Analogues of the Tp* Ligand Containing a 3-Me but Non-Methyl 5-R Groups

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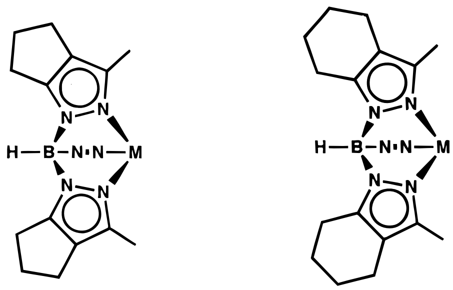
Introduction

Although more than 170 scorpionate (polypyrazolylborate) ligands are known,[1] a very large percentage of research in this area was, and is, being done with the ancient ligand Tp* (= Tp^{Me2}).[2] This work horse of the "first generation" Tp ligands has provided interesting results in numerous areas, such as in C−H bond activation.[3] Despite the importance of regiochemical considerations in C−H bond activation and other catalytic and stoichiometric processes, no efforts have been made to fine-tune this system by introducing regiochemically pure modifications of Tp* containing the 3-Me group next to the coordinated metal but having something other than a methyl group in the 5 position. Only one ligand of this type has been reported: Tp^{4Bo,3Me} (Bo = benzo-) in which 5-R was the C−H of a 4,5-fused benzo ring.[5] Modifications of Tp*, containing an alkyl 4-R group, including Me and *n*-Bu,[6] as well as Et, Am, (Am = amyl) and Bn,[7] are known, but in terms of steric effects, they are all essentially equivalents of Tp* because each of them contains a 5-Me group.

We wanted to synthesize analogues of the Tp* ligand, Tp^{Me,R}, which would contain an aliphatic non-methyl 5-substituent. Offhand, this task appeared difficult, because experience has shown that when homoscorpionate ligands were prepared from 3(5)-Me-5(3)-R-substituted pyrazoles, in which R was large, only Tp^{R,Me} ligands containing the R group in the 3-position, along with 5-Me, were produced exclusively (R = *t*-Bu,[8] Ph,[9] and other aryl groups[10]), or predominantly (R = *i*-Pr).[11] At the same time, in the case of medium-sized R (Et, *i*-Bu), inseparable mixtures of regioisomers were obtained.[12] Our approach was based on making the 5-alkyl group "smaller" than Me, thus precluding, or minimizing, the formation of regioisomers by pinning a straight-chain 5 substituent to the pyrazole 4 position. To this end, we chose 3-methylpyrazoles containing 4,5-trimethylene and 4,5-tetramethylene loops, leading to Tp^{x} species that could be viewed as analogues of Tp* or, more accurately, of the Tp*^{R} ligands.

Reported herein is the synthesis of such ligands, Tp^{Me,mt3} and Tp^{Me,mt4},[13] and structures of their representative cobalt and rhodium complexes, Co[Tp^{Me,3mt}][Tp^{Np}] and Rh[κ^2-Tp^{Me,4mt}]-(COD).



Tp^{Me,mt3} Tp^{Me,mt4}

(-N=N- represents the third, hidden pz^{x} ring)

Experimental Section

All chemicals were commercial reagent grade and were used as received. 2-Acetylcyclopentanone and 2-acetylcyclohexanone were obtained from Aldrich. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls, or as KBr pellets, with a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. Proton NMR spectra (in $CDCl_3$) 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-Methyl-4,5-(1,3-propylene)pyrazole, Hpz^{Me,mt3}. To a solution of 18 mL (0.36 mol) of hydrazine monohydrate in 150 mL of methanol was added 45.4 g (0.36 mol) of 2-acetylcyclopentanone in 100 mL of methanol. After the exothermic reaction subsided, the solution was stripped to dryness, yielding a solid in a 45 g (100%) yield. The product was sublimable in vacuo and was recrystallized from an octane/toluene mixture. Mp: 141−142 °C. ^{1}H NMR: 12.0 (1H, NH) 2.69 (t, 2H, 5-CH_2), 2.54 (t, 2H, 5-CH_2), 2.42 (m, 2H, central CH_2), 2.22 (s, Me). The ^{13}C NMR has already been reported.[14] Anal. Calcd for $C_7H_{10}N_2$: C, 68.9; H, 8.2; N, 23.0. Found: C, 69.0; H, 8.1; N, 22.8.

Thallium Hydrotris(3-methyl-4,5-propylene-5-methylpyrazol-1-yl)borate, Tl[Tp^{Me,mt3}]. A mixture of 49 g (0.4 mol) of 3-methyl-4,5-(1,3-propylene)pyrazole and 4.3 g of KBH_4 (0.08 mol, a 5:1 mole ratio) was stirred and heated in an oil bath, ultimately at 256 °C. Hydrogen evolution was brisk at first, up to about 4.5 L, then slowed as the solid began to precipitate. The solid did not melt even at 256 °C, despite continued hydrogen evolution. After hydrogen was no longer evolved (5.5 L, 92% theory), 7 h, the flask was cooled, and the solid was removed mechanically. It was crushed into small pieces, which were briefly stirred into 200 mL of refluxing toluene. This mixture was filtered and the solid was dried. The potassium salt, which had a BH stretch at 2445 cm^{-1}, was obtained in a 33 g (92%) yield. It was dissolved in 100 mL of a 50/50 THF/DMF mixture and was stirred with an excess of aqueous $TlNO_3$ and 500 mL of methylene chloride.

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(13) Abbreviations: "mt" stands for "methylene", 3 and 4 refer to the number of methylene groups, with the connection points to the pyrazolyl ring being, by default, the 4 and 5 positions.
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The Tl complex did not dissolve completely in methylene chloride. The total mixture was filtered, and the solid was washed with methanol. The filtrate phases were separated, and the organic phase was stripped to dryness. This residue was stirred with methanol and filtered, yielding more product, for a combined yield of 41 g (84%). The analytical sample was recrystallized from mesitylene. Mp 266−267 °C dec. IR: BH at 2470 cm^{-1}. ^1H NMR: 2.82 (m, 2H), 2.54 (broad d, 4H), 2.33 (s, 3H, Me). Anal. Calcd for $C_{21}H_{28}BN_6Tl$: C, 46.8; H, 4.55; N, 13.7. Found: C, 47.5; H, 4.67; N, 13.4.

Co[$Tp^{Me,mt3}$][Tp^{Np}], 1. An equimolar mixture of Co[Tp^{Np}]Cl and Tl[$Tp^{Me,mt3}$] was stirred in methylene chloride until the blue color disappeared. The slurry was filtered to remove TlCl, and the filtrate was chromatographed on alumina, collecting the yellow band. Evaporation of the filtrate yielded the heteroleptic product, isolated in 62% yield. Mp: 262−264 °C to a red melt. IR: BH at 2443, sh 2445 cm^{-1}. NMR (ppm): singlets at 104 and 103 (BH, BH′), 78.6 (3H, H5), 46.2 (3H, H4), 42.2 (6H, "5"-CH_2), 15.0 (6H, "4"-CH_2), −1.7 (6H, central CH_2), −17.2 (27H, *t*-Bu), −71.7 (9 H, Me), −96 (6H, neopentyl CH_2). Anal. Calcd for $C_{45}H_{68}B_2CoN_{12}$: C, 63.0; H, 7.9, N, 19.6. Found: C, 62.6; H, 8.22; N, 19.4.

3-Methyl-4,5,6,7-tetrahydroindazole, Hpz^{Me,mt4}. A methanol solution of 100 g of 2-acetylcyclohexanone (0.71 mol) was added drowpise to 38 g (0.76 mol) of stirred hydrazine hydrate in methanol. After the exothermic reaction subsided, the solvent was stripped, and the product was distilled at 124−128°/ 0.8 Torr, yielding 85 g (82%) of a pale yellowish syrup, which partially crystallized upon standing overnight. NMR: 11.77 (s, 1H, NH); 2.59 (t, 2H, 5-CH_2), 2.30 (t, 2H, 4-CH_2), s 2.16 (3H, Me) 1.67 (m, 4H, central two methylenes). The ^{13}C NMR has already been reported.[14] Anal. Calcd for $C_8H_{12}N_2$: C, 70.6; H, 8.82; N, 20.6. Found: C, 70.8; H, 8.47; N, 20.7.

Tl[$Tp^{Me,mt4}$]. All 85 g (0.63 mol) of the above 3-methyl-4,5,6,7-tetrahydroindazole was heated with 6.75 g (0.13 mol) of KBH_4 (mole ratio 5:1). Hydrogen evolution proceeded rapidly from 150° up to 250 °C when 9.5 L of hydrogen was evolved (theory 9.75), at which point the melt suddenly solidified. After the melt was cooled, it was broken up and boiled in a mixture of 400 mL of octane and 50 mL of toluene. The hot slurry was filtered, and the solid was washed with boiling heptane, yielding 37.5 g (62.5%) of the dry K salt, containing a very sharp BH peak at 2405 cm^{-1}. It was converted to the Tl complex (which was quite soluble in dichloromethane) as was described for the $Tp^{Me,mt3}$ ligand. Tl[$Tp^{Me,mt4}$] was obtained in 46.1 g (89.9%) yield. Mp: darkening from 270 °C, but still remaining as a tan solid at 307 °C. IR: BH at 2476 cm^{-1}. NMR: 2.77 (t, 2H, 5-CH_2), 2.29 (t, 2H, 4-CH_2), s 2.20 (3H, Me), 1.67 (doublet of quintuplets, 4H, central two methylenes) plus very broad BH in the 4.0−5.4 ppm range (1/3 H). Anal. Calcd for $C_{24}H_{34}BN_6Tl$: C, 46.4; H, 5.48; N, 13.5. Found: C, 46.3; H, 5.23; N, 13.5.

Co[$Tp^{Me,mt4}$][Tp^{Np}]. This complex was prepared as in the case of Co[$Tp^{Me,mt3}$][Tp^{Np}]. Mp: 271−272 °C dec. IR: BH at 2439, 2480 cm^{-1}. NMR (ppm): 104 (2H, BH, BH′), 79.3 (3H, H5), 48.4 (6H, "5"-CH_2), 45.9 (3H, H4), 12.7 (6H, methylene next to "5"-CH_2), 5.3 (6H, methylene next to "4"-CH_2) −6.9 (6H, "4"-CH_2), −17.6 (27H, *t*-Bu), −73.1 (9 H, Me), −97.8 (6H, neopentyl CH_2). Anal. Calcd for $C_{48}H_{74}B_2CoN_{12}$: C, 64.1; H, 8.23; N, 18.7. Found: C, 63.6; H, 8.37; N, 18.5.

Rh[$Tp^{Me,mt4}$](COD). Equimolar quantities of Tl[$Tp^{Me,mt4}$] and $[RhCl(COD)]_2$ were stirred in methylene chloride for 1 h. The slurry was filtered, and the filtrate was evaporated to dryness, producing an 84% yield of the crude product, which was recrystallized from xylene to form orange crystals. Mp: 199−200 °C. IR: BH at 2445 cm^{-1}. ^1H NMR: 4.26 (s, 4H, olefinic Hs), 2.50 (bt 6H, CH_2), 2.42 (bt 6H, CH_2), 2.34 (s, 9H, Me); 2.17 (m, 4H, COD), 1.76 (bs, 12H, CH_2), 1.66 (m, 4H, COD). Anal. Calcd for $C_{32}H_{42}BN_6Rh$: C, 61.5; H, 6.73; N, 13.4. Found: C, 61.9; H 6.91; N 13.1.

Crystallographic Structure Determination. A suitable crystal for single-crystal X-ray diffraction was selected and mounted with epoxy cement on the tip of a thin glass fiber. Data for **1** were collected on a Siemens-P4 diffractometer with a SMART/CCD detector and **2** with a scintillation detector.

No evidence of symmetry higher than triclinic was observed in the diffraction data of **1**, and the systematic absences in the diffraction data were uniquely consistent for the reported space group for **2**. *E*-statistics suggested the centrosymmetric space group option, $P\bar{1}$, for **1**. The 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. An absorption correction, using SADABS, was applied to the data for **1**, and no absorpion corrections were required for **2** because there was less than 10% variation in the integrated intensities of the Ψ-scan reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the boron atoms of 1 were located from the difference map and allowed to refine. All other hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL Plus (Version 4.2) or the SHELXTL (5.10) program libraries (Sheldrick, G. Siemens XRD, Madison, WI).

Results and Discussion

The reaction of the two pyrazoles, 3-methyl-4,5-(1,3-propylene)pyrazole and 3-methyl-4,5-(1,4-butylene)pyrazole (= 3-methyl-4,5,6,7-tetrahydroindazole), with KBH_4 was carried out in the melt, in a manner analogous to the preparation of Tp*. The new ligands were isolated in good yields and were characterized as their Tl complexes. In each case, the proton NMR spectrum indicated a C_{3v} symmetry of the ligand and, thus, the presence of only one regioisomer, but this did not establish whether it was the one with a 3-Me or a 5-Me substituent. We resolved this issue by means of synthesizing the heteroleptic complexes, Co[$Tp^{Me,mt3}$][Tp^{Np}] and Co[$Tp^{Me,mt4}$][Tp^{Np}]. These particular compounds were chosen over the homoleptic ones because they had better solubility, and because the signals for the Tp^{Np} ligand were well-known. As had been established before, the ^1H NMR spectra of octahedral Co$[Tp^x]_2$ complexes are a sensitive probe for the location of protons and alkyl substituents on the pyrazolyl rings. In particular, a 3-Me group was found at about −72 ppm, whereas the 5-Me appeared around +47 ppm.[5]

In the NMR spectrum of Co[$Tp^{Me,mt3}$][Tp^{Np}], the Me appeared at −71.7 ppm and, thus, in the 3-Me range, similar to the 3-Me in Co[Tp*][Tp^{Np}], which was at −76 ppm.[15] The methylenes were at 42.2, 15.0, and −1.7 ppm and were assigned to the 5-, the central one, and the 4-methylene, respectively. This assignment was based on the spectrum of the related complex Co[Tp^{Me3}][Tp^{Np}], for which the 5-, 4-, and 3-Me groups were at 43.3, −0.7, and −74.9 ppm, respectively. The remaining 15.0 ppm peak in Co[$Tp^{Me,mt3}$][Tp^{Np}] was assigned, by default, to the central methylene, and it could be compared with the 19.8 ppm peak of the methyl of the 5-Et group in Co$[Tp^{Et2}]_2$.[15]

In the NMR spectrum of Co[$Tp^{Me,mt4}$][Tp^{Np}], the methyl peak was at −73.1 ppm, again in the 3-Me range. The methylene peaks were at 48.4, 12.2, 5.3, and −6.9 ppm and were assigned to the 5-CH_2, the CH_2 next to it, the CH_2 next to the 4-CH_2, and the 4-CH_2, respectively. This assignment was based on correlation with the spectrum of the related complex Co[$Tp^{4Bo,Me3}$][Tp^{Np}], for which the 3-Me was at −71.3 ppm, the "5-CH" (= indazolyl 7H) at 49.2 ppm, the "4-CH" (= indazolyl 4H) at −7.8 ppm, whereas the indazolyl 6H and 5H peaks were at 19.0 and 11.5 ppm, respectively.[5]

An even more definitive proof of the nature of the $Tp^{Me,mt3}$ ligand was obtained by determining the crystal structure of the Co[$Tp^{Me,mt3}$][Tp^{Np}] complex, **1**, by X-ray crystallography (see Figure 1). The cobalt ion was in an octahedral environment, with the Co−N bond distances to the $Tp^{Me,mt3}$ ligand being slightly shorter than those of Tp^{Np} (average 2.149 versus 2.172 Å) but longer than those found in Co$[Tp]_2$ (average 2.124 Å),[16]

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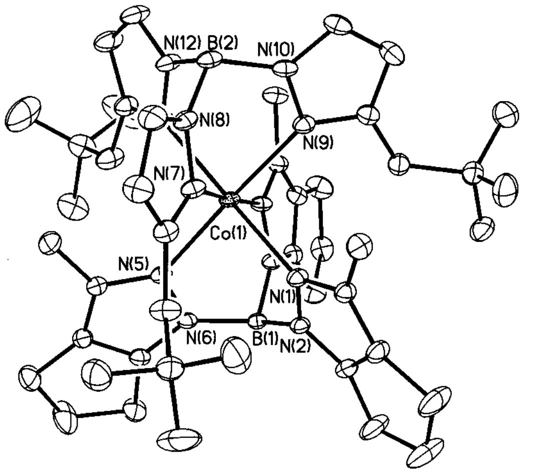

Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) and angles (deg): Co−N(1) 2.149; Co−N(3) 2.152; Co−N(5) 2.145; Co−N(7) 2.164; Co−N(9) 2.168; Co−N(11) 2.185; N(1)−Co−N(3) 88.8; N(1)−Co−N(5) 86.1; N(3)−Co−N(5) 87.3; N(7)−Co−N(9) 87.1; N(9)−Co−N(11) 87.4; N(7)−Co−N(11) 85.3.

and shorter than those found in $[CoTp_2]^+$ (2.195 Å).[17] In the related complex Co[$Tp^{3Bo,7Me}$][Tp^{Np}], the Co−N bonds of the rather hindered $Tp^{3Bo,7Me}$ ligand averaged 2.236 Å, and those of Tp^{Np} averaged 2.137 Å, whereas in the complex Co[$Tp^{a*,3Me}$][Tp^{Np}], these values were 2.206 and 2.153 Å, respectively.[5] By comparison, the average M−N distances in the octahedral iron(II) complexes, $FeTp_2$ and $FeTp*_2$, were 1.975 and 2.172 Å, respectively.[18]

The structural information on the $Tp^{Me,mt4}$ ligand was obtained from the rhodium complex, Rh[$Tp^{Me,mt4}$](COD), **2** (see Figure 2). Prior experience with Tp^xRh(COD) species led us to expect a κ^2-structure,[19] and this expectation was reinforced by observing a B−H stretch at 2445 cm^{-1}, in line with the findings that a B−H stretch below 2500 cm^{-1} is indicative of κ^2-coordination in similar complexes.[20] In compound **2**, the $Tp^{Me,mt4}$ ligand was bidentate, with the third $pz^{Me,mt4}$ arm essentially orthogonal to the C2 axis. Although Rh[Tp*](COD) has not been structurally characterized, the present κ^2 motif was also displayed in the related complex Rh[$Tp^{4Bo,3Me}$](COD).[5]

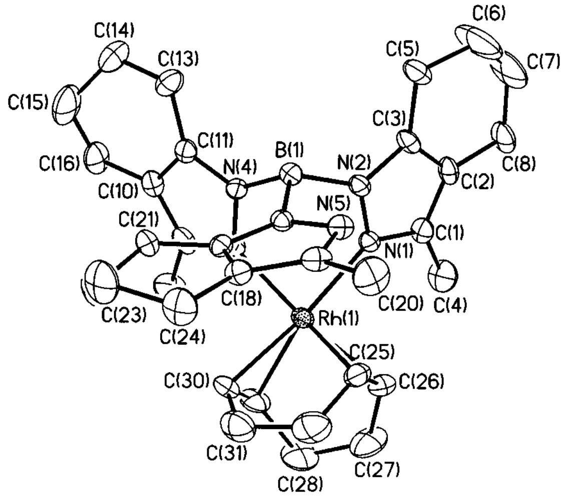

Figure 2. ORTEP drawing of **2**. Selected bond lengths (Å) and angles (deg): Rh−N(1) 2.083; Rh−N(3) 2.133; Rh−C(5) 2.115; Rh−C(26) 2.132; Rh−C(29) 2.117; Rh−C(30) 2.120; N(1)−Rh−N(3) 83.9; N(1)−Rh−C(25) 96.7; N(1)−Rh−C(26) 90.3; N(1)−Rh−C(29) 154.0; N(1)−Rh−C(30) 168.4; N(3)−Rh−C(25) 151.0; N(3)−Rh−C(26) 170.0; N(3)−Rh−C(29) 101.0; N(3)−Rh−C(30) 92.4.

Altogether, the regiochemical purity of the $Tp^{Me,mt4}$ ligand was somewhat surprising. Although we were reasonably confident that the short trimethylene loop in $Tp^{Me,mt3}$ would pull the 5-CH_2 sufficiently back so that it would not compete sterically with the methyl group, thus leading to a single $Tp^{Me,mt3}$ ligand isomer; in the case of the tetramethylene loop, there could have been enough competition to produce other ligand isomers, in addition to $Tp^{Me,mt4}$. However, only trace amounts of unidentified impurities were observed. This is in contrast to Tp ligands derived from pyrazoles containing only 3,4-polymethylene loops of 3, 4, 6, and 10 units, from which product mixtures with varying degrees of complexity were formed.[15]

In summary, we have prepared two novel Tp^x ligands, $Tp^{Me,mt3}$ and $Tp^{Me,mt4}$, each containing a 3-Me group but having non-methyl substituents in the 5-position. These ligands may prove to be useful to fine-tune systems for which Tp* has been traditionally employed.

Supporting Information Available: Tables of detailed crystallographic data, atomic position parameters, and bond lengths and angles for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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