

## Coordination Chemistry of Novel Scorpionate Ligands Based on 3-Cyclohexylpyrazole and 3-Cyclohexyl-4-bromopyrazole

Swiatoslaw Trofimenko,\* Arnold L. Rheingold, and Louise M. Liable Sands

Department of Chemistry and Biochemistry, The University of Delaware, Newark, Delaware 19716

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The ligands [hydrotris(3-cyclohexylpyrazol-1-yl)borate,  $[\text{Tp}^{\text{Cy}}]^-$ , tetrakis(3-cyclohexylpyrazol-1-yl)borate,  $[\text{pz}^{\text{o}}\text{Tp}^{\text{Cy}}]^-$ , and hydrotris(3-cyclohexyl-4-bromopyrazol-1-yl)borate,  $[\text{Tp}^{\text{Cy,4Br}}]^-$  were synthesized and characterized as their TI(I) derivatives. They were converted to a variety of tetrahedral LMX and octahedral LML' complexes, as well as to the dinuclear nickel carbonate complex  $[\text{Ni}(\text{Tp}^{\text{Cy}})]_2(\text{CO}_3)$ , **4**, and the compound  $\text{Ni}[\text{Tp}^{\text{Cy,4Br}}][\text{pz}^{\text{Cy,4Br}}]_3(\text{H})_2$ , **5**. The structures of  $\text{Co}[\text{Tp}^{\text{Cy}}]\text{Cl}$ , **1**,  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]\text{Cl}$ , **2**,  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]\text{NCS}$ , **3**,  $[\text{Ni}(\text{Tp}^{\text{Cy}})]_2(\text{CO}_3)$ , **4**,  $\text{Ni}[\text{Tp}^{\text{Cy,4Br}}][\text{pz}^{\text{Cy,4Br}}]_3(\text{H})_2$ , **5**, and  $\text{Mo}[\text{Tp}^{\text{Cy}}](\text{CO})_2(\eta^3\text{-methallyl})$ , **6**, were determined by X-ray crystallography. The structures of paramagnetic heteroleptic complexes  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}]$ ,  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}^*]$ ,  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}][\text{Tp}]$ , and  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}][\text{Tp}^*]$  were established by NMR. The homoleptic compounds  $\text{Co}[\text{Tp}^{\text{Cy}}]_2$  and  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]_2$  rearrange thermally to  $\text{Co}[\text{Tp}^{\text{Cy}}]_2$  and to  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]_2$ , respectively, containing one 5-cyclohexyl group/ligand.

### Introduction

The rich and differentiated chemistry derived from 3-R-substituted homoscorpionate (tris(pyrazolyl)borate) ligands,  $\text{Tp}^{\text{R}}$ ,<sup>1</sup> where the R group is of intermediate steric hindrance, such as isopropyl,  $\text{Tp}^{\text{iPr}}$ ,<sup>2</sup> along with its variants  $\text{Tp}^{\text{iPr,4Br}}$ ,<sup>2</sup>  $\text{Tp}^{\text{iPr,Me}}$ ,<sup>3</sup> and  $\text{Tp}^{\text{iPr}_2}$ ,<sup>4</sup> as well as  $\text{Tp}^{\text{Ph}}$ , including ligands with diverse phenyl substituents<sup>1</sup> and those with a tethered phenyl group,<sup>5</sup> has led us to prepare and examine the new ligands  $\text{Tp}^{\text{Cy}}$ , where R is a cyclohexyl group, along with its 4-bromo analogue,  $\text{Tp}^{\text{Cy,4Br}}$ , and also the tetrakis ligand  $[\text{B}(\text{pz}^{\text{Cy}})_4]^-$  ( $= \text{pz}^{\text{o}}\text{Tp}^{\text{Cy}}$ ). The cyclohexyl substituent, while similar to the isopropyl group in the steric screening effected by its 2,6-methylene groups, has the additional features of providing a substantially larger hydrophobic pocket around the metal. Moreover, the possibility of the pyrazolyl ring being bonded to the cyclohexyl group through either axial or

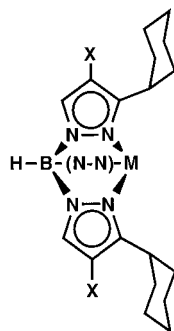
equatorial position could not be discounted. Such features were apt to provide additional fine-tuning of the coordinative behavior of the ligand, modulating accessibility of the coordinated metal to other prospective reaction partners. This would be in marked contrast to the  $\text{Tp}^{\text{CPr}}$  ligand, where the cyclopropyl substituent offered no significant steric screening and the coordination chemistry of  $\text{Tp}^{\text{CPr}}$  resembled very much that of the parent Tp ligand.<sup>6,7</sup> Some  $\text{Tp}^{\text{Cy}}$  complexes, such as  $[\text{Tp}^{\text{Cy}}\text{H}][\text{CuCl}_2]$  and  $[\text{Tp}^{\text{Cy}}\text{Cu}]_2[\mu\text{-CO}_3]$ , have been reported in our earlier preliminary communication,<sup>8</sup> as was, more recently, the formation of  $[\text{Tp}^{\text{Cy}}\text{Cu}][\text{pz}^{\text{Cy}}]_2\text{H}^9$  and of  $\text{Cu}[\text{Tp}^{\text{Cy}}]_2$ .<sup>10</sup> The  $\text{Tp}^{\text{Cy}}$  complex of Cu(I) was found to be an excellent catalyst for cyclopropene formation from acetylenes.<sup>11</sup>

3-Cyclohexylpyrazole, 3-cyclohexyl-4-bromopyrazole, and the homoscorpionate ligands derived therefrom, hydrotris(3-cyclohexylpyrazol-1-yl)borate,  $[\text{Tp}^{\text{Cy}}]^-$ , tetrakis(3-cyclohexylpyrazol-1-yl)borate,  $[\text{pz}^{\text{o}}\text{Tp}^{\text{Cy}}]^-$ , and hydrotris(3-cyclo-

\* To whom correspondence should be addressed. E-mail: trofimen@udel.edu.

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X = H or Br

-(N-N)- is the third, hidden, 3-cyclohexyl-4-(X)-pyrazolyl group

hexyl-4-bromopyrazol-1-yl)borate,  $[\text{Tp}^{\text{Cy},4\text{Br}}]^-$ , were synthesized, and their coordination chemistry was examined in high-spot fashion, with the structures of key complexes being established by NMR and by X-ray crystallography.

### Experimental Section

All chemicals were of the highest commercial reagent grade and were used as received. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls 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.

**Cyclohexyl Methyl Ketone.** Acetophenone was hydrogenated to 1-cyclohexylethanol in a 1 L autoclave, until cessation of hydrogen uptake, using 5% Ru on Alumina as catalyst, at 200 psi hydrogen and 150 °C. The product was obtained quantitatively after vacuum distillation, and its structure was supported by NMR. The “as-prepared” material was catalytically dehydrogenated to cyclohexyl methyl ketone, using as catalyst a mixture in equal proportions of cupric oxide, basic copper carbonate, and calcium hydroxide. A mixture of 200 g of 1-cyclohexylethanol (1.39 mol) and 20 g of the catalyst was heated on an oil bath allowing the temperature to rise slowly. From 180 °C there was a moderate but steady evolution of hydrogen, and the temperature was raised until the liquid refluxed gently. After 24 h there was 36.5 L hydrogen evolved (theory 39 L), and further gas evolution ceased. The pot contents were distilled at atmospheric pressure, collecting 180 g (91%) of material boiling constantly around 180 °C. It had no OH in the IR spectrum and only a very strong CO at 1713  $\text{cm}^{-1}$ . NMR: 2.33 (s, 1H), 2.11 (s 3 H), 1.97 (m 2 H), 1.78 (m, 2 H), 1.67 (m 1 H), complex m 1.14–1.26 (complex m, 5 H) ppm.

**3-Cyclohexylpyrazole.** A mixture of 263 g (2.09 mol) of methyl cyclohexyl ketone and 222 g (3 mol) of ethyl formate was added in one portion to a suspension of 2.09 mol of dry sodium methoxide powder, rapidly stirred in 1.5 L dry toluene. After a short induction period, an exothermal reaction took place and a clear solution was obtained, but on stirring of the mixture for 3 h, a white solid precipitated. It was extracted with 1 L of cold water, and to this extract 2.1 mol of hydrazine hydrate was added, followed by 2.1 mol of acetic acid. After 30 min, ice was added, plus enough NaOH solution to make the mixture basic. An orange oil separated, which was taken up in methylene chloride, filtered through a shallow bed of alumina, stripped, and distilled in vacuo, bp 150°/2.7 Torr. The yield was 205 g (64%). NMR: 7.48 (d, 1 H), 6.05 (d, 1 H), 2.74 (tt, 1 H), 2.03 (d, 2 H), 1.80 (dt, 2 H), 1.72 (d 1 H), 1.41 (sextet, 4 H), 1.25 (m, 1 H) ppm. The NH was not discernible.  $^{13}\text{C}$  NMR:

25.9 (C-4'), 26.1 (C-3',5'), 33.0 (C-2',6'), 36.0 (C-1'), 101.1 (C-4), 134.9 (C-5), 152.2 (C-3). Anal. Calcd for  $\text{C}_9\text{H}_{14}\text{N}_2$ : C, 72.00; H, 9.33; N, 18.7. Found: C, 71.9; H, 9.47; N, 18.7.

**3-Cyclohexyl-4-bromopyrazole.** To a solution of 80 g (0.5 mol) of 3-cyclohexylpyrazole in a mixture of 500 mL of methanol, 50 mL of water, and 5 mL of concentrated HCl was added dropwise 0.5 mol of  $\text{Br}_2$ . After completion of the addition and neutralization with NaOH, the product was extracted with methylene chloride and the extracts were stripped, yielding on standing 105 g (92%) of a solid. After recrystallization from hexane it had mp 84–85 °C.  $^1\text{H}$  NMR: 11.5 (1 H, NH), 7.48 (s, 1 H, H-5), 2.76 (tt, 1 H, tertiary H), 1.7–2.0 (m, 5 H, Cy), 1.2–1.6 (m, 5 H, Cy) ppm.  $^{13}\text{C}$  NMR: 26.1 (C'-1), 26.5 (C'-2), 31.8 (C'-3), 35.5 (C'-4), 91.8 (C-4), 136.9 (C-3) and 148.7 (C-5) ppm. Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{BrN}_2$ : C, 47.2; H, 5.68; N, 12.1. Found: C, 47.0; H, 5.76; N, 12.1.

**Tl[Tp<sup>Cy</sup>].** A mixture of 205 g (1.37 mol) of 3-cyclohexylpyrazole and 12.3 g (0.228 mol) of  $\text{KBH}_4$  was stirred and heated on an oil bath. Hydrogen evolution became brisk around 200 °C. After 24 L of hydrogen was evolved, as measured by a wet-test-meter, excess pyrazole was distilled out in vacuo and the residue solidified. There were still some unreacted  $\text{KBH}_4$  particles present. The residue was dissolved in DMF, filtered, and converted to the Tl salt, which was extracted into chloroform, filtered through alumina, and evaporated. The resulting solid was stirred with methanol, filtered out, and washed with methanol. The dried product was obtained in 100 g (66.2%) yield; mp 142–143 °C. IR: BH 2430  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 7.71 (broadened d, 1 H, H-5), 5.97 (even broader d, 1 H, H-4), 2.77 (very broad m, 1 H), 1.93 (broad s, 2 H), 1.81 (m, 2 H), 1.74 (d, 2 H), 1.40 (quintet, 4 H), 1.25 (tt, 1H) ppm.  $^{13}\text{C}$  NMR: 26.1 (Cy C-4), 26.6 (Cy C-3,5), 34.2 (d,  $J = 51.4$ , Cy C-2,6), 37.6 (d,  $J = 27$ , Cy C-1), 100.9 (C-4), 135.7 (C-5), 159.1 (d,  $J = 47$ , C-3) ppm. Anal. Calcd for  $\text{C}_{27}\text{H}_{40}\text{BN}_6\text{Tl}$ : C, 48.9; H, 6.03; N, 12.7. Found: C, 49.2; H, 6.19; N, 12.6.

**Tl[Tp<sup>Cy,4Br</sup>].** A mixture 105 g (0.46 mol) of 3-cyclohexyl-4-bromopyrazole and 8 g (0.15 mol) of  $\text{KBH}_4$  was refluxed in 400 mL of 4-methylanisole until 10.6 L of hydrogen (theory 11.1 L) was evolved, which took 4 h. The solvent was distilled out in vacuo, and the residue was dissolved in DMF and stirred with an excess of aqueous  $\text{TlNO}_3$  solution. The resulting slurry was diluted with water and was filtered and washed with hot water and with methanol. After drying there was obtained 111 g (82.2%) of a white solid. The product was recrystallized from toluene; mp 239–240 °C. IR: BH, 2434  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 7.22 (s, 1 H, H-5), 2.38 (broad t, 1 H, tertiary H), 1.98–0.94 (broad m, with peaks at 1.4 and 1.0, 10 H, cyclohexyl) ppm.  $^{13}\text{C}$  NMR: 26.1 (Cy C-4), 26.8 (Cy C-3), 32.8 ( $J = 50$ , Cy C-2), 37.3 (Cy C-1), 92.2 (pz C-4), 136.9 (pz C-5), 156.2 (pz C-3) ppm. Anal. Calcd for  $\text{C}_{27}\text{H}_{37}\text{BBr}_3\text{N}_6\text{Tl}$ : C, 36.0; H, 4.11; N, 9.33. Found: C, 36.4; H, 4.28; N, 9.12.

**M[Tp<sup>Cy,4z</sup>]X Complexes (M = Co, Ni, Zn; z = H, Br; X = Cl, I, NCS).** A mixture of  $\text{Tl}[\text{Tp}^{\text{Cy},4z}]$  and an excess of solid  $\text{MX}_2$  was stirred in methylene chloride for several hours at room temperature. The slurry was filtered, and the filtrate was passed through a column of alumina. Evaporation yielded the  $\text{M}[\text{Tp}^{\text{Cy},4z}]\text{X}$  product, which was purified by recrystallization. Yields were in the 75–90% range.

**Co[Tp<sup>Cy</sup>]Cl (1):** blue solid, recrystallized from octane; mp 193–195 °C. IR: BH 2488  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{40}\text{BCoClN}_6$ : C, 58.5; H, 6.27; N, 13.2. Found: C, 58.5; H, 6.37; N, 13.0.

**Co[Tp<sup>Cy</sup>]NCS:** dark blue solid; mp 205–207 °C. IR: BH 2501, NCS 2054  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{40}\text{BCoN}_7\text{S}$ : C, 58.3; H, 6.94; N, 17.0. Found: C, 58.7; H, 7.13; N, 16.9.

**Ni[Tp<sup>Cy</sup>]Cl**: red solid, recrystallized from octane; mp 200–202 °C. IR: BH 2493 cm<sup>-1</sup>. Anal. Calcd for C<sub>27</sub>H<sub>40</sub>BClNi<sub>6</sub>: C, 58.5; H, 6.27; N, 13.2. Found: C, 58.9; H, 6.43; N, 12.9.

**[Ni(Tp<sup>Cy</sup>)<sub>2</sub>(CO<sub>3</sub>)] (4)**. A dichloromethane solution of Ni[Tp<sup>Cy</sup>]Cl was stirred rapidly with an aqueous solution of NaHCO<sub>3</sub> until the red organic layer became green. The layers were separated, and the organic layer was passed through alumina. Evaporation of the eluate yielded a green solid, which was purified by recrystallization from toluene; mp 268–270 °C (dec). IR: BH 2480, CO 1568 cm<sup>-1</sup>. Anal. Calcd for C<sub>55</sub>H<sub>40</sub>B<sub>2</sub>N<sub>12</sub>NiO<sub>3</sub>: C, 63.7; H, 7.71; N, 16.2. Found: C, 64.0; H, 7.89; N, 16.1.

**Zn[Tp<sup>Cy</sup>]Cl**: white solid, recrystallized from octane/toluene; mp 193–195 °C. IR: BH 2487 cm<sup>-1</sup>. NMR: 7.52 (d, 1 H), 5.97 (d, 1 H), 3.00 (tt, 1 H), 1.92 (dd, 2 H), 1.75 (“t”, 3 H), 1.16–1.58 (m, 5 H) ppm. Anal. Calcd for C<sub>27</sub>H<sub>40</sub>BClCoN<sub>6</sub>Zn: C, 52.3; H, 6.46; N, 13.6. Found: C, 51.9; H, 6.22; N, 13.4.

**Zn[Tp<sup>Cy</sup>]I**: white solid, recrystallized from octane/xylene, mp 257–258 °C. IR: BH at 2485 cm<sup>-1</sup>. NMR: 7.50 (d, 1 H), 5.98 (d, 1 H), 3.18 (tt, 1 H), 1.95 (broad d, 2 H), 1.76 (m, 3 H), 1.51 (quartet of triplets, 2 H), 1.30 (quartet of doublets, 2 H), 1.22 (quartet of triplets, 1 H) ppm. Anal. Calcd for C<sub>27</sub>H<sub>40</sub>BCoIN<sub>6</sub>Zn: C, 45.6; H, 5.63; N, 11.8. Found: C, 45.5; H, 5.70; N, 11.7.

**Co[Tp<sup>Cy,4Br</sup>]Cl (2)**: blue solid; mp none up to 300 °C. IR: BH 2496 cm<sup>-1</sup>. It had very high solubility in boiling cyclohexane. Anal. Calcd for C<sub>27</sub>H<sub>37</sub>BBR<sub>3</sub>CoClN<sub>6</sub>: C, 41.0; H, 4.68; N, 10.6. Found: C, 41.4; H, 4.77; N, 10.5.

**Co[Tp<sup>Cy,4Br</sup>]NCS (3)**: blue solid with low solubility in boiling cyclohexane; mp 280–282 °C (dec). IR: BH 2535, NCS 2065 cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>37</sub>BBR<sub>3</sub>CoN<sub>7</sub>S: C, 41.3; H, 4.55; N, 12.1. Found: C, 41.5; H, 4.68; N, 11.8.

**Tp<sup>Cy,4Br</sup>NiCl**. This product, which was red in solution, turned greenish on evaporation and was difficult to purify. The crude material was used in the reaction below.

**Ni[Tp<sup>Cy,4Br</sup>][pz<sup>Cy,4Br</sup>]<sub>3</sub>(H)<sub>2</sub> (5)**. The above crude Ni[Tp<sup>Cy,4Br</sup>]Cl was stirred in a mixture of methylene chloride and methanol. Triethylamine was added, followed by oxalic acid in small portions until the color changed to a greenish one. After addition of much water, the organic layer was separated and passed through alumina. Evaporation of the eluate gave a pale blue-violet solid. It was recrystallized from toluene, yielding blueish-violet crystals; mp 270–272 °C. IR: BH 2458 cm<sup>-1</sup>. Anal. Calcd for C<sub>54</sub>H<sub>75</sub>BBR<sub>6</sub>-N<sub>12</sub>Ni: C, 45.0; H, 5.20; N, 11.7. Found: C, 45.2; H, 5.32; N, 11.5.

**Co[Tp<sup>Cy</sup>]<sub>2</sub> and Co[Tp<sup>Cy\*</sup>]<sub>2</sub>**. To a solution of Ti[Tp<sup>Cy</sup>] in chloroform was added 0.5 equiv of Co(ClO<sub>4</sub>)<sub>2</sub> in a minimum amount of water, followed by half the volume of 2-propanol. A deep purple color appeared immediately. After 30 min twice the volume of water was added, and the separated organic layer was passed through a layer of alumina. The purple residue from evaporation of the solvent was stirred with acetone and was filtered out. IR: BH 2395 cm<sup>-1</sup>. Mp: 150–153 °C; on further heating the color lightens, becoming salmon, and the melt solidifies. Further heating does not melt the solid up to 330 °C. The same yellow product (by IR) was obtained by boiling the purple solid in dodecane. IR: BH 2494 cm<sup>-1</sup>. Anal. Calcd for C<sub>54</sub>H<sub>80</sub>B<sub>2</sub>CoN<sub>12</sub>: C, 66.3; H, 8.19; N, 17.2. Found (purple compound): C, 66.5; H, 8.33; N, 17.0. Found (yellow compound): C, 66.3; H, 8.25; N, 16.9.

**Co[Tp<sup>Cy,4Br</sup>]<sub>2</sub> and Co[Tp<sup>(Cy,4Br)\*</sup>]<sub>2</sub>**. The reaction was run as above, using Ti[Tp<sup>Cy,4Br</sup>], and a purple product was obtained. However, after passage of the purple eluate through alumina and evaporation of the solvent, the purple color started fading within 15 min, and after 2 h a yellow solid was obtained. IR: BH 2448

cm<sup>-1</sup>. Anal. Calcd for C<sub>54</sub>H<sub>74</sub>B<sub>2</sub>Br<sub>6</sub>CoN<sub>12</sub>: C, 44.7; H, 5.10; N, 11.6. Found: C, 45.3; H, 5.47; N, 11.2.

**Zn[Tp<sup>Cy</sup>]<sub>2</sub> and Zn[Tp<sup>Cy\*</sup>]<sub>2</sub>**. These complexes were prepared as in the case of cobalt. The white tetrahedral Zn complex had IR matching that of the Co(II) complex, with BH at 2396 cm<sup>-1</sup>. NMR: 7.30 (d, 1H, H-5), 6.05 (d, 1H, H-4), 2.25 (broad hump, 1H, H-1'), 1.6 (m, 5H) and 1.2 (m, 5H) ppm. Upon heating, the compound melted around 155–157 °C and quickly resolidified. The BH was now at 2484 cm<sup>-1</sup>, and the NMR spectrum was now quite complex and different from the starting material. Anal. Calcd for C<sub>54</sub>H<sub>80</sub>B<sub>2</sub>N<sub>12</sub>Zn: C, 65.9; H, 8.14; N, 17.1. Found (low melting point complex): C, 66.0; H, 8.21; N, 16.9. Found (high melting point complex): C, 65.9; H, 8.28; N, 17.0.

**Co[Tp<sup>Cy</sup>][Tp], Co[Tp<sup>Cy</sup>][Tp\*], Co[Tp<sup>Cy,4Br</sup>][Tp], and Co[Tp<sup>Cy,4Br</sup>][Tp\*]**. These heteroleptic complexes were prepared by stirring an equimolar mixture of the appropriate Co[Tp<sup>x</sup>]Cl and Ti[Tp<sup>y</sup>] components in methylene chloride at room temperature for several hours. The resulting slurry, which was sometimes still blue and sometimes peach-colored, was filtered through Celite, and the filtrate was chromatographed on alumina, collecting the yellowish-orange eluate. After evaporation of the solvent, the residue was recrystallized several times from toluene, to remove the impurities which included unreacted starting materials and the homoleptic Co[Tp]<sub>2</sub> or Co[Tp\*]<sub>2</sub> complexes. The purification was continued until the characteristic peaks of Co[Tp]<sub>2</sub> or Co[Tp\*]<sub>2</sub> were no longer present in the NMR spectra. The yields averaged 40–60%.

**Co[Tp<sup>Cy</sup>][Tp]**: pale yellow solid; mp 301–302 °C. IR: BH 2471 cm<sup>-1</sup> with a lower-frequency shoulder. <sup>1</sup>H NMR: 117.5 (1 H, BH), 114.5 (1 H, BH'), 91.8 (3 H, H-5), 81.7 (3H, H-5'), 43.8 (3 H, H-4), 41.6 (3H, H-4'), -6.6 (3H, Cy 4-H axial), -13.2 (3H, Cy 4-H equatorial), -13.7 (12 H, Cy H-3 axial and equatorial), -29.6 (6 H, Cy H-2 axial), -55.4 (6 H, Cy H-2 equatorial), -103.8 (3 H, H-3), -130.2 (3H, Cy H-1) ppm. Anal. Calcd for C<sub>36</sub>H<sub>50</sub>-B<sub>2</sub>CoN<sub>12</sub>: C, 59.1; H, 6.84; N, 23.0. Found: C, 59.0; H, 6.98; N, 22.9.

**Co[Tp<sup>Cy</sup>][Tp\*]**: yellow-orange solid; mp 254–256 °C. IR: BH 2518 (Tp\*) and 2474 (Tp<sup>Cy</sup>) cm<sup>-1</sup>. <sup>1</sup>H NMR: 101 (1 H, BH), 98 (1 H, BH'), 71.5 (3 H, H-5), 49.4 (3 H, H-5'), 44.3 (3 H, H-4'), 41.2 (9 H, 5-Me), -5.9, 3 H, Cy H-4, axial), -10.8 (9 H, Cy H-4 equatorial + H-3 equatorial), -12.8 (6 H, Cy H-3, axial), -24.7 (6 H, Cy H-2 axial), -42.4 (6 H, Cy H-2, equatorial), -71.8 (9 H, 3-Me), -104.9 (3 H, Cy H-1) ppm. Anal. Calcd for C<sub>42</sub>H<sub>62</sub>B<sub>2</sub>-CoN<sub>12</sub>: C, 61.8; H, 7.61; N, 20.6. Found: C, 61.7; H, 7.83; N, 20.2.

**Co[Tp<sup>Cy,4Br</sup>][Tp]**: dark yellow solid; mp 304–305 °C (dec). IR: BH 2458 cm<sup>-1</sup> with a higher-frequency shoulder. NMR: 113 (1H, BH), 114 (1 H, BH'), 90.4 (3 H, H-5), 88.4 (3 H, H-5'), 43.1 (3 H, H-4), -6.1 (3 H, Cy H-4 axial), -13.1 (3 H, Cy H-4 equatorial), -13.3 (6 H, Cy H-3 equatorial), -13.7 (6 H, Cy H-3 axial), -28.6 (6 H, Cy H-2 axial), -55.7 (6 H, Cy H-2 equatorial), -102.7 (1 H, Cy H-1) and -135 (3 H, H-3) ppm. Anal. Calcd for C<sub>36</sub>H<sub>47</sub>BBR<sub>3</sub>CoN<sub>6</sub>: C, 44.6; H, 4.86; N, 17.4. Found: C, 44.9; H, 5.08; N, 17.2.

**Co[Tp<sup>Cy,4Br</sup>][Tp\*]**: orange solid; mp 261–262 °C. IR: BH 2517 (Tp\*) and 2450 (Tp<sup>Cy,4Br</sup>) cm<sup>-1</sup>, both of equal intensity. <sup>1</sup>H NMR: 101 (1 H, BH), 97 (1 H, BH'), 77.8 (3 H, H-5), 52.4 (3 H, H-4), 42.5 (9 H, Me-5), -5.4 (3 H, Cy H-4 axial), -10.7 (9-H, Cy H-4 equatorial plus Cy H-3 equatorial), -12.7 (6 H, Cy H-3 axial), -23.8 (6 H, Cy H-2 axial), -42.5 (6 H, Cy H-2 equatorial), -70.7 (9 H, 3-Me), -111.8 (3 H, Cy H-1) ppm. Anal. Calcd for C<sub>42</sub>H<sub>59</sub>-BBR<sub>3</sub>CoN<sub>12</sub>: C, 47.9; H, 5.61; N, 16.0. Found: C, 47.8; H, 5.70; N, 15.8.

**Table 1.** Crystal, Data Collection, and Refinement Parameters

	1	2	3	4	5	6
formula	C <sub>27</sub> H <sub>40</sub> BClCoN <sub>6</sub>	C <sub>27</sub> H <sub>37</sub> BBBr <sub>3</sub> ClCoN <sub>6</sub>	C <sub>28</sub> H <sub>37</sub> BBBr <sub>3</sub> CoN <sub>7</sub> S	C <sub>55</sub> H <sub>80</sub> B <sub>2</sub> N <sub>12</sub> Ni <sub>2</sub> O <sub>3</sub>	C <sub>61</sub> H <sub>80</sub> BBBr <sub>6</sub> N <sub>12</sub> Ni	C <sub>33</sub> H <sub>47</sub> BMoN <sub>6</sub> O <sub>2</sub>
fw	553.8	790.55	813.18	1096.35	1530.35	1096.35
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pnma</i>	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.228(2)	18.284	18.9317(11)	12.8778(7)	13.649(4)	9.479(3)
<i>b</i> , Å	16.690(4)	15.873(2)	15.6134(9)	12.9667(7)	18.566(6)	14.041(4)
<i>c</i> , Å	16.873(3)	10.5741(14)	10.9964(6)	20.4134(12)	26.411(8)	14.375(6)
$\alpha$ , deg				85.2880(10)	87.92(2)	69.50(3)
$\beta$ , deg	93.187(16)			76.3410(10)	88.39(2)	80.32(3)
$\gamma$ , deg				62.3490(10)	88.69(2)	71.00(3)
<i>V</i> , Å <sup>3</sup>	2875.7(1)	3068.7(7)	3250.4(3)	2935.5(3)	6684(4)	1961(2)
<i>Z</i> , <i>Z'</i>	4, 1	4, 1/2	4, 1/2	2, 1	4, 2	2, 1
cryst color, habit	blue cube	blue needle	blue needle	green needle	blue block	yellow block
<i>D</i> (calc), g cm <sup>-3</sup>	1.279	1.711	1.662	1.242	1.521	1.302
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	7.16	45.81	43.11	6.93	39.23	4.23
temp, K	295(2)	173(2)	173(2)	173(2)	293(2)	255(2)
diffractometer	Siemens P4	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD	Siemens P4/CCD	Siemens P4
radiation			Mo K $\alpha$ ( $\lambda$ = 0.71073 Å)			
<i>R</i> ( <i>F</i> ), % <sup>a</sup>	4.76	3.84	5.44	4.21	8.35	3.31
<i>R</i> ( <i>wF</i> <sup>2</sup> ), % <sup>a</sup>	5.25	6.01	8.36	7.72	14.34	3.73

<sup>a</sup> Quantity minimized =  $R(wF^2) = \sum[\omega(F_o^2 - F_c^2)^2] / \sum[wF_o^2]^2$ ;  $R = \sum\Delta / \sum(F_o)$ ,  $\Delta = |(F_o - F_c)|$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$ .

**Mo[TP<sup>Cy</sup>](CO)<sub>2</sub>( $\eta^3$ -methallyl) (6).** This complex was obtained by stirring equimolar quantities of Ti[TP<sup>Cy</sup>] and Mo(MeCN)<sub>2</sub>(Cl)-(CO)<sub>2</sub>( $\eta^3$ -methallyl)<sup>12</sup> in methylene chloride for 1 h. The slurry was filtered through Celite to remove TiCl<sub>4</sub>, and the filtrate was evaporated yielding a yellow solid, which was recrystallized from heptane and turns orange around 135 °C; mp (dec) 203–205 °C. IR: BH 2468, CO 1934, 1842 cm<sup>-1</sup>. NMR: 7.52 (d, 2 H, H-5), 7.07 (d, 1 H, H-5), 6.02 (d, 2 H, H-4), 5.80 d, 1 H, H-4), 3.98 (tt, 1 H), 3.44 (tt, 2 H), 3.26 (s, 2 H, *syn*), 1.2–2.1 (m, 15 H, including singlets at 1.42 (3 H, Me) and 1.19 (2 H, *anti*)) ppm. Anal. Calcd for C<sub>33</sub>H<sub>47</sub>BMoN<sub>6</sub>O<sub>2</sub>: C, 59.5; H, 7.06; N, 12.6. Found: C, 59.9; H, 7.21; N, 12.3.

**K[pz<sup>o</sup>TP<sup>Cy</sup>].** A mixture of 24 g of 3-cyclohexylpyrazole and 1.7 g of KBH<sub>4</sub> (molar ratio 4.8:1) was stirred and heated until cessation of hydrogen evolution, which occurred at 280–290 °C, at which point the theoretical amount (3.3 L) had evolved and the flask contents were partially solidified. The partly cooled residue was stirred and boiled with heptane, and the resulting white slurry was filtered hot, yielding 15.2 g of a white solid. Since the Ti salt could not be obtained crystalline, being too soluble in all solvents, the crude K salt was used to prepare the metal complexes.

**M[pz<sup>o</sup>TP<sup>Cy</sup>]<sub>2</sub> Complexes.** The M[pz<sup>o</sup>TP<sup>Cy</sup>]<sub>2</sub> complexes were synthesized by mixing a THF solution of crude K[pz<sup>o</sup>TP<sup>Cy</sup>] with a concentrated aqueous solution of the appropriate metal perchlorate. After dilution with much water, the products were extracted with methylene chloride and filtered through alumina, and the filtrates were evaporated, followed by trituration of the residue with methanol. The complexes were recrystallized from octane.

**Co[pz<sup>o</sup>TP<sup>Cy</sup>]<sub>2</sub>:** purple solid, decomp from 260 °C. The NMR had two sets of pz<sup>o</sup> groups: one broad; the other relatively sharp. The tertiary H, which is usually broad anyway, was not visible. The broad bands were at (ppm) 69 (1 H), 37 (1 H), -24 (2 H), and -43 (2 H); the sharp ones at 28.7, 15.9, 10.2, 7.9 (2 H), 7.3 (2 H), -4.9 (4 H), and -9.4 (4 H). Anal. Calcd for C<sub>72</sub>H<sub>104</sub>B<sub>2</sub>CoN<sub>16</sub>: C, 67.9; H, 8.17; N, 17.6. Found: C, 67.8; H, 8.24; N, 17.3.

**Ni[pz<sup>o</sup>TP<sup>Cy</sup>]<sub>2</sub>:** fuchsia solid, decomp from 210 °C. Anal. Calcd for C<sub>72</sub>H<sub>104</sub>B<sub>2</sub>N<sub>16</sub>Ni: C, 67.9; H, 8.17; N, 17.6. Found: C, 68.0; H, 8.29; N, 17.5.

**Zn[pz<sup>o</sup>TP<sup>Cy</sup>]<sub>2</sub>:** white solid, mp 272–274 °C. NMR: 7.19 (d, 1 H), 6.16 (d, 1 H), 6.13 (d, 1 H), 5.95 (d, 1 H), 3.64 (quint, 1 H),

1.92 (m, 3 H), 1.64–1.80 (m, 3 H), 1.0–1.5 (m, 14 H) ppm. <sup>13</sup>C NMR: 24.12, 25.92, 26.39, 26.59, 33.11, 33.66, 35.80, 37.79, 102.13, 103.05, 133.79, 141.19, 160.59, 163.67 ppm. Anal. Calcd for C<sub>72</sub>H<sub>104</sub>B<sub>2</sub>N<sub>16</sub>Zn: C, 67.6; H, 8.13; N, 17.5. Found: C, 67.9; H, 8.30; N, 17.4.

### Crystallographic Structural Determination

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of the a fine glass. Data were collected either with a Siemens P4 diffractometer equipped with a serial detector or a Siemens P4/CCD diffractometer, both of which employed graphite-monochromated Mo K $\alpha$  X-radiation ( $\lambda$  = 0.710 73 Å).

The diffraction data for **1–3** are uniquely consistent with the reported space groups and yielded chemically reasonable and computationally stable results of refinement. No symmetry higher than triclinic was observed in the diffraction data of **4–6**. In all three cases the *E*-statistics suggested the centrosymmetric space group option, *P* $\bar{1}$ . All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Structures **2** and **3** reside on crystallographic mirror planes. There are two chemically equivalent but crystallographically independent molecules in the asymmetric unit of **5**. The positions of the borato protons of **1**, **3**, **4**, and **6** were determined from the electron difference map, and the isotropic displacement coefficients were allowed to refine freely. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms, with the exceptions noted, were treated as idealized contributions.

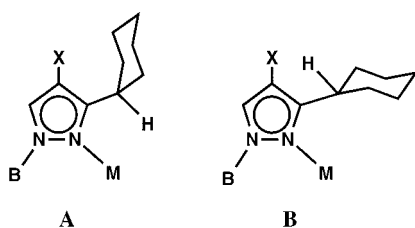
All software and sources of the scattering factors are contained in the SHELXTL program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

### Results and Discussion

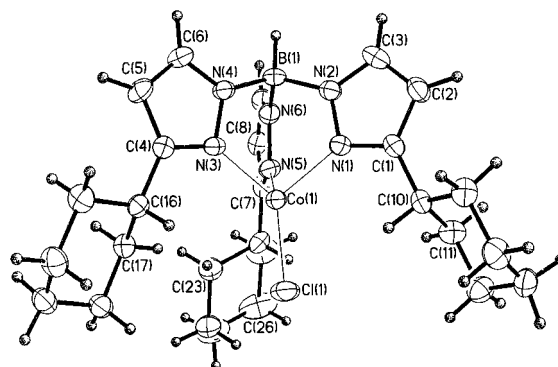
The starting pyrazoles, 3-cyclohexylpyrazole and 3-cyclohexyl-4-bromopyrazole, were prepared in conventional manner and were converted to the respective ligands, TP<sup>Cy</sup> and TP<sup>Cy,4Br</sup>, by the reaction with KBH<sub>4</sub>. This was done either neat or, to avoid possible overheating and decomposition of

(12) Hayter, R. C. *J. Organomet. Chem.* **1968**, *13*, P1–P3.

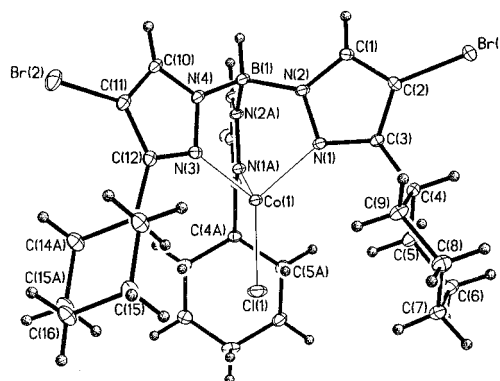
3-cyclohexyl-4-bromopyrazole, as was noted in the case of 3-isopropyl-4-bromopyrazole,<sup>2</sup> in *p*-methylanisole. Both ligands were isolated as their crystalline Tl salts. This contrasts with the analogous pair Tl[Tp<sup>iPr</sup>] and Tl[Tp<sup>iPr,4Br</sup>], where only the latter could be readily obtained in crystalline form. The <sup>13</sup>C NMR spectra of Tl[Tp<sup>Cy</sup>] and Tl[Tp<sup>Cy,4Br</sup>] showed <sup>13</sup>C–<sup>205</sup>Tl coupling to the 2,6-carbons of the cyclohexyl group and in the case of Tl[Tp<sup>Cy</sup>] also to the cyclohexyl C-1 and to the pyrazole C-4. The structures of Tl[Tp<sup>Cy</sup>] and Tl[Tp<sup>Cy,4Br</sup>] were determined by X-ray crystallography.<sup>13</sup> In each, the ligand was  $\kappa^3$ -bonded to Tl. The average Tl–N distances in Tl[Tp<sup>Cy</sup>] and Tl[Tp<sup>Cy,4Br</sup>] were 2.53 and 2.63 Å, respectively, implying slight loosening of the Tl–N bond in the Tl[Tp<sup>Cy,4Br</sup>] complex or some relaxation of the bite angle due to nonbonding interactions of the 4-Br and the cyclohexyl group. The cone angles of Tl[Tp<sup>Cy</sup>] and Tl[Tp<sup>Cy,4Br</sup>] were 281 and 273°, respectively, and thus much larger than the cone angle of Tl[Tp<sup>iPr,4Br</sup>], which was 243°. There was, however, a significant difference in the disposition of the cyclohexyl rings, all of which were bonded to the pyrazole C-3 through the equatorial position. In the case of Tl[Tp<sup>Cy</sup>], two cyclohexyl rings were straddling the pyrazolyl plane so that the tertiary hydrogen was pointed toward the metal, as in **A**, but one was turned the opposite way, as in **B**. This was the first proven instance, at least in the crystal, of the three 3-CHR<sub>2</sub> substituents of a Tp<sup>CHR<sub>2</sub></sup> ligand not being all pointed in the same direction, either toward or away from the coordinated metal. In the structure of Tl[Tp<sup>Cy,4Br</sup>], all three cyclohexyl rings were positioned as in **B**, placing Tl in a symmetric pocket of three cyclohexyl rings. This is exactly as in the structure of the related Tl[Tp<sup>iPr,4Br</sup>] complex, where all isopropyl groups were also in the **B** rotameric orientation.<sup>13</sup>



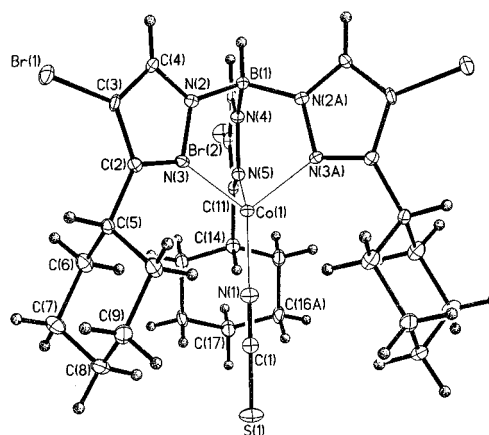
The reaction of Tl[Tp<sup>Cy</sup>] and Tl[Tp<sup>Cy,4Br</sup>] with divalent metal chlorides produced the complexes M[Tp<sup>Cy</sup>]Cl and M[Tp<sup>Cy,4Br</sup>]Cl, respectively (M = Co, Ni, Zn), and the structures of Co[Tp<sup>Cy</sup>]Cl, **1**, and Co[Tp<sup>Cy,4Br</sup>]Cl, **2**, were determined by X-ray crystallography (Figures 1 and 2). They both had the same tetrahedral structure, with very similar Co–N distances (2.03 and 2.04 Å, respectively). This compares with 2.05 Å for the related Co[Tp<sup>iPr,4Br</sup>]Cl complex.<sup>2</sup> One thing that set M[Tp<sup>Cy</sup>]Cl and M[Tp<sup>Cy,4Br</sup>]Cl apart in the crystal structure was again the orientation of the cyclohexyl groups. In the case of Co[Tp<sup>Cy</sup>]Cl all cyclohexyl groups had the tertiary hydrogen pointed at the metal (as in **A**), while in Co[Tp<sup>Cy,4Br</sup>]Cl two tertiary hydrogens were pointing away from the metal (as in **B**) and one at the metal,



**Figure 1.** ORTEP plot of the structure of Co[Tp<sup>Cy</sup>]Cl, **1**. Selected bond distances (Å) and angles (deg): Co–N(1) 2.023(4); Co–N(3) 2.029(4); Co–N(5) 2.025(4); Co–Cl 2.189(2); N(1)–Co–N(3) 92.9(1); N(1)–Co–N(5) 94.8(2); N(5)–Co–N(3) 92.1(1).



**Figure 2.** ORTEP plot of the structure of Co[Tp<sup>Cy,4Br</sup>]Cl, **2**. Selected bond distances (Å) and angles (deg): Co(1)–N(3) 2.028(4); Co(1)–N(1) 2.050(3); Co(1)–N(1)#1 2.050(3); Co(1)–Cl 2.2014(14); N(3)–Co–N(1)#1 93.35(10); N(3)–Co–N(1) 93.35(10); N(1)–Co–N(1)#1 94.19(14).

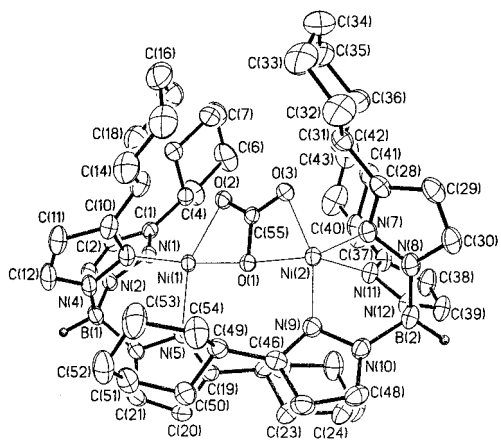


**Figure 3.** ORTEP plot of the structure of Co[Tp<sup>Cy,4Br</sup>]NCS, **3**. Selected bond distances (Å) and angles (deg): Co(1)–N(1) 1.910(6); Co(1)–N(5) 2.005(5); Co(1)–N(3) 2.026(4); Co(1)–N(3)#1 2.026(4); N(1)–Co(1)–N(3) 124.24(13); N(5)–Co(1)–N(3) 94.84(14).

so that the orientation was **ABB**. A similar **ABB** orientation was also found in the case of Co[Tp<sup>Cy,4Br</sup>]NCS, **3** (Figure 3). In this complex the Co–N bond of the NCS ligand deviated by about 5° from the boron–cobalt axis. By way of comparison, in the two structurally characterized tetrahedral species Co[Tp<sup>iPr,4Br</sup>]NCS<sup>2</sup> and Co[Tp<sup>iPr,4Br</sup>]Cl,<sup>14</sup> the

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(14) Olson, M. D.; Rettig, S. J.; Storr, A.; Trotter, J.; Trofimenko, S. *Acta Crystallogr.* **1991**, *C47*, 1543.

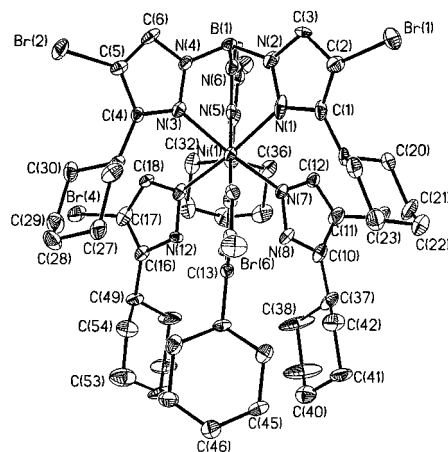


**Figure 4.** ORTEP plot of the structure of  $[\text{Ni}(\text{Tp}^{\text{Cy},4\text{Br}})]_2[\text{CO}_3]$ , **4**. Selected bond distances (Å) and angles (deg): Ni(1)–N(3) 2.020(2); Ni(1)–N(5) 2.029(2); Ni(1)–N(1) 2.033(2); Ni(2)–N(9) 2.028(2); Ni(2)–N(7) 2.035(2); Ni(2)–N(11) 2.038(2); N(1)–O(2) 2.0345(17); N(1)–O(1) 2.0945(16); N(2)–O(3) 2.0313(19); N(2)–O(1) 2.0824(16); N(3)–Ni(1)–N(5) 95.24(9); N(3)–Ni(1)–N(1) 88.62(9); N(1)–Ni(1)–N(5) 89.89(9); N(3)–Ni(1)–O(2) 103.85(8); N(5)–Ni(1)–O(2) 156.37(7); N(1)–Ni(1)–O(2) 104.18(8).

isopropyl group configuration was **BBB**. In all other complexes, octahedral or five-coordinate as, for instance, in  $\text{Co}[\text{Tp}^{\text{Pr},4\text{Br}}][\text{Tp}]$ ,  $\text{Co}[\text{Tp}^{\text{Pr},4\text{Br}}][\text{Tp}^{\text{Ph}}]$ ,  $\text{Co}[\text{Tp}^{\text{Pr},4\text{Br}}][\text{Bp}^{\text{Ph}}]$ , and  $\text{Co}[\text{Tp}^{\text{Pr},4\text{Br}}][\text{Ph}_2\text{Bp}]^{15}$  or in the dimer  $[\text{Ni}[\text{Tp}^{\text{Pr},4\text{Br}}]\text{NCS}]_2$ ,<sup>16</sup> the orientation of the methyl groups was invariably away from the coordinated metal (**AAA**). The same orientation was also found in  $\text{Co}[\text{Tp}^{\text{Pr},\text{Me}}]\text{I}$ ,<sup>17</sup> in  $\text{Cd}[\text{Tp}^{\text{Pr}_2}]\text{I}$ ,<sup>18</sup> and in  $\text{Cu}[\text{Tp}^{\text{Pr}_2}]\text{Cl}$ .<sup>19</sup>

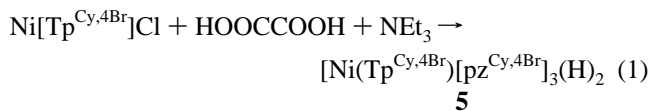
The dinuclear carbonate complex  $[\text{Ni}(\text{Tp}^{\text{Cy}})]_2[\mu\text{-CO}_3]$ , **4**, was obtained via a two-phase reaction of  $\text{Ni}[\text{Tp}^{\text{Cy}}]\text{Cl}$  in dichloromethane with aqueous  $\text{NaHCO}_3$  solution. The structure of this complex (Figure 4) is quite similar to the previously reported copper analogue  $[\text{Cu}(\text{Tp}^{\text{Cy}})]_2[\mu\text{-CO}_3]$ ,<sup>8</sup> although the Ni–O bond lengths are slightly longer, averaging 2.088 Å versus 2.022 Å to the shared oxygen and 2.033 Å versus 1.992 Å to the unshared oxygen. Compared to the related carbonate complex  $[\text{Ni}(\text{Tp}^{\text{Pr}_2})_2](\mu\text{-CO}_3)$ ,<sup>20</sup> the Ni–O distances to the common oxygen atom are longer (average 2.088 Å versus 2.048 Å), while those to the unique oxygens are shorter (average 2.033 Å versus 2.067 Å), pointing to subtle differences in the geometry of these rather similar complexes. By contrast in the respective copper analogues, the  $\text{Tp}^{\text{Cy}}$  complex had the Cu–O distances to the unique oxygen slightly longer (average 2.030 Å versus 2.024 Å), but the distance to the unique oxygens were essentially identical (1.997 Å versus 1.999 Å).

In an attempt to prepare the dinuclear oxalate complex,  $[\text{Ni}(\text{Tp}^{\text{Cy},4\text{Br}})]_2[\text{C}_2\text{O}_4]$ , the crude  $\text{Ni}[\text{Tp}^{\text{Cy},4\text{Br}}]\text{Cl}$  was treated



**Figure 5.** ORTEP plot of the structure of  $\text{Ni}[\text{Tp}^{\text{Cy},4\text{Br}}][\text{pz}^{\text{Cy},4\text{Br}}]_3(\text{H})_2$ , **5**. Selected bond distances (Å) and angles (deg): Ni(1)–N(1) 2.166(9); Ni(1)–N(3) 2.134(7); Ni(1)–N(5) 2.201(8); Ni(1)–N(7) 2.099(7); Ni(1)–N(9) 2.099(8); Ni(1)–N(1) 2.102(8); Ni(1)–N(1)–N(7) 88.1(3); Ni(1)–N(1)–N(11) 89.9(3); N(11)–Ni(1)–N(7) 94.6(3); N(9)–Ni(1)–N(3) 95.3(3); N(7)–Ni(1)–N(3) 175.5(3); N(11)–Ni(1)–N(3) 88.4(3); N(9)–Ni(1)–N(1) 93.6(3); N(1)–Ni(1)–N(7) 89.9(3); N(11)–Ni(1)–N(1) 174.5(3); N(93)–Ni(1)–N(1) 87.0(3); N(9)–Ni(1)–N(5) 177.2(3); N(5)–Ni(1)–N(7) 89.6(3); N(11)–Ni(1)–N(5) 88.8(3); N(3)–Ni(1)–N(5) 87.1(3); N(1)–Ni(1)–N(5) 88.0(3).

with oxalic acid and triethylamine (eq 1). However, the resulting pale violet crystalline product turned out to be the complex **5**, as was established by X-ray crystallography (Figure 5). This reaction had to involve partial degradation of the ligand to generate the pyrazole  $\text{Hpz}^{\text{Cy},4\text{Br}}$ . The above complex may be regarded as the free acid of a novel dianionic ligand  $[\text{Ni}(\text{Tp}^{\text{Cy},4\text{Br}})(\text{pz}^{\text{Cy},4\text{Br}})_3]^{2-}$ , which could be made monoanionic through replacement of nickel(II) with a trivalent ion, such as cobalt(III) or chromium(III). That would make it an all-pyrazole-based analogue of the Kläui ligand,<sup>21</sup>  $[(\text{Cp}^*)\text{Co}[\text{P}(\text{=O})\text{R}_2]^-]$ . Related ligands partially based on pyrazole, such as the anion  $[(\text{Cp}^*)\text{Ir}(\text{pz})_3]^-$ , which was structurally characterized as the dinuclear complex  $[(\text{Cp}^*)\text{Ir}(\text{pz})_3\text{Ni}(\text{Tp}^{\text{Pr},4\text{Br}})]$ ,<sup>22</sup> and  $[(\text{Cp}^*)\text{Ir}(\mu\text{-pz})_3\text{PtMe}_3]$ ,<sup>23</sup> have already been reported, as was  $[(\text{CO})_3\text{Re}(\text{pz})_3]^-$ .<sup>24</sup>



In the molybdenum methallyl complex,  $\text{Mo}[\text{Tp}^{\text{Cy}}](\text{CO})_2(\eta^3\text{-CH}_2\text{CMeCH}_2)$ , **6**, the structure was stereochemically rigid on the NMR time scale, with the inequivalent  $\text{pz}^{\text{Cy}}$  arms appearing as a 2:1 pattern in the NMR spectrum, indicative of  $C_2$  symmetry. The structure (Figure 6) resembled that of the related complex  $\text{Mo}[\text{Tp}^{\text{Ms}}](\text{CO})_2(\eta^3\text{-CH}_2\text{CMeCH}_2)$ .<sup>25</sup>

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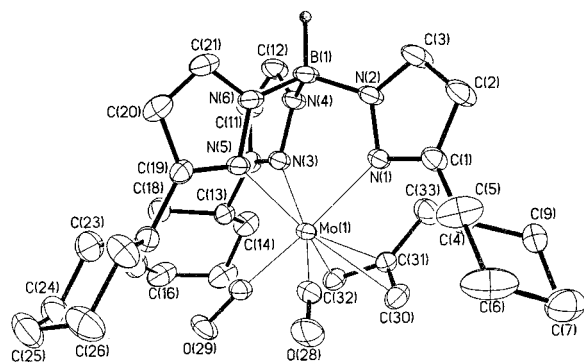
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**Figure 6.** ORTEP plot of the structure of  $\text{Mo}[\text{Tp}^{\text{Cy}}](\text{CO})_2(\eta^3\text{-CH}_2\text{-CMeCH}_2)$ , **6**. Selected bond distances (Å) and angles (deg): Mo–N(1) 2.347(3); Mo–N(3) 2.299(2); Mo–N(5) 2.225(2); Mo–C(30) 2.345(3); Mo–C(31) 2.244(2); Mo–C(32) 2.345(3); N(1)–Mo–N(3) 92.3(1); N(1)–Mo–N(5) 77.5(1); N(5)–Mo–N(3) 75.7(1).

Treatment of  $\text{Tl}[\text{Tp}^{\text{Cy}}]$  or  $\text{Tl}[\text{Tp}^{\text{Cy,4Br}}]$  with  $\text{Co}[\text{ClO}_4]_2$  gave deep purple products, typical of tetrahedral cobalt(II) complexes with  $\text{Bp}^x$  ligands. Evaporation of a solution of  $\text{Co}[\text{Tp}^{\text{Cy}}]_2$  produced a deep purple solid, which was assumed to contain a  $\kappa^2\text{-Tp}^{\text{Cy}}$  ligand and tetrahedral coordination of the cobalt ion. This compound was quite stable in the dry state or in hydrocarbon solvents and had the BH peak at  $2395\text{ cm}^{-1}$ . Upon melting at  $154\text{ }^\circ\text{C}$ , it changed color to peachy yellow, resolidified, and then did not melt up to  $300\text{ }^\circ\text{C}$ . This behavior was indicative of a  $\text{Co}[\text{Tp}^{\text{R}}]_2$  to  $\text{Co}[\text{Tp}^{\text{R}*}]_2$  rearrangement (eq 2), well-precedented in the  $\text{M}[\text{Tp}^{\text{Pr,4X}}]_2$  series, to the octahedral species  $\text{Co}[\text{Tp}^{\text{Cy}*}]_2$ , containing two  $\kappa^3$ -coordinated rearranged ligands, in which one of the  $\text{pz}^{\text{Cy}}$  arms per ligand has the cyclohexyl substituent in the 5-position. One result of this rearrangement was a  $100\text{ cm}^{-1}$  wavenumber shift of the BH peak from  $2395$  to  $2494\text{ cm}^{-1}$ . It should be noted that the analogous, structurally characterized  $\text{Cu}[\text{Tp}^{\text{Cy}}]_2$  complex also contained  $\kappa^2\text{-Tp}^{\text{Cy}}$  ligands but they were in a planar rather than tetrahedral arrangement.<sup>10</sup>



By contrast, the originally purple solution of  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]_2$  started changing color already during evaporation, and the peachy-yellow rearranged octahedral complex precipitated at room temperature. For this reason, we were unable to isolate the pure purple  $\kappa^2$ -coordinated tetrahedral  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]_2$  complex but only the octahedral  $\kappa^3$ -coordinated rearranged species  $\text{Co}[\text{Tp}^{\text{Cy,4Br}*}]_2$ , which had the BH stretch at  $2469\text{ cm}^{-1}$ .

The reaction of  $\text{Co}[\text{Tp}^{\text{Cy}}]\text{X}$  or  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]\text{X}$ , ( $\text{X} = \text{Cl}$  or  $\text{NCS}$ ) with  $\text{TlTp}$  or  $\text{TlTp}^*$  gave rise to the heteroleptic octahedral complexes  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}]$ ,  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}^*]$ ,  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}][\text{Tp}]$ , and  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}][\text{Tp}^*]$ . These reactions proceeded rapidly with  $\text{TlTp}$  and more slowly with  $\text{TlTp}^*$ , and they were not fully stoichiometric. Thus, stirring equimolar amounts of the blue  $\text{Co}[\text{Tp}^{\text{Cy}}]\text{X}$  or  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}]\text{X}$  and  $\text{TlTp}$  did not result in complete discharge of the blue color, until additional amounts of  $\text{TlTp}$  were added in small portions. One could, in essence, “titrate” the blue solution to the disappearance of the blue color and obtain a mixture of the appropriate heteroleptic complex along with the homoleptic

**Table 2.** NMR Peaks of Heteroleptic 3-Cyclohexyl  $\text{Co}(\text{II})$  Complexes of  $\text{Tp}^{\text{Cy}}$  and  $\text{Tp}^{\text{Cy,4Br}}$  Ligands (in ppm)<sup>a</sup>

protons	$\text{Tp}^{\text{Cy}}\text{CoTp}$	$\text{Tp}^{\text{Cy}}\text{CoTp}^*$	$\text{Tp}^{\text{Cy,4Br}}\text{CoTp}$	$\text{Tp}^{\text{Cy,4Br}}\text{CoTp}^*$
H5, H5'	91.8, 81.7	71.5	90.4, 88.4	77.8
Me5		41.2		42.5
H4, H4'	43.8, 41.6	49.4, 44.3	43.1	52.4
H3	–130.2		–135	
Me3		–71.8		–70.7
Cy-H1	–103.8	–104.9	–102.7	–111.8
Cy-H2 <sup>e</sup>	–55.4	–42.4	–55.6	–42.5
Cy-H2 <sup>a</sup>	–29.6	–24.7	–28.6	–23.8
Cy-H3 <sup>a</sup>	–13.7	–12.8	–13.7	–12.7
Cy-H3 <sup>e</sup>	–13.7	–10.8	–13.3	–10.7
Cy-H4 <sup>e</sup>	–13.2	–10.8	–13.1	–10.7
Cy-H4 <sup>a</sup>	–6.6	–5.9	–6.1	–5.4

<sup>a</sup> The superscripts “e” and “a” refer to equatorial and axial protons, respectively.

complex  $\text{Co}[\text{Tp}]_2$ . If the blue solution resulting from the reaction of stoichiometric amounts of, for instance,  $\text{Co}[\text{Tp}^{\text{Cy}}]\text{X}$  and  $\text{TlTp}$  was chromatographed, one obtained unchanged starting material, plus  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}]$  and some  $\text{Co}[\text{Tp}]_2$ . It appears that  $\text{TlTp}$  reacts in two ways, forming the heteroleptic complex  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}]$  and also wresting the cobalt ion from the  $\text{Tp}^{\text{Cy}}$  ligand and producing the very stable  $\text{Co}[\text{Tp}]_2$ . The exact mechanism of this reaction is unclear, but it might entail the formation of an anionic intermediate  $[\text{Co}(\text{Tp}^{\text{Cy}})(\text{Tp})_2]^-$  containing three  $\kappa^2$ -bonded ligands, which could then lose either the  $[\text{Tp}^{\text{Cy}}]^-$  or the  $[\text{Tp}]^-$  anion to produce the observed octahedral products. Once formed,  $\text{Co}[\text{Tp}^{\text{Cy}}][\text{Tp}]$  and  $\text{Co}[\text{Tp}]_2$  remain unreactive and can be separated by chromatography and fractional crystallization, the heteroleptic complex being always the more soluble one. The same dual reaction pathway was also observed with the  $\text{TlTp}^*$  ligand, except that  $\text{Co}[\text{Tp}^{\text{Cy,4Br}}][\text{Tp}^*]$  required numerous recrystallizations to be completely freed of  $\text{Co}[\text{Tp}^*]_2$ . In the impure “as-produced” complex, the  $2517\text{ cm}^{-1}$  peak characteristic of  $\text{Tp}^*$  was much stronger than the  $2450\text{ cm}^{-1}$  peak, belonging to the  $[\text{Tp}^{\text{Cy,4Br}}]$  ligand. Upon progressive purification, the  $2517\text{ cm}^{-1}$  peak kept shrinking, until it remained equal in size to the  $2450\text{ cm}^{-1}$  peak. In the related  $\text{Co}[\text{Tp}^{\text{Pr,4Br}}][\text{Tp}^*]$  complex the respective peaks were at  $2520$  and  $2575\text{ cm}^{-1}$ .<sup>16</sup>

The purification of these heteroleptic complexes could be easily followed by NMR, since the proton peaks in their spectra were very sharp and spaced over  $200\text{ ppm}$ , showing even separate signals for the axial and equatorial protons of the cyclohexyl group. As can be seen from Table 2, the most upfield protons were those of the pyrazolyl H-3 ( $-130$ ,  $-135\text{ ppm}$ ) and of the cyclohexyl tertiary proton ( $-103$  to  $-112\text{ ppm}$ ), followed by the 2,6-protons at about  $-55$  and  $-30\text{ ppm}$  for complexes containing the  $\text{Tp}$  ligand and about  $-42$  and  $-24$  for complexes containing  $\text{Tp}^*$ . The change from  $\text{Tp}$  to  $\text{Tp}^*$  has a greater effect on the chemical shifts than a change from  $\text{Tp}^{\text{Cy}}$  to  $\text{Tp}^{\text{Cy,4Br}}$  and is in line with the  $\text{pz}^{\text{Cy}}$  arm being pushed away from the metal by the 3-Me groups of the  $\text{Tp}^*$  ligand. The same effect was observed earlier in the  $\text{Co}[\text{Tp}^{\text{Pr,4Br}}][\text{Tp}]$  and  $\text{Co}[\text{Tp}^{\text{Pr,4Br}}][\text{Tp}^*]$  pair, where the isopropyl methyls were at  $-35.5$  in the former complex but  $-28.5$  in the latter.<sup>15</sup> The  $-55$  and  $-42$  peaks in Table 2 were assigned to the equatorial protons, and the  $-30$  and

–24 peaks to the axial ones. The signals of the 3,5-cyclohexyl protons were too close together to permit distinction between the axial and equatorial positions. On the other hand, the 4-protons were sufficiently separated, so that the –13 and –11 peaks could be assigned to the equatorial and those around –6 ppm to the axial protons.<sup>26</sup> In light of these more accurate results, we have to reverse the assignment of the previously reported peaks for the H-3 (–96.3 ppm) and the isopropyl tertiary H (–126.1 ppm).<sup>17</sup>

Important information could be deduced from the NMR spectra as to the structure of these heteroleptic complexes in solution. The spectra confirmed the intuitive assumption that the cyclohexyl group is stereochemically rigid and is symmetrically straddling the pyrazolyl plane, with the tertiary hydrogen directed at the metal. If rapid rotation of the cyclohexyl group were taking place, then the cyclohexyl tertiary hydrogen, which appears as a sharp peak in the –103 to –112 ppm range, would be averaged over the full space/time distribution and present a fairly broad signal roughly where a 3-methyl group normally shows up, i.e., around –70 ppm, and the cyclohexyl methylene proton peaks would be very broad with multiple overlaps. Second, if a rigid structure were to exist in solution, with the cyclohexyl group straddling the pyrazolyl plane and the tertiary hydrogen turned away from the metal, then the tertiary hydrogen peak should be in the –50 to –60 ppm range. This is clearly not the case.

The tetrakis ligand,  $\text{pz}^o\text{Tp}^{\text{Cy}}$ , was also synthesized by prolonged heating of 3-isopropylpyrazole with  $\text{KBH}_4$ . It behaved just like its isopropyl analogue,  $\text{pz}^o\text{Tp}^{\text{iPr}}$ , in forming

(26) The sensitivity of the chemical shifts of protons in octahedral Tp-derived Co(II) complexes to their position with respect to the cobalt is such that a  $5^\circ$  angular variation at a constant distance of 3 Å results in a 11 ppm change of the chemical shift, while a 0.1 Å distance change at a constant angle of  $110^\circ$ , produces a 13 ppm shift: (a) Lamar, G. N.; Jesson, J. P.; Meakin, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 3, 1286. (b) Domaille, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5392.

a series of tetrahedral complexes,  $\text{M}[\text{pz}^o\text{Tp}^{\text{Cy}}]_2$ , which had essentially superimposable IR spectra, thus being isomorphous. The structure of  $\text{Co}[\text{pz}^o\text{Tp}^{\text{Cy}}]_2$  was determined by X-ray crystallography but was of poor quality ( $R_f = 30$ ) and unpublizable. Nevertheless, it did confirm each ligand coordinating in bidentate fashion. The lack of exchange between the coordinated and uncoordinated pyrazolyl arms was indicated by the presence of two pairs of very sharp signals of identical intensity for the 4- and 5-protons on the pyrazolyl rings in the isomorphous zinc complex,  $\text{Zn}[\text{pz}^o\text{Tp}^{\text{Cy}}]_2$  and also by the presence of two sets of 3-cyclohexylpyrazolyl peaks in the spectrum of the paramagnetic Co(II) complex. This spectrum was much less sharp than the spectra of octahedral  $\text{Co}[\text{Tp}^{\text{x}}]_2$  complexes.

## Conclusions

A comparison of the  $\text{Tp}^{\text{Cy}}$ ,  $\text{Tp}^{\text{Cy.4Br}}$ , and  $\text{pz}^o\text{Tp}^{\text{Cy}}$  ligands with their analogues  $\text{Tp}^{\text{iPr}}$ ,  $\text{Tp}^{\text{iPr.4Br}}$ , and  $\text{pz}^o\text{Tp}^{\text{iPr}}$  shows, as a first approximation, similar coordination chemistry, although complexes derived from the first set of ligands exhibited greater stability. Thus, the unrearranged  $\text{Co}[\text{Tp}^{\text{Cy}}]_2$  was isolable and stable at room temperature, although it could be thermally rearranged to  $\text{Co}[\text{Tp}^{\text{Cy}*}]_2$ . Such stability was lowered in the  $\text{Co}[\text{Tp}^{\text{Cy.4Br}}]_2$  complex which slowly rearranged even at room temperature. By contrast, in the  $\text{Tp}^{\text{iPr}}$  and  $\text{Tp}^{\text{iPr.4Br}}$  analogues the unrearranged complex could not be isolated at all. Another distinction was in the reaction of  $\text{Ni}[\text{Tp}^{\text{Cy.4Br}}]\text{X}$  with oxalate ion, where formation of the unusual complex  $\text{Ni}[\text{Tp}^{\text{Cy.4Br}}][\text{pz}^{\text{Cy.4Br}}](\text{H})_2$  contrasted with the isolation of the simple oxalate-bridged dinuclear species,  $[\text{Ni}(\text{Tp}^{\text{iPr.4Br}})]_2(\text{C}_2\text{O}_4)$ , in the similar reaction of  $\text{Ni}[\text{Tp}^{\text{iPr.4Br}}]\text{X}$ .<sup>27</sup>

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