

Homoscorpionate (Tris(pyrazolyl)borate) Ligands Containing Tethered 3-Phenyl Groups

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Four new homoscorpionate ligands have been prepared, three of them involving a 3-phenyl substituent subject to steric control via tethering to the 4-position of the pyrazole ring. The tethering prevents major departure from parallel alignment of the phenyl and pyrazolyl rings. In addition, the choice of the tether (methylene or 1,2-ethylene) results in the phenyl 6'-CH being either pulled away from the metal in the former case or thrust toward the metal in the latter. The effect of the 5-methyl substituent on the bite of the ligand was also explored. The new ligands were hydrotris(2*H*-benz[*g*]-4,5-dihydroindazol-2-yl)borate (=Tp^a), hydrotris(3-methyl-2*H*-benz[*g*]-4,5-dihydroindazol-2-yl)borate (=Tp^{a,Me}), hydrotris(1,4-dihydroindeno[1,2-*c*]pyrazol-1-yl)borate (=Tp^b), and hydrotris(3-phenyl-5-methylpyrazol-1-yl)borate (=Tp^{Ph,Me}), each of which differed subtly in its coordinative behavior from the other three. Complexes of the type L₂M, LMX, LRh(COD), LRh(CO)₂, LPd(η³-methallyl), and LMo(CO)₂(η³-methallyl) were synthesized, and the structures of Tp^aRh(CO)₂, Tp^{a,Me}ZnI, Tp^bTl, and Tp^{Ph,Me}ZnI were determined by X-ray crystallography. Tp^aRh(CO)₂ crystallizes in the space group *P* $\bar{1}$, with *a* = 8.574(2) Å, *b* = 20.113(6) Å, *c* = 20.188(6) Å, α = 61.68(2)°, β = 84.14(2)°, γ = 85.15(2)°, and *V* = 3046.0(15) Å³ for *Z* = 4. Tp^{a,Me}ZnI crystallizes in the space group *P*2₁2₁2₁, with *a* = 10.002(1) Å, *b* = 16.237(3) Å, *c* = 19.952(3) Å, and *V* = 3240.3(8) Å³ for *Z* = 4. Tp^bTl crystallizes in the space group *P*2₁/*n*, with *a* = 11.363(2) Å, *b* = 11.09692) Å, *c* = 21.010(4) Å, β = 99.33(2)°, and *V* = 2614.0(9) Å³ for *Z* = 4. The phenyl and pyrazolyl planes are essentially coplanar. Tp^{Ph,Me}ZnI crystallizes in the space group *P*na2₁, with *a* = 32.645(6) Å, *b* = 11.327(3) Å, *c* = 16.180(3) Å, and *V* = 5983.1(22) Å³ for *Z* = 8. Cone and wedge angles were calculated for the new ligands and compared with revised previously reported values.

Introduction

In the known complexes containing the HB(3-phenylpyrazol-1-yl)₃ ligand (=Tp^{Ph}) and its analogs Tp^{Tol} and Tp^{An},¹ the phenyl group is free to rotate around the pyrazolyl-phenyl bond. Such structures, as determined by X-ray crystallography, usually contain the aromatic ring rotated at some angle with respect to the pz plane, the extent of such rotation being often governed by packing forces. Typically, in compounds such as Tp^{Ph}CoNCS·THF,² Tp^{Ph}₂Fe,³ Tp^{Ph}Cu(pterin),⁴ Tp^{Ph}₂Yb,⁵ Tp^{Ph}₂Sm,⁵ Tp^{Tol}Tl,⁶ and Tp^{An}Mo(CO)₂NO,⁷ the twist angles between the aromatic ring and the pyrazolyl plane range from 2 to 62° and are most commonly between 20 and 40°.

We were recently interested in constructing homoscorpionate (tris(pyrazolyl)borate) ligands in which, through appropriate substitution, the phenyl group would be almost frozen in a particular twist orientation around the pz-Ph bond with only a small degree of oscillatory freedom, leading to a more predictable and controllable environment around the coordinated metal. The first such ligands, [HB(3-mesityl-pz)₃]⁻ (=Tp^{Me}) and [HB(3-mesityl-pz)₂(5-mesityl-pz)]⁻ (=Tp^{Me*}), contained phenyl groups which were prevented from rotation around the pyrazolyl plane by the 2',6'-methyl substituents. The phenyl rings in these ligands,

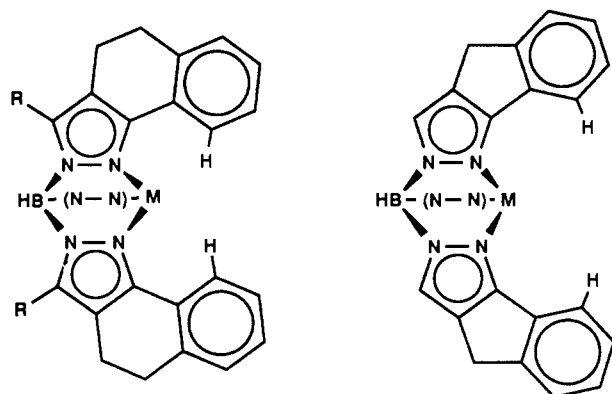
while not exactly orthogonal, were restricted to a 15–20° oscillation around the phenyl-pyrazolyl bond, as was shown by X-ray crystallographic structure determination of the complexes Tp^{Me}Mo(CO)₂(η³-methallyl) and Tp^{Me*}ZnI.⁸ A similar type of rotational blocking was achieved in the HB[3-(9-anthryl)pz]₃ (=Tp^{An}) ligand. However, orthogonality in complexes of this ligand was prevented by the nonbonding repulsions of the 2',3',6',7'-hydrogens, and this resulted in each anthryl group being twisted with respect to the pyrazolyl plane.⁹

We planned to achieve a different type of fixed twist angle, one in which the phenyl group approaches coplanarity to the pyrazolyl plane, through tethering of the phenyl group by means of a link from its 2'-(ortho-) position to the pyrazolyl 4-position. The model ligand chosen was hydrotris(4,5-dihydro-2*H*-benz[*g*]-indazol-2-yl)borate (=Tp^a), differing from Tp^{Ph} in having the phenyl 2'-position tied to the pyrazolyl 4-position by a 1,2-ethylene tether. This tether pushes the phenyl group toward the metal and prevents major departure from coplanarity of the phenyl and pyrazolyl groups. With a suitable combination of metal and coligands, oxidative addition of the phenyl C-H to the metal would be facilitated, as compared with the Tp^{Ph} ligand. To assess the effect of modest structural changes on the coordinative behavior of this ligand type, we also prepared the following related ligands: hydrotris(3-methyl-4,5-dihydro-2*H*-benz[*g*]indazol-2-yl)borate (=Tp^{a,Me}), where in addition to the 1,2-ethylene tether there is a methyl group in the pyrazolyl 5-position, such substitution having been found to impart additional stability to the ligand by providing steric protection to the B-H bond and by tightening the ligand bite; hydrotris(1,4-dihydroindeno[1,2-*c*]pyrazol-1-yl)borate (=Tp^b), differing from Tp^a in having a shorter tether, -CH₂-, pulling the phenyl group away from the coordinated metal; hydrotris(3-phenyl-5-pyrazol-1-yl)borate (=Tp^{Ph,Me}), differing from Tp^{a,Me} in having the phenyl group untethered.

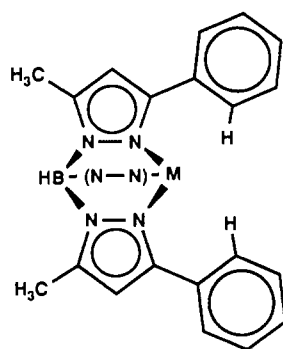
[†] University of Delaware.[‡] duPont.[⊙] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

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Tp^a: R = HTp^a.Me: R = CH₃

[-(N-N)- denotes the third, hidden, pz* group]

Tp^{Ph,Me}

The appropriate pyrazoles, 2*H*-benz[*g*]-4,5-dihydroindazole, 3-methyl-2*H*-benz[*g*]-4,5-dihydroindazole, 1,4-dihydroindeno[1,2-*c*]pyrazole, and 3-phenyl-5-methylpyrazole, were synthesized and converted to the corresponding homoscorpionate ligands, Tp^a, Tp^a.Me, Tp^b, and Tp^{Ph,Me}, and selected features of their coordinative behavior were studied.

Experimental Section

The compounds 3-phenyl-5-methylpyrazole,¹⁰ [PdCl(η³-CH₂CMeCH₂)₂]₂,¹¹ (MeCN)₂MoCl(CO)₂(η³-CH₂CMeCH₂),¹² Tp^bNpCoCl,¹³ and [RhCl(COD)]¹⁴ were prepared by literature methods. All the other chemicals were 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.

Synthesis of the Various Pyrazoles. 2*H*-Benz[*g*]-4,5-dihydroindazole. A mixture of 250 g of 1-tetralone (1.7 mol) and 275 mL of ethyl formate (3.4 mol, 100% excess) was poured in one portion into a nitrogen-blanketed slurry of 92.5 g of sodium methoxide (1.7 mol) in 2 L of toluene. After a few minutes, the slurry cleared and set up to a thick paste. After 30 min, 2 L of water was added and the mixture was stirred until the solids dissolved. The aqueous layer was separated from the mixture and treated with 1.7 mol of hydrazine hydrochloride. The resulting red product was extracted with methylene chloride, and the extracts were filtered through a 4-cm layer of alumina. The eluate was stripped, yielding a bright

orange-red solid to which was added 400 mL of isopropyl alcohol and 45 mL of hydrazine hydrate (for hydrazinolysis of some of the red byproducts to the desired compound). The solvent was slowly boiled off (oil bath), and when the bath temperature approached 200 °C, water started distilling out, and the color of the product lightened. The product was distilled in vacuo, with the main cut boiling at 181 °C/0.6 Torr, and was obtained in 156 g (54%) yield. The yellow distillate solidified and was recrystallized from toluene: mp 123–124 °C (lit. mp 123,¹⁵ 135 °C¹⁶); ¹H NMR δ 7.77 (1H), s 7.35 (1H), m 7.14–7.24 (3H), t 2.90 (2H), t 2.74 (2H) ppm. The ¹³C NMR of this compound has been reported.¹⁷ Anal. Calc for C₁₁H₁₀N₂: C, 77.6; H, 5.88; N, 16.5. found: C, 77.7; H, 5.94; N, 16.4.

3-Methyl-2*H*-benz[*g*]-4,5-dihydroindazole. To 25 g (0.13 mol) of 2-acetyl-1-tetralone stirred in 200 mL of a 50:50 methanol/isopropyl alcohol mixture was added dropwise 8 mL (excess) of hydrazine hydrate. An exothermic reaction took place, and a clear solution resulted. It was stripped to dryness, and the product was obtained in 22.5 g (94%) yield. After recrystallization from toluene/heptane, the product melted at 142–143 °C. NMR: broad NH around 12.2 ppm m (1H); m 7.70 (1H), m 7.18 (1H), m 7.12 (2H), t 2.87 (2H), t 2.58 (2H), s 2.14 (3H) ppm. The ¹³C NMR of this compound has been reported.¹⁷ Anal. Calc for C₁₂H₁₂N₂: C, 78.3; H, 6.52; N, 15.2. Found: C, 77.8; H, 6.47; N, 15.3.

1,4-Dihydroindeno[1,2-*c*]pyrazole. A mixture of 100 g (0.76 mol) of 1-indanone and 200 g (large excess) of ethyl formate was added in one portion to a stirred, nitrogen-blanketed suspension of 41 g (0.76 mol) of anhydrous NaOMe in 1 L of toluene. Within seconds a thick paste resulted, which was stirred mechanically and then diluted with hexane, and the product was extracted with a mixture of 1 L of water plus 300 mL of 2-propanol. The aqueous layer was separated from the mixture and treated with an aqueous solution of 0.76 mol of hydrazine hydrochloride. The red product was extracted with methylene chloride, and the extract was passed through alumina and stripped, yielding a yellow solid, which was refluxed for 1 h in isopropyl alcohol, containing 25 mL of hydrazine hydrate. The solution was then stripped to dryness, and the residue was heated to 220 °C. The product was sublimed in vacuo from the dark residue and was further purified by recrystallization from 2-propanol: yield 45 g (46%); mp 203–204 °C with prior sintering around 200 °C. Because of low solubility in chloroform, the NMR was run in acetone-*d*₆: δ 7.65 (1H), s 7.57 (1H), d 7.48 (1H), t 7.30 (1H), t 7.22 (1H), broad hump 3.8–4.8 (1H), s 3.61 (2H) ppm. The ¹³C NMR of this compound has been reported.¹⁷ Anal. Calc for C₁₀H₈N₂: C, 76.9; H, 5.13; N, 18.0. Found: C, 77.1; H, 5.22; N, 17.8.

Synthesis of the Ligands Tp^a, Tp^a.Me, Tp^b, and Tp^{Ph,Me}. Thallium Hydrotris(2*H*-benz[*g*]-4,5-dihydroindazol-2-yl)borate (=L^aTl). A mixture of 5.4 g (0.1 mol) of KBH₄ and 68 g (0.4 mol) of 2*H*-benz[*g*]-4,5-dihydroindazole was stirred and refluxed overnight in 200 mL of anisole, during which time white solid precipitated. The hot slurry was filtered, and the fluffy solid was washed with anisole, and obtained after drying in 40 g (56%) yield. It contained a strong BH stretch at 2398 cm⁻¹ and was very soluble in DMF but sparingly in chloroform. The ligand was converted to the Tl salt, which on heating in a capillary started turning amber only at the air-exposed surface and decomposed at 302 °C. IR: BH 2425 cm⁻¹. NMR: unresolved d (but not nearly as broad as in the case of Tp^a.Me analog; *vide infra*) 7.82 (3H, 6'-H) ppm; s 7.54 (3H, 5-H), m 7.15–7.30 (9H, 3',4',5'-H) ppm; A₂B₂ set of two triplets at 2.86 (6H, CH₂) and 2.70 (6H, CH₂) ppm. ¹³C NMR: 19.5 ppm; 30.1, 116.5, 122.6 ppm (broad, but still "singlet", unlike the well-resolved doublet of Tp^a.Me, with *J* = 317.3 Hz); 126.6, 127.1, 128.7, 130.0, 133.0, 137.5 ppm; 149.7 ppm (again, this peak of 3-C is sharp here but broad in for Tp^a.Me analog). Anal. Calc for C₃₃H₂₈BN₆Tl: C, 54.8; H, 3.87; N, 11.6. Found: C, 54.4; H, 3.92; N, 11.4.

Thallium Hydrotris(3-methyl-2*H*-benz[*g*]-4,5-dihydroindazol-2-yl)borate (=L^a.MeTl). A mixture of 55 g of 3-methyl-2*H*-benz[*g*]-4,5-dihydroindazole (0.30 mol) and 2.7 g (0.05 mol) of KBH₄ was melted with stirring and heated by means of an oil bath. Hydrogen evolution commenced around 190–200 °C and continued up to 245 °C, the theoretical amount being evolved within 1 h. The melt was cooled and dissolved in THF, and this solution was added to a stirred mixture of chloroform plus excess aqueous TiNO₃. The organic layer was filtered through a short layer of alumina, and the solvent was stripped off. After trituration with methanol, a white solid was obtained, which was isolated by filtration, thoroughly washed with methanol, and dried, yielding 31

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g (81%) of the Tl salt, which gradually darkened from 240 °C but did not melt up to 290 °C. IR: BH 2430 cm⁻¹. ¹H NMR: broad d 7.6–7.9 (3H, 6'-H), m 7.1–7.25 (9H, 3',4',5'-H), broad BH 4.7–5.6 (1H), t 2.86 (6H, CH₂), t 2.60 (6H, CH₂), s 2.40 (9H, CH₃). ¹³C NMR: 11.3 (Me), 19.2 and 30.1 (both CH₂), 115.1 (C4), 122.5 (d, *J* = 317.3 Hz, 6'-C), 126.5, 126.9, and 128.5 (3',4',5'-C), 130.2 (1'-C), 137.4 (5-C), 140.0 (2'-C), 148.3 (broadened, 3-C) ppm. Anal. Calc for C₃₆H₃₄BN₆Tl: C, 56.5; H, 4.44; N, 11.0. Found: C, 56.7; H, 4.56; N, 10.9.

Thallium Hydrotris(1,4-dihydroindeno[1,2-*c*]pyrazol-1-yl)borate (=L^bTl). A mixture of 1,4-dihydroindeno[1,2-*c*]pyrazole and KBH₄ in a 4:1 molar ratio was refluxed in anisole for over 30 h. The mixture was stripped to dryness, and the residue was dissolved in THF and treated with excess saturated aqueous TiNO₃ solution. The product was extracted with methylene chloride, the extracts were filtered through alumina and evaporated, and the residue was stirred with methanol, affording L^bTl in 42% yield. The product was recrystallized from xylene: mp 243–244 °C; IR BH 2438 cm⁻¹; ¹H NMR d 7.74 (3H, 6'-H), s 7.65 (3H, 5-H), d 7.41 (3H, 3'-H), t 7.31 (3H, 4'- or 5'-H), t of d 7.22 (3H, 4'- or 5'-H), s 3.55 (6H, CH₂) ppm; ¹³C NMR 28.9 (CH₂), 120.1 (6'-C), 123.8 (4-C), 126.1, 126.5, 126.8 (3',4',5'-C), 130.2 (3-C), 134.8 (1'-C), 149.1 (2'-C), 161.3 (3-C) ppm. Anal. Calc for C₃₀H₂₂BN₆Tl: C, 52.9; H, 3.23; N, 12.2. Found: C, 53.2; H, 3.34; N, 12.1.

Thallium Hydrotris(3-phenyl-5-methylpyrazol-1-yl)borate (=Tp^{Ph,Me}.Tl). A mixture of 200 g (1.27 mol) of 3-phenyl-5-methylpyrazole and 10.8 g of KBH₄ (0.2 mol) was melted, stirred, and heated (oil bath) until the theoretical amount of hydrogen (15 L) was evolved. Excess 3-phenyl-5-methylpyrazole was distilled out in vacuo. The residue was cooled and dissolved in THF, and the solution was poured into excess aqueous TiNO₃, also containing methylene chloride. A white solid precipitated, poorly soluble in the organic phase. The mixture was filtered, and the solid was washed with methanol and then with methylene chloride. The yield of the dry solid was 53 g. The organic layer from the filtrate was passed through a 5-cm layer of alumina, stripped, and triturated with isopropyl alcohol, yielding 62 g of white solid identical to the first crop. Total yield was 115 g (84%). Recrystallization from toluene afforded crystals melting sharply at 242–243 °C. IR: BH 2502 cm⁻¹. ¹H NMR: d 7.57 (6H, 2',6'-H), m 7.1–7.3 (9H, 3',4',5'-H), s 6.28 (3H, 4-H), 4.4–5.6 (1H, BH), s 2.50 (9H, CH₃) ppm. ¹³C NMR: 13.2 (Me), 104.5 (C4), 127.1 (2',6'-C), 127.7 (4'-C), 128.9 (3',5'-C), 134.4 (5-C), 145.4 (1'-C), 152.4 (3-C) ppm. Anal. Calc for C₃₀H₂₈BN₆Tl: C, 52.4; H, 4.08; N, 12.2. Found: C, 52.5; H, 4.13; N, 12.1.

Preparation of Complexes of the Tp^a, Tp^{a,Me}, Tp^b, and Tp^{Ph,Me} Ligands. Octahedral Homoleptic Complexes L₂M. A typical preparation involved the dropwise addition of 0.5 equiv of a THF solution of MCl₂ or M(ClO₄)₂ to a stirred methylene chloride solution of the Tl salt of the appropriate ligand. The "end point" in some cases was clearly indicated by a color change (e.g. by the cessation of disappearance of the deep blue color of CoCl₂(THF)_n and appearance of a yellow color). The TiCl was filtered off, the filtrate was passed through a column of alumina, and the eluate was stripped. The products were recrystallized from xylene/octane or toluene/heptane mixtures.

Tp^aCo: yellow crystals; darkens from 285 °C, dec 292–298 °C; IR BH 2448 cm⁻¹. Anal. Calc for C₆₆H₅₆B₂CoN₁₂: C, 72.2; H, 5.10; N, 15.3. Found: C, 72.3; H, 5.18; N 15.1.

L₂Fe: pale greenish crystals; darkens gradually from 285 °C, dec 298–302 °C; IR BH 2443 cm⁻¹. Anal. Calc for C₆₆H₅₆B₂FeN₁₂: C, 72.4; H, 5.12, N, 15.4. Found: C, 72.1; H, 5.22; N, 15.2.

Tp^aZn: white crystals; mp 242–244 °C dec; IR BH 2447 cm⁻¹; NMR s 7.61 (3H), d 6.76 (3H), m 6.65 (6H), t 6.13 (1H), t 2.26 (6H), t 1.83 (6H) ppm. Anal. Calc for C₆₆H₅₆B₂N₁₂Zn: C, 71.8; H, 5.08; N, 15.2. Found: C, 72.1; H, 5.30; N, 14.9.

Tp^{a,Me}Co: yellowish orange crystals; no mp up to 310 °C; IR BH 2547 cm⁻¹. Anal. Calc for C₇₂H₆₈B₂CoN₁₂: C, 73.2; H, 5.76; N, 14.2. Found: C, 73.3; H, 5.77; N, 14.0.

Tp^{a,Me}Fe: pale greenish crystals; no mp up to 310 °C; IR 2544 cm⁻¹. Anal. Calc for C₇₂H₆₈B₂FeN₁₂: C, 73.34; H, 5.77; N, 14.26. Found: C, 73.38; H, 5.70; N, 14.16.

Tp^{a,Me}Zn: white crystals; mp 288–290 °C; IR 2522 cm⁻¹; NMR d 6.93 (3H), d 6.73 (3H), t 6.61 (3H), t 6.05 (3H), s 2.53 (9H), t 2.11 (6H), t 1.85 (6H) ppm. Anal. Calc for C₇₂H₆₈B₂N₁₂Zn: C, 72.8; H, 5.73; N, 14.2. Found: C, 73.0; H, 5.84; N, 14.0.

Tp^bCo: yellow crystals; no mp up to 320 °C; IR BH 2449 cm⁻¹. Anal. Calc for C₆₀H₄₄B₂CoN₁₂: C, 71.1; H, 4.34; N, 16.6. Found: C, 71.5; H, 4.47; N, 16.4.

Tp^{Ph,Me}Co: salmon-colored crystals; sinters from 253 °C, changes color through purple to amber, melts with bubbling around 258 °C, and

then partly resolidifies; no further change occurs until around 290 °C, when darkening takes place only at the surface exposed to air; IR BH 2542 cm⁻¹; NMR b 87.5 (BH), 50.0 (4-H), 35.8 (Me), -0.1 (*m*-H's), -0.2 (*p*-H), b -39.3 (*o*-H's) ppm in 2:3:9:6:3:6 ratio. Anal. Calc for C₆₀H₅₆B₂CoN₁₂: C, 70.2; H, 5.46; N, 16.4. Found: C, 69.8; H, 5.47; N, 16.2.

Tp^{Ph,Me}Fe: white solid; sinters from 251 °C, melts with partial resolidification around 253 °C, remelts around 268 °C with a brown ring at the surface exposed to air; IR BH 2543 cm⁻¹. Anal. Calc for C₆₀H₅₆B₂FeN₁₂: C, 70.5; H, 5.48; N, 16.4. Found: C, 70.6; H, 5.55; N, 16.3.

Tp^{Ph,Me}Zn: white solid; mp 166–169 °C with bubbling; IR BH 2473 cm⁻¹; NMR: d 7.59 (6H, 2',6'-H), overlapping triplets centered at 7.3 (9H, 3',4',5'-H), b s 6.16 (3H, 5-H), s 2.50 (9H, CH₃) ppm. Anal. Calc for C₆₀H₅₆B₂N₁₂Zn: C, 69.8; H, 16.3; N, 16.3. Found: C, 70.0; H, 5.52; N, 16.1.

Octahedral Heteroleptic Complexes LMTp^{Np}. These complexes were prepared by stirring an equimolar mixture of the Tl salt of the appropriate ligand with Tp^{Np}CoCl in methylene chloride overnight. The blue color had faded by that time, and the slurry was chromatographed on alumina, collecting the peach-colored band. Evaporation yielded the product, which was recrystallized from toluene/heptane.

Tp^aCoTp^{Np}: peach-colored crystals, mp 266–268 °C; IR BH 2469, 2441 cm⁻¹; NMR 96 (2H, BH), 76 (3H, 5-H of Tp^{Np}), 68 (3H, 5-H of Tp^a), 51 (3H, 4-H), 7.6 (6H, Tp^a CH₂), 6.3 (3H), -0.9 (3H), -4.5 (3H), -8.0 (6H, Tp^a CH₂), -17 (27H, *t*-Bu), -57 (3H, Tp^a CH nearest Co), -89 (6H, Tp^{Np} CH₂). Assignments were correlated with known paramagnetic spectra involving heteroleptic octahedral Co(II) complexes of Tp^{Np}. Anal. Calc for C₅₇H₆₈B₂CoN₁₂: C, 68.3; H, 6.79; N, 16.8. Found: C, 68.5; H, 6.88; N, 16.6.

L^{a,Me}CoTp^{Np}: peach-colored crystals; mp 280–281 °C; IR BH 2442, 2471, 2545 cm⁻¹; NMR 96 (2H, BH), 76.3 (3H, 5-H), 49.6 (3H, 4-H), 38.0 (9H, CH₃), 6.8 (3H, CH), 6.7 (6H, L^a CH₂), -1.1 (3H), -4.7 (3H), -8.1 (6H, L^a CH₂), -17.2 (27H, *t*-Bu), -90.6 ppm (6H, Tp^{Np} CH₂). Anal. Calc for C₆₀H₇₄B₂CoN₁₂: C, 69.03; H, 7.09; N, 16.1. Found: C, 69.3; H, 7.21; N, 16.0.

Tp^bCoTp^{Np}: yellow solid, no mp to 310 °C; IR BH 2470, 2441 cm⁻¹; NMR 109 (1H, BH), 106 (1H, BH), 81.3 (3H, 5-H of Tp^{Np}), 73.6 (3H, 5-H of L^a), 48.3 (3H, 4-H), 35.0 (6H, Tp^b CH₂), 1.40 (3H, Ph CH), -2.96 (3H, Ph CH), -5.31 (3H, Ph CH), -19.2 (27H, Me), -30.1 (3H, Ph 6-H), -98.9 (6H, Tp^{Np} CH₂). Anal. Calc for C₅₄H₆₂B₂CoN₁₂: C, 67.6; H, 6.47; N, 17.5. Found: C, 67.7; H, 6.54; N, 17.3.

Tp^{Ph,Me}CoTp^{Np}. Attempts to prepare this complex by prolonged stirring of a solution of Tp^{Np}CoCl and Tp^{Ph,Me}Tl in methylene chloride gave no reaction, and the starting materials were recovered unchanged.

Tp^aMX Complexes (M = Co, Ni, Zn; X = Cl, I, NCO, NCS). These complexes were prepared by stirring a sample of the ligand Tl salt in a 50:50 mixture of DMF and methylene chloride. A large excess of the metal halide, plus additional alkali halide (which resulted in better yields), or metal perchlorate and KNCO or KNCS was added, and the mixture was stirred overnight. Water plus additional methylene chloride was added, and the methylene chloride layer was separated from the mixture and washed with water three times to remove DMF. It was then filtered rapidly through a shallow bed of Celite/alumina, and the filtrate was evaporated to dryness. The residue was recrystallized from toluene or xylene. In some instances (Co and Ni, but not Zn) five-coordinate solvated species were obtained, but the solvate molecule could be removed by heating in vacuo. In the case of Tp^a, the Tp^aTl solution was added very slowly to a large excess of MX₂ in order to minimize formation of Tp^a₂M.

Tp^aZnI: white solid; mp 285–287 °C; IR BH 2452 cm⁻¹; NMR d 8.61 (3H), s 7.57 (3H), m 7.18–7.32 (9H), t 2.86 (6H, CH₂), t 2.68 (6H, CH₂) ppm. Anal. Calc for C₃₃H₂₈BN₆Zn: C, 55.7; H, 3.94; N, 11.8. Found: C, 55.5; H, 4.05; N, 11.9.

Tp^aZnNCS: white solid; mp to 315 °C; IR BH 2466, NCS 2075 cm⁻¹; NMR d 8.28 (3H), s 7.56 (3H), t 7.55 (3H), m 7.25 (6H), t 2.88 (6H, CH₂), t 2.71 (6H, CH₂) ppm. Anal. Calc for C₃₄H₂₈BN₇SZn: C, 63.6; H, 4.36; N, 15.2. Found: C, 63.7; H, 4.45; N, 15.0.

Tp^aZnNCO: white solid; mp to 315 °C; IR BH 2467, NCO 2246 cm⁻¹; NMR d 8.37 (3H), s 7.56 (3H), t 7.46 (3H), m 7.25 (6H), t 2.88 (6H, CH₂), t 2.70 (6H, CH₂) ppm. Anal. Calc for C₃₄H₂₈BN₇OZn: C, 65.2; H, 4.47; N, 15.7. Found: C, 64.9; H, 4.55; N, 15.6.

Tp^{a,Me}CoCl: bluish-green solid; attempted chromatography on alumina converts it to Tp^{a,Me}Co; no mp to 330 °C; IR 2556 cm⁻¹. Anal. Calc for C₃₆H₃₄BClCoN₆: C, 65.9; H, 5.19; N, 12.8. Found: C, 66.1; H, 5.27; N, 12.7.

Table 1. Crystal Data for Rh(CO)₂Tp^a (1), ZnITp^aMe (2), TITp^b (3), and ZnITp^bMe (4)

	1	2	3	4
formula	C ₃₅ H ₂₈ BN ₆ O ₂ Rh	C ₃₆ H ₃₄ BN ₆ ZnI	C ₃₀ H ₂₂ BN ₆ Tl	C ₃₀ H ₂₈ BN ₆ ZnI
fw	454.7	753.8	681.7	675.7
space group	P $\bar{1}$	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n	Pna2 ₁
a, Å	8.574(2)	10.002(1)	11.363(2)	32.645(6)
b, Å	20.113(6)	16.237(3)	11.096(2)	11.327(3)
c, Å	20.188(6)	19.952(3)	21.010(4)	16.180(3)
α , deg	61.68(2)			
β , deg	84.14(2)		99.33(2)	
γ , deg	85.15(2)			
V, Å ³	3046.0(15)	3240.3(8)	2614.0(9)	5983.1(22)
Z	4	4	4	8
temp, K	298	233	296	296
λ , Å (Mo K α)	0.710 73	0.710 73	0.710 73	0.710 73
ρ (calc), g cm ⁻³	1.479	1.545	1.732	1.500
μ (Mo K α), cm ⁻¹	6.04	17.47	62.10	18.82
R(F) ^a	0.0360	0.0419	0.0430	0.0476
R _w (F) ^b	0.0388	0.0492	0.0424	0.0523

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|, \quad ^b [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; \quad w^{-1} = \sigma^2(F_o) + gF_o^2.$$

Tp^aMeCoNCO: bluish-green solid; no mp to 310 °C; IR BH 2555, NCO 2211 cm⁻¹. Anal. Calc for C₃₇H₃₄BCoN₇O: C, 67.1; H, 5.14; N, 14.8. Found: C, 67.0; H, 5.02; N, 14.6.

Tp^aMeCoNCS: bluish-green solid; dec 311–313 °C; IR BH 2549, NCS 2060 cm⁻¹. Anal. Calc for C₃₇H₃₄BCoN₇S: C, 65.5; H, 5.01; N, 14.4. Found: C, 65.6; H, 5.14; N, 14.1.

Tp^aMeNiCl: pale wine-red solid; sinters from 325 °C, dec 328–330 °C; IR BH 2548 cm⁻¹. Anal. Calc for C₃₆H₃₄BClN₆Ni: C, 65.9; H, 5.19; N, 12.8. Found: C, 66.2; H, 5.29; N, 12.6.

Tp^aMeNiNCO: pale wine-red solid; dec 315–316 °C; IR BH 2542, NCO 2203 cm⁻¹. Anal. Calc for C₃₇H₃₄BCoN₇O: C, 67.1; H, 5.14; N, 14.8. Found: C, 67.3; H, 5.12; N, 14.5.

Tp^aMeNiNCS: maroon-brown solid; mp 310–311 °C dec; IR BH 2540, NCS 2042 cm⁻¹. Anal. Calc for C₃₇H₃₄BCoN₇S: C, 65.5; H, 5.01; N, 14.4. Found: C, 65.8; H, 5.13; N, 14.3.

Tp^aMeZnCl: white solid; mp 332–334 °C dec; IR BH 2548 cm⁻¹; NMR d 8.57 (3H), t 7.35 (3H), m 7.2 (6H), t 2.85 (6H), t 2.58 (6H), s 2.46 (9H) ppm. Anal. Calc for C₃₆H₃₄BClN₆Zn: C, 65.3; H, 5.19; N, 12.7. Found: C, 65.6; H, 5.27; N, 12.6.

Tp^aMeZnI: white solid; mp 303–305 °C; IR 2553 cm⁻¹; NMR d 8.52 (3H, 6'-H), m 7.16–7.22 (9H, 3',4',5'-H), t 2.85 (6H, CH₂), t 2.57 (6H, CH₂), s 2.46 (9H, CH₃) ppm. Anal. Calc for C₃₆H₃₄BI₆Zn: C, 57.4; H, 4.52; N, 11.2. Found: C, 57.5; H, 4.49; N, 11.2.

Tp^aMeZnNCO: white solid; sinters from 335 °C, mp 338–340 °C; IR BH 2553, NCO 2225 cm⁻¹; NMR d 8.35 (3H, 6'-H), t 7.44 (3H, Ph), q 7.24 (6H, Ph), t 2.87 (6H, CH₂), t 2.59 (6H, CH₂), s 2.36 (9H, CH₃) ppm. Anal. Calc for C₃₇H₃₄BN₇OZn: C, 66.5; H, 5.14; N, 14.7. Found: C, 66.6; H, 5.22; N, 14.5.

Tp^bZnNCO: white solid; mp 302–304 °C; IR BH 2473, NCO 2227 cm⁻¹; NMR d 8.08 (3H, 6'-H), s 7.63 (3H, 5-H), t 7.42 (6H, 3',4'-H), t 7.26 (3H, 5'-H), s 3.55 (6H, CH₂). Anal. Calc for C₃₁H₂₂BN₇OZn: C, 63.7; H, 3.77; N, 16.8. Found: C, 63.8; H, 3.85; N, 16.7.

Tp^bZnNCS: mp none up to 310 °C; IR BH asymmetric peak, sharpest point 2481, midpoint 2461, NCS 2064 cm⁻¹; NMR d 8.07 (3H, 6'-H), s 7.64 (3H, 5-H), m 7.44 (6H, 3',4'-H), t 7.29 (3H, 5'-H), s 3.58 (6H, CH₂) ppm. Anal. Calc for C₃₁H₂₂BN₇SZn: C, 62.0; H, 3.67; N, 16.3. Found: C, 61.9; H, 3.75; N, 16.4.

Tp^aMeCoNCS: mp 222–224 °C; IR BH 2547, NCS 2072 cm⁻¹. Anal. Calc for C₃₁H₂₈BCoN₇S: C, 62.0; H, 4.67; N, 16.3. Found: C, 61.8; H, 4.64; N, 16.1.

Tp^aMeNiNCS: "As obtained" the product was green. Upon sublimation of Hp₂* at 240 °C/1 Torr, it became chestnut red. Mp 250–252 °C. IR: BH 2542, NCS 2052 cm⁻¹. Anal. Calc for C₃₁H₂₈BN₇NiS: C, 62.0; H, 4.67; N, 16.3. Found: C, 61.8; H, 4.71; N, 16.2.

Tp^aMeZnNCS: mp 250–241 °C; IR BH 2551, NCS 2089 cm⁻¹; NMR d 7.62 (6H, 2',6'-H), m 7.4–7.5 (9H, 3',4',5'-H), s 2.53 (9H, CH₃) ppm in 2:2:1:3 ratio, BH by integration as 1H at 4.4–5.4 ppm. Anal. Calc for C₃₁H₂₈BN₇SZn: C, 61.4; H, 4.62; N, 16.2. Found: C, 61.4; H, 4.56; N, 16.0.

Tp^bMeZnCl: sintering from 264 °C, mp 275–277 °C; IR BH 2547 cm⁻¹; NMR d 7.68 (6H, 2',6'-H), m 7.36 (9H, 3',4',5'-H), s 6.22 (3H, 4-H), s 2.53 (9H, CH₃) ppm, BH by integration as 1H in the 4.22–5.3 ppm range. Anal. Calc for C₃₁H₂₈BClN₆Zn: C, 61.6; H, 4.80; N, 14.4. Found: C, 61.8; H, 4.93; N, 14.2.

Tp^bMeZnI: white solid; mp 279–280 °C; IR BH 2548 cm⁻¹; NMR m 7.59 (6H, 2',6'-H), m 7.33 (9H, 3',4',5'-H), s 6.17 (3H, 4-H), s 2.54 (9H, CH₃) ppm. Anal. Calc for C₃₁H₂₈BI₆Zn: C, 53.4; H, 4.15; N, 12.5. Found: C, 53.4; H, 4.22; N, 12.4.

LRh(COD) and LRh(CO)₂ Complexes. The LRh(COD) complexes were prepared by stirring equimolar amounts of the appropriate TI salt with [RhCl(COD)]₂ in methylene chloride for several hours. After removal of the precipitated TlCl by filtration, the solvent was evaporated, and the yellow residue was recrystallized from toluene/heptane. Yields were in the 80–90% range. The LRh(CO)₂ complexes were prepared, in the case of Tp^a, Tp^aMe, and Tp^b, by bubbling CO through a solution of LRh(COD), stripping to dryness, and recrystallization from toluene/heptane. In the case of Tp^bMe, there was no reaction upon bubbling CO through a solution of Tp^bMeRh(COD); however, bubbling CO through a solution of [RhCl(COD)]₂, followed by the addition of Tp^bMeTl, yielded readily Tp^bMeRh(CO)₂.

Tp^aRh(COD): darkens from 238 °C, dec 242–244 °C; IR BH 2414 cm⁻¹; NMR two sharp doublets in 1:2 ratio at 9.28 and 9.10 ppm (6'-H's), two sharp singlets in 2:1 ratio at 7.86 and 7.74 ppm (5-H's), the remaining aromatic and aliphatic peaks overlapping, but the aromatic/aliphatic peak ratio is correct. Anal. Calc for C₄₁H₄₀BN₆Rh: C, 67.4; H, 5.48; N, 11.5. Found: C, 67.7; H, 5.55; N, 11.4.

Tp^aRh(CO)₂: darkens from 210 °C, mp 226–228 °C; IR BH 2456, CO 2064, 2000 cm⁻¹; NMR d 8.74 (2H), d 8.61 (1H), d 8.00 (1H), s 7.71 (1H), s 7.54 (2H), t 7.50 (2H), m 7.1–7.3 (6H), m 2.4–3.1 (12H) ppm. Anal. Calc for C₃₅H₂₈BN₆RhO₂: C, 62.0; H, 4.13; N, 12.3. Found: C, 62.1; H, 4.22; N, 12.1.

Tp^aMeRh(COD): yellow-orange solid; mp ~300 °C; IR BH 2463 cm⁻¹; NMR unresolved d 9.42, broad peaks 7.88, 7.52, 7.1–7.3, 4.15, 3.78, 2.9, 2.7, 2.9 with spike at 2.2, b d 1.95, 1.5, 1.2 ppm. Anal. Calc for C₄₄H₄₆BN₆Rh: C, 68.4; H, 5.96; N, 10.9. Found: C, 68.5; H, 6.08; N, 11.0.

Tp^aMeRh(CO)₂: yellow solid; mp 256–258 °C dec; IR BH 2526, CO 2064, 1990 cm⁻¹; NMR d 8.75 (3H, 6'-H), td 7.35 (3H, Ph), m 7.23 (6H, Ph), t 2.89 (6H, CH₂), t 2.61 (6H, CH₂), s 2.36 (9H, CH₃) ppm. Anal. Calc for C₃₈H₃₄BN₆O₂Rh: C, 63.3; H, 4.72; N, 11.7. Found: C, 63.7; H, 4.89; N, 11.5.

Tp^bRh(COD): dark yellow solid; mp 215–216 °C; IR BH 2417 cm⁻¹; NMR broad peak 8.11, broad hump 7.5, triplets 7.38 and 7.23, broad humps 4.36, 3.55, 2.64, 2.0, and 1.6 ppm. Anal. Calc for C₃₈H₃₄BN₆Rh: C, 66.3; H, 4.94; N, 12.2. Found: C, 66.5; H, 5.12; N, 12.0.

Tp^bRh(CO)₂: yellow solid; some darkening but no change up to 305 °C. IR: BH 2470 and CO 2084, 2056, 2020, 1988 cm⁻¹, the 2056, 1988 cm⁻¹ peaks being stronger than the other two. NMR: the aromatic peaks exhibit considerable overlap due to the isomers present; prominent peaks include d 8.10, s 7.61 ppm; the methylene protons appear as a strong singlet at 3.58 ppm and three smaller, identical singlets at 3.75, 3.52, and 3.50 ppm. Anal. Calc for C₃₂H₂₂BN₆O₂Rh: C, 60.4; H, 3.46; N, 13.2. Found: C, 60.5; H, 3.52; N, 13.0.

Tp^bMeRh(COD): yellow solid; sinters partly from 235 °C, melts 245–247 °C to a clear orange melt, without decomposition; IR BH 2462 cm⁻¹; NMR d 8.04 (6H, 2',6'-H), t 7.46 (6H, 3',5'-H), t 7.35 (3H, 4'-H), s 6.29 (3H, 4-H), s (b) 3.34 (4H, COD olefinic protons), s 2.34 (9H, CH₃), m

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Rh	1893(1)	1476(1)	1129(1)	36(1)	Rh'	4193(1)	6454(1)	-3862(1)	33(1)
O(1)	-442(4)	426(2)	2257(2)	68(2)	O(1')	6858(4)	6664(2)	-5006(2)	57(2)
O(2)	-126(5)	1594(3)	-44(2)	72(2)	O(2')	6450(4)	5419(2)	-2757(2)	62(2)
N(1)	3303(4)	1415(2)	1945(2)	37(2)	N(1')	2670(4)	7256(2)	-4639(2)	32(1)
N(2)	4894(4)	1355(2)	1820(2)	39(2)	N(2')	1129(4)	7070(2)	-4560(2)	36(2)
N(3)	3449(4)	2265(2)	336(2)	36(1)	N(3')	2432(4)	6389(2)	-3026(2)	35(1)
N(4)	5024(4)	2101(2)	409(2)	40(2)	N(4')	899(4)	6349(2)	-3145(2)	35(2)
N(5)	4107(4)	346(2)	1228(2)	42(2)	N(5')	2483(4)	5448(2)	-3911(2)	37(2)
N(6)	5528(4)	672(2)	1046(2)	43(2)	N(6')	919(4)	5648(2)	-3903(2)	37(2)
C(1)	445(5)	828(3)	1842(3)	45(2)	C(1')	5819(5)	6601(3)	-4586(2)	37(2)
C(2)	647(6)	1565(3)	392(3)	46(2)	C(2')	5581(5)	5815(3)	-3169(3)	41(2)
C(11)	5583(6)	1175(3)	2457(3)	45(2)	C(11')	384(5)	7597(3)	-5162(3)	41(2)
C(12)	4451(6)	1107(3)	3014(3)	48(2)	C(12')	1413(5)	8125(3)	-5635(2)	39(2)
C(13)	4485(7)	885(3)	3830(3)	63(3)	C(13')	1302(6)	8830(3)	-6382(3)	54(2)
C(14)	2979(7)	470(3)	4239(3)	65(3)	C(14')	2868(6)	8913(3)	-6847(3)	54(2)
C(15)	1542(7)	935(3)	3867(3)	53(2)	C(15')	4246(6)	8848(3)	-6404(3)	47(2)
C(16)	184(7)	986(3)	4288(3)	65(3)	C(16')	5269(7)	9265(3)	-6758(3)	65(3)
C(17)	-1111(7)	1426(4)	3929(3)	70(3)	C(17')	6808(7)	9215(3)	-6347(4)	72(3)
C(18)	-1089(6)	1810(3)	3153(3)	59(3)	C(18')	6763(6)	8756(3)	-5583(3)	59(3)
C(19)	238(6)	1766(3)	2722(3)	50(2)	C(19')	5474(5)	8323(3)	-5218(3)	44(2)
C(20)	1547(6)	1319(3)	3073(3)	42(2)	C(20')	4233(5)	8346(2)	-5623(2)	36(2)
C(21)	3046(6)	1271(3)	2671(3)	41(2)	C(21')	2833(5)	7905(2)	-5289(2)	34(2)
C(31)	5840(6)	2634(3)	-182(3)	47(2)	C(31')	1(5)	6189(3)	-2512(3)	44(2)
C(32)	4805(5)	3160(3)	-651(3)	42(2)	C(32')	904(5)	6118(3)	-1964(3)	43(2)
C(33)	4983(6)	3872(3)	-1393(3)	54(2)	C(33')	606(7)	5900(3)	-1142(3)	61(3)
C(34)	3617(6)	3944(3)	-1857(3)	55(2)	C(34')	2079(1)	5474(3)	-740(3)	62(3)
C(35)	2046(6)	3865(3)	-1422(3)	46(2)	C(35')	3530(6)	5924(3)	-1118(3)	51(2)
C(36)	734(7)	4293(3)	-1765(3)	64(3)	C(36')	4663(7)	5989(3)	-710(3)	62(3)
C(37)	-684(7)	4236(3)	-1361(4)	72(3)	C(37')	5957(7)	6408(4)	-1064(3)	66(3)
C(38)	-821(6)	3756(3)	-594(3)	61(3)	C(38')	6137(6)	6793(3)	-1847(3)	59(3)
C(39)	456(6)	3316(3)	-234(3)	48(2)	C(39')	5022(6)	6746(3)	-2271(3)	46(2)
C(40)	1885(6)	3349(3)	-637(3)	41(2)	C(40')	3721(5)	6307(3)	-1917(3)	41(2)
C(41)	3318(5)	2920(2)	-308(2)	37(2)	C(41')	2432(5)	6258(2)	-2307(2)	37(2)
C(51)	6623(6)	249(3)	856(3)	49(2)	C(51')	45(5)	5080(3)	-3812(3)	41(2)
C(52)	5924(6)	-362(3)	919(3)	45(2)	C(52')	1030(5)	4492(3)	-3767(3)	39(2)
C(53)	6450(7)	-1033(3)	800(3)	64(3)	C(53')	821(6)	3716(3)	-3667(3)	54(3)
C(54)	5579(8)	-1705(3)	1374(3)	72(3)	C(54')	2165(6)	3182(3)	-3231(3)	57(3)
C(55)	3813(7)	-1560(3)	1437(3)	57(2)	C(55')	3770(5)	3514(3)	-3552(3)	44(2)
C(56)	2752(10)	-2130(4)	1653(4)	82(4)	C(56')	5083(6)	3058(3)	-3569(3)	55(3)
C(57)	1177(10)	-2005(5)	1748(4)	88(4)	C(57')	6541(6)	3363(3)	-3854(3)	60(3)
C(58)	583(8)	-1305(5)	1635(4)	84(4)	C(58')	6703(6)	4124(3)	-4132(3)	53(3)
C(59)	1593(7)	-718(4)	1408(3)	66(3)	C(59')	5431(5)	4589(3)	-4115(3)	46(2)
C(60)	3212(6)	-843(3)	1323(3)	48(2)	C(60')	3960(5)	4285(3)	-3828(2)	37(2)
C(61)	4354(5)	-279(3)	1148(2)	41(2)	C(61')	2544(5)	4750(3)	-3835(2)	37(2)
B	5717(6)	1407(3)	1082(3)	40(2)	B'	407(6)	6381(3)	-3877(3)	37(2)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(b) 1.63 (4H, COD), sextet 1.09 (4H, COD) ppm. Anal. Calc for $C_{38}H_{40}BN_6Rh$: C, 65.7; H, 5.76; N, 12.1. Found: C, 65.5; H, 5.75; N, 11.9.

Tp^{Ph}Mo(CO)₂(η^3 -CH₂CMeCH₂)₂: orange crystals; mp 227–229 °C dec; IR BH 2512, CO 2073, 2001 cm⁻¹; NMR dd 7.86 (6H, 2',6'-H), m 7.30–7.44 (9H, 3',4',5'-H), s 6.126 (3H, 4-H), s 2.47 (9H, CH₃) ppm. Anal. Calc for $C_{32}H_{28}BN_6O_2Rh$: C, 59.8; H, 4.36, N, 13.1. Found: C, 59.6; H, 4.41; N, 12.8.

LMo(CO)₂(η^3 -CH₂CMeCH₂) Complexes. These complexes were prepared by stirring equimolar amounts of the appropriate Tl salt of the ligand plus (MeCN)₂MoCl(CO)₂(η^3 -CH₂CMeCH₂) in methylene chloride for several hours. The mixtures were filtered, and the filtrates were chromatographed on alumina, collecting the yellow band. Stripping and recrystallization of the residue from xylene yielded the pure complexes. No product was isolated from Tp^{Ph}Mo(CO)₂(η^3 -CH₂CMeCH₂)₂.

Tp^{Ph}Mo(CO)₂(η^3 -CH₂CMeCH₂): The initially obtained, very soluble orange solid, on recrystallization from boiling xylene yields a yellow solid; it darkens gradually from 200 °C, dec 267–269 °C. IR: BH 2478, CO 1930, 1839 cm⁻¹. NMR: d 9.52 (1H), d 8.30 (2H), s 7.52 (2H), m 7.2–7.8 (10H), s 3.18 (2H), m 2.6–3.0 (12H), s 0.79 (2H), s 0.55 (3H) ppm. Anal. Calc for $C_{35}H_{35}BN_6O_2$: C, 64.5; H, 4.82, N, 11.6. Found: C, 64.5; H, 4.93; N, 11.5.

Tp^{Ph}Mo(CO)₂(η^3 -CH₂CMeCH₂)₂: yellow solid; mp 290–291 °C dec; IR BH 2445, CO 1931, 1828 cm⁻¹; NMR d 8.96 (1H), d 8.45 (2H), s 7.60 (2H), m 7.24–7.58 (7H), d 4.04 (2H), s 3.61 (2H), s 3.56 (2H), s 3.48 (2H), s 1.69 (2H), s 0.98 (2H) ppm. Anal. Calc for $C_{36}H_{29}BN_6O_2$: C, 63.2; H, 4.24; N, 12.3. Found: C, 63.5; H, 4.31; N, 12.1.

Tp^{Ph}Mo(CO)₂(η^3 -CH₂CMeCH₂)₂: yellow solid; mp 227–229 °C dec; IR BH 2548, CO 1931, 1845 cm⁻¹; NMR d 7.85 (2H), overlapping

multiplets 7.30–7.62 (11H), s 6.08 (1H), s 6.04 (2H), s 2.58, (2H) s 2.47 ((6H), s 2.31 (3H), s 0.91 (3H), s 0.12 (2H) ppm. Anal. Calc for $C_{36}H_{35}BN_6O_2$: C, 62.6; H, 5.07; N, 12.2. Found: C, 63.0; H, 5.16; N, 12.0.

[Tp^{Ph}Mo(CO)₂][Et₄N]. An equimolar mixture of Tp^{Ph}Tl and Mo(CO)₆ was refluxed overnight in THF, and the resulting yellow solution was poured into an excess of tetraethylammonium bromide solution. The bright yellow solid was isolated by filtration and was obtained after washing and drying in 78% yield: darkens from 177 °C, dec ~190 °C; IR BH 2521, CO 1897, 1777, 1735 cm⁻¹; NMR (DMSO-*d*₆) dd 9.54 (3H), s 7.59 (3H), m 7.1–7.2 (9H), quartet 3.11 (8H), t 2.71 (6H), t 2.54 (6H), td 1.08 (12H) ppm. Anal. Calc for $C_{44}H_{48}BN_7O_3$: C, 63.7; H, 5.79; N, 11.8. Found: C, 64.0; H, 5.89; N, 11.5.

[Tp^{Ph}W(CO)₃][Et₄N]. This complex was prepared as above, starting with W(CO)₆, and was obtained as a dark yellow solid with ν (BH) at 2453 and ν (CO) at 1887 and 1749 (vb) cm⁻¹. NMR (DMSO-*d*₆): dd 9.63 (3H), s 7.67 (3H), m 7.1–7.2 (9H), quartet 3.17 (8H), t 2.75 (4H), t 2.57 (4H), tt 1.14 (12H) ppm. It gradually decomposes at 225–230 °C. Anal. Calc for $C_{44}H_{48}BN_7O_3W$: C, 59.7; H, 4.97; N, 10.2. Found: C, 60.0; H, 5.12; N, 9.98.

LPd(η^3 -CH₂CMeCH₂) Complexes. These complexes were prepared by stirring equimolar mixtures of the appropriate ligand Tl salt with [CIPd(η^3 -CH₂CMeCH₂)₂]. The precipitated TiCl was filtered off, and the filtrate was evaporated to dryness; the products were purified by chromatography on alumina, followed by recrystallization from toluene/heptane.

Tp^{Ph}Pd(η^3 -CH₂CMeCH₂): white solid; darkens gradually from 150 °C, dec 210–215 °C; IR 2423 cm⁻¹; NMR only broad humps in the aliphatic

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for **2**

	x	y	z	$U(\text{eq})^a$
I	82.5(4)	4979.0(3)	5136.6(2)	34.9(1)
Zn	-55.2(7)	5091.2(4)	6390.3(3)	23.3(2)
N(1)	685(5)	6068(3)	7516(3)	30(2)
N(2)	543(5)	6167(3)	6836(3)	25(2)
N(3)	886(5)	4526(3)	7662(3)	27(2)
N(4)	1005(5)	4302(3)	6996(3)	23(2)
N(5)	-1385(5)	5205(3)	7639(3)	26(2)
N(6)	-1723(4)	5026(3)	6981(2)	24(1)
C(1)	1279(6)	6749(4)	7791(4)	33(2)
C(2)	1544(6)	7277(4)	7272(4)	28(2)
C(3)	2182(8)	8112(5)	7250(4)	44(3)
C(4)	2914(7)	8168(4)	6567(4)	41(3)
C(5)	1962(7)	7996(4)	5991(4)	36(2)
C(6)	1998(8)	8446(5)	5398(4)	52(3)
C(7)	1115(9)	8298(5)	4894(4)	51(3)
C(8)	179(9)	7667(4)	4955(4)	56(3)
C(9)	141(8)	7197(4)	5539(3)	41(2)
C(10)	1052(7)	7352(4)	6050(4)	34(2)
C(11)	1036(6)	6912(4)	6695(3)	28(2)
C(12)	1584(8)	6828(5)	8508(3)	46(3)
C(21)	1650(7)	4026(4)	8051(3)	31(2)
C(22)	2267(7)	3473(5)	7638(4)	35(2)
C(23)	3280(8)	2802(5)	7753(4)	46(3)
C(24)	4269(8)	2817(5)	7164(4)	48(3)
C(25)	3557(7)	2778(4)	6501(4)	35(2)
C(26)	4092(7)	2360(5)	5968(4)	42(3)
C(27)	3430(8)	2312(4)	5354(4)	41(3)
C(28)	2204(8)	2677(4)	5283(4)	39(3)
C(29)	1645(7)	3117(4)	5813(3)	31(2)
C(30)	2318(6)	3194(4)	6415(3)	26(2)
C(31)	1839(6)	3652(4)	6994(3)	26(2)
C(32)	1758(8)	4105(5)	8803(3)	49(3)
C(41)	-2491(6)	5361(4)	7998(3)	27(2)
C(42)	-3584(6)	5274(4)	7578(3)	29(2)
C(43)	-5074(7)	5346(4)	7690(3)	42(2)
C(44)	-5688(7)	5650(5)	7052(4)	50(3)
C(45)	-5244(6)	5169(4)	6435(3)	35(2)
C(46)	-6107(6)	5019(5)	5908(4)	43(2)
C(47)	-5709(8)	4577(5)	5352(4)	45(3)
C(48)	-4441(8)	4272(5)	5317(4)	41(3)
C(49)	-3538(7)	4437(4)	5820(3)	32(2)
C(50)	-3927(6)	4888(4)	6386(3)	27(2)
C(51)	-3055(5)	5064(4)	6957(3)	25(2)
C(52)	-2428(7)	5563(5)	8733(3)	41(3)
B	93(9)	5299(4)	7856(3)	28(2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

and aromatic regions, at the correct proton ratio. Anal. Calc for $\text{C}_{37}\text{H}_{35}\text{BN}_6\text{Pd}$: C, 65.3; H, 5.15; N, 12.4. Found: C, 65.7; H, 5.27; N, 12.3.

Tp^aMePd($\eta^3\text{-CH}_2\text{CMeCH}_2$): white solid; darkens gradually from 166 °C, dec 187–190 °C; IR BH 2474 cm^{-1} ; NMR only very broad humps in the aliphatic and aromatic regions. Anal. Calc for $\text{C}_{40}\text{H}_{41}\text{BN}_6\text{Pd}$: C, 66.5; H, 5.68; N, 11.6. Found: C, 66.4; H, 5.61; N, 11.8.

Tp^bPd($\eta^3\text{-CH}_2\text{CMeCH}_2$): white solid; sinters from 165 °C, gradually decomposes from 177 °C; IR 2421 cm^{-1} ; NMR (all peaks broadened, aromatic ones less so) d 7.72 (3H), d 7.43 (3H), t 7.29 (3H), t 7.22 (3H), b s 3.87 (2H), vb s 2.65 (6H), vb s 2.08 (3H) ppm. Anal. Calc for $\text{C}_{34}\text{H}_{29}\text{BN}_6\text{Pd}$: C, 64.0; H, 4.55; N, 13.2. Found: C, 64.2; H, 4.67; N, 13.1.

Tp^aPhMePd($\eta^3\text{-CH}_2\text{CMeCH}_2$): white solid; darkens from 188 °C, dec 196–197 °C; IR BH 2477 cm^{-1} ; NMR d 7.74 (6H, 2',6'-H), m 7.24–7.40 (9H, 3',4',5'-H), s 6.27 (3H, 4-H), s 2.54 (2H, syn), 2.30 (9H, CH₃), s 2.72 (2H, anti), s 2.62 (3H, η^3 -allyl CH₃) ppm. Anal. Calc for $\text{C}_{34}\text{H}_{35}\text{BN}_6\text{Pd}$: C, 63.4; H, 5.43; N, 13.0. Found: C, 63.7; H, 5.55; N, 12.9.

Crystallographic Analysis. Crystallographic data for $\text{Rh}(\text{CO})_2\text{Tp}^a$ (**1**), ZnITp^aMe (**2**), TiTp^b (**3**), and $\text{ZnITp}^b\text{PhMe}$ (**4**) are collected in Table 1. Crystals of $\text{Rh}(\text{CO})_2\text{Tp}^a$ (**1**), ZnITp^aMe (**2**), TiTp^b (**3**), and $\text{ZnITp}^b\text{PhMe}$ (**4**) were obtained respectively from slow evaporation of a methylene chloride/toluene mixture, benzene, xylene, and benzene. Preliminary photographic characterization showed the following Laue symmetries: $\bar{1}$ for **1**, $2/m$ for **3**, and mmm for both **2** and **4**. Systematic absences in the diffraction data uniquely established the space groups as $P2_12_12_1$ for

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for **3**

	x	y	z	$U(\text{eq})^a$
Tl	217.1(4)	1412(4)	973(2)	44(1)
N(1)	1180.7(6)	2149.4(7)	2564.4(4)	35.6(3)
N(2)	423.1(7)	1333.7(7)	2199.3(3)	40.4(3)
N(3)	1277.6(7)	3925(6)	1834.5(4)	38.3(3)
N(4)	457.9(7)	3602.5(8)	1305.3(4)	41.3(3)
N(5)	2846.2(7)	2283.6(6)	1901.3(4)	37.3(3)
N(6)	2408(7)	1468.7(7)	1426.7(3)	38.5(3)
C(1)	1002(9)	2094(9)	3190(4)	42(4)
C(2)	146(9)	1218(8)	3236(4)	41(4)
C(3)	-566(9)	592(10)	3676(5)	52(4)
C(4)	-1312(9)	-257(9)	3218(5)	45(4)
C(5)	-2133(10)	-1077(10)	3354(6)	60(5)
C(6)	-2721(11)	-1776(10)	2846(7)	66(5)
C(7)	-2488(11)	-1676(9)	2238(6)	65(5)
C(8)	-1665(9)	-822(9)	2091(5)	47(4)
C(9)	-1067(8)	-139(8)	2580(5)	35(3)
C(10)	-173(8)	801(8)	2612(4)	32(3)
C(11)	1259(9)	5131(8)	1912(5)	43(4)
C(12)	415(9)	5608(9)	1449(5)	46(4)
C(13)	-152(11)	6751(10)	1180(6)	69(5)
C(14)	-1061(9)	6271(9)	623(5)	53(4)
C(15)	-1895(12)	6919(11)	191(6)	71(5)
C(16)	-2584(11)	6267(14)	-317(6)	74(6)
C(17)	-2469(10)	5056(13)	-377(5)	64(5)
C(18)	-1660(9)	4422(11)	58(5)	57(4)
C(19)	-954(9)	5012(9)	551(5)	44(4)
C(20)	-45(8)	4632(9)	1077(4)	39(4)
C(21)	4047(8)	2258(9)	2016(4)	38(3)
C(22)	4414(8)	1396(10)	1622(5)	42(3)
C(23)	5467(9)	696(11)	1474(5)	57(4)
C(24)	4875(9)	-201(10)	976(5)	50(4)
C(25)	5393(11)	-1076(10)	645(6)	63(5)
C(26)	4684(14)	-1781(11)	200(6)	74(6)
C(27)	3451(13)	-1600(10)	74(6)	67(5)
C(28)	2912(9)	-726(10)	396(5)	47(4)
C(29)	3619(9)	-37(9)	846(4)	38(3)
C(30)	3368(8)	926(9)	1270(4)	38(3)
B	2000(10)	3004(10)	2280(5)	39(4)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2 and $P2_1/n$ for **3** and indicated $P\bar{1}$ or $P1$ for **1** and $Pna2_1$ or $Pnma$ for **4**. Analysis of the E values indicated the centrosymmetric choice $P\bar{1}$ for **1** and the noncentrosymmetric choice $Pna2_1$ for **4**. Crystals of **1**, **2**, and **4** were well shaped, and azimuthal ψ scans of six reflections indicated that absorption corrections were unnecessary; for **3**, however, an empirical absorption correction¹⁸ was applied.

All structures were solved by Patterson methods and completed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were treated as idealized, updated isotropic contributions with the exception of the boron hydrogen atoms in **1** and **3**, which were located on difference maps and refined isotropically. Structures **1** and **4** contain two chemically identical but crystallographically independent molecules in the asymmetric unit. A Rogers test, $\eta = 1.08(5)$, confirms that the absolute structure of complex **2** is as shown in Figure 2. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens, Madison, WI).

Discussion

The synthesis of ligands Tp^a and Tp^b was accomplished by prolonged refluxing of the appropriate pyrazoles with KBH_4 in anisole, while ligands Tp^aMe and Tp^bPhMe were prepared by heating KBH_4 in a large excess of the appropriate molten pyrazole. All the above ligands were isolated and characterized as their stable Tl salts. Each was a single isomer, with boron bonded to the least hindered nitrogen atom.

The proximity of the H and C atoms of the pyrazolyl 3-substituent in Tl-type Tl salts to the Tl atom is usually associated with their coupling to ^{205}Tl , although the exact mode of this

(18) Hope, H.; Moezzi, B. Personal communication, Department of Chemistry, University of California, Davis.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for 4

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Zn	7244(1)	5001(1)	10000	43(1)	Zn'	5225(1)	10364(1)	5189(2)	39(1)
I	6990(1)	2983(1)	9703(2)	62(1)	I'	5367(1)	12368(1)	5761(2)	70(1)
N(1)	7244(4)	5663(12)	11166(11)	56(6)	N(1')	5314(3)	9862(10)	3964(8)	40(4)
N(2)	7378(4)	6820(11)	11203(10)	55(5)	N(2')	5257(3)	8666(10)	3900(8)	37(4)
N(3)	7004(4)	6478(10)	9433(8)	46(5)	N(3')	4665(3)	9530(10)	5187(9)	45(4)
N(4)	7179(4)	7482(10)	9769(10)	50(5)	N(4')	4711(3)	8353(10)	4956(8)	44(4)
N(5)	7843(3)	5497(10)	9868(9)	46(4)	N(5')	5533(3)	8972(9)	5686(8)	36(4)
N(6)	7893(4)	6685(11)	10048(10)	56(5)	N(6')	5449(3)	7930(10)	5306(9)	41(4)
C(1)	7527(8)	8405(18)	12239(14)	101(10)	C(1')	5266(5)	7089(14)	2799(12)	62(7)
C(2)	7404(5)	7178(17)	11982(12)	59(7)	C(2')	5294(4)	8339(14)	3104(11)	46(6)
C(3)	7283(5)	6222(20)	12493(14)	75(8)	C(3')	5369(5)	9353(13)	2633(10)	48(6)
C(4)	7198(5)	5321(17)	11947(12)	54(7)	C(4')	5374(4)	10262(12)	3202(10)	39(5)
C(5)	6692(7)	3699(20)	11969(19)	115(12)	C(5')	5582(7)	12349(16)	3493(11)	73(8)
C(6)	6553(9)	2535(26)	12181(19)	123(13)	C(6')	5613(8)	13535(18)	3270(15)	96(11)
C(7)	6847(13)	1875(30)	12616(19)	160(19)	C(7')	5477(7)	13923(17)	2522(14)	81(9)
C(8)	7228(12)	2216(27)	12792(25)	175(21)	C(8')	5294(6)	13108(16)	2006(12)	74(8)
C(9)	7340(10)	3336(26)	12523(22)	158(17)	C(9')	5275(6)	11924(16)	2240(12)	69(8)
C(10)	7060(6)	4116(18)	12166(12)	65(8)	C(10')	5416(5)	11515(14)	2981(10)	47(6)
C(11)	7105(6)	9697(13)	9670(16)	86(8)	C(11')	4278(6)	6560(15)	4797(16)	91(9)
C(12)	6981(5)	8439(13)	9448(11)	54(6)	C(12')	4345(5)	7790(14)	5050(10)	50(6)
C(13)	6682(5)	8054(15)	8942(12)	57(6)	C(13')	4061(5)	8627(18)	5310(12)	65(7)
C(14)	6697(5)	6844(13)	8945(11)	48(6)	C(14')	4271(4)	9687(14)	5361(11)	48(6)
C(15)	6022(6)	6307(17)	8393(13)	77(8)	C(15')	4255(5)	11884(16)	5319(13)	67(7)
C(16)	5758(6)	5569(20)	7930(14)	79(9)	C(16')	4094(8)	12977(17)	5561(18)	101(11)
C(17)	5914(7)	4630(20)	7540(14)	77(9)	C(17')	3771(9)	12903(35)	6143(23)	139(19)
C(18)	6305(8)	4327(17)	7621(13)	81(9)	C(18')	3623(11)	11891(39)	6429(24)	164(23)
C(19)	6577(5)	5057(15)	8085(11)	61(7)	C(19')	3789(6)	10874(22)	6179(13)	83(9)
C(20)	6435(5)	6030(14)	8474(11)	49(6)	C(20')	4111(5)	10804(16)	5630(12)	55(7)
C(21)	8444(5)	8218(15)	10054(17)	98(10)	C(21')	5658(5)	5811(12)	5350(11)	64(7)
C(22)	8287(5)	6960(15)	9921(15)	72(8)	C(22')	5684(5)	7072(14)	5632(11)	53(6)
C(23)	8495(5)	5977(13)	9695(13)	62(7)	C(23')	5932(5)	7583(13)	6186(12)	54(6)
C(24)	8210(4)	5093(11)	9677(11)	41(5)	C(24')	5836(4)	8768(12)	6234(10)	42(5)
C(25)	8118(4)	2939(13)	9902(12)	56(6)	C(25')	6396(5)	9910(16)	6842(13)	68(7)
C(26)	8192(6)	1784(16)	9761(17)	79(8)	C(26')	6533(6)	10716(21)	7422(17)	90(10)
C(27)	8451(7)	1483(19)	9126(19)	96(11)	C(27')	6291(7)	11182(17)	8021(14)	78(9)
C(28)	8643(7)	2368(21)	8650(16)	93(10)	C(28')	5893(7)	10908(19)	7989(13)	88(9)
C(29)	8557(6)	3508(18)	8826(15)	80(9)	C(29')	5739(6)	10147(18)	7389(14)	89(9)
C(30)	8287(4)	3819(15)	9470(11)	52(6)	C(30')	6000(4)	9638(13)	6822(10)	43(5)
B	7533(6)	7429(15)	10399(15)	61(8)	B'	5134(5)	7911(15)	4618(13)	46(6)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

coupling is unclear. Thus, for $\text{Tp}^{\text{a}}\text{Ti}$, the 6'-H NMR peak was moderately broadened, as was the 6'-C peak in the ^{13}C NMR spectrum. Addition of the 5-Me group to Tp^{a} greatly intensified this coupling, and for $\text{Tp}^{\text{a,Me}}\text{Ti}$ the 6'-H peak was extremely broad while the ^{13}C - ^{205}Ti coupling of 6'-C was 316 Hz. This value is substantially higher than that found for $\text{Tp}^{\text{b}}\text{Ti}$ (171 Hz),¹⁹ or even for $\text{Tp}^{\text{b,Me}}\text{Ti}$ ($J = 197$ Hz).²⁰ For the salt $\text{Tp}^{\text{b}}\text{Ti}$ there was no indication of coupling to ^{205}Ti , as all the ^1H and ^{13}C signals were sharp, consistent with the short methylene tether pulling the phenyl group away from the Ti atom. Finally, for $\text{Tp}^{\text{b,Me}}\text{Ti}$ there was some broadening of the peaks derived from 2',6'-H's and 2',6'- ^{13}C 's, suggesting either free rotation or oscillation of the phenyl group, which would make the 2'- and 6'-positions magnetically equivalent.

With regard to the formation of LMX ($X = \text{halide}$ or pseudohalide) complexes, the ligand Tp^{a} did form them with both Co(II) and Zn(II) . However, the $\text{Tp}^{\text{a}}\text{CoX}$ complexes were unstable and self-converted to $\text{Tp}^{\text{a}_2}\text{Co}$. Even with Zn(II) , formation of $\text{Tp}^{\text{a}}\text{ZnX}$ was accompanied by that of $\text{Tp}^{\text{a}_2}\text{Zn}$ in

about equal proportions. Nevertheless, by a suitable choice of conditions it was possible to prepare each type of the Zn(II) complex separately. The NMR spectrum of the $\text{Tp}^{\text{a}_2}\text{Zn}$ complex showed large upfield shifts of all peaks (methylene peaks by 0.4 and 0.66 ppm and the aromatic proton peaks by 1–2 ppm, as compared to those of $\text{Tp}^{\text{a}}\text{ZnX}$), probably arising from the ring current effect of the interpenetrating aromatic rings in an octahedral structure. The $\text{Tp}^{\text{a}}\text{ZnX}$ complexes had the 6'-H signal shifted downfield to around 8.6 ppm, as compared with that of the starting pyrazole, while the remaining peaks were hardly changed.

The $\text{Tp}^{\text{a,Me}}\text{MX}$ complexes could be obtained with Co(II) , Ni(II) , and Zn(II) , and they did not self-convert to $\text{Tp}^{\text{a,Me}_2}\text{M}$ species when recrystallized from aromatic hydrocarbons. However, attempts to purify $\text{Tp}^{\text{a,Me}}\text{CoX}$ complexes by chromatography on alumina resulted in disappearance of the blue color and elution of the yellow-orange $\text{Tp}^{\text{a,Me}_2}\text{Co}$. Both Co(II) and Ni(II) , but not Zn(II) , $\text{Tp}^{\text{a,Me}}\text{MX}$ species readily added donor molecules, forming five-coordinate complexes which could be reconverted to $\text{Tp}^{\text{a,Me}}\text{MX}$ by heating in vacuo. The $\text{Tp}^{\text{a,Me}}\text{Ni(NCS)}$ complex was red-brown (five-coordinate adducts were green), and thus monomeric, in contrast to the NCS-bridged green dimer formed by $\text{Tp}^{\text{Pr,4Br}}\text{Ni(NCS)}$.²⁰ The complex $\text{Tp}^{\text{a,Me}_2}\text{Zn}$, just like $\text{Tp}^{\text{a}_2}\text{Zn}$, had all its ^1H NMR peaks shifted upfield, as compared with those of the tetrahedral LMX species, except that shifts for the methylene groups were even larger (0.77, 0.73 ppm).

The ligand Tp^{b} formed isolable and stable $\text{Tp}^{\text{b}}\text{MX}$ complexes only with Zn(II) for $X = \text{NCO}$ or NCS , channeling all the other reactions toward the formation of $\text{Tp}^{\text{b}_2}\text{M}$ species. By contrast, the ligand $\text{Tp}^{\text{b,Me}}$ favored the formation of tetrahedral $\text{Tp}^{\text{b,Me}}\text{MX}$

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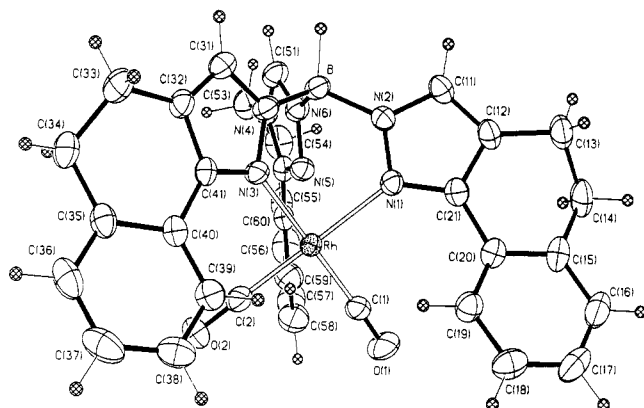


Figure 1. Molecular structure of $\text{Rh}(\text{CO})_2\text{Tp}^a$ (1) drawn with 35% probability ellipsoids (one of two chemically similar but crystallographically independent molecules).

complexes with both $\text{Co}(\text{II})$ and $\text{Zn}(\text{II})$; still, $\text{Tp}^{\text{Ph,Me}}\text{Co}$ could be prepared from the perchlorate salt, and its structure assignment was supported by the ^1H NMR spectrum, where each shifted peak could be appropriately assigned. Its melting behavior of going through a purple (tetrahedral) and yellow (octahedral) stage before the final melt suggests ligand rearrangement to the less hindered asymmetric complex, such rearrangements being known to occur in more hindered Tp^{R} systems, e.g. in Tp^{Np} .¹³ Similar melting behavior was observed for other $\text{M}(\text{II})$ complexes of $\text{Tp}^{\text{Ph,Me}}$.

Heteroleptic complexes $\text{Tp}^{\text{a}}\text{CoTp}^{\text{Np}}$, $\text{Tp}^{\text{a,Me}}\text{CoTp}^{\text{Np}}$, and $\text{Tp}^{\text{b}}\text{CoTp}^{\text{Np}}$ were prepared from $\text{Tp}^{\text{Np}}\text{CoCl}$ and the TI salt of the appropriate ligand. The reaction with Tp^{b} at room temperature was instantaneous, with that of Tp^{a} somewhat slower and with that of $\text{Tp}^{\text{a,Me}}$ slower yet, but all these heteroleptic complexes could be obtained within hours. There was no discernible reaction with $\text{Tp}^{\text{Ph,Me}}\text{Ti}$ even after 2 days, and the starting materials were recovered. This clearly sets up the steric hindrance hierarchy of these ligands as $\text{Tp}^{\text{Ph,Me}} > \text{Tp}^{\text{a,Me}} > \text{Tp}^{\text{a}} > \text{Tp}^{\text{b}}$, with the last one being about as unhindered as Tp itself. The ^1H NMR spectra of these paramagnetic octahedral Co complexes spanned over 200 ppm and were sharp, with most peaks clearly assignable to one or the other ligand.

Each of the new ligands reacted easily with $\text{Rh}(\text{COD})\text{Cl}$ to form the $\text{LRh}(\text{COD})$ complex. The NMR spectrum of $\text{Tp}^{\text{a}}\text{Rh}(\text{COD})$ had the $6'\text{-H}$ doublets in a 2:1 pattern, shifted downfield to 9.10 and 9.28 ppm, respectively, the COD olefinic and aliphatic protons appeared each as three broad and asymmetric peaks, and there was considerable overlap of the sharp aromatic signals. For $\text{Tp}^{\text{a,Me}}\text{Rh}(\text{COD})$ all the peaks were indistinctly broad, the sharpest being the $6'\text{-H}$ doublet at 9.42 ppm. For $\text{Tp}^{\text{b}}\text{Rh}(\text{COD})$ only the aromatic triplets ($4',5'\text{-H}$) were sharp; the $6'\text{-H}$ (at 8.11 ppm), 5-H , and $3'\text{-H}$ signals were broad humps, as were those of all the aliphatic and olefinic protons, suggestive of slow exchange. By contrast, the NMR spectrum of $\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{COD})$ was very sharp, indicating equivalence of all three pyrazolyl groups and of the $2',6'\text{-}$ and $3',5'\text{-}$ protons; it was thus indicative of a dynamic, fluxional structure. The olefinic protons appeared as a broadened singlet, while the aliphatic ones appeared as a quadruplet at 1.08 ppm and an unresolved multiplet at 1.60 ppm.

Upon bubbling of carbon monoxide into a methylene chloride solution of $\text{Tp}^{\text{a}}\text{Rh}(\text{COD})$, $\text{Tp}^{\text{a,Me}}\text{Rh}(\text{COD})$, or $\text{Tp}^{\text{b}}\text{Rh}(\text{COD})$, the corresponding dicarbonyl derivatives, $\text{LRh}(\text{CO})_2$, were obtained. No reaction occurred at all with $\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{COD})$, presumably due to the steric hindrance around the Rh atom; however, prolonged passing of carbon monoxide into a solution of $\text{Rh}(\text{COD})\text{Cl}$, followed by the addition of $\text{Tp}^{\text{Ph,Me}}\text{Ti}$, gave rise to $\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{CO})_2$. The NMR spectrum of $\text{Tp}^{\text{a}}\text{Rh}(\text{CO})_2$ was sharp with the $6'\text{-H}$ doublets at 8.74 and 8.61 ppm in 2:1 ratio; considerable overlap prevented identification of the other peaks.

Table 6. Selected Bond Distances and Angles for 1

Bond Distances (Å)				
	molecule 1	molecule 2	molecule 1	molecule 2
Rh–N(1)	2.093(4)	2.105(3)	B–N(2)	1.542(7)
Rh–N(3)	2.091(3)	2.109(4)	B–N(4)	1.540(5)
Rh–C(1)	1.855(4)	1.848(6)	B–N(6)	1.537(8)
Rh–C(2)	1.850(6)	1.843(4)		1.526(8)
Nonbonding Distances (Å)				
	molecule 1	molecule 2	molecule 1	molecule 2
Rh–N(5)	2.779(4)	2.641(4)	Rh–H(59A)	3.355
Rh–B	3.263(6)	3.267(7)	B–H(19A)	5.285
Rh–H(19A)	3.023	2.980	B–H(39A)	5.281
Rh–H(39A)	2.950	3.032	B–H(59A)	5.135
				5.102
Bond Angles (deg)				
	molecule 1		molecule 2	
N(1)–Rh–N(3)	86.2(1)		85.8(1)	
N(1)–Rh–C(1)	93.3(2)		93.8(2)	
N(1)–Rh–C(2)	178.0(2)		175.3(2)	
N(3)–Rh–C(1)	176.1(2)		173.5(2)	
N(3)–Rh–C(2)	92.5(2)		93.6(2)	
C(1)–Rh–C(2)	87.9(2)		86.3(2)	
N(2)–B–N(4)	108.9(4)		109.0(4)	
N(2)–B–N(6)	110.0(3)		111.5(4)	
N(4)–B–N(6)	111.9(5)		110.3(3)	
Twist Angles (deg) ^a				
	molecule 1		molecule 2	
Pz(1)–Ph(19) ^b	24.1		22.2	
Pz(3)–Ph(39) ^b	22.4		25.5	
Pz(5)–Ph(59) ^b	17.8		18.3	
Cone Angles (deg) ^c				
	molecule 1	molecule 2	molecule 1	molecule 2
H(19A)	261	262	H(59A)	232
H(39A)	265	260		234

^a The twist angle is the dihedral angle between the least-squares planes defined by the pyrazolyl atoms and the phenyl ring atoms. ^b Pz stands for the pyrazolyl ring with the number in parentheses being the lowest numbered nitrogen atom in that ring. Ph is the phenyl ring, and the parenthetical number is that of the carbon atom closest to the metal. ^c The cone angle is twice the angle defined by B–M–H_i , where H_i is the van der Waals surface of the phenyl ring hydrogen atom nearest the metal atom.

In the case of $\text{Tp}^{\text{a,Me}}\text{Rh}(\text{CO})_2$, all the peaks were very sharp, the three pyrazolyl groups were equivalent, consistent with rapid exchange, and the $6'\text{-H}$ doublet was at 8.75 ppm. The IR of $\text{Tp}^{\text{b}}\text{Rh}(\text{CO})_2$ had four CO peaks, at 2084, 2056, 2020, and 1988 cm^{-1} , consistent with presence of Tp^{b} bonding in $\eta^2\text{-}$ and $\eta^3\text{-}$ fashions. The higher frequency peak pair is usually associated with the $\eta^2\text{-}$ structure, and the lower frequency pair, with the $\eta^3\text{-}$ structure.²¹ The presence of coordination isomers was also confirmed by the NMR spectrum, which had four peaks for the methylene protons: one large singlet for the identical methylenes in the dynamic $\eta^3\text{-}$ structure; three smaller peaks in 1:1:1 ratio, two for the "inner" and "outer" protons of the coordinated pz^* groups and one for the methylene in the uncoordinated pz^* group in the $\eta^2\text{-}$ structure. This phenomenon was noted before for $\text{Tp}^{\text{Ph}}\text{Rh}(\text{CO})_2$ and $\text{Tp}^{\text{CF}_3\text{,Me}}\text{Rh}(\text{CO})_2$, where the ratios of the $\eta^2\text{-}$ and $\eta^3\text{-}$ species depend on both the ligand structure and the temperature.²¹ The spectrum of $\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{CO})_2$ was just as sharp as that of $\text{Tp}^{\text{a,Me}}\text{Rh}(\text{CO})_2$, and the $2',6'\text{-}$ doublet was at 7.86 ppm.

Different types of reaction took place upon reacting $(\text{MeCN})_2\text{Mo}(\text{CO})_2(\eta^3\text{-methylallyl})\text{Cl}$ with the TI salts of the four ligands.

With Tp^aTl , an orange material was obtained upon low-temperature isolation of the product. Its IR spectrum contained two BH peaks in the agostic range ($2056, 2085\text{ cm}^{-1}$) and CO peaks at $1957, 1872\text{ cm}^{-1}$. But even on short standing in chloroform solution, additional peaks started appearing (BH at 2478 cm^{-1} , CO at 1930 and 1838 cm^{-1}) as the original peaks declined. Eventually, only the second product was present, which was isolated as a bright yellow solid and identified as the "normal" $\text{Tp}^a\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$ complex. It was also obtained as the only product upon recrystallization of the original "agostic" material from xylene. We conclude that the initial product is the agostic complex containing a B–H–Mo bond, which is unstable with respect to the "normal" $\text{Tp}^a\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$ complex and rearranges to it, amidst some decomposition.

When Tp^aMeTl was treated with $(\text{MeCN})_2\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})\text{Cl}$, a brown solution was obtained, and the unknown product was totally retained on alumina. Tp^b behaved normally and produced the yellow $\text{Tp}^b\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$ complex (IR BH 2444 , CO $1931, 1828\text{ cm}^{-1}$) as the only product. This complex was stereochemically rigid, as indicated by NMR, with the CH_2 protons appearing as three singlets in 1:1:1 ratio ("unique", "outer", and "inner" protons in a molecule of C_3 symmetry) and the aromatic peaks as 2:1 patterns. In the case of the $\text{Tp}^{\text{Ph,Me}}$ ligand, the normal product, $\text{Tp}^{\text{Ph,Me}}\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$, was obtained with $\nu(\text{BH})$ at 2548 and $\nu(\text{CO})$ at 1931 and 1845 cm^{-1} ; its NMR spectrum had the 2',6'-protons, the 4-proton, and the methyl proton signals in 2:1 patterns, consistent with a stereochemically rigid structure. It is noteworthy that while the BH and the lower-frequency CO bands showed considerable variation in the three complexes, the high-frequency CO band remained essentially constant.

The reaction of Tp^aK with $\text{Mo}(\text{CO})_6$ readily formed the bright yellow anion $[\text{Tp}^a\text{Mo}(\text{CO})_3]^-$, isolated as the tetraethylammonium salt. It had a BH peak at 2521 and sharp CO peaks at $1897, 1777, \text{ and } 1735\text{ cm}^{-1}$. The tungsten analog was prepared similarly; it had a BH peak at 2454 , a sharp CO peak at 1887 , and a very strong and broad one at 1748 cm^{-1} . Similar reactions with the other ligands were not tried.

Each of the new ligands reacted readily with $[\text{PdCl}(\eta^3\text{-CH}_2\text{-CMeCH}_2)]_2$ to produce the $\text{LPd}(\eta^3\text{-CH}_2\text{-CMeCH}_2)$ complexes. They contain square-planar Pd and a bidentately coordinated ligand. While analogous compounds derived from Tp or pzTp had sharp NMR spectra, indicating equivalence of all pz groups (via rapid exchange of the coordinated and uncoordinated pz substituents), the new ligands had rather broad and indistinct NMR spectra, consistent with slow exchange. Of the two complexes, $\text{Tp}^a\text{Pd}(\eta^3\text{-CH}_2\text{-CMeCH}_2)$ and $\text{Tp}^a\text{MePd}(\eta^3\text{-CH}_2\text{-CMeCH}_2)$, the NMR of the latter was even less well defined. By contrast, $\text{Tp}^{\text{Ph,Me}}\text{Pd}(\eta^3\text{-CH}_2\text{-CMeCH}_2)$ had a very sharp NMR spectrum, indicative of rapid exchange.

Structural Analysis by X-ray Crystallography

In order to have some quantitative comparison features for the presently reported ligands, we have calculated the cone angles and the wedge angles for each of them, taking into account the van der Waals radii of the hydrogen atoms. This included recalculation of some of the previously reported cone angle values, for which the van der Waals radii were ignored. The wedge angle in a complex was determined as the angle between the 6'-H of the phenyl group, its orthogonal projection point on the B–M axis, and the 6'-H of the adjacent phenyl group, rotated in such a way as to be a mirror image of the first one. The wedge angles provided a rough measure of the open space available for a reacting molecule to penetrate sideways between the 3-phenylpyrazolyl planes to the metal.

For comparison purposes, we have also calculated the wedge and cone angles for some previously reported Tp^a ligands, taking into account the hydrogen van der Waals radii, which led to

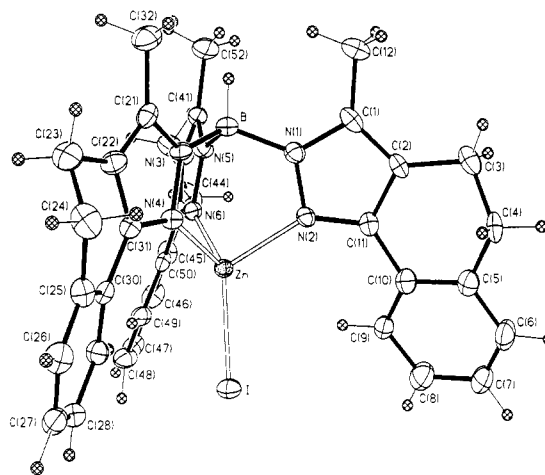


Figure 2. Molecular structure of $\text{ZnITp}^a\text{,Me}$ (**2**) drawn with 35% probability ellipsoids.

revision of some of the angles. Respective cone and wedge angles are as follows: for Tp (based on Tp_2Co)²⁷ 198.5 and 91.0° ; for Tp^* (based on $\text{Tp}^*\text{MoO}(\text{SPh})_2$)²⁸ 235.7 and 74.7° ; for $\text{Tp}^{\text{Pr,4Br}}$ (based on $\text{Tp}^{\text{Pr,4Br}}\text{Co}(\text{NCS})$)²⁹ 262.0 and 35.5° ; for Tp^{tBu} (based on $\text{Tp}^{\text{tBu}}\text{Co}(\text{NCS})$)² 264.9 and 34.8° . The Tp^{Me} ligand had the largest cone angle (281.1°) and the smallest wedge angle (7.0°) calculated on the basis of $\text{Tp}^{\text{Me}}\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$ and of $\text{Tp}^{\text{Me}}\text{ZnI}$.⁸

Figure 1 shows the structure of the $\text{Tp}^a\text{Rh}(\text{CO})_2$ complex. It contains Rh in a square-planar configuration, with two short (2.09 \AA) N–Rh bonds and one of the pyrazolyl groups connected by a long (2.78 \AA) apical bond. The geometry and bond lengths are similar to those found in the complex $\text{Tp}^{\text{CF}_3\text{,Me}}\text{Rh}(\text{CO})_2$ ($2.10, 2.11$ and 2.62 \AA), but the structure differs from that found for $\text{Tp}^{\text{Ph}}\text{Rh}(\text{CO})_2$, where the uncoordinated phenylpyrazolyl group is turned away from the Rh atom and where the Rh–N bonds are somewhat shorter (2.06 \AA).²¹ The sp^3 carbons of the ethylene tether are not coplanar with the pyrazolyl plane but cross it in zigzag fashion, causing a twist between the phenyl and pyrazolyl planes of 21.4° (average). The cone angle is remarkably large (262°), almost equal to that of Tp^{tBu} (265°). Yet the ligand forms octahedral species Tp^a_2M readily, indeed preferentially, as opposed to Tp^aMX . The answer lies in a relatively large wedge angle (44.3°).

Figure 2 shows the structure of $\text{Tp}^a\text{,MeZnI}$. The Zn–N bond lengths are almost all identical at 2.05 \AA , in line with those reported for $\text{Tp}^{\text{Me}}\text{ZnI}$,⁸ $\text{Tp}^{\text{tBu}}\text{ZnI}$,²² $\text{Tp}^{\text{tBu,Me}}\text{ZnOH}$,²³ $\text{Tp}^{\text{Ph}}\text{ZnX}$,²⁴ and $\text{Tp}^{\text{tBu,Me}}\text{ZnX}$.²⁵ Again, the ethylene tether is zigzagging, resulting in an average phenyl twist angle of 22.6° . The cone angle is slightly larger (average 263°) than that in Tp^a . Still, $\text{Tp}^a\text{,Me}_2\text{M}$ complexes form readily, although somewhat less readily than with Tp^a and, conversely, the $\text{Tp}^a\text{,MeMX}$ complexes are somewhat more stable than their Tp^aMX analogs. The wedge angle averages 43.5° , being marginally smaller than that in Tp^a .

The structure of Tp^bTl shows clearly the pullback of the phenyl ring away from the metal by the short $-\text{CH}_2-$ tether, so that the cone angle is only 242° , substantially smaller than in Tp^a or $\text{Tp}^a\text{,Me}$. With the phenyl and pyrazolyl planes being essentially coplanar, the wedge angle is rather large, averaging 82.4° , as compared with 91.0° in the parent Tp ligand itself, and accordingly the chemical behavior of Tp^b is close to that of Tp. The N–Tl bond lengths range from 2.52 to 2.55 \AA and are thus somewhat shorter than those in $\text{Tp}^{\text{tBu}}\text{Tl}$ ¹⁸ or in the recently reported $\text{Tp}^{(4\text{tBuPh})_2}\text{Tl}$.²⁶

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Table 7. Selected Bond Distances and Angles for 2

Bond Distances (Å)			
Zn-N(1)	2.050(5)	B-N(1)	1.539(9)
Zn-N(3)	2.056(5)	B-N(3)	1.534(9)
Zn-N(5)	2.046(4)	B-N(5)	1.547(10)
Zn-I	2.512(1)		
Nonbonding Distances (Å)			
Zn-B	2.947(8)	B-H(9A)	5.134
Zn-H(9A)	3.163	B-H(29A)	5.259
Zn-H(29A)	3.178	B-H(49A)	5.267
Zn-H(49A)	3.232		
Bond Angles (deg)			
I-Zn-N(2)	118.5(1)	N(4)-Zn-N(6)	92.8(2)
I-Zn-N(4)	120.8(1)	N(1)-B-N(3)	110.7(6)
I-Zn-N(6)	127.9(1)	N(1)-B-N(5)	109.0(5)
N(2)-Zn-N(4)	97.2(2)	N(3)-B-N(5)	110.0(5)
N(2)-Zn-N(6)	91.8(2)		
Twist Angles (deg) ^a			
Pz(1)-Ph(9) ^b	24.1	Pz(5)-Ph(49) ^b	19.0
Pz(3)-Ph(29) ^b	24.7		
Cone Angles (deg) ^c			
H(9A)	259	H(29A)	267
		H(49A)	263

^{a-c} See the footnotes at the bottom of Table 6.

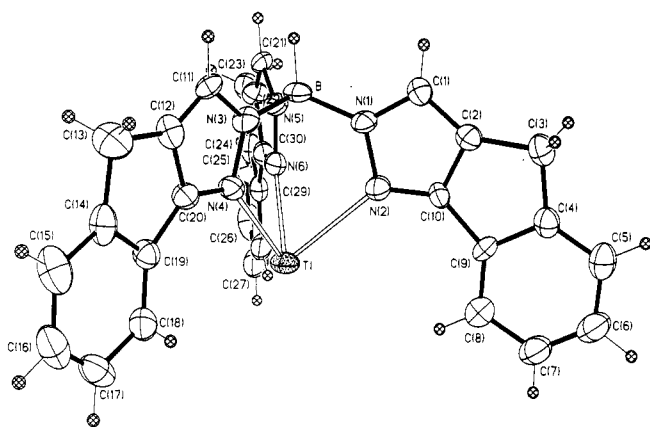


Figure 3. Molecular structure of TITp^b (3) drawn with 35% probability ellipsoids.

Table 8. Selected Bond Distances and Angles for 3

Bond Distances (Å)			
Tl-N(2)	2.550(7)	B-N(1)	1.518(14)
Tl-N(4)	2.530(8)	B-N(3)	1.531(13)
Tl-N(6)	2.518(7)	B-N(5)	1.563(14)
Nonbonding Distances (Å)			
Tl-B	3.595(11)	B-H(8A)	5.750
Tl-H(8A)	3.534	B-H(18A)	5.767
Tl-H(18A)	3.550	B-H(28A)	5.770
Tl-H(28A)	3.506		
Bond Angles (deg)			
N(2)-Tl-N(4)	76.5(2)	N(1)-B-N(3)	110.8(8)
N(2)-Tl-N(6)	72.3(2)	N(1)-B-N(5)	110.4(8)
N(4)-Tl-N(6)	79.4(2)	N(3)-B-N(5)	110.1(8)
Twist Angles (deg) ^a			
Pz(1)-Ph(8) ^b	0.5	Pz(5)-Ph(28) ^b	4.7
Pz(3)-Ph(18) ^b	2.0		
Cone Angles (deg) ^c			
H(8A)	242	H(18A)	242
		H(28A)	245

^{a-c} See the footnotes at the bottom of Table 6.

In Tp^{Ph,Me}ZnI (Figure 4) the N-Zn distances are unexceptional. The cone angles, based on the diversely twisted phenyl groups, average about 250°, but the unrestrained twist angles of the phenyl groups are rather large (-67, 40, 41° and 31, 32, -63° for the two independent molecules). This leads to substantially smaller wedge angles (averaging 31.6°) than in the preceding complexes

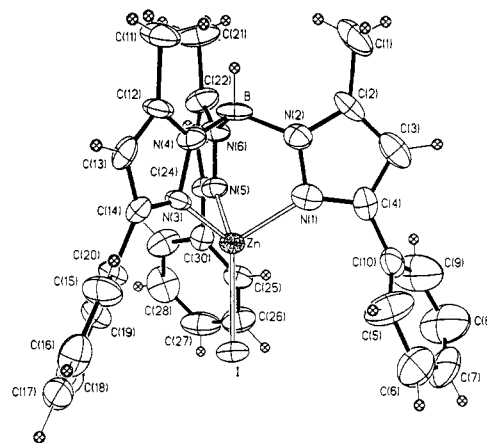


Figure 4. Molecular structure of ZnITp^{Ph,Me} (4) drawn with 35% probability ellipsoids (one of two chemically similar but crystallographically independent molecules).

Table 9. Selected Bond Distances and Angles for 4

Bond Distances (Å)					
	molecule 1	molecule 2	molecule 1	molecule 2	
Zn-N(1)	2.031(17)	2.082(13)	B-N(2)	1.556(27)	1.496(23)
Zn-N(3)	2.063(12)	2.056(11)	B-N(4)	1.542(26)	1.567(21)
Zn-N(5)	2.046(11)	2.036(11)	B-N(6)	1.556(23)	1.516(23)
Zn-I	2.479(2)	2.495(2)			
Nonbonding Distances (Å)					
	molecule 1		molecule 2		
Zn-B	2.978(21)		Zn'-B'	2.943(19)	
Zn-H(5A)	3.913		Zn'-H(5'A)	3.095	
Zn-H(19A)	3.269		Zn'-H(15B)	2.996	
Zn-H(25A)	3.133		Zn'-H(29B)	3.647	
B-H(5A)	5.563		B'-H(5'A)	5.147	
B-H(19A)	5.161		B'-H(15B)	4.987	
B-H(25A)	5.043		B'-H(29B)	5.135	
Bond Angles (deg)					
	molecule 1		molecule 2		
I-Zn-N(1)	121.1(4)		125.2(3)		
I-Zn-N(3)	122.3(4)		125.7(3)		
I-Zn-N(5)	123.6(3)		117.8(3)		
N(1)-Zn-N(3)	96.5(5)		89.9(5)		
N(1)-Zn-N(5)	89.8(5)		95.5(5)		
N(3)-Zn-N(5)	95.4(5)		94.8(4)		
N(2)-B-N(4)	109.1(14)		109.0(12)		
N(2)-B-N(6)	108.1(13)		112.3(12)		
N(4)-B-N(6)	110.3(16)		109.7(14)		
Twist Angles (deg) ^a					
Pz(1)-Ph(5) ^b	-67.5	Pz(1)-Ph(5) ^b	31.2		
Pz(3)-Ph(19) ^b	39.7	Pz(3)-Ph(15) ^b	31.8		
Pz(5)-Ph(25) ^b	41.2	Pz(5)-Ph(29) ^b	-62.5		
Cone Angles (deg) ^c					
H(5A)	238		H(5'A)	265	
H(19A)	252		H(15B)	261	
H(25A)	253		H(29B)	230	

^{a-c} See the footnotes at the bottom of Table 6.

and is reflected in the chemical behavior of Tp^{Ph,Me}. Thus, Tp^{Ph,Me}MX complexes show much higher stability, and the Tp^{Ph,Me}₂M complexes, while capable of existence, give evidence of thermal rearrangement to the less hindered octahedral species containing one "reversed" pyrazolyl group. Also, Tp^{Ph,Me}Rh(COD) is inert toward CO at room temperature, unlike the three other analogous complexes of Tp^a, Tp^{Ph,Me}, and Tp^b. Since the molecule Tp^{Ph,Me}Rh(CO)₂ is perfectly stable, one can deduce that it is the necessary transition state for the displacement of

COD by CO in $\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{COD})$ that is too crowded. Another example of the more hindered nature of the $\text{Tp}^{\text{Ph,Me}}$ ligand is the inability to form the heteroleptic octahedral $\text{Tp}^{\text{Ph,Me}}\text{CoTp}^{\text{Np}}$ complex. But not all reactions proceed less readily with the $\text{Tp}^{\text{Ph,Me}}$ ligand: in the reaction with $(\text{MeCN})_2\text{MoCl}(\text{CO})_2(\eta^3\text{-methallyl})$ the $\text{Tp}^{\text{Ph,Me}}$ ligand functions normally, just like Tp itself, or Tp^{b} . Here, it is the $\text{Tp}^{\text{a,Me}}$ ligand that gives none of the desired product, and even the less hindered Tp^{a} produces initially an agostic product, and then only a low yield of $\text{Tp}^{\text{a}}\text{Mo}(\text{CO})_2(\eta^3\text{-methallyl})$.

Conclusion

The tethering of the 3-phenyl group leads to an increase or decrease of the cone angle of the ligand, depending on the length of the tether, and to an increase of the wedge angle, as compared with an untethered 3-phenyl group. In the case of the short tether, $-\text{CH}_2-$, the wedge angle is 82.4° , and thus close to that of the parent ligand Tp. With the longer zigzagging tether, $-\text{CH}_2\text{CH}_2-$, the

cone angle is very large, especially when a 5-Me group is present on the pyrazolyl ring, approaching that of the 3-*t*-Bu group, the wedge angle still being relatively open (about 44°). The coordination chemistry of these ligands reflects such spatial restrictions. All the tethered ligands display significant tendency to form octahedral L_2M complexes, while the formation and stability of half-sandwich complexes is inverse to the tightness of the tether.

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Supplementary Material Available: Tables of structure determination parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters plus eight additional ORTEP drawings for 1–4 (28 pages). Ordering information is given on any current masthead page.