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Complexes of heteroscorpionate trispyrazolylborate ligands. Part IX. X-ray crystallographic studies on cobalt(II) complexes of hydrobis(3-phenyl,5-methylpyrazolyl)(3,5-diethylpyrazolyl)borate

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Abstract

The synthesis of the sodium salt of a new anionic heteroscorpionate trispyrazolylborate ligand as of sodium hydrobis(3-phenyl,5-methylpyrazolyl)(3,5-diethylpyrazolyl)borate (NaTp″) was described. Two cobalt(II) complexes: Tp″Co(NCS)(THF) and Tp″CoTp were synthesized and characterized crystallographically. Trispyrazolylborate ligands (Tp″ and Tp) are coordinated in a κ^3 fashion in both complexes. The dependence of the Co–N bond length from the steric hindrance of the Tp″ ligand was discussed. The steric hindrance imposed by the Tp″ ligand was also probed by in situ conversions of Tp″Co(NCS)(CD_3OD) into Tp″Co(lactate) and Tp″CoTp with ^{1}H NMR spectral monitoring and compared with other similar systems.

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Keywords: Poly(3-rpyrazolyl)borate cobalt(II) complexes; Structures; NMR

1. Introduction

The tris(pyrazolyl)borate anionic ligand (Tp) was synthesized by Trofimenko in 1967 [1].

Since then structural modifications by introduction of substituents at the 3–5 positions of the pyrazolyl residues have resulted in more than one hundred tris(pyrazolyl)borates of the second generation (Tp′) [2]. Some 3-R_1,5-R_2-pyrazoles are able to form hydrotris(3-R_1,5-R_2pyrazolyl)borate (homoscorpionate) and hydrobis(3-R_1,5-R_2pyrazolyl)(3-R_2,5-R_1pyrazolyl)borate (heteroscorpionate) [2,3]. The latter are especially interesting because they provide C_s symmetry to the metal center when coordinated in a κ^3 fashion in contrary to C_{3v} symmetry of homoscorpionates. The heteroscorpionates, which can also be constructed by condensation of two different pyrazoles with borohydride will be named hereafter the third generation trispyrazolylborates (Tp″). In this paper, we have described the synthesis of a new Tp″ composed of two 3-phenyl,5-methylpyrazolyl and one 3,5-diethylpyrazolyl residues. The ligand was bound to a cobalt(II) center and two complexes, the mono-ligand Tp″Co(NCS) and heteroleptic Tp″CoTp, were characterized structurally by X-ray crystallography.

2. Experimental

2.1. Syntheses

2.1.1. 3,5-Diethylpyrazole (3,5-diEtpzH)

Hydrazine monohydrate (15 cm^3, 15.45 g, 0.309 mol) was added dropwise to a warm solution of 3,5-heptanodione (25 g, 0.195 mol) in ethanol (100 cm^3). The mixture was then refluxed for 0.5 h and cooled to room temperature. The solvents were removed under reduced pressure and the product was distilled in vacuo. The fraction boiling at 125–127 °C (3.5 mmHg) was collected. The product crystallized at room temperature. Yield 21 g, 86.7%.

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^{1}H NMR ($CDCl_3$, 293 K): 8.18 (1H, br s, N(1,2)-H); 5.89 (1H, s, 4-H); 2.64 (4H, q, 3,5-C*H*$_2$CH$_3$, *J*(CH$_2$–CH$_3$) = 7.6 Hz); 1.24 (6H, t, 3,5-CH$_2$C*H*$_3$).

Mass spectrum (ESI, positive polarization) *m/e*: [3,5-diEtpzH]$^+$ 124 (100%).

2.1.2. Sodium hydrobis(3-phenyl,5-methylpyrazolyl)(3,5-diethylpyrazolyl)borate (Na[HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)])

NaBH$_4$ (0.7578 g, 20.0 mmol) was heated with 3(5)-phenyl,5(3)-methylpyrazole (3-Ph,5-MepzH, 6.0120 g, 38.0 mmol) and 3,5-diEtpzH (2.7292 g, 22.0 mmol) in octadecane (60 cm^3) with vigorous stirring in a 250 cm^3 three-neck round-bottom 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 octadecane (317 °C). Heating was continued until 1600 cm^3 of hydrogen was collected. Heptane (100 cm^3) was added to the solution after cooling to about 100 °C and left for 2 h, the deposited precipitate was filtered off, washed with petroleum ether and vacuum dried. Crude product was collected (2.97 g), suspended in 90 cm^3 heptane, boiled for 5 min and filtered off while hot. The same procedure was repeated again and finally the solid was washed twice with 30 cm^3 of hot heptane, petroleum ether and vacuum dried. 2.05 g of pure Na[HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)] was collected (21.7% yield).

^{1}H NMR ((CD$_3$)$_2$SO, 293 K): 7.81–7.20 (10H, m, *o*-, *m*- and *p*-H(3-Ph)); 6.22 (2H, s, 4-H(3-Ph,5-Mepz)); 5.67 (1H, s, 4-H(3,5-diEtpz)); 2.35–2.55 (4H, m, CH$_2$CH$_3$(3,5-diEtpz)); 2.15 (6H, s, 5-CH$_3$(3-Ph,5-Mepz)); 1.20–0.90 (6H, m, 3,5-CH$_2$CH$_3$).

*2.1.3. Tetrahydrofuran thiocyanatohydrobis(3-phenyl,5-methylpyrazolyl)(3,5-diethylpyrazolyl)boratocobalt(II) ([HB(3-Ph,5-Mepz)2(3,5-diEtpz)]Co(NCS)(THF), **1-THF**)*

Na[HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)] (100 mg, 0.212 mmol) dissolved in THF (10 cm^3) was added dropwise into 50 cm^3 of aqueous 0.1 M cobalt(II) nitrate and 0.5 M potassium thiocyanate solution. The blue cobalt complex was extracted with methylene dichloride (100 cm^3), the organic layer was washed twice with water (100 cm^3) and dichloromethane was removed on a rotary evaporator. The solid residue was dissolved in THF and left for crystallization from THF/heptane solvents. **1-THF** was collected as violet–blue crystals (70 mg, 0.110 mmol, 51.9%). One of the crystals was analyzed crystallographically.

Elemental analysis: Calc. for $C_{32}H_{38}N_7OSBCo$ (MW 638.49): C, 60.20; H, 6.00; N, 15.36. Found: C, 59.95; H, 6.16; N, 15.43.

^{1}H NMR (CD$_3$OD, 298 K): −64.3 (4H, *o*-H(3-Ph,5-Mepz)), −32.4 (2H, 3-C*H*$_2$CH$_3$(3,5-diEtpz)), −23.2 (3H, 3-CH$_2$C*H*$_3$(3,5-diEtpz)), 2.0 (4H, (*m*-H(3-Ph,5-Mepz))); 2.4 (2H, *p*-H(3-Ph,5-Mepz)), 10.9 (3H, 5-CH$_2$C*H*$_3$(3,5-diEtpz)), 30.2 (2H, 5-C*H*$_2$CH$_3$(3,5-diEtpz)), 42.6 (1H, 4-H(3,5-diEtpz)), 52.1 (6H, C*H*$_3$(3-Ph,5-Mepz)), 63.3 (2H, 4-H(3-Ph,5-Mepz)), 90.8 (1H, B-*H*).

IR (KBr, cm^{-1}): 2536 (ν_{BH}) 2080 (ν_{NCS}).

*2.1.4. [Hydrobis(3-phenyl,5-methylpyrazolyl)(3,5-diethylpyrazolyl)borato][hydrotris(pyrazolyl)borato]cobalt(II), ([HB(3-Ph,5-Mepz)2(3,5-diEtpz)]CoTp, **2**)*

The conversion of **1-CD$_3$OD** into **2** was performed on a micromolar scale by titration of 6 mg of the starting complex (**1-THF**, 9.4 μmol) in methanol-*d*$_4$ (400 μl) with 0.35 M KTp in methanol-*d*$_4$. The reaction was followed by ^{1}H NMR spectroscopy. The formation of fine yellow crystals of **2** was observed immediately after conversion was completed. One of the crystals was analyzed crystallographically. The larger scale synthesis (32 mg of **1-THF**, 50 μmol) gave 34 mg of **2** (47.1 μmol, 94% yield).

Elemental analysis: Calc. for $C_{36}H_{40}N_{12}B_2Co$ (MW 721.35): C, 59.94; H, 5.59; N, 23.30. Found: C, 59.85; H, 5.60; N, 23.13.

^{1}H NMR (CD$_3$OD, 298 K): −101.3 (2H, 3-H(Tp)), −82.5 (1H, 3-H(Tp)), −71.7 (2H, 3-C*H*$_2$CH$_3$(3,5-diEtpz)), −56.8 (4H, *o*-H(3−Ph,5-Mepz)), −27.9 (3H, 3-CH$_2$C*H*$_3$(3,5−diEtpz)), −2.4 (4H, *m*-H(3-Ph,5-Mepz)), −0.7 (2H, *p*-H(3-Ph,5-Mepz)), 21.4 (3H, 5-CH$_2$C*H*$_3$(3,5-diEtpz)), 40.2 (6H, 5-CH$_3$(3-Ph,5-Mepz)), 40.9, 45.0 and 52.8 (2H, 2H, 2H, 4-H(Tp) + 4-H(3-Ph,5-Mepz) + 5-C*H*$_2$CH$_3$(3,5-diEtpz)), 46.0 and 47.0 (1H, 1H, 4-H(3,5-diEtpz) and 4-H(Tp)), 86.2 (1H, 5-H(Tp)), 88.5 (2H, 5-H(Tp)), 107.1 and 110.0 (B-*H*(Tp,Tp″)).

IR (KBr, cm^{-1}): 2548, 2478 (ν_{BH} Tp″and Tp).

Mass spectrum (ESI, positive polarization) *m/e*: [**2**]$^+$ 721.3 (100%); [**2**-C$_3$N$_2$H$_3$]$^+$ 654.3 (8%).

*2.1.5. Conversion of **1-CD$_3$OD** into [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Co(OOCCH(OH)CH$_3$) in situ*

The conversion of **1-CD$_3$OD** into [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Co(OOCCH(OH)CH$_3$) (6 mg of **1-THF**, 9.4 μmol dissolved in 400 μl of methanol-*d*$_4$) has been performed in situ by titration with 0.55 M sodium lactate in methanol-*d*$_4$ under ^{1}H NMR spectral control.

^{1}H NMR (CD$_3$OD, 298K, δ): −68.8, −64.3 (2H + 2H, *o*-H(3-Ph,5-Mepz)), −13.2 (3H, 3-CH$_2$C*H*$_3$(3,5-diEtpz)), −1.9 (2H, 3-C*H*$_2$CH$_3$(3,5-diEtpz) or *p*-H(3-Ph,5-Mepz)), −0.1 (4H, *m*-H(3-Ph,5-Mepz)), 1.5 (2H, *p*-H(3-Ph,5-Mepz) or 3-C*H*$_2$CH$_3$(3,5-diEtpz)), 8.1 (3H, 5-CH$_2$C*H*$_3$(3,5-diEtpz)), 28.1, 28.3 (1H, 1H, 5-C*H*$_2$CH$_3$(3,5-diEtpz)), 43.7, 45.0, 45.1 (3H, 3H, 3H, CH$_3$(L), 2 × 5-CH$_3$(3-Ph,5-Mepz)), 46.0, 62.1, 65.5, 76.3 (1H, 1H, 1H, 1H, 3 × 4-H(Tp″), CH(L)), 84.7 (B-*H*), where L = lactate (OOCCH(OH)CH$_3$).

Table 1
Crystal data and structure refinement

Compound	**1-THF**	**2**
Empirical formula	$C_{32}H_{38}BN_7OSCo$	$C_{36}H_{40}B_2N_{12}Co$
Formula weight	638.49	721.35
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	11.218(2)	27.585(6)
b (Å)	11.614(2)	16.798(3)
c (Å)	12.629(3)	19.224(4)
α (°)	95.54(3)	–
β (°)	97.00(3)	124.74(3)
γ (°)	105.80(3)	–
V (Å^3)	1556.8(5)	7320(3)
Z	2	8
D_{calc} (Mg m^{-3})	1.362	1.309
μ (mm^{-1})	0.656	0.513
F(0 0 0)	670	3016
Crystal size (mm)	0.20 × 0.18 × 0.15	0.19 × 0.15 × 0.15
θ Range for data collection (°)	3.68–28.44	3.40–28.48
Index ranges	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 11$	$-35 \leqslant h \leqslant 35$, $-21 \leqslant k \leqslant 22$, $-25 \leqslant l \leqslant 23$
Reflections collected	10 773	24 348
Independent reflections	6848 (0.0264)	8614 (0.0470)
Data/parameters	6848/392	8614/464
Goodness of fit on F^2	1.074	1.032
Final R_1/wR_2 indices ($I > 2\sigma(I)$)	0.0361/0.0905	0.0526/0.0834
Largest difference peak/hole (e Å^{-3})	0.384/−0.404	0.324/−0.391

2.2. Methods

Crystal data for **1** and **2** are given in Table 1, together with refinement details. All measurements of crystals were performed at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. Both crystals were positioned at 65 mm from the CCD camera. Six hundred and twelve frames were measured at 0.75° intervals with a counting time of 15 s. Accurate cell parameters were determined and refined by least-squares fit of the 3300 (**1-THF**) and 2600 (**2**) strongest reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o (formerly Kuma Diffraction Wroclaw, Poland) programs. The structure was solved by direct methods (program SHELXS-97 [4]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 [5] programs. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from the geometry of molecules and $\Delta\rho$ maps but were not refined.

^{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. IR spectra were recorded on a Perkin-Elmer 1725X instrument. Mass spectra were obtained on a Finnigan MAT TSQ 700 spectrometer by the ESI method in chloroform.

3. Results and discussion

Heteroscorpionate Tp″ ligands obtained by condensation of two different pyrazoles with sodium borohydride are potential tripodal anionic ligands with precisely tunable geometry [6–13]. In the course of our systematic studies, we have focused on the synthesis of [HB(3-R_1,5-R_2pz)$_2$(3,5-diR_3pz)]$^-$ ligands (where pz = pyrazol-1-yl moiety). Previously, it was demonstrated that two such heteroscorpionate ligands, with R_1 = Ph, R_2 = Me, R_3 = Me [9], and with R_1 = Ph, R_2 = *i*Pr, R_3 = Me [13] underwent borotropic shift of one 3-R_1,5-R_2pz into 3-R_2,5-R_1pz in their Tp″Co(NCS) complexes. The chiral Tp* ligands, which formed via that rearrangement were still bound to the cobalt(II) center. Eventually we have isolated and characterized crystallographically the dimeric [HB(3-Ph,5-*i*Prpz)(3-*i*Pr,5-Phpz)(3,5-diMepz)Co(NCS)]$_2$ complex as a *meso* compound bearing two Tp* ligands of opposite boron-centered chirality [13]. The ligand described in this paper is another tripod of C_s symmetry, which can be successfully applied for such a rearrangement. It is composed of two 3-Ph,5-Mepz and one 3,5-diEtpz moieties. It has been synthesized in good yield by condensation of 2 equiv. of 3(5)-methyl,5(3)-phenylpyrazole (3-Ph,5-MepzH) and 1 equiv. of 3,5-diethylpyrazole (3,5-diEtpzH) with sodium borohydride under well-controlled conditions, i.e., in high-boiling solvent instead of melted pyrazoles. The sodium salt of the ligand has been isolated and applied to construct the corresponding Tp″Co(NCS)(THF) complex (**1-THF**) as it was previously presented in the case of all Tp″ ligands obtained in our laboratory [7–13].

3.1. Structure of **1-THF**

The view of a molecule of **1-THF** is shown in Fig. 1. The ligand is coordinated in a κ^3 fashion as it was found in the case of other heteroscorpionates: [HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)]$^-$ [8], [HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]$^-$ [9], [HB(3-*i*Pr,5-Mepz)$_2$(3-Ph,5-*i*Prpz)]$^-$ [13] and [HB(3-Ph,5-Mepz)$_2$(5-*i*Prpz)]$^-$ [12]. All mentioned Tp″ ligands form pentacoordinate Tp″Co(NCS)(THF) complexes. However, the increase of steric hindrance both at pyrazolyl C-3 and/or C-5 by introducing 3-*t*Bupz [7] or 3,5-di-*t*Bupz [8] resulted in the

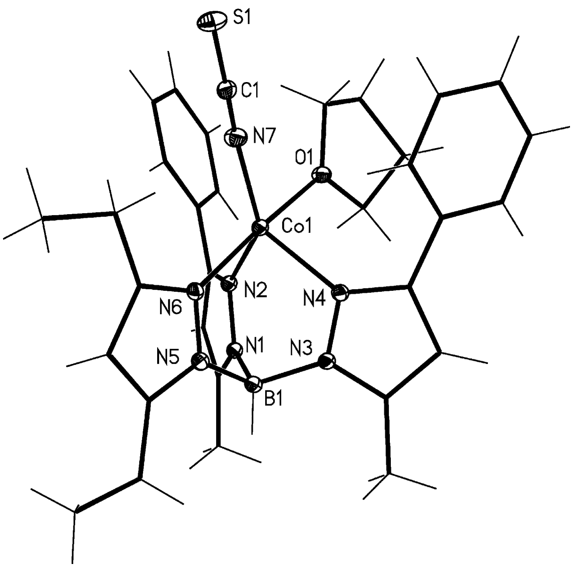

Fig. 1. Molecular structure of 1-THF. Selected bond lengths (Å) and angles (°): Co(1)–N(2), 2.0788(16); Co(1)–N(4), 2.0523(16); Co(1)–N(6), 2.1206(15); Co(1)–N(7), 1.9764(18); Co(1)–O(1), 2.1567(13); N(4)–Co(1)–N(2), 93.83(6); N(2)–Co(1)–N(6), 87.64(6); N(4)–Co(1)–N(6), 87.53(6); N(7)–Co(1)–N(2), 138.11(7); N(7)–Co(1)–N(4), 127.95(7); N(7)–Co(1)–N(6), 96.11(6); N(2)–Co(1)–O(1), 87.12(6); N(4)–Co(1)–O(1), 90.88(6); N(6)–Co(1)–O(1), 174.41(5); N(7)–Co(1)–O(1), 89.09(6).

formation of tetracoordinate Tp″Co(NCS) complexes under the same conditions. Generally, the cobalt(II) center is able to adopt a neutral THF ligand with the formation of pentacoordinate Tp″Co(NCS)(THF) complexes when the cobalt-centered bite angle of Tp″ is not lower than 148.6° (or the boron-centered bite angle α is not lower than 80.4°) (Table 2).

Other experimental measures describing the steric hindrance of Tp″ ligands successfully applied to Tp″Co(NCS)(CD$_3$OD) complexes [8–13] were based on metathesis of thiocyanate into trispyrazolylborate (Tp) or lactate (L) anions followed by ^{1}H NMR spectroscopy (see the following section).

Table 2
The dependence of coordination number (n) on cobalt-centered (β) and boron-centered (α) bite angles of Tp″ ligands in Tp″Co(NCS)(THF)$_{n-4}$ complexes

Entry	Tp″ ligand, [Ref.]	α	β	n
1	[HB(3-Ph,5-Mepz)$_2$(5-*i*Prpz)]$^-$, [12]	85.2	163.3	5
2	[HB(3-*i*Pr,5-Phpz)$_2$(3-Ph,5-*i*Prpz)]$^-$, [13]	86.4	159.0	5
3	[HB(3-Ph,5-Mepz)$_2$(3-Me,5-Phpz)]$^-$, [8]	81.9	149.2	5
4	[HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]$^-$, this paper	81.4	149.0	5
5	[HB(3-Ph,5-Mepz)$_2$(3,5-diMepz)]$^-$, [9]	80.4	148.6	5
6	[HB(3-Ph,5-*i*Prpz)$_2$(3,5-diMepz)]$^-$, [13]	77.6	141.3	4
7	[HB(3-Phpz)$_2$(3,5-di-*t*Bupz)]$^-$, [8]	75.6	134.5	4
8	[HB(3-Phpz)$_2$(3-*t*Bupz)]$^-$, [7]	75.1	133.5	4

Bite angles were defined in Ref. [9].

3.2. Metathesis of thiocyanate into lactate and trispyrazolylborate

The pentacoordinate [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Co(NCS)(CD$_3$OD) complex (**1-CD$_3$OD**) forms immediately upon dissolving **1-THF** in methanol-d_4. The ^{1}H NMR spectrum of **1-CD$_3$OD** is presented in Fig. 2(A). The resonances of protons of 3-substituents are typically shifted upfield, whereas those of 5-substituents, 4-H and B-H resonances are shifted downfield. The replacement of thiocyanate with chiral lactate produced the spectrum characteristic for pentacoordinate species

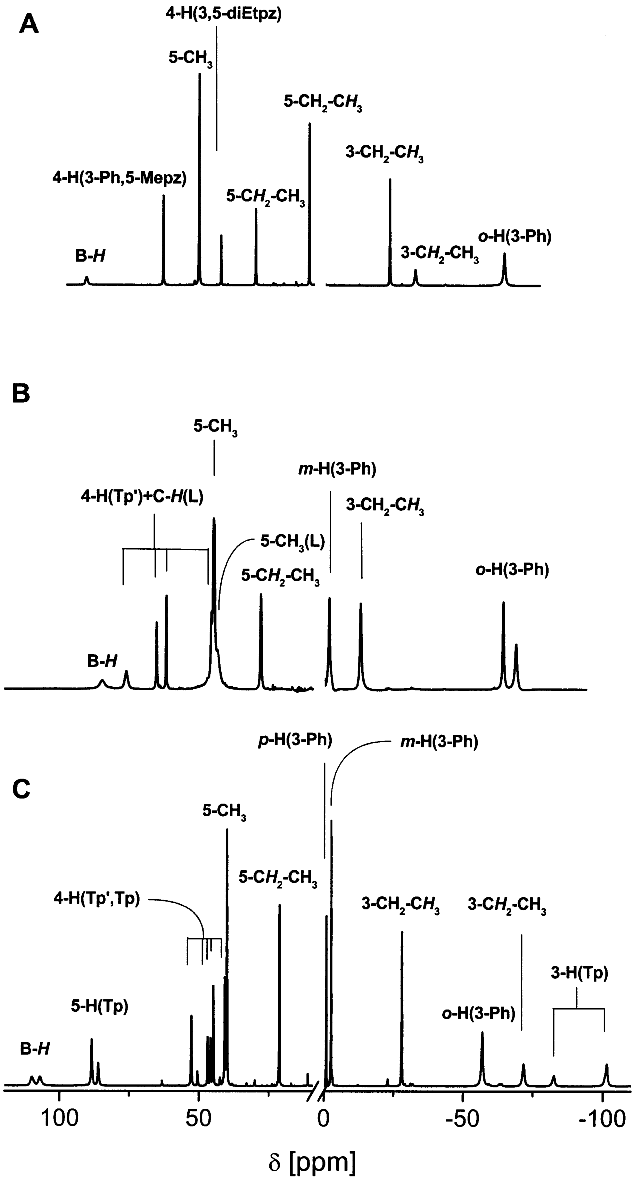

Fig. 2. The ^{1}H NMR spectra of: **1-CD$_3$OD** (A); **[HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Co(OOCCH(OH)CH$_3$)** (B); **2** (C) in methanol-d_4 at 298 K. The resonances from lactate anion in trace B are labelled with L. The 0–10 ppm region is omitted for the sake of clarity in traces A–C.

with carboxylate and α-hydroxy oxygens coordinated to the metal center (Fig. 2, trace B). The diastereotopic splitting of *o*-H(3-Ph) which are placed in close vicinity of the chiral ancillary ligand is the most pronounced (the chemical shift difference of 4.5 ppm between two *o*-H(3-Ph) resonances is observed), while those for remote 5-CH_3 groups and 5-$C\mathit{H}_2CH_3$ are much smaller. The diastereotopic splitting of 3-$C\mathit{H}_2CH_3$ could not be observed due to considerable broadening of the corresponding resonance (not shown in trace B). Additionally, three 4-H resonances are found accordingly to the lack of elements of symmetry in [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]Co(OOCCH(OH)CH_3).

Careful titration of **1-CD_3OD** with KTp led to quantitative formation of the [HB(3-Ph,5-Mepz)$_2$(3,5-diEtpz)]CoTp complex (**2**). The ^{1}H NMR spectrum of **2** (trace C) demonstrated the slow mutual rotation of Tp″ and Tp ligands around the metal center similarly as it was shown for other Tp″CoTp complexes [8–11]. Consequently, the pairs of 3-H and 5-H resonances of Tp and 4-H resonances of both Tp and Tp″, all at the 2:1 integral intensity ratio, are observed. The resonance of methylene protons of the 3-$C\mathit{H}_2CH_3$ group is considerably shifted upfield in comparison with that of **1-CD_3OD** (~41 ppm) while the methyl protons resonance of 3-$CH_2C\mathit{H}_3$ remains almost unshifted. That strongly suggests the increase in population of the rotational isomer around the C(3)–CH_2CH_3 bond in which the methyl group is pointing away from the metal ion in **2** in comparison with **1-THF**. However, in the solid state in both **1-THF** and **2** this conformation was found (see the section below).

3.3. Structure of 2

Crystals of **2** grow easily from methanol upon addition of an equimolar amount of KTp to **1-THF**. The molecular structure of **2** is presented in Fig. 3. Both ligands are coordinated in a κ^3 manner via three pyrazolyl nitrogen atoms. The averaged Co–N bond distances are 2.20 and 2.13 Å for Tp″ and Tp ligands, respectively. The bite angles of Tp″ are 155.9° (β) and 87.7° (α), i.e. considerably larger in comparison with those for the same ligand in **1-THF**. Although X-ray data are available for many heteroleptic bis-trispyrazolylborate complexes, **2** is the only example with unsubstituted Tp for which the bond lengths and angles are known from solid state studies. Therefore a comparison can be done only with Tp_2Co complex [14]. Surprisingly, the mean Co–N(Tp) distance in **2** is exactly the same as that in Tp_2Co (2.13 Å). Also the β and α values for Tp in **2** (222.9° and 111.5°, respectively) are almost the same as those in Tp_2Co (222.8° and 111.6°, respectively). However, the Co–N(Tp) distances in **2** depend on the character of the pyrazolyl residues of Tp″. Thus, Co–N(10) which is bonded *trans* to N(6) is about 0.05 Å shorter in comparison with the averaged value for Co–N(8) and Co–N(12). This structural feature is retained in the dynamic molecule as can be concluded from the ^{1}H NMR spectrum of **2**. The 3-H(Tp) resonances of 2:1 intensity ratio are found at −101.3 and −82.5 ppm, respectively. The higher intensity resonance belongs to the two pyrazolyl residues *synclinal* to 3,5-diEtpz(Tp″). It should be also mentioned, that the molecule is considerably distorted from C_{3v} symmetry (neglecting the 3- and 5-substituents of Tp″). The N_t–Co–N_t angles (N_t—*trans* bonded nitrogen donors) are 177.0°, 177.5° and 179.5° instead of the expected 180.0°. It might result from a substantial difference in steric hindrance imposed by the different 3-substituents of Tp″.

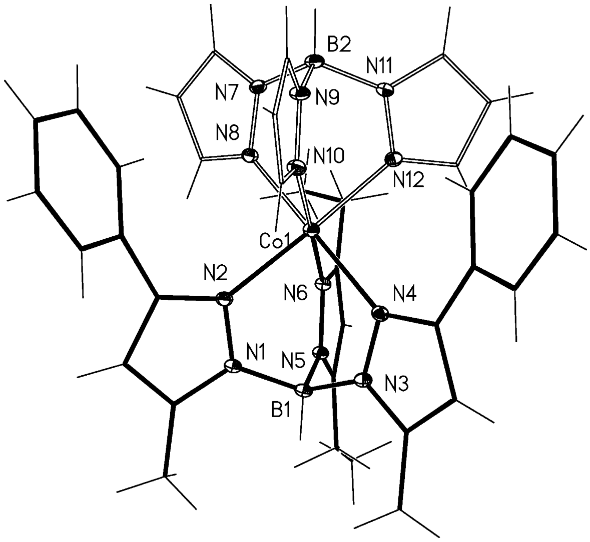

Fig. 3. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Co(1)–N(2), 2.170(2); Co(1)–N(4), 2.269(2); Co(1)–N(6), 2.1670(19); Co(1)–N(8), 2.133(2); Co(1)–N(10), 2.097(2); Co(1)–N(12), 2.161(2); N(2)–Co(1)–N(4), 84.08(7); N(6)–Co(1)–N(2), 89.80(7); N(6)–Co(1)–N(4), 88.95(7); N(10)–Co(1)–N(8), 86.60(7); N(8)–Co(1)–N(12), 82.73(8); N(10)–Co(1)–N(12), 86.87(7); N(8)–Co(1)–N(2), 95.91(8); N(8)–Co(1)–N(4), 179.49(7); N(8)–Co(1)–N(6), 90.54(7); N(10)–Co(1)–N(2), 91.02(7); N(10)–Co(1)–N(4), 93.92(7); N(10)–Co(1)–N(6), 177.09(8); N(12)–Co(1)–N(2), 177.55(7); N(12)–Co(1)–N(4), 97.29(8); N(12)–Co(1)–N(6), 92.25(7).

4. Supplementary data

Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 189 812 for compound **1-THF**, CCDC No. 189 813 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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