The Ambivalent Bonding of the 3(5)-Isopropylpyrazolyl Moiety in Homo- and Heteroscorpionate Hydrobis(3-R_1-5-R_2-pyrazolyl)(*y*-isopropylpyrazolyl)-boratocobalt(II) Complexes (*y* = 3 or 5)[‡]

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The synthesis of hydrotris(pyrazol-1-yl)borate ligands (Tp^x) by condensation of sodium borohydride with 3(5)-isopropylpyrazole and either 5(3)-methyl-3(5)-phenylpyrazole or 3,5-diphenylpyrazole gave the novel heteroscorpionate ligands hydrobis(5-methyl-3-phenylpyrazolyl)(5-isopropylpyrazolyl)-borate and hydrobis(3,5-diphenylpyrazolyl)(5-isopropylpyrazolyl)borate, respectively. These were converted into $CoTp^x(NCS)$ complexes as well as $CoTp^x_2$ in the case of the former ligand. In an attempted synthesis of heteroscorpionates bearing two y-isopropylpyrazolyl moieties (y = 3 or 5) formation of the homoscorpionate hydrotris(3-isopropylpyrazolyl)borate along with the above-mentioned heteroscorpionates was noticed; no formation of the desired heteroscorpionates could be detected. The bis[hydrobis(5-methyl-3-phenylpyrazolyl)(5-isopropylpyrazolyl)borato]cobalt(II) and tetrahydrofuranothiocyanatobis[hydrobis(5-methyl-3-phenylpyrazolyl)(5-isopropylpyrazolyl)borato]cobalt(II) tetrahydrofuran solvate complexes were studied by X-ray crystallography. Two Tp^x ligands provide six nitrogen donors from pyrazol-1-yl residues to form a Tp^x_2Co complex in which two 5-isopropylpyrazolyl rings are placed in a plane of symmetry, whereas the same Tp^x ligand is bound in an η^3 fashion in the pentacoordinate $[CoTp^x(NCS)(THF)]\cdot THF$ complex, in which a nitrogen atom from thiocyanate and an oxygen atom from THF complete the coordination sphere of the central metal ion. These compounds as well as the complexes thiocyanatohydrobis(3,5-diphenylpyrazolyl)(5-isopropylpyrazolyl)boratocobalt(II) and thiocyanatohydrotris(3-isopropylpyrazolyl)boratocobalt(II) were characterized by ^1H NMR and IR spectroscopy.
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Introduction

Tris(pyrazolyl)borate anions (Tp^x) provide three *cis*-arranged nitrogen donors that are able to coordinate to transition metal ions, leaving the remaining coordination sites of the central metal ion to perform extraneous chemistry with more weakly bound ligands.[1] The stereochemistry of these reactions can be influenced by the symmetry of the Tp^x moiety, including the induction of asymmetry in catalytic reactions. One of the approaches used successfully for the latter is based on the preparation of Tp^x ligands containing chiral substituents attached to the periphery of Tp^x.[2−4] Another approach for the formation of chiral Tp^x ligands is the synthesis of heteroscorpionates composed of three different pyrazolyl residues.[5] Here we describe the synthesis of heteroscorpionates composed of two different pyrazoles, which were separated from the post-synthetic mixture as their cobalt(II) complexes.

Results and Discussion

Spontaneously formed heteroscorpionate tris(pyrazolyl)borate ligands can be obtained during the condensation of the borohydride anion with 3(5)-R-pyrazoles or 3(5)-R_1-5(3)-R_2-pyrazoles. The first spontaneous heteroscorpionate ligand was synthesized by Trofimenko, who isolated the bis-ligand complex $[Co\{HB(3\text{-}i\mathrm{Prpz})_2(5\text{-}i\mathrm{Prpz})\}_2]$.[6] At that time it was not clear if the heteroscorpionate was formed during the synthesis of $NaTp^x$ or exclusively during the conversion of the homoscorpionate $[HB(3\text{-}i\mathrm{Prpz})_3]^-$ ($Tp^{i\mathrm{Pr}}$) into the heteroscorpionate upon heating of the $[Co(Tp^{i\mathrm{Pr}})_2]$ complex. In the latter case the driving force of the borotropic shift of the 3-isopropyl- into the 5-isopropylpyrazolyl moiety could be the release of steric clashes between six 3-isopropyl substituents around the metal ion. Later it was demonstrated that heteroscorpionate ligands are also formed during the condensation of pyrazoles with borohydrides.[7,8] This ambivalency of 3- versus 5- substitution of 3(5)-R_1-5(3)-R_2-pyrazoles can be used to construct mixed-pyrazole or even chiral Tp^x ligands.

We have used 3(5)-isopropylpyrazole for the synthesis of heteroscorpionate Tp^x ligands in order to study the bonding ambivalency of 3(5)-isopropylpyrazole in synthetic, mixed-pyrazole heteroscorpionates. The 5(3)-methyl-3(5)-phenyl-

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[‡] Complexes of Heteroscorpionate Trispyrazolylborate Anionic Ligands, VII. Part VI: Ref. [9]

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pyrazole or 3,5-diphenylpyrazole provided the additional pyrazolyl moieties to construct heteroscorpionates.

Structures of 1 and 2 in the Solid State

The heteroscorpionate obtained from condensation of $NaBH_4$ with 3-*i*PrpzH and 5-Me-3-PhpzH was found to be $[HB(5\text{-Me-3-Phpz})_2(5\text{-}i\text{Prpz})]^-$. Two cobalt(II) complexes of this anion were synthesized and studied by X-ray crystallography: the bis-ligand homoleptic complex $[Co\{HB(3\text{-Ph,5-Mepz})_2(5\text{-}i\text{Prpz})\}_2]$ (**1**) and the mono-ligand complex $[Co\{HB(3\text{-Ph,5-Mepz})_2(5\text{-}i\text{Prpz})\}(NCS)(THF)]\cdot THF$ (**2**). The molecular structures of the complexes are shown in Figure 1 and 2, respectively. The cobalt-centered bite angles (β) of the ligand in complexes **1** and **2** are 168.9° and 163.3°, respectively, while the corresponding boron-centered bite angles (α) are 88.5° and 85.2°, respectively (the bite angles were calculated as previously, i.e. disregarding hydrogen atoms).[5] The molecule of **1** is centrosymmetric. The boron-cobalt distance is 3.17 Å in **1**, while that in **2** is 3.12 Å. Thus the Tp^x ligand in **1** is bound less tightly to the cobalt center than in **2**. Accordingly, the average Co−N distance in **1** is 2.17 Å, while that in **2** is 2.09 Å (see captions to Figure 1 and 2). Such a structural difference could be anticipated due to substantial crowding around the metal ion in hexacoordinate $CoTp^x_2$ complexes. Nevertheless, this is only the second case of structurally characterized mono- and bis-ligand pentacoordinate $[CoTp^x(NCS)(THF)]$ and hexacoordinate $CoTp^x_2$ complexes constructed with the same Tp^x ligand. The first example was demonstrated for the heteroscorpionate ligand $[HB(5\text{-Me-3-Phpz})_2(3\text{-Me-5-Phpz})]^-$, for which a similar relationship was found: $\beta = 154.6°$ and 149.2°, $\alpha = 85.7°$ and 81.9°; average Co−N bond length = 2.26 Å and 2.23 Å; Co−B distance = 3.15 Å and 3.09 Å, for $CoTp^x_2$ and $[CoTp^x(NCS)(THF)]$ complexes, respectively.[8,9]

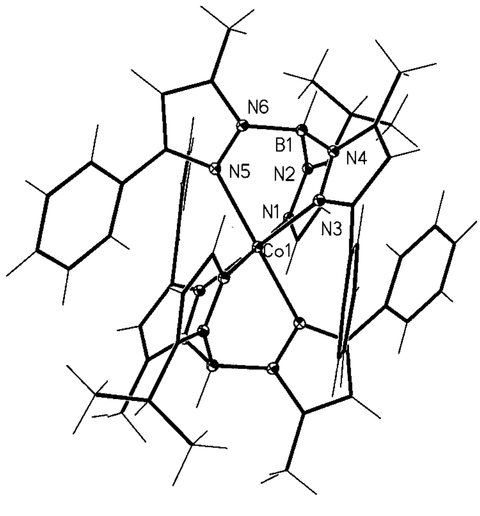

Figure 1. View of **1**; selected bond lengths [Å] and angles [°]: Co(1)−N(1) 2.0469(12), Co(1)−N(3) 2.2341(12), Co(1)−N(5) 2.2194(13); N(1)−Co(1)−N(5) 89.43(5), N(1)−Co(1)−N(3) 90.66(5), N(5)−Co(1)−N(3) 79.55(5)

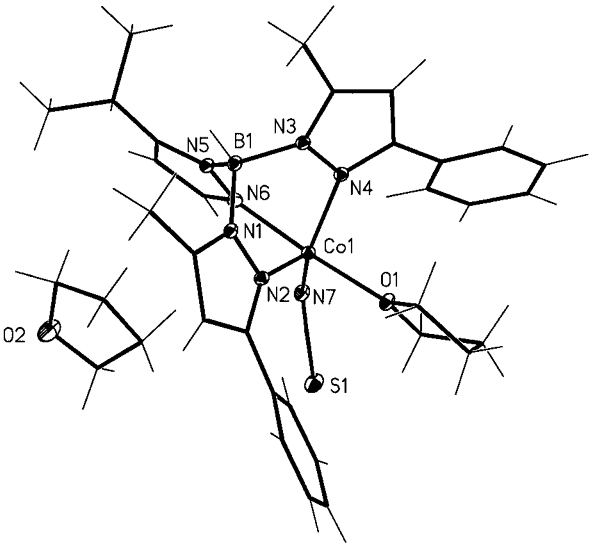

Figure 2. View of **2**; selected bond lengths [Å] and angles [°]: Co(1)−N(2) 2.0830(19), Co(1)−N(4) 2.0540(19), Co(1)−N(6) 2.1351(19), Co(1)−N(7) 1.999(2), Co(1)−O(1) 2.1193(16); N(2)−Co(1)−N(4) 93.03(7), N(2)−Co(1)−N(6) 88.05(7), N(4)−Co(1)−N(6) 84.25(7), N(7)−Co(1)−N(2) 124.92(8), N(7)−Co(1)−N(4) 141.39(8), N(7)−Co(1)−N(6) 89.73(7), N(7)−Co(1)−O(1) 88.46(7), N(2)−Co(1)−O(1) 96.76(7), N(4)−Co(1)−O(1) 94.32(7), N(6)−Co(1)−O(1) 175.06(7)

The β and α bite angles of Tp^x in **1** are much lower than those found in $[HB(3\text{-}i\text{Prpz})_2(5\text{-}i\text{Prpz})]_2Co$, which are 191.5° and 103.0°, respectively.[6] However, the Tp^x ligand in the latter is bound more tightly than that in **1**; the cobalt-boron distance is 3.15 Å. The ^1H NMR spectra of **1** and **2** are consistent with the crystal structures (see below).

A detailed analysis of the molecular structure of **2** shows some unexpected features. The 5-isopropylpyrazolyl moiety is bound more weakly than two 5-methyl-3-phenylpyrazolyl residues (see caption of Figure 2) whereas one might have expected the opposite effect due to the lack of a bulky 3-substituent and the presence of a large 5-isopropyl substituent which should result in a shortening of the Co−N(5-*i*Prpz) bond. This may be due to the specific arrangement of the remaining monodentate ligands: the coordinated THF molecule is placed within the pocket formed by the two 5-phenyl substituents, while the N-coordinated thiocyanate is very close to, and placed almost co-planar with, the 5-isopropylpyrazolyl ring. This close proximity induces a considerable weakening of the Co−N(5-*i*Prpz) bond. There are two additional intermolecular contacts (2.95 Å and 2.94 Å) between the thiocyanato sulfur atom and the *m*-H(3-Ph) and 4-H(5-Me-3-Phpz) atoms of two different molecules.

^1H NMR Spectra

The ^1H NMR spectroscopy of high-spin cobalt(II) complexes is a convenient method for the structural elucidation of $CoXTp^x$ and $CoTp^x_2$ complexes in solution[5−12] as the chemical shifts are dominated by the dipolar contribution.[12] The resonances of the 3-*i*Pr hydrogens are shifted considerably upfield, whereas those of the 5-*i*Pr hydrogens are shifted in opposite directions. The ^{1}H NMR spectrum of a side-product obtained in the synthesis of Tp^x from 3(5)-*i*PrpzH and 3,5-diPhprH, i.e. [Co(Tp^{iPr})(NCS)(CD$_3$OD)] (**4**, Figure 3A) indicated that heteroscorpionate [HB(3-*i*Prpz)$_2$(5-*i*Prpz)]$^-$. From this one can conclude that the driving force for the borotropic shift converting homo- to heteroscorpionates is the steric hindrance in [CoTp*i*Pr$_2$].[6] On the other hand, the ^{1}H NMR spectrum of the heteroscorpionate [Co{HB(5-*i*Prpz) (3,5-diPhpz)$_2$}(NCS)(CD$_3$OD)] (**3**, Figure 3B) clearly indicates the presence of a 5-*i*Pr substituent in the [CoTp^x(NCS)] complex on the basis of the methyl(*i*Pr) resonance at δ = 16.3 ppm. The presence of a 5-*i*Pr-pyrazolyl moiety in the mono-ligand complex **3** suggests that steric repulsion between the two 3-*i*Pr-pyrazolyl residues in the CoTp$^x_2$ complex is not necessary for the borotropic shift. This is strongly supported by the fact that 5-*i*Pr-pyrazolyl is present also in the synthetic heteroscorpionate Tp^x ligand both in the mono-ligand complex **2** (Figure 3C) and the bis-ligand complex **1** (Figure 3D). The symmetry of the ^{1}H NMR spectrum of **1** suggests that the Tp^x ligands are arranged in an antiperiplanar (*trans*) conformation similarly to those in [Co{HB(3-*i*Prpz)$_2$(5-*i*Prpz)}$_2$].[6] The Tp^x ligands in **1** are more sterically demanding and the boron-attached hydrogen atoms are about 0.02 Å more distant than those in [Co{HB(3-*i*Prpz)$_2$(5-*i*Prpz)}$_2$] (see above). Therefore, the 5-*i*Pr-pyrazolyl moiety is bound more weakly in **1** than in [Co{HB(3-*i*Prpz)$_2$(5-*i*Prpz)}$_2$]; the B-*H* and 3-H resonances are observed at δ = 75.2 and -29.4 ppm, respectively, while they are found at about δ = 93 and -63 ppm in the latter complex. However, the steric hindrance of [HB(3-Ph,5-Mepz)$_2$(5-*i*Prpz)]$^-$ ligand is still small enough to form the CoTp$^x_2$ complex **1**. The synthesized heteroscorpionate is a typical case of a Tp^x ligand with intermediate steric hindrance, which, depending on the synthetic procedure, forms both the stable mono-ligand complex **2** and its bis-ligand counterpart **1**. A slight structural modification by introducing a 5-phenyl- instead of a 5-methyl-substituent, resulting in formation of the heteroscorpionate [HB(5-*i*Prpz)(3,5-diPhpz)$_2$]$^-$ produces a more demanding ligand, which in the same synthetic procedure gives only the mono-ligand complex **3**.

We also varied the stoichiometry of 3(5)-*i*PrpzH and 3,5-diPhpzH in favor of the former to obtain another heteroscorpionate, [HB(*y*-*i*Prpz)$_2$(3,5-diPhpz)]$^-$ (where *y* = 3 or 5). However, we found that a higher percentage of homoscorpionate was obtained, without detectable amounts of the desired heteroscorpionate.

Because we were aiming for the latter, another modified pyrazole, namely 5(3)-isopropyl-3(5)-phenylpyrazole was subsequently successfully used to construct the heteroscorpionate [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]$^-$ anion which was thermally converted when isolated as its cobalt complex [CoTp^x(NCS)] into [Co{HB(5-*i*Pr-3-Phpz)(3-*i*Pr-5-Phpz)-(3,5-diMepz)}(NCS)] (**5**) in about 50% yield.[13]

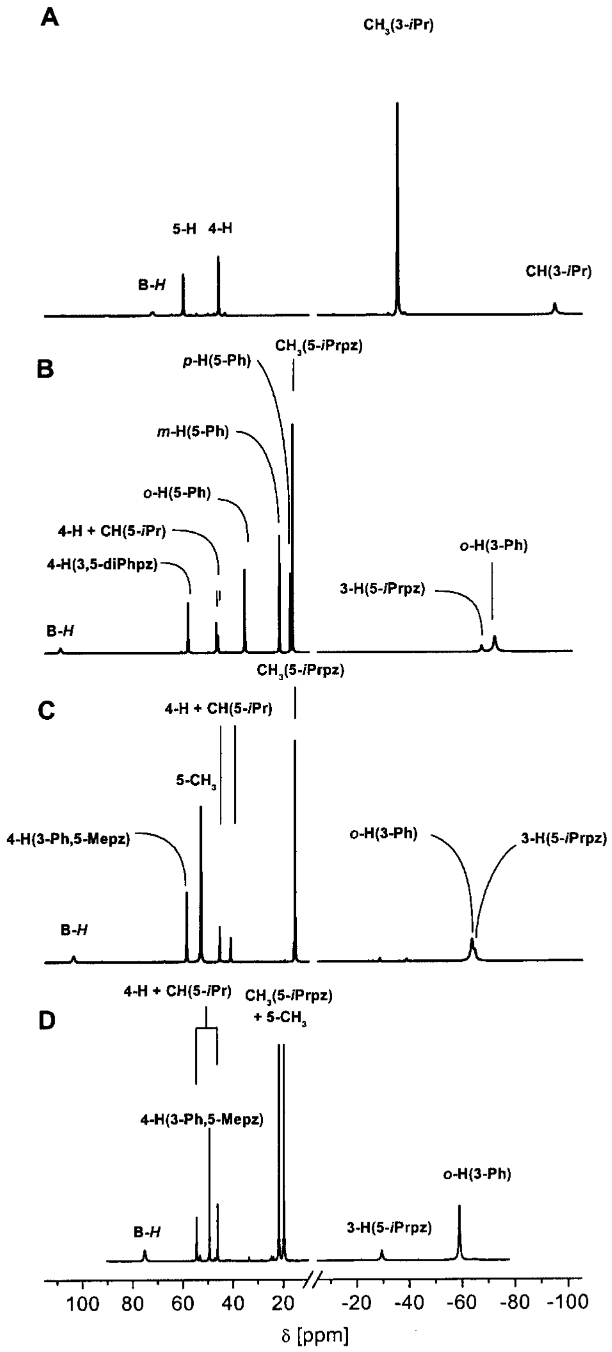

Figure 3. ^{1}H NMR spectra of: [Co(Tp^{iPr})(NCS)(CD$_3$OD)] (**A**); [Co{HB(5-*i*Prpz)(3,5-diPhpz)$_2$}(NCS)(CD$_3$OD)] (**B**); [Co{HB(5-Me-3-Phpz)$_2$(5-*i*Prpz)}(NCS)(CD$_3$OD)] (**C**) in [D$_4$]methanol; and [Co{HB(3-Ph,5-Mepz)$_2$(5-*i*Prpz)}$_2$] in [D]chloroform (**D**)

Experimental Section

Methods and Instruments: Elemental analyses were performed with Perkin−Elmer 2400 CHN analyzer. The ^{1}H NMR spectra were obtained with a Bruker AMX300 spectrometer operating in the quadrature mode at 300 MHz. The residual peaks of deuterated solvents were used as internal standards. The FT IR spectra were recorded in KBr pellets on a Perkin−Elmer 1725X instrument.

Syntheses: 5(3)-Methyl-3(5)-phenylpyrazole (5-Me-3-PhpzH), 3(5)-isopropylpyrazole (3-*i*PrpzH) and 3,5-diphenylpyrazole (3,5-diPhpzH) were synthesized by known methods.[5,6] [CoTp^{x}(NCS)] complexes were synthesized in the presence of an excess of metal ion and thiocyanate anion, followed by extraction of the product into dichloromethane, as previously reported.[5]

Bis[hydrobis(5-methyl-3-phenylpyrazolyl)(5-isopropylpyrazolyl)-borato]cobalt(II) ([Co{HB(3-Ph,5-Mepz)$_2$(5-*i*Prpz)}$_2$], 1), and Tetrahydrofuranothiocyanatohydrobis(5-methyl-3-phenylpyrazolyl)(5-isopropylpyrazolyl)boratocobalt(II) Tetrahydrofuran Solvate ([Co{HB-(3-Ph,5-Mepz)$_2$(5-*i*Prpz)}(NCS)(THF)]·THF, 2): $NaBH_4$ (0.57 g, 15.04 mmol) was heated with 5-Me-3-PhpzH (4.15 g, 26.2 mmol) and 3-*i*PrpzH (2.06 g, 18.75 mmol) in heptadecane (30 cm^3) with vigorous stirring in a 250-cm^3 three-necked round-bottomed flask attached to a wet-test meter and condenser. The device was flushed with nitrogen before heating was started. The temperature was gradually increased up to the boiling point of heptadecane (302 °C). Heating was continued until 1010 cm^3 of hydrogen had been collected. Heptane (60 cm^3) was added to the solution after cooling to about 100 °C and the mixture was left overnight at room temperature. The deposited precipitate was filtered off, washed with petroleum ether and vacuum dried (0.89 g, 1.94 mmol, ca. 13% yield). The crude product was converted into [CoTp^{x}(NCS)] complexes by standard methods. These complexes were then dissolved in THF. Dissolution was accompanied by the formation of a yellowish-white precipitate, which was filtered off, washed with small amount of THF and crystallized from dichloromethane. Yellowish-orange crystals of **1** were collected after re-concentration of the solution (256 mg, 0.275 mmol, 14.2% yield). One of the crystals was examined crystallographically (Table 1). The THF filtrate was layered with heptane. From this fraction reddish-violet crystals of **2** were collected (104 mg, 0.15 mmol, ca. 7.7% yield). One of the crystals was used for an X-ray crystallographic measurement (Table 1).

Thiocyanatohydrobis(3,5-diphenylpyrazolyl)(5-isopropylpyrazolyl)-boratocobalt(II) ([Co{HB(3,5-diPhpz)$_2$(5-*i*Prpz)}(NCS)(CH_3OH)], 3) and Thiocyanatohydrotris(3-isopropylpyrazolyl)boratocobalt(II) ([Co(Tp^{iPr})(NCS)], 4): $NaBH_4$ (0.46 g, 12.1 mmol) was heated with 3-*i*PrpzH (2.54 g, 23.05 mmol) and 3,5-diPhpzH (2.93 g, 13.3 mmol) in octadecane (40 cm^3) with vigorous stirring in a 250-cm^3 three-necked round-bottomed flask attached to a wet-test meter and condenser. The temperature was gradually increased up to the boiling point of octadecane (315 °C). Heating was continued until 930 cm^3 of hydrogen had been collected and then for a further hour. A white precipitate formed after cooling the mixture to about 100 °C. Heptane (80 cm^3) was then added to the suspension, which was then stirred for 2 hours at room temperature. The crude product was filtered off, washed with petroleum ether and dried to give 1.66 g of a mixture of NaTp^{x} salts. NaTp^{x} (210 mg) was converted into a mixture of [CoTp^{x}(NCS)] complexes and this mixture was dissolved in methanol (5 cm^3). The insoluble blue material, identified as [Co(Tp^{Ph_2})(NCS)],[7] was separated by passing the solution through a short bed of celite. The filtrate contained 44% [Co(Tp^{iPr})(NCS)] and 56% [Co{HB(3,5-diPhpz)$_2$(5-*i*Prpz)}(NCS)] which were identified by their ^{1}H NMR spectra. The filtrate was left to crystallize by slow evaporation of methanol. In the first instance pink, plate-shaped crystals of [Co{HB(3,5-diPhpz)$_2$(5-*i*Prpz}(NCS)(CH_3OH)]·CH_3OH were separated and collected (yield 65 mg, 0.092 mmol), and finally pink, cube-shaped crystals of [Co(Tp^{iPr})(NCS)] were collected, which turned blue upon drying at high vacuum (48 mg, 0.105 mmol).

1: $C_{52}H_{56}B_2CoN_{12}$ (929.64): calcd. C 67.18, H 6.07, N 18.81; found C 66.98, H 6.16, N 18.64. ^{1}H NMR ($CDCl_3$, 298 K): δ: = −59.0 [4 H, *o*-H(3-Ph)], −29.4 [1 H, 3-H(5-*i*Prpz)], 0.2 [4 H, *m*-H(3-Ph)], 2.5[2 H, *p*-H(3-Ph)], 19.7 and 21.7 [6 H and 6 H, 5-CH_3(3-Ph,5-Mepz) and CH_3(5-*i*Prpz)], 46.2 [1 H, HC(5-*i*Pr) or 4-H(5-*i*Prpz)], 49.4 [2 H, 4-H(3-Ph,5-Mepz)], 54.5 [1 H, 4-H(5-*i*Prpz) or HC(5-*i*Pr)], 75.2 (1 H, BH) ppm. IR (KBr): $\tilde{\nu}$ = 2536 cm^{-1} ν(BH).

2: $C_{35}H_{44}BCoN_7O_2S$ (696.57): calcd. C 60.35, H 6.37, N 14.76; found C 60.20, H 6.28, N 14.66. ^{1}H NMR (CD_3OD, 298 K): δ = −64.7 [1 H, 3-H(5-*i*Prpz)], −63.2 [4 H, *o*-H(3-Ph)], 1.7 [4 H, *m*-H(3-Ph)], 3.6 [2 H, *p*-H(3-Ph)], 15.4 (6 H, CH_3, 5-*i*Prpz), 41.1 and 45.5 [1 H, CH(5-*i*Prpz) and 1 H, 4-H(5-*i*Prpz)], 53.1 (6 H, 5-CH_3), 58.7 [2 H, 4-H(3-Ph,5-Mepz)], 103.8 (B-H) ppm. IR (KBr): $\tilde{\nu}$ = 2545 cm^{-1} ν(BH), 2056 ν(NCS).

3: $C_{38}H_{36}BCoN_7OS$ (708.56): calcd. C 64.41, H 5.12, N 13.84; found C 64.86, H 5.37, N 13.89. ^{1}H NMR (CD_3OD, 298 K): δ = −72.4 [4 H, *o*-H(3-Ph)], −67.4 [1 H, 3-H(5-*i*Prpz)], 1.5 [4 H, *m*-H(3-Ph)], 3.4 [2 H, *p*-H(3-Ph)], 16.3 (6 H, CH_3, 5-*i*Prpz), 17.2 [2 H, *p*-H(5-Ph)], 21.6 [4 H, *m*-H(5-Ph)], 35.3 [4 H, *p*-H(5-Ph)], 46.2 and 46.8 [1 H, CH(5-*i*Prpz) and 1 H, 4-H(5-*i*Prpz)], 58.1 [2 H, 4-H(3,5-diPhpz)], 109.0 (1 H, BH) ppm. IR (KBr): $\tilde{\nu}$ = 2579 cm^{-1} ν(BH), 2063 ν(NCS).

4: $C_{19}H_{28}BCoN_7S$ (456.29): calcd. C 50 01, H 6.18, N 21.49; found C 50.21, H 5.71, N 21.32. ^{1}H NMR (CD_3OD, 298 K): δ = −86.0 [3 H, CH(3-*i*Prpz)], −28.6 [18 H, CH_3(3-*i*Prpz)], 49.7 [3 H, 5-H(3-*i*Prpz)], 63.2 [3 H, 4-H(3-*i*Prpz)], 75.0 (1 H, B-H) ppm. IR (KBr): $\tilde{\nu}$ = 2484 cm^{-1} ν(BH), 2059 ν(NCS).

Crystal data are given in Table 2, together with refinement details. All measurements of crystals were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation. Both crystals were positioned at 65 mm from the KM4CCD camera. 612 Frames were measured at 0.75° intervals with a counting time of 45 sec. The data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) (formerly Kuma Diffrac-

Table 1. The structure-chemical shift relationship

Compound	Geometric factors[a]			Chemical shifts[b]			
	β [°]	α [°]	B···Co [Å]	δ(B-H) [ppm]	δ(CH,3-*i*Pr) [ppm]	δ(CH_3,3-*i*Pr) [ppm]	δ(*o*-H,3-Ph) [ppm]
1-CD_3OD	140.6	75.5	3.07	93.7	–	–	−57.4
2-CD_3OD[c]	–	–	–	92.7	−34.8	−24.8	−57.9
3-CD_3OD	159.0	86.4	3.11	86.7	−71.1	−29.8[d]	−81.2
4-CD_3OD[e]	141.3	77.6	2.97	95.6	–	–	−69.6
5-CD_3OD[e]	152.5	83.0	3.11	85.0	−70.2	−29.1[d]	−78.2

[a] Data from X-ray crystallographic measurements for [CoTp^{x}(NCS)(THF)] complexes, unless stated otherwise. [b] Measured in [D$_4$]methanol. [c] No X-ray data available. [d] Average value for two separate resonances. [e] Geometric factors measured for tetracoordinate [CoTp^{x}(NCS)] and pentacoordinate [CoTp^{x}(NCS)]$_2$, respectively

Table 2. Crystal data and structure refinement

Compound	**1**	**2**
Empirical formula	$C_{52}H_{56}B_2N_{12}Co$	$C_{35}H_{44}BN_7O_2SCo$
Molecular weight	929.64	696.57
T /K	100(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	Pbca
a (Å)	10.782(2)	15.6114(15)
b (Å)	10.905(3)	19.8342(15)
c (Å)	12.2209(19)	22.0406(17)
α (°)	87.45(2)	−
β (°)	74.763(16)	−
γ (°)	60.72(2)	−
V (Å^3)	1203.3(5)	6824.6(10)
Z	1	8
D_c (Mg·m^{-3})	1.283	1.356
μ (mm^{-1})	0.407	0.607
F(000)	489	2936
Crystal size (mm)	0.20 × 0.18 × 0.16	0.20 × 0.17 × 0.14
θ range for data collection (°)	3.47−28.41	3.23−28.53
Ranges of *h*,*k*,*l*	$-14\rightarrow14$, $-12\rightarrow14$, $-16\rightarrow14$	$-20\rightarrow12$, $-26\rightarrow26$, $-28\rightarrow29$
Reflections collected	8288	45044
Independent reflections(R_{int})	5285 (0.0187)	8203 (0.0527)
Data/parameters	5285/416	8203/601
GOF(F^2)	1.078	1.161
Final R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0323/0.0810	0.0565/0.0970
Extinction	−	0.00012(12)
Largest diff. peak/hole (e·Å^{-3})	0.337/-0.429	0.620/-0.303

tion Wrocław, Poland) programs. The structures were solved by the heavy-atom method (program SHELXS-97) and refined by full-matrix least-squares on all F^2 data using the SHELXL-97 programs.[14,15] Non-hydrogen atoms were refined with anisotropic vibrational parameters; hydrogen atoms were included from geometry of molecules and/or $\Delta\rho$ maps and were refined with isotropic vibrational parameters.

CCDC-185198 (**1**) and -185199 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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