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Indium(III) Complexes of Potentially Tridentate Poly(pyrazolyl)borate Ligands. Ionization of Molecular $[HB(pz)_3]_2InCl$ in CD_2Cl_2 Solution

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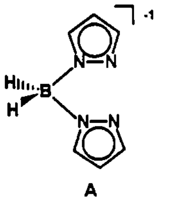
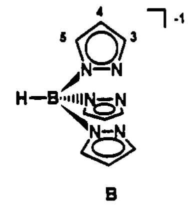
The reaction of 3 equiv of $[B(pz)_4]^-$ with $InCl_3$ in either THF or THF/H_2O results in the formation of $[B(pz)_4]_3In$. The reaction of 2 equiv of $[B(pz)_4]^-$ with $InCl_3$ in THF results in the formation of $[B(pz)_4]_2InCl$. Variable-temperature NMR studies indicate that the latter complex has an octahedral structure with one bidentate and one tridentate ligand. An analogous reaction using $InCH_3Cl_2$ yields $[B(pz)_4]_2InCH_3$, a complex shown crystallographically to have an octahedral structure with one bidentate and one tridentate ligand. The reaction of $[B(pz)_4]^-$ with $In(CH_3)_2Cl$ yields $[B(pz)_4]In(CH_3)_2$, a complex believed to have a four-coordinate structure. The six-coordinate complexes $[HB(pz)_3]InCl_2{\cdot}THF$ and $[HB(pz)_3]_2InCl$ form in the reaction with $InCl_3$ of 1 and 2 equiv of $[HB(pz)_3]^-$, respectively. Low-temperature NMR studies in the nonpolar solvent toluene-d_8 indicate that $[HB(pz)_3]_2InCl$ has a six-coordinate structure with one bidentate and one tridentate ligand. In CD_2Cl_2, the chloride ligand ionizes yielding a solution of the ionic compound $\{[HB(pz)_3]_2In\}Cl$. Dissolving $[HB(pz)_3]_2InCl$ in $CDCl_3$ or a 1/1 mixture of CD_2Cl_2/toluene-d_8 yields solutions containing both the ionic and covalent forms. The cation $\{[HB(pz)_3]_2In\}^+$ can also be prepared from a number of other routes, including the reaction of 1 equiv of $[HB(pz)_3]^-$ and $InCl_3$ in a THF/H_2O solvent system to yield $\{[HB(pz)_3]_2In\}\{InCl_4\}$. The reaction of 3 equiv of $[HB(pz)_3]^-$ with 2 equiv of $InCl_3$ in a mixed THF/H_2O solvent system yields $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}$, as characterized by X-ray crystallography. The reaction of $In(CH_3)Cl_2$ with 2 equiv of $[HB(pz)_3]^-$ leads to the formation of $[HB(pz)_3]_2InCH_3$, another example of a complex believed to have a six-coordinate structure. The reaction of either 1 or 2 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCl_3$ in THF leads to the isolation of $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}H(3,5\text{-}Me_2pz)$ forms in similar reactions in toluene or in THF in the presence of added $H(3,5\text{-}Me_2pz)$. The reaction of either 1 or 2 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCH_3Cl_2$ yields $[HB(3,5\text{-}Me_2pz)_3]In(Cl)(CH_3)$, a complex believed to be four coordinate. Crystal data: $[B(pz)_4]_2InCH_3{\cdot}2tol$ (tol = toluene), triclinic, $P\bar{1}$, $a = 8.637(4)$ Å, $b = 12.549(6)$ Å, $c = 18.815(10)$ Å, $\alpha = 104.45(4)°$, $\beta = 96.94(4)°$, $\gamma = 98.09(4)°$, $V = 1929.1(16)$ Å^3, $Z = 2$, $T = 243$ K, $R(F) = 10.46\%$; $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}{\cdot}THF{\cdot}CH_2Cl_2$, orthorhombic, *Pbca*, $a = 18.688(8)$ Å, $b = 16.584(5)$ Å, $c = 29.640(12)$ Å, $V = 9183.8(6)$ Å^3, $Z = 8$, $T = 238$ K, $R(F) = 5.99\%$.

Introduction

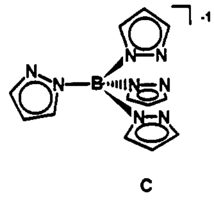
We have undertaken an investigation into the coordination and organometallic chemistry of the post-transition metals using the unique properties of the poly(pyrazolyl)borate ligand system.[1] These ligands are extremely versatile because the number of donor atoms in each ligand can be varied from two to three in going from the bidentate ligands A to the potentially tridentate ligands B and C, and the substituents on the pyrazolyl rings can be changed. As shown in our recent studies with complexes of tin(II) and lead(II), varying the fourth boron substituent from hydrogen (**B**) to a pyrazolyl ring (**C**) can also change the coordination mode of the ligand.[2]


A

$[H_2B(pz)_2]^-$


B

$[HB(pz)_3]^-$


C

$[B(pz)_4]^-$

Our initial synthetic efforts with the group 13 metals gallium(III)[3] and indium(III)[4] used the dihydrobis(pyrazolyl)borate ligand, A. Two series of compounds with the general formula $[H_2B(pz)_2]_mMCl_n(CH_3)_p$ ($m + n + p = 3$; M = Ga, In; pz = pyrazolyl ring) have been prepared. These investigations clearly demonstrated that the poly(pyrazolyl)borate ligands form extremely stable, monomeric complexes with these post-transition metals.

The chemistry of gallium(III) has been studied with the potentially tridentate ligands B and C.[5,6] The reaction of these ligands with $GaCl_3$ yields the cationic complexes $\{[\text{ligand}]_2Ga\}^+$. Starting with $GaCl_x(CH_3)_y$ ($x + y = 3$), a series of complexes of the general formula $[\text{ligand}]_mMCl_n(CH_3)_p$ ($m + n + p = 3$) have been prepared. An important feature of this chemistry is

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the tendency for gallium to prefer either four- or six-coordination. Thus, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ is four-coordinate with a bidentate hydrotris(pyrazolyl)borate ligand and $[B(pz)_4]_2GaCH_3$ is six-coordinate containing both a tridentate and bidentate tetrakis(pyrazolyl)borate ligand.

The synthesis and characterization of a series of indium complexes containing the ligands $[HB(pz)_3]^-$, $[HB(3,5\text{-}Me_2pz)_3]^-$, or $[B(pz)_4]^-$ are reported here. The solid-state structures of $[B(pz)_4]_2In(CH_3)\cdot 2tol$ (tol = toluene) and $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}\cdot THF\cdot CH_2Cl_2$ have been determined crystallographically and the solution-state structures of several of these new complexes studied by variable-temperature NMR. An unusual case of a molecular complex, $[HB(pz)_3]_2InCl$, undergoing ionization of a chloride ligand to form an ionic compound when dissolved in CD_2Cl_2 is also reported.

Experimental Section

General Procedure. All solvents were dried, degassed, and distilled prior to use. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. $K[HB(pz)_3]$,[7a] $K[HB(3,5\text{-}Me_2pz)_3]$[7b] (pz* is used as an abbreviation for $3,5\text{-}Me_2pz$), and $K[B(pz)_4]$[7a] were prepared according to published methods. The preparation of $InCl_2CH_3$ and $InCl(CH_3)_2$ (in situ) were carried out following the published methods.[4] Anhydrous $InCl_3$ was purchased from Cerac Inc. and Strem. MeLi (in diethyl ether) was purchased from Aldrich. Both reagents were used without further purification. Elemental analyses were performed by Robertson Laboratory, Inc. Molecular weights were determined by freezing point depression measurements as described elsewhere.[8]

Tris[tetrakis(1-pyrazolyl)borato]indium(III) $\{[B(pz)_4]_3In\}$. $InCl_3$ (0.25 g, 1.1 mmol) and $K[B(pz)_4]$ (1.08 g, 3.39 mmol) were charged into a flask. THF (40 mL) was added via syringe and the mixture stirred for 5 h at room temperature. The THF was removed under vacuum. Benzene (40 mL) was added to the residue and the solution filtered. The benzene was removed under vacuum to reveal a white solid (0.94 g, 0.98 mmol, 87%), dec 315–320 °C. ^1H NMR ($CDCl_3$): δ 7.67, 7.15, 6.64, 6.27 (all 6; all d; $J = 2$ Hz; 3,5-H pz); 6.16, 6.09 (6, 6; t, t; $J = 2.3$ Hz; 4-H pz). Mass spectrum: m/z 955 ($M^+ + 3H$), 673 ($M^+ - B(pz)_4$). Anal. Calcd for $C_{36}H_{36}N_{24}B_3In$: C, 45.35; H, 3.81. Found: C, 45.20; H, 3.54.

Bis[tetrakis(1-pyrazolyl)borato]chloroindium(III) $\{[B(pz)_4]_2InCl\}$. $InCl_3$ (0.25 g, 1.1 mmol) and $K[B(pz)_4]$ (0.72 g, 2.3 mmol) were charged into a flask. THF (40 mL) was added via syringe. The mixture was stirred at room temperature for 4 h. The THF was evaporated under vacuum. The product was then extracted with benzene (40 mL) and filtered. The benzene was removed under vacuum to reveal a white solid (0.60 g, 0.85 mmol, 75%), mp 254–257 °C. ^1H NMR ($CDCl_3$, ambient temperature): δ 7.7, 7.4 (8, 8; br; 3,5-H pz); 6.3 (8; br; 4-H pz). ^1H NMR (CD_2Cl_2, −79 °C): δ 8.06, 7.99, 7.55, 7.25 (all 2; all d; $J = 2$ Hz; 3,5-H pz); 8.04, 7.95, 7.80, 7.63, 6.99, 6.74, 6.49, 6.29 (all 1; all d, $J = 2$ Hz; 3,5-H pz); 6.41, 6.37 (2, 2; t, t; $J = 2$ Hz; 4-H pz); 6.64, 6.27, 6.27, 5.92 (all 1; all t; $J = 2$ Hz; 4-H pz). Mass spectrum: m/z 707 ($M^+ - H$), 673 ($M^+ - Cl$). Cryoscopic molecular weight, benzene solution, formula weight 708 (observed molality, observed molecular weight): 0.0253, 718; 0.0487, 729.

Bis[tetrakis(1-pyrazolyl)borato]methylindium(III) $\{[B(pz)_4]_2InCH_3\}$. Method A. $InCl_2CH_3$ (0.50 g, 2.5 mmol) and $K[B(pz)_4]$ (1.59 g, 5.00 mmol) were charged into a flask. THF (40 mL) was added via syringe, and the mixture was stirred overnight. The THF was removed under vacuum. The product was extracted with benzene (40 mL) and filtered. The benzene was removed under vacuum to reveal a white solid. Colorless crystals were grown from toluene at −20 °C (0.57 g, 0.83 mmol, 33%).

Method B. $[B(pz)_4]_2InCl$ (0.20 g, 0.28 mmol) was charged into a flask along with Et_2O (25 mL) and the resulting solution cooled to −78 °C. MeLi (0.20 mL, 1.4 M, 0.28 mmol) was added via syringe and the solution allowed to warm to room temperature (1 h). The solution was stirred at room temperature for 3 h and the Et_2O evaporated under vacuum. The product was extracted with benzene (35 mL). The solution was filtered, and the solvent was removed under vacuum to leave a white solid. This solid was recrystallized from toluene at −20 °C. The resulting solid was dried under vacuum and contained 0.5 equiv of toluene (0.11 g, 0.16 mmol, 58%), mp 132–135 °C. ^1H NMR ($CDCl_3$): δ 7.52, 7.35 (8, 8; d, d; $J = 1.5$ Hz, 2.2 Hz; 3,5-H pz); 6.25 (8; t; $J = 2.2$ Hz; 4-H pz); −0.72 (3; s; CH_3). ^{13}C NMR ($CDCl_3$): δ 141.8, 136.2 (3,5-C pz); 106.2 (4-C pz); −3.10 (broad, CH_3). Mass spectrum: m/z 673 ($M^+ - CH_3$). Anal. Calcd for $C_{25}H_{27}N_{16}B_2In\cdot {}^1/_2C_7H_8$: C, 46.56; H, 4.25; N, 30.05. Found: C, 46.96; H, 4.05; N, 30.10.

Dimethyl[tetrakis(1-pyrazolyl)borato]indium(III) $\{[B(pz)_4]In(CH_3)_2\}$. $In(CH_3)_2Cl$ (0.41 g, 2.3 mmol) and $K[B(pz)_4]$ (0.72 g, 2.3 mmol) were charged into a flask along with 25 mL of THF, and the solution was stirred for 5 h. The THF was removed under vacuum. The product was then extracted with hexane (2 × 25 mL) and filtered. The hexane was evaporated under vacuum to reveal a white solid (0.56 g, 1.3 mmol, 59%), mp 86–88 °C. ^1H NMR (CD_3COCD_3): δ 7.82, 6.92 (4, 4; br, br; 3,5-H pz); 6.33 (4; br; 4-H pz); −0.33 (6; s, CH_3). Mass spectrum: m/z 409 ($M^+ - CH_3$), 394 ($M^+ - 2CH_3$).

[Hydrotris(1-pyrazolyl)borato]dichloro(tetrahydrofuran)indium(III) $\{[HB(pz)_3]InCl_2\cdot THF\}$. $InCl_3$ (0.44 g, 2.0 mmol) and $K[HB(pz)_3]$ (0.50 g, 2.0 mmol) were charged into a flask. THF (30 mL) was added via syringe and the mixture stirred for 4 h. The THF was evaporated under vacuum and benzene (30 mL) added to extract the product. The solution was filtered and the benzene evaporated under vacuum to reveal a white solid (0.10 g, 0.22 mmol, 11%), mp 155–158 °C. ^1H NMR ($CDCl_3$): δ 7.96, 7.62 (3, 3; s, s; 3,5-H pz); 6.19 (3; s, 4-H pz); 3.83, 1.88 (4, 4; m, m; THF). Mass spectrum: m/z 397 ($M^+ - H$, THF), 363 ($M^+ - Cl$, THF).

Bis[hydrotris(1-pyrazolyl)borato]chloroindium(III) $\{[HB(pz)_3]_2InCl\}$. $InCl_3$ (0.33 g, 1.5 mmol) and $K[HB(pz)_3]$ (0.75 g, 3.0 mmol) were charged into a round-bottomed flask. THF (40 mL) was added via syringe and the mixture stirred at room temperature for 5 h. The THF was evaporated under vacuum. The residue was extracted with benzene (35 mL) and filtered. The benzene was removed under vacuum to yield a white solid (0.95 g, 1.3 mmol, 84%), mp 199–203 °C. ^1H NMR (C_6D_6, ambient temperature): δ 7.48, 7.15 (6, 6; br, br; 3,5-H pz); 5.77 (6; br; 4-H pz). ^1H NMR (C_7D_8, −68 °C): δ 8.10, 7.79, 7.67, 7.62, 7.00, 6.84, 6.71, 6.31 (1, 1, 2, 2, 2, 1, 2, 1; all d; 3,5-H pz); 5.61, 5.59, 5.30 (3, 2, 1; all t; 4-H pz); 4.4 (2; br; BH pz). Mass spectrum: m/z 575 ($M^+ - H$), 540 ($M^+ - HCl$). Anal. Calcd for $C_{18}H_{20}N_{12}B_2ClIn$: C, 37.47; H, 3.49. Found: C, 37.38; H, 3.37.

{Bis[hydrotris(1-pyrazolyl)borato]indium(III)}tetrachloroindate $\{[HB(pz)_3]_2In\}InCl_4$. $InCl_3$ (0.22 g, 1.0 mmol) was dissolved in H_2O (50 mL) and $K[HB(pz)_3]$ (0.25 g, 1.0 mmol) in THF (50 mL). The two solutions were shaken together in a separatory funnel, and the product was extracted with CH_2Cl_2 (2 × 25 mL). The CH_2Cl_2 layer was separated and the solvent removed to leave a white solid. This solid was washed twice with benzene (10 mL) and dried in vacuo to yield the title salt containing 1.5 equiv of THF of crystallization (0.36 g, 0.45 mmol, 90%), mp 216–220 °C. ^1H NMR ($CDCl_3$): δ 8.11, 7.41 (6, 6; d, d; $J = 2.2$ Hz; 3,5-H pz); 6.46 (6; t; $J = 2.3$ Hz; 4-H pz); 4.8 (2; br; BH pz), 3.82, 1.87 (6, 6: m, m; THF). FAB mass spectrum: m/z 541 ($\{[HB(pz)_3]_2In\}^+$). Anal. Calcd for $C_{18}H_{20}N_{12}B_2Cl_4In_2\cdot 3/2C_4H_8O$ (confirmed by ^1H NMR): C, 31.82; H, 3.56. Found: C, 32.03; H, 3.40.

Bis[hydrotris(1-pyrazolyl)borato]indium(III) [Hydrotris(1-pyrazolyl)borato]trichloroindate ($\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}$). $InCl_3$ (0.25 g, 1.1 mmol) was dissolved in H_2O (50 mL) and $K[HB(pz)_3]$ (0.40 g, 1.6 mmol) in THF (50 mL). The two solutions were shaken together in a separatory funnel, and the product was extracted with CH_2Cl_2 (2 × 25 mL). The CH_2Cl_2 layer was separated and the solvent removed to leave a white solid of the title salt containing 1 equiv of THF of crystallization (0.55 g, 0.53 mmol, 93%), dec 89–93 °C. ^1H NMR (CD_2Cl_2, ambient temperature): δ 7.99, 7.54, 7.42 (6, 3, 9; all br; 3,5-H pz); 6.40, 6.06 (6, 3; br, br; 4-H pz). ^1H NMR (CD_2Cl_2, −80 °C): δ 8.00, 7.50, 7.40, 7.33 (6, 3, 6, 3; all s; 3,5-H pz); 6.36, 6.06 (6, 3; s, s; 4-H pz); 4.8 (3; br; BH pz), 3.69, 1.82 (4, 4; m, m; THF). FAB mass spectrum: m/z 541 ($\{[HB(pz)_3]_2In\}^+$).

Bis[hydrotris(1-pyrazolyl)borato]methylindium(III) $\{[HB(pz)_3]_2InCH_3\}$. Method A. $InCl_2CH_3$ (0.46 g, 2.3 mmol) and $K[HB(pz)_3]$ (1.14 g, 4.52 mmol) were charged into a flask along with THF (25 mL), and the mixture was stirred at room temperature for 4 h. The THF was evaporated under vacuum and benzene (30 mL) added to extract the product. The solvent was then evaporated under vacuum to yield a white solid (0.57 g, 1.0 mmol, 45%).

Method B. $[HB(pz)_3]_2InCl$ (0.50 g, 0.87 mmol) was charged into a flask along with Et_2O (25 mL) and the resulting solution cooled to −78 °C. MeLi (0.62 mL, 1.4 M, 0.87 mmol) was added via syringe and the solution allowed to warm to room temperature (1 h). The solution was

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stirred at room temperature for 3 h and the Et_2O evaporated under vacuum. The product was extracted with benzene (35 mL). The solution was filtered, and the solvent was removed under vacuum to leave a white solid. This solid was recrystallized from toluene at -20 °C (0.25 g, 0.45 mmol, 52%), mp 203-205 °C. ^1H NMR ($CDCl_3$): δ 7.62, 7.24 (6, 6; br, br, 3,5-H pz); 6.14 (6; br; 4-H pz); -0.18 (3; br; CH_3). ^1H NMR (C_7D_8, -80 °C): δ 8.17, 7.94, 7.89, 7.29, 7.13, 7.03, 6.82, 6.35 (1, 1, 2, 2, 2, 1, 2, 1; 3,5-H pz); 5.72, 5.69, 5.67, 5.27 (2, 1, 2, 1; 4-H pz); 0.72 (3; CH_3). Mass spectrum: *m/z* 555 ($M^+ - H$), 541 ($M^+ - CH_3$). Anal. Calcd for $C_{19}H_{23}N_{12}B_2In$: C, 41.00; H, 4.17. Found: C, 40.93; H, 4.22. Cryoscopic molecular weight, benzene solution, formula weight 556 (observed molality, observed molecular weight): 0.0266, 557; 0.0356, 532.

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloroindium(III) {[HB(3,5-Me_2pz)$_3$]$InCl_2$·THF}. $InCl_3$ (0.22 g, 1.0 mmol) and K[HB(3,5-Me_2pz)$_3$] (0.34 g, 1.0 mmol) were charged into a flask. THF (25 mL) was added via syringe and the solution stirred overnight. The THF was removed under vacuum and the product extracted with benzene (25 mL). The solution was filtered and the solvent removed under vacuum to yield a white solid (0.34 g, 0.62 mmol, 62%), dec 53-54 °C. ^1H NMR ($CDCl_3$): δ 5.77 (3; s, 4-H pz*); 4.01, 1.97 (4, 4; m, m; THF); 2.50, 2.34 (9, 9; s, s; 3,5-Me pz*). Mass spectrum: *m/z* 481 ($M^+ - H$, THF); 447 ($M^+ -$ Cl, THF); 387 ($M^+ -$ pz*, THF).

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloroindium(III) {[HB(3,5-Me_2pz)$_3$]$InCl_2$·H(3,5-Me_2pz)}. $InCl_3$ (0.22 g, 1.0 mmol), K[HB(3,5-Me_2pz)$_3$] (0.34 g, 1.0 mmol), and H(3,5-Me_2pz) (0.096 g, 1.0 mmol) were charged into a flask. Et_2O (35 mL) was added via syringe and the solution stirred overnight. The Et_2O was removed under vacuum and the product extracted with benzene (30 mL). The solution was filtered and the solvent removed under vacuum to yield a white solid (0.51 g, 0.88 mmol, 88%), dec 187-195 °C. ^1H NMR ($CDCl_3$): δ 11.0 (1; s; Hpz*); 5.85, 5.78, 5.73 (1, 1, 2; all s; 4-H pz*): 2.69, 2.36, 2.34, 2.02, 1.38 (3, 6, 6, 6, 3; all s; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 151.8, 150.9, 150.2, 145.2, 145.0, 142.1 (1, 2, 1, 2, 1, 1; 3,5-C pz*); 107.1, 107.0, 106.4 (1, 2, 1; 4-C pz*); 14.0, 13.4, 13.2, 13.1, 11.7, 11.6 (1, 2, 2, 1, 1, 1; 3, 5-Me pz*). Mass spectrum: *m/z* 481 ($M^+ - H$, Hpz*); 447 ($M^+ -$ Cl, Hpz*); 387 ($M^+ -$ pz*, Hpz*). Anal. Calcd for $C_{20}H_{30}N_8BCl_2In$: C, 41.48; H, 5.23. Found: C, 41.97; H, 5.18.

[Hydrotris(3,5-dimethylpyrazolyl)borato]chloromethylindium(III) {[HB(3,5-Me_2pz)$_3$]In(Cl)(CH_3)}. Method A. $InCl_2CH_3$ (0.20 g, 1.0 mmol) and K[HB(3,5-Me_2pz)$_3$] (0.34 g, 1.0 mmol) were charged into a flask. THF (25 mL) was added via syringe and the solution stirred for 4 h. The THF was removed under vacuum and the product extracted with benzene (25 mL). The solution was filtered and the solvent removed under vacuum to yield a white solid. This solid was recrystallized in toluene at -20 °C.

Method B. [HB(3,5-Me_2pz)$_3$]$InCl_2$·THF (0.27 g; 0.50 mmol) was charged into a flask along with THF (25 mL) and the solution cooled to -78 °C. MeLi (0.35 mL; 0.50 mmol) was added via syringe and the resulting solution allowed to warm to room temperature (1 h). The solution was stirred an additional 3 h and the solvent removed under vacuum. The product was extracted with benzene (25 mL) and filtered, and the benzene was removed under vacuum to leave a white solid (0.17 g, 0.37 mmol; 74%), mp 249-251 °C. ^1H NMR ($CDCl_3$, ambient temperature): δ 5.78 (3; s, 4-H pz*); 2.37, 2.35 (9, 9; s, s; 3,5-Me pz*); 0.75 (3; s; CH_3). ^1H NMR (CD_2Cl_2, -85 °C): δ 5.91, 5.70 (2, 1; s; 4-H pz*); 4.5 (1; br; BH pz*); 2.38, 2.36, 2.25, 2.13 (6, 6, 3, 3; all s; 3,5-Me pz*); 0.68 (3; s, CH_3). ^{13}C NMR ($CDCl_3$): δ 150.2, 146.0 (3,5-C pz*); 106.6 (4-C pz*); 14.4, 13.1 (3,5-Me pz*). The In-CH_3 resonance was not observed, presumably due to line broadening caused by the quadrupolar indium atom. Mass spectrum: *m/z* 461 ($M^+ - H$), 447 ($M^+ - CH_3$), 427 (M^+ - Cl).

Crystallographic Analyses. Crystal, data collection, and refinement parameters for the two structures are collected in Table 1. Colorless crystals of $[B(pz)_4]_2InCH_3$·2tol were grown from toluene, and those of {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2 were grown from a CH_2Cl_2 solution of {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF by the slow evaporation of the solvent. They were mounted in Lidemann glass capillary tubes and photographically characterized. $\bar{1}$ and *mmm* Laue symmetry was found for $[B(pz)_4]_2InCH_3$·2tol and {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2, respectively. For $[B(pz)_4]_2InCH_3$·2tol, the centrosymmetric space group alternative was selected by its frequency of occurrence; the well-behaved results of refinement support this choice. Systematic absences in the diffraction data allowed a unique assignment of the space group for {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2. Semiempirical corrections of absorptions were applied to both data sets.

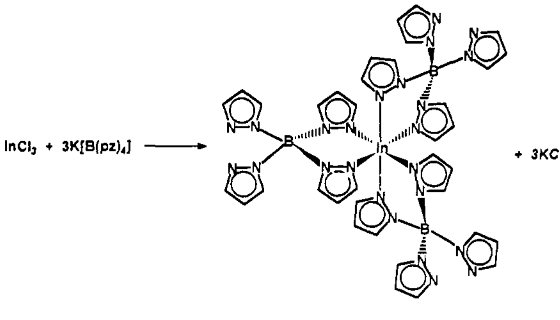
Table 1. Crystallographic Data for $[B(pz)_4]_2InCH_3 \cdot 2C_7H_8$ and {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2

	$[B(pz)_4]_2InCH_3\cdot 2C_7H_8$	{$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2
formula	$C_{38}H_{40}B_2InN_{16}$	$C_{32}H_{40}B_3Cl_5In_2N_{18}O$
fw	857.3	1132.2
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a, Å	8.637(4)	18.688(8)
b, Å	12.549(6)	16.584(5)
c, Å	18.815(10)	29.640(12)
α, deg	104.45(4)	
β, deg	96.94(4)	
γ, deg	98.09(4)	
V, Å^3	1929.1(16)	9183.8(6)
Z	2	8
ρ(calc), g cm^{-3}	1.476	1.637
temp, K	243	238
λ, Å	0.710 73	0.710 73
R(*F*), %	10.46	5.99
R_w(F), %	17.38	7.56

The indium atoms were located by direct methods. For $[B(pz)_4]_2InCH_2$·2tol, two molecules of toluene per indium atom were found in the crystal lattice. Both solvent molecules are severely disordered; for one of the molecules the methyl-group location could not be identified (this ring was constrained to a planar hexagon). In {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2, one molecule each of THF and CH_2Cl_2 was found for each pair of ions. For $[B(pz)_4]_2InCH_3$·2tol, all non-hydrogen atoms, except those in the more disordered solvent molecule, were refined anisotropically. For disordered solvent molecule, were refined anisotropically. For {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2, only the indium, chlorine, and nitrogen atoms were anisotropically refined to conserve data. Hydrogen atoms were idealized except for the more disordered solvent molecule in $[B(pz)_4]_2InCH_3$·2tol where they were ignored. All computer programs and the sources of the scattering factors are contained in the SHELXTL-PLUS program library (4.2) (G. Sheldrick, Siemens Corp., Madison, WI). Tables 2 and 3 contain the atomic coordinates and isotropic thermal parameters for $[B(pz)_4]_2InCH_3$·2tol and {$[HB(pz)_3]_2In$}{$[HB(pz)_3]InCl_3$}·THF·CH_2Cl_2, respectively.

Results and Discussion

Tetrakis(pyrazolyl)borate Complexes. The reaction of 3 equiv of $[B(pz)_4]^-$ with $InCl_3$ in either THF or THF/H_2O results in the formation of $[B(pz)_4]_3In$ in good yield (eq 1). This compound is soluble in aromatic hydrocarbon and halocarbon solvents. It is air stable in solution and the solid state.



(1)

The ^1H NMR spectrum of this complex at ambient temperature shows resonances arising from two types of pyrazolyl rings in a 1:1 ratio. As pictured, a six-coordinate structure similar to that shown crystallographically for the analogous dihydrobis(pyrazolyl)borate complex, $[H_2B(pz)_2]_3In$, is reasonable.[9] The coordinated and noncoordinated pyrazolyl rings do not exchange rapidly with each other on the NMR time scale, but the noncoordinated rings, rendered nonequivalent by the typical boat configuration of the six-membered InN_4B rings, must equilibrate

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(9) Nicholson, B. K.; Thomson, R. A.; Watts, F. D. *Inorg. Chim. Acta* **1988**, *148*, 101.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for $[B(pz)_4]_2InCH_3{\cdot}2C_7H_8$

	x	*y*	*z*	*U*(eq)[a]
In	200(1)	730(1)	12540(1)	35(1)
N(1)	2909(15)	1511(10)	12725(7)	47(5)
N(2)	3515(13)	2059(9)	12247(6)	34(4)
N(3)	−68(14)	2189(10)	11963(7)	46(5)
N(4)	1115(12)	2571(8)	11652(6)	32(4)
N(5)	884(12)	49(10)	11404(6)	37(4)
N(6)	1810(12)	719(9)	11091(6)	33(4)
N(7)	5013(14)	2295(10)	10975(7)	45(5)
N(8)	3497(12)	2436(9)	10990(6)	34(4)
N(9)	−2240(12)	−225(9)	11992(6)	35(4)
N(10)	−2938(12)	−1188(8)	12117(6)	30(3)
N(11)	665(11)	−939(9)	12705(7)	49(4)
N(12)	−454(13)	−1754(8)	12693(6)	34(4)
N(13)	−3770(19)	−619(13)	13563(8)	67(6)
N(14)	−2485(12)	−1107(9)	13472(6)	36(4)
N(15)	−4192(18)	−3368(13)	12925(9)	67(7)
N(16)	−3214(13)	−2948(9)	12514(7)	38(4)
C(1)	−1035(19)	2870(12)	12094(10)	53(6)
C(2)	−484(21)	3832(12)	11869(10)	57(7)
C(3)	885(18)	3619(12)	11598(8)	47(6)
C(4)	510(16)	−943(12)	10911(8)	45(5)
C(5)	1226(17)	−944(11)	10279(8)	43(5)
C(6)	2015(16)	119(11)	10419(7)	37(5)
C(7)	3911(18)	1778(14)	13343(8)	54(6)
C(8)	5220(20)	2521(13)	13293(9)	54(6)
C(9)	4916(18)	2680(13)	12586(9)	48(6)
C(10)	2910(16)	2776(11)	10389(8)	39(5)
C(11)	4164(19)	2935(13)	9997(9)	50(6)
C(12)	5398(19)	2591(14)	10386(9)	53(6)
C(13)	−3311(18)	120(13)	11576(9)	49(6)
C(14)	−4770(17)	−630(11)	11448(9)	46(6)
C(15)	−4535(16)	−1448(11)	11804(8)	40(5)
C(16)	2062(19)	−1231(18)	12822(9)	62(7)
C(17)	1862(19)	−2390(15)	12903(10)	56(7)
C(18)	244(20)	−2668(12)	12822(9)	50(6)
C(19)	−1627(21)	−1036(13)	14149(9)	52(6)
C(20)	−2394(25)	−458(18)	14666(10)	71(8)
C(21)	−3703(29)	−255(18)	14294(10)	78(9)
C(22)	−3223(17)	−3687(11)	11851(8)	44(5)
C(23)	−4260(24)	−4577(14)	11841(12)	71(8)
C(24)	−4891(20)	−4436(12)	12485(10)	60(7)
C(25)	−220(26)	1564(15)	13614(10)	71(8)
B(1)	2507(16)	1982(13)	11503(9)	34(5)
B(2)	−2261(17)	−1756(12)	12697(8)	31(5)
C(31)	1371(47)	−3344(20)	14598(14)	109(14)
C(32)	3195(115)	−3217(60)	14673(32)	299(6)
C(33)	3958(129)	−3829(92)	14495(44)	411(95)
C(34)	3224(47)	−4708(40)	14164(22)	134(23)
C(35)	1827(55)	−5143(25)	13958(17)	128(17)
C(36)	523(37)	−4413(36)	14209(17)	130(18)
C(37)	−1055(46)	−4478(57)	14146(27)	543(100)
C(41)	−855(25)	5400(16)	10421(11)	75(5)
C(42)	−1880	4638	9824	222(22)
C(43)	−1269	3975	9251	154(13)
C(44)	367	4072	9276	50(188)
C(45)	1392	4834	9873	50(188)
C(46)	781	5498	10446	50(188)

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

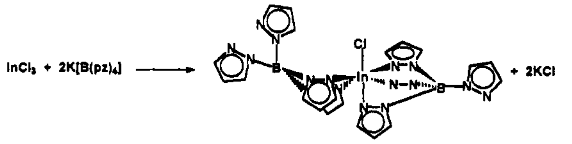
Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}{\cdot}THF{\cdot}CH_2Cl_2$

	x	*y*	*z*	*U*(eq)[a]
In(1)	2658.5(6)	4937.5(7)	3554.3(3)	30(1)
In(2)	6989.7(6)	3469(7)	3994.3(4)	33(1)
Cl(1)	5828(2)	2758(3)	3979(2)	46(2)
Cl(2)	7441(3)	2701(3)	4636(1)	56(2)
Cl(3)	7479(3)	2678(3)	3376(1)	51(2)
Cl(4)	5805(5)	3467(7)	658(4)	192(6)
Cl(5)	4852(5)	2643(5)	115(3)	139(4)
N(1)	2003(8)	5374(8)	4134(4)	40(5)
N(2)	1348(7)	5659(8)	4041(4)	29(4)
N(3)	1626(7)	4396(8)	3339(4)	37(5)
N(4)	1028(6)	4862(8)	3358(4)	29(4)
N(5)	2274(8)	6031(8)	3220(4)	41(5)
N(6)	1562(7)	6237(8)	3262(4)	34(5)
N(7)	3248(7)	4468(8)	2964(4)	33(5)
N(8)	3894(7)	4117(7)	3048(4)	27(4)
N(9)	3708(7)	5466(8)	3722(4)	37(5)
N(10)	4289(6)	4966(9)	3696(4)	34(5)
N(11)	3025(8)	3857(8)	3895(4)	46(5)
N(12)	3740(6)	3619(7)	3834(4)	25(4)
N(13)	6530(7)	4429(8)	4472(4)	34(5)
N(14)	6709(7)	5240(7)	4385(4)	33(5)
N(15)	6620(7)	4414(8)	3491(4)	40(5)
N(16)	6791(7)	5203(8)	3540(4)	43(5)
N(17)	7978(8)	4290(9)	3996(4)	45(5)
N(18)	7893(7)	5114(9)	4011(4)	44(5)
C(1)	2095(9)	5388(10)	4575(5)	42(5)
C(2)	1464(10)	5651(10)	4775(6)	48(5)
C(3)	1003(10)	5804(10)	4432(5)	43(5)
C(4)	1426(10)	3686(12)	3173(6)	50(5)
C(5)	708(9)	3688(10)	3104(5)	42(4)
C(6)	473(10)	4441(11)	3216(5)	47(5)
C(7)	2559(9)	6565(10)	2930(5)	36(4)
C(8)	2050(9)	7132(11)	2813(5)	45(5)
C(9)	1427(9)	6917(10)	3008(5)	38(4)
C(10)	3087(10)	4337(10)	2525(6)	44(4)
C(11)	3670(9)	3961(10)	2319(5)	39(4)
C(12)	4164(9)	3814(10)	2652(5)	33(4)
C(13)	3942(11)	6154(12)	3909(6)	54(5)
C(14)	4671(11)	6118(12)	3960(6)	60(6)
C(15)	4868(10)	5350(11)	3837(5)	50(5)
C(16)	2771(9)	3323(10)	4201(5)	41(4)
C(17)	3286(9)	2756(10)	4322(6)	44(5)
C(18)	3883(10)	2975(10)	4081(5)	44(5)
C(19)	6124(9)	4410(10)	4830(5)	38(4)
C(20)	6036(10)	5178(12)	4998(6)	60(6)
C(21)	6396(9)	5698(12)	4708(6)	48(5)
C(22)	6314(9)	4373(10)	3082(6)	40(5)
C(23)	6266(9)	5127(11)	2883(6)	51(5)
C(24)	6589(10)	5640(12)	3182(6)	53(5)
C(25)	8684(10)	4128(11)	4010(6)	48(5)
C(26)	9040(11)	4846(11)	4025(6)	59(5)
C(27)	8553(10)	5463(12)	4021(6)	57(5)
O(1)	4180(9)	6918(10)	2016(5)	94(5)
C(101)	4029(10)	6149(11)	2138(6)	54(5)
C(102)	4426(10)	5960(10)	2510(6)	48(5)
C(103)	4771(10)	6674(10)	2610(5)	51(5)
C(104)	4660(9)	7233(10)	2313(5)	38(4)
C(105)	5751(13)	3018(15)	132(8)	93(8)
B(1)	1036(10)	5731(11)	3554(6)	34(5)
B(2)	4229(10)	4077(11)	3508(6)	31(5)
B(3)	7155(11)	5504(14)	3981(7)	52(6)

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

by rapid flips of these rings. These flips equilibrate the noncoordinated pyrazolyl rings with each other and coordinated pyrazolyl rings with each other but do not equilibrate these two types of rings. The resonances broaden at lower temperature, but a limiting low-temperature spectrum was not attained.

The reaction of 2 equiv of $[B(pz)_4]^-$ with $InCl_3$ in THF results in the formation of $[B(pz)_4]_2InCl$ in good yield (eq 2). This compound is soluble in aromatic hydrocarbon solvents and freely soluble in halocarbon solvents. A molecular weight study indicates that it is monomeric in solution.



(2)

The ambient-temperature ¹H NMR spectrum shows equivalent, but broad, resonances for each type of hydrogen atom in the pyrazolyl rings. The −89 °C spectrum in CD_2Cl_2 is complicated with each type of hydrogen atom in the pyrazolyl rings showing resonances in a 2:2:1:1:1:1 ratio (Figure 1). These data can be explained by a square pyramidal structure in which the two InN_4B

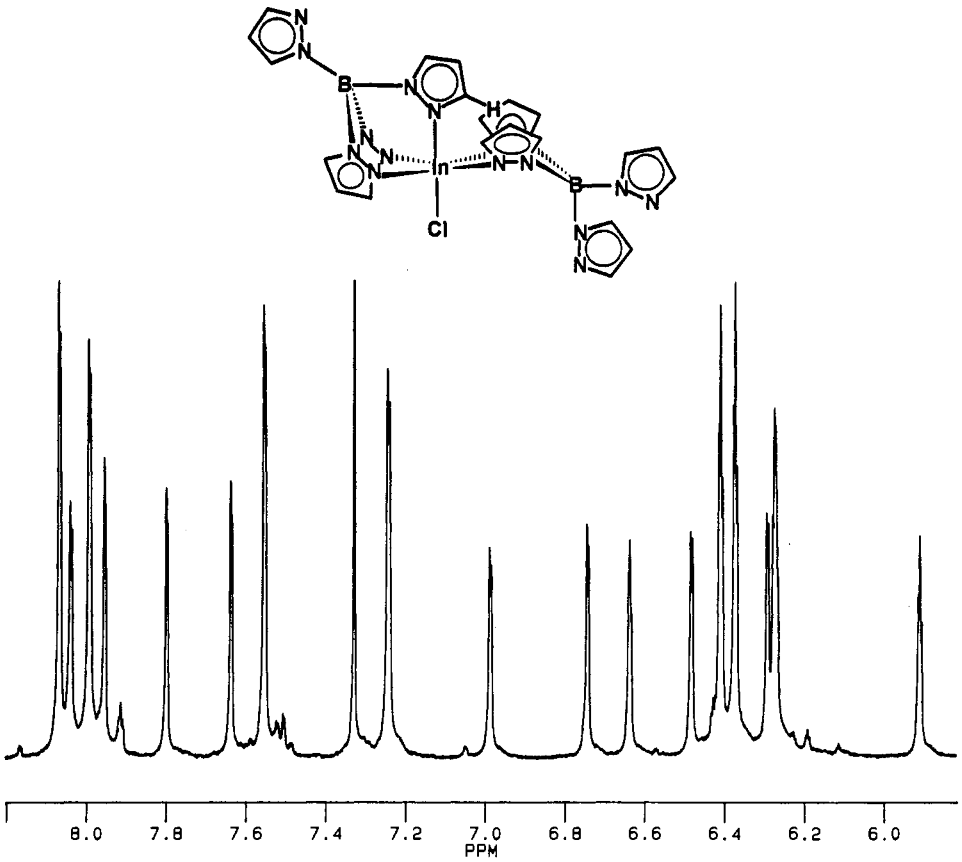
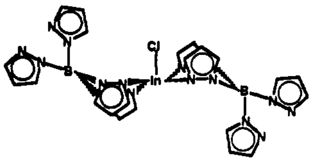
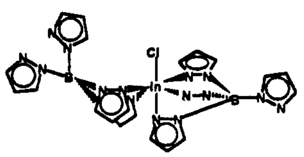


Figure 1. ^{1}H NMR spectrum for $[B(pz)_4]_2InCl$ in CD_2Cl_2 at -89 °C.

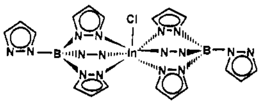
boats are flipped differently relative to the axial Cl (**D**), an



D



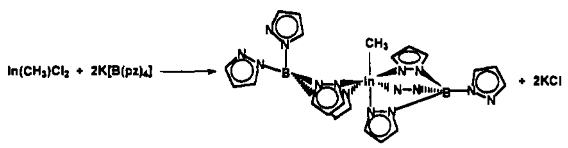
E



F

octahedral structure with one bidentate and one tridentate ligand (**E**), or a seven-coordinate capped octahedron with the chloride ligand in the capping position (**F**). The difference in the first two possibilities is whether a third pyrazolyl ring of the ligand pictured to the right is coordinated or noncoordinated. In both cases there must be a plane of symmetry which passes through the indium, chlorine, and both boron atoms. We favor the six-coordinate structure **E** because X-ray crystallography has shown that the solid-state structures of the methyl analogs, $[B(Pz)_4]_2InCH_3$ (vide infra) and $[B(pz)_4]_2GaCH_3$,[6] are six-coordinate. The observation by ^{1}H NMR that one of the resonances assigned to a 3-position hydrogen atom on a pyrazolyl ring is shifted to high field is also strongly indicative of a six-coordinate complex containing one bidentate and one tridentate poly(pyrazolyl)borate ligand (vide infra).[10] These results and the fact that we have been unable to prepare any seven-coordinate complexes of gallium and indium with these ligands tend to rule out structure **F**.

The methyl analog is prepared from $In(CH_3)Cl_2$ and 2 equiv of $[B(pz)_4]^-$ in good yield (eq 3). The complex is freely soluble



(3)

in aromatic hydrocarbon and halocarbon solvents and slightly soluble in hydrocarbon solvents. It is stable in air in the solid state. This compound can also be prepared from the reaction $[B(pz)_4]_2InCl$ and CH_3Li at -78 °C.

The ^{1}H NMR spectrum of this complex at ambient temperature shows the pyrazolyl rings as equivalent and a resonance at -0.72 ppm for the methyl ligand. These resonances broaden and collapse at lower temperatures, but a limiting low-temperature spectrum was not attained. The structure in the solid state was determined by X-ray crystallography.

An ORTEP drawing of $[B(pz)_4]_2InCH_3$ is shown in Figure 2. Important bond angles and distances are listed in Table 4. The structure shows that the complex is six-coordinate with a bidentate and a tridentate tetrakis(pyrazolyl)borate ligand. This result is similar to that found in the gallium analog.[6] The arrangement of the donor atoms is nearly octahedral with *cis* N–In–N bond angles ranging from 77.2(5) to 94.0(4)°. The largest interligand N–In–N bond angles involve the pyrazolyl rings *cis* to the methyl group. The *cis* C–In–N angles range from 96.4(6) to 101.8(6)°, with the two angles from the bidentate ligand the larger ones. These angles are larger as a consequence of the orientation of the boat configuration of the InN_4B ring. The boat is oriented such that the boron atom is "up" on the same side of the octahedron as the methyl ligand pushing "down" the coordinated nitrogen atoms of this ligand. This orientation, also observed with $[B(pz)_4]_2GaCH_3$, minimizes the interligand contact of the

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(10) Reger, D. L.; Mason, S. S.; Reger, L. B.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.*, following paper in this issue.

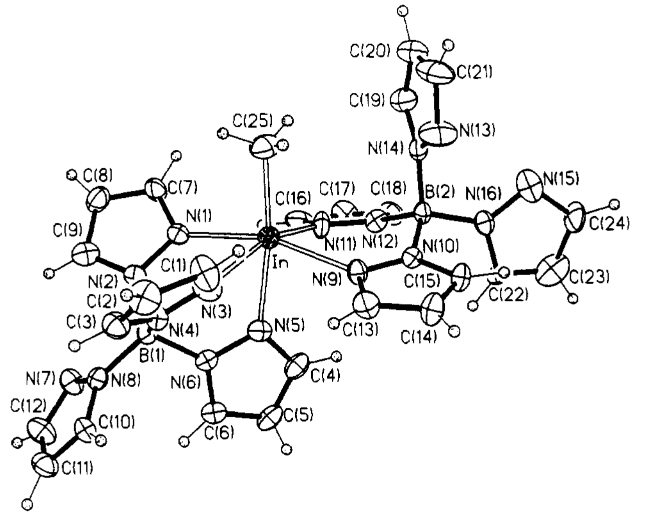


Figure 2. ORTEP drawing of $[B(pz)_4]_2In(CH_3)$.

Table 4. Selected Bond Distances and Angles for $[B(pz)_4]_2InCH_3{\cdot}2C_7H_8$

(a) Bond Distances (Å)			
In–N(1)	2.354(12)	In–N(9)	2.256(10)
In–N(3)	2.374(15)	In–N(11)	2.275(12)
In–N(5)	2.277(11)	In–C(25)	2.132(18)
(b) Bond Angles (deg)			
N(1)–In–N(3)	82.5(4)	N(3)–In–C(25)	97.9(6)
N(1)–In–N(5)	77.3(4)	N(5)–In–N(9)	84.4(4)
N(1)–In–N(9)	161.7(4)	N(5)–In–N(11)	83.2(4)
N(1)–In–N(11)	94.0(4)	N(5)–In–C(25)	172.4(6)
N(1)–In–C(25)	96.4(6)	N(9)–In–N(11)	84.7(4)
N(3)–In–N(5)	77.2(5)	N(9)–In–C(25)	101.8(6)
N(3)–In–N(9)	92.6(4)	N(11)–In–C(25)	101.7(6)
N(3)–In–N(11)	160.3(4)		

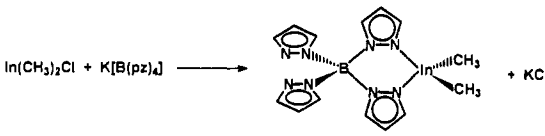
noncoordinated pyrazolyl rings of the bidentate ligand with the coordinated ring of the tridentate ligand *trans* to the methyl group.

This orientation also places the hydrogen atom on C(4) between the coordinated pyrazolyl rings of the bidentate ligand. As mentioned above for $[B(pz)_4]_2InCl$, we observe in all six-coordinate complexes containing one bidentate and one tridentate poly(pyrazolyl)borate ligand a resonance, assigned to a 3-position hydrogen atom on a pyrazolyl ring, that is shifted to high field. This effect is even more pronounced in complexes of this type containing the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand.[10] With this ligand, one 3-position methyl resonance is substantially shifted to high field. We attribute this shielding effect to the proximity of the 3-position hydrogen atom or methyl group on the tridentate ligand that is oriented close to the aromatic ring currents in the coordinated pyrazolyl rings of the bidentate ligand.

The In–C distance of 2.132(18) Å is normal. It is the same as those found in the four-coordinate $[H_2B(pz)_2]In(CH_3)_2$ (2.133(5) and 2.138(6) Å) and slightly longer than those in the weakly associated dimer $\{[H_2B(pz)_2]In(CH_3)Cl\}_2$ (2.091(5) and 2.102(4) Å in two crystallographically independent molecules).[4] The shortest In–N distance in the tridentate ligand (2.277(11) Å) is the one *trans* to the methyl ligand. This result is surprising considering the *trans* influence of a methyl ligand would be expected to be greater than that of a nitrogen donor ligand,[11] although the same result is observed in $[B(pz)_4]_2GaCH_3$. The In–N distances for the bidentate ligand are about the same length (2.256(10) and 2.275(12) Å) and about 0.1 Å shorter than the analogous In–N distances *cis* to the methyl in the tridentate ligand.

$[B(pz)_4]_2InCH_3$ is the second example of a six-coordinate organometallic complex of indium. Barron has very recently reported the first example, InMe(diphenyltriazenato)$_2$(3,5-Me$_2$pyridine).[12] We are finding that six coordination for gallium(III) and indium(III) is common in complexes of these potentially tridentate poly(pyrazolyl)borate ligands.[6,10]

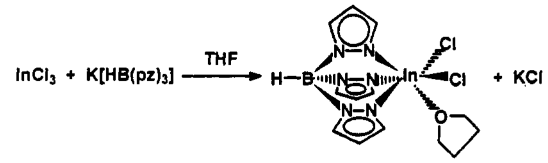
The reaction of 1 equiv of $[B(pz)_4]^-$ with $In(CH_3)_2Cl$ results in the formation of $[B(pz)_4]In(CH_3)_2$ (eq 4). This compound is



(4)

freely soluble in hydrocarbon and halocarbon solvents. The pyrazolyl rings show equivalent resonances at ambient temperature, an indication that the molecule is fluxional, but a limiting low-temperature spectrum was not observed. We anticipate that this complex is four-coordinate analogous to $[HB(3,5\text{-}Me_2pz)_3]Ga(Cl)(CH_3)$ and $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ that have been shown crystallographically to be four-coordinate.

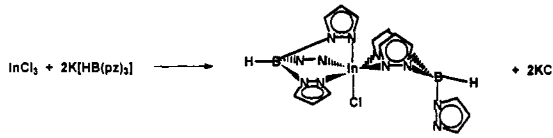
Hydrotris(pyrazolyl)borate Complexes. The reaction of 1 equiv of $[HB(pz)_3]^-$ with $InCl_3$ results in the formation of the THF adduct of $[HB(pz)_3]InCl_2$ (eq 5), but in low yield. This compound is soluble in both aromatic hydrocarbon and halocarbon solvents. It is also air stable in solution and the solid state.



(5)

The pyrazolyl rings of $[HB(pz)_3]InCl_2{\cdot}THF$ show equivalent resonances in its ^1H NMR spectra at all temperatures, with no evidence of line broadening even at −80 °C. These results are best interpreted as arising from fast dissociation–association of the THF ligand, although equilibration can also be achieved by rotation of the $[HB(pz)_3]^-$ ligand about the B–In axis.

The reaction of 2 equiv of $[HB(pz)_3]^-$ with $InCl_3$ in THF results in the formation of $[HB(pz)_3]_2InCl$ (eq 6). This compound also



(6)

forms in a reaction with 3 equiv of $[HB(pz)_3]^-$, rather than $[HB(pz)_3]_3In$, the expected product given the analogous chemistry observed for ligands **A** and **C**. It is soluble in aromatic hydrocarbon and halocarbon solvents and is air stable in solution and the solid state.

The ^1H NMR spectra of $[HB(pz)_3]_2InCl$ in toluene-d_8 are as expected for a six-coordinate structure containing one bidentate and one tridentate ligand, analogous to other $[ligand]_2MX$ (M = Ga, In: X = CH_3, Cl) complexes of these ligands. At room temperature, a broad resonance is observed for each type of hydrogen atom in the pyrazolyl rings. At low temperatures, each type of hydrogen atom shows resonances in a 2:2:1:1 ratio. The top part of Figure 3 shows this spectrum for the 5-position hydrogen atoms. An unusually high-field-shifted doublet is also observed at δ 6.29 and is assigned to the 3-position hydrogen atom on the ring of the tridentate ligand in proximity to the pyrazolyl rings of the bidentate ligand, as discussed above.

The ^1H NMR spectra of this complex in halocarbon solvents are very unusual. The ambient-temperature spectrum run in $CDCl_3$ shows a single broad resonance for each of the three types of pyrazolyl ring hydrogen atoms. Both ambient- and low-

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(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience; New York, 1988; p 1300.

(12) Leman, J. T.; Roman, H. A.; Barron, A. R. *Organometallics* **1993**, *12*, 2986.

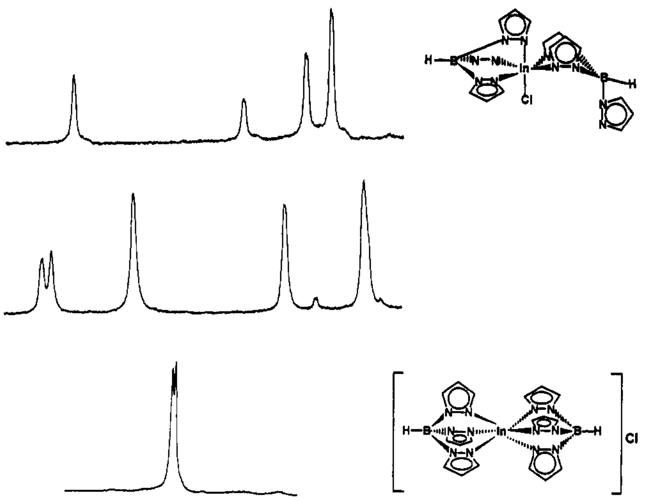
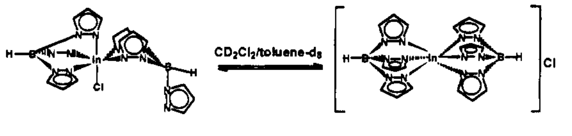


Figure 3. ${}^1H$ NMR spectra, run at −65 °C, of the 5-position hydrogen atoms on the pyrazolyl rings recorded when $[HB(pz)_3]_2InCl$ solid is dissolved in three different solvents. The portions of the spectra shown are the most deshielded resonances and are centered at about δ 7.8. Scales have been omitted from the spectra for clarity due to the strong solvent dependence of the chemical shifts. (a) Top: In toluene-d_8 the resonances for $[HB(pz)_3]_2InCl$ are observed. (b) Middle: In a 1/1 mixture of toluene-d_8/CD_2Cl_2 the resonances for both $[HB(pz)_3]_2InCl$ and $\{[HB(pz)_3]_2In\}Cl$ are observed. (c) Bottom: In CD_2Cl_2 in resonance for $\{[HB(pz)_3]_2In\}Cl$ are observed.

temperature spectra run in CD_2Cl_2 show just three sharp resonances, one for each type of hydrogen atom in the pyrazolyl rings. The bottom part of Figure 3 shows the resonance for the 5-position hydrogen atoms. Given the broad singlets observed in $CDCl_3$, a complex low-temperature spectrum, as observed in toluene-d_8, was expected. From the chemical shifts of the resonances in CD_2Cl_2, we were able to assign them as arising *not from* $[HB(pz)_3]_2InCl$ *but from cationic* $\{[HB(pz)_3]_2In\}^+$ (vide infra). This cation must form from *ionization of the chloride ligand from the covalent* $[HB(pz)_3]_2InCl$ *complex in the polar* CD_2Cl_2 *solvent.* Evaporation of the CD_2Cl_2 leads to the re-formation of the covalent complex, $[HB(pz)_3]_2InCl$. The low-temperature spectrum in $CDCl_3$ shows resonances for both $[HB(pz)_3]_2InCl$ and $\{[HB(pz)_3]_2In\}Cl$, with those arising from the cation dominating. In a 1/1 mixture of toluene-d_8/CD_2Cl_2, both compounds are clearly observed. The middle part of Figure 3 shows this spectrum for the 5-position hydrogen atoms (note that the chemical shifts of the resonances are strongly solvent dependent). The resonance for $\{[HB(pz)_3]_2In\}Cl$ is distinctive for this cation, and the resonances for $[HB(pz)_3]_2InCl$ show an equally distinctive 2:2:1:1 ratio pattern for each type of pyrazolyl ring hydrogen atom. The resonances for the two compounds coalesce at higher temperatures.

Thus, dissolving $[HB(pz)_3]_2InCl$ in a 1/1 mixture of toluene-d_8/CD_2Cl_2 *produces a solution containing both the ionic and covalent forms*, and they are in fast equilibrium on the NMR time scale at higher temperatures (eq 7). The same situation is true in $CDCl_3$ solution. We are not aware of other molecular complexes of the post-transition metals that show this unusual solvent dependence.



(7)

The cation of the ionic compound has been previously prepared in our laboratory by several methods, by abstraction of the chloride ligand from $[HB(pz)_3]_2InCl$ by $AgBF_4$, by removal of the methyl ligand by protonation of $[HB(pz)_3]_2InCH_3$ with $[HNEt_3][BPh_4]$, and from the reaction of $K[HB(pz)_3]$ with InCl. The hydrotris(3,5-dimethylpyrazolyl) analog, $\{[HB(3,5\text{-}Me_2pz)_3]_2In\}^+$, has recently been reported and strucurally characterized.[13] The $\{[HB(pz)_3]_2In\}^+$ cation is best prepared as the $InCl_4^-$ compound from the reaction of 1 equiv of $[HB(pz)_3]^-$ and $InCl_3$ in a THF/H_2O solvent system (eq 8).

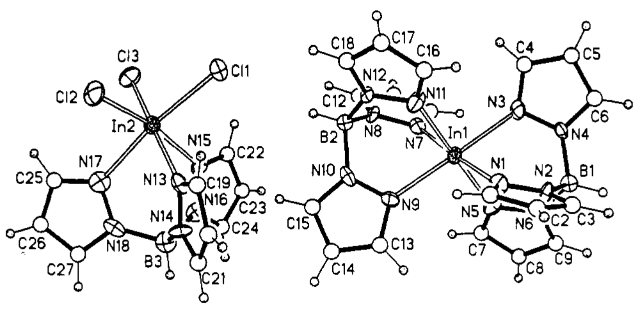
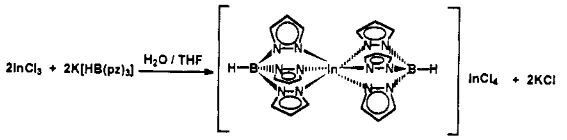


Figure 4. ORTEP drawing of $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}$.



(8)

The reaction of *three* equivalents of $[HB(pz)_3]^-$ with *two* equivalents of $InCl_3$ in a mixed THF/H_2O solvent system yields $\{[HB(pz)_3]_2In\}\{[HB)pz)_3]InCl_3\}$ (eq 9).

$$2InCl_3 + 3K[HB(pz)_3] \xrightarrow{H_2O/THF} \{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\} + 3KCl \quad (9)$$

The ${}^1H$ NMR spectra of this compound in CD_2Cl_2 show resonances for the cation and a second set of pyrazolyl resonances assigned to the anion. These resonances are sharp at low temperatures but start to broaden at room temperature indicating the onset of ligand exchange between the two ions. The structure of $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}\cdot THF\cdot CH_2Cl_2$ has been determined crystallographically. An ORTEP drawing of the molecule is shown in Figure 4. There are no close interactions, either between the ions or between the ions and the solvent molecules. Important bond distances and angles are listed in Table 5.

The cation and anion show approximately octahedral coordination about the indium atoms. For $\{[HB(pz)_3]_2In\}^+$, the intraligand N–In–N angles, restrained by the chelate rings, vary from 82.8(5) to 86.7(5)°. The interligand N–In–N angles are larger, ranging from 93.6(5) to 100.7(5)°. Comparable angles are found in $\{[HB(3,5\text{-}Me_2pz)_3]_2In\}^+$.[13] The indium–nitrogen bond distances (average 2.20 Å) are slightly shorter than those in the tris(3,5-dimethylpyrazolyl) analog (average 2.25 Å).

The anion, $\{[HB(pz)_3]InCl_3\}^-$, has N–In–N angles ranging 79.3(5)–83.6(5)°, *cis* N–In–Cl angles of 89.5(5)–92.9(4)°, and Cl–In–Cl angles of 93.4(2)–100.1(2)°. The In–N distances (average 2.29 Å) are almost 0.1 Å longer than those in the cation. The In–Cl bonds (average 2.45 Å) are only slightly longer than those found in the neutral six-coordinate octahedral compound $[HB(3,5\text{-}Me_2pz)_3]InCl_2NCCH_3$ (average = 2.43 Å).[5]

Thus, the reactions of $InCl_3$ and $[HB(pz)_3]^-$ are dependent on the solvent system used and the stoichiometry of the reactions. A 1/1 reaction in THF yields $[HB(pz)_3]InCl_2\cdot THF$. The 1/1 reaction in a THF/H_2O mixture yields $\{[HB(pz)_3]_2In\}InCl_4$. A 1/2 (indium/ligand) reaction in THF yields $[HB(pz)_3]_2InCl$, a compound that ionizes into $\{[HB(pz)_3]_2In\}Cl$ in CD_2Cl_2 solution. The reaction of a 2/3 mixture in THF/H_2O yields the bimetallic indium salt $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}$.

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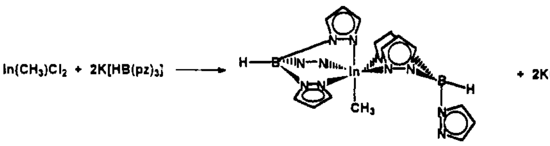
(13) Frazer, A.; Piggott, B.; Harman, M.; Mazid, M.; Hursthouse, M. B. *Polyhedron* **1992**, *11*, 3013.

Table 5. Selected Bond Distances and Angles for $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}\cdot THF\cdot CH_2Cl_2$

(a) Bond Distances for $\{[HB(pz)_3]_2In\}^+$ (Å)			
In(1)–N(1)	2.230(13)	In(1)–N(7)	2.209(12)
In(1)–N(3)	2.223(13)	In(1)–N(9)	2.205(14)
In(1)–N(5)	2.187(13)	In(1)–N(11)	2.168(14)
(b) Bond Angles for $\{[HB(pz)_3]_2In\}^+$ (deg)			
N(1)–In(1)–N(3)	82.8(5)	N(3)–In(1)–N(11)	94.3(5)
N(1)–In(1)–N(5)	84.2(5)	N(5)–In(1)–N(7)	95.6(5)
N(1)–In(1)–N(7)	176.4(5)	N(5)–In(1)–N(9)	93.7(5)
N(1)–In(1)–N(9)	100.7(5)	N(5)–In(1)–N(11)	178.9(5)
N(1)–In(1)–N(11)	94.8(5)	N(7)–In(1)–N(9)	82.8(5)
N(3)–In(1)–N(5)	85.4(5)	N(7)–In(1)–N(11)	85.4(5)
N(3)–In(1)–N(7)	93.6(5)	N(9)–In(1)–N(11)	86.7(5)
N(3)–In(1)–N(9)	176.2(5)		
(c) Bond Distances for $\{[HB(pz)_3]InCl_3\}^-$ (Å)			
In(2)–Cl(1)	2.472(4)	In(2)–N(13)	2.296(13)
In(2)–Cl(2)	2.441(5)	In(2)–N(15)	2.271(13)
In(2)–Cl(3)	2.433(5)	In(2)–N(17)	2.294(15)
(d) Bond Angles for $\{[HB(pz)_3]InCl_3\}^-$ (deg)			
Cl(1)–In(2)–Cl(2)	93.9(2)	Cl(1)–In(2)–Cl(3)	93.4(2)
Cl(2)–In(2)–Cl(3)	100.1(2)	Cl(3)–In(2)–N(13)	168.2(3)
Cl(1)–In(2)–N(13)	90.8(3)	Cl(3)–In(2)–N(15)	89.5(4)
Cl(1)–In(2)–N(15)	92.9(4)	Cl(3)–In(2)–N(17)	91.1(4)
Cl(1)–In(2)–N(17)	172.1(4)	N(13)–In(2)–N(15)	79.3(5)
Cl(2)–In(2)–N(13)	90.6(3)	N(13)–In(2)–N(17)	83.6(5)
Cl(2)–In(2)–N(15)	167.9(4)	N(15)–In(2)–N(17)	80.6(5)
Cl(2)–In(2)–N(17)	91.7(4)		

The reaction of $In(CH_3)Cl_2$ with 2 equiv of $[HB(pz)_3]^-$ leads to the formation of $[HB(pz)_3]_2InCH_3$ (eq 10). This compound is soluble in aromatic hydrocarbon and halocarbon solvents. It is air stable in solution and the solid state. It can also be prepared from the reaction of CH_3Li with $[HB(pz)_3]_2InCl$ at −78 °C. Molecular weight studies indicate $[HB(pz)_3]_2InCH_3$ is a monomer in benzene solution. This product, rather than $[HB(pz)_3]InCH_3Cl$, is also isolated from the reaction of 1 equiv of $[HB(pz)_3]^-$ with $In(CH_3)Cl_2$.



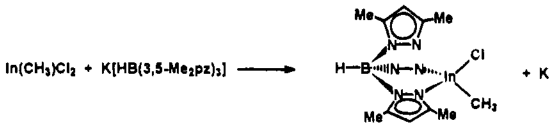
(10)

The ^1H NMR spectrum of $[HB(pz)_3]_2InCH_3$ is very broad at ambient temperature but sharpens on a lower field instrument to three resonances indicating equivalent pyrazolyl rings. Upon cooling of the sample to −80 °C, each resonance goes to a 2:2:1:1 pattern. The observation of an unusually shielded 3-position resonance, this time by more than 0.8 ppm, suggests an octahedral structure with one tridentate and one bidentate ligand.

Hydrotris(3,5-dimethylpyrazolyl)borate Complexes. The reaction of 1 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCl_3$ in THF leads to the isolation of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$. This complex has been mentioned previously, and the acetonitrile adduct analog, $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot NCCH_3$, characterized crystallographically.[5] $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ is also the product isolated from the reaction of 2 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCl_3$.

The preference for indium(III) to attain six-coordination in complexes of these ligands is emphasized by the reaction of 1 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCl_3$ in toluene. The product of this reaction is $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot H(3,5\text{-}Me_2pz)$. The only source of the $H(3,5\text{-}Me_2pz)$ ligands is decomposition of $[HB(3,5\text{-}Me_2pz)_3]^-$. The formation of the six-coordinate adduct is apparently favored over the formation of five-coordinate $[HB(3,5\text{-}Me_2pz)_3]InCl_2$. This pyrazole adduct is prepared in higher yield in reactions in which 1 equiv of pyrazole is added at the start.

The reaction of either 1 or 2 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCH_3Cl_2$ yields $[HB(3,5\text{-}Me_2pz)_3]In(Cl)(CH_3)$ (eq 11). In contrast to the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ligands, it has not proven possible to prepare $(ligand)_2InX$ complexes with the bulky $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand, even though we have prepared $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(3,5\text{-}Me_2pz)_2]Cl$.[10]



(11)

Although fluxional at ambient temperatures, the low-temperature ^1H NMR spectrum of $[HB(3,5\text{-}Me_2pz)_3]In(Cl)(CH_3)$ shows each of the resonances for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand in a 2/1 ratio. This spectrum is very similar to that observed with $[HB(3,5\text{-}Me_2pz)_3]Ga(Cl)(CH_3)$ and $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$, complexes that have been shown crystallographically to be four-coordinate with bidentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligands. We propose a similar structure for $[HB(3,5\text{-}Me_2pz)_3]In(Cl)(CH_3)$.

Conclusions

The results of this study and previous results on the analogous chemistry of gallium(III) indicate that in complexes of potentially multidentate poly(pyrazolyl)borate ligands the metal atoms prefer either four- or six-coordination. The only five-coordinate complexes, $[H_2B(pz)_2]_2MX$, that we have prepared contain the dihydrobis(pyrazolyl)borate ligands.[3a,4] The tendency for the formation of cationic complexes of the type $\{[poly(pyrazolyl)borate]_2M\}^+$ is higher for gallium than indium. The complex $[HB(pz)_3]_2InCl$ is molecular in toluene but ionizes a chloride ligand and forms such a cation in CD_2Cl_2 solution. Both the ionic and covalent forms of $[HB(pz)_3]_2InCl$ are present in a 1/1 mixture of toluene-d_8/CD_2Cl_2. $[B(pz)_4]_2InCl$ does not ionize in CD_2Cl_2. The difference in the behaviors of $[HB(pz)_3]_2InCl$ and $[B(pz)_4]_2InCl$ is best explained by the greater propensity of the $[HB(pz)_3]^-$ ligand to achieve tridentate coordination.[14] Although six-coordinate $(ligand)_2InX$ complexes form readily with $[HB(pz)_3]^-$ and $[B(pz)_4]^-$, we have been unable to prepare analogous complexes with $[HB(3,5\text{-}Me_2pz)_3]^-$.

Acknowledgment is made to the National Science Foundation (Grants CHE-9115158 and OSR-9108772). The NSF (Grants CHE-8411172 and CHE-8904942) and NIH (Grant RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment at the University of South Carolina.

Supplementary Material Available: A stereoview of the unit cell and tables of complete data collection information, bond distances and angles, anisotropic thermal parameters, and positional parameters of H atoms (16 pages). Ordering information is given on any current masthead page.

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