λ_{max} (ε [mol^{-1} dm^3 cm^{-1}]) = 498 (61.2), 538 nm (64.2).

3: $C_{40}H_{40}B_2CoN_8$ (713.35): calcd. C 67.33, H 5.65, N 15.71; found C 67.53, H 5.63, N 15.68.

IR (KBr): $\tilde{\nu}$ = 2493 (m) ν(BH), 2400 cm^{-1} (m). Magnetic moment (Evans method): μ = 3.9 B.M. UV/Vis: λ_{max} (ε [mol^{-1} dm^3 cm^{-1}]) = 580 (510), 555 (640), 512 nm (356).

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