Coordination Chemistry of Homoscorpionate Ligands with 3-Cyclopropyl Substituents

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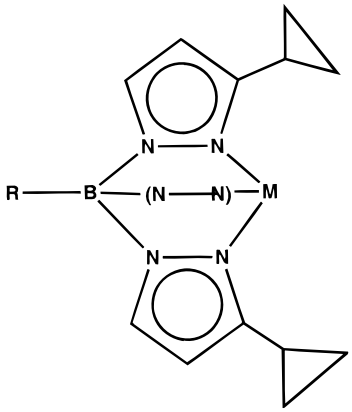
In a quest for precisely sterically tuned ligand systems, the new scorpionate ligands hydrotris(3-cyclopropylpyrazol-1-yl)borate, Tp^{Cpr}, and tetrakis(3-cyclopropylpyrazol-1-yl)borate, pz^*Tp^{Cpr}, have been synthesized. They readily form octahedral homoleptic and heteroleptic complexes with first-row transition metal compounds, but their $[M(Tp^{Cpr})(X)]$ complexes are unstable with respect to the octahedral ones. The complex $[Mo(Tp^{Cpr})(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$ was also prepared. Structures of the paramagnetic $[Co(Tp^{Cpr})_2]$, $[Co(pz^*Tp^{Cpr})_2]$, and $[Co(Tp^{Cpr})(Tp^{Ph})]$ complexes have been determined by ^{1}H NMR and those of $[Fe(Tp^{Cpr})_2]$ and $[Fe(pz^*Tp^{Cpr})_2]$, as well as that of $[Co(Tp^{Cpr})(Tp^{Ph})]$, by X-ray crystallography, indicating facile accommodation of six cyclopropyl groups in the equatorial belt of octahedral complexes. In its coordination behavior, Tp^{Cpr} is quite different from Tp^{iPr} and resembles Tp^{Me}.

Introduction

A wide scope of remarkable coordination chemistry, including complexes resembling bioinorganic systems, has been found employing the homoscorpionate[1] ligand Tp^{iPr} (ref 2) and its analogs, such as $Tp^{iPr,4Br}$ (ref 2), $Tp^{iPr,Me}$ (refs 3 and 4), and Tp^{iPr2} (ref 5)—all containing a 3-isopropyl group on the pyrazolyl ring. This substituent is of intermediate steric hindrance, and while allowing the formation of tetrahedral LMX complexes, the substituent makes it impossible to obtain octahedral L_2M species, except with the rearrangement of one 3-iPrpz group to a 5-iPrpz group per ligand.[2] In seeking to fine-tune the Tp^x ligand system, we aimed for a symmetrical 3-substituent to fill the gap between Tp^{Me} and Tp^{iPr}. To reduce the steric hindrance of the isopropyl 3-substituent, we chose to tie together the terminal methyl carbons, thus converting an isopropyl into a cyclopropyl group. Since the isopropyl group usually straddles the pyrazolyl plane with its methyl groups pointed away from the metal,[6] such modification would increase the wedge angle[7] of the ligand while keeping the cone angle essentially unchanged. The new ligands $[HB(3\text{-cyclopropylpyrazol-1-yl})_3]^-$ (Tp^{Cpr}) and $[B(3\text{-cyclopropylpyrazol-1-yl})_4]^-$ (pz^*Tp^{Cpr}) were prepared, being characterized as their Tl salts, **1** and **2**, respectively, and their coordination chemistry was explored. The coordination chemistry differed dramatically from that of Tp^{iPr} and pz^*Tp^{iPr}. The unusual tetrameric tetrahedral structure of **1** has already been reported.[8]



1 $[Tl(Tp^{Cpr})]$ R = H, M = Tl

2 $[Tl(pz^*Tp^{Cpr})]$ R = 3-(Cpr)pz, M = Tl

-(N-N)- represents the third, hidden, 3-(Cpr)pz group

Experimental Section

All the chemicals were reagent grade and used as received. Elemental analyses were performed by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. ^{1}H 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. Evolution of hydrogen during ligand synthesis was measured quantitatively by a wet-test meter.

3-Cyclopropylpyrazole was synthesized in 58% yield from methyl cyclopropyl ketone by the method used for making 3-isopropylpyrazole.[2] Bp: 122−124 °C/2.8 Torr. ^{1}H NMR: 12.45 (1 H, NH), 7.46 (s, 1 H, H-5), 5.93 (d, 1 H, H-4), 1.97 (sept, 1 H, tertiary H), 0.93 (dt, 2 H, cyclopropyl), 0.74 (db, 2 H, cyclopropyl) ppm. ^{13}C NMR: 7.89, 101.1, 134.0, 150.6 ppm (the fifth peak is hidden under the 7.9 peak). Anal. Calcd for $C_6H_8N_2$: C, 66.7; H, 7.41; N, 25.9. Found: C, 66.9; H, 7.51; N, 25.7.

$Tl(Tp^{Cpr})$ (1) was prepared by refluxing 3-cyclopropylpyrazole with KBH_4 (3.6:1 mol ratio) in 4-methylanisole until the theoretical amount

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of hydrogen was evolved. After the solvent was distilled off and excess 3-cyclopropylpyrazole at reduced pressure, the residue was dissolved in THF and stirred with a saturated aqueous solution of Tl_2SO_4. The product was extracted with chloroform, and the extracts were filtered through alumina and stripped. Stirring the residue with methanol gave **1** in 77% yield. Mp: 144−146 °C. IR: BH 2438 cm^{-1}. ^1H NMR: 7.50 (d, 1 H, H-5), 5.74 (d, 1 H, H-4), 2.04 (sept, 1 H, tertiary H), 0.93 (dt, 2 H, cyclopropyl), 0.566 (db, 2 H, cyclopropyl) ppm. ^{13}C NMR: 8.1, 9.0, 99.7, 135.9, and 155.8 ppm. Anal. Calcd for $C_{18}H_{22}BN_6Tl$: C, 40.2; H, 4.10; N, 15.6. Found: C, 40.1; H, 4.18; N, 15.4.

Tl(pz*Tp^{Cpr}) (2) was prepared by refluxing KBH_4 in an excess of 3-cyclopropylpyrazole until the theoretical amount of hydrogen was evolved. Excess 3-cyclopropylpyrazole was distilled in vacuo, and the residue was converted to the Tl salt as described above. Mp: 182−184 °C. ^1H NMR: 7.34 (d, 1 H, H-5), 5.83 (d, 1 H, H-4), 2.01 (sept, 1 H, tertiary H), 0.92 (dt, 2 H, cyclopropyl), 0.68 (dt, 2 H, cyclopropyl) ppm. ^{13}C NMR: 7.9, 9.2, 101.2, 136.1, 156.7 ppm. Anal. Calcd for $C_{24}H_{29}BN_8Tl$: C, 44.7; H, 4.50; N, 17.4. Found: C, 44.8; H 4.66; N, 17.1.

Compounds L_2M were prepared from **1** and **2**, respectively, by treatment of their THF solutions with the appropriate aqueous metal chlorides or perchlorates. After the mixture was diluted with water, the complexes were extracted with chloroform, and the extracts were purified by filtration through alumina and isolated by stirring the evaporation residue with methanol. Final purification was by recrystallization from a toluene/heptane mixture.

[Co(Tp^{Cpr})$_2$] (**3**): Yellow crystals; no mp detected up to 300 °C. IR: BH 2434 cm^{-1}. ^1H NMR: 111.5 (1H, BH), 83.4 (3 H, H-5), 45.2 (3 H, H-4), −28.5 (6 H, "far" cyclopropyl Hs), −31.6 (6 H, "close" cyclopropyl Hs), −118.9 (3 H, tertiary H) ppm. Anal. Calcd for $C_{36}H_{42}BCoN_{12}$: C, 59.8; H, 5.81; N, 23.2. Found: C, 59.5; H, 6.08; N, 23.1.

[Fe(Tp^{Cpr})$_2$] (**4**): Pale greenish crystals; no mp detected up to 300 °C. IR BH 2433 cm^{-1}. Anal. Calcd for $C_{36}H_{42}BFeN_{12}$: C, 60.0; H, 5.83; N, 23.3. Found C, 59.8; H, 6.01; N, 23.2.

[Co(pz*Tp^{Cpr})$_2$] (**5**): Yellow crystals; no mp detected up to 300 °C. ^1H NMR: 84.3 (3 H, 3 H, H-5), 61.3 (1 H, H-5′), 43.1 (3 H, H-4), 28.9 (1 H, H-4′), 19.3 (1 H, tertiary H′), 15.8 (2 H, "near" cyclopropyl H′), 11.6 (2 H, "far" cyclopropyl H′), −28.3 (6 H, "far" cyclopropyl Hs), −32.3 (6 H, "near" cyclopropyl Hs), −122.4 (tertiary H) ppm. Anal. Calcd for $C_{48}H_{58}BCoN_{16}$: C, 61.3; H, 6.18; N, 23.9. Found: C, 61.2; H, 6.25; N, 23.8.

[Fe(pz*Tp^{Cpr})$_2$] (**6**): Pale greenish crystals; no mp detected up to 300 °C. Anal. Calcd for $C_{48}H_{58}BFeN_{16}$: C, 61.5; H, 6.20; N, 23.9. Found: C, 61.4; H, 6.33; N, 23.7.

[Co(Tp^{Cpr})(Tp^{Ph})] (**7**) was prepared by stirring equimolar quantities of **1** and [Co(Tp^{Ph})NCS],[9] in methylene chloride for 2 h, filtration of this mixture through Celite, and chromatography of the filtrate on alumina, collecting the orange band. Orange crystals; mp 246−248 °C. IR: BH 2438, 2469 cm^{-1}. ^1H NMR: 95.2 (2 H, BH), 76.0, 68.8 (each 3 H, H-5 and H-5′), 50.11, 43.7 (each 3 H, H-4 and H-4′), 7.5 (6 H, *meta*), 6.9 (3 H, *para*), −24.6, −28.3 (6 H each, cyclopropyl methylene Hs), −42.4, (6 H, *ortho*), −98.9 (tertiary H) ppm. Anal. Calcd for $C_{45}H_{44}B_2CoN_{12}$: C, 64.8; H, 5.28; N, 20.2. Found: C, 65.0; H, 5.38; N, 20.1.

[Co(Tp^{Cpr})(Tp^{An})] (**8**) was prepared as described above using Tp^{An}-CoNCS and was obtained as orange crystals, mp 206−208 °C. IR: 2440 cm^{-1}. ^1H NMR: 97 (2 H, BH and BH′), 76.6 (3 H, H-5, Tp^{Cpr}), 69.1 (3 H, H-5, Tp^{An}), 49.6 (3 H, H-4 Tp^{Cpr}), 44.0 (3 H, H-4 Tp^{An}), 1.96 (2 H, *meta*), 1.69 (9 H, Me), −24.9, −28.6 (6 H each, cyclopropyl methylene Hs), −42.1 (6 H, *ortho*), −100 (3 H, tertiary H) ppm. Anal. Calcd for $C_{48}H_{50}B_2CoN_{12}O_3$: C, 62.4; H, 5.42; N, 18.2. Found: C, 62.5; H, 5.55; N, 18.1.

[Zn(Tp^{Cpr})$_2$] (**9**): White crystals; mp 279−280 °C. IR: BH 2435 cm^{-1}. ^1H NMR: 7.45 (d, 1 H, H-5), 5.44 (d, 1 H, H-4), 1.05 (sept, 1 H, tertiary H), 0.33 (dt, 2 H, cyclopropyl), 0.30 (dt, 2 H, cyclopropyl) ppm. Anal. Calcd for $C_{36}H_{42}BN_{12}Zn$: C, 59.3; H, 5.76; N, 23.1. Found: C, 59.1; H, 5.87; N, 22.8.

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Table 1. Crystallographic Data for **4**, **6**, and **7**

	4	**6**	**7**
formula	$C_{36}H_{38}B_2FeN_{12}$	$C_{51.5}H_{62}B_2FeN_{16}$	$C_{45}H_{44}B_2CoN_{12}$
fw	716.3	982.6	833.47
space group	*C*2/*m*	*P*$\bar{1}$	*P*2$_1$/*c*
a, Å	15.136.(7)	12.239(2)	10.509(3)
b, Å	13.031(6)	12.369(2)	35.514(6)
c, Å	10.219(4)	18.031(4)	11.388(5)
α, deg		90.62(3)	
β, deg	112.48(3)	104.41(3)	91.03(2)
γ, deg		106.68(3)	
V, Å^3	1862(2)	2522.5(8)	4249(2)
Z	2	2	2
cryst color/habit	colorless block	colorless block	pink block
D(calcd), g cm^{-3}	1.277	1.294	1.303
μ(Mo Kα), cm^{-1}	4.48	3.53	4.52
temp, °C	23(2)	23(2)	−30(2)
radiation	Mo Kα (*λ* = 0.710 73 Å)		
R(*F*), %	5.04[a]	4.84[a]	7.46[b]
R(*wF*), %	6.89[a]	6.54[a]	16.42[b,c]

[a] Quantity minimized = $\sum\Delta^2$; R = $\sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |F_o - F_c|$. [b] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [c] $R(wF^2)$, %.

[Zn(pz*Tp^{Cpr})$_2$] (**10**): White crystals; mp 160−162 °C. ^1H NMR: 7.14 (d, 1 H, H-5), 5.70 (d, 1 H, H-4), 1.33 (sept, 1 H, tertiary H), 0.61 (db, 2 H, cyclopropyl), 0.45 (db, 2 H, cyclopropyl) ppm.

[Zn(Tp^{Cpr})NCS] (**11**) was prepared by vigorously stirring a chloroform solution of **1** with aqueous zinc perchlorate containing excess potassisum thiocyanate for 2 h. The organic layer was separated, filtered through Celite, and chromatographed on alumina. The product was obtained as white crystals in 73% yield; mp 188−190 °C. IR: BH 2509, NCS 2063 cm^{-1}. ^1H NMR: 7.49 (d, 1 H, H-5), 5.70 (d, 1 H, H-4), 2.12 (sept, 1 H, tertiary H), 1.10 (db, 2 H, cyclopropyl), 0.67 (db, 2 H, cyclopropyl) ppm. Anal. Calcd for $C_{19}H_{22}BN_7SZn$: C, 50.0; H, 4.82; N, 21.2. Found: C, 49.7; H, 5.02; N, 21.0.

[Mo(Tp^{Cpr})(CO)$_2$(η^3-CH$_2$CMeCH$_2$) (12). This complex was prepared by stirring an equimolar mixture of **1** and [(MeCN)$_2$Mo(CO)$_2$-(η^3-CH$_2$CMeCH$_2$)],[10] in methylene chloride for 2 h at room temperature. The resulting slurry was filtered to remove TlCl (which had a tendency to pass through alumina), and the filtrate was chromatographed on alumina, collecting the yellow band. Solvent evaporation produced a residue, which was recrystallized from a toluene/octane mixture. Mp: darkens from 195 °C, 218−220 °C (dec). IR: BH 2464; CO 1929, 1834 cm^{-1}. ^1H NMR: 7.45 (d, 2 H, H-5), 7.08 (d, 1 H, H-5), 5.64 (d, 2 H, H-4), 5.56 (d, 1 H, H-4), 4.25 (s, 2 H, *syn*), 3.08(sept, 1 H, tertiary H), 2.53 (sept, 2 H, tertiary H) 1.42 (s, 2 H, *anti*), 1.22 (m, 4 H, cyclopropyl), 1.19 (s, 3 H, Me), 1.15 (m, 2 H, cyclopropyl), 0.90 (m, 4 H, cyclopropyl), 0.71 (m, 2 H, cyclopropyl) ppm. Anal. Calcd for $C_{24}H_{29}BMoN_6O_2$: C, 53.3; H, 5.37; N, 15.6. Found: C, 3.5; H, 5.48; N, 15.4.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were selected and mounted on the tip of a glass fiber with epoxy cement. The data for **7** were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector, while for **4** and **6** the datawere collected using a scintillation detector.

The photographic and diffraction data for **4** and **7** indicated a monoclinic crystal system and a *C*-centered lattice for **4**, and no evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **6**. The *E*-statistics, along with the presence of a molecular 2-fold axis and a mirror plane in **4**, suggested the centrosymmetric space group *C*2/*m*; the *E*-statistics suggested the centrosymmetric space group, *P*$\bar{1}$ for **6**; the systematic absences in the diffraction data were uniquely consistent with the reported space group for **7**. Solution in the respective space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. No absorption corrections were required because there was

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less than a 10% variation in the integrated Ψ-scan intensity data. The molecule in **4** is located on a 2-fold axis and a mirror plane, with the carbon atoms C(8), C(9), and C(11) of the unique cyclopropyl groups disordered over the 2-fold axis. The asymmetric unit of **6** consists of two independent, but chemically equivalent, half molecules and a toluene solvent molecule, each of which is on an inversion center with the carbon atoms of the toluene equally disordered over the inversion center. All non-hydrogen atoms were refined with anisotropic displacements parameters, except for the carbon atoms of toluene in **6**, which were refined isotropically and fixed as a rigid planar group. The hydrogen atoms on both of the unique cyclopropyl groups of **4** and on the toluene molecule of **6** were omitted. All other hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL PLUS (version 4.2) of the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

The ligand Tp^{Cpr} was synthesized in the usual fashion by heating the new 3-cyclopropylpyrazole with KBH_4 and was purified by conversion to the Tl salt, **1**. This salt has an unexpected tetrameric solid-state structure containing a tetrahedron of Tl atoms capped at each apex with a Tp^{Cpr} ligand, thus placing each Tl in an octahedral environment—a structure unique among all the known $[Tl(Tp^x)]$ salts.[8] The ligand Tp^{Cpr} did not form stable tetrahedral $[M(Tp^{Cpr})(X)]$ complexes; attempts to prepare them with first-row divalent transition metals (Co, Ni, Fe, Cu) resulted only in the isolation of the octahedral $[M(Tp^{Cpr})_2]$ species. Only with Zn(II) was it possible to isolate the tetrahedral complex $Tp^{Cpr}ZnNCS$, **11**, by treating the ligand with a large excess of $Zn(NCS)_2$, prepared in situ. Even then, some $[Zn(Tp^{Cpr})_2]$ was still formed as a minor component, although it could be removed by fractional recrystallization. The octahedral complexes $[M(Tp^{Cpr})_2]$, formed with Co(II), Ni(II), Fe(II), and Cu(II), contained unrearranged Tp^{Cpr} ligands. This was confirmed by the well-resolved ^1H NMR spectrum of the paramagnetic $[Co(Tp^{Cpr})_2]$ complex, **3**, showing only one type of cyclopropylpyrazolyl group present, and consistent with the cyclopropyl substituent being only in the 3-position. The peaks were sharp and well-separated, with the tertiary proton at −119 ppm, the "near" and "far" (with respect to the Co atom) cyclopropyl protons at −31.6 and −28.5, respectively, while the 4-H, 5-H, and BH peaks were at 45.2, 83.4, and 111 ppm, as is typical for other $[Co(Tp^x)_2]$ complexes. The analogous Ni, Cu, and Fe complexes had IR spectra almost identical to the Co complex and were, thus, isomorphous.

The ligand $[Tp^{Cpr}]^-$ also reacts with $[(MeCN)_2Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$, producing the complex $[Mo(Tp^{Cpr})(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$, **12**, which has a stereochemically rigid structure with the (Cpr)pz groups appearing as 2:1 patterns in the sharp ^1H NMR spectrum.

Additional details of the ligand were obtained from the structures of $[Fe(Tp^{Cpr})_2]$, **4**, and $[Fe(pz*Tp^{Cpr})_2]$, **6**, established by X-ray crystallography (Figures 1 and 2). They show unrearranged ligands, with six cyclopropyl groups somewhat disordered, all with their methylene groups turned away from the metal. Unlike 3-isopropyl groups, six 3-cyclopropyl substituents are easily accommodated in the equatorial belt of the molecule. The Fe−N bond lengths in both **4** and **6** are an average of 2.190(3) Å; in **4** all Fe−N bonds are equal while in **6** they range from 2.170(3) to 2.218(2) Å due to reduced symmetry, which arises from the presence of the fourth 3-cyclopropylpyrazolyl substituent on boron. In comparison, octahedral Fe(II) complexes containing no 3-substituents on the Tp ligand have much shorter Fe−N bond lengths: in $[Fe(Tp)_2]$,[11] $[Fe(PhTp)_2]$,[12] and $[Fe(pzTp)_2]$[12] they are 1.971(5) Å—again, the value is an average for the complexes containing a non-hydrogen substituent on boron. Thus, in terms of Fe−N bond lengths, **4** and **6** are more similar to $[Fe(Tp^{Me2})_2]$, where the Fe−N bond lengths are 2.172(4) Å. As expected, the Fe(III) complex, $[Fe(Tp^{Me2})_2]^+$, contains much shorter Fe−N bonds, 1.966(3) Å, as compared with its Fe(II) analog,[13] as does $[Fe(Tp^{Me})_2]^+$ (1.956(6) Å)[14] and $[Fe(Tp)_2]^+$ (1.956(4) Å).[15]

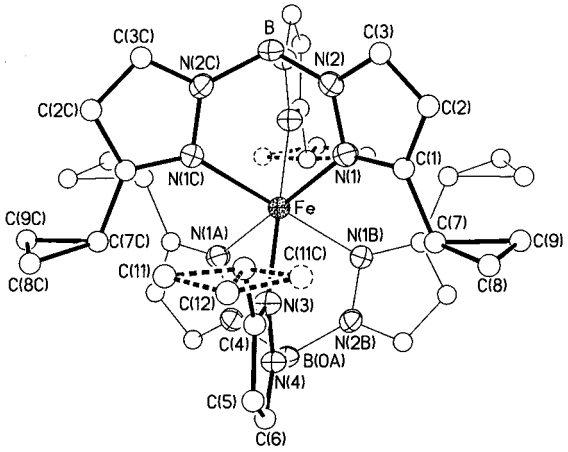

Figure 1. ORTEP plot of the structure of $[Fe(Tp^{Cpr})_2]$, **4**. C(11) is disordered by the crystallographic mirror plane as shown. Unlabeled pyrazolyl ring atoms are labeled using the same scheme as the labeled pyrazolyl ring atoms. Carbon atoms are shown as spheres, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 30% probability.

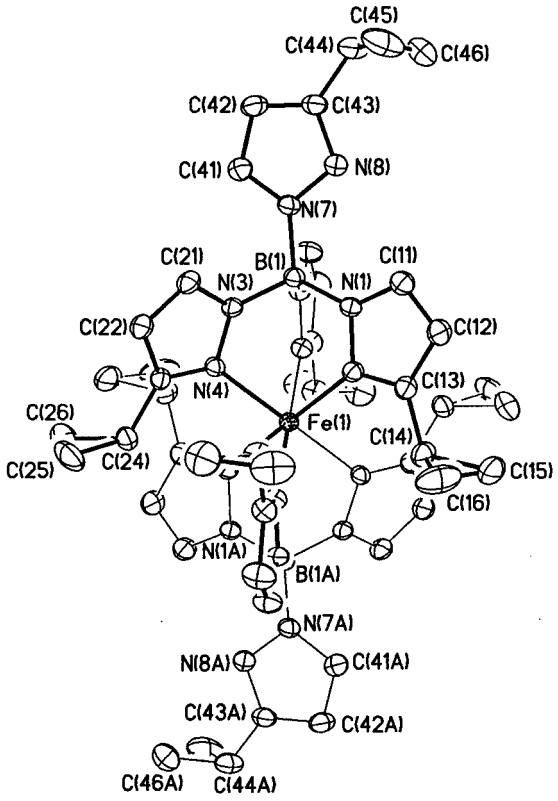

Figure 2. ORTEP plot of the structure of $[Fe(pz*Tp^{Cpr})_2 \cdot 0.5toluene]$, **6**. Only one of the two independent molecules is shown. The solvent molecule and the hydrogen atoms are omitted for clarity. Unlabeled pyrazolyl ring atoms are labeled using the same scheme as the labeled pyrazolyl ring atoms. Thermal ellipsoids are at 30% probability.

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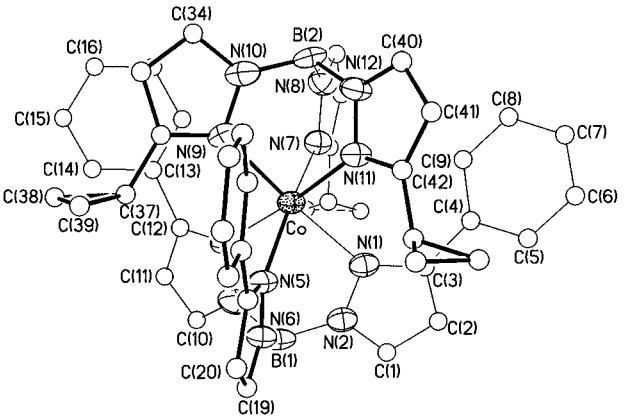
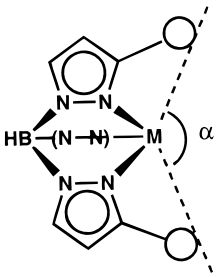


Figure 3. ORTEP plot of the structure of [Fe(Tp^{Cpr})(Tp^{Ph})], **7**. Unlabeled pyrazolyl ring atoms are numbered using the same scheme as the labeled pyrazolyl ring atoms. Carbon atoms are shown as spheres, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 30% probability.

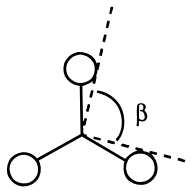
The greatly reduced spatial demand of the cyclopropyl versus isopropyl group as a 3-substituent was also evidenced in the heteroleptic complexes [Co(Tp^{Cpr})(Tp^{Ph})], **7**, and [Co(Tp^{Cpr})(Tp^{An})], **8**, prepared from **1** and [Co(Tp^{Ph})(NCS)] and [Co(Tp^{An})(NCS)], respectively. In both complexes, the Tp^{Ar} ligand is clearly *N*,*N*,*N*-tridentate, as indicated by ^{1}H NMR which showed all three 3-Arpz groups to be identical. This was confirmed further by an X-ray crystallographic structure determination for **7** (Figure 3), which showed the Tp^{Ph} ligand coordinating through all three of its N atoms. The molecule has Co in an octahedral environment, the Co−N distances averaging 2.121(6) Å for Tp^{Cpr} and 2.223(6) Å for Cp^{Ph}, with one phenyl ring being almost coplanar with the pz plane (a twist of 4.7°) and the other two twisted by 44° about the pz-Ph bond. The B−Co −B sequence is not colinear, with Co being about 5° off the B−B axis. The accommodation of three phenyls and three cyclopropyl groups in the equatorial belt of the molecule contrasts with the analogous [Co($Tp^{iPr,4Br}$)(Tp^{Ph})] complex, where only two of the three 3-phenylpz groups are able to coordinate to Co, the sixth coordination site being occupied by an agostic B−H−Co bond.[16]

Another clear difference in the coordination behavior between scorpionate ligands with 3-isopropyl and 3-cyclopropyl substitutents was demonstrated by the corresponding $[B(pz^*)_4]^-$ species. The ^{1}H and ^{13}C NMR spectra of **2** showed all pz* groups to be identical, implying either a rapid exchange of the coordinated and uncoordinated pz* groups or this salt being dissociated in chloroform and existing there as an ion pair. While with [pz*Tp^{iPr}]$^-$ the homoleptic complexes [M(pz*Tp^{iPr})$_2$] of the first-row transition metals are invariably tetrahedral and of dynamic D_{2d} symmetry with the ^{1}H NMR showing pz* groups in a 2:2 pattern, the [M(pz*Tp^{Cpr})$_2$] complexes are octahedral and of local D_{3d} symmetry with the pz* groups in 3:1 patterns. There was no evidence for exchange of the coordinated and uncoordinated 3-(Cpr)pz groups, as clearly established from the NMR spectrum of [Co(pz*Tp^{Cpr})$_2$], **5**, in which the three coordinated pz* groups were all identical but different from the uncoordinated fourth pz* group, all the corresponding peak sets appearing as 3:1 patterns. The peaks of intensity 3 corresponded closely to those found in [Co(Tp^{Cpr})$_2$], while those of the uncoordinated 3-(Cpr)pz exhibited smaller shifts, commensurate with their greater distance from the Co center. In the case of the tetrahydrophilic Zn(II), all 3-(Cpr)pz groups in both [Zn(Tp^{Cpr})$_2$], **9**, and [Zn(pz*Tp^{Cpr})$_2$], **10**, were identical in the NMR spectra, implying rapid exchange of the coordinated and uncoordinated groups. This sharply contrasts with the NMR spectrum of [Zn(pz*Tp^{iPr})$_2$], where the two coordinated and two uncoordinated pz* rings are not identical and do not exchange, 2:2 peak patterns being observed.

In order to quantify the difference in the steric hindrance between the 3-isopropyl and 3-cyclopropyl groups in Tp ligands, the cone and wedge angles, defined as shown below, were recalculated for a series of representative Tp^x complexes.



Cone angle = 360°- α



Wedge angle = β

(View down the M-B axis)

Table 2. Cone and Wedge Angles for Complexes of Tp^R Ligands Based On Either H or C

compound	cone angle H/(C) (deg)		wedge angle H/(C) (deg)	
[Co(Tp)$_2$]	210	214	68[a]	
[Fe(Tp^{Me})$_2$]	248	247	63	56
[Ni($Tp^{iPr,4Br}$)(Tp)]	257	239	37	41
Tp derived from **3**	213	219	54[a]	
[Co($Tp^{iPr,4Br}$)NCS]	278	280	27	18
[Fe(Tp^{Cpr})$_2$]	252	233	68	57
[Co(Tp^{tBu})(NCS)]	268	284	17	14

[a] These values were based on the van der Waals radius of carbon.

While, ideally, we wanted to base these values on octahedral Co(II) complexes, they were not available for all Tp^x ligands, so Co, Ni, and Fe complexes were used in some cases. Also, since octahedral complexes derived from Tp^{iPr} contain rearranged 3,3,5-ligands, values from the heteroleptic complex [Ni($Tp^{iPr,4Br}$)(Tp)] were taken. In addition, cone and wedge angles for two tetrahedral complexes are provided. It should be noted that the distinction between octahedral and tetrahedral complexes is not just one of coordination numbers. In the tetrahedral complex [Co($Tp^{iPr,4Br}$)(NCS)] the isopropyl group straddles the pz plane with its methyl groups pointed *toward* the metal, while in [Ni($Tp^{iPr,4Br}$)(Tp)] (and in other octahedral complexes of the Tp^{iPr}-type ligand) the methyls are pointed *away* from the metal. This results in the "tetrahedral" $Tp^{iPr,4Br}$ having a significantly larger cone angle and smaller wedge angle (278° vs 257° and 27° vs 63°), respectively) than the "octahedral" one.

The calculations were based on both the outermost hydrogens of the R group, the one that forms the largest B−M−H(or C) angle to maximize the cone angle of the Tp^x ligand, and also on the corresponding carbons, using the average van der Waals radius of a hydrogen atom and of a methylene group, respectively. As given in Table 2, the Tp^{Cpr} ligand has a much larger cone angle than the parent Tp but their wedge angles are remarkably similar. At the same time, the cone angle of Tp^{Cpr} is only slightly smaller than that of $Tp^{iPr,4Br}$ and slightly larger than that of Tp^{Me}, yet its wedge angle is much larger than that

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(15) Cho, S.-H.; Whang, D.; Kim, K. *Bull. Korean Chem. Soc.* **1991**, *12*, 107.
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of $Tp^{iPr,4Br}$; this difference is borne out by the coordination chemistry of these two ligands. It is also noteworthy that the cone and wedge angles of the same ligand, $Tp^{iPr,4Br}$, differ substantially when taken from an octahedral or a tetrahedral complex, with larger steric hindrance being manifested in the tetrahedral complex.

Conclusions

One can conclude that converting a 3-isopropyl substituent in Tp ligands to 3-cyclopropyl results in a major decrease of the steric hindrance through enlargement of the wedge angle, to the point that the coordination behavior of the ligand approximates that of Tp^{Me}. At the same time, the plurality of cyclopropyl groups on the periphery of the molecule renders Tp^{Cpr} derivatives more lipophilic and soluble than their Tp^{Me} analogs.

Supporting Information Available: Tables of detailed crystallographic data, atomic position parameters, and bond lengths and angles and ORTEP diagrams of **4**, **6**, and **7** (26 pages). Ordering information is given on any current masthead page.

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