Homoscorpionate Ligands Based on 3-(Cyclobutyl)pyrazole and 3-(Cyclopentyl)pyrazole

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Keywords: Scorpionates / Cobalt / Borates / N ligands

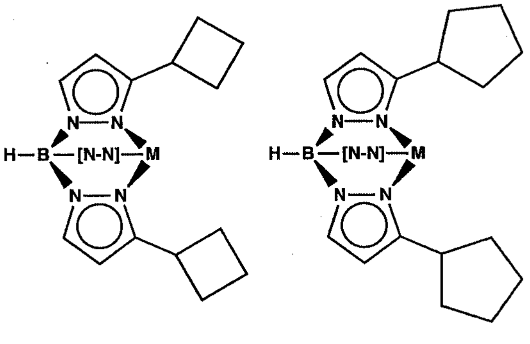
The novel scorpionate ligands hydrotris[3-(cyclobutyl)pyrazol-1-yl]borate (Tp^{Cbu}), hydrotris[3-(cyclopentyl)pyrazol-1-yl]borate (Tp^{Cpe}), tetrakis[3-(cyclobutyl)pyrazol-1-yl]borate (pz^oTp^{Cbu}), tetrakis[3-(cyclopentyl)pyrazol-1-yl]borate (pz^oTp^{Cpe}), have been synthesized, converted into a variety of homo- and heteroleptic complexes, and studied by NMR spectroscopy. The complexes $Tl[Tp^{Cbu}]$ (**1**), $Tl[Tp^{Cpe}]$ (**2**), $Co[Tp^{Cbu}]_2$ (**3**), $Co[Tp^{Cpe*}]_2$ (**4**), $Co[Tp^{Cpe}][Tp]$ (**5**), $Co[pz^oTp^{Cbu}]_2$ (**6**), and $Co[pz^oTp^{Cpe}]_2$ (**7**) have been structurally characterized by X-ray crystallography. The coordination behavior of Tp^{Cpe} is similar to that of Tp^{Cy} or Tp^{iPr} in producing stable tetrahedral $Tp^{Cpe}MX$ complexes, but octahedral homoleptic complexes only with ligand rearrangement, yielding $M[Tp^{Cpe*}]_2$. By contrast, Tp^{Cbu} is unusual in forming both tetrahedral $Tp^{Cbu}MX$, and homoleptic $M[Tp^{Cbu}]_2$ complexes, without rearrangement. The complex **6** is tetrahedral in solution but octahedral in the crystal, while complex **7** is tetrahedral in solution and in the crystal.

Introduction

Among the many known homoscorpionate [tris(pyrazolyl)borate] ligands of the type Tp^R,[1] where the R substituent is in the 3-position, there are only two in which R is a cycloalkyl group. One is Tp^{Cpr},[2,3] where R is cyclopropyl, and the other Tp^{Cy},[4–7] where R is cyclohexyl. Their coordinative behavior is strikingly different. Tp^{Cpr} coordinates very much like the parent Tp ligand, forming octahedral $M[Tp^{Cpr}]_2$ complexes with great ease, as does its tetrakis analog, pz^oTp^{Cpr} $\{= [B(pz^{Cpr})_4]^-\}$ and, conversely, it is very reluctant to form stable tetrahedral species $M[Tp^{Cpr}]X$. By contrast, Tp^{Cy} readily forms stable tetrahedral complexes $M[Tp^{Cy}]X$, and its $M[Tp^{Cy}]_2$ complexes are not octahedral but tetrahedral, containing κ^2-Tp^{Cy} ligands. It is only through thermally induced rearrangement, which converts one 3-(cyclohexyl)pyrazolyl arm to 5-(cyclohexyl)pyrazolyl, that octahedral complexes are obtained.[7] We decided to study the coordination chemistry of scorpionates with 3-R = cycloalkyl substituents intermediate in size between cyclopropyl and cyclohexyl, in order to determine where the transition from one type of behavior to the other occurs.

That the variations in the size and geometry of 3-R substituents have a pronounced effect on the coordination chemistry, and on the catalytic effectiveness of specific Tp^R metal complexes, has been conclusively demonstrated in the studies, where a series of Tp^R copper(I) complexes was used in achieving carbene transfer, and C-bond activation. Thus, in the cyclopropanation reaction by way of carbene transfer from ethyl diazoacetate to styrene and to other olefins, the by far most active ligand was Tp^{Ms} (Ms = mesityl).[8] On the other hand, in the rather similar cyclopropenation of acetylenes, catalysts derived from Tp^{Ms} gave only mediocre results, but catalysts based on Tp^{Cy} were stellar performers.[9]

We have, therefore, synthesized Tp^R ligands where R was 3-cyclobutyl (= Tp^{Cbu}) or 3-cyclopentyl (= Tp^{Cpe}), as well as their tetrakis analogs pz^oTp^{Cbu} and pz^oTp^{Cpe}, and have examined their coordination chemistry in high-spot fashion.



$M[Tp^{Cbu}]$ $M[Tp^{Cpe}]$

-(N-N)- is the third, hidden, 3-cycloalkylpyrazolyl ring

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Results and Discussion

The two new pyrazoles, 3-(cyclobutyl)pyrazole and 3-(cyclopentyl)pyrazole, were synthesized by way of formylating cyclobutyl methyl ketone, and cyclopentyl methyl ketone, respectively, and treatment of the resulting dicarbonyl intermediates with hydrazine. Reaction of these pyrazoles with KBH_4 produced the respective ligands, characterized as their Tl derivatives, Tl[Tp^{Cbu}] (**1**) and Tl[Tp^{Cpe}] (**2**). Comparing the cone and wedge angles of the structurally characterized compounds **1** and **2** (Figure 1 and 2), which were 234 and 253°, respectively,[11] with those of Tl[Tp^{Cpr}] (223°) and Tl[Tp^{Cy}] (281°), one can see that the cone angle of **1** is still relatively close to Tl[Tp^{Cpr}], in differing by only 11°, but the cone angle of **2** is roughly midway between those of Tl[Tp^{Cpr}] and Tl[Tp^{Cy}]. One could expect, therefore, at first approximation, the ligand [Tp^{Cbu}] to be somewhat similar in terms of its coordination behavior to [Tp^{Cpr}], while [Tp^{Cpe}] might resemble [Tp^{Cy}]. The average Tl−N bond lengths of **1** and **2** were both 2.562 Å, although in the case of **1** all lengths were exactly equal, while in **2** they ranged from 2.530 to 2.607 Å. The respective N−Tl−N angles averaged 75.2 and 75.5°, again being all identical in the case of **1**, but ranging from 72.3 to 77.3° in the case of **2**. Both, the Tl−N bond lengths and N−Tl−N bond angles fall right into the middle range of known Tl[Tp^R] complexes.[12]

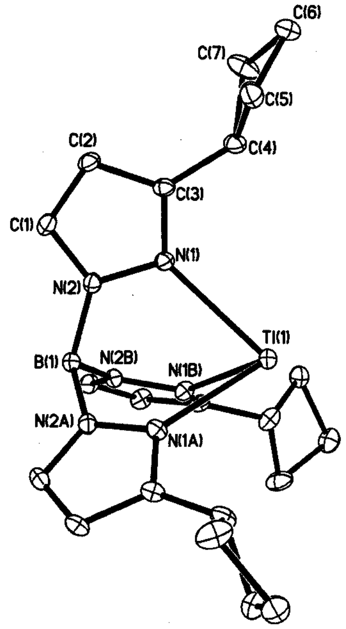

Figure 1. ORTEP plot of the structure of Tl[Tp^{Cbu}] (**1**); selected bond length [Å] and angle [°]: Tl−N(1) 2.562(2); N(1)−Tl−N(1A) 75.20(7)

The cyclopropyl group in Tp^{Cpr} compounds has the angle between its 2- and 3-C atoms very close to the theoretical 60°.[2,3] The cyclopropyl ring is thus very constrained, as compared to an isopropyl (or cyclohexyl) group, the two methylene groups being pinned back and offering little in terms of steric hindrance. Hence, the coordination behavior of Tp^{Cpr} resembles that of the parent Tp or of Tp^{Me}. Going to the less tight angle between the 2- and 4-C atoms in the cyclobutyl group, which was 86.4° in Co[Tp^{Cbu}]$_2$ (**3**) and 86.7° in Co[pz°Tp^{Cbu}]$_2$ (**6**) for the cyclobutyl groups in the equatorial belt, such small contraction of the angle is perhaps necessary in order to accommodate there the six cyclobutyl groups. The angle was 96° for the cyclobutyl groups in **6** on the uncoordinated pyrazolyl ring. Clearly, one would expect an increase in steric hindrance in Tp^{Cbu}, as compared to Tp^{Cpr}. A further increase in steric hindrance is anticipated in the case of Tp^{Cpe}, where the angle between the 2- and 5-C atoms of a planar cyclopentyl group would be 108°, and thus almost equal to the tetrahedral angle of 109° present in isopropyl or cyclohexyl groups. In the Co[Tp^{Cpe*}]$_2$ complex **4** the angle in the inner cyclopentyl groups was 101°, while it was 103° in the cyclopentyl group on the rearranged pz^{Cpe} arm. This increased loosening of the 2- and 5-methylene groups would make the cyclopentyl substituent even closer, in terms of steric effects, to a cyclohexyl or isopropyl group.

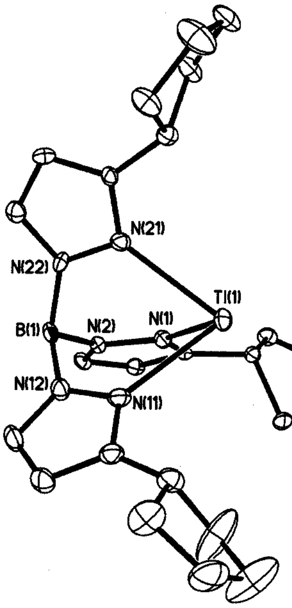

Figure 2. ORTEP plot of the structure of Tl[Tp^{Cpe}] (**2**); selected bond lengths [Å] and angles [°]: Tl−N(1) 2.530(10), Tl−N(11) 2.607(10), Tl−N(21) 2.59(9); N(1)−Tl−N(11) 77.3(3), N(1)−Tl−N(21) 76.7(3), N(1)−Tl−N(11) 72.6(3)

The Tp^{Cbu} ligand was found to form isolable tetrahedral M[Tp^{Cbu}]X complexes, differing in this respect from Tp^{Cpr}, where such complexes with transition metals were spontaneously converted into octahedral homoleptic species, M[Tp^{Cpr}]$_2$.[3] At the same time homoleptic complexes M[Tp^{Cbu}]$_2$ could also be prepared. In the case of the paramagnetic Co[Tp^{Cbu}]$_2$ (**3**) its NMR spectrum was extremely sharp and indicated all pz^{Cbu} arms to be identical, which meant that no rearrangement of the ligands to Tp^{Cbu*} had taken place. The structure of **3** was determined by X-ray crystallography, and showed the molecule to be of D_{3d} symmetry (Figure 3). There appeared to be no problem of accommodating the six cyclobutyl groups in the equatorial belt of the molecule. The N−Co distances averaged 2.142 Å, and this is very close to the values found in Co[Tp]$_2$ (2.129 Å),[13] Co[Tp*]$_2$ (2.143 Å),[14] and to the N−Co distances of the Tp^{Cpr} component in Co[Tp^{Cpr}][Tp^{Ph}], where the N−Co distances average 2.121 Å for Tp^{Cpr}, and 2.223 Å for Tp^{Ph}.[3]

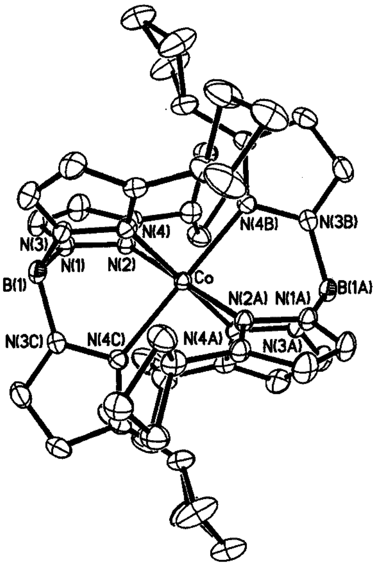

Figure 3. ORTEP plot of the structure of Co[Tp^{Cbu}]$_2$ (**3**); selected bond lengths [Å] and angle [°]: Co−N(2) 2.139(5), Co−N(4) 2.143(4); N(2)−Co−N(4) 88.7(1)

As an example of heteroleptic complexes, Co[Tp^{Cbu}][Tp] was synthesized by the reaction of Co[Tp^{Cbu}]Cl with Tl[Tp]. The NMR of this complex was very sharp and indicative of C_{3v} symmetry for the molecule, with each proton readily identifiable, even to the point of separating the *cis*- and *trans*-protons of the cyclobutyl ring. We assumed that the protons nearer to the metal center would exhibit the larger chemical shift.[15]

The ligand [Tp^{Cpe}]$^-$ readily formed tetrahedral Co[Tp^{Cpe}]X complexes, which were stable, yet reactive enough to serve as precursors to a variety of heteroleptic compounds of the type Co[Tp^{Cpe}][Tp^R], as discussed further on.

The homoleptic complex Co[Tp^{Cpe}]$_2$ was prepared readily from Tl[Tp^{Cpe}] and Co(ClO$_4$)$_2$. It was purple in solution, but wine-red in the solid state. Heating in hydrocarbon solvents, such as toluene or xylene produced a purple solution, suggestive of tetrahedral coordination, and on concentration the wine-red solid was recovered unchanged. However, when Co[Tp^{Cpe}]$_2$ was refluxed briefly in benzonitrile, the purple color changed to amber, and layering of the solution with heptane resulted in the formation of bright yellow crystals, m.p. 286−288 °C. This color is typical of octahedral cobalt homoscorpionates, and so the crystals were assumed to be Co[Tp^{Cpe*}]$_2$ (**4**). Heating of Co[Tp^{Cpe}]$_2$ in a melting point tube, resulted in a purple melt at 142−144 °C, resolidification with a color change to amber at around 166−168 °C, and melting of that solid at around 280 °C. That this, indeed, involved rearrangement of Co[Tp^{Cpe}]$_2$ to **4**, containing one 5-(cyclopentyl)pyrazolyl group per ligand, was suggested by the proton NMR spectrum. It was rather complicated, as each proton of the two 3-(cyclopentyl) rings was unique [*cis* and *trans*, inner and outer protons with respect to the C_2 axis, plus the tertiary one for a total of nine peaks for the two 3-(cyclopentyl) rings], the 5-(cyclopentyl) ring had four pairs of 2,5- and 3,4-protons, plus the tertiary one for a total of five peaks. In addition, there were the pyrazolyl protons (three 4-H, two 5-H, and one 3-H), for a total of 19 peaks. Nevertheless, they all could be assigned, on the basis of the protons closer to the cobalt center exhibiting the greater shifts.[15] The four 2,5-protons of the 3-(cyclopentyl) rings were well separated in the $\delta = -32$ to -49 ppm range, while those of the 3,4-protons were closely bunched together in the $\delta = -14$ to -15 ppm area. Such thermal rearrangements [Equation (1)] have been observed before as, for instance, in converting Co[Tp^{Np}]$_2$ to Co[Tp^{Np*}]$_2$,[16] or Co[Tp^{Cy}]$_2$ to Co[Tp^{Cy*}]$_2$.[7]

$$\mathrm{M[HB(3\text{-}Rpz)_3]_2} \rightarrow \mathrm{M[HB(3\text{-}Rpz)_2(5\text{-}Rpz)]_2} \qquad (1)$$

The rearranged structure of **4** was confirmed by X-ray crystallography. In this structure (Figure 4) the two pyrazolyl arms with the 5-(cyclopentyl) group are *trans* to each other, and their Co−N bond lengths are 2.11 Å, while those with the 3-(cyclopentyl) group have Co−N bond lengths of 2.16 Å, thus being significantly longer (see Table 1).

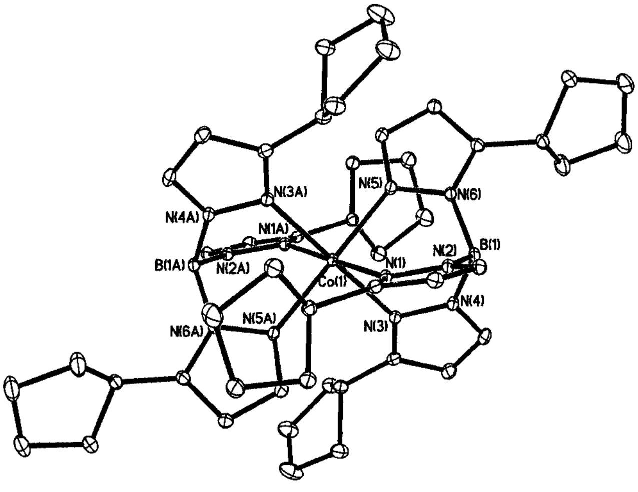

Figure 4. ORTEP plot of the structure of Co[Tp^{Cpe*}]$_2$ (**4**); selected bond lengths [Å] and angles [°]: Co−N(5) 2.1154(14), Co−N(3) 2.1576(13), Co−N(1) 2.11619(13); N(5)−Co−N(3) 88.18(5), N(5)−Co−N(1) 87.21(5), N(1)−Co−N(3) 84.44(5)

A series of heteroleptic complexes Co[Tp^{Cpe}][Tp^R] was also prepared, to check how large an R group in 3-position of the Tp^R ligand can still be accommodated in such complexes without causing rearrangement of [Tp^{Cpe}] to [Tp^{Cpe*}], or altering the octahedral structure. Three such compounds were prepared: Co[Tp^{Cpe}][Tp] (**5**), Co[Tp^{Cpe}][Tp*] and Co[Tp^{Cpe}][Tp^{Cpr}]. In each of them, the octahedral structure was maintained without rearrangement of the Tp^{Cpe} ligand, as was clearly indicated by the NMR spectra of these paramagnetic complexes. All the

Table 1. Average Co−N bond lengths in octahedral homoleptic Co[Tp^{x}]$_2$ and heteroleptic Co[Tp^{x}][Tp^{y}] complexes

Tp$^{\mathrm{R}}$ ligand	Co−N [Å]	Found in complex	Ref.
Tp	2.129(7)	Co[Tp]$_2$	[13]
Tp	2.129(4)	Co[Tp$^{\mathrm{Cpe}}$][Tp]	this work
Tp	2.131(5)	Co[Tp$^{\alpha\mathrm{Nt}}$][Tp]	[19]
Tp	2.143(2)	Co[Tp$^{\beta\mathrm{Nt}}$][Tp]	[19]
Tp	2.142(3)	Co[Tp$^{\mathrm{CHPh2}}$][Tp]	[21]
Tp	2.124(3)	Co[Tp$^{\mathrm{Ph,4Me}}$][Tp]	[21]
Tp	2.122(2)	Co[Tp$^{\mathrm{Ph,4Et}}$][Tp]	[21]
Tp	2.124(2)	Co[Tp$^{\mathrm{Tol}}$][Tp]	[21]
Tp^{4}*t*Bu	2.165(6)	Co[Tp$^{\mathrm{CHPh2}}$][Tp$^{\mathrm{4tBu}}$]	[21]
Tp^{4}*t*Bu	2.129(2)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{4tBu}}$]	[21]
Tp*	2.144(2)	Co[Tp*]$_2$	[14]
Tp*	2.141(5)	Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*]	[19]
Tp$^{\mathrm{Cpr}}$	2.121(6)	Co[Tp$^{\mathrm{Cpr}}$][Tp$^{\mathrm{Ph}}$]	[3]
Tp$^{\mathrm{Cbu}}$	2.142(2)	Co[Tp$^{\mathrm{Cbu}}$]$_2$	this work
Tp$^{\mathrm{Cbu}}$	2.124(3)	Co[pz$^{\mathrm{o}}$Tp$^{\mathrm{Cbu}}$]$_2$	this work
Tp$^{\mathrm{Cpe}}$	2.160(2)[a]	Co[Tp$^{\mathrm{Cpe}*}$]$_2$	this work
Tp$^{\mathrm{Cpe}}$	2.168(3)	Co[Tp$^{\mathrm{Cpe}}$][Tp]	this work
Tp$^{\mathrm{iPr}}$	2.167(2)[b]	Co[Tp$^{\mathrm{iPr}*}$]	[10]
Tp$^{\mathrm{iPr,4Br}}$	2.179(3)[c]	Co[Tp$^{\mathrm{(iPr,4Br)}*}$]	[10]
Tp$^{\mathrm{Np}}$	2.167(6)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{4tBu}}$]	[21]
Tp$^{\mathrm{Np}}$	2.175(4)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{Br3}}$]	[22]
Tp$^{\mathrm{Np}}$	2.137(7)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{3Bo,7Me}}$]	[20]
Tp$^{\mathrm{Np}}$	2.172(3)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{Me,mt3}}$]	[23]
Tp$^{\mathrm{Np}}$	2.153(15)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{a}*,\mathrm{3Me}}$]	[20]
Tp$^{\mathrm{Me,mt3}}$	2.149(3)[d]	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{Me,mt3}}$]	[23]
Tp$^{\mathrm{a}*,\mathrm{3Me}}$	2.207(2)	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{a}*,\mathrm{3Me}}$]	[20]
Tp$^{\mathrm{3Bo,7Me}}$	2.236(7)[e]	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{3Bo,7Me}}$]	[20]
Tp$^{\mathrm{Br3}}$	2.139(2)	Co[Tp$^{\mathrm{Br3}}$]$_2$	[21]
Tp$^{\mathrm{Br3}}$	2.128(3)	Co[Tp$^{\mathrm{Br3}}$][Tp$^{\mathrm{Np}}$]	[21]
Tp$^{\mathrm{Tn}}$	2.155(3)	Co[Tp$^{\mathrm{Tn}}$]$_2$(CHCl$_3$)	[18]
Tp$^{\mathrm{Tn}}$	2.170(2)	Co[Tp$^{\mathrm{Tn}}$]$_2$(C$_6$H$_6$)	[18]
Tp$^{\mathrm{Ph}}$	2.223(6)	Co[Tp$^{\mathrm{Cpr}}$][Tp$^{\mathrm{Ph}}$]	[3]
Tp$^{\mathrm{Ph,4Me}}$	2.223(3)	Co[Tp$^{\mathrm{Ph,4Me}}$][Tp]	[21]
Tp$^{\mathrm{Ph,4Et}}$	2.222(2)	Co[Tp$^{\mathrm{Ph,4Et}}$][Tp]	[21]
Tp$^{\mathrm{Tol}}$	2.226(2)	Co[Tp$^{\mathrm{Tol}}$][Tp]	[21]
Tp$^{\mathrm{a}*,\mathrm{3Me}}$	2.207(15)[f]	Co[Tp$^{\mathrm{Np}}$][Tp$^{\mathrm{a}*,\mathrm{3Me}}$]	[20]
Tp$^{\alpha\mathrm{Nt}}$	2.238(5)	Co[Tp$^{\alpha\mathrm{Nt}}$][Tp]	[19]
Tp$^{\alpha\mathrm{Nt}}$	2.233(4)	Co[Tp$^{\alpha\mathrm{Nt}}$][Tp*]	[19]
Tp$^{\beta\mathrm{Nt}}$	2.228(2)	Co[Tp$^{\beta\mathrm{Nt}}$][Tp]	[19]
Tp$^{\mathrm{CHPh2}}$	2.214(4)	Co[Tp$^{\mathrm{CHPh2}}$][Tp]	[21]
Tp$^{\mathrm{CHPh2}}$	2.206(1)	Co[Tp$^{\mathrm{CHPh2}}$][Tp$^{\mathrm{4tBu}}$]	[21]

[a] Values taken from the two 3-cyclopentylpyrazolyl arms per ligand. [b] Values taken from the two 3-isopropylpyrazolyl arms per ligand. [c] Values taken from the two 4-bromo-3-isopropylpylpyrazolyl arms per ligand. [d] Tp$^{\mathrm{Me,mt3}}$ = hydrotris(3-methyl-4,5-propylenepyrazol-1-yl)borate. [e] Tp$^{\mathrm{3Bo,7Me}}$ = hydrotris(7-methylindazol-1-yl)borate. [f] Tp$^{\mathrm{a}*,\mathrm{3Me}}$ = hydrotris(3-methyl-2*H*-benz[*g*]indazol-2-yl)borate.

spectra were extremely sharp, as is the case with octahedral cobalt(II) bis(homoscorpionates), and showed each proton to be in a specific environment, with assignments based on the previously established ranges for the chemical shifts of the pyrazolyl ring protons, and protons of pyrazolyl substituents in the various positions. The structure of **5** was determined by X-ray crystallography (Figure 5). It was of C_{3v} symmetry, and contained slightly longer Co−N bonds for the Tp$^{\mathrm{Cpe}}$ ligand than for Tp (2.168 versus 2.129 Å).

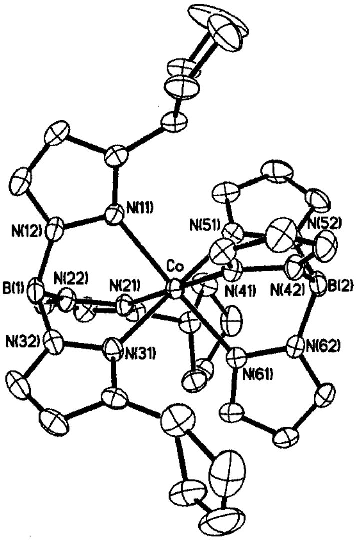

Figure 5. ORTEP plot of the structure of Co[Tp$^{\mathrm{Cpe}}$][Tp] (**5**); selected bond lengths [Å] and angles [°]: Co−N(11) 2.173(3), Co−N(21) 2.167(3), Co−N(31) 2.165(4), Co−N(41) 2.132(3), Co−N(51) 2.130(4), Co−N(61) 2.126(4); N(11)−Co−N(21) 87.4(1), N(11)−Co−N(31) 87.5(1), N(31)−Co−N(21) 87.3(1), N(41)−Co−N(51) 85.7(1), N(41)−Co−N(61) 84.7(1), N(51)−Co−N(61) 85.2(1)

When the reaction of KBH$_4$ with 3-(cyclobutyl)pyrazole or 3-(cyclopentyl)pyrazole was carried out without solvent, and long reaction times were employed, the tetrakis ligands [B(pz$^{\mathrm{Cbu}}$)$_4$]$^-$ (= pz$^{\mathrm{o}}$Tp$^{\mathrm{Cbu}}$) and [B(pz$^{\mathrm{Cpe}}$)$_4$]$^-$ (= pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpe}}$) were obtained and were converted into their thallium derivatives, Tl[pz$^{\mathrm{o}}$Tp$^{\mathrm{Cbu}}$] and Tl[pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpe}}$]. While Tl[pz$^{\mathrm{o}}$Tp$^{\mathrm{Cbu}}$] could be isolated in crystalline form and characterized, Tl[pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpe}}$] was very difficult to crystallize and, for this reason, the crude K salt was used to prepare [pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpe}}$] complexes. The coordination chemistry of the two new ligands fitted neatly between that of pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpr}}$ and pz$^{\mathrm{o}}$Tp$^{\mathrm{Cy}}$. Whereas pz$^{\mathrm{o}}$Tp$^{\mathrm{Cpr}}$, just like the parent pzTp,[17] coordinated only in a κ^3-fashion, forming with first-row transition metals octahedral complexes M[Tp$^{\mathrm{Cpr}}$]$_2$, in which the three-coordinated and one uncoordinated pz$^{\mathrm{Cpr}}$ arms did not exchange, giving rise to NMR signals for each pyrazolyl arm in 3:1 ratio, the ligand pz$^{\mathrm{o}}$Tp$^{\mathrm{Cy}}$ coordinated only in a κ^2-fashion, yielding tetrahedral complexes, as was also the case with the ligand pz$^{\mathrm{o}}$Tp$^{\mathrm{iPr}}$.[10] This distinction between octahedral and tetrahedral complexes is most apparent in the Co[pz$^{\mathrm{o}}$Tp$^{\mathrm{R}}$]$_2$ species, where the octahedral complexes are yellow, while the tetrahedral ones are deep purple.

The solid complex $\mathrm{Co[pz^{o}Tp^{Cbu}]_2}$ (**6**) was yellow, but when in solution, be it in chloroform at room temperature or in boiling toluene, the color changed to deep purple, indicating dissociation of one of the $\mathrm{pz^{Cbu}}$ arms per ligand, and formation of a dynamic tetrahedral structure. Upon crystallization of the complex from the purple solution, the resulting crystals were again bright yellow, indicative of octahedral coordination. The NMR of this compound was quite different from that of $\mathrm{Co[pz^{o}Tp^{Cpr}]_2}$ in which the signals corresponding to the three-coordinated and one uncoordinated pyrazolyl arms per ligand were sharp and well separated, consistent with a lack of exchange between the coordinated and uncoordinated pyrazolyl arms. The NMR spectrum of **6**, by contrast, contained broad peaks at positions averaging the peaks of the two-coordinated and two uncoordinated pyrazolyl arms per ligand. Nevertheless, the structure determination of **6** (Figure 6) confirmed the octahedral nature of the complex in the crystal, with each ligand being κ^3-coordinated, and the fourth $\mathrm{pz^{Cbu}}$ arm remaining free.

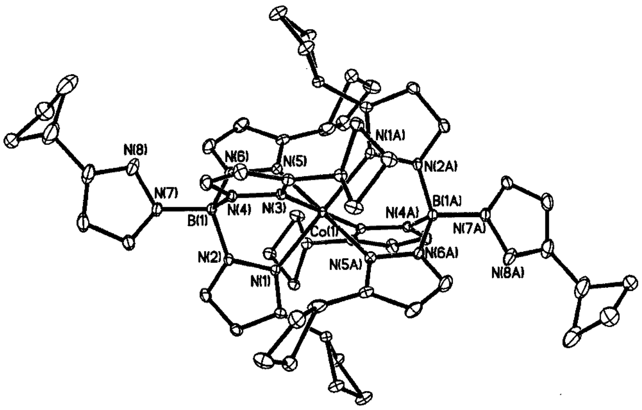

Figure 6. ORTEP plot of the structure of $\mathrm{Co[pz^{o}Tp^{Cbu}]_2}$ (**6**); selected bond lengths [Å] and angles [°]: Co−N(1) 2.1317(18), Co−N(3) 2.0923(18), Co−N(5) 2.1469(18), N(1)−Co−N(3) 88.33(7), N(1)−Co−N(5) 88.14(7), N(5)−Co−N(3) 88.41(7)

The $\mathrm{[pz^{o}Tp^{Cpe}]}$ ligand also formed a 2:1 cobalt complex, $\mathrm{Co[pz^{o}Tp^{Cpe}]_2}$ (**7**), which was purple in solution, and remained purple on concentration suggestive of a tetrahedral structure throughout, with κ^2-coordination of each ligand. It is similar, in this regard, to the ligands $\mathrm{[pz^{o}Tp^{iPr}]}$ and $\mathrm{[pz^{o}Tp^{Cy}]}$. The NMR spectrum of **7** showed broad peaks, indicative of exchange of all four pyrazolyl arms at room temperature. In the crystal (Figure 7) the complex also exhibited a tetrahedral structure, similar to that found in the case of $\mathrm{Co[pz^{o}Tp^{Cy}]_2}$ and $\mathrm{Co[pz^{o}Tp^{iPr}]_2}$. The Co−N distances for the coordinated $\mathrm{pz^{Cpe}}$ arms averaged 1.997 Å, and were thus considerably shorter than the values of 2.158 Å found in **4** or 2.168 Å encountered in **5**, implying a lesser degree of congestion in the tetrahedral structure.

The steric hindrance imposed on $\mathrm{Tp^{R}}$ ligands by the R substituents in 3-position manifests itself in the slight, but persistent, M−N bond lengthening in their octahedral homo- and heteroleptic complexes. In Table 1 we have collected Co−N bond length data from structurally determined $\mathrm{Co[Tp^{R}]_2}$ and $\mathrm{Co[Tp^{R}][Tp^{R'}]}$ complexes. As can be seen there, the parent Tp ligand is indeed, and expectedly, the least hindered, while the ligand $\mathrm{Tp^{Cbu}}$ resembles Tp*, in terms of steric hindrance, as expressed in terms of Co−N bond lengths. The $\mathrm{Tp^{Cpe}}$ ligand appears closest in its Co−N bond length values to $\mathrm{Tp^{iPr}}$, which is also in consonance with its observed coordination chemistry.

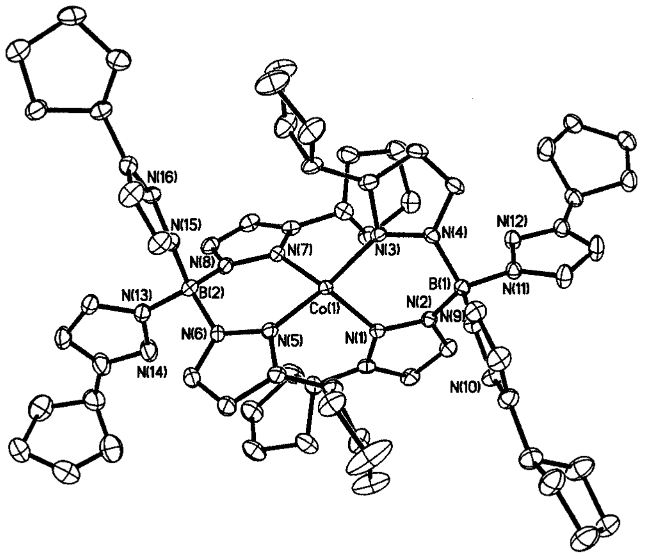

Figure 7. ORTEP plot of the structure of $\mathrm{Co[pz^{o}Tp^{Cpe}]_2}$ (**7**); selected bond lengths [Å] and angles [°]: Co−N(1) 1.991(3), Co−N(3) 1.986(3), Co−N(5) 1.985(3), Co−N(7) 1.984(3); N(1)−Co−N(3) 96.79(13), N(1)−Co−N(5) 115.56(13), N(5)−Co−N(3) 125.76(15), N(1)−Co−N(7) 109.01(14), N(3)−Co−N(7) 112.82(13)

We also compared the propensity for dynamic exchange of the coordinated and uncoordinated pyrazolyl arms in a series of $\mathrm{[pz^{o}Tp^{R}]}$ ligands by examining the NMR spectra for the 4- and 5-protons in a series of diamagnetic zinc complexes $\mathrm{Zn[pz^{o}Tp^{R}]_2}$, where R was methyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. For the complexes where R was methyl or cyclopropyl, there were only two very sharp peaks for the 4- and 5-protons, implying very rapid exchange of all the pyrazolyl arms. When R was cyclobutyl, there were still only two peaks present, but they ceased to be sharp, with one of them being more of a hump than a peak and the other significantly broadened. The broadest peak was the one for 5-H, as was the C-5 peak in the ^{13}C NMR spectrum of this compound. When R was cyclopentyl, there were already four peaks for the 4- and 5-protons, although they could not be discerned as doublets, implying still a small degree of exchange. In the case where R was cyclohexyl, the four peaks were narrow and sharp with their doublets clearly resolved. These comparisons indicate that the ligand $\mathrm{[pz^{o}Tp^{Cbu}]}$ exhibits a hybrid type of behavior which, in turn, implies that the energy difference in solution between the tetrahedral and octahedral forms is quite small.

Conclusion

In summary, we have prepared and characterized new Tp^{Cbu} and Tp^{Cpe} ligands and their tetrakis analogs, [pz^oTp^{Cbu}] and [pz^oTp^{Cpe}], establishing the main features of their coordination chemistry. The ligands Tp^{Cpe} and [pz^oTp^{Cpe}] act very much like the more hindered analogs Tp^{Cy} and [pz^oTp^{Cy}]. However, the Tp^{Cbu} and [pz^oTp^{Cbu}] ligands are, in some ways, special. Tp^{Cbu} is a Tp^R ligand with the largest cycloalkyl group which still permits the formation of homoleptic Co[Tp^R]$_2$ complexes without rearrangement of the ligand to Tp^{R*}, while [pz^oTp^{Cbu}] exhibits a very facile conversion from octahedral to tetrahedral when going into solution. Being relatively unhindered, this tetrahedral form of [pz^oTp^{Cbu}] might interact/coordinate with some small molecules and, perhaps, exhibit interesting catalytic properties. We are planning to investigate these aspects in the future.

Experimental Section

General: All chemicals were of the highest commercial reagent grade and were used as received. Cyclobutyl methyl ketone and cyclopentylmagnesium chloride were purchased from Aldrich. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls of 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 16 K data points, a sweep width of 3000−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s.

3-(Cyclobutyl)pyrazole: This compound was prepared by formylation of cyclobutyl methyl ketone (125 g 1.27 mol) with methyl formate, and anhydrous sodium methoxide, followed by the reaction with hydrazine, as has been done in the synthesis of 3-isopropylpyrazole.[10] The product, b.p. 123 °C/1.7 Torr, was obtained in 98 g (63%) yield. ^{1}NMR: δ = 7.49 (d, J = 2.0 Hz, 1 H, 5-H), 6.12 (d, J = 2.0 Hz, 1 H, 4-H), 3.59 (quint, 1 H, tertiary H), 2.14 (m, 2 H, cyclobutyl), 2.20 (quint of d, 2 H, cyclobutyl), 2.1−1.8 (m, 4 H, cyclobutyl) ppm. ^{13}C NMR: δ = 18.8 (unique methylene), 29.6 (2 methylenes), 32.5 (tertiary C), 102.0 (C-4), 135 (C-5), 151.6 (C-3) ppm. $C_7H_{10}N_2$ (122.09): calcd. C 68.9, H 8.20, N 23.0; found C 68.8, H 8.29, N 22.8.

3-(Cyclopentyl)pyrazole: Cyclopentyl methyl ketone was prepared by adding 1.20 mol of cyclopentylmagnesium chloride to a solution of 1.35 mol of acetic anhydride in 1 L of THF. After completion of the addition and another hour of stirring, saturated aqueous ammonium chloride was added, and the two layers were separated. The upper layer was passed through alumina, and the filtrate was stripped and distilled in vacuo, saving the cut with b.p. 163−165 °C. The yield was 56 g (41%). 3-(Cyclopentyl)pyrazole was prepared from the above cyclopentyl methyl ketone, methyl formate, and anhydrous sodium methoxide, followed by the reaction with hydrazine as has been done in the case of 3-isopropylpyrazole.[10] The redistilled pyrazole, b.p. 145−150 °C/5.8 Torr, was obtained in 26 g (42%) yield. ^{1}H NMR: δ = 12.4 (br., 1 H, NH), 7.47 (d, J = 2.0, 1 H, 5-H), 6.06 (d, J = 2.0, 1 H, 4-H), 3.14 (quint, 1 H, tertiary H), 2.07 (m, 2 H, cyclopentyl), 1.5−1.9 (m, 6 H, cyclopentyl) ppm. ^{13}C NMR: δ = 15.1, 33.2, 37.5 (tertiary C), 101.6 (C-4), 135.0 (C-5), 151.4 (C-3) ppm. $C_8H_{12}N_2$ (136.10): calcd. C 70.6, H 8.82, N 20.6; found C 70.6, H 8.94, N 20.6%.

Thallium Hydrotris[3-(cyclobutyl)pyrazol-1-yl]borate, Tl[Tp^{Cbu}] (1): A mixture of 96 g (0.79 mol) of 3-(cyclobutyl)pyrazole and 11.6 g (0.215 mol) of KBH_4 was stirred and refluxed in 200 mL of 4-methylanisole. Hydrogen evolution was steady, and the theoretical amount was evolved within 4 h. The solvent was distilled off under vacuum, and the residue was boiled with 300 mL of heptane, and the solution was filtered hot. The crude K[Tp^{Cbu}] had a B−H band at $\tilde{\nu}$ = 2383 cm^{-1}. The compound was converted into Tl[Tp^{Cbu}] in standard fashion, and this product was obtained in 58 g (48%) overall yield. M.p. 132−134 °C. IR: $\tilde{\nu}$ = 2428 (B−H) cm^{-1}. ^{1}H NMR: δ = 7.54 (d, J = 2.0, 3 H, 5-H), 6.05 (d, J = 2.0, 3 H, 4-H), 3.65 (quint, 3 H, tertiary H), 2.33 (m, 6 H, cyclobutyl), 2.16 (m, 6 H, cyclobutyl), 1.99 (m, 3 H, cyclobutyl), 1.86 (m, 3 H, cyclobutyl) ppm; the BH signal of intensity 1 is visible by integration in the δ = 3.6−5.2 ppm region. ^{13}C NMR: δ = 18.9 (Cbu C-3), 30.0 (Cbu C-2,4), 33.9 (Cbu C-1), 101.6 (C-4), 135.9 (C-5), 157.8 (C-3) ppm. $C_{21}H_{28}BN_6Tl$ (579.67): calcd. C 43.5, H 4.84, N 14.5; found C 43.6, H 4.98, N 14.3.

Thallium Hydrotris[3-(cyclopentyl)pyrazol-1-yl]borate, Tl[Tp^{Cpe}] (2): This compound was prepared as above from 50 g (0.37 mol) of 3-(cyclopentyl)pyrazole and 5.6 g (0.10 mol) of KBH_4 in 75 mL of 4-methylanisole. The residue, after removal of the solvent in vacuo, was converted into Tl[Tp^{Cpe}], which was obtained in 30 g (47%) overall yield. IR: $\tilde{\nu}$ = 2438 (B−H) cm^{-1}. ^{1}H NMR: δ = 7.51 (3 H, 5-H), 5.98 (3 H, 4-H), 3.21 (3 H, quint, Cpe 1-H), 2.07 (6 H, Cpe), 1.75 (m, 6 H, Cpe), 1.64 (m, 12 H, Cpe) ppm; the BH (1 H) signal is visible by integration in the δ = 3.6−5.2 ppm region. ^{13}C NMR: δ = 25.4, 34.1, 38.9 (Cpe, C-1), 101.1 (C-4), 135.8 (C-5), 157.9 (C-3) ppm. $C_{24}H_{34}BN_6Tl$ (621.75): calcd. C 46.4, H 5.48, N 13.5; found C 46.3, H 5.56, N 13.4.

Co[Tp^{Cbu}]Cl: A solution of Tl[Tp^{Cbu}] (1.2 g, 2.0 mmol) in 50 mL of dichloromethane was stirred vigorously with a large excess of anhydrous $CoCl_2$. After 2 h, the blue slurry was filtered through a pad of Celite, and the filtrate was concentrated, yielding a blue solid in 0.64 g (68%) yield. It was obtained after recrystallization from a toluene/heptane mixture as dark blue crystals, m.p. 148−150 °C. IR: $\tilde{\nu}$ = 2504 (B−H) cm^{-1}. $C_{21}H_{28}BClCoN_6$ (469.46): calcd. C 53.6, H 5.96, N 17.9; found C 54.0; H 6.14, N 17.7.

Co[Tp^{Cpe}]Cl: This compound was synthesized in the same way as Co[Tp^{Cbu}]Cl, and was obtained in 63% yield as dark blue crystals, m.p. 161−163 °C. IR: $\tilde{\nu}$ = 2478 (B−H) cm^{-1}. $C_{24}H_{34}BClCoN_6$ (505.49): calcd. C 56.3, H 6.64, N 16.4; found C 56.4, H 6.83, N 16.3.

Zn[Tp^{Cpe}]NCS: The compound was prepared by stirring vigorously in dichloromethane Tl[Tp^{Cpe}] with a large excess of zinc perchlorate and potassium thiocyanate (1:4 mol ratio) in a minimum amount of water. After 2 h, the organic layer was separated, passed through alumina, and the solvents were evaporated, yielding the product in 64% yield. M.p. 160−162 °C. IR: $\tilde{\nu}$ = 2496 (B−H), 2063 (NCS) cm^{-1}. ^{1}H NMR: δ = 7.54 (3 H, 5-H), 6.03 (d, 3 H, 4-H), 3.24 (3 H, quint, Cp 1-H), 2.13 (m, 6 H, Cpe), 1.77 (m, 12 H, Cpe), 1.58 (m, 6 H, Cpe) ppm. $C_{35}H_{34}BN_7SZn$ (660.63): calcd. C 55.6, H 6.30, N 18.2; found C 55.7, H 6.41, N 18.0.

Co[Tp^{Cbu}]$_2$ (3): To a stirred solution of Tl[Tp^{Cbu}] (1.2 g, 2.0 mmol) in 50 mL of THF was added dropwise a concentrated aqueous solution of 0.26 g (1 mmol) of $Co(ClO_4)_2$·$(H_2O)_6$ followed, after 1 h, by 200 mL of water and 100 mL of chloroform. The layers were separated, and the chloroform layer was passed through a shallow bed of alumina, and the solvents were evaporated, yielding 0.67 g (83%) of yellow $\mathrm{Co[Tp^{Cbu}]_2}$, which was purified by recrystallization from xylene. M.p. 254−256 °C. IR: ṽ = 2439, 2467 cm^{-1}. ^{1}H NMR: δ = 97 (1 H, BH), 74.0 (3 H, 5-H), 48.9 (3 H, 4-H), −12.0 (6 H, 3′-H), −26.1 and 26.7 (6 H each, *cis* and *trans* 2′-H), −92.5 (3 H, 1′-H) ppm. $\mathrm{C_{42}H_{56}B_2CoN_{12}}$ (809.50): calcd. C 62.3, H 6.92, N 20.8; found C 62.5, H 7.14, N 20.6.

$\mathrm{Co[Tp^{Cpe*}]_2}$ (4): The complex $\mathrm{Co[Tp^{Cpe}]_2}$ was prepared as above, but using $\mathrm{Tl[Tp^{Cpe}]}$ instead of $\mathrm{Tl[Tp^{Cbu}]}$, and it was obtained in 76% yield, as a pale purplish-red solid. It melted to a purple melt at 142−144 °C, then the melt resolidified with a color change to amber at around 166−168 °C, melting again at around 280 °C. Boiling of a sample of the product in benzonitrile resulted in an amber solution, after passing through a deep purple stage. Overlayering this solution with heptane resulted, on standing, in the formation of bright yellow needles, m.p. 286−288 °C. NMR: δ = 84.9 (2 H, 5-H of 3-Cpe), 59.2 (1 H, 4-H of 5-Cpe), 49.5 (2 H, 4-H of 3-Cpe), 38.6 (1 H, tertiary H of 5-Cpe), 24.8 (2 H, *trans*-2,4-H of 5-Cpe), 16.9 (2 H, *cis*-2,4-H of 5-Cpe), 13.5 (2 H, *trans*-3,4-H of 5-Cpe), 9.12 (2 H, *cis*-3,4-H of 5-Cpe), −14.104 (2 H, 3,4-H of 3-Cpe), −14.7 (2 H, 3,4-H of 3-Cpe), −14.7 (2 H, 3,4-H of 3-Cpe) −15.0 (2 H, 3,4-H of 3-Cpe), −31.9 (2 H, *trans*-2,5-H of 3-Cpe), −36.3 (2 H, *trans*-2,5-H of 3-Cpe), −40.9 (2 H, *cis*-2,5-H of 3-Cpe, −46.8 (2 H, *cis*-2,5-H of 3-Cpe), −94 (1 H, 3-H), −108 (2 H, tertiary H of 3-Cpe) ppm. $\mathrm{C_{48}H_{68}B_2CoN_{12}}$ (893.69): calcd. C 64.5, H 7.61, N 18.8; found C 65.1, H 7.80, N 19.0.

$\mathrm{Zn[Tp^{Cbu}]_2}$: M.p. 186−188 °C. IR: ṽ = 2466, 2438 (B−H) cm^{-1}. ^{1}H NMR: δ = 7.57 (d, *J* = 2.0, 3 H, 5-H), 6.16 (d, *J* = 2.0, 3 H, 4-H), 2.73 (quint, 3 H, tertiary H), 1.81 (m, 6 H, cyclobutyl), 1.62 (m, 6 H, cyclobutyl), 1.57 (m, 6 H, cyclobutyl) ppm; the BH (1 H) signal can be discerned by integration in the δ = 3.5−5.0 ppm range. ^{13}C NMR: δ = 18.1 (C-3′), 30.1 (C-2′), 32.9 (C-1′), 102.1 (C-4), 135.9 (C-5), 159.3 (C-3) ppm. $\mathrm{C_{42}H_{56}B_2N_{12}Zn}$ (815.55): calcd. C 61.8, H 6.87, N 20.6; found C 62.0, H 7.01, N 20.5.

$\mathrm{Zn[Tp^{Cpe}]_2}$: M.p. 182−184 °C. ^{1}H NMR: δ = 7.31 (d, 3 H, 5-H), 6.06 (d, 3 H, 4-H), 2.60 (3 H, quint, Cpe 1-H), 1.63 (m, 12 H, Cpe), 1.47 (m, 12 H, Cpe) ppm. ^{13}C NMR: δ = 25.3, 33.8, 38.9, 102.0, 137.5, 161.0 ppm. $\mathrm{C_{48}H_{68}B_2N_{12}Zn}$ (899.61): calcd. C 64.1, H 7.56, N 18.7; found C 64.2, H 7.69, N 18.5.

Preparation of Heteroleptic $\mathrm{Co[Tp^{R}][Tp^{R'}]}$ Complexes. A: One method to synthesize octahedral cobalt complexes containing two different $\mathrm{Tp^R}$ ligands was to stir equimolar amounts of $\mathrm{Co[Tp^R]Cl}$ (R = Cbu, Cpe) and $\mathrm{Tl[Tp^{R'}]}$ (R′ = H, Me, cyclopropyl) in dichloromethane until the disappearance of the characteristic blue color of $\mathrm{Co[Tp^R]Cl}$. This took from a few minutes to several hours, depending on the steric hindrance of $\mathrm{Tp^{R'}}$. The slurry was then filtered through a bed of Celite to remove TlCl, and the filtrate was chromatographed on alumina, collecting the yellow band. Concentration of the eluate yielded the crude product, which was recrystallized from toluene or xylene. **B:** An alternative way was to stir $\mathrm{Tl[Tp^R]}$ in dichloromethane with a large excess of anhydrous $\mathrm{CoCl_2}$, to filter the blue slurry after 4 h, and without isolation of $\mathrm{Co[Tp^R]Cl}$, adding an equimolar amount of the appropriate $\mathrm{Tl[Tp^{R'}]}$ salt. When the color of the slurry changed from blue to yellowish, the slurry was filtered to remove TlCl, the filtrate was chromatographed on alumina, and concentration of the eluate yielded the crude $\mathrm{Co[Tp^R][Tp^{R'}]}$ complex, which was purified by recrystallization. The unoptimized yields in these reactions ranged from 55 to 82%.

$\mathrm{Co[Tp^{Cbu}][Tp]}$: This complex was prepared by method A, was obtained in 82% yield, and recrystallized from toluene. M.p. 267−268 °C. IR: ṽ = 2469, 2445 (B−H) cm^{-1}. ^{1}H NMR: δ = 114.2 and 111.8 (1 H each, BH), 90.4 and 82.5 (3 H each, 5-H), 44.8 and 41.5 (3 H each, 4-H), −14.5 and − 15.0 (3 H each, *cis*- and *trans*-3′-H), −31.5 and −35.4 (6 H each, *cis*- and *trans*-2′-H), −102.1 (3 H, 1′-H), −124.3 (3 H, 3-H) ppm. $\mathrm{C_{30}H_{38}B_2CoN_{12}}$ (646.97): calcd. C 55.6, H 5.87, N 26.0; found C 55.5, H 6.01, N 25.7.

$\mathrm{Co[Tp^{Cpe}][Tp]}$ (5): This complex was prepared by method A and was obtained in 77% yield. M.p. 278−280 °C. IR: ṽ = 2473, 2440 (B−H) cm^{-1}. ^{1}H NMR: δ = 118.5 and 115.7 (1 H each, BH and BH′), 92.9 and 93.4 (3 H each, 5-H and 5′-H), 45.3 and 42.0 (3 H each, 4-H and 4′-H), −13.6 and − 14.5 (6 H each, Cp 3-H, *cis* and *trans*), −35.5 (6 H, Cp 2-H, *trans*) −45.6 (6 H, Cp 2-H, *cis*), −106.3 (3 H, Cp 1-H), −131.7 (3 H, 3-H) ppm. $\mathrm{C_{33}H_{44}B_2N_{12}}$ (689.40): calcd. C 57.5, H 6.39, N 24.4; found 57.8, H 6.48, N 24.1.

$\mathrm{Co[Tp^{Cpe}][Tp^*]}$: This complex was prepared by method B and was obtained in 69% yield. M.p. 282−284 °C. IR: ṽ = 2515, 1475, 2443 (B−H) cm^{-1}. ^{1}H NMR: δ = 105.5 (2 H, BH and BH′), 77.6 (3 H, 5-H), 48.1 and 44.8 (3 H each, 4-H and 4′-H), 42.9 (9 H, 5-Me), −12.3 and −12.9 (6 H each, Cp 3-H, *cis* and *trans*), −31.5 (6 H, Cp 2-H, *trans*), −38.4 (6 H, Cp 2-H, *cis*), −75.7 (9 H, 3-Me), −113.6 (3 H, Cp 1-H) ppm. $\mathrm{C_{39}H_{56}B_2CoN_{12}}$ (773.06): calcd. C 60.5, H 7.24, N 21.7; found C 60.4, H 7.31, N 21.6.

$\mathrm{Co[Tp^{Cpe}][Tp^{Cpr}]}$: This complex was prepared by method B and was obtained in 55% yield. M.p. 247−248 °C. IR: ṽ = 2438, 2473 (B−H) cm^{-1}. ^{1}H NMR: δ = 99.6 and 97.2 (1 H each, BH and BH′), 76.0 and 69.4 (3 H each, 5-H and 5′-H), 47.6 and 45.4 (3 H each, 4-H and 4′-H), −11.2 (12 H, Cpr 3-H), −23.8 (3 H, Cpr 2-H, *trans*), −25.6 (6 H, Cpr 2-H, *cis*), −28.9 (6 H, Cpr 2-H, *trans*) −32.4 (6 H Cpe 2-H, *cis*), −97.3 and −100.0 (3 H each, Cpr and Cpe 1-H) ppm. $\mathrm{C_{42}H_{56}B_2CoN_{12}}$ (809.09): calcd. C 56.6, H 6.92, N 20.8; found C 56.5, H 7.04, N 20.7.

Preparation of the $\mathrm{[pz^oTp^{Cbu}]}$ and $\mathrm{[pz^oTp^{Cpe}]}$ Ligands: These ligands were prepared by heating with stirring the appropriate pyrazole and $\mathrm{KBH_4}$ in a 5:1 mol ratio, bringing the oil-bath temperature slowly up to 250−270 °C, and maintaining this temperature under a gentle nitrogen stream for 24 h. After some cooling, the excess pyrazoles were distilled off in vacuo, and the residues were refluxed for 1 h in heptane, cooled and filtered, yielding the crude K salts $\mathrm{K[pz^oTp^{Cbu}]}$ and $\mathrm{K[pz^oTp^{Cpe}]}$, respectively. Samples of each were converted into the Tl salts, $\mathrm{Tl[pz^oTp^{Cbu}]}$ and $\mathrm{Tl[pz^oTp^{Cpe}]}$. However, only $\mathrm{Tl[pz^oTp^{Cbu}]}$ could be recrystallized, as the resinous $\mathrm{Tl[pz^oTp^{Cpe}]}$ resisted all attempts at crystallization. For this reason, the crude $\mathrm{K[pz^oTp^{Cpe}]}$ salt was employed for preparing $\mathrm{M[pz^oTp^{Cpe}]}$ complexes.

$\mathrm{Tl[pz^oTp^{Cbu}]}$: It was recrystallized from octane. M.p. 129−132 °C. ^{1}H NMR: δ = 7.41 (d, *J* = 2 Hz, 1 H, 5-H), 6.15 (d, *J* = 2 Hz, 1 H, 4-H), 3.65 (quint, 1 H, tertiary H), 2.34 (m, 2 H, Cbu), 2.18 (m, 2 H, Cbu), 1.8−2.1 (m, 2 H, Cbu) ppm. ^{13}C NMR: δ = 18.8 (Cbu C-3), 29.7 (Cbu C-2), 33.9 (Cbu C-1), 102.7 (C-4), 136.0 (C-5), 158.9 (C-3) ppm. $\mathrm{C_{28}H_{36}BN_8Tl}$ (699.55): calcd. C 48.1, H 5.15, N 16.0; found C 48.2, H 5.23, N 15.8.

$\mathrm{Co[pz^oTp^{Cbu}]_2}$ (6): This complex was prepared from $\mathrm{Tl[pz^oTp^{Cbu}]}$ and $\mathrm{Co[ClO_4]_2{\cdot}(H_2O)_6}$. It turns gradually deep purple above 150 °C, and melts at around 250 °C. ^{1}H NMR: δ = 63.9 (1 H), 34.8 (1 H), −5.0 (1 H), − 5.6 (1 H), −14.8 (16 H), −57 (1 H) ppm. $\mathrm{C_{56}H_{72}B_2CoN_{16}}$ (1049.85): calcd. C 64.1, H 6.86, N 21.4; found C 63.9, H 6.92, N 21.2.

$\mathrm{Co[pz^oTp^{Cpe}]_2}$ (7): This complex was prepared from $\mathrm{Tl[pz^oTp^{Cpe}]}$ and $\mathrm{Co[ClO_4]_2{\cdot}(H_2O)_6}$. M.p. 251−253 °C. ^{1}H NMR: very broad

Table 2. Crystallographic data of compounds **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{21}H_{28}BN_6Tl$	$C_{24}H_{34}BN_6Tl$	$C_{42}H_{56}B_2CoN_{12}$	$C_{48}H_{68}B_2CoN_{12}$	$C_{33}H_{44}B_2CoN_{12}$	$C_{56}H_{72}B_2CoN_{16}$	$C_{64}H_{88}B_2CoN_{16}$
Formula mass	579.67	621.75	809.5	893.69	689.4	1049.85	1162.05
Space group	$Pa\bar{3}$	$P2_1/c$	$Pnnm$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	16.5976(1)	26.5969(2)	11.932(5)	9.1733(5)	13.741(4)	10.9923(4)	10.4526(5)
b [Å]	???	16.3566(1)	12.580(6)	11.3770(6)	15.592(3)	19.0910(7)	41.7982(19)
c [Å]	???	18.3532(2)	13.669(8)	11.7241(6)	17.279(4)	12.9080(5)	14.9597(7)
α [°]	???	???	???	76.188(1)	???	???	???
β [°]	???	105.793(1)	???	78.193(1)	104.93(2)	98.674(1)	109.851(1)
γ [°]	???	???	???	87.916(1)	???	???	???
V [Å^3]	4572.31(5)	7682.88(11)	2052(2)	1163.0(1)	3577(2)	2677.8(2)	6147.3(5)
Z/Z'	24/8	4/12	8/2	2/1	4/4	4/2	4/4
Crystal color, habit	colorless, block	colorless, block	yellow, block	yellow, block	yellow, cube	yellow, block	purple, plate
D(calcd.) [g cm^{-3}]	1.684	1.613	1.310	1.276	1.280	1.302	1.256
μ(Mo-K_α) [cm^{-1}]	7.083	6.329	4.66	4.17	5.22	3.75	3.34
T [K]	173(2)	203(2)	298	120.0(0.1)	298	120.0(0.1)	173.0(0.1)
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Bruker Smart Apex CCD	Siemens P4	Bruker Smart Apex CCD	Bruker Smart Apex CCD
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
$R(F)$ (%)[a]	2.32	6.82	5.80	4.08	3.81	5.94	9.37
$R(wF^2)$ (%)[b]	4.85[c]	16.06	9.09[c]	10.65	4.00[c]	15.98	21.92

[a] $R = \|F_o| - |F_c\|/|F_o|$. [b] $R(wF^2) = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$. [c] $R(wF) = \{[w(|F_o| - |F_c|)^2]/[wF_o^2]\}^{1/2}$; $w = 1/\sigma^2(F_o)$.

peaks at δ = 70, 36, 30, 16, −10, −26 ppm, with a very large indistinct hump centered at δ = 5 ppm. $C_{64}H_{88}B_2CoN_{16}$ (1162.05): calcd. C 66.1, H 7.58, N 19.3; found C 65.9, H 7.70, N 19.0.

Zn[pz^{o}Tp^{Cbu}]$_2$: This complex was prepared from Tl[pz^{o}Tp^{Cbu}] and $Zn[ClO_4]_2\cdot(H_2O)_6$. M.p. 266−268 °C. ^{1}H NMR: δ = 6.86 (br. hump, 1 H, 5-H), 6.20 (d, 1 H, 4-H), 2.97 (very br. hump, 1 H, tertiary H), 1.66−2.10 (m, 6 H, cyclobutyl) ppm. ^{13}C NMR: δ = 18.5 (Cbu C-4), 29.7 (Cbu C-2,3), 33.7 (Cbu C-1), 102.9 (C-4), 138 (C-5), 161.1 (C-4) ppm. $C_{56}H_{72}B_2N_{16}Zn$ (1055.73): calcd. C 63.7, H 6.82, N 21.2; found C 64.0, H 6.98, N 21.0.

Zn[pz^{o}Tp^{Cpe}]$_2$: This complex was prepared from Tl[pz^{o}Tp^{Cpe}] and $Zn[ClO_4]_2\cdot(H_2O)_6$. M.p. 221−223 °C. ^{1}H NMR: δ = 7.15 (d, 2 H, 5-H), 6.33 (d, 2 H, 5-H), 6.07 (d, 2 H, 4-H), 5.94 (d, 2 H, 4-H), 3.08 (2 H, quint, Cpe 1-H), 2.17 (2 H, quint, Cpe 1-H), 1.95 (m, 4 H, Cpe), 1.4−1.8 (m, 20 H, Cpe), 1.27 (m, 8 H, Cpe) ppm. ^{13}C NMR: δ = 25.4, 33.6, 34.2, 37.7, 39.4, 102.1, 102.3, 133.4, 140.4, 159.5, 163.6 ppm. $C_{64}H_{88}B_2N_{16}Zn$ (1.167.81): calcd. C 65.8, H 7.54, N 19.2; found C 66.0, H 7.71, N 19.1.

X-ray Crystal Structure Determinations: Diffraction intensity data were collected with Siemens P4 (**1**−**3**, **5**) and Bruker Smart Apex CCD (**4**, **6**, **7**) diffractometers. Crystal, data collection, and refinement parameters are given in Table 2. The systematic absences in the diffraction data of **1**−**3**, **5**−**7** structures are uniquely consistent with the reported space groups. The space group for **4** has been chosen by intensity statistics. The structures were solved by direct methods (**1**−**6**) and the Patterson function (**7**), completed by subsequent Fourier syntheses and refined by full-matrix, least-squares procedures on reflection intensities (F^2). SADABS absorption corrections were applied to the data of **1**, **3**−**6** and DIFABS[22] corrections to the data of **2** (T_{min} = 0.48, T_{max} = 1.00) and **7** (T_{min} = 0.28, T_{max} = 1.00).[23] All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. In the structure of **6**, two C_4 rings are disordered in two positions with occupation multiplicity μ = 0.60, 0.40 and 0.59, 0.41, respectively. All software and sources scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). CCDC-178940 (**1**), -178941 (**2**), -178942 (**3**), -178943 (**4**), -178944 (**5**), -178945 (**6**) and -178946. (**7**) 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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[23] Confronted with a difficult correction for absorption, a prudent crystallographer will sample the output of the many programs at his disposal, and then select the one that does the job best. In the realm of empirical and semi-empirical correction schemes, many programs have been written, some old and some new. Each analyzes the data in a somewhat different way, and each can produce different results. While DIFABS may be one of the older methods, it is, on occasion, the one that performs best, and because its routines are well known and some newer routines are undocumented "black boxes," its idiosyncrasies are also well known. We are unaware that anyone has declared DIFABS ineffective or fatally flawed, and until such time, it is a useful procedure that we intend to keep using.

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Received February 27, 2002
[I02103]