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Hydrotris[3-(1-naphthylpyrazol-1-yl)]borate and Hydrotris[3-(2-naphthylpyrazol-1-yl)]borate: Two Novel Homoscorpionate Ligands of Varying Coordination Behavior

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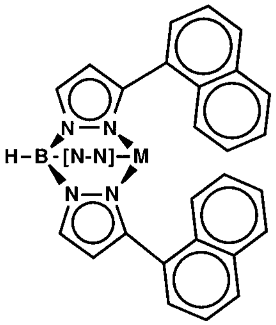
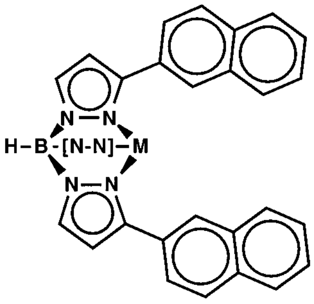
Introduction

The adjustment of the coordinating behavior of homoscorpionate ligands is often accomplished by changing the nature of the 3-substitutent, which is closest to the coordinated metal.[1] Apart from the aliphatic substituents of varying size, such as methyl,[2] isopropyl,[3] cyclopropyl,[4] cyclohexyl,[5] neopentyl,[6] *tert*-butyl,[7] and triptycyl,[8] there is also the 3-phenyl substituent[7] and its variants. For instance, in addition to the 4-substituents on the phenyl group, such as methyl,[9] methoxy,[10] i-propyl,[11] *tert*-butyl,[12] and fluoro,[13] which affect the electron density of the phenyl group and extend a protective pocket around the coordinated metal, there are also examples of a 3-phenyl group being tied to the pyrazolyl 4-position with methylene, ethylene,[14] or an ethyne tether,[15] which are used in order to achieve coplanarity of the phenyl and pyrazolyl rings. Conversely, orthogonality of the phenyl and pyrazolyl planes is aimed at through placement of 2,4,6-methyl substituents (3R = mesityl) on the phenyl ring in $\mathrm{Tp}^{\mathrm{Ms}}$ (= hydrotris(3-mesitylpyrazol-1-yl)borate)[16] or fusing two benzo rings thereon, as in the case where 3R is 9-anthryl in $\mathrm{Tp}^{\mathrm{Ant}}$ (= hydrotris[3-(9-anthryl)pyrazol-1-yl)]borate).[17]

In this context, we were interested in Tp ligands containing a single benzo ring fused to the 3-phenyl group in the two possible ways, 2,3- and 3,4-, as the steric effects of these two ligands promised to be different both, in terms of their cone and wedge angles and in the twists of the naphthyl plane with respect to the pyrazolyl ring. The two isomeric 3-naphthylpyrazoles were synthesized and converted to the corresponding ligands, $\{\mathrm{HB[3\text{-}(1\text{-}naphthylpyrazol\text{-}1\text{-}yl)]_3}\}^-$ (= $\mathrm{Tp}^{\alpha\mathrm{Nt}}$) and $\{\mathrm{HB[3\text{-}(2\text{-}naphthylpyrazol\text{-}1\text{-}yl)]_3}\}^-$ (= $\mathrm{Tp}^{\beta\mathrm{Nt}}$), which were characterized as their Tl derivatives, $\mathrm{Tl[Tp}^{\alpha\mathrm{Nt}}]$ and $\mathrm{Tl[Tp}^{\beta\mathrm{Nt}}]$. The coordination chemistry of these ligands was briefly explored and compared with that of other related homoscorpionates.





[-[N-N]- represents the third, hidden, 3-naphthylpyrazolyl group]

$\mathrm{Tp}^{\alpha\mathrm{Nt}}\mathrm{M}$ **$\mathrm{Tp}^{\beta\mathrm{Nt}}\mathrm{M}$**

Experimental Section

All chemicals were commercial reagent grade and used as received. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls or KBr pellets with a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. The compounds were studied with typical conditions of 16K data points, a sweep width of 3000−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s.

Preparation of 3-(1-Naphthyl)pyrazole. To a rapidly stirred slurry of 54 g (1.0 mol) of anhydrous sodium methoxide, stirred in a mixture of 800 mL toluene and 1 L THF, was added in one portion of a mixture of 170 g (1 mol) of 1′-acetonaphthone and 150 mL (large excess) of ethyl formate. After stirring for 1 h, the resulting slurry was diluted with 1 L of hexane and filtered, and the solid was washed with ether and dried overnight. It was dissolved in 2 L of methanol, and a solution of 74 g (1 mol) of hydrazine monohydrochloride in 1 L of water was added with stirring. A yellow oil separated. The reaction mixture was basified with 50% aqueous NaOH, cooled by adding ice, and extracted with methylene chloride. The dark red extract was stripped, and the red residue was refluxed with 20 mL of hydrazine hydrate in 500 mL of isopropyl alcohol for 2 h, whereupon the color became much lighter. This solution was poured into 2 L of ice-water, whereupon a solid precipitated. It was isolated by filtration and distilled in vacuo, collecting the fraction at bp 190−192 °C/0.6 Torr. 3-(1-Naphthyl)pyrazole was recrystallized from aqueous methanol and obtained in 128 g (66.0%) yield; mp 120−121 °C. ^{1}H NMR: 8.27 (d, 1 H, $J = 7.5$), 7.82 (m, 2 H), 7.56 (d, 1 H, $J = 7.0$), 7.44 (m, 3 H), 7.29 (d, 1 H, $J = 1.9$, pyrazole H-5), 6.47 (d 1 H, $J = 1.9$, pyrazole H-4) ppm. The ^{13}C NMR spectrum has already been reported.[17] Anal. Calcd for $\mathrm{C_{13}H_{10}N_2}$: C, 80.4; H, 5.15; N, 14.4%. Found: C, 80.2; H, 5.31; N, 14.6%.

Preparation of 3-(2-Naphthyl)pyrazole. This was done as above, substituting 2′-acetonaphthone for 1′-acetonaphthone. After the initial clearing up of the mixture, the sodium salt precipitated rapidly to form a thick mass which, after standing for 2 days, became easily filtrable. The filtered solid was washed with hexane, dissolved in methanol,

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processed as above, and produced 3-(2-naphthyl)pyrazole in 157 g (80.9%) yield. It was recrystallized from toluene, yielding fine needles, mp 159−160 °C. ^{1}H NMR (dmso-d_6): 8.31 (d, 1 H, H-5), 8.05−7.80 (m, 5 H, Ar, 7.48 (t, 2 H, Ar), 6.84 (d, 1 H, H-4) ppm. The ^{13}C NMR spectrum has already been reported.[17] Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.4; H, 5.15; N, 14.4%. Found: C, 80.2; H, 5.34; N, 14.7%.

Preparation of Thallium Hydrotris[3-(1-naphthyl)pyrazolyl]borate, Tl[Tp$^{\alpha\mathrm{Nt}}$]. A mixture of 5.4 g (0.1 mole) of KBH_4 and 97 g of 3-(1-naphthyl)pyrazole (0.5 mol) was melted and heated with stirring as hydrogen evolution was measured with a wet-test meter. When 7.5 L of hydrogen had evolved, the melt was partly cooled, dissoved in 300 mL of DMAC, and stirred with excess aqueous $TlNO_3$. After dilution with water, extraction with methylene chloride, filtration of the extract through Celite, and stripping of the extracts, there was obtained, after stirring the residue with methanol, 61 g (76%) of Tl[Tp$^{\alpha\mathrm{Nt}}$]; mp 216−218 °C. IR: BH 2432 cm^{-1}. The ^{1}H and ^{13}C NMR spectra have already been reported.[18] Anal. Calcd for $C_{39}H_{28}BN_6Tl$: C, 58.9; H, 3.52; N, 10.6%. Found: C, 58.4; H, 3.56; N, 10.1%.

Thallium Hydrotris[3-(2-naphthyl)pyrazolyl]borate, Tl[Tp$^{\beta\mathrm{Nt}}$]. This was done as above, using 3-(2-naphthyl)pyrazole instead of 3-(1-naphthyl)pyrazole. After hydrogen evolution ceased (7.5 L evolved), the melt was poured into 600 mL of rapidly stirred toluene. The crude K[Tp$^{\beta\mathrm{Nt}}$] precipitated, was filtered off hot after brief boiling of the slurry, washed with hot toluene, and air-dried. It was converted to Tl[Tp$^{\beta\mathrm{Nt}}$] as above, and the product was obtained in 56 g (71%) yield; mp 142−146 °C. IR: BH 2432 cm^{-1}. ^{1}H and ^{13}C NMR spectra have already been reported.[18] Anal. Calcd for $C_{39}H_{28}BN_6Tl$: C, 58.9; H, 3.52; N, 10.6%. Found: C, 59.4; H, 4.07; N, 10.0%.

Mo[Tp$^{\alpha\mathrm{Nt}}$](CO)$_2$(η^3-methallyl). A mixture of 1.6 g (2 mmol) of Tl[Tp$^{\alpha\mathrm{Nt}}$] and 0.65 g (2 mmol) of Mo(CO)$_2$(Cl)(η^3-methallyl)(MeCN)$_2$ in methylene chloride was stirred overnight, filtered through Celite to remove TlCl, and chromatographed on alumina; the bright yellow band was collected. The product was obtained in 1.4 g (87%) yield, mp 243−244 °C dec. IR: BH 2465, CO 1942, 1853 cm^{-1}. NMR: 7.35−8.16 (overlapping multiple peaks, 23 Hs), 6.55 (overlapping d in 2:1 ratio, 3 H, H-4), 2.37 (bs, 1 H, syn), 2.10 (bs, 1 H, syn), 1.04 (s, 3 H, Me), −0.15 (s, 1 H, anti), −0.28 (s, 1 H, anti) ppm. Anal. Calcd for $C_{45}H_{35}BMoN_6O_2$: C, 67.7; H, 4.39; N, 10.5%. Found: C, 67.6; H, 4.44; N, 10.7%.

Mo[Tp$^{\beta\mathrm{Nt}}$](CO)$_2$(η^3-methallyl). This was done as above, but using Tl[Tp$^{\beta\mathrm{Nt}}$]. The product was obtained as bright yellow solid, mp 257−258 °C (d) in 1.3 g (82%) yield. IR: BH 2467, CO 1934, 1842 cm^{-1}. NMR: 8.57 (s, 1 H), 7.4−8.2 (overlapping m, 23 H), 6.45 (d, 1 H, H-4), 6.39 (d, 2 H, H-4′), 2.56 (s, 2 H, syn), 0.94 (s, 3 H, Me), 0.04 (s, 2 H, anti) ppm. Anal. Calcd for $C_{45}H_{35}BMoN_6O_2$: C, 67.7; H, 4.39; N, 10.5%. Found: C, 68.0; H, 4.43; N, 10.6%.

Preparation of Co[Tp$^{\alpha\mathrm{Nt}}$]Cl. A mixture of 8.0 g (10 mmol) of Tl[Tp$^{\alpha\mathrm{Nt}}$] and 2.6 g (20 mmol) of anhydrous $CoCl_2$ was stirred overnight in methylene chloride. The slurry was filtered through Celite, and evaporation produced a blue solid in 4.7 g (68%) yield, which was recrystallized from toluene; mp 225−227 °C. IR: BH 2474 cm^{-1}. Anal. Calcd for $C_{39}H_{28}BClCoN_6$: C, 68.2; H, 4.08; N, 12.1%. Found: C, 68.5; H, 4.26; N, 12.1%.

Preparation of Zn[Tp$^{\alpha\mathrm{Nt}}$]NCS and Zn[Tp$^{\beta\mathrm{Nt}}$]NCS. These compounds were prepared by adding a THF solution of Tl[Tp$^{\alpha\mathrm{Nt}}$] or Tl[Tp$^{\beta\mathrm{Nt}}$] to an aquomethanolic solution of 1 equiv of zinc nitrate and 4 equiv of KSCN. The products, obtained in 75−85% yields, were extracted with methylene chloride after the mixture was diluted with much water. The organic extracts were washed several times with water, filtered through a layer of alumina, and stripped to dryness, and the residue was recrystallized from toluene.

Zn[Tp$^{\alpha\mathrm{Nt}}$]NCS: mp 247−249 °C. IR: BH 2502, NCS 2088 cm^{-1}. NMR: 7.98 (d, 3 H, J = 1.9, pyrazole H-5), 7.86 (“ty”, 9 H), 7.52 (m, 6 H), 7.40 (t, 3 H, J =) 7.12 (t, 3 H, J =), 6.61 (d, 3 H, J = 1.9, pyrazole H-4), BH (1 H) visible by integration at 4.2−5.2 ppm. Anal. Calcd for $C_{40}H_{28}BN_7SZn$: C, 67.2; H, 3.92; N, 13.7%. Found: C, 67.4; H, 4.15; N, 13.5%.

Zn[Tp$^{\beta\mathrm{Nt}}$]NCS: mp sinters from about 240 °C, but does not melt up to 300 °C. IR: 2491, NCS 2077 cm^{-1}. NMR: 8.25 (d, 3 H, J = 1.9, pyrazole H-5), 8.03 (“t”, 6 H), 7.85 (m, 9 H), 7.48 (m, 6 H), 6.84 (d, 3 H, J = 1.9, pyrazole H-4), BH (1 H) by integration at 4.0−5.1 ppm. Anal. Calcd for $C_{40}H_{28}BN_7SZn$: C, 67.2; H, 3.92; N, 13.7%. Found: C, 67.1; H, 4.18; N, 13.6%.

Preparation of Co[Tp$^{\alpha\mathrm{Nt}}$][Tp] and Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*]. An equimolar mixture of Co[Tp$^{\alpha\mathrm{Nt}}$]Cl with TlTp or TlTp* [Tp* = HB(3,5-dimethylpyrazol-1-yl)$_3$] was stirred in methylene chloride overnight. The slurry was filtered through Celite to remove TlCl, and the filtrate was chromatographed on alumina, collecting the yellow/orange band. After evaporation of the eluate, the residue was recrystallized several times from toluene to remove the byproducts, Co[Tp]$_2$ and Co[Tp*]$_2$, respectively. The purified Co[Tp$^{\alpha\mathrm{Nt}}$][Tp] and Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*] complexes were obtained in about 50% yield.

Co[Tp$^{\alpha\mathrm{Nt}}$][Tp]: yellow solid, mp 230−232 °C. IR: BH 2453 cm^{-1}. ^{1}H NMR: 115.6 (1 H, BH), 116.0 (1 H, BH), 89.3 (3 H, pz H-5), 79.9 (3 H, pz H-5′), 42.4 (3 H, pz H-4), 39.8 (3 H, pz H-4′), 0.6 (3 H, H-8), −0.6 (3 H, H-7), −1.7 (3 H, H-6), − 2.6 (3 H, H-5), −6.1 (3 H, H-4), −19.8 (3 H, H-3), −93.7 (3 H, H-2), −103.8 (3 H, pz 3-H) ppm. Anal. Calcd for $C_{42}H_{38}B_2CoN_{12}$: C, 63.7; H, 4.80; N, 21.2%. Found: C, 63.9; H, 5.07; N, 21.1%.

Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*]: pink solid, mp 224−226 °C. IR: BH 2514 (Tp*), 2448 (Tp$^{\alpha\mathrm{Nt}}$) cm^{-1}. Anal. Calcd for $C_{42}H_{38}B_2CoN_{12}$: C, 63.7; H, 4.80, N, 21.2%. Found: C, 64.0; H, 4.96; N, 21.0%.

Preparation of Co[Tp$^{\beta\mathrm{Nt}}$][Tp]. This complex was prepared by stirring Tl[Tp$^{\beta\mathrm{Nt}}$] with an excess of anhydrous $CoCl_2$ in methylene chloride overnight, filtering the blue slurry, and then stirring the blue filtrate with an equivalent amount of TlTp overnight. After filtration of the mixture through Celite, the filtrate was chromatographed on alumina, collecting the yellow-orange band, and after evaporation of the eluate, the product was recrystallized from xylene. Orange solid, mp 240−242 °C. IR: 2454 cm^{-1}. ^{1}H NMR: 112 (1 H, BH), 110 (1 H, BH′), 87.4 (3 H, pz H-5), 76.1 (3 H, pz H-5′), 44.2 (3 H, pz H-4), 41.9 (3 H, pz H-4′), 10.13 (3 H, H-8), 9.58 (3 H, H-7), 6.50 (3 H, H-6), 3.33 (3 H, H-5), −3.43 (3 H, H-4), −42.7 (3 H, H-3), −63.9 (3 H, H-1) and −97.3 (3 H, pz H-3) ppm. Anal. Calcd for $C_{48}H_{50}B_2CoN_{12}$: C, 65.8; H, 5.71; N, 19.2%. Found: C, 65.9; H, 5.87; N, 18.9%.

Results and Discussion

The new pyrazoles, 3-(α-naphthyl)pyrazole and 3-(β-naphthyl)pyrazole, and their homoscorpionate ligands, [Tp$^{\alpha\mathrm{Nt}}$] and [Tp$^{\beta\mathrm{Nt}}$], were prepared in the standard fashion and characterized as their Tl salts. Compared to the ligand [Tp$^{\mathrm{Ph}}$], one would expect the following differences in their coordination behavior.

The ligand Tp$^{\alpha\mathrm{Nt}}$ with its 2,3-fusion of the benzo ring on the phenyl substituent would not extend much beyond a phenyl group, so that its cone angle might be comparable. On the other hand, it would have a much smaller wedge angle, with the fused benzo ring blocking side access to the coordinated metal. At the same time, compared to the 9-anthryl group, which is quite rigid and cannot rotate around the plane of the pyrazolyl ring at all, there should be less problem with rotation around the C−C bond connecting the pyrazolyl and naphthyl groups. At least one could envisage, if not full rotation, a windshield-wiper motion on the metal side, assuming the existence of a barrier to rotation around the pyrazolyl ring via nonbonding interactions with its 4-H.

By contrast, the Tp$^{\beta\mathrm{Nt}}$ ligand would have little problem with rotation around the naphthyl−pyrazolyl bond, as the 3,4-fusion of the benzo ring would not add much in the way of wedge angle reduction. On the other hand, the 3,4-benzo ring would provide a much deeper pocket around the metal, even compared with a phenyl group containing large 4-substituents (such as isopropyl or *tert*-butyl).

In the complexes Mo[Tp$^{\alpha\mathrm{Nt}}$](CO)$_2$-η^3-methallyl and Mo[Tp$^{\beta\mathrm{Nt}}$](CO)$_2$-η^3-methallyl, one observes an asymmetric

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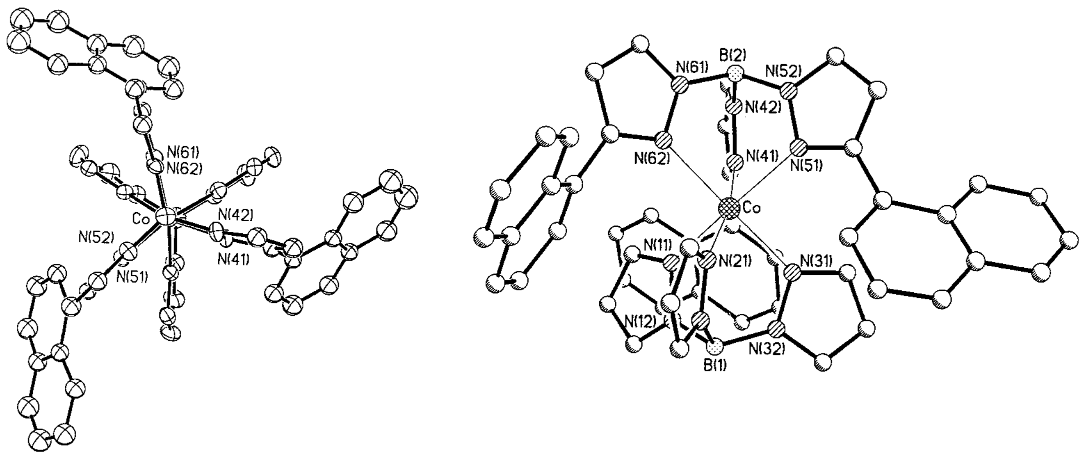

Figure 1. Structure of the complex **1**, Co[$\mathrm{Tp}^{\alpha\mathrm{Nt}}$][Tp], viewed along the B−Co−B axis and side-on. Selected bond lengths (Å) and angles (°): Co−N(11) 2.117; Co−N(21) 2.143; Co−N(31) 2.132; Co−N(41) 2.242; Co−N(51) 2.211; Co−N(61) 2.261; N(11)−Co−N(21) 85.1; N(11)−Co−N(31) 86.8; N(11)−Co−N(41) 86.7; N(11)−Co−N(51) 171.5; N(11)−Co−N(61) 97.7; N(21)−Co−N(31) 84.7.

Table 1. Crystallographic Data for (**1**), (**2**), and (**3**)

	(**1**)	(**2**)	(**3**)
formula	$C_{48.75}H_{40.25}B_2CoN_{12.75}O_{0.75}$	$C_{48}H_{38}B_2CoN_{12}$	$C_{54.5}H_{51}B_2ClCoN_{16}$
fw	886.35	863.45	946.55
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
temp, K	298	228	223
a, Å	15.052(1)	17.0174(1)	10.7538(3)
b, Å	15.477(2)	13.7697(2)	16.6928(4)
c, Å	19.618(2)	18.3586(2)	28.8725(8)
α, deg	81.417(8)		
β, deg	87.803(6)	90.6447(7)	97.7491(12)
γ, deg	77.328(7)		
V, Å^3	4409.0(5)	4301.6(8)	5135.6(4)
Z	4	4	4
d(calc), g cm^{-3}	1.335	1.333	1.281
μ(Mo Kα), cm^{-1}	4.42	4.50	4.36
R(F)[a],%	7.01	4.93	7.25
R(wF^2)[a],%	14.50	10.76	17.23

[a] As defined in ref.

environment for the methallyl group of the former complex in solution, with the syn and anti protons appearing as two separate peaks each (total 5 methallyl peaks), whereas in the latter complex they appeared as singlets (total 3 methallyl peaks). Furthermore, in the β complex, the 4-H peaks were clearly separated in a 2:1 pattern, while in the α complex, they overlapped closely, being almost a single peak. The asymmetry of the η^3-methallyl environment in Mo[$\mathrm{Tp}^{\alpha\mathrm{Nt}}$]$(CO)_2$($\eta^3$-methallyl) must arise from the α naphthyl rings of the $\mathrm{Tp}^{\alpha\mathrm{Nt}}$ ligand being all twisted in the same direction around the pyrazolyl plane and incapable of free rotation around the pyrazolyl C3 and naphthyl C1 bond. This would make the environments of the two CH_2 groups of the η^3-methallyl ligand quite different. It is known that in the case of the complex Mo[$\mathrm{Tp}^{\alpha*}$]$(CO)_2$(η^3-methallyl), where a 3-phenyl substituent is tied to the pyrazole 4-position by an ethyne tether so that the phenyl plane is coplanar with the pyrazole ring, the $\mathrm{Tp}^{\alpha*}$ [= HB(2H-benz[*g*]-indazol-2-yl)$_3$] ligand is κ^2 and with an agostic B−H−Mo bond, the reason for this is the inability of the coplanar phenyl group to intrude into the space occupied by the η^3-methallyl ligand.[15]

By contrast, in the Mo[$\mathrm{Tp}^{\beta\mathrm{Nt}}$]$(CO)_2$($\eta^3$-methallyl) complex, the β-naphthyl group is free to rotate without interfering with the η^3-methallyl ligand, thereby imparting C_2 symmetry to the environment of the latter. It should be noted that such C_2 symmetry prevailed in the complex Mo[$\mathrm{Tp}^{\mathrm{Ms}}$]$(CO)_2$($\eta^3$-methallyl), in which the 3-mesityl groups are almost orthogonal to the pyrazolyl plane.[16]

The question regarding which ligand would be more hindered was approached via the formation of heteroleptic octahedral complexes Co[$\mathrm{Tp}^{\alpha\mathrm{Nt}}$][Tp], **1**, and Co[$\mathrm{Tp}^{\beta\mathrm{Nt}}$][Tp], **2**. Both of them were synthesized by the reaction of Co[$\mathrm{Tp}^{\alpha\mathrm{Nt}}$]Cl or Co[$\mathrm{Tp}^{\beta\mathrm{Nt}}$]Cl with TlTp, with the yellow color of the products suggesting octahedral coordination of cobalt(II) and thus both ligands coordinating in κ^3 fashion. The NMR spectrum of **1** was very sharp, consisting of twelve peaks, with each proton being quite distinct. While the pyrazolyl protons and the 2-, 3-, and 4-protons of the naphthyl group could be asigned with a good degree of assurance, the remaining protons relatively far from the cobalt ion were close together in the diamagnetic range, and their assignment was tentative. Nevertheless, the proton at −93.7 ppm could be assigned to the naphthyl H-2, the one at −19.8 ppm to the naphthyl H-3, and the one at −6.1 to the naphthyl H-4. The remaining four naphthyl protons were bunched together in a narrow range (0.6 to −2.6 ppm) and were difficult to assign, while the pyrazolyl 4- and 5-protons were in their usual range, around 40 and 80 ppm, respectively. The essential point is that all three 3-(1-naphthyl)pyrazolyl arms were in an identical magnetic environment. The structure of **1** was established by X-ray crystallography (Figure 1, Table 1). The naphthyl substituents were all twisted in the same direction by approximately 53°. The average Co−N distances for the Tp ligand were slightly shorter than those for $\mathrm{Tp}^{\alpha\mathrm{Nt}}$ (2.143 versus 2.228 Å).

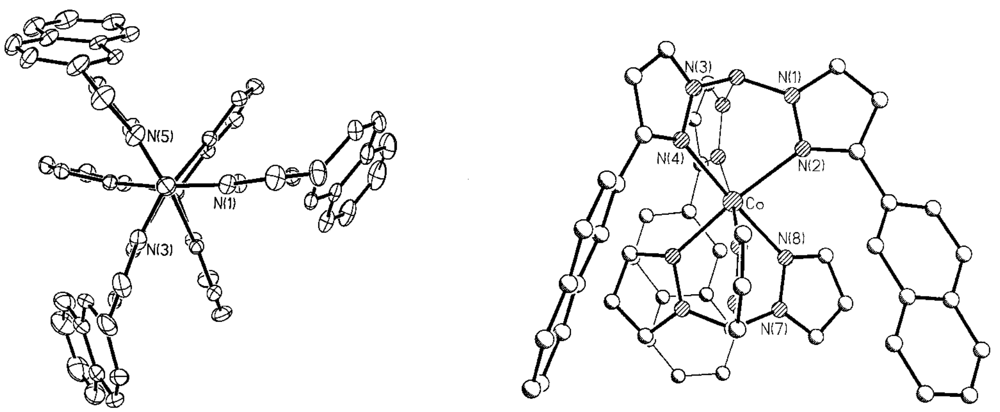

Figure 2. Structure of the complex **2**, Co[Tp$^{\beta\text{Nt}}$][Tp], viewed along the B−Co−B axis, and side-on. Selected bond lengths (Å) and angles (°): Co−N(2) 2.221; Co−N(4) 2.219; Co−N(6) 2.194; Co−N(8) 2.129; Co−N(10) 2.091; Co−N(12) 2.111; N(2)−Co−N(4) 87.7; N(4)−Co−N(6) 87.0; N(6)−Co−N(8) 98.9; N(8)−Co−N(10) 86.4; N(10)−Co−N(12) 86.0; N(8)−Co−N(12) 85.3.

Similarly, in the very sharp NMR spectrum of **2**, also consisting of twelve peaks, the naphthyl H-3 and H-1 protons were at −63.9 and − 42.4 ppm, respectively, the −3.2 ppm signal was assigned to the H-4, and the remaining naphthyl protons were in the 3.6 to 10.4 ppm range, and their assignments were tentative. As before, the pyrazolyl 4 and 5 protons were in the expected ranges around 40 and 80 ppm, respectively. Again, the three 3-(2-naphthyl)pyrazolyl arms of the Tp$^{\beta\text{Nt}}$ ligand were spectroscopically identical. The structure of **2** was also determined by X-ray crystallography (Figure 2). The Tp$^{\beta\text{Nt}}$ ligand provided a much deeper pocket than Tp$^{\alpha\text{Nt}}$, so that the Tp ligand was totally buried within it. At the same time, the twist angle of the naphthyl group, with respect to the pyrazolyl plane, was smaller by about 7° in the Tp$^{\beta\text{Nt}}$ part of the ligand than in Tp$^{\alpha\text{Nt}}$ (on the average 46.1 versus 52.8°). The Co−N distances for the Tp ligand were again slightly shorter than those for Tp$^{\beta\text{Nt}}$ (2.110 versus 2.221 Å).

The complex Co[Tp$^{\alpha\text{Nt}}$][Tp*], **3**, was synthesized from Co-[Tp$^{\alpha\text{Nt}}$]Cl and TlTp*. Unlike **1**, it was pink rather than yellow. Its NMR spectrum was baffling; instead of the expected twelve peaks, as in **1** or **2**, here was a forest of about 40 peaks, some of them overlapping. The situation became clearer when the structure of **3** was determined by X-ray crystallography (Figure 3). The molecule had no symmetry elements at all; the 1-naphthyl substituents were not twisted in the same direction, as in **1**, but one substituent was twisted in the opposite direction from the other two. This made each pyrazolyl arm unique, so that one would have expected 36 separate peaks in the NMR. It was very difficult to identify the overlapping peaks, and impossible to assign them, except by grouping them roughly in the “pyrazolyl H-5” or “pyrazolyl H-4” areas. It is surprising that the asymmetric structure, found in the solid state, seems to also be present in solution, since any rotational freedom of the 1-naphthyl substituents would have resulted in dynamic symmetrization of the molecule and the presence of only the expected 12 peaks.

While the heteroleptic complex Co[Tp$^{\beta\text{Nt}}$][Tp*] was also prepared, it could not be properly characterized, as it was contaminated with hard to remove Co[Tp*$_2$], and crystals suitable for X-ray structure detrmination could not be grown. It was too insoluble in common NMR solvents, but from the yellow−orange color comparable to that of complexes **1** and **2** and the IR spectrum, which showed the B−H stretches for the each of the respective scorpionate ligands, we surmise that the molecule is of C_{3v} symmetry, with a rigid structure in which the Tp* 3-methyl groups intercalate between the 2-naphthyl rings.

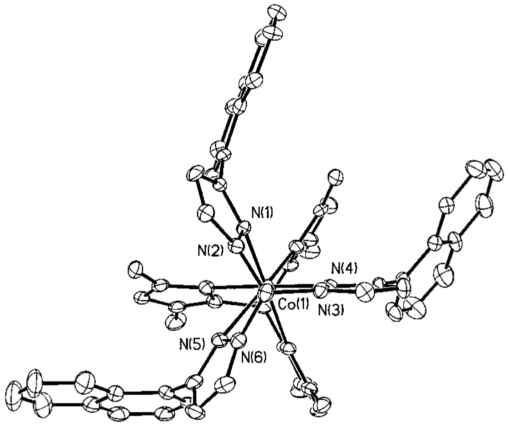

Figure 3. Structure of the complex **3**, Co[Tp$^{\alpha\text{Nt}}$][Tp*]. Selected bond lengths (Å) and angles (°): Co−N(1) 2.203; Co−N(3) 2.178; Co−N(5) 2.380; Co−N(7) 2.140; Co−N(9) 2.142; Co−N(11) 2.112; N(1)−Co−N(3) 81.7; N(1)−Co−N(5) 86.1; N(1)−Co−N(7) 101.0; N(1)−Co−N(9) 166.7; N(1)−Co−N(11) 99.3; N(3)−Co−N(5) 93.7; N(3)−Co−N(7) 95.7; N(3)−Co−N(9) 90.2; N(3)−Co−N(11) 177.7; N(5)−Co−N(7) 169.0; N(5)−Co−N(9) 83.9; N(5)−Co−N(11) 84.4; N(7)−Co−N(9) 90.2; N(7)−Co−N(11) 86.2; N(9)−Co−N(11) 88.5.

The tetrahedral zinc complexes, Zn[Tp$^{\alpha\text{Nt}}$]NCS and Zn[Tp$^{\beta\text{Nt}}$]-NCS, were also prepared and characterized by their well-defined NMR spectra. Tetrahedral homoscorpionte zinc complexes have been studied as models for various zinc-based enzymes, notably carbonic anhydrase.[20]

An unusual heteroleptic complex of the [Tp$^{\alpha\text{Nt}}$] ligand, Co-[Tp$^{\alpha\text{Nt}}$][3,4-bis(diphenylphosphinoyl)-1,2,3-triazolato], has been recently reported in a communication dealing with the [3,4-bis(diphenylphosphinoyl)-1,2,3-triazolato] ligand.[21] It contains cobalt in a five coordinate environment, where, in addition to the three nitrogen atoms of the [Tp$^{\alpha\text{Nt}}$] ligand, it is also coordinated to the oxygen of one −P(O)Ph$_2$ group and to the nearest nitrogen atom of the triazole ring.

Summary

Two novel homoscoprionate ligands, containing a naphthyl substituent in the 3-position and bonded either through the

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1-position, [Tp$^{\alpha\mathrm{Nt}}$], or through the 2-position, [Tp$^{\beta\mathrm{Nt}}$], have been synthesized, and the nature of their complexes was elucidated by NMR and by X-ray crystallography. The [Tp$^{\beta\mathrm{Nt}}$] ligand resembled other Tp$^{\mathrm{Ar}}$ ligands, where Ar is a para-substituted phenyl group, although the 2-naphthyl substituent provided a substantially deeper pocket around the coordinated metal while retaining rotational freedom. By contrast, rotation of the 1-naphthyl substituent in [Tp$^{\alpha\mathrm{Nt}}$] was restricted, which led to complexes of lower symmetry that those of the [Tp$^{\beta\mathrm{Nt}}$] ligand and, at times, as in the case of Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*], to a structure devoid of any symmetry elements. It is possible that the [Tp$^{\alpha\mathrm{Nt}}$] ligand might find some use in the preparation of asymmetric catalysts.

Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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