Synthesis, X-ray Crystallographic and ^{1}H NMR Spectroscopic Structural Studies on Cobalt(II) Complexes of Homoscorpionate, Heteroscorpionates and Chiral Tris(pyrazolyl)borates Obtained from 5(3)-*Iso*propyl-3(5)-phenylpyrazole and 3,5-Dimethylpyrazole[‡]

Tomasz Ruman,[a] Zbigniew Ciunik,[b] and Stanislaw Wołowiec*[a]

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Condensation of 5(3)-isopropyl-3(5)-phenylpyrazole with sodium borohydride led to a mixture of tris(pyrazolyl)borate ligands (Tp^x) – the homoscorpionate hydrotris(5-isopropyl-3-phenylpyrazolyl)borate and the heteroscorpionates hydro(3-isopropyl-5-phenylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borate and hydrobis(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borate – that were converted into Tp^{x}Co(NCS) complexes. The molecular structures of pentacoordinate[hydrotris(5-isopropyl-3-phenylpyrazolyl)borato](tetrahydrofuran)(thiocyanato)cobalt(II) (**1-THF**) and [hydrobis(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borato](tetrahydrofuran)(thiocyanato)cobalt(II) (**3-THF**) were elucidated crystallographically. Hydro(3,5-dimethylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borate was also obtained by condensation of 2.1 equiv. of 5(3)-isopropyl-3(5)-phenylpyrazole and 0.9 equiv. of 3,5-dimethylpyrazole with sodium borohydride, and it was converted into [hydro(3,5-dimethylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) (**4**), which was characterized by X-ray crystallography. The latter was converted thermally under mild conditions (358 K in toluene) into [hydro(3,5-dimethylpyrazolyl)(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) (**9**) in 45% yield, as was concluded from the ^{1}H NMR spectrum of the post-reaction mixture. The dimer of **9** was obtained as single crystals from toluene/hexane and its structure was determined crystallographically. Two chiral Tp^x ligands of opposite boron-centered configurations are coordinated to cobalt(II) ions in a κ^3 fashion. The pentacoordinate metal ions are bridged head-to-tail by the thiocyanate anions. This chiral Tp^x ligand is the first example of a borate with fixed boron-centered chirality.

Introduction

Some 3(5)-R^1,5(3)-R^2-substituted pyrazoles (3-R^1,5-R^{2}pzH) form spontaneously both homo- and heteroscorpionate tris(pyrazolyl)borate anions when condensed with borohydride (BH_4^-).[1−10] The phenomenon was noticed originally by Trofimenko, who found that 3-isopropylpyrazole gave homoscorpionate tris(3-isopropylpyrazolyl)borate (Tp^{iPr}), which underwent thermal conversion in the Tp^{iPr2}Co complex into bis[hydrobis(3-isopropylpyrazolyl)-(5-isopropylpyrazolyl)borato]cobalt(II).[1] Metal-ion complexes of homoscorpionate Tp^x ligands have potentially C_{3v} symmetry when coordinated in a κ^3 manner, while the same type of coordination in case of heteroscorpionate Tp^x results in the formation of C_s local symmetry around the metal ion. Tp^x ligands of C_s symmetry form spontaneously from one pyrazole or by the use of two different pyrazoles. Hereafter, the latter species are named synthetic heteroscorpionates. Many synthetic heteroscorpionates have been prepared to date.[10−17] Recently, [hydro(3,5-dimethylpyrazolyl)bis(5-methyl-3-phenylpyrazolyl)borato](thiocyanato)-cobalt(II) was converted thermally into [hydro(3,5-dimethylpyrazolyl)(3-methyl-5-phenylpyrazolyl)(5-methyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) in ca. 30% yield upon heating the starting heteroscorpionate complex at 428 K in propylbenzene under reflux.[10] Encouraged by that result, we have replaced 5(3)-methyl-3(5)-phenylpyrazole with 5(3)-isopropyl-3(5)-phenylpyrazole to synthesize heteroscorpionates bearing 3- and 5-substituents of comparable size on the two pyrazolyl residues of Tp^x. We observed the ready formation of homo- and two heteroscorpionates when sodium borohydride was condensed with 3 equiv. of 5(3)-isopropyl-3(5)-phenylpyrazole. Three Tp^{x}Co(NCS) complexes were obtained and separated from this synthetic mixture, and two of them were characterized crystallographically. The ambivalent binding of 5(3)-isopro-

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[‡] Complexes of Heteroscorpionate Trispyrazolylborate Ligands, VIII. Part VII: Ref.[17]

[a] Faculty of Chemistry, Rzeszów University of Technology,
6 Powstanców Warszawy Ave., 35-959 Rzeszów, Poland
[b] Faculty of Chemistry, University of Wroclaw,
14 Joliot-Curie Str., 50-383 Wroclaw, Poland

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pyl-3(5)-phenylpyrazole was then used for the thermal conversion in good yield under mild conditions of the synthetic heteroscorpionate in [hydro(3,5-dimethylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) into its counterpart bearing a chiral Tp^x ligand.

Results and Discussion

Heteroscorpionate tris(pyrazolyl)borates formed spontaneously when the pyrazoles used to construct Tp^x were 3(5)-isopropylpyrazole,[1] 4-bromo-3(5)-isopropylpyrazole,[1,2] 3(5)-neopentylpyrazole,[3] 3(5)-mesitylpyrazole,[4] 5-methyl-3,4-diphenylpyrazole,[5] 3(5)-methylpyrazole,[6] 3(5)-phenylpyrazole,[7] 3(5)-cyclohexylpyrazole,[8] 4-bromo-3(5)-cyclohexylpyrazole,[8] (4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydroindazole,[9] and 5(3)-methyl-3(5)-phenylpyrazole.[10] In the latter case, the sodium salt of heteroscorpionate Na[HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)] was separated from the homoscorpionate $NaTp^{Ph,Me}$ counterpart because of the good solubility of $NaTp^{Ph,Me}$ in hot heptane. Moreover, prolonged heating of sodium homoscorpionate in heptane under reflux caused considerable conversion of $NaTp^{Ph,Me}$ into sodium heteroscorpionate.[10,11] On the other hand, the heteroscorpionate Tp^x ligands were obtained by deliberate synthesis with the use of two different pyrazoles.[10–17]

Previously, we demonstrated that heating of [hydro(3,5-dimethylpyrazolyl)bis(5-methyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) {[HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS)} in propylbenzene at 428 K led to the formation of [hydro(3,5-dimethylpyrazolyl)(3-methyl-5-phenylpyrazolyl)(5-methyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) complex, containing a chiral Tp^x ligand, in ca. 30% yield.[14] The reaction was accompanied by formation of other products, namely [hydro(3,5-dimethylpyrazolyl)bis(3-methyl-5-phenylpyrazolyl)borato](thiocyanato)cobalt(II) and complexes later identified as Tp^xCo(NCS) species containing Tp^x ligands of different composition resulting from cross-exchange of pyrazole units between the two Tp^x ligands.[11] These products form readily when thiocyanate in [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS) is replaced with carboxylates, such as lactate, pyruvate, or 2-hydroxybutyrate.[11] This instability of Tp^x ligands containing the 3,5-dimethylpyrazolyl residue led to the formation of hydrobis(3,5-dimethylpyrazolyl)[5(3)-methyl-3(5)-phenylpyrazolyl]borate and even hydrotris(3,5-dimethylpyrazolyl)borate anions that are able to form bis(ligand) homo- and heteroleptic Tp^xCo$Tp^{x'}$ complexes because of the low steric hindrance of the Tp^x ligands. Consequently, the dismutation of Tp^xCo(OOCR) into Tp^xCo$Tp^{x'}$ and Co(OOCR)$_2$ took place. To avoid the dismutation of Tp^xCo(X) complexes, we have synthesized the Tp^x ligand composed of the 3(5)-isopropyl-5(3)-phenylpyrazole unit, with medium-sized substituents placed at both the 3- and 5-positions of the pyrazole unit. Thus, we have produced homo- and heteroscorpionate anionic ligands that are sterically more crowded in comparison with hydro(3,5-dimethylpyrazolyl)bis(5-methyl-3-phenylpyrazolyl)borate and have performed thermal conversion of the corresponding Tp^xCo(NCS) complex into chiral Tp^x at lower temperature.

Spontaneously Formed Tp^x Heteroscorpionates Constructed of 5(3)-Isopropyl-3(5)-phenylpyrazole

Condensation of sodium borohydride with 5(3)-isopropyl-3(5)-phenylpyrazole and prolonged heating of the reaction mixture in heptane under reflux led to the formation of three Tp^x anions. These anions were bound into isolated Tp^xCo(NCS) complexes − namely, [hydrotris(5-isopropyl-3-phenylpyrazolyl)borato](tetrahydrofuran)(thiocyanato)cobalt(II) [$Tp^{Ph,iPr}$Co(NCS)(THF), **1-THF**], [hydro(3-isopropyl-5-phenylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) {[HB(3-Ph,5-*i*Prpz)$_2$(3-*i*Pr,5-Phpz)]Co(NCS), **2**}, and [hydrobis(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borato](tetrahydrofuran)(thiocyanato)cobalt(II) {[HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]Co(NCS)(THF), **3-THF**} − and two of them (**1-THF** and **3-THF**) were characterized by X-ray crystallography. Views of the molecules of **1-THF** and **3-THF** are presented in Figures 1 and 2, respectively.

Both Tp^x ligands are coordinated in a κ^3 manner to the central metal ion. The complexes are pentacoordinate, with a nitrogen atom donor of a thiocyanate unit and an oxygen atom of THF completing the coordination sphere. The cobalt-centered (β) and boron-centered (α) bite angles (measured disregarding the hydrogen atoms) in **1-THF** and **3-THF** are β = 75.6 and 86.4°, respectively, and α = 140.7 and 159.1°, respectively. We see that the Tp^x ligand in **3-THF** is much more relaxed. The release of the steric hindrance in the Tp^x ligand in **3-THF**, relative to that in **1-THF**, is probably the reason for the spontaneous transformation, even in the case of the sodium salt. On the other

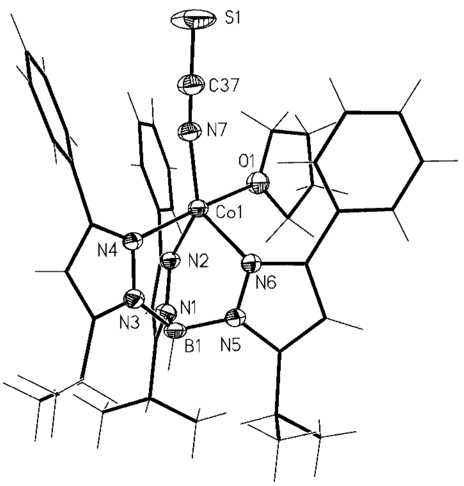


Figure 1. View of **1-THF**; selected bond lengths [Å] and angles [°]: Co(1)−N(7) 1.946(3), Co(1)−N(2) 2.053(3), Co(1)−N(4) 2.154(3), Co(1)−N(6) 2.048(3), Co(1)−O(1) 2.189(3); N(2)−Co(1)−N(4) 84.65(11), N(2)−Co(1)−N(6) 95.02(12), N(4)−Co(1)−N(6) 88.56(12), N(7)−Co(1)−N(2) 139.30(14), N(7)−Co(1)−N(4) 96.96(12), N(7)−Co(1)−N(6) 125.64(14), N(2)−Co(1)−O(1) 89.88(11), N(4)−Co(1)−O(1) 174.52(11), N(6)−Co(1)−O(1) 91.58(11), N(7)−Co(1)−O(1) 87.41(12)

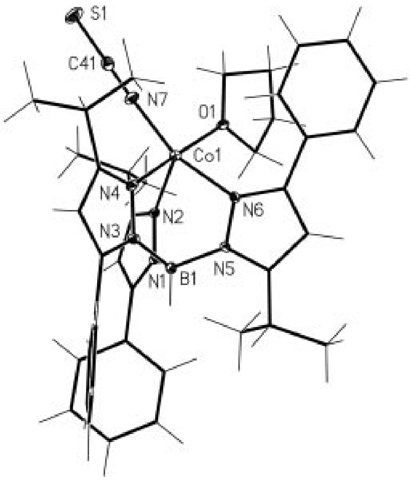


Figure 2. View of **3-THF**; selected bond lengths [Å] and angles [°]: Co(1)−N(7) 1.980(3), Co(1)−N(2) 2.056(3), Co(1)−N(4) 2.125(3), Co(1)−N(6) 2.067(2); Co(1)−O(1) 2.133(2), N(7)−Co(1)−N(2) 110.06(10), N(7)−Co(1)−N(4) 95.42(10), N(7)−Co(1)−N(6) 159.12(11), N(2)−Co(1)−N(4) 90.12(10), N(2)−Co(1)−N(6) 90.78(10), N(4)−Co(1)−N(6) 85.61(9), N(7)−Co(1)−O(1) 86.71(9), N(2)−Co(1)−O(1) 95.61(9), N(4)−Co(1)−O(1) 172.82(9), N(6)−Co(1)−O(1) 89.96(9)

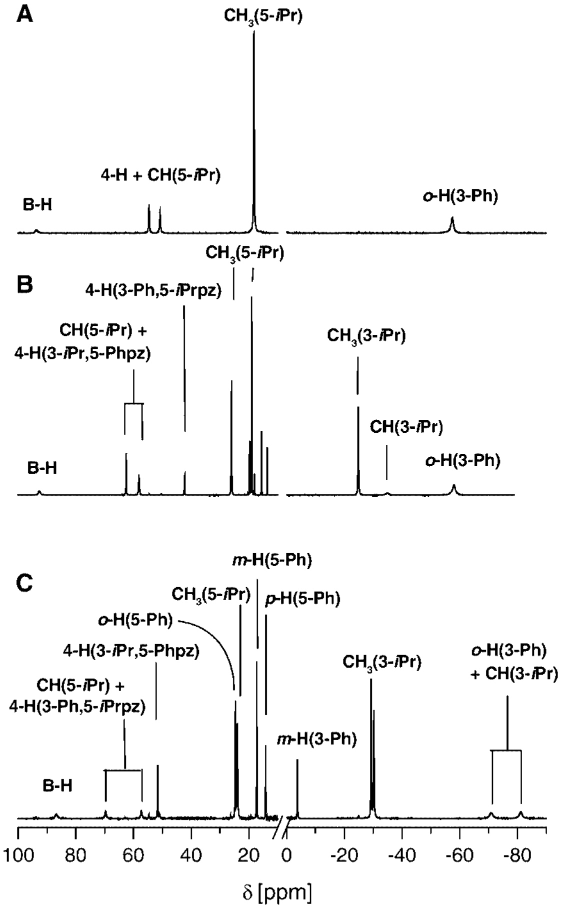


Figure 3. ^{1}H NMR spectra of **1-CD$_3$OD** (A), **2-CD$_3$OD** (B), and **3-CD$_3$OD** (C) in [D$_4$]methanol at 298 K; the 10−0-ppm region has been omitted for the sake of clarity.

hand, the boron−cobalt distance in **1-THF** is considerably shorter (3.07 Å) than that in **3-THF** (3.11 Å). The chemical shifts observed in the ^{1}H NMR spectra of **1**−**3** taken in [D$_4$]methanol corroborate strictly with those structural features (Figure 3).

The spectrum of **1-CD$_3$OD** is simple because of the effective C_{3v} symmetry of the complex and is composed of an upfield-shifted *o*-H(3-Ph) resonance at δ = −57.4 ppm, and a single downfield-shifted resonance at δ = 18.3 ppm for all of the 18 methyl group protons of the 5-*i*Pr substituent (Figure 3, trace A). The resonance of the methyl group protons of the 3-*i*Pr unit, which integrates to six protons at δ = −24.8 ppm in spectrum B, is diagnostic of **2-CD$_3$OD**. The methyl group protons of two 5-*i*Pr substituents show two separate signals at δ = 19.1 and 26.1 ppm because of diastereotopicity at the boron side of Tp^x in **2-CD$_3$OD**. The local chirality is caused by the fact that the 5-*i*Prpz residues are flanked by two different pyrazolyl moieties, i.e., the units 3-Ph,5-*i*Prpz and 3-*i*Pr,5-Phpz. The resonance of C*H*(3-*i*Prpz) is shifted upfield, as is that of *o*-H(3-Ph), which was anticipated on the basis of previous studies.[1,3,4,9−11,13−18] All other resonances − i.e., B-*H*, 4-H, and those of the 5-substituents − are shifted downfield (Figure 3, trace B). This feature is also observed for **3-CD$_3$OD** (Figure 3, trace C). In this case, the resonance of the methyl group protons of two 3-*i*Pr substituents are split into a doublet because of diastereotopicity at the cobalt side of Tp^x in **3-CD$_3$OD**. The chemical shift of CH_3(3-*i*Pr) is similar in both **2-CD$_3$OD** and **3-CD$_3$OD**.

Although the relationship between the solid-state structures of pentacoordinate ***n*-THF** complexes and ***n*-CD$_3$OD** counterparts (where ***n*** = **1** or **3**) is not straightforward, the correlation demonstrated by the data in Table 1 is remarkable.

Table 1. Relationship between structures and their ^{1}H NMR chemical shifts

Compound	Geometric factors[a]			Chemical shifts[b]			
	β [°]	α [°]	B···Co [Å]	δ(B-*H*) [ppm]	δ(C*H*,3-*i*Pr) [ppm]	δ(CH_3,3-*i*Pr) [ppm]	δ(*o*-H,3-Ph) [ppm]
1-CD$_3$OD	140.6	75.5	3.07	93.7	–	–	−57.4
2-CD$_3$OD[c]	–	–	–	92.7	−34.8	−24.8	−57.9
3-CD$_3$OD	159.0	86.4	3.11	86.7	−71.1	−29.8[d]	−81.2
4-CD$_3$OD[e]	141.3	77.6	2.97	95.6	–	–	−69.6
9-CD$_3$OD[e]	152.5	83.0	3.11	85.0	−70.2	−29.1[d]	−78.2

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

The correlation between the chemical shift of the B-*H* proton and the cobalt−boron distance is obvious; the longer the distance between the cobalt atom and the boron-attached hydrogen atom in an ***n*-THF** complex, the lower is the value of the chemical shift of the B-*H* proton in ***n*-CD$_3$OD**. A similar trend is found on the cobalt side of the Tp^x ligands; the mean distances between the C(*ortho*) atom of the 3-phenyl substituents and the cobalt ion in **1-THF** and **3-THF** are 3.52 and 3.46 Å, respectively, and, consequently, the chemical shifts of *o*-H(3-Ph) are $\delta = -57.4$ and -81.2 ppm in **1-CD$_3$OD** and **3-CD$_3$OD**, respectively. A comparison of the bite angles in **1-THF** and **3-THF** indicates that steric crowding imposed by three 3-phenyl substituents around the cobalt ion in **1-CD$_3$OD** keeps the *o*-H(3-Ph) protons remote from the paramagnetic center, while the more relaxed surrounding of cobalt(II) in **3-CD$_3$OD** allows for the closer contact between the *o*-H(3-Ph) protons and the metal ion. Thus, the intermediate position of the resonances of the B-*H* and *o*-H(3-Ph) protons of **2-CD$_3$OD** is a rather expected result. The unexpected feature in the spectrum of **2-CD$_3$OD** is the considerably smaller chemical shift of the C-*H*(3-*i*Pr) proton in comparison with that in **3-CD$_3$OD**. This feature may be caused by the 3-*i*Pr substituent being pushed away by the two flanking 3-Ph substituents in the former complex. The ^{1}H NMR spectroscopic results obtained for the other two complexes described here will be discussed later.

Synthesis, Structure and Properties of [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS) (4)

The ambivalent bonding of 3(5)-isopropyl-5(3)-phenylpyrazole to boron resulted in spontaneous formation of heteroscorpionates, which was demonstrated above. We did not intend to optimize the yield of the synthesis of the Tp^x ligands described. Instead, we have constructed the synthetic heteroscorpionate composed of two pyrazole units, i.e., two 3-Ph,5-*i*Prpz units and one 3,5-diMepz unit. The sodium salt of the Tp^x ligand was obtained as a pure product in good yield. We have assumed that the ligand remained unchanged during the synthesis of the [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS) complex, which was obtained by a standard procedure under mild conditions. During workup, we found that prolonged heating (12 h) of the complex in methanol was accompanied by formation of bis(ligand) complexes, similar to that found in the case of [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS).[10,11] Examination by mass spectrometry of the white precipitate of side-products isolated from hot methanol indicated that a series of the following complexes were formed by cross-exchange of the pyrazolyl moieties: [HB(Ph,*i*Prpz)$_2$(3,5-diMepz)]$_2$Co [*m*/*z* (%) = 1014 (80)], [HB(Ph,*i*Prpz)$_2$(3,5-diMepz)][HB(Ph,*i*Prpz)(3,5-diMepz)$_2$]Co [*m*/*z* (%)= 923 (100)], [HB(Ph,*i*Prpz)(3,5-diMepz)$_2$]$_2$Co [*m*/*z* (%) = 832 (40)], [HB(Ph,*i*Prpz)(3,5-diMepz)$_2$][HB(3,5-diMepz)$_3$]Co [*m*/*z* (%) = 742 (10)], and [HB(3,5-diMepz)$_3$]$_2$Co [*m*/*z* (%) = 651 (40)]. The [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS) complex was much less prone, however, to undergo this conversion than was the [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS) one.[11] Thus, we were able to isolate and grow crystals of **4** from the polar solvent THF. The molecular structure of **4** is presented in Figure 4. The cobalt is tetracoordinate in **4** despite the replacement of one pyrazolyl residue of medium steric demand (3-Ph,5-*i*Prpz in **1-THF**) by a sterically rather nondemanding one (3,5-diMepz). The cobalt-centered and boron-centered bite angles of the latter ligand in tetracoordinate **4** are slightly larger (141.3 and 77.6°, respectively) in comparison with those in **1-THF** (see Table 1). Nevertheless, the ligand is bound more tightly than are homo- and heteroscorpionate in **1-THF** and **3-THF**, respectively, which can be concluded from the relatively short cobalt−boron distance and the largest chemical shift of the B-*H* proton in **4-CD$_3$OD** (Table 1).

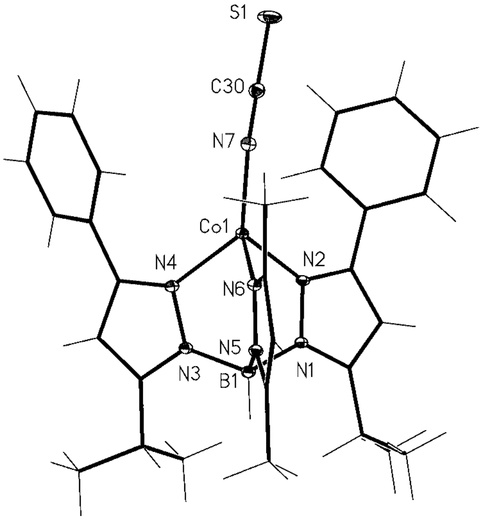


Figure 4. View of **4**; selected bond lengths [Å] and angles [°]: Co(1)−N(7) 1.9178(15), Co(1)−N(2) 2.0154(14), Co(1)−N(4) 2.0124(15), Co(1)−N(6) 2.0020(15); N(7)−Co(1)−N(2) 120.60(6), N(7)−Co(1)−N(4) 130.29(6), N(7)−Co(1)−N(6) 116.50(6), N(4)−Co(1)−N(2) 92.42(6), N(6)−Co(1)−N(2) 95.74(6), N(6)−Co(1)−N(4) 93.28(6)

Steric Demands of Tp^x Ligands in [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]CoTp (5), [HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]CoTp (6), [HB(3-Ph,5-*i*Prpz)$_2$(3-*i*Pr,5-Phpz)]CoTp (7), and Tp$^{\mathrm{Ph},i\mathrm{Pr}}$CoTp (8); Tp = Tris(pyrazolyl)borate

The presence of small- or medium-sized substituents at positions 3 and 5 of pyrazole units renders the Tp^{x}Co(X) complexes able to coordinate Tp as the X unit in all of the compounds studied. Previously, it has been noted that the presence of merely one sterically demanding 3-*tert*-butyl or 3,5-di-*tert*-butylpyrazolyl residue precluded such a conversion.[13,10]

The comparison of the steric demands of Tp^x ligands has been made for their Tp^{x}CoTp complexes, which were generated in situ. The ^{1}H NMR spectra of pentacoordinate Tp^{x}Co(NCS)(CD$_3$OD) complexes are shown in Figures 3 and 5 (A). The metathesis of the thiocyanate ion and the Tp unit occurred quantitatively without formation of Tp$_2$Co except in the case of Tp$^{\mathrm{Ph},i\mathrm{Pr}}$Co(NCS). The Tp^x ligands of intermediate steric hindrance described here were expected to form stable hexacoordinate Tp^{x}CoTp com-

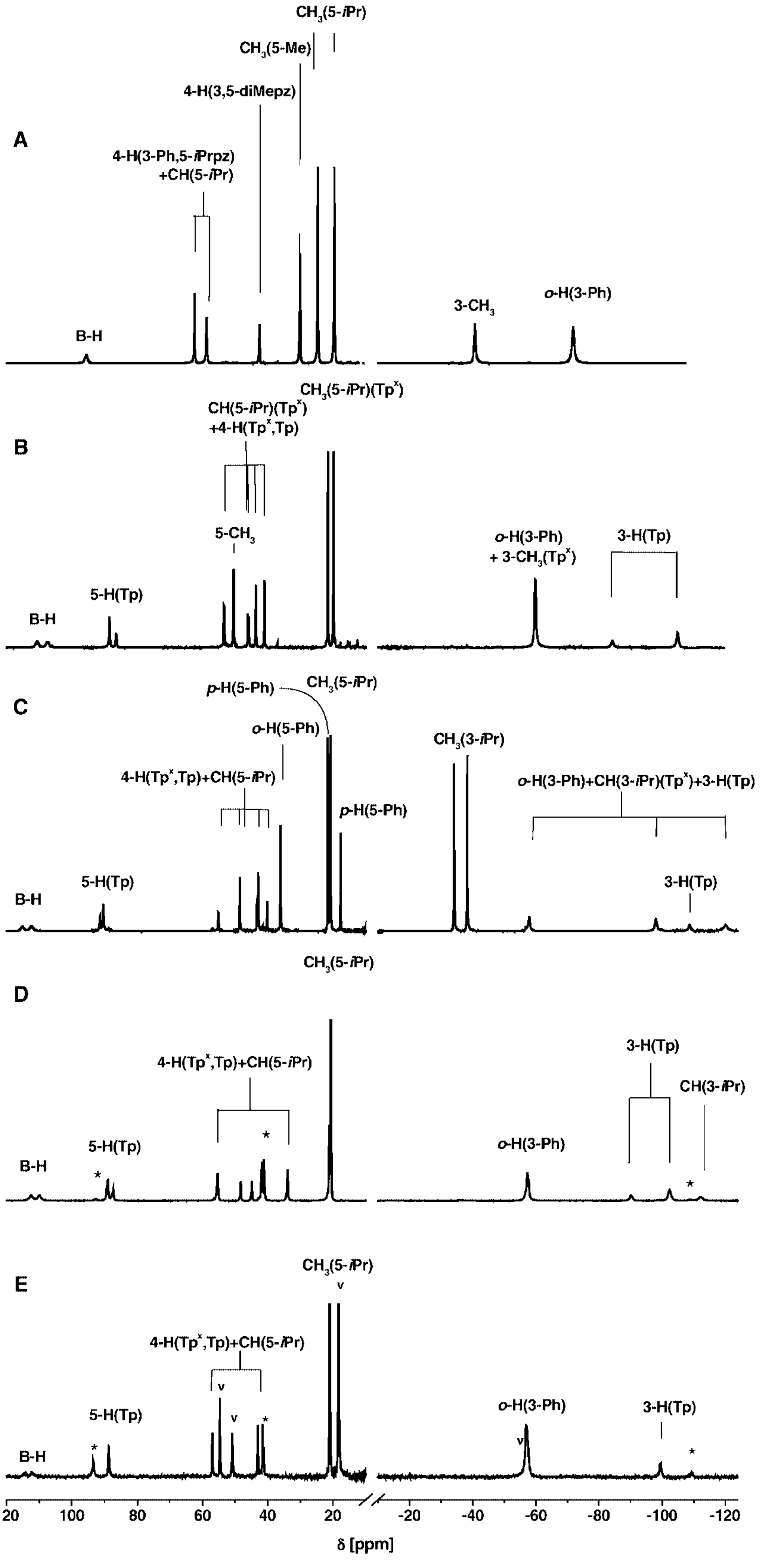


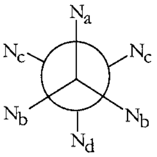
Figure 5. ^{1}H NMR spectra of [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS)(CD_3OD) (**4-CD_3OD**) (A), [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]CoTp (**5**) (B), [HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]CoTp (**6**) (C), [HB(3-*i*Pr,5-Phpz)(3-Ph,5-*i*Prpz)$_2$]CoTp (**7**) (D), and Tp^{Ph,iPr}CoTp (**8**) (E) in [D$_4$]methanol at 298 K; the resonances of Tp_2Co are labeled with asterisks (traces D and E), the resonances of starting Tp^{Ph,iPr}Co(NCS)(CD_3OD) complex (**1-CD_3OD**) are labeled with a "v"

plexes, as was found in other cases.[1,3,5,9–11,13–17,20–25] The reactions between the thiocyanate-bearing starting complexes and KTp were monitored by ^{1}H NMR spectroscopy of [D_4]methanol solutions. The resulting spectra are presented in Figure 5 (B–E).

The ^{1}H NMR spectra of [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]CoTp, (**5**, trace B), [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)$_2$]CoTp (**6**, trace C), and [HB(3-*i*Pr,5-Phpz)(3-Ph,5-*i*Prpz)$_2$]CoTp (**7**, trace D) reveal that mutual rotation of the Tp and heteroscorpionate Tp^x ligands around the central metal ion at 298 K is slow on the timescale of the method; the resonances of the 3-H, 4-H, and 5-H protons of the Tp ligand appear as two signals with a ratio of intensities of 2:1. Other Tp^xCoTp complexes bearing Tp^x heteroscorpionates – [HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)]$^-$,[10] [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]$^-$,[14] and [HB(3-Ph,5-Mepz)$_2$-(3,5-diEtpz)]$^-$,[24] – behave similarly.

Considering the chemical shifts of the 3-H and/or 5-H signals of the Tp ligand as a measure of the strength of the Co–N(Tp) bonds, we find that shorter Co–N(Tp) bonds are observed for those pyrazolyl(Tp) units that are flanked by the sterically less demanding pyrazolyl residues of Tp^x.

Thus, in the antiperiplanar isomer – in which N_a and N_b stand for nitrogen donor atoms of the pz_a and pz_b units, respectively, of Tp and N_c and N_d are the nitrogen donor atoms of the pz_c and pz_d units, respectively, of heteroscorpionate Tp^x – the chemical shifts of the 3-H(pz_a,Tp) signals are higher in comparison with those of the 3-H(pz_b,Tp) signals when the 3-R substituents at pz_c are smaller than the 3-R substituents at pz_d. This situation was found for **6**, in which pz_c is 3-*i*Pr,5-Phpz, whereas pz_d is 3-Ph,5-*i*Prpz (Table 2). In all other cases of Tp^xCoTp complexes (where Tp^x is the heteroscorpionate ligand), the pz_c units are sterically more demanding, resulting in the 2:1 pattern observed for the resonances of the 3-H(Tp) and, 5-H(Tp) protons of pz_b and pz_a, respectively, and the peaks with intensity of two hydrogen atoms are shifted more paramagnetically. For example, in **5** the two 3-Ph(pz_c,Tp^x) substituents are in a *synclinal* position with respect to the pz_a(Tp) unit. Thus, the pz_a(Tp) unit is bound more weakly in comparison to the two pz_b(Tp) units, which are flanked by *synclinal* 3-Ph,5-*i*Prpz and 3,5-diMepz units. Consistently, the isotropic shifts of 3-H(pz_a,Tp) and 5-H(pz_a,Tp) are smaller in comparison to those of 3-H(pz_b,Tp) and 5-H(pz_b,Tp) (Table 2).



Tp^x ligands with intermediate-sized 3- and 5-substituents weaken the bonding of Tp at the cobalt(II) center in Tp^xCoTp complexes, as is demonstrated by the hyperfine shift of the B-*H* signal being lower by 1.3–13.6 ppm (the average values of chemical shifts for Tp^x and Tp units are listed in column 5 of Table 2) in comparison with that in Tp_2Co. A more precise parameter is the shift of the 3-H and 5-H(Tp) signals (Δ_3 and Δ_5 in column 6). For Tp^xCoTp complexes with homoscorpionate Tp^x ligands, this weakening, composed of both steric and electronic effects (*trans*

Table 2. Characteristic features of ^{1}H NMR spectra of Tp^xCoTp complexes

Entry	Formula of complex	Chemical shift (intensity) [mean]of 3-H(Tp)	5-H(Tp)	B-*H*[c]	Δ[a] Δ_3; Δ_5	SD[b] SD_3; SD_5
1	Tp_2Co[d]	−109.1	93.1	120.4	–	–
2	$Tp^{Ph,Me}$CoTp[10]	−100.3	89.3	113.9	8.8; 3.8	–
3	$Tp^{Ph,iPr}$CoTp[d]	−99.3	88.7	113.1	9.8; 4.4	–
4	$Tp^{iPr,4Br}$CoTp[25]	−96.3	86.2	107.6	15.5; 6.9	–
5	Tp^{Cy}CoTp[9]	−103.8	91.8	116.7	5.3; 1.3	–
6	$Tp^{Cy,4Br}$CoTp[9]	−102.7	90.4	113.5	6.4; 2.7	–
7	[HB(3-Me,5-Phpz)(3-Ph,5-Mepz)$_2$]CoTp[10]	−86.9(1H); −101.4(2H); [−96.6]	88.1(1H); 91.1(2H); [90.1]	112.6	12.5; 3.0	14.5; 3.0
8	[HB(3,5-diMepz)(3-Ph,5-Mepz)$_2$]CoTp[14]	−81.1(1H); −100.1(2H); [−93.8]	85.6(1H); 88.2(2H); [87.3]	107.8	15.3; 5.8	19.0; 2.6
9	[HB(3,5-diEtpz)(3-Ph,5-Mepz)$_2$]CoTp[24]	−82.5(1H); −101.3(2H); [−95.0]	86.2(1H); 88.5(2H); [87.7]	108.6	14.1; 5.4	18.8; 2.3
10	[HB(3-*i*Pr,5-Phpz)(3-Ph,5-*i*Prpz)$_2$]CoTp[d]	−90.3(1H); −102.5(2H); [−98.4]	87.7(1H); 89.3(2H); [88.8]	111.5	10.7; 4.3	12.2; 1.6
11	[HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)$_2$]CoTp[d]	−98.1(2H); −108.8(1H); [−101.7]	90.4(2H); 91.4(1H); [90.7]	113.7	7.4; 2.4	10.7; 1.0
12	[HB(3,5-diMepz)(3-Ph,5-*i*Prpz)$_2$]CoTp[d]	−81.8(1H); −101.7(2H); [95.1]	86.4(1H); 88.5(2H); [87.8]	109.0	14.0; 5.3	19.9; 2.1
13	[HB(5-*i*Prpz)(3-Ph,5-Mepz)$_2$]CoTp[17]	−84.2(1H); −97.2(2H); [−92.9]	79.5(1H); 91.1(2H); [87.2]	109.1	16.2; 5.9	13.0; 11.6
14	[HB(3,5-diMepz)(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)]-CoTp[d]	−89.0; −96.8; −108.3; [98.0]	89.0; 96.9; 108.3; [98.1]	110.6	11.1; 5.0	

[a] Calculated as chemical shifts [ppm] of 3-H(Tp) and 5-H(Tp) in the Tp^xCoTp complex minus those in Tp_2Co (Entry 1, columns 3 and 4). [b] Calculated as the absolute value of the chemical shift difference [ppm] between 3-H(Tp) [or 5-H(Tp)] in Tp^xCoTp complexes. [c] Averaged for B-*H* resonances of Tp and Tp^x. [d] This paper.

effect) imposed by the 3−5-substituents, of the Tp^{x} ligands can be put into order: Tp$^{i\mathrm{Pr},4\mathrm{Br}}$ > Tp$^{\mathrm{Ph},i\mathrm{Pr}}$ > Tp$^{\mathrm{Ph,Me}}$ > Tp$^{\mathrm{Cy},4\mathrm{Br}}$ > Tp$^{\mathrm{Cy}}$.

Unfortunately, the crystallographic data are not available for those compounds, with one exception,[24] therefore a strict relationship between chemical shift observed in the ^{1}H NMR spectra and distances cannot be made. The difference between the effective size of the 3- and/or 5-substituents can be precisely derived, however, from the data of the heteroscorpionate Tp^{x}CoTp complexes based upon the differences between the chemical shifts of pairs of resonances of the 3-H proton and those of the 5-H(Tp) proton (SD$_3$ and SD$_5$, respectively, column 7 in Table 2). These resonances were assigned (Entries 7−14, Table 2) according to the symmetry of the studied species. Thus, the pairs of pyrazolyl residues resulting in differentiation of steric hindrance can be put in order: 3-Ph,5-*i*Prpz/3,5-diMepz > 3-Ph,5-Mepz/3,5-diMepz > 3-Ph,5-Mepz/3,5-diEtpz > 3-Ph,5-Mepz/3-Me,5-Phpz > 3-H,5-*i*Prpz/3-Me,5-Phpz > 3-H,5-*i*Prpz/3-Ph,5-*i*Prpz.

This comparison seems to be reliable. It shows, for instance, even a subtle difference in steric hindrance between 3,5-diMepz and 3,5-diEtpz (Entries 8 and 9), and the influence of steric hindrance imposed by 5-substituents, 5-Me vs. 5-*i*Pr (Entries 8 and 12) or 5-Me vs. 5-Ph (Entries 7 and 8).

Thermal Conversion of 4 into [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)]Co(NCS) (9)

Previously, we have demonstrated that [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS) underwent conversion into chiral [HB(3-Me,5-Phpz)(3-Ph,5-Mepz)(3,5-diMepz)]-Co(NCS) in 30% yield when heated in propylbenzene for a prolonged time. That reaction was accompanied by the formation of [HB(3-Me,5-Phpz)$_2$(3,5-diMepz)]Co(NCS) and some other products − including bis(ligand) complexes Tp^{x}CoTp$^{x\prime}$ which were formed with Tp^{x} ligands of lower steric hindrance − obtained as a mixture.[10] These complexes also form as a result of scrambling of the pyrazolyl residues when the attempt was made to exchange the thiocyanate anion of [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS) for carboxylate anions.[11] To avoid this kind of reactivity and to construct a ligand of higher steric demand, with the hope of leading to the thermal conversion under less dramatic conditions, we have replaced the 5-methyl-3-phenylpyrazolyl residue with the 5-isopropyl-3-phenylpyrazolyl one and converted the synthesized [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS) complex thermally. The reaction was monitored by ^{1}H NMR spectroscopy. Figure 6 presents the series of spectra taken for the [D$_8$]toluene solutions containing the starting complex and the species formed upon heating them. The ^{1}H NMR spectra of the Tp^{x}Co(NCS) complexes in this solvent are particularly easy to interpret because the low-field region of the spectra show exclusively the resonances of the 4-H protons of the 3,5-disubstituted Tp^{x} ligands. Thus, at 357 K the starting compound is represented by two resonances at δ = 60.7 and 53.1 ppm of 2:1 intensity ratio (Figure 6). Upon heating the starting complex at this temperature, three resonances for the 4-H protons, of 1:1:1 intensity ratio, appeared at δ = 62.3, 57.4, and 56.7 ppm, which were attributed to [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Ph)(3,5-diMepz)]Co(NCS) (**9**). The chiral complex was formed in 45% yield within 450 min (Figure 7). The formation of the chiral product was accompanied by formation of [HB(3-*i*Pr,5-Phpz)$_2$(3,5-diMepz)]Co(NCS) (see the resonances labeled as 10 in Figure 6) resulting from double borotropic shift in [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS). Although yet another product was formed under those condition, the yield of chiral product was much improved in comparison with the conversion performed for [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]Co(NCS).[10]

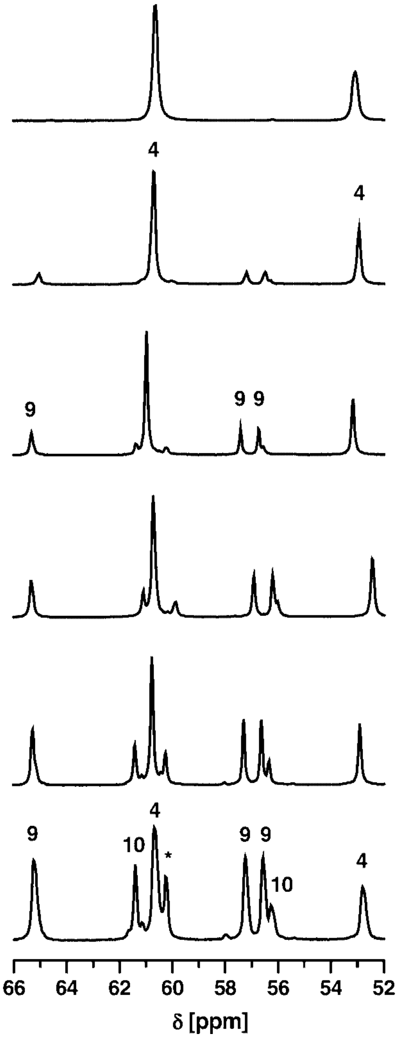


Figure 6. Selected fragments of the ^{1}H NMR spectra of the complexes formed during thermal conversion of [HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]Co(NCS) (**4**) in [D$_8$]toluene; the resonances of the 4-H protons of the starting compound (trace A), [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)]Co(NCS) (**9**), [HB(3-*i*Pr,5-Phpz)$_2$(3,5-diMepz)]Co(NCS) (**10**), and unidentified side-product, are denoted by the arabic numerals 4, 9, and 10, and an asterisk, respectively

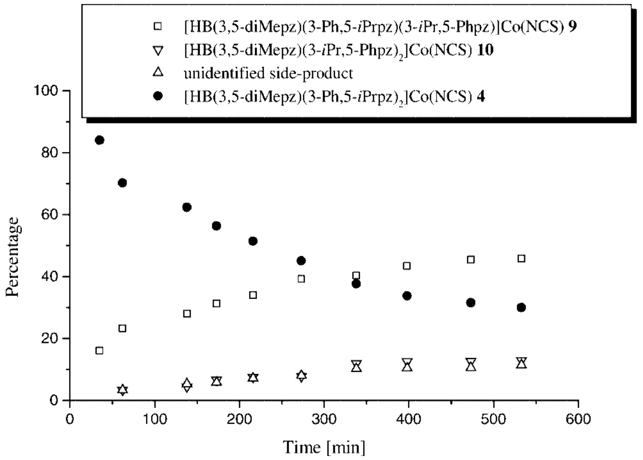


Figure 7. Percentage of the complexes formed during thermal conversion of **4** at 357 K in [D$_8$]toluene over the course of time

A large-scale procedure eventually gave pure **9**, which was obtained from the post-reaction mixture by fractional crystallization from toluene/heptane as a second crop of crystals. The structure of isolated dimeric compound **9$_2$** was determined crystallographically (Figure 8). Tp^x ligands impose intermediate steric hindrance and, therefore, the central cobalt(II) ion in **9** is pentacoordinate. Typically, the three coordination sites are occupied by the pyrazolyl nitrogen atoms, the thiocyanate nitrogen atom and, additionally, by the sulfur atom of a second thiocyanate anion that bridges to another cobalt(II) center in the dimeric complex. Two Tp^x ligands have opposite configuration at the chiral boron atom. Thus, the *meso* form of dimer of **9$_2$** was obtained in the solid state. The ^{1}H NMR spectrum of **9-CD$_3$OD** in [D$_4$]methanol is presented in Figure 9 (trace A). The upfield-shifted resonances belong to protons of the C-3 substituents − *o*-H(3-Ph) (δ = − 78.2 ppm), C*H*(3-*i*Pr) (δ = −70.2 ppm), 3-CH$_3$ (δ = −57.1 ppm), and diastereoisotopic C*H*$_3$(3-*i*Pr) (δ = −30.1, −28.1 ppm) − whereas the three resonances of the 4-H protons, and those belonging to the protons of the 5-substituent and the B-*H* unit, are shifted downfield. The conversion in situ of **9-CD$_3$OD** into Tp^{x}CoTp by simple titration of **9-CD$_3$OD** with KTp in [D$_4$]methanol produced the heteroleptic complex, which showed seven resonances, with intensity corresponding to one proton, of six 4-H (Tp^x and Tp) protons and one C*H*(5-*i*Pr) proton in the region of the spectrum between δ = 38 and 53 ppm (see inset in trace B). The diastereoisomers of Tp^{x}Co[OOCC(*S*)H(OH)CH$_3$] generated in situ by titration of **9-CD$_3$OD** with sodium (*S*)-lactate are present in solution in equal concentrations, as is concluded from the 1:1 intensity pattern of all the resonances of the two diastereoisomers in the ^{1}H NMR spectrum of

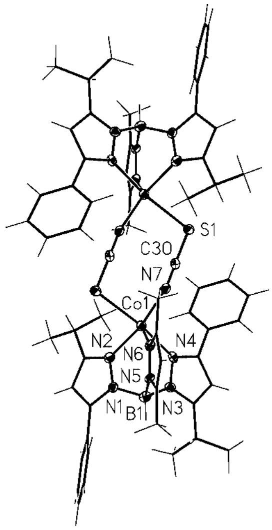


Figure 8. View of the dimer of **9**; selected bond lengths [Å] and angles [°]: Co(1)−N(7) 1.976(7), Co(1)−N(6) 2.031(6), Co(1)−N(2) 2.053(7), Co(1)−N(4) 2.142(7), Co(1)−S(1) 2.581(3); N(7)−Co(1)−N(6) 113.6(3), N(7)−Co(1)−N(2) 150.8(3), N(6)−Co(1)−N(2) 95.6(3), N(7)−Co(1)−N(4) 95.8(3), N(6)−Co(1)−N(4) 88.8(2), N(2)−Co(1)−N(4) 83.7(3), N(7)−Co(1)−S(1) 89.69(19), N(6)−Co(1)−S(1) 95.90(19), N(2)−Co(1)−S(1) 87.81(19), N(4)−Co(1)−S(1) 170.64(19)

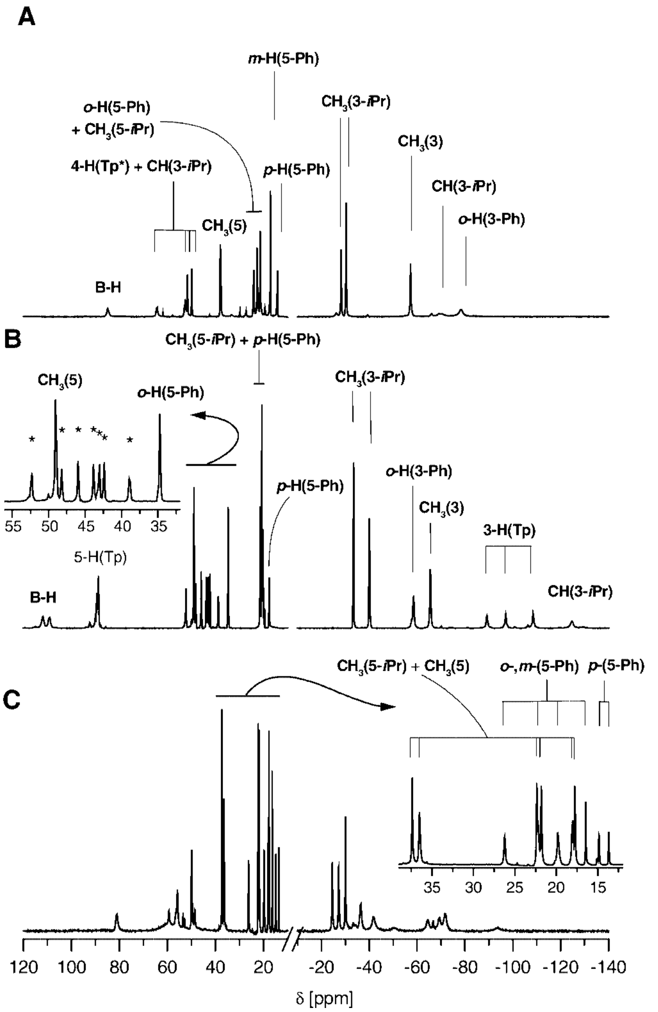


Figure 9. ^{1}H NMR spectra of [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)]Co(NCS)(CD$_3$OD) (A), [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)]CoTp (B), and [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)]Co(OOCCH(OH)CH$_3$] (C) in [D$_4$]methanol at 298 K; seven resonances of intensity corresponding to one hydrogen atom are labeled with asterisks in the inset of trace B and are attributed to the 4-H(Tp,Tp^x) and C*H*(5-*i*Pr) protons

$Tp^xCo[OOCC(S)H(OH)CH_3]$ presented as trace C. The bottom inset in Figure 9 shows the details of the 13−37-ppm region of the spectrum, in which we observe six methyl group resonances of the 3-CH_3 and CH_3(5-*i*Pr) groups and six *o*-, *m*-, and *p*-(5-Ph) resonances. The two diastereoisomers differ in energy and consequently have considerably different spectra. The spectrum remains unchanged over the course of time (24 h) indicating that rather little inversion of configuration at the boron atom takes place.

No tetracoordinate anionic borates with boron-centered chirality have been obtained to date. Tetrahedral (or nearly tetrahedral) neutral boron compounds with boron-centered chirality have been reported.[26−31] Several compounds of this type, with boron-centered chirality imposed by peripheral chiral substituents, have been structurally characterized.[28−31] Generally, separable enantiomers (diastereoisomers) of opposite boron-centered chirality interconvert rapidly at ambient temperatures ($\Delta G^{\ddagger}_{25}$ = 60−90 kJ/mol).[28−33] The chiral tripodal Tp^x ligand described in this report was designed as a chiral ancillary for facial Tp^xML_n complexes with catalytic activity. Currently, we are working on the isolation of the enantiomerically pure sodium salts of the chiral ligands and their thallium(I) complexes and the preparation of the catalytically active complexes of those ligands.

Experimental Section

Syntheses

5(3)-Isopropyl-3(5)-phenylpyrazole (3-Ph,5-*i*PrpzH): The 3(5)-Ph,5(3)-*i*PrpzH unit was synthesized from the corresponding diketone obtained by the general procedure of Swamer and Hauser.[19] Sodium hydride (19.2 g, 0.80 mol) was suspended in diethyl ether (100 mL) containing ethyl isobutyrate (106.8 mL, 92.6 g, 0.80 mol) under nitrogen in a 2-L three-neck round-bottom flask. The flask was later connected to a wet test-meter, condenser and a dropping funnel. The glass device was flushed with nitrogen. Acetophenone (46.6 mL, 47.86 g, 0.4 mol), dissolved in diethyl ether (100 mL), was added dropwise to the mixture. The reaction was initiated by gentle heating of the mixture. The progress of the reaction was monitored by measuring the volume of hydrogen gas evolved. The reaction was stopped after the evolution of hydrogen had ceased (8 L of gas was collected). Ice-cold water (300 mL) and hydrochloric acid were added to the reaction mixture. The diethyl ether phase was extracted with water (2 × 0.8 L) and the combined water extracts, which contained diketone, were left overnight to react with hydrazine monohydrate (20 mL 20.2 g, 0.4 mol). The solution turned orange and turbid. The pyrazole was extracted three times with diethyl ether (2 L). The solvent was evaporated in a rotary evaporator and the oily product was kept under reduced pressure overnight. Hexane (100 mL) was added to the crude product and the mixture was stirred at room temperature for 24 h. The light-yellow powder of 3(5)-Ph,5(3)-*i*PrpzH was collected and dried under high vacuum (8.8 g, 11.8%). ^{1}H NMR ($CDCl_3$): δ = 1.31 [d, J^3 = 6.7 Hz, 6 H,CH_3(*i*Pr)], 3.01 [sept, 1 H, CH(*i*Pr)], 6.36 (s, 1 H, 4-H), 7.3−7.8 (m, 5 H, *o*-, *m*-, *p*-phenyl), 8.5 (br. s, 1 H, NH) ppm. MS (ESI, positive polarization): *m*/*z* (%) = 186.3 (100) $[C_{12}H_{14}N_2]^+$.

Synthesis of Sodium Tris(pyrazolyl)borates

Sodium Hydrotris(5-isopropyl-3-phenylpyrazolyl)borate {Na[HB(3-Ph,5-*i*Prpz)$_3$]}, Sodium Hydro(3-isopropyl-5-methylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borate, and Sodium Hydrobis(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borate: $NaBH_4$ (0.1389 g, 3.67 mmol) and 3-Ph,5-*i*PrpzH (2.0033 g, 10.77 mmol) in octadecane (40 mL) were heated with vigorous stirring in a 250-mL three-neck round-bottom flask equipped to a wet test-meter and condenser. The mixture was heated until 400 mL of hydrogen gas was evolved and then heating was continued for 40 min. Heptane (100 mL) was added to the solution after it had cooled to ca. 100 °C and then left overnight at room temperature. The solid was separated by filtration, washed with petroleum ether and dried under high vacuum. Yield 0.305 g (0.60 mmol, 16.3%). The mixture of sodium salts of Tp^x ligands was converted into Tp^xCo(NCS) complexes as reported earlier[10] and was quantified as a mixture based upon the intensity of the integrals of the resonances in the ^{1}H NMR spectrum. The mixture comprised [HB(3-*i*Pr,5-Phpz)(3-Ph,5-*i*Prpz)$_2$]Co(NCS) (80.4%), [HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]Co(NCS) (10.8%), and [HB(3-Ph,5-*i*Prpz)$_3$]Co(NCS) (8.8%). The complexes were separated and identified by their ^{1}H NMR spectra (see below).

Synthesis and Separation of and [Hydrotris(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) [$Tp^{Ph,iPr}$Co(NCS)(THF), 1-THF], [Hydro(3-isopropyl-5-phenylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) {[HB(3-Ph,5-*i*Prpz)$_2$(3-*i*Pr,5-Phpz)]Co(NCS), 2}, and [Hydrobis(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borato](thiocyanato)cobalt(II) {[HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]Co(NCS)(THF), 3-THF}: The complexes were synthesized as described previously[10] starting from NaTp^x mixture (0.305 g, 0.52 mmol) and separated by fractional crystallization from THF/heptane at 4 °C. The blue, cube-shaped crystals of **1-THF** were collected as the first product (30 mg, 0.040 mmol, 7.7% yield), dark-blue needle-shaped crystals of **2-THF** (150 mg, 0.20 mmol, 38.5% yield) were obtained as the second crop and, finally, violet-blue crystals of analytically pure **3-THF** (38 mg, 0.050 mmol, 9.6% yield) were obtained. The crystals of **1-THF** and **3-THF** were examined by X-ray crystallography (Table 3), whereas all attempts to grow the crystals of **2-THF** gave crystalline material that was very sensitive to change of temperature, which precluded good-quality X-ray crystallographic measurement.

1-THF: $C_{41}H_{48}BCoN_7OS$ (756.66): calcd. C 65.08, H 6.39, N 12.96; found C 65.21, H 6.41, N 12.62. ^{1}H NMR (CD_3OD, 298 K): δ = −57.4 [6 H, *o*-H(3-Ph)], 3.7 [3 H, *p*-H(3-Ph)], 4.5 [6 H, *m*-H(3-Ph)], 18.3 [18 H, CH_3(5-*i*Pr)], 50.8 and 54.7 [3 H, CH(5-*i*Pr) and 3 H, 4-H(3-Ph,5-*i*Prpz)], 93.7 (B-H) ppm. IR (KBr): ṽ = 2588 (ν_{BH}), 2059 (ν_{NCS}) cm^{-1}.

2-THF: $C_{41}H_{48}N_7BCoOS$ (756.66): calcd. C 65.08, H 6.39, N 12.96; found C 65.12, H 6.23, N 12.48. ^{1}H NMR (CD_3OD, 298 K): δ = −57.9 [4 H, *o*-H(3-Ph)], −34.8 [1 H, CH(3-*i*Pr)], −24.8 [6 H, CH_3(3-*i*Pr)], 0.9 [2 H, *p*-H(3-Ph)], 1.2 [4 H, *m*-H(3-Ph)], 13.7 [1 H, *p*-H(5-Ph)], 15.8 [2 H, *m*-H(5-Ph)], 19.1 [6 H, CH_3(5-*i*Pr)], 19.8 [2 H, *o*-H(5-Ph)], 26.1 [6 H, CH_3(5-*i*Pr)], 42.4 [1 H, 4-H(3-*i*Pr,5-Phpz)], 58.2 and 62.6 [2 H, CH(5-*i*Pr) and 2 H, 4-H(3-Ph,5-*i*Prpz)], 92.7 (B-H) ppm. IR (KBr): ṽ = 2557 (ν_{BH}), 2062 (ν_{NCS}) cm^{-1}.

3-THF: $C_{41}H_{48}N_7BCoOS$ (756.66): calcd. C 65.08, H 6.39, N 12.96; found C 65.40, H 6.61, N 13.02. ^{1}H NMR (CD_3OD, 298 K): δ = −80.8, −70.8 [2 H, *o*-H(3-Ph) and 2 H, CH(3-*i*Pr)], −30.3, −29.4 [6 H, two diastereoisotopic CH_3(3-*i*Pr)], −3.8 [2 H, *m*-H(3-Ph)], 0.4 [1 H, *p*-H(3-Ph)], 14.2 [2 H, *p*-H(5-Ph)], 17.3 [4 H, *m*-H(5-Ph)], 23.9

Table 3. Crystal data and structure refinement

Compound	**1-THF**	**3-THF**	**4**	**9_2**
Empirical formula	$C_{41}H_{48}BCoN_7OS$	$C_{41}H_{48}BCoN_7OS$	$C_{30}H_{34}BCoN_7S$	$C_{30}H_{34}BCoN_7S$
Formula mass	756.66	756.66	594.44	594.44
T [K]	293(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.960(2)	9.860(2)	8.5970(17)	10.618(4
b [Å]	14.731(3)	19.415(3)	12.048(2)	11.717(4)
c [Å]	23.516(3)	20.782(3)	15.011(3)	13.128(4)
α [°]	90	90	89.59(3)	111.95(3)
β [°]	90.858(12)	91.762(15)	88.05(3)	99.83(3)
γ [°]	90	90	75.07(3)	93.96(3)
V [Å^3]	4142.8(12)	3976.5(12)	1501.4(5)	1476.8(9)
Z	4	4	2	2
$D_{calcd.}$ [Mg·m^{-3}]	1.213	1.264	1.315	1.337
μ [mm^{-1}]	0.504	0.525	0.673	0.684
F(000)	1596	1596	622	622
Crystal size [mm]	0.24 × 0.20 × 0.16	0.20 × 0.13 × 0.13	0.18 × 0.16 × 0.14	0.33 × 0.07 × 0.05
θ range for data collection [°]	3.36−28.54	3.50−26.00	3.59−28.34	3.42−28.40
Ranges of *h*, *k*, *l*	−15/15, −19/15, −30/31	−8/12, −23/23, −25/24	−11/11, −10/16, −19/19	−14/9, −15/15, −16/17
Reflections collected	28281	22893	10451	10255
Independent reflections/R_{int}	9651/0.0891	7672/0.0741	6606/0.0197	6500/0.1089
Data/parameters	9651/476	7672/476	6606/367	6500/367
GOF(F^2)	1.102	1.072	1.075	0.959
Final R_1/wR_2 indices ($I > 2\sigma_I$)	0.0852/0.1300	0.0671/0.0741	0.0330/0.0790	0.0867/0.1433
Extinction coefficient	0.0002(3)	0.00095(15)		
Min./max. Transmission				0.8670/0.9695
Largest diff. peak/hole [e·Å^{-3}]	0.323/−0.304	0.289/−0.303	0.319/-0.386	0.365/-0.432

[6 H, CH_3(5-*i*Pr)], 24.7 [4 H, *o*-H(5-Ph)], 51.6 [2 H, 4-H(3-*i*Pr,5-Phpz)], 57.2, 69.7 [1 H, CH(5-*i*Pr) and 1 H, 4-H(3-Ph,5-*i*Prpz)], 86.8 (B-H) ppm. IR (KBr): $\tilde{\nu}$ = 2597 (ν_{BH}), 2083 (ν_{NCS}) cm^{-1}.

Sodium Hydro(3,5-dimethylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)borate {Na[HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]}: A mixture of $NaBH_4$ (0.2848 g, 7.53 mmol), 3-Ph,5-*i*PrpzH (2.9401 g, 15.81 mmol) and 3,5-diMepzH (0.6517 g, 6.78 mmol) in octadecane (40 mL) was heated with vigorous stirring in a 250-mL three-neck round-bottom flask equipped with a wet test-meter and condenser. The device was flushed with nitrogen before heating began. The temperature was increased gradually to the boiling point of octadecane (317 °C). Heating was continued until 630 mL of hydrogen gas was collected. Heptane (100 mL) was added to the solution after it had been cooled to ca. 100 °C and then the mixture was left overnight at 4 °C. The solid (0.6150 g, 16.4%) was separated by filtration at room temperature, washed with petroleum ether and then dried under high vacuum. From the heptane filtrate another sodium salt was recovered, i.e., sodium hydrotris(5-isopropyl-3-phenylpyrazolyl)borate (12%), which was synthesized also by a separate procedure (vide supra). ^{1}H NMR (CD_3OD, 298 K): δ = 1.53 [d, 12 H, CH_3(*i*Pr)], 2.19 [s, 6 H, 3- and 5-CH_3], 3.02 [sept, 2 H, CH(3-*i*Pr)], 5.91 [s, 1 H, 4-H(3,5-diMepz)], 6.43 [s, 2 H, 4-H(3-*i*Pr,5-Phpz)], 7.8−7.2 [10 H, m, *o*-, *m*-, and *p*-H(3-*i*Pr,5-Phpz)] ppm.

[Hydro(3,5-dimethylpyrazolyl)bis(5-isopropyl-3-phenylpyrazolyl)-borato](thiocyanato)cobalt(II) {[HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]-Co(NCS), 4}: This complex was synthesized by adding Na[HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)] (110 mg, 0.22 mmol) in THF (5 mL) into an aqueous solution (50 mL) of 0.1 M $Co(NO_3)_2$ and 0.5 M KNCS. The resulting blue product was extracted into CH_2Cl_2 (100 mL), the organic layer was washed with water (2 × 100 mL), the CH_2Cl_2 was evaporated in a rotary evaporator. The solid residue was dissolved in THF (5 mL) and recrystallized by the co-diffusion of hexane (ca. 80 mL) at 4 °C. After two weeks, the product was collected as blue crystals (123 mg, 0.18 mmol, 82% yield). One of the crystals was analyzed crystallographically (Table 3).

4: $C_{30}H_{34}N_7BCoS$ (594.44): calcd. C 60.61, H 5.76, N 16.49; found C 60.42, H 5.61, N 16.40. ^{1}H NMR (CD_3OD, 298 K): δ = −69.6 [4 H, *o*-H(3-Ph)], −39.5 (3 H, 3-CH_3), 1.6 [4 H, *m*-H(3-Ph)], 2.8 [2 H, *p*-H(3-Ph)], 19.7 [6 H, CH_3(5-*i*Pr)], 24.7 [6 H, CH_3(5-*i*Pr)], 30.1 (3 H, 5-CH_3), 42.5 [1 H, 4-H(3,5-diMepz)], 58.7 [2 H, CH(5-*i*Pr)], 62.4 [2 H, 4-H(3-Ph,5-*i*Prpz)], 95.6 (1 H, BH) ppm. IR (KBr): $\tilde{\nu}$ = 2557 (ν_{BH}), 2064 (ν_{NCS}) cm^{-1}.

In Situ Conversions of Tp^{x}Co(NCS) into Tp^{x}CoTp Complexes: The complexes were converted into their Tp^{x}CoTp counterparts in [D$_4$]methanol on a micromolar scale by the stepwise addition of 1 M KTp in [D$_4$]methanol into the starting thiocyanate complex (ca. 6 mg), dissolved in [D$_4$]methanol (400 μL). The progress of reaction was monitored by ^{1}H NMR spectroscopy.

Thermal Conversion of 4 into [Hydro(3,5-dimethylpyrazolyl)(3-isopropyl-5-phenylpyrazolyl)(5-isopropyl-3-phenylpyrazolyl)borato]-(thiocyanato)cobalt(II) (9): Heteroscorpionate complex **4** (6.3 mg, 9.5 μmol) was dissolved in [D$_8$]toluene (450 μL) in an NMR tube, which was placed in the cavity of the NMR instrument and heated at 357 K for 23 h or at 377 K for 14 h. The progress of reaction was monitored by ^{1}H NMR spectroscopy. Large-scale conversion was performed with **4** (300 mg) in toluene (30 mL) at 357 K for 500 min. The resulting solution was layered with heptane and left to crystallize at room temperature. The first crop of crystals was identified as **4** by its ^{1}H NMR spectrum, while violet needles of **9_2** were obtained as the second crop (67 mg, 22% yield). The structure of **9_2** was determined crystallographically (Table 3).

9: $C_{30}H_{34}BCoN_7S$ (594.44): calcd. C 60.61, H 5.76, N 16.49; found C 60.63, H 5.80, N 16.59. ^1H NMR (CD_3OD, 298 K): $\delta = -78.2$ [2 H, *o*-H(3-Ph)], −70.2 [1 H, CH(3-*i*Pr)], −57.2 (1 H, 3-CH_3), −30.1, −28.1 [3 H, 3 H, CH_3(3-*i*Pr)], −4.2 [2 H, *m*-H(3-Ph)], 0.8 [1 H, *p*-H(3-Ph)], 14.4 [1 H, *p*-H(5-Ph)], 17.4, [2 H, *m*-H(3-Ph)], 21.5, 22.8 [3 H, 3 H, CH_3(5-*i*Pr)], 24.3 [2 H, *o*-H(3-Ph)], 33.1 (3 H, 5-CH_3), 50.0, 51.9, 52.9 [1 H, 1 H, 1 H, 4-H(pz)], 64.7 [1 H, CH(5-*i*Pr)], 85.0 (1 H, BH) ppm. IR (KBr): $\tilde{\nu} = 2557$ (ν_{BH}), 2121, 2058 (ν_{NCS}) cm^{-1}.

Methods: ^1H 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. IR spectra were recorded with a Perkin−Elmer 1725X spectrophotometer. Elemental analyses were performed with an EA 1108 apparatus (Carbo Erba) at the Department of Organic Chemistry, Faculty of Chemistry, Rzeszów University of Technology. Mass spectra were obtained using a Finnigan MAT TSQ 700 spectrometer by the ESI method from chloroform with a 4.5-kV ionization potential and a capillary temperature of 250 °C. Crystal data are given in Table 1 together with refinement details. Measurements were performed at 293 K for **1-THF** and at 100 K for **3-THF**, **4** and $\mathbf{9_2}$ using an Oxford Cryosystem device with a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were positioned at 65 mm from the CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 10−15 s. Accurate cell parameters were determined and refined by least-squares fit of 2500−3800 of the strongest reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied for **1-THF**, **3-THF** and **3**, and analytical absorption correction was applied for $\mathbf{9_2}$. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o (formerly Kuma Diffraction Wroclaw, Poland) programs. Structures were solved by direct methods (program SHELXS-97)[34] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 programs.[35] Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and Δρ maps but were not refined. CCDC-200532 (**1-THF**), -200533 (**3-THF**), -200534 (**4**) and -189010 ($\mathbf{9_2}$) 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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