Hydrotris(3-mesitylpyrazol-1-yl)borate and Hydrobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)borate: Symmetric and Asymmetric Ligands with Rotationally Restricted Aryl Substituents

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Two novel ligands, hydrotris(3-mesitylpyrazol-1-yl)borate $[HB(3Mspz)_3]^-$ (=Tp^{Ms}) and its isomer hydrobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)borate (=Tp^{Ms*}), were synthesized; the latter is the first example of an asymmetric tris(pyrazolyl)borate ligand. They were used to form the complexes $Tp^{Ms}ZnX$, $Tp^{Ms*}MX$ (M = Zn, Cd; X = Cl, I, NCS), $Tp^{Ms}Pd(\eta^3\text{-methallyl})$, $Tp^{Ms*}Pd(\eta^3\text{-methallyl})$, $Tp^{Ms}Rh(COD)$, $Tp^{Ms*}Rh(COD)$, $Tp^{Ms}Rh(CO)_2$, $Tp^{Ms*}Rh(CO)_2$, $Tp^{Ms}Mo(CO)_2(\eta^3\text{-methallyl})$, and $Tp^{Ms*}Mo(CO)_2(\eta^3\text{-methallyl})$. Above 220 °C some of the Tp^{Ms*} complexes rearrange into their Tp^{Ms} analogs. Structures of $Tp^{Ms}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ and of $Tp^{Ms*}ZnI$ were established by X-ray crystallography. The complex $Tp^{Ms}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ crystallizes in the space group $P2_1/m$ (No. 11) with parameters a = 12.709(3) Å, b = 21.085(4) Å, c = 17.856(4) Å, β = 108.66(3)°, V = 4533(2) Å^3 for Z = 4. It contains octahedrally coordinated Mo, with the mesityl groups deviating by 0–17.2° from orthogonality to the pyrazolyl plane. The complex $Tp^{Ms*}ZnI$ crystallizes in the space group $P\bar{1}$ (No. 2) with parameters a = 12.188(3) Å, b = 12.905(4) Å, c = 14.1104(6) Å, α = 97.21(3)°, β = 113.61(3)°, γ = 109.45(2)°, and V = 1828.6(6) Å^3 for Z = 2. It contains tetrahedral Zn(II), and the mesityl groups deviate from orthogonality to the pyrazolyl plane by 10.2–31.8°.

Introduction

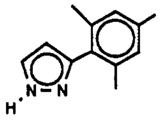
The presence of bulky substituents at the 3-position in tris(pyrazolyl)borate moieties $HB(3\text{-}Rpz)_3M$ imposes steric restrictions on ligands bonding at the remaining coordination sites.[1] Thus, the $[Tp^{Ph}M]^+$ fragment [Tp^{Ph} = $HB(3\text{-}Phpz)_3$] can still form three N–M bonds with an additional $[Tp^{Ph}]^-$ to give octahedral $Tp^{Ph}{}_2M$ complexes, albeit reluctantly,[2] but it will not do so with the ligand $[HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_3]^-$. The resulting complex $M[HB(3\text{-}Phpz)_3][HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_3]$ contains five M–N bonds and one agostic B–H–N bond from the Tp^{Ph} ligand.[3] Another feature of the 3-phenyl group involves its addition (internal cyclometalation) in some half-sandwich compounds of Rh(I). For instance, irradiation of a benzene solution of $Tp^{Ph}Rh(CO)_2$ resulted in the loss of one CO and oxidative addition of one 3-phenyl group, producing an octahedral structure, containing one Rh–H bond and one Rh–C bond to the ortho carbon of the phenyl group.[4] This reaction was possible because the phenyl group was free to rotate and assumed the necessary orientation for oxidative addition.

In Tp^{Ph} complexes where the structue was determined by X-ray crystallography, one finds the phenyl group neither parallel with nor orthogonal to the pyrazolyl plane. In the five-coordinate complex $Tp^{Ph}CoNCS\cdot THF$, the twist angles differ for each ring, being 32.3, 36.2, and 36.6°, respectively.[1b] In the octahedral complex $Tp^{Ph}{}_2Fe$ the twist angles range from 21 to 31°,[2] while in $Tp^{Ph}Cu(pterin)$[5] they are 38, 40, and 54°, the large angle being caused by steric interaction with the pterin ligand. Other twist angles of the Tp^{Ph} ligand are 21–28° for $Tp^{Ph}{}_2Yb$ and 11, 26, and 31° for $Tp^{Ph}{}_2Sm$.[6]

In the related compound $HB[3\text{-}(4\text{-methylphenyl})pz]_3Tl$, there are two molecules of different geometries in the unit cell, containing dihedral angles of about 2 and 30°, respectively. This difference is due to packing forces.[7] By contrast, in $HB[3\text{-}(4\text{-methoxyphenyl})pz]_3Mo(CO)_2NO$ the twist angles range from 52 to 62°.[8]

We were interested in the coordination chemistry of $HB(3Rpz)_3$ ligands where R would be an aromatic group, bulky enough to prevent formation of $L^*{}_2M$ complexes and also incapable of coplanarity with the pyrazolyl ring, being, preferably, orthogonal to it. Such a ligand would permit reactions at the metal without the interfering oxidative addition of the phenyl group. This orthogonality was to be achieved by means of 2,6-substituents, which would preclude or inhibit rotation of the phenyl group around the C–C bond to the pyrazole ring. The mesityl substituent was chosen as the 3-R group.

The hitherto unknown 3-mesitylpyrazole (**1**) was synthesized and converted to the $HB(3Mspz)_3$ ligand (=Tp^{Ms}, Ms = mesityl), characterized as $Tp^{Ms}Tl$ (**2**) and as various derivatives of type **3**.



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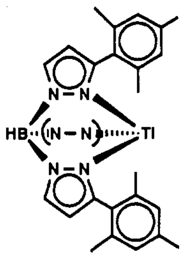

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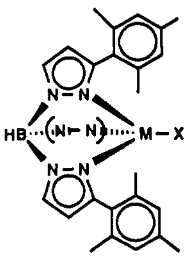

3

(-(N-N)- denotes the third 3-mesitylpyrazolyl group)

Its coordinative behavior was investigated in high-spot fashion,

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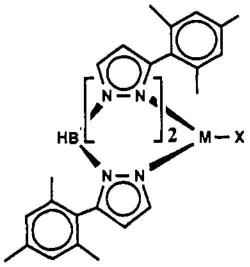
including an X-ray crystallographic structure determination of the derivative Tp^{Ms}Mo(CO)$_2$(η^3-CH$_2$CMeCH$_2$).

In the course of Tp^{Ms} synthesis, an isomeric ligand was isolated with one the mesityl groups in the 5-position. This ligand was abbreviated as Tp^{Ms*}, and complexes derived therefrom, such as **4**, **5**, and others, were prepared and contrasted with those based on the symmetrical ligand Tp^{Ms}. The structure of Tp^{Ms*}ZnI was determined by X-ray crystallography.



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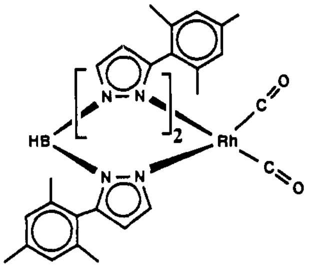

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Experimental Section

The precursors (MeCN)$_2$Mo(CO)$_2$Cl(η^3-CH$_2$CMeCH$_2$),[9] [PdCl(η^3-CH$_2$CMeCH$_2$)]$_2$,[10] and [RhCl(COD)]$_2$[11] were prepared by literature methods. All the other chemicals were reagent grade and were used as received. Elemental analyses were done by Microanalysis, Inc., of 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.

Preparation of 3-Mesitylpyrazole. To a slurry of 60 g (1.1 mol) of anhydrous sodium methoxide in 1.4 L of toluene, rapidly stirred in a 4-L beaker, was added in one portion a mixture of 178 g (1.1 mol) of 2,4,6-trimethylacetophenone and 300 mL (large excess) of ethyl formate. The slurry cleared up almost completely. After a few minutes of induction period, a moderately exothermal reaction took place, and a solid started precipitating. To facilitate stirring, 1 L of hexane was added. After 1 h of stirring, the slurry was filtered, and the white solid was washed with hexane and pressed dry. The material was dissolved in 1.5 L of methanol, and a solution of 76 g (1.1 mol) of hydrazine hydrochloride in 500 mL of water was added over a few minutes. A bright yellow color developed. Addition of 1.5 L of cold water precipitated a bright, canary-yellow solid. The slurry was extracted with 1.5 L of methylene chloride, and the dark yellow-orange extract was stripped to dryness. The residue was refluxed in 400 mL of isopropyl alcohol along with 25 mL (0.5 mol) of hydrazine hydrate for 2 h (which resulted in fading of the color to pale yellow), followed by distillation of all volatiles, ultimately at reduced pressure (oil bath at 250 °C). This resulted in completion of hydrazinolysis and in conversion of some of the byproducts to 3-mesitylpyrazole. There was obtained 162 g (79.2% yield) of crude pale yellow product. After recrystallization from toluene, it was obtained as fine white needles (first crop 132 g, 64.5%; second crop 15 g 6.0%; sublimation of the yellow residue from evaporation of the mother liquor gave an additional 3.2 g of 3-mesitylpyrazole), mp 184–186 °C. Anal. Calc for C$_{12}$H$_{14}$N$_2$: C, 77.4; H, 7.53; N, 15.0. Found: C, 77.2; H, 7.38; N, 14.4. NMR: d 7.49, s 6.91, d 6.13, s 2.29, and s 2.00 ppm in 1:2:1:3:6 ratio, assigned to 5-H, 3′,5′-H, 4-H, 4′-Me and 2′,6′-Me, respectively. ^{13}C NMR: 144.0 (3-C), 137.9 (4′-C), 137.7 (2′,6′-C), 135.6 (5-C), 128.3 (1′-C), 128.0 (3′,5′-C), 105.5 (4-C), 21.2 (4′-Me), 20.2 (2′,6′-Me) ppm.

Preparation of Thallium Hydrotris(3-mesitylpyrazol-1-yl)borate (=Tp^{Ms}Tl) and of Thallium Hydrobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)borate (=Tp^{Ms*}Tl). A mixture of 117 g (0.63 mol) of 3-mesitylpyrazole and 8.5 g (0.16 mol) of KBH$_4$ was refluxed in 250 mL of anisole. Hydrogen evolution at reflux was slow but steady, slowing down gradually. After 60 h of reflux, there was obtained 11.1 L of H$_2$ (vs 11.8 L theory). Anisole was distilled out at reduced pressure, and the residue was dissolved in 400 mL of THF. The cloudy solution was stirred with Celite; it was then filtered, and the clear filtrate was added to a stirred solution of 50 g of TlNO$_3$ in 800 mL of water, mixed with 800 mL of methylene chloride. The mixture was stirred vigorously for 30 min, and the layers were allowed to separate. Much of the upper aqueous layer was decanted and replaced with fresh water. The stirring and separation were repeated twice. The mixture, which contained a substantial amount of crystalline solid in the methylene chloride layer, was transferred to a 2-L separatory funnel, and the organic layer was filtered through a coarse-frit funnel, collecting the solid. It was washed with a few small portions of methylene chloride and yielded after drying 33.8 g (28%) of pure Tp^{Ms}Tl. The filtrate was evaporated to dryness and was stirred with 1 L of methanol. The resulting slurry was filtered, and the solid was washed thoroughly with methanol to remove excess 3-mesitylpyrazole and air-dried, yielding 66.8 g (56%) of a mixture of Tp^{Ms}Tl and Tp^{Ms*}Tl.

The methanol filtrate was mixed with aqueous acetic acid, and the mixture was refluxed for 1 h to hydrolyze any ligand which may have been present. The mixture was then diluted with water and neutralized with sodium hydroxide, which resulted in precipitation of 3-mesitylpyrazole, obtained after drying in 41-g yield. Based on converted 3-mesitylpyrazole, the combined yield of Tp^{Ms}Tl and Tp^{Ms*}Tl was 96%, and the individual yields were 32% for Tp^{Ms}Tl and 64% for the second crop (mixture of Tp^{Ms}Tl and Tp^{Ms*}Tl).

By NMR analysis, where the two isomeric ligands could be clearly distinguished, the second fraction of Tl salts was 83% Tp^{Ms*}Tl and 17% Tp^{Ms}Tl. One recrystallization from toluene yielded a 5.7-g first crop of the low-solubility Tp^{Ms}Tl, leaving a residue which consisted of 91% Tp^{Ms*}Tl and 9% Tp^{Ms}Tl. This material was used to prepare Tp^{Ms*} derivatives, which were then purified directly.

Tp^{Ms}Tl was recrystallized from toluene. Mp: 303–305 °C. IR: BH at 2430 cm^{-1} with a weaker peak at 2457 cm^{-1}. ^{1}H NMR s 7.83 (5-H), s 6.84 (3′,5′-H), s 6.07 (4-H), s 2.27 (4′-Me), s 1.90 (2′,6′-Me) ppm in 3:6:3:9:18 ratio. The BH was detectable by integration (relative intensity = 1) in the 4.1–5.3 ppm range. ^{13}C NMR: d 20.3 (J = 62.0 Hz, 2′,6′-Me), s 21.1 (4′-Me), d 104.9 (J = 25.2 Hz, 4-C), s 127.9 (3′,5′-C), s 131.0 (1′-C), s 135.8 (5-C), s 137.3 (2′,6′-C), s 137.4 (4′-C), d 151 (J = ~20 Hz, 3-C) ppm. Anal. Calc for C$_{36}$H$_{40}$BN$_6$Tl: C, 56.0; H, 5.19; N, 10.9. Found: C, 56.1; H, 5.36; N, 10.8.

Tp^{Ms*}Tl was recrystallized from octane and was obtained as fine fibrous needles. Mp: 222–223 °C; the melt resolidifies around 225 °C, melting again with decomposition at 305–308 °C. IR: 2492 cm^{-1} with a shoulder 2466 cm^{-1}. ^{1}H NMR: d 7.54, d, 7.48, s 6.97, s 6.88, broad, partly merged doublets 6.04, 6.02, s 2.39, s 2.29, s 1.95, s 1.84 ppm in 2:1:2:4:1:2:3:6:12:6 ratio. ^{13}C NMR, where each of the peaks present in the Tp^{Ms}Tl spectrum is split into 2:1 patterns (ppm): 19.8, 20.3 (broad, unresolved d) (1:2, 2′,6′-Me); 21.0, 21.2 (2:1, 4′-Me); 104.7, 105.0 (2:1, 4-C); 127.6, 127.9 (1:2, 3′,5′-C); 130.7, 131.1 (1:2, 1′-C); 136.0, 137.3, 137.5, 137.9, 138.3, 146.5, 150.4 (1:2, 3-C). IR: BH at 2490 cm^{-1}. Anal. Calc for C$_{36}$H$_{40}$BN$_6$Tl: C, 56.0; H, 5.19; N, 10.9. Found: C, 55.9; H, 5.24; N, 10.7.

Thermal Isomerization of Tp^{Ms*}Tl to Tp^{Ms*}TL. A sample of pure Tp^{Ms*}Tl was heated to 236 °C in a test tube and maintained at this temperature for 1 h. The sample melted and then gradually solidified. After cooling, the darkened solid plug was crushed and recrystallized from xylene. The IR of the purified material was identical with that of authentic Tp^{Ms}Tl. Evaporation of the filtrate yielded a solid residue which was, by IR, also Tp^{Ms}Tl.

Preparation of Tp^{Ms}MX and Tp^{Ms*}MX Complexes (M = Zn, Cd). The complexes were prepared by rapidly stirring a mixture consisting of a methylene chloride solution of either Tp^{Ms}Tl or Tp^{Ms*}Tl with an aqueous solution of Zn(NO$_3$)$_2$ along with an excess of KX or NaX, plus a catalytic amount of tetrabutylammonium bromide as phase-transfer agent. After 4 h the phases were separated, and the organic phase was filtered through a layer of Celite and alumina. The filtrate was evaporated, and the residue was purified by recrystallization from toluene or xylene (in the case of Tp^{Ms}MX complexes) or from heptane (in the case of Tp^{Ms*}MX complexes). The Tp^{Ms}CdCl and Tp^{Ms*}CdCl complexes were prepared similarly.

Tp^{Ms}ZnCl: white solid, recrystallized from mesitylene (250 mL of saturated solution in boiling mesitylene deposited on cooling 2.3 g of the granular product). Mp: softens at 323 °C, melts with decomposition from 327 to 334 °C. IR: BH 2472 cm^{-1}. ^{1}H NMR: d 7.85, s 6.84, d 6.12, s 2.24, s 1.90 ppm in 1:2:1:3:6 ratio. Anal. Calc for C$_{36}$H$_{40}$BClN$_6$Zn: C, 64.7; H, 5.99; N, 12.6. Found: C, 65.0; H, 5.97; N, 12.5.

Tp^{Ms*}ZnCl. Tp^{Ms*}ZnCl is much more soluble in mesitylene than Tp^{Ms}ZnCl and crystallizes in needles which trap much solvent. It softens and

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starts flowing at 274 °C, is still a hazy paste at 284 °C, then it solidifies, and starts melting again with decomposition from 316 °C. IR: BH 2515 cm^{-1}. ^{1}H NMR: d 7.70, d 7.62, s 7.01, s 6.89, d 6.11, s 2.43, s 2.28, s 1.90, s 1.87 ppm in 1:2:2:4:3:3:6:12:6 ratio. Anal. Calc for $C_{36}H_{40}BClN_6Zn$: C, 64.7; H, 5.99; N, 12.6. Found: C, 64.6; H, 6.03; N, 12.4.

Tp^{Ms}ZnI. Mp (from xylene): softens from 307 °C, melts with decomposition at 312–314 °C. IR: BH 2471 cm^{-1}. NMR: d 7.83, s 6.82, d 6.12, s 2.24, s 1.90 ppm in 1:2:1:3:6 ratio. Anal. Calc for $C_{36}H_{40}BIN_6Zn$: C, 56.9; H, 5.27; N, 11.1. Found: C, 57.0; H, 5.02; N, 10.9.

TP^{Ms*}ZnI (=Compound II in X-ray Study). Mp (from xylene): 241–242 °C. The melt does not resolidify up to 300 °C. IR: BH 2515 cm^{-1}. NMR: d 7.71, d 7.62, s 7.01, s 6.88, d 6.09, s 2.42, s 2.29, s 1.93, s 1.88, s 1.86 ppm in 1:2:2:4:3:3:6:6:6:6 ratio. Anal. Calc for $C_{36}H_{40}BIN_6Zn$: C, 56.9; H, 5.27; N, 11.1. Found: C, 57.1; H, 5.07; N, 10.9.

Tp^{Ms}ZnNCS. Mp (from xylene): sinters from 292 °C, melts around 295 °C. IR: very sharp BH at 2478 cm^{-1}, NCS at 2053 cm^{-1}. NMR: d 7.83, s 6.90, d 6.17, s 2.29, s 1.96 ppm in 1:2:1:3:6 ratio. Anal. Calc for $C_{37}H_{40}BN_7SZn$: C, 64.3; H, 5.80; N, 14.2. Found: C, 64.1; H, 5.92; N, 14.1.

Tp^{Ms*}ZnNCS. Mp (from toluene): 243–244 °C, followed by immediate resolidification, and then melting again at 292–302 °C. IR: BH 2511, NCS 2053 cm^{-1}. ^{1}H NMR: 7.68, 7.62, 7.01, 6.96, 6.94, 6.15, 6.12, 2.41, 2.32, 1.92, 1.84 ppm in 1:2:2:2:2:2:1:3:6:12:6 ratio. Anal. Calc for $C_{37}H_{40}BN_7SZn$: C, 64.3; H, 5.80; N, 14.2. Found: C, 64.0; H, 5.87; N, 14.0.

Tp^{Ms}ZnNCO. Mp (from toluene): sinters from 296 °C, mp 305–307 °C dec. IR: BH 2469 cm^{-1}, NCO 2236 cm^{-1}. ^{1}H NMR: d 7.83, s 6.87, d 6.16, s 2.25, s 1.87 ppm in 1:2:1:3:6 ratio. Anal. Calc for $C_{37}H_{40}BN_7OZn$: C, 65.9; H, 5.93; N, 14.5. Found: C, 65.7; H, 6.04; N, 14.2.

Tp^{Ms*}ZnNCO. Mp (from octane): 247–249 °C, no solidification up to 300 °C. IR: BH 2514 cm^{-1} NCO 2222 cm^{-1}. ^{1}H NMR: d 7.66, d 7.61, s 7.00, s 6.93, d 6.12, d 6.10, s 2.40, s 2.30, s 1.92, s 1.85 ppm in 1:2:2:4:2:1:3:6:6:12 ratio. Anal. Calc for $C_{37}H_{40}BN_7OZn$: C, 65.9; H, 5.93; N, 14.5. Found: C, 65.6; H, 6.01; N, 14.3.

Tp^{Ms}CdCl: crystals from xylene; sinters around 265 °C and then melts with bubbling at 266–268 °C. IR: BH 2458 cm^{-1}. ^{1}H NMR: d 7.88, s 6.85, d 6.16, s 2.24, s 1.90 ppm in 1:2:1:3:6 ratio. Anal. Calc for $C_{37}H_{40}BClCdN_6$: C, 60.4; H, 5.59; N, 11.7. Found: C, 60.2; H, 5.68; N, 11.5.

Tp^{Ms*}CdCl: crystals from xylene; sinters from 268 °C, mp 275–277 °C (with bubbling). IR: 2497 cm^{-1}. ^{1}H NMR: d 7.57, s 6.99, s 6.89, d 6.05, d 6.04, s 2.40, s 2.24, s 1.92, s 1.83 ppm in 3:2:4:1:2:3:6:6:12 ratio. Anal. Calc for $C_{37}H_{40}BClCdN_6$: C, 60.4; H, 5.59; N, 11.7. Found: C, 60.5; H, 5.66; N, 11.6.

Preparation of Tp^{Ms}CoNCO. This complex was prepared similarly to the Tp^{Ms}ZnNCS analog, except that the product had to be heated at 240 °C/1 Torr to remove coordinated solvent and/or 3-mesitylpyrazole. The blue crystals sinter from 256 °C and melt at 265–267 °C. IR: BH 2472 cm^{-1}, NCS 2065 cm^{-1}. Anal. Calc for $C_{37}H_{40}BCoN_7S$: C, 64.9; H, 5.85; N, 14.3. Found: C, 64.5; H, 5.94; N, 14.2.

Preparation of Tp^{Ms}Mo(CO)$_2$(η^3-CH$_2$CMeCH$_2$) (=Compound I in X-ray Study). Equimolar amounts of Tp^{Ms}Tl and (MeCN)$_2$Mo(CO)$_2$(Cl)(π-methallyl) were stirred in methylene chloride for 2 h. The slurry was filtered, and the filtrate was chromatographed on alumina, collecting the yellow band. After evaporation of solvent and recrystallization of the residue from toluene, there was obtained a yellow solid in 75% yield, darkening gradually from 228 °C and decomposing at 238–239 °C. IR: BH 2502 cm^{-1}, CO 1943, 1857 cm^{-1}. ^{1}H NMR: d 7.75 (2H, 5-H), d 7.63 (1H, 5-H), s 6.95 (6H, 3′,5′-H), d 6.15 (1H, 4-H), d 6.08 (2H, 4-H), s 2.94 (2H, π-allyl syn-H), s 2.32 (9H, 4′-Me), s 2.20 (12H, 2′,6′-Me), s 2.03 (6H, 2′,6′-Me), s 1.48 (3H, π-allyl Me), s 0.17 ppm (2H, π-allyl anti-H). Anal. Calc for $C_{42}H_{47}BMoN_6O_2$: C, 65.1; H, 6.07; N, 10.8. Found: C, 65.4; H, 6.35; N, 10.5.

Preparation of Tp^{Ms*}Mo(CO)$_2$(η^3-CH$_2$CMeCH$_2$). This was done as above, but using Tp^{Ms*}Tl instead of Tp^{Ms}Tl. The complex was purified by chromatography, eluting with ether. The eluate was stripped and triturated with isopropyl alcohol, which yielded yellow crystals. The complex was extremely soluble in toluene and was recrystallized from octane. It darkens gradually from 240 °C; dec pt 241–242 °C. IR: BH 2496 cm^{-1}, CO 1950 and 1861 cm^{-1}. The ^{1}H NMR was very complex with five 5(3)-H peaks (8.50, 7.97, 7.55, 7.53 (broad), 7.29 (broad)), four 3′,5′-H peaks (7.03, 6.97, 6.95, 6.91 (all broad)), four 4-H peaks (6.08, 6.05 (broad), 6.02, 5.98 (broad)), and the syn-, anti-, and 2,6-methyl peaks as a complex scattering of 19 peaks, ranging from 3.49 to 0.30 ppm. The ratio of total aromatic:aliphatic protons was about 1:3 (theory 12:34). Anal. Calc for $C_{42}H_{47}BMoN_6O_2$: C, 65.1; H, 6.07; N, 10.8. Found: C, 65.0; H, 6.16; N, 10.6.

Preparation of Tp^{Ms}Rh(COD). A mixture of 0.05 mol of Tp^{Ms}Tl and 0.05 mol (as monomer) of [RhCl(COD)]$_2$ was stirred in 100 mL of methylene chloride for 15 min, and the mixture was then chromatographed on alumina, collecting the yellow band. Evaporation of solvent yielded 74% of a yellow solid, which was recrystallized from octane/toluene. Mp: 230–232 °C. IR: BH at 2420 cm^{-1}. ^{1}H NMR: d 7.61 (2H, 5-H), d 7.14 (1H, 5-H), s 6.97 (4H, 3′,5′-H), s 6.90 (2H, 3′,5′-H), d 6.06 (2H, 4′-H), d 5.95 (1H, 4-H), broad s 3.70 (4H, olefinic H), s 2.34 (3H, 4′-Me), s 2.28 (6H, 2′,6′-Me), s 2.14 (12H, 2′,6′-Me), s 1.79 (6H, 2′,6′-Me), unresolved m 1.50 (4H), m 1.20 (4H) ppm. Anal. Calc for $C_{44}H_{52}BN_6Rh$: C, 67.9; H, 6.68; N, 10.8. Found: C, 68.0; H, 6.75; N, 10.6.

Preparation of Tp^{Ms*}Rh(COD). This complex was prepared as above, using Tp^{Ms*}Tl as the starting material. Mp (from toluene/octane): 197–200 °C. IR: BH at 2450 cm^{-1}. ^{1}H NMR: instead of the simple 2:1 pattern for all peaks, found in Tp^{Ms}Rh(COD), there were three pyrazole 5(3)-H peaks (8.12, 7.85, and 7.56 ppm in approximately 1:2:2 relative ratio) and three pyrazole 4-H peaks (6.31, 6.17, and 5.95 ppm, again in relative 1:2:2 ratio); the mesityl 3,5-protons appeared as four overlapping peaks (6.98, 6.94, 6.91, 6.83 ppm, relative ratio difficult to assess); there were three COD vinylic protons at 4.07, 3.52, and 3.37 ppm (in 2:2:1 relative ratio); the methylene protons also appeared as several clusters of signals, as did the methyl protons. Anal. Calc for $C_{44}H_{52}BN_6Rh$: C, 67.9; H, 6.68; N, 10.8. Found: C, 68.2; H, 6.79; N, 10.5.

Preparation of Tp^{Ms}Rh(CO)$_2$. This complex was synthesized by bubbling CO for 30 min through a methylene chloride solution of Tp^{Ms}Rh(COD), followed by stripping of the solvent and removal of COD in vacuo. The yellow product was recrystallized from toluene. Mp: sinters from 241 °C, dec pt 245–248 °C. IR: BH at 2450 cm^{-1}, CO at 2063 and 1984 (vs) cm^{-1} (Nujol), 2062, 1986 cm^{-1} (cyclohexane). ^{1}H NMR: d 7.73, s 6.87, d 6.13, s 2.26, s 2.04 ppm in 1:2:1:3:6 ratio. ^{13}C NMR: 20.7, 21.1, 106.1, 127.4, 131.1, 136.0, 138.0, 138.1, 153.6, 183.3, 184.2. Anal. Calc for $C_{38}H_{40}BN_6O_2Rh$: C, 62.8; H, 5.51; N, 11.6. Found: C, 62.6; H, 5.66; N, 11.3.

Preparation of Tp^{Ms*}Rh(CO)$_2$. This complex was prepared as above and was purified by recrystallization from heptane. Mp: sinters from 192 °C, melts at 196–199 °C. IR: BH at 2506 cm^{-1}, CO at 2060 and 1964 (vs) cm^{-1} (Nujol), 2062, 1965 cm^{-1} (cyclohexane). ^{1}H NMR: d 7.69, d 7.52, s 6.98, s 6.88, d 6.06, s 2.38, s 2.28, s 1.99, s 1.84 ppm in 1:2:2:4:3:3:6:6:12 ratio. ^{13}C NMR (ppm): 19.8, 20.3 (1:2, 2′,6′-Me); 21.2, 21.2 (2:1, 4′-Me); 105.3, 106.3 (2:1, 4-C); 127.7 (3′,5′-C); 129.2, 131.6 (1:2, 4′-C); 135.4, 137.8, 137.9, 138.2, 143.1, 146.9, 152.8, 187.2, 188.1. Anal. Calc for $C_{38}H_{40}BN_6O_2Rh$: C, 62.8; H, 5.51; N, 11.6. Found: C, 62.5; H, 5.61; N, 11.4.

Preparation of Tp^{Ms}Pd(η^3-CH$_2$CMeCH$_2$). This complex was prepared by stirring equivalent amounts of Tp^{Ms}Tl and PdCl(η^3-methallyl) in methylene chloride, and the product was purified by chromatography on alumina, eluting with methylene chloride. Stripping of the eluate and trituration of the residue with methanol gave a pale creamy solid. It darkens gradually from 210 °C; dec pt 227–228 °C. IR: BH at 2419 cm^{-1}. ^{1}H NMR: d 7.75 (5-H), s 6.86 (3′,5′-H), d 6.11 (4-H), s 2.38 (π-allyl syn-H), s 2.27 (4′-Me), s 2.02 (2′,6′-Me), s 1.72 (π-allyl anti-H), s 1.22 (π-allyl Me) ppm in 3:6:3:2:9:18:2:3 ratio. Anal. Calc for $C_{40}H_{47}BN_6Pd$: C, 65.9; H, 6.46; N, 11.5. Found: C, 65.8; H, 6.42; N, 11.4.

Preparation of Tp^{Ms*}Pd(η^3-CH$_2$CMeCH$_2$). This complex was prepared as above, but using Tp^{Ms*}Tl instead of Tp^{Ms}Tl, and it was obtained as a pale creamy solid, which was recrystallized from heptane, yielding white crystals. They darken gradually from 180 °C; dec pt 185–188 °C. IR: BH at 2484 cm^{-1}. ^{1}H NMR: d 7.47, s 6.93, b s 6.06, d 6.00, b s 2.71, s 2.35, s 2.27, s 2.01, s 1.97, s 1.90, s 1.50 ppm in 3:2:4:1:2:3:6:2:12:6:3 ratio. The broadening of the π-allyl peaks and of one of the 4-H peaks is indicative of a dynamic process. Anal. Calc for $C_{40}H_{47}BN_6Pd$: C, 65.9; H, 6.4; N, 11.5. Found: C, 65.7; H, 6.53; N, 11.3.

Crystal and Molecular Structures of Tp^{Ms}Mo(CO)$_2$(η^3-CH$_2$CMeCH$_2$) (I) and Tp^{Ms*}ZnI (II). Crystallographic data for these structures are presented in Table I. A yellow, platelike crystal of compound **I**, recrystallized from an acetone/toluene/hexane solution, and a colorless, cube-shaped crystal of compound **II**, recrystallized from heptane, were each mounted on a fine glass fiber with epoxy cement. Preliminary photographic characterizations revealed $2/m$ Laue symmetry for **I** and $\bar{1}$ Laue symmetry for **II**. The unit-cell parameters were obtained from the least-squares fit of 26 reflections ($15 \leq 2\theta \leq 20°$) for **I** and 20 reflections

Table I. Crystallographic Parameters for $\mathrm{Mo(CO)_2[\eta^3\text{-}CH_2C(CH_3)CH_2][(3\text{-}mesityl\text{-}pz)_3BH]}$ (I) and $\mathrm{ZnI[(3\text{-}mesityl\text{-}pz)_2(5\text{-}mesityl\text{-}pz)BH]}$ (II)

	I	II
formula	$C_{42}H_{47}BMoN_6O_2$	$C_{36}H_{40}BIN_6Zn$
fw	774.60	759.8
space group	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)
a, Å	12.709(3)	12.188(3)
b, Å	21.085(4)	12.905(4)
c, Å	17.856(4)	14.104(6)
α, deg		97.21(3)
β, deg	108.66(3)	113.61(3)
γ, deg		109.45(2)
V, Å^3	4533(2)	1828.6(6)
Z	4	2
d(calc), g/cm^3	1.135	1.380
μ, cm^{-1}	3.27	15.5
T, °C	25	23
λ(Mo Kα), Å	0.710 73	0.710 73
$R(F)$,[a] %	7.70	3.75
$R_w(F)$,[b] %	8.04	4.79

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; $w^{-1} = \sigma^2(F_o) + gF_0^2$.

($15 \leq 2\theta \leq 25°$) for **II**. The systematic absences in the diffraction data of **I** were consistent with either of the space groups $P2_1$ and $P2_1/m$. E statistics suggested the centrosymmetric alternatives, $P2_1/m$ and $P\bar{1}$, for **I** and **II**, respectively, and the chemically sensible results of refinement supported these choices. A correction for absorption was not required for **I** (low μ, well-shaped crystal). A semiempirical absorption correction was applied to **II** (XEMP, $T_{max}/T_{min} = 1.17$).

Both structures were solved by direct methods, which located the heavy atoms. The remaining non-hydrogen atoms were found through subsequent Fourier syntheses. The unit cell of compound **I** contains two crystallographically independent, but chemically similar, half-molecules on a mirror plane perpendicular to the b axis. After completion of the structure of the Mo complex, two clusters of atoms were located, which are assumed to be disordered solvent molecules. The first, labeled C(43), C(44), and C(46), was arbitrarily refined as full-occupancy carbon atoms, but no satisfactory chemical identity could be assigned. The second appeared to be disordered acetone and was labeled O(51), C(51), C(52), and C(53). Both solvent molecules, located on the crystallographic mirror plane, were excluded from the calculation of density and formula weight and from the unit-cell formula. All non-hydrogen atoms in both compounds, except the carbon atoms in **I**, were refined with anisotropic parameters, and all hydrogen atoms, except the one on the boron atom in **I**, were idealized (d(CH) = 0.960 Å; $U = 1.2U$ for attached C).

All programs and the sources of the scattering factors are contained in the SHELXTL/PC (Version 4.2) program library (G. Sheldrick, Nicolet (Siemens), Madison, WI).

Atom coordinates for **I** and **II** are given in Table II, and relevant bond distances and angles are given in Table III.

Results and Discussion

The novel pyrazole 3-mesitylpyrazole (=3-MspzH) was prepared from 2,4,6-trimethylacetophenone via formylation with ethyl formate and reaction with hydrazine. It reacted with potassium borohydride, forming two ligands in about 2:1 ratio.

$$\text{3-mesitylpyrazole} + \mathrm{KBH_4} \rightarrow \\ \mathrm{[HB(3\text{-}Mspz)_3]K} + \mathrm{[HB(3\text{-}Mspz)_2(5\text{-}Mspz)]K} \quad (1)$$

After conversion to their Tl salts, these ligands were separated by fractional crystallization. Although the symmetrical ligand, $\mathrm{[HB(3\text{-}mesityl\text{-}pz)_3]Tl}$ (=Tp$^{\mathrm{Ms}}$Tl), was the minor component, it was easier to isolate pure because of its low solubility. The much more soluble isomeric salt, $\mathrm{[HB(3\text{-}mesityl\text{-}pz)_2(5\text{-}mesityl\text{-}pz)]Tl}$ (=Tp$^{\mathrm{Ms}*}$Tl), was difficult to obtain pure, as it tenaciously retained a few percent of Tp$^{\mathrm{Ms}}$Tl, requiring numerous recrystallizations.

The ^{1}H NMR of Tp$^{\mathrm{Ms}}$Tl indicated C_{3v} symmetry for the molecule, showing all 3-mesitylpyrazol-1-yl groups to be equivalent. It also exhibited ^{205}Tl coupling to the pyrazole 4- and 5-protons, making these peaks appear as broad singlets. In the ^{13}C spectrum, ^{205}Tl coupling was observed to the 2′,6′-methyls (62 Hz), as well as to the 4-C (25 Hz) and 3-C (20 Hz). This is in contrast to the ^{13}C spectra of $\mathrm{[HB(3\text{-}Phpz)_3]Tl}$,[12] [HB(3-($p$-tolyl)pz$_3$]Tl,[7] and [HB(3-($p$-methoxyphenyl)pz)$_3$]Tl,[13] where no ^{205}Tl coupling to the pyrazole 4-C and 3-C is observed.

While fairly simple NMR spectra were expected, and observed, for Tp$^{\mathrm{Ms}}$ complexes, a considerably more involved situation existed for Tp$^{\mathrm{Ms}*}$ derivatives. With the ligand exhibiting C_s symmetry, one would have expected in tetrahedral and dynamic pseudotetrahedral complexes 2:1 patterns for the pyrazolyl 4- and 3(5)-protons and for the 4′-methyl signals. At the same time, one should have observed 1:1:1 patterns for the 2′,6′-methyls and for the 3′,5′-protons, since the plane of symmetry, passing through the 5-Mspz group is separating the 2′,6′-methyls of the 3-Mspz groups into "outer" and "inner" sets with respect to that plane, so that singlets of intensity 6 would be observed for each of these sets, as well as for the equivalent 2′,6′-methyls of the 5-Mspz group. The same situation should apply to the 3′,5′-protons, leading to their 1:1:1 pattern.

In actual practice this was not observed, presumably because the differences between the "inner" and "outer" 2′,6′-methyls and 3′,5′-protons were too small to cause significant differences in chemical shifts. What was observed throughout were 2:1 patterns not only for 4-H and 3(5)-H signals but also for the 2′,6′-methyls and 3′,5′-protons. In many instances the peaks with relative intensity of 2 were broadened, suggesting the presence of two unresolved peaks. The only exceptions were Tp$^{\mathrm{Ms}*}$ZnI, which showed a clear 1:1:1 pattern for the 2′,6′-methyls (but a 2:1 pattern for the 3,5-protons), and Tp$^{\mathrm{Ms}*}$ZnNCS, which had a 1:1:1 pattern for the 3,5-protons (but a 2:1 pattern for the 2′,6′-methyls).

Another spectroscopic feature differing substantially for the two isomeric ligands was the B–H stretch: 2430 cm^{-1} for Tp$^{\mathrm{Ms}}$Tl and 2492 cm^{-1} for Tp$^{\mathrm{Ms}*}$Tl. The higher frequency B–H stretch for Tp$^{\mathrm{Ms}*}$ complexes, as compared with those for Tp$^{\mathrm{Ms}}$, was also observed for all other Tp$^{\mathrm{Ms}}$/Tp$^{\mathrm{Ms}*}$ derivative pairs.

The Tp$^{\mathrm{Ms}*}$ ligand represents the first instance where an asymmetric species of the type $\mathrm{[HB(3\text{-}Rpz)_2(5\text{-}Rpz)]}$ could be conveniently isolated. While octahedral bis complexes $\mathrm{L^*_2M}$ containing the ligands $\mathrm{[HB(3\text{-}Pr^ipz)_2(5\text{-}Pr^ipz)]}$ and $\mathrm{[HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_2(5\text{-}Pr^i\text{-}4\text{-}Brpz)]}$ were reported,[14] they were formed from an initially symmetrical ligand, by way of rearrangement of $\mathrm{L_2M}$ complexes, and the asymmetric ligand was never isolated. Isolation of small quantities of a related asymmetric ligand was reported in the synthesis of $\mathrm{[HB(3\text{-}neopentyl\text{-}pz)_3]}$, but it was obtained as a minor byproduct and was not investigated in detail.[15] In the present case the asymmetric tris(pyrazolyl)borate ligand is the major product and lends itself to more detailed studies, especially in comparison with its symmetrical counterpart. On heating above 220 °C, the lower-melting complexes Tp$^{\mathrm{Ms}*}$Tl, Tp$^{\mathrm{Ms}*}$ZnCl, and Tp$^{\mathrm{Ms}*}$ZnNCS rearranged to their higher-melting Tp$^{\mathrm{Ms}}$ analogs, but Tp$^{\mathrm{Ms}*}$ZnI and Tp$^{\mathrm{Ms}*}$ZnNCO gave no evidence for rearrangement. The rearrangement observed is exactly the opposite from what takes place in the rearrangement of the $\mathrm{HB(3\text{-}Pr^i\text{-}4\text{-}Xpz)_3}$ ligand (X = H or Br) to $\mathrm{[HB(3\text{-}Pr^i\text{-}4\text{-}Xpz)_2(5\text{-}Pr^i\text{-}4\text{-}Xpz)]}$ in $\mathrm{L_2M}$ complexes, where the more symmetrical ligand is transformed into the less symmetrical one. We may assume that Tp$^{\mathrm{Ms}*}$ is the kinetic product but Tp$^{\mathrm{Ms}}$ is the thermodynamically favored one.

Several other pairs of related complexes based on Tp$^{\mathrm{Ms}}$ and Tp$^{\mathrm{Ms}*}$ were synthesized. As expected, complexes derived from the less symmetrical ligand, Tp$^{\mathrm{Ms}*}$, were lower melting and had much higher solubility than those derived from Tp$^{\mathrm{Ms}}$. The only

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Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
				(A) Compound I					
Mo	8505.0(11)	2500	6055.6(7)	29.7(5)[a]	C(26)	7036(8)	3059(5)	5188(6)	44(3)
Mo′	2123.0(11)	2500	1510.6(7)	30.6(5)[a]	C(27)	7287(12)	2500	4829(8)	33(4)
N(1)	9548(7)	3295(4)	5620(4)	35(3)[a]	C(29)	7821(9)	3087(6)	6590(7)	50(3)
N(2)	10600(7)	3101(4)	5664(5)	39(4)[a]	C(1′)	3898(9)	3855(6)	1899(7)	50(3)
N(3)	10074(10)	2500	7089(6)	34(5)[a]	C(2′)	4830(10)	4053(7)	2515(8)	73(4)
N(4)	11049(10)	2500	6919(7)	52(6)[a]	C(3′)	5070(10)	3563(6)	3046(8)	66(4)
N(1′)	3583(7)	3264(4)	2035(4)	38(3)[a]	C(4′)	3370(9)	4261(5)	1191(7)	53(3)
N(2′)	4332(7)	3096(4)	2761(5)	40(3)[a]	C(5′)	2382(9)	4573(5)	1117(7)	50(3)
N(3′)	2153(9)	2500	2794(6)	32(5)[a]	C(6′)	1867(10)	4931(6)	451(7)	64(4)
N(4′)	3158(10)	2500	3381(6)	39(5)[a]	C(7′)	2299(11)	4959(6)	−150(8)	69(4)
O(1)	7355(7)	3400(4)	6921(5)	78(4)[a]	C(8′)	3323(10)	4675(6)	−79(7)	66(4)
O(1′)	83(7)	3391(4)	1059(4)	68(4)[a]	C(9′)	3866(9)	4331(6)	604(7)	55(3)
B(1)	11166(17)	2500	6082(10)	51(9)[a]	C(10′)	1896(11)	4656(6)	1787(7)	77(4)
B(1′)	4269(14)	2500	3211(10)	37(7)[a]	C(11′)	5008(11)	4053(7)	679(8)	89(5)
C(1)	9450(8)	3888(5)	5308(6)	38(3)	C(12′)	1740(13)	5318(8)	−910(9·)	118(6)
C(2)	10417(9)	4051(6)	5138(6)	52(3)	C(13′)	1351(12)	2500	3143(9)	39(4)
C(3)	11108(10)	3553(5)	5387(7)	54(3)	C(14′)	1878(14)	2500	3960(10)	59(5)
C(4)	8505(9)	4339(5)	5214(6)	42(3)	C(15′)	2971(13)	2500	4091(10)	49(4)
C(5)	8383(9)	4642(5)	5894(6)	50(3)	C(16′)	133(12)	2500	2756(8)	34(4)
C(6)	7541(10)	5092(6)	5804(7)	63(4)	C(17′)	−435(8)	3078(5)	2613(6)	39(3)
C(7)	6842(11)	5241(6)	5076(8)	66(4)	C(18′)	−1597(8)	3057(5)	2291(6)	43(3)
C(8)	6992(10)	4971(6)	4424(7)	62(4)	C(19′)	−2168(13)	2500	2130(9)	46(4)
C(9)	7812(9)	4526(5)	4460(6)	47(3)	C(22′)	155(9)	3700(5)	2831(7)	58(3)
C(10)	9253(10)	4526(6)	6688(7)	78(4)	C(24′)	−3412(12)	2500	1775(10)	71(6)
C(11)	7951(10)	4278(6)	3714(7)	65(4)	C(25′)	3702(13)	2500	403(10)	63(5)
C(12)	5939(12)	5741(8)	4997(9)	118(6)	C(26′)	1868(9)	3051(5)	335(6)	46(3)
C(13)	10330(15)	2500	7885(10)	56(5)	C(27′)	2486(12)	2500	354(8)	38(4)
C(14)	11478(20)	2500	8206(15)	109(8)	C(29′)	894(9)	3071(5)	1259(6)	43(3)
C(15)	11905(23)	2500	7571(14)	113(9)	C(43)	5437(33)	8141(19)	3193(21)	484(33)
C(16)	9557(12)	2500	8364(9)	44(4)	C(44)	4832(53)	7500	2665(34)	375(34)
C(17)	9259(10)	3060(6)	8628(7)	58(3)	C(46)	5273(30)	7500	3688(21)	205(15)
C(18)	8594(10)	3069(7)	9113(7)	73(4)	O(51)	6925(49)	5896(29)	2061(25)	1022(98)[a]
C(19)	8279(16)	2500	9330(11)	71(6)	C(51)	5858(27)	5633(17)	2148(21)	253(16))
C(22)	9691(11)	3684(6)	8457(8)	89(5)	C(52)	5365(26)	6288(17)	1641(21)	347(23)
C(24)	7550(20)	2500	9863(14)	166(12)	C(53)	4396(28)	6038(17)	1945(21)	392(25)
C(25)	7791(14)	2500	4170(10)	61(5)					
				(B) Compound II[a]					
Zn	−1780.6(5)	−1594.9(5)	5489.3(5)	44.7(3)	C(15)	−4033(5)	−2571()4)	6170(4)	45(3)
I	57.5(4)	132.1(4)	6958.8(4)	80.0(2)	C(16)	−3335(5)	−1668(4)	7232(4)	47(3)
B	−4144(5)	−3565(5)	3588(5)	44(3)	C(17)	−3291(6)	−564(5)	7242(5)	58(3)
N(1)	−2897(4)	−1431(3)	4045(3)	49(2)	C(18)	−2627(7)	272(5)	8245(5)	75(4)
N(2)	−3920(4)	−2435(3)	3292(3)	47(2)	C(19)	−2025(7)	62(6)	9214(5)	76(4)
N(3)	−3480(4)	−2566(3)	5523(3)	42(2)	C(20)	−2099(6)	−1027(6)	9180(5)	68(4)
N(4)	−4385(4)	−3436(3)	4576(3)	43(2)	C(21)	−2743(5)	−1900(5)	8211(4)	53(3)
N(5)	−1710(4)	−3054(3)	4796(3)	44(2)	C(22)	−3912(7)	−273(5)	6215(5)	77(4)
N(6)	−2878(4)	−3778(3))	3897(3)	42(2)	C(23)	−1341(8)	994(7)	10283(6)	122(6)
C(1)	−2967(6)	−591(5)	3602(5)	63(3)	C(24)	−2811(6)	−3082(5)	8235(5)	70(4)
C(2)	−4027(6)	−1037(5)	2575(5)	74(4)	C(25)	−2739(5)	−4672(4)	3452(4)	49(3)
C(3)	−4606(5)	−2207(5)	2381(4)	56(3)	C(26)	−1471(5)	−4537(4)	4059(4)	53(3)
C(4)	−5719(5)	−3133(5)	1408(5)	59(3)	C(27)	−852(5)	−3517(4)	4901(4)	45(3)
C(5)	−5457(6)	−3512(6)	575(5)	72(4)	C(28)	488(5)	−3021(4)	5844(4)	47(3)
C(6)	−6487(7)	−4407(7)	−349(5)	91(4)	C(29)	634(5)	−3090(4)	6861(5)	53(3)
C(7)	−7726(7)	−4929(7)	−447(6)	95(4)	C(30)	1901(5)	−2658(5)	7729(5)	56(3)
C(8)	−7951(6)	−4541(6)	379(6)	85(4)	C(31)	3013(5)	−2168(5)	7611(5)	57(3)
C(9)	−6974(6)	−3646(5)	1314(5)	65(3)	C(32)	2842(5)	−2137(5)	6597(5)	60(3)
C(10)	−4103(6)	−2981(7)	673(5)	96(5)	C(33)	1599(5)	−2563(4)	5694(4)	52(3)
C(11)	−8801(7)	−5905(8)	−1441(6)	142(6)	C(34)	−550(6)	−3615(6)	7039(5)	78(4)
C(12)	−7270(6)	−3256(6)	2203(6)	86(4)	C(35)	4370(6)	−1691(6)	8574(5)	89(4)
C(13)	−5472(5)	−3977(4)	4665(5)	51(3)	C(36)	1485(6)	−2526(5)	4598(5)	73(4)
C(14)	−5304(5)	−3460(4)	5650(5)	56(3)					

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

exception was the pair Tp^{Ms}CdCl/Tp^{Ms*}CdCl, where Tp^{Ms*}CdCl was the higher-melting compound. The BH stretch was typically 2470 cm^{-1} for Tp^{Ms}ZnX complexes (as well as for the Tp^{Ms}CoNCO complex) and 2514 cm^{-1} for their Tp^{Ms*}ZnX analogs. A shift to lower frequencies occurred upon going to the heavier Cd(II) analogs, Tp^{Ms}CdCl and Tp^{Ms*}CdCl (2458 and 2497 cm^{-1}, respectively).

The ^{1}H NMR spectra of the tetrahedral derivatives L*ZnX (L* = Tp^{Ms} or Tp^{Ms*}; X = Cl, I, NCS, NCO) reflected their inherent symmetries. All 3-mesitylpyrazol-1-yl groups were identical in Tp^{Ms}ZnX complexes, while in their Tp^{Ms}ZnX analogs, they appeared as 2:1 patterns, except in Tp^{Ms*}ZnI and Tp^{Ms*}ZnNCS, as mentioned above. The scarcity of the expected 1:1:1 patterns for the 2′,6′-methyls and for the 3′,5′-hydrogens has to be explained in terms of an accidentally very small difference in the chemical shifts between the "inner" and "outer" 2′,6′-methyls and the 3′,5′-hydrogens. A full rotation of the mesityl groups, which would also give the same result, appears unlikely. A surprising feature appeared in the NMR spectra of Tp^{Ms}CdCl and Tp^{Ms*}CdCl. While the former was essentially identical to that of Tp^{Ms}ZnCl, the latter differed from that of Tp^{Ms*}ZnCl by having only a single peak for the pyrazolyl 3(5)-hydrogens (the other peaks appearing as the usual 2:1 patterns).

The reaction of Tp^{Ms}Tl with (MeCN)$_2$Mo(CO)$_2$(Cl)(π-

Table III. Selected Bond Distances and Bond Angles

(A) $Mo(CO_2)[\eta^3\text{-}CH_2C(CH_3)CH_2][(3\text{-mesityl-pz})_3BH]$ (I)

	I	I′
Bond Distances (Å)		
Mo–N(1)	2.414(9)	2.408(8)
Mo–N(3)	2.242(10)	2.279(12)
Mo–C(29)	1.932(11)	1.909(11)
Mo–C(26)	2.329(13)	2.330(11)
Mo–C(27)	2.241(12)	2.256(17)
C(25)–C(27)	1.509(26)	1.519(23)
C(26)–C(27)	1.425(14)	1.397(14)
Bond Angles (deg)		
Mo–C(29)–O(1)	174.4(11)	174.7(8)
Mo–C(27)–C(25)	115.4(9)	116.7(9)
Mo–C(27)–C(26)	75.2(6)	75.2(8)
Mo–C(26)–C(27)	68.5(6)	69.4(8)
C(25)–C(27)–C(26)	124.2(7)	123.7(7)
C(26)–C(27)–C(26A)	111.6(14)	112.6(14)
N(1)–Mo–N(3)	80.2(3)	81.1(3)
N(1)–Mo–N(1A)	87.9(4)	83.9(4)
C(29)–Mo–C(29A)	79.7(8)	78.2(7)
N(1)–Mo–C(26))	80.8(3)	83.4(3)
N(1)–Mo–C(27)	87.9(3)	89.9(3)
N(1)–Mo–C(26A)	122.9(3)	123.5(4)
N(3)–Mo–C(26)	149.3(3)	149.2(3)
N(3)–Mo–C(27)	163.4(5)	167.9(4)
N(3)–Mo–C(26A)	149.3(5)	149.2(3)
N(1)–Mo–C(29)	95.4(4)	98.1(4)
N(1)–Mo–C(29A)	169.9(4)	169.7(4)
N(3)–Mo–C(29)	90.0(4)	89.2(4)

(B) $ZnI[(3\text{-mesityl-pz})_2(5\text{-mesityl-pz})]BH$ (II)

Bond Distances (Å)			
Zn–I	2.465(1)	Zn–N(1)	2.031(4)
Zn–N(3)	2.056(4)	Zn–N(5)	2.054(5)
Bond Angles (deg)			
I–Zn–N(1)	119.6(1)	I–Zn–N(3)	124.5(1)
I–Zn–N(5)	128.0(1)	N(1)–Zn–N(3)	89.3(2)
N(1)–Zn–N(5)	94.1(2)	N(3)–Zn–N(5)	91.1(2)

Table IV. Dihedral Plane Calculations of the Rings in the Pyrazolylborate Ligand and Their Corresponding Mesityl Rings

	I	I′
N(1)–N(2)–C(1)–C(2)–C(3)/ C(4)–C(5)–C(6)–C(7)–C(8)–C(9)	72.8	76.7
N(3)–N(4)–C(13)–C(14)–C(14)/ C(16)–C(17)–C(18)–C(19)–C(17A)–C(18A)	90.0	90.0

	II
N(1)–N(2)–C(1)–C(2)–C(3)/ C(4)–C(5)–C(6)–C(7)–C(8)–C(9)	79.8
N(3)–N(4)–C(13)–C(14)–C(15)/ C(16)–C(17)–C(18)–C(19)–C(20)–C(21)	102.8
N(5)–N(6)–C(25)–C(26)–C(27)/ C(28)–C(29)–C(30)–C(31)–C(32)–C(33)	121.8

methallyl) produced the yellow compound $Tp^{Ms}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ in good yield. In its ^1H NMR, the ligand pyrazolyl groups were in a clean 2:1 pattern, as in the case of simple Tp and Tp* analogs, and there was no evidence of rotation around the B–Mo axis at room temperature. By contrast, the ^1H NMR spectrum of the analogous $Tp^{Ms*}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ was rather complicated and suggestive of more than one isomer being present, presumably as rotamers around the B–Mo axis differing in the disposition of mesityl rings with respect to the π-methallyl group, plus possible rotamers of the π-methylallyl group itself.

The Rh(I) complex $Tp^{Ms}Rh(COD)$ was readily obtained by the reaction of $Tp^{Ms}Tl$ with $[RhCl(COD)]_2$. It was a stable yellow solid, the NMR of which had the 3-mesitylpyrazolyl signals in a 2:1 pattern, and the COD protons appeared as three distinct peaks, indicative of the presence of a plane of symmetry in the molecule. Conversely, in the $Tp^{Ms*}Rh(COD)$ complex the pyrazole 4- and 5-hydrogens appeared as three peaks, in roughly 1:2:2 ratio. There were four peaks for the phenyl 3,5-hydrogens and five different methyl groups. The COD proton peak patterns present in $Tp^{Ms}Rh(COD)$ were now split up into three, or more, components, which was indicative of lack of a plane of symmetry.

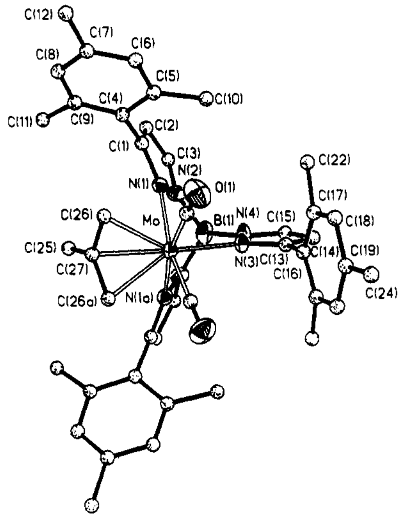

Figure 1. Molecular structure and labeling scheme for $Mo(CO)_2[\eta^3\text{-}CH_2C(CH_3)CH_2][(3\text{-mesityl-pz})_3BH]$ (I). Ellipsoids are drawn at 35% probability. Hydrogen atoms are omitted for clarity.

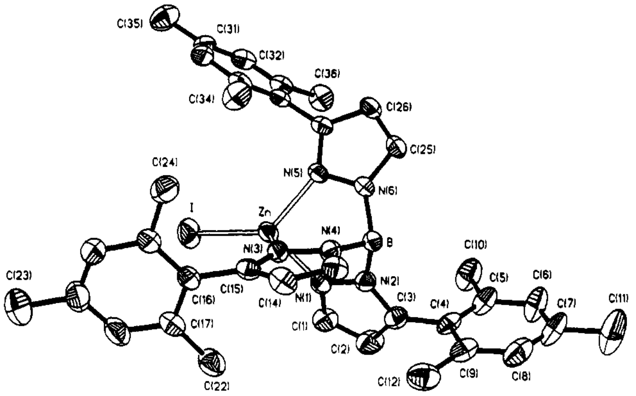

Figure 2. Molecular structure and labeling scheme for $ZnI[(3\text{-mesityl-pz})_2(5\text{-mesityl-pz})]BH$ (II). Ellipsoids are drawn at 35% probability. Hydrogen atoms are omitted for clarity.

Similar differences were also encountered in the ^1H NMR spectra of $Tp^{Ms}Rh(CO)_2$ and $Tp^{Ms*}Rh(CO)_2$, although the latter spectrum did indicate C_s symmetry, unlike that of $Tp^{Ms*}Rh(COD)$. $Tp^{Ms}Rh(CO)_2$ had all three mesitylpyrazol-1-yl groups equivalent at room temperature, with sharp single peaks for the pyrazole 4- and 5-hydrogens, as well as for the 3′,5′-hydrogens and for the 2′,6′- and 4′- methyl groups. Assuming a square planar structure for $Tp^{Ms}Rh(CO)_2$, these findings would be consistent with exchange of the three 3-Mspz coordinating groups and rotation of the $Rh(CO)_2$ fragment around the B–Rh axis. In the case of $Tp^{Ms*}Rh(CO)_2$, all the peaks present in $Tp^{Ms}Rh(CO)_2$ were split into 2:1 patterns, with the surprising exception of that of the pyrazole 4-H, which remained a single peak.

The Pd(II) derivative $Tp^{Ms}Pd(\eta^3\text{-}CH_2CMeCH_2)$, just like $Tp^{Ms}Rh(CO)_2$, showed dynamic C_{3v} symmetry, in having all three mesitylpyrazolyl groups identical. Since the complex is most likely square planar, we are dealing here with two dynamic processes, similar to those in $Tp^{Ms}Rh(CO)_2$: exchange of the coordinated and uncoordinated mesitylpyrazolyl groups, accompanied by rotation of the $(\eta^3\text{-}CH_2CMeCH_2)$ group around the B–Pd axis. The same exchange process is taking place in $Tp^{Ms*}Pd(\eta^3\text{-}CH_2CMeCH_2)$, and the signals observed fall into typical 2:1 patterns, corresponding to the 3-mesityl- and 5-mesitylpyrazolyl rings.

The structure of $Tp^{Ms}Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$ was determined by X-ray crystallography. The molecule has a plane of symmetry, bisecting the π-methallyl group, with the mesityl groups being all in the 3-position. This is consistent with the NMR spectrum, indicative of the molecule being stereochemically rigid at room temperature. However, all the mesityl groups are not quite orthogonal to the pyrazolyl plane: those adjacent to the η^3-$\mathrm{CH_2CMeCH_2}$ ligand are twisted away from orthogonality by about 13.3 and 17.2°, respectively (these values represent the crystallographically distinct molecules in the unit cell), in the direction which moves the mesityl 2-Me group away from the η^3-$\mathrm{CH_2CMeCH_2}$ group. The third mesityl group, flanked by the sterically unassuming carbonyls, is exactly orthogonal. Steric repulsions for the rings flanking the η^3-$\mathrm{CH_2CMeCH_2}$ group are also suggested by the longer Mo–N bond lengths, as compared with those in the ring trans to it (average of 2.41 Å versus 2.26 Å). In the related complex $\mathrm{TpMo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)}$, all the Mo–N bonds are shorter, although the distinction between the adjacent and trans pz groups remains (average 2.30 Å for the former versus 2.21 Å for the latter).[16]

The other structural study, that of $\mathrm{Tp^{Ms*}ZnI}$, confirmed the presence of one mesityl group per ligand in the 5-position. The deviations of the mesityl groups from orthogonality were 10.2, 12.8, and 31.8°, the lowest value again being obtained for the 5-mesityl group. This tetrahedral molecule exhibits only small differences in the Zn–N bond lengths: 2.03, 2.05, and 2.06 Å, with the shortest distance associated with the pyrazolyl ring containing the 5-mesityl group. These distances are typical for tetrahedral $\mathrm{HB(pz^*)_3ZnX}$ complexes, such as $\mathrm{HB(3\text{-}Bu^t\text{-}pz)_3ZnCN}$, $\mathrm{HB(3\text{-}Bu^tpz)_3ZnI}$,[17] $\mathrm{HB(3\text{-}Bu^t\text{-}5\text{-}Mepz)_3ZnOH}$,[18] $\mathrm{HB(3\text{-}Phpz)_3ZnX}$,[19] and $\mathrm{HB(3\text{-}Bu^t\text{-}3\text{-}Mepz)_3ZnX}$.[20]

Conclusions

The new ligands $\mathrm{Tp^{Ms}}$ and $\mathrm{Tp^{Ms*}}$ represent the first examples of a tris(pyrazolyl)borate where the 3-aromatic substituent is permanently twisted at a large angle, at times aproaching orthogonality, with respect to the pyrazolyl plane. This creates a differently shaped pocket around the coordinated metal, compared with hitherto known $\mathrm{HB(3\text{-}aryl\text{-}pz)_3}$ ligands.

A further first is the facile isolation of an asymmetrically substituted tris(pyrazolyl)borate ligand, $\mathrm{Tp^{Ms*}}$, which complements the $\mathrm{Tp^{Ms}}$ ligand, by screening two-thirds of the access to the coordinated metal just as $\mathrm{Tp^{Ms}}$ does but leaving a specifically-shaped entry sector for other coordinating ligands or reactants. The noncompactness of the $\mathrm{Tp^{Ms*}}$ ligand is relieved in some complexes by thermal rearrangement to the more symmetrical (C_{3v}) $\mathrm{Tp^{Ms}}$ ligand.

Supplementary Material Available: Tables of structure determination parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for I and II (15 pages). Ordering information is given on any current masthead page.

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