Hydrotris(indazolyl)borates: Homoscorpionates with Tunable Regiochemistry

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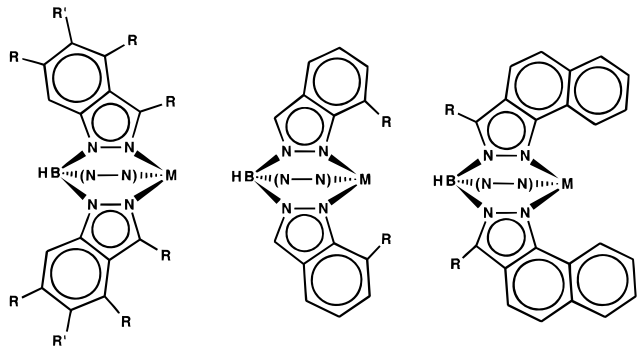
A series of hydrotris(indazolyl)borates containing diverse substituents on the indazole ring and representing two types of regiochemistries have been synthesized. Indazoles with a 7-alkyl substituent or a 6,7-fused benzo ring formed ligands with boron bonded to the less hindered N-2 (=Tp^{3Bo}), while those with alkyl or aryl substituents in any other position yielded ligands with boron bonded to the more hindered N-1 (=Tp^{4Bo}), thus being the first example of homoscorpionates with 4,5-substituents. Octahedral homo- and heteroleptic complexes of Co, Fe, and Zn have been prepared and characterized, as well as complexes of the types [M(L)(NCS)], [Mo(L)$(CO)_2$(η^3-CH_2CMeCH_2)], [Rh(L)(COD)], and [Rh(L)$(CO)_2$]. X-ray crystallography provided structures of the complexes [Rh(HB{3-methylindazol-1-yl}$_3$)(COD)], **1** (space group $P2_1/n$; a = 11.766(2), b = 16.189(2), c = 15.149(2) Å; β = 92.51(1)°; Z = 4; R = 0.0306 for 4318 independent reflections), [Co(HB{7-methylinazol-2-yl}$_3$)(HB{3-neopentylpyrazol-1-yl}$_3$)], **2** (space group $P\bar{1}$; a = 13.368(4), b = 13.652(4), c = 16.203(9) Å; α = 73.73(4), β = 71.26(3), γ = 63.54(2)°; Z = 2; R = 0.0761 for 7721 independent reflections), and [Co(hydrotris{3-methyl-2*H*-benz[*g*]indazol-2-yl}borate)(hydrotris{3-neopentylpyrazol-1-yl}borate)]·C_6H_5CN, **3** (space group $P\bar{1}$; a = 13.216(6), b = 13.706(4), c = 17.881(6) Å; α = 73.79(2), β = 86.71(3), γ = 85.61(3)°; Z = 2; R = 0.1138 for 6698 independent reflections).

Introduction

It has been a well-established fact that, in the reaction of KBH_4 with 3-R-substituted pyrazoles, which leads to the corresponding substituted hydrotris(pyrazol-1-yl)borates, boron always bonds to the less hindered N, so that the R substituent ends up in the 3-position and the resulting $[HB(3\text{-}Rpz)_3]^-$ ligand is of C_{3v} symmetry.[1] This preference was explained on steric grounds, as the transition state leading to the 5-R isomer would be more sterically crowded and thus energetically unfavorable. Boron also bonds to the less hindered nitrogen in the case of 3,5-disubstituted pyrazoles, when the 3- and 5-substituents differ significantly in size as, for instance, Me and tBu, so that the only product formed is $Tp^{tBu,Me}$.[2] Only in the case of R = mesityl is the "as formed" product predominantly [$HB(3Rpz)_2$(5Rpz)] (=Tp^{Ms*}), but even then, 3-R substitution dominates (2:1) and heating the asymmetric [Tl(Tp^{Ms*})] salt converts it to the more stable symmetrical [Tl(Tp^{Ms})] derivative.[3] In some cases, where 3-R is fairly bulky as, for instance Tp^{iPr} [4] or Tp^{Np},[5] one also obtains a small amount of the 3,3,5-ligand, the major product still being 3,3,3. It is during the formation of octahedral complexes, where six isopropyl groups cannot be accommodated in the equatorial belt of the molecule, that rearrangement of the Tp^{iPr} ligand to the 3,3,5-isomer occurs. The ligand Tp^{Np} produces octahedral 3,3,3-complexes, but on heating, they rearrange to the 3,3,5-isomers. Thus, even in cases where the 3,3,3-ligand is not the exclusive product, 3-substitution is still the dominant one.

However, when the pyrazole 3,4-substituents are part of a fused benzo ring, as in benzopyrazole (indazole), the above empirical expectations no longer hold true. In the ligand derived from benzopyrazole (indazolyl-1-ylborate = Tp^{4Bo}), boron was



(—(N—N)— represents the third, hidden, pz* group)

A. Tp^{4Bo}-type ligands	**B.**	**C.**
R = H or Me	$Tp^{3Bo,7Me}$: R = Me	Tp^{a*} : R = H
R' = H, Me, Et, t-Bu, Ph	$Tp^{3Bo,7tBu}$: R = tBu	$Tp^{a*,3Me}$; R = Me

found to be bonded exclusively to the more hindered,[6] but electronically richer,[7] nitrogen atom. Here, the interplay of steric and electronic factors tilts in favor of the latter, giving rise to a ligand with steric hindrance around boron, but not at the coordinated metal. At the same time, homoscorpionate ligands derived from 7-substituted indazoles (=Tp^{3Bo}), as well as from benzindazole (naphthopyrazole), (=Tp^{a*}),[8] had the boron bonded exclusively to the less hindered nitrogen. This substituent-dependent regiospecificity exceeded that found during the methylation of indazoles.[9] We sought to establish the rules governing such regioselectivity during the formation of substituted poly(indazolyl)borates by synthesizing diversely substituted poly(indazolyl)borate ligands and their transition-metal

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Table 1. Crystallographic Data for [Rh(HB{3-methylindazol-1-yl}$_3$)(COD)] (**1**), [Co(HB{7-methylindazol-2-yl}$_3$)(HB{3-neopentylpyrazol-1-yl}$_3$)] (**2**), and [Co(HB{3-methyl-2*H*-benz[*g*]indazol-2-yl}$_3$)(HB{3-neopentylpyrazol-1-yl}$_3$)]·C_6H_5CN (**3**)

	1	**2**	**3**
formula	$C_{32}H_{34}BN_6Rh$	$C_{48}H_{62}B_2CoN_{12}$	$C_{67}H_{73}B_2CoN_{13}$
fw	616.4	887.6	1140.9
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	11.766(2)	13.368(4)	13.216(6)
b, Å	16.189(2)	13.652(4)	13.706(4)
c, Å	15.149(2)	16.203(9)	17.881(6)
α, deg		73.73(4)	73.79(2)
β, deg	92.51(1)	71.26(3)	86.71(3)
γ, deg		63.54(2)	85.61(3)
V, Å^3	2882.8(7)	2474(1)	3099(2)
Z	4	2	2
crystal color, habit	orange block	orange block	yellow block
D(calc), g cm^3	1.420	1.192	1.223
μ(Mo Kα), cm^{-1}	6.25	3.92	3.29
temp, °C	23	23	23
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
R,[a] %	4.92	7.02	11.38
R_w,[a] %	5.38	9.11	11.28

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

complexes and by determining their structures by NMR techniques and by X-ray crystallography.

Experimental Section

5-Phenylindazole,[10] 5-methylindazole,[11] 3-methylindazole,[12] 1*H*-benz[*g*]indazole,[13] 3-methyl-1*H*-benz[*g*]indazole,[14] [$(MeCN)_2Mo(CO)_2$-(η^3-CH_2CMeCH_2)],[15] and [RhCl(COD)]$_2$[16] were prepared by literature methods. All other chemicals were of reagent grade and were used as received. Elemental analyses were performed 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 300−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s. The ^{13}C NMR spectra of some of the indazoles[17] and benzindazoles[18] have already been reported. The new indazoles were prepared by a modification of the general method described for indazole synthesis,[19] involving condensation of ethyl formate with a substituted cyclohexanone, conversion of the product with hydrazine to the tetrahydroindazole, and dehydrogenation with a palladium catalyst. The procedure is exemplified by the preparation of 7-methylindazole.

Crystallographic Structure Determinations. Crystal, data collection, and refinement parameters are given in Table 1. A suitable crystal for single-crystal X-ray diffraction was selected and mounted on the tip of a glass fiber with epoxy cement. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 25°$). Despite several recrystallizations, the best crystals that could be obtained for all samples were extremely weak diffractors and the reflections were diffuse.

The systematic absences in the diffraction data are uniquely consistent for the reported space group for **1**, and no evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **2** or **3**. *E* statistics suggested the centrosymmetric space group $P\bar{1}$ for **2** and **3**, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, the refinements were completed by subsequent difference Fourier syntheses and full-matrix least-squares procedures. No absorption corrections were required because there was less than 10% variation in the integrated *ψ*-scan intensities. A molecule of the recrystallization solvent, benzonitrile, was located in the asymmetric unit of **3**, and the phenyl ring was fixed as a rigid planar group to conserve data. The carbon atoms and the atoms of the solvent molecule in **3** were refined isotropically; all other non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom on boron in **1** was located from the difference map and allowed to refine. The hydrogen atoms in **3** were omitted, and 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) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Synthesis of 7-Methylindazole. To a rapidly stirred suspension of 121 g (2.23 mol) of anhydrous sodium methoxide in 1.2 L of dry toluene was added in one portion a mixture of 250 g (2.23 mol) of 2-methylcyclohexanone and 190 g (2.56 mol) of ethyl formate. After the exothermic reaction subsided, the yellowish Na salt was extracted with 2 L of water. To the stirred aqueous layer was added 114 g (2.23 mol) of hydrazine hydrate, followed by 134 g (2.23 mol) of acetic acid. After the mixture was allowed to cool to room temperature, the product was extracted with 2 L of methylene chloride, the extracts were stripped to dryness (oil bath at 220 °C), and the residue was distilled in vacuo. Yield of the main cut, bp 126−129 °C/2.8−3.0 Torr, was 178 g (56%). ^{1}H NMR: NH 12.0−12.4 (1 H), s 7.28 (1 H), m 2.37 (1 H), m 2.50 (2 H), very complex m 1.90 (2 H), very complex m 1.62 (1 H), quadruplet with additional structure 1.39 (1 H) and d 1.31 (3 H, Me) ppm. Anal. Calc for $C_8H_{12}N_2$: C, 70.6; H, 8.82; N, 20.6. Found: C, 70.8; H, 8.54; N, 20.3.

To the above product was added 5 g of 10% Pd/C, and the mixture was heated with stirring until hydrogen evolution commenced around 270−280 °C and proceeded at a good rate. After cessation of hydrogen evolution, the product was distilled at reduced pressure (bp 155−160°/2.5−2.8 Torr) and was obtained in 162 g (98%) yield. The molten distillate was poured into stirred heptane, yielding a solid that had a tendency to absorb hydrocarbon solvents; mp 100−102 °C. NMR: s 8.13 (1 H, H-3), d 7.56 (1 H, H- 4), d.7.10 (1 H, H-6), t 7.03 (1 H, H-5), s 2.58 (3 H, Me) ppm. For ^{13}C NMR see ref 17.

7-*tert*-Butylindazole. The tetrahydro precursor was obtained in 54% yield (from heptane); mp 127−128 °C. Dehydrogenation produced 7-*tert*-butylindazole in 84% yield (from octane); mp 156−157 °C. ^{1}H NMR: s 8.12 (1 H, H-3), d 7.63 (1 H, H-4), d 7.28 (1 H, H-6), t 7.11 (1 H, H- 5), s 1.54 (9 H, tBu) ppm; NH (1 H) at 11.5 ppm. ^{13}C NMR: 30.1 (CCH_3), 34.6 (CCH_3), 118.7, 121.1, 122.7, 124.1, 133.3, 134.7, 138.3 ppm. Anal. Calc for $C_{11}H_{14}N_2$: C, 75.9; H, 8.05; N, 16.1. Found: C, 76.0; H, 16.3; N, 16.0.

5-Ethylindazole was obtained in 65% yield (from heptane); mp 116−117 °C. ^{1}H NMR: s 8.06 (1 H, H-3), d 7.53 (1 H, H-4), d 7.41 (1 H, H-6), dd 7.24 (1 H, H-7), quad 1.75 (2 H, CH_2), t 1.28 (3 H, CH_3) ppm. Anal. Calc for $C_9H_{10}N_2$: C, 74.0; H, 6.85; N, 19.2. Found: C, 74.1; H, 6.95; N, 19.1.

4,6-Dimethylindazole was obtained in 61% yield (from toluene/heptane); mp 113−114 °C. ^{1}H NMR: broad hump 10−12 (NH), s 8.07 (1 H, H-3), s 7.08 (1 H, H-6), 6.75 (1 H, H-7), s 2.55 (3 H, Me), s 2.41 (3 H, Me) ppm. ^{13}C NMR: 18.6, 21.8, 106.8, 121.8, 123.0, 130.5, 132.8, 137.0, 140.7 ppm. Anal. Calc for $C_9H_{10}N_2$: C, 74.0; H, 6.85; N, 19.2. Found: C, 74.2; H, 6.97; N, 19.0.

Preparation of Hydrotris(indazolyl)borate Ligands. A typical preparation involved refluxing a mixture of the appropriate indazole and KBH_4 (3.7:1 mole ratio) in 4-methylanisole (500 mL/0.1 mol of KBH_4), the emanating hydrogen being measured with a wet-test meter. The reaction was continued until the theoretical amount of hydrogen was evolved. With some indazoles, the solution remained clear; with others, the K salt precipitated. 4-Methylanisole was then distilled at

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reduced pressure, the residue was boiled with toluene, and the mixture was filtered to remove unreacted indazole, yielding the crude K salt of the ligand.

The potassium salt was dissolved in THF (or DMF, if necessary) and converted to the Tl salt, by mixing the K salt solution with an equivalent amount of aqueous Tl nitrate or sulfate. After dilution with more water, the product was extracted with methylene chloride and purified by filtration through alumina, and the filtrate was evaporated, yielding the crude Tl salt. This was stirred with methanol, removing any residual indazole, and the mixture was filtered. The white Tl salt was purified by recrystallization from toluene or from toluene/octane mixtures. Yields ranged from 60 to 80%.

Thallium hydrotris(indazol-1-yl)borate (=[Tl(Tp^{4Bo})]: mp 254−256 °C. IR: BH 2450 cm^{-1}. ^{1}H NMR: d 8.12 (1 H, H-7), s 8.00 (1 H, H-3), d 7.62 (1 H, H-4), t 7.38 (1 H, H-6), t 7.02 (3 H, H-5) ppm. ^{13}C NMR: 112.7, 120.3, 120.5, 123.2, 126.3, 132.9, 144.3 ppm. Anal. Calc for $C_{21}H_{16}BN_6Tl$: C, 44.4; H, 2.82; N, 14.8. Found: C, 44.7; H, 2.96; N, 14.5.

Thallium hydrotris(5-methylindazol-1-yl)borate (=[Tl(Tp^{4Bo,5Me})]: mp 292−294 °C dec. IR: BH 2471 cm^{-1}. ^{1}H NMR: d 7.96 (1 H, H-6), s 7.91 (1 H, H-3), s 7.36 (1 H, H-4), d 7.17 (1 H, H-7), s 2.37 (3 H, Me) ppm. ^{13}C NMR: 21.3 (Me), 112.35, 119.8, 128.5, 129.5, 132.1 ppm. Anal. Calc for $C_{24}H_{22}BN_6Tl$: C, 47.3; H, 3.61; N, 13.8. Found: C, 47.2; H, 3.77; N, 13.5.

Thallium hydrotris(3-methylindazol-1-yl)borate (=[Tl(Tp^{4Bo,3Me})]: mp 288−290 °C dec. IR: BH 2475 cm^{-1}. ^{1}H NMR: dt 8.04 (1 H, H-7), dt 7.51(1 H, H-4), td 7.35 (1 H, H-6), td 6.99 (1 H, H-5), s 2.66 (3 H, Me) ppm. Anal. Calc for $C_{24}H_{22}BN_6Tl$: C, 47.3; H, 3.61; N, 13.8. Found: C, 47.3; H, 3.72; N, 13.6.

Thallium hydrotris(7-methylindazol-2-yl)borate (=[Tl(Tp^{3Bo,7Me})]: mp dec from 282 °C. IR: BH 2455 cm^{-1}. ^{1}H NMR: s 8.36 (1 H, H-3), d 7.51 (1 H, H-6), d 7.03 (1 H, H-4), t 6.91 (1 H, H-5), s 2.78 (9 H, Me) ppm. ^{13}C NMR: d 20.8 (J = 416 Hz), 118.7, 121.1, d 121.5 (J = 65 Hz), 125.4, 131.5, d 150.8 (J = 59 Hz) ppm. Anal. Calc for $C_{24}H_{22}BN_6Tl$: C, 47.3; H, 3.61; N, 13.8. Found: C, 47.1; H, 3.81; N, 13.7.

Thallium hydrotris(5-ethylindazol-1-yl)borate (=[Tl(Tp^{4Bo,5Et})]: mp 238−240 °C. IR: BH 2471 cm^{-1}. ^{1}H NMR: d 8.02 (1 H, H-7), s 7.87 (1 H, H-3), s 7.37 (1 H, H-4), dd 7.23 (1 H, H-6), quartet 2.66 (2 H, CH_2, t 1.20 (3 H, Me) ppm. ^{13}C NMR: 16.2, 28.8, 112.5, 117.9, 123.4, 127.5, 132.3, 136.1, 143.2 ppm. Anal. Calc for $C_{27}H_{28}BN_6Tl$: C, 49.8; H, 4.30; N, 12.9. Found: C, 49.8; H, 4.43; N, 12.6.

Thallium hydrotris(5-phenylindazol-1-yl)borate (=[Tl(Tp^{4Bo,5Ph})]: mp 290−292 °C dec. IR: BH 2477 cm^{-1}. Anal. Calc for $C_{39}H_{28}BN_6Tl$: C, 58.9; H, 3.52; N, 10.6. Found: C, 59.0; H, 3.55; N, 10.2.

Thallium Hydrotris(5-*tert*-butylindazol-1-yl)borate (=[Tl(Tp^{4Bo,5tBu})]: mp 255−257 °C. IR: BH 2468 cm^{-1}. ^{1}H NMR: dd 8.01 (1 H, H-7), s 7.96 (1 H, H-3), d 7.56 (1 H, H-4), dd 7.48 (1 H, H-6), s 1.32 (9H, tBu) ppm. ^{13}C NMR: 31.55 (tBu Me), 34.52 (tBu *C*Me$_3$), 112.2, 115.3, 125.3, 132.7, 143.0 ppm. Anal. Calc for $C_{33}H_{40}BN_6Tl$: C, 53.9; H, 5.44; N, 11.4. Found: C, 53.6; H, 5.67; N, 11.2.

Thallium hydrotris(7-*tert*-butylindazol-2-yl)borate (=[Tl(Tp^{3Bo,7tBu})]: mp 265−266 °C. IR: BH 2457 cm^{-1}. ^{1}H NMR: s 8.42 (3 H, H-3), d 7.60 (3 H, H-4), d 7.13 (3 H, H-6), t (3 H, H-5), s 1.60 (27 H, tBu), BH (1 H) by integration 6.0−4.4 ppm. ^{13}C NMR: 30.7 (broad), 35.6, 119.6, 121.2, 122.1, 123.9 (C-4), 132.4 (C-5), 138.9 (C-5), 149.4 (C-3) ppm. Anal. Calc for $C_{33}H_{40}BN_6Tl$: C, 53.9; H, 5.44; N, 11.4. Found: C, 53.8; H, 5.53; N, 11.3.

Thallium hydrotris(4,6-dimethylindazol-1-yl)borate (=[Tl(Tp^{4Bo,4,6Me2})]: mp 286−288 °C dec. IR: BH 2486 cm^{-1}. ^{1}H NMR: s 7.92 (1 H, H-3), s 7.68 (1 H, H-5), s 6.64 (1 H, H-7), 2.49 (3 H, Me), 2.46 (3 H, Me) ppm. ^{13}C NMR: 18.6 (Me), 22.2 (Me), 109.5, 122.5, 130.1, 131.6, 136.4, 144.9 ppm. Anal. Calc for $C_{27}H_{28}BN_6Tl$: C, 49.8; H, 4.30; N, 12.9. Found: C, 49.5; H, 4.53; N, 12.8.

Thallium hydrotris(2*H*-benz[*g*]indazol-2-yl)borate (=[Tl(Tp^{a*}): mp 286−289 °C dec. IR: BH 2450 cm^{-1}. ^{1}H NMR: d (vb) 8.4−8.9 (1 H, H-9), s 8.36 (1 H, H-3), d 7.79 (1 H, H-5), m 7.55 (3 H, H-6,7,8), d 7.29 (1 H, H-4) ppm. ^{13}C NMR: 119.2, 123.0, 124.7, 126.0, 126.2, 126.5, 128.8, 131.8, 133.1, 148.2, 162.4. Anal. Calc for $C_{33}H_{22}BN_6Tl$: C, 55.2; H, 3.07; N, 11.7. Found: C, 55.1; H, 3.14; N, 11.5.

Thallium Hydrotris(3-methyl-2*H*-benz[*g*]indazol-2-yl)borate (=[Tl(Tp^{a*,3Me})]. The "as produced" Tl salt was a mixture consisting of 40% of the symmetrical product and 60% of the 3,3,5-species, hydrobis(3-methyl-2*H*-benz[*g*]indazol-2-yl)(3-methyl-2*H*-benz[*g*]indazol-1-yl)borate, characterized by Me singlets at 2.80 and 2.61 ppm in a 2:1 ratio. The 3,3,5-species was preferentially (4:1) extracted with boiling chloroform, and boiling the undissolved fraction with xylene yielded pure 3,3,3-species as the insoluble material. The xylene filtrate contained the 3,3,3- and 3,3,5-species in a 7:3 ratio. We did not seek to isolate the asymmetric 3,3,5-isomer. Mp of [Tl(Tp^{a*,3Me})]: 303−304 °C dec. IR: BH 2515 cm^{-1}. ^{1}H NMR: vb d 8.4 (1 H, H-9), dd 7.83 (1 H, H-6), d 7.53 (1 H, H-4), quintet (two overlapping td), 7.50 (1 H, H-7,8), d 7.31(1 H, H-5), s 2.81 (3 H, Me). Anal. Calc for $C_{36}H_{28}BN_6Tl$: C, 56.9; H, 3.69; N, 11.1. Found: C, 57.2; H, 3.82; N, 11.1.

Homoleptic Complexes. These complexes were prepared by stirring a 2:1 molar mixture of TlTp^x and MCl_2 in a 1:1 mixture of THF and methylene chloride at room temperature for 2−3 h. The slurry was diluted with much water, additional methylene chloride was added, and the mixture was filtered through Celite to remove TlCl. The yellow organic layer was chromatographed through a short alumina column, and solvent evaporation yielded the product, which was stirred with methanol, filtered off, and purified further by recrystallization from toluene or xylene.

[Co(Tp^{4Bo})$_2$]: yellow solid; mp 446 °C (DSC). IR: BH 2450 cm^{-1}. Anal. Calc for $C_{42}H_{32}B_2CoN_{12}$: C, 64.2; H, 4.08; N, 21.1. Found: C, 64.3; H, 4.13; N, 20.9.

[Fe(Tp^{4Bo})$_2$]: reddish solid; mp none to 310 °C. Anal. Calc for $C_{42}H_{32}B_2FeN_{12}$: C, 63.7; H, 4.05; N, 21.2. Found: C, 63.7; H, 4.12; N, 21.1.

[Co(Tp^{4Bo,5Me})$_2$]: yellow solid; mp none to 310 °C. IR: BH 2473 cm^{-1}. Anal. Calc for $C_{48}H_{44}B_2CoN_{12}$: C, 66.3; H, 5.06; N, 19.3. Found: C, 66.1; H, 5.17; N, 19.0.

[Zn(Tp^{4Bo,5Me})$_2$]: white solid; mp none to 310 °C. IR: BH 2476 cm^{-1}. ^{1}H NMR: d 8.10 (1 H, H-7), s 7.59 (1 H, H-3), d 7.30 (1 H, H-6), s 7.28 (1 H, H-4), s 2.38 (3 H, Me). Anal. Calc for $C_{48}H_{44}B_2N_{12}Zn$: C, 63.7; H, 4.05; N, 21.2. Found: C, 63.9; H, 4.17; N, 21.0.

[Fe(Tp^{4Bo,5Me})$_2$]: red solid; mp none to 310 °C. IR: BH 2478 cm^{-1}. Anal. Calc for $C_{48}H_{44}B_2FeN_{12}$: C, 66.3; H, 5.06; N, 19.3. Found: C, 66.1; H, 5.17; N, 19.0.

[Co(Tp^{4Bo,5Et})$_2$]: yellow solid; mp none up to 310 °C. IR: BH 2472 cm^{-1}. Anal. Calc for $C_{54}H_{56}B_2CoN_{12}$: C, 68.0; H, 5.88; N, 17.6. Found: C, 68.3; H, 5.94; N, 17.2.

[Fe(Tp^{4Bo,5Et})$_2$]: red solid; mp none up to 310 °C. IR: BH 2469 cm^{-1}. Anal. Calc for $C_{54}H_{56}B_2FeN_{12}$: C, 68.2; H, 5.89; N, 17.7. Found: C, 68.3; H, 6.01; N 17.6.

[Co(Tp^{4Bo,3Me})$_2$]: yellow solid; mp none to 310 °C. IR: BH 2477 cm^{-1}. Anal. Calc for $C_{48}H_{44}B_2CoN_{12}$: C, 66.3; H, 5.06; N, 19.3. Found: C, 66.1; H, 5.23; N, 19.0.

[Fe(Tp^{4Bo,3Me})$_2$]: pale greenish solid; mp none to 300 °C. IR: BH 2472 cm^{-1}. Anal. Calc for $C_{48}H_{44}B_2FeN_{12}$: C, 66.3; H, 5.06; N, 19.3. Found: C, 66.5; H, 5.27; N, 19.1.

[Co(Tp^{3Bo,7Me})$_2$]: yellow solid; mp none to 310 °C. IR: BH 2461 cm^{-1}. Anal. Calc for $C_{48}H_{44}B_2CoN_{12}$: C, 66.3; H, 5.06; N, 19.3. Found: C, 65.9; H, 5.22; N, 19.3.

[Co(Tp^{4Bo,4,6Me2})$_2$]: yellow solid; mp lower than 300 °C. IR: BH 2484 cm^{-1}. Anal. Calc for $C_{54}H_{56}B_2CoN_{12}$: C, 68.0; H, 5.88; N, 17.6. Found: C, 68.3; H, 5.84; N, 17.2.

[Fe(Tp^{4Bo,4,6Me_2})$_2$]: red solid; mp none up to 310 °C. IR: BH cm^{-1}. Anal. Calc for $C_{54}H_{56}B_2FeN_{12}$: C, 68.2; H, 5.89; N, 17.7. Found: C, 68.4; H, 6.11; N, 17.5.

[Co(Tp^{a*,3Me})$_2$]: yellow solid; mp none to 310 °C. IR: BH 2505 cm^{-1}. Anal. Calc for $C_{72}H_{56}B_2CoN_{12}$: C, 73.9; H, 4.79; N, 14.4. Found: C, 74.1; H, 4.90; N, 14.1.

Heteroleptic Complexes of Type [Co(L)(Tp^{Np})]. These complexes were prepared by stirring an equimolar mixture of TlTp^x and [Co(Tp^{Np})(Cl)] in methylene chloride at room temperature until the blue color disappeared or overnight. After filtration through Celite to remove TlCl, the filtrate was chromatographed on alumina, collecting the

Table 2. NMR Data for Homoleptic and Heteroleptic* (with Tp^{Np}) Co(II) Complexes of Tp^{4Bo}-Type Hydrotris(indazolyl)borates[a]

indazole	3R	4R	5R	6R	7R
unsubstituted	−102	−10	11	20	51
unsubstituted*	−96	−9	11	19	47
3-methyl	−89 (Me)	−8	5	14	50
3-methyl*	−71 (Me)	−8	12	19	47
5-methyl	−102	−11	7 (Me)	21	52
5-methyl*	−97	−10	2 (Me)	20	49
5-ethyl	−101	−11	3 (CH_2)	21	51
			0.0 (Me)		
5-*tert*-butyl*	−95	−10	0.0 (tBu)	20	49
5-phenyl*	−95	−9	6 (Ph)	21	48
4,6-dimethyl*	−97	−14 (Me)	12	15 (Me)	53

[a] Signals are in ppm. Peaks for the Tp^{Np} protons in heteroleptic complexes are not shown; they average −96 (CH_2), −21 (tBu), 46 (H-4), and 79 (H-5) ppm.

yellow-orange band. The residue from evaporation of the solvent was stirred with methanol, the mixture was filtered to remove any residual azole present, and the product was then recrystallized from toluene/octane. Yields ranged from 45 to 65%. For ^{1}H NMR of these complexes, see Table 2.

L = $Tp^{4Bo,5Me}$: yellow solid; mp 240−242 °C. IR: BH 2471, 2467 cm^{-1}. Anal. Calc for $C_{48}H_{62}B_2CoN_{12}$: C, 64.9; H, 6.99; N, 18.9. Found: C, 65.0; H, 7.25; N, 18.8.

L = $Tp^{4Bo,3Me}$: yellow solid; mp 290−293 °C. IR: BH 2468, 2433 cm^{-1}. Anal. Calc for $C_{48}H_{62}B_2CoN_{12}$: C, 64.9; H, 6.99; N, 18.9. Found: C, 65.2; H, 7.28; N, 18.6.

L = $Tp^{4Bo,4,6Me_2}$: pale yellow solid; mp 304−307 °C. IR: BH 2480, 2445 cm^{-1}. Anal. Calc for $C_{51}H_{68}B_2CoN_{12}$: C, 65.9; H, 7.32; N, 18.1. Found: C, 66.1; H, 7.39; N, 17.8.

L = $Tp^{4Bo,5tBu}$: yellow solid; mp 304−306 °C. IR: BH cm^{-1}. Anal. Calc for $C_{57}H_{77}B_2CoN_{12}$: C, 67.7; H, 7.62; N, 16.6. Found: C, 67.9; H, 7.66; N, 16.5.

L = $Tp^{4Bo,5Ph}$: yellow solid; mp 280−282 °C. IR: BH cm^{-1}. Anal. Calc for $C_{63}H_{68}B_2CoN_{12}$: C, 70.5; H, 6.36; N, 15.7. Found: C, 70.7; H, 6.47; N, 15.3.

L = $Tp^{3Bo,7Me}$: peach-colored solid; mp 248−250 °C. IR: BH 2471, 2445 cm^{-1}. ^{1}H NMR: 95.3 (1 H, BH), 93.3 (1 H, BH′), 75.0 (3 H, Tp^{Np} H-5), 66.1 (3 H, H-3), 52.5 (3 H, Tp^{Np} H-4), 26.5 (3 H, H-4), −3.6 (3 H, H-5), −12.7 (3 H, H-6), −16.4 (27 H, tBu), −37.7 (Me), −87.8 (6 H, CH_2) ppm. Anal. Calc for $C_{48}H_{62}B_2CoN_{12}$: C, 64.9; H, 6.99; N, 18.9. Found: C, 65.1; H, 7.18; N, 18.6.

L = Tp^{a*}: orange-pink solid; mp 284−286 °C. IR: BH 2473, 2452 cm^{-1}. ^{1}H NMR: 97.2 (1 H, BH), 95.3 (1 H, BH′), 75 (3 H, Tp^{Np} H-5), 68 (3 H, H-3), 51 (3 H, Tp^{Np} H-4), 27 (3 H, H-4), 6.5 (3 H, H-8), −0.10 (3 H, H-7), −3.2 (3 H, H-5), −3.6 (3 H, H-6), −17 (27 H, tBu), −53 (3 H, H9), −89 (6 H, CH_2) ppm. Anal. Calc for $C_{57}H_{64}B_2CoN_{12}$: C, 68.6; H, 6.42; N, 16.9. Found: C, 68.5; H, 6.36; N, 16.5.

L = $Tp^{a*,3Me}$: peach-colored solid; mp 290−292 °C. IR: BH 2472, 2442 cm^{-1}. ^{1}H NMR: 98 (1 H, BH), 96 (1H, BH′), 75.8 (3 H, Tp^{Np} H-5), 50.1 (3 H, Tp^{Np} H-4), 41.2 (9 H, Me), 24.5 (3 H, H-8), 7.0 (3 H, H-7), −0.6 (3 H, H-6), −3.9 (3 H, H-5), −4.0 (3 H, H-4), −17.6 (27 H, tBu), −55.0 (3 H, H-9), −90.1 (6 H, CH_2) ppm. Anal. Calc for $C_{50}H_{68}B_2CoN_{12}$: C, 65.4; H, 7.42; N, 18.3. Found: C, 65.5; H, 7.56; N, 18.2.

Complexes $LMo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$. These complexes were prepared by stirring an equimolar mixture of $TlTp^x$ and $[(MeCN)_2Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$[13] in methylene chloride for 2−3 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 or orange band. Solvent evaporation produced a residue, which was recrystallized from a toluene/octane mixture. All the complexes were yellow, except for those of $Tp^{3Bo,7Me}$ and Tp^{a*}, which were orange. Yields ranged from 50 to 75%.

L = $Tp^{4Bo,5Me}$: mp darkens from about 270 °C, dec from 290 °C. IR: BH 2485, CO 1946, 1855 cm^{-1}. Anal. Calc for $C_{30}H_{29}BMoN_6O_2$: C, 58.8; H, 4.73; N, 13.7. Found: C, 58.9; H, 4.86; N, 13.5.

L = $Tp^{4Bo,5tBu}$: mp dec 308−310 °C. IR: BH 2479, CO 1951, 1871 cm^{-1}. ^{1}H NMR: vvb 8.5 (3H), vb 7.7 (3 H), s 7.58 (3 H), d 7.48 (3 H), s 3.67 (2 H, *syn*), s 1.62 (2 H, *anti*), s 1.53 (3 H, Me), s 1.29 (9 H) ppm. Anal. Calc for $C_{39}H_{47}BMoN_6O_2$: C, 63.4; H, 6.37; N, 11.4. Found: C, 63.7; H, 6.52; N, 11.0.

L = $Tp^{4Bo,5Ph}$: mp dec 234−237 °C. IR: BH 2488, CO 1947, 1856 cm^{-1}. ^{1}H NMR: vvb 8.8 (3 H), vb (8.0 (3 H), s 7.82 (3 H, H-3), s 7.67 (3 H), d 7.56 (6 H, ortho), t 7.38 (6 H, meta), t 7 25 (3 H, para), s 3.69 (2 H, *syn*), s 1.65 (2 H, *anti*), s 1.56 (3 H, Me) ppm. Anal. Calc for $C_{45}H_{35}BMoN_6O_2$: C, 67.7; H, 4.39; N, 10.5. Found: C, 67.5; H, 4.55; N, 10.3.

L = $Tp^{4Bo,3Me}$: mp darkens from 280 °C, dec 292−298 °C. IR: BH 2479, CO 1937, 1838 cm^{-1}. ^{1}H NMR: d 8.18 (1 H), d 7.97 (2 H), dt 7.58 (2 H), dt 7.52 (1 H), td 7.43 (2 H), td 7.16 (1 H), td 7.08 (2 H), td 6.91 (1 H), s 3.66 (2 H, *syn*), 3.25 (3 H, 3-Me), 2.95 (6 H, 3-Me), 1.78 (2 H, *anti*), 1.21 (3 H, Me) ppm. Anal. Calc for $C_{30}H_{29}BMoN_6O_2$: C, 58.8; H, 4.73; N, 13.7. Found: C, 59.0; H, 4.89; N, 13.4.

L = $Tp^{4Bo,4,6Me_2}$: mp darkens from about 270 °C, dec from 300 °C. ^{1}H NMR: vvb 8.5 (3 H), vb 7.5 (3 H), s 6.66 (3 H), s 3.70 (2 H, *anti*), s 2.50 (6 H, 6-Me), s 2.46 (3 H, 4-Me), 1.62 (2 H, *anti*), 1.52 (3 H, Me) ppm. Anal. Calc for $C_{33}H_{35}BMoN_6O_2$: C, 60.6; H, 5.35; N, 12.8. Found: C, 60.4; H, 5.53; N, 12.6.

L = $Tp^{3Bo,7Me}$: IR: BH 2459, 2185, sh 2180, CO 1966, 1878 cm^{-1}. ^{1}H NMR: s 8.43 (1 H), s 8.16 (1 H), s 8.15 (1 H), d 7.60 (1 H), t 7.45 (2 H), d 7.28 (1 H), d 7.18 (1 H), d 7.13 (1 H), quintet 7.02 (3 H), d 3.80 (1 H, *syn*), t 3.50 (1 H, *syn*), 3.32 (3 H), 3.00 (3 H), 2.79 (3 H), s 1.92 (1 H, *anti*), s 1.58 (3 H), d 1.33 (1 H, *anti*) ppm. Anal. Calc for $C_{30}H_{29}BMoN_6O_2$: C, 58.8; H, 4.73; N, 13.7. Found: C, 59.0; H, 4.91; N, 13.4.

L = Tp^{a*}: mp darkens from 150 °C, dec 170−174 °C. IR: CO 1940, 1855 cm^{-1}. ^{1}H NMR: d 10.21(1 H), d 9.46 (1 H), d 8.85 (1 H), s 8.46 (1 H), s 8.30 (1 H), s 8.17 (1 H), overlapping m 7.58−7.96 (9 H), m 7.36−7.50 (6 H), d 3.90 (1 H, *syn*), t 3.61 (1 H, *syn*), s 2.03 (1 H, *anti*), s 1.58 (3 H, Me), d 1.48 (1 H, *anti*) ppm. Anal. Calc for $C_{39}H_{29}BMoN_6O_2$: C, 65.0; H, 4.03; N, 11.7. Found: C, 65.2; H, 4.39; N, 12.1.

[Co($Tp^{3Bo,7Me}$)(NCS): mp 242−245 °C. IR: BH 2494, NCS 2065 cm^{-1}. ^{1}H NMR: 28.7 (3 H, H-6), 25.6 (3 H, H-5), 14.7 (9 H, Me), 8.4 (3 H, H-4), 3.6 (3 H, H-3), −8.9 (1 H) ppm. Anal. Calc for $C_{25}H_{22}BCoN_7S$: C, 57.5; H, 4.21; N, 18.8. Found: C, 57.9; H, 4.33; N, 18.7.

[Co($Tp^{3Bo,7tBu*}$)(NCS): mp 266−269 °C. IR: BH 2601, NCS 2072 cm^{-1}. Anal. Calc for $C_{34}H_{40}BCoN_7S$: C, 63.0; H, 6.17; N, 15.1. Found: C, 63.3; H, 6.29; N, 15.0.

[Zn($Tp^{3Bo,7Me}$)(NCS): mp 270−273 °C. IR: BH 2494, NCS 2084 cm^{-1}. ^{1}H NMR: s 8.78, d 7.51, d 7.15, t 6.99, s 2.91 ppm. Anal. Calc for $C_{25}H_{22}BN_7SZn$: C, 56.8; H, 4.17; N, 18.6. Found: C, 57.0; H, 4.28; N, 18.5.

[Rh($Tp^{4Bo,3Me}$)(COD)]: orange solid; mp 218−220 °C dec. ^{1}H NMR: d 7.56 (3 H), d 7.32 (3 H), t 7.17 (3 H), t 7.01 (3 H), m 4.15 (4 H COD arom), s 2.74 (9 H, Me), m 1.56 (4 H, COD aliph), m 1.42 (4 H, COD aliph) ppm. Anal. Calc for $C_{32}H_{34}BN_6Rh$: C, 62.3; H, 5.52; N, 13.6. Found: C, 62.0; H, 5.71; N, 13.2.

[Rh(Tp^{a*})(COD)]: yellow solid; mp 258−260 °C dec. Anal. Calc for $C_{41}H_{34}BN_6Rh$: C, 68.0; H, 4.70; N, 11.6. Found: C, 68.4; H, 4.98; N, 11.6.

[Rh($Tp^{a*,3Me}$)(COD)]: yellow solid; mp darkens from 245 °C. IR: BH 2478 cm^{-1}. Anal. Calc for $C_{44}H_{40}BN_6Rh$: C, 68.9; H, 5.22; N, 11.0. Found: C, 69.1; H, 5.37; N, 10.7.

[Rh(Tp^{a*})($CO)_2$]: light yellow solid; mp darkens from 210 °C, dec 250−260 °C. IR: BH 2480, CO 2080 and 2030 cm^{-1}. Anal. Calc for $C_{35}H_{22}BN_6O_2Rh$: C, 62.5; H, 3.27; N, 12.5. Found: C, 62.1; H, 3.42; N, 12.2.

[Rh($Tp^{a*,3Me}$)($CO)_2$]: light yellow solid; mp 272−274 °C. IR: BH 2494, CO 2078, 2014 plus small peak at 1983 cm^{-1}. ^{1}H NMR: d 9.47 (1 H, H-9), dd 7.83 (1 H, H-6), td 7.61 (1 H, H-7), td 7.56 (1 H, H-8), d 7.53 (1 H, H-4), d 7.35 (1 H, H-5), s 2.75 (3 H, Me) ppm. Anal. Calc for $C_{38}H_{28}BN_6O_2Rh$: C, 63.9; H, 3.92; N, 11.8. Found: C, 64.0; H, 4.12; N, 11.7.

Results and Discussion

The various indazoles were prepared by first synthesizing the tetrahydro derivatives from the appropriately substituted cyclohexanones and then aromatizing them to the indazoles via catalytic dehydrogenation over 5−10% Pd/C catalysts. Reaction of these indazoles with KBH_4 in 4-methylanisole gave cleanly a single product, the regiochemistry of which was investigated by means of ^{1}H NMR of their octahedral paramagnetic Co(II) complexes, as the chemical shifts of pyrazolyl protons in Co(II) tris(pyrazolyl)borates had been found to be a sensitive probe of their relative positions in space with regard to the Co atom.[20] Whenever their solubility was adequate, homoleptic complexes were used, but when they were too insoluble in typical NMR solvents, we resorted to the heteroleptic ones, prepared by the reaction of the Tl salt of the new ligand with [Co(Tp^{Np})Cl],[5] since such mixed somplexes had much better solubility.

It was established in advance that the chemical shifts of the indazolyl protons were essentially the same in homoleptic and heteroleptic complexes, with Tp^{Np} as the second ligand (Table 1). There was a small difference (5−6 ppm) in the shifts for the 3-H and 7-H, with homoleptic complexes displaying the greater shifts, suggestive of their more compact structure. For instance, the 3-H in homoleptic complexes was around −102 ppm, while in heteroleptic ones it was at −95 to −97 ppm. Similarly, the 7-H was at 51 ppm in the homoleptic complexes and 47−48 ppm in the heteroleptic ones. These discrepancies were negligible, compared to the specific chemical shifts of the indazolyl protons.

While its large shift made the 3-H immediately recognizable, the assignment of the 4-, 5-, 6-, and 7-protons was made by selectively placing methyl (or other) substituents at various positions of indazole and noting the disappearance of the appropriate proton peak. For instance, the ligand derived from 4,6-dimethylindazole had, in addition to the immediately identifiable 3-H peak at −97 ppm, single proton peaks at 12 and 53 ppm. These clearly belonged to the 5- and 7-protons. In the ligand from 5-methylindazole (as well as in those from 5-ethylindazole, 5-*tert*-butylindazole, and 5-phenylindazole), the 12 ppm proton peak disappeared and was thus assigned to 5-H, while, by default, the 53 ppm peak had to be that of the 7-H. The remaining peaks of the 4- and 6-protons were assigned to the −10 and + 20 ppm signals present (in addition to those mentioned above) in the spectra of the ligands from indazole itself and from 3-methylindazole. Clearly, as the protons become more and more distant from the cobalt atom, in the sequence 3, 4, 5, 6, 7, their chemical shifts become progressively more positive being, approximately, −100, −10, +10, +20, and +50 ppm. In the same manner the corresponding methyl peaks at the 3-, 4-, 5-, and 6-positions were determined to be at −70, −14, +7, and +15 ppm (see Table 1). There was no example for 7-Me in the Tp^{4Bo} ligand system, since 7-substitution leads to Tp^{3Bo}-type ligands (see below), but in view of the observed trend, it would probably be around 20−30 ppm. In the same manner, it was possible to assign proton signals for the Tp^{3Bo} ligands. For the 3-, 4-, 5-, and 6-protons they are +66, +26, −4, and −13 ppm. Again, no direct values for the 7-H could be obtained, since indazoles with a 7-H formed Tp^{4Bo} ligands. One could estimate that 7-H would be around −70 ppm, its spatial position with reference to the Co atom being close to that of the hydrogens from the 3-Me group in the $Tp^{4Bo,3Me}$ ligand.

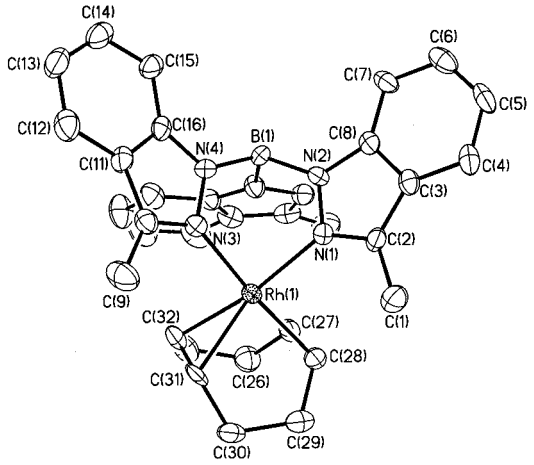

Figure 1. Molecular structure of [Rh(HB{3-methylindazol-1-yl}$_3$)(COD)], **1**, drawn with 30% probability ellipsoids. Unlabeled indazolyl ring atoms are numbered using the same numbering scheme as that for the numbered indazolyl ring atoms. Hydrogen atoms are omitted for clarity.

In the case of 3-methylindazole, there was little doubt *a priori* as to its regiochemistry, since the 3-methyl group was clearly larger than the benzo CH. Still, we determined the structure of its Rh derivative, [Rh($Tp^{4Bo,3Me}$)(COD)], and found the expected regiochemistry confirmed. The ligand coordinates in κ^2 fashion, as would be expected for a moderately hindered Tp^x ligand and a relatively bulky diene,[21] with the 2-N of the uncoordinated indazolyl group pointing away from the metal atom (Figure 1). In the NMR spectrum, the structure is fluxional, with all indazolyl groups identical. Rh−N distances are 2.105(6) and 2.120(6) Å, as compared with 2.099 Å in the analogous complex [Rh(pzTp)(COD)].[22] In related complexes [Rh($MeTp^{Me}$)(NBD)[23] and [Rh(Tp^{Me})(NBD),[24] where the diene is a more compact NBD and the Tp^x ligand is κ^3, the Rh−N distances are longer (2.242, 2.145, 2.229 Å and 2.248, 2.148, 2.25(1) Å, respectively).

The coordination chemistry of the Tp^{4Bo}-type ligands was consistent with their lack of steric hindrance at the coordinating end, close to the metal. In each instance, there was facile formation of homoleptic octahedral L_2M complexes with first-row transition metals, and Tp^{4Bo}-type ligands reacted rapidly with tetrahedral precursors such as [M(Tp^{Np})X] to yield heteroleptic octahedral species [M(Tp^{4Bo})(Tp^{Np})]. At the same time, attempts to prepare tetrahedral [M(Tp^{4Bo})(X)] species yielded only the homoleptic octahedral [M(Tp^{4Bo})$_2$] complexes.

All Tp^{4Bo}-type ligands reacted with [$(MeCN)_2Mo(CO)_2(\eta^3$-$CH_2CMeCH_2)$], producing the complexes [Mo(L)$(CO)_2(\eta^3$-CH_2-$CMeCH_2)$]. Their NMR spectra indicated fluxionality at room temperature for Tp^{4Bo} ligands containing 4-, 5-, or 6-substituents, similar to that observed with the parent Tp ligand, while, in the case of $Tp^{4Bo,3Me}$, the structure was a rigid one, with all indazolyl protons falling into 2:1 patterns, the spectrum resembling that of the Tp^{Me2} analog.[25]

Ligands of the Tp^{3Bo} type were formed only in the presence of a non-hydrogen substituent in the 7-position. Two of them,

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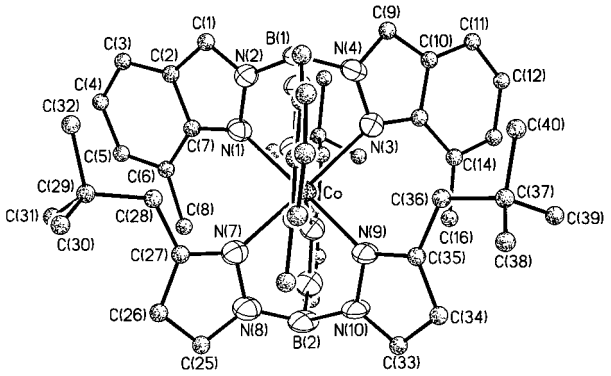

Figure 2. Molecular structure of [Co(HB{7-methylindazol-2-yl}$_3$)(HB{3-neopentylpyrazol-1-yl}$_3$)], **2**, drawn with 30% probability ellipsoids. Unlabeled pyrazolyl and indazolyl ring atoms are numbered using the same numbering scheme as that for the numbered pyrazolyl and indazolyl ring atoms. Carbon atoms are shown as spheres, and hydrogen atoms are omitted for clarity.

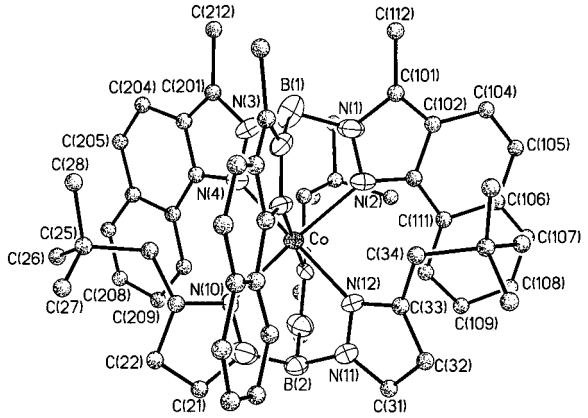

Figure 3. Molecular structure of [Co(HB{3-methyl-2*H*-benz[*g*]indazol-2-yl}$_3$)(HB{3-neopentylpyrazol-1-yl}$_3$)]·C_6H_5CN, **3,** drawn with 30% probability ellipsoids. Unlabeled pyrazolyl and indazolyl ring atoms are numbered using same numbering scheme as that for the numbered pyrazolyl and indazolyl ring atoms. Hydrogen atoms are omitted for clarity.

Tp^{3Bo,7Me} and Tp^{3Bo,7tBu}, were prepared, containing a 7-Me and a 7-tBu substituent, respectively. Here, the coordination chemistry was dominated by the close proximity of these 7-substituents to the metal. In the case of the 7-Me derivative, this was manifested by the largest $^{13}C-^{205}Tl$ coupling known for homoscorpionates, 416 ppm, for the 7-methyl group. The steric hindrance also caused reactions, such as the formation of the heteroleptic octahedral species [Co(Tp^{3Bo,7Me})(Tp^{Np})], to proceed very slowly, as compared with reactions of any of the Tp^{4Bo} ligands. Still, the heteroleptic complex was the expected, unrearranged one, as proven by the correct ^{1}H NMR spectrum, which confirmed that each set of three pyrazolyl groups within the ligand was identical**.** In addition, the Tp^{3Bo,7Me} structure of the ligand was established by X-ray crystallography (Figure 2), which shows the neopentyl substituents aligned with the pyrazolyl plane, so as to minimize interference with the 7-Me groups. The molecule is of approximate C_{3v} symmetry, with the Co−N bonds longer for the Tp^{3Bo,7Me} ligand than for Tp^{Np} (averaging 2.23 Å versus 2.14 Å). The complex [Mo(Tp^{3Bo,7Me})(CO)$_2$(η^3-methallyl) was also prepared. Its ^{1}H NMR spectrum had three unique methyl groups at 2.79, 3.00, and 3.32 ppm, and also each methallyl proton was unique, thus strongly suggesting the presence of a κ^2 Tp^{3Bo,7Me} ligand plus an agostic B−H−Mo bond, just as has been established for the the Tp^{a*} analog.[8] In contrast to the Tp^{4Bo}-type ligands, Tp^{3Bo,7Me} was sufficiently sterically encumbered at the metal end to permit isolation of the stable tetrahedral complex, [Co(Tp^{3Bo,7Me})(NCS)]. This complex was green, just as that derived from Tp^{3Bo,7tBu}, but unlike the latter it contained an unrearranged Tp^{3Bo,7Me} ligand, since ^{1}H NMR indicated C_{3v} symmetry and equivalence of all three 7-methylindazolyl groups.

In the case of the superhindered Tp^{3Bo,7tBu} ligand, no homoleptic or heteroleptic octahedral complexes could be prepared, and even the formation of a simple tetrahedral complex, [Co(L)NCS], was accompanied by steric-relief-driven rearrangement of the ligand to [HB(7-tBu-indazol-2-yl)$_2$(7-tBu-indazol-1-yl)] (=Tp^{3Bo,7tBu*}). The X-ray structures of the representative compounds, [Tl(Tp^{3Bo,7tBu})], and the rearranged derivative, [Co(Tp^{3Bo,7tBu*})(NCS)], have already been communicated.[26]

Another type of indazolylborate ligand, Tp^{a*}, contained a benzo group fused to the indazole ring in such a manner that the 9-H approached the coordinated metal.[8] In this case, the regiochemistry was exclusively of the Tp^{3Bo} type, with boron bonded to the less hindered nitrogen, and was consistent with the overruling of electronic factors by steric ones. Although the flat benzindazolyl group offered a wide wedge angle, and thus had low steric obstruction for side-on fit of other ligands, it had a large cone angle. As a result of this combination of features, homoleptic and heteroleptic octahedral complexes, such as [Co(Tp^{a*})(Tp^{Np})], could be formed, with the benzindazolyl rings interpenetrating in an orderly fashion. However, in the case of the [Mo(Tp^{a*})(CO)$_2$(η^3-methallyl) complex, the ligand functioned only in a bidentate fashion, the third coordination site being occupied by an agostic B−H−Mo bond, as was confirmed by X-ray crystallography.[8]

A modified Tp^{a*} ligand, containing an additional methyl group in the 3-position, was also synthesized. The 3-methyl group partly counterbalanced the steric effect of the fused benzo ring, so that the "as produced" Tl salt contained only 40% of the symmetrical ligand, Tp^{a*,3Me}, the rest being the 3,3,5-species. Still, the more symmetrical 3,3,3-ligand had lower solubility and could be obtained through selective extraction of the more soluble asymmetric species, followed by recrystallization. The presence of the 3-Me group gave rise to a tighter "bite" of the ligand and a larger cone angle, so that the reaction with [Mo(CO)$_2$(η^3-methallyl)(MeCN)(Cl)] failed to yield an isolable product, in contrast to the results obtained with Tp^{a*} or with Tp^{3Bo,7Me}. On the other hand, Tp^{a*,3Me} reacted with [Co(Tp^{Np})(Cl)], forming the heteroleptic octahedral complex, [Co(Tp^{Np})(Tp^{a*,3Me})], in which both ligands were κ^3, as was shown both by ^{1}H NMR and by an X-ray crystallographic structure determination of the benzonitrile adduct, **3** (Figure 3). The Co-N bond distances in Tp^{a*,3Me} are slightly longer than those in Tp^{Np}, averaging 2.21 Å versus 2.15 Å, and the bond length disparity between the two ligands is less than in [Co(Tp^{3Bo,7Me})(Tp^{Np})]. The ligand also formed the [Rh(Tp^{a*,3Me})(CO)$_2$] complex, which showed equivalence of all three indazolyl groups in the NMR spectrum, although the type of structure in the crystal is uncertain.

Conclusions

The regiochemistry of homoscorpionate ligands prepared from indazoles can be controlled as follows:

1. Indazole itself and indazoles containing alkyl or aryl substituents in positions 3, 4, 5, and 6 form ligands where boron is bonded to the more hindered N-1 and represent a special class of homoscorpionate ligands containing a protective pocket

(26) Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1233−1234.

around boron but sterically unencumbered at the coordinating end and behaving much like the parent Tp. Tp^{4Bo}-type ligands also represent the first example of 4,5-disubstituted homoscorpionates.

2. Indazoles having alkyl substituents at the 7-position or containing a 6,7-fused benzo ring yield ligands with boron bonded to the less hindered N-2. They possess very large cone angles, with the 7-R or 9-H (for naphthopyrazolyl) being very close to the metal. Nevertheless, they do form octahedral complexes, thanks to their large wedge angles. On the other hand, in the complexes $[Mo(L)(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$ they only bond in κ^2 fashion, also providing an agostic B−H−Mo bond.

3. Indazoles containing both 3- and 7- substituents (including a fused 6,7-benzo ring) do not yield regiochemically pure ligands, although bonding to the less hindered N-2 is still preferred. While there is insufficient information on this class (only one example), regiochemically pure ligands might be obtainable, given sufficient disparity in size between the 3- and 7-substituents.

Supporting Information Available: Tables listing atomic positional parameters, thermal parameters, and bond lengths and angles (24 pages). Ordering information is given on any current masthead page.

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