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Poly(pyrazolyl)borate complexes of gallium and indium*

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Contents

Abstract

The poly(pyrazolyl)borate family of ligands has been used to prepare a variety of stable complexes of gallium and indium of the general formula [poly(pyrazolyl)borate]$_m$MCl$_n$(CH$_3$)$_p$ ($m+n+p=3$), and the cationic complexes $\{$[poly(pyrazolyl)borate]$_2$M$\}^+$. The results of these studies show that in complexes of potentially multidentate poly(pyrazolyl)borate ligands these two metals prefer four- or six-coordination. The only five-coordinate complexes, [$H_2B(pz)_2$]$_2$MX, that have been prepared contain the dihydrobis(pyrazolyl)borate ligands. These complexes, even the organometallics, are unusually stable. The complex [HB(3,5-Me$_2$pz)$_3$]InCl$_2$(THF) is an excellent starting material for the formation of complexes containing one poly(pyrazolyl)borate ligand and other types of ligands and also intermetallic complexes. A bulky poly(pyrazolyl)borate ligand stabilizes indium(I) in the complex [HB(3-Phpz)$_3$]In.

Keywords: Gallium; Indium; Borate complexes

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1. Introduction

The poly(pyrazolyl)borate family of ligands were first introduced by Trofimenko in the 1960s [1]. These ligands are extremely versatile because the number of donor

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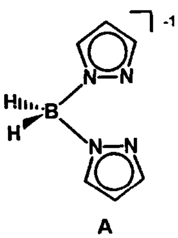
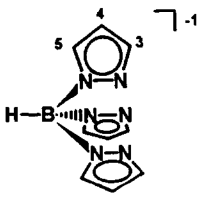
atoms in each ligand can be varied from two to three in going from the bidentate ligands **A** to the potentially tridentate ligands **B** and **C**. The steric properties of the ligands can be altered by changing the substituents on the pyrazolyl rings.



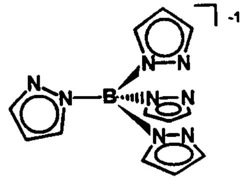
A

$[H_2B(pz)_2]^-$



B

$[HB(pz)_3]^-$



C

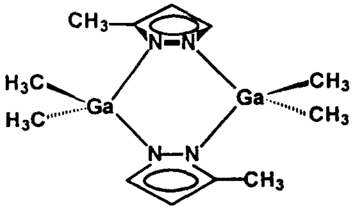
$[B(pz)_4]^-$

These ligands have been used extensively to prepare complexes of the transition metals [1]. The introduction by Trofimenko of poly(pyrazolyl)borate ligands substituted with bulky alkyl and aryl substituents, such as $[HB(3\text{-}^{t}Bupz)_3]^-$ (pz = pyrazolyl ring), has provided new impetus for this area of chemistry [2]. Reviewed here are results using these ligands with the metals gallium and indium.

2. Pyrazolylgallium dimers

While not poly(pyrazolyl)borate complexes of gallium, the symmetrical pyrazolylgallium dimers were the first related complexes of gallium prepared and characterized. The first report was on the synthesis and solid-state structure of $D_2Ga(pz)_2GaD_2$ (**1**) [3]. This complex was prepared by heating equimolar amounts of pyrazole and $(CH_3)_3N \cdot GaD_3$. The solid-state structure is shown in Fig. 1. As is typical for this class of molecules, the six-member ring is in a boat configuration.

The syntheses of a number of additional $R_2Ga(pz)_2GaR_2$ were reported [4]. The solid-state structures of four pyrazolylgallium dimethyl dimers were studied to determine the effects of substitution on both the gallium atoms and the bridging pyrazolyl groups. The complexes studied were $(CH_3)_2Ga(pz^*)_2Ga(CH_3)_2$, where pz* = pyrazolyl (**2**), 3-methylpyrazolyl (**3**), indazolyl (**4**) [5] and 3,5-dimethylpyrazolyl (**5**) [6]. For the two asymmetrically substituted complexes **3** and **4**, the substituents of the pyrazolyl rings are on opposite sides of the molecule.



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The most interesting trend in these five complexes is the change in the boat configuration of the six-member ring. Table 1 shows the Ga–Ga distances and

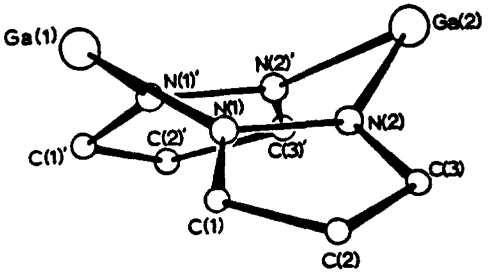


Fig. 1. Solid-state structure of $D_2Ga(pz)_2GaD_2$.

Table 1
Intramolecular parameters for $R_2Ga(pz^*)_2GaR_2$ complexes

Compound	Ga–Ga distance (Å)	V-angle (deg)
1	3.529	127.4
2	3.652	131.5
3	3.663	139.5
4	3.736	147.8
5	3.840	180

V-angle for each of these compounds. The V-angle is the angle between the two planar $Ga_2N_2C_3$ groups and defines the amount of pucker of the boat configuration. As the steric demands in the molecules increase, the shape of the ring flattens until, with compound **5**, the ring is planar. The increase in steric strain for **5** is also indicated by its reactivity. Compounds **1**–**4** are air-stable, but **5** hydrolyzes to $(CH_3)_2Ga(OH)(3,5\text{-}Me_2pz)Ga(CH_3)_2$.

A series of additional dimethylgallylazoles were also prepared by treatment of various azoles (imidazoles, benzimidazoles, pyrazoles, s-triazole and benzotriazole) with Me_3Ga [7]. The reaction of the dimethylgallylpyrazole derivative with alkyl halides and acid chlorides was also studied [8].

3. Bis(pyrazolyl)borate complexes of gallium

The reaction of two and three equivalents of $[H_2B(pz)_2]^-$ with $GaCl_3$ leads to the formation in high yield of $[H_2B(pz)_2]_2GaCl$ (**6**) and $[H_2B(pz)_2]_3Ga$ (**7**), respectively [9]. The solid-state structure of **6** was determined crystallographically [9,10] and is shown in Fig. 2. The structure is a nearly perfect trigonal bipyramid. Each $[H_2B(pz)_2]^-$ ligand occupies one axial and one equatorial position, with the chlorine atom in the remaining equatorial site. The angles formed from the axial and equatorial sites are 89.2(1)° and 91.0(1)°, and within the equatorial plane the Cl–Ga–N angles are 121.2(1)° and the N–Ga–N angle is 117.5(1)°. This compound is a

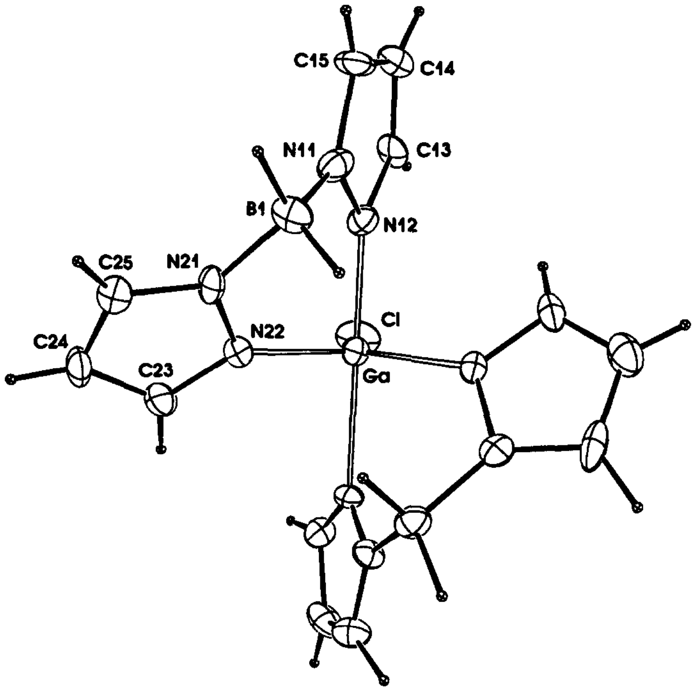


Fig. 2. Solid-state structure of $[H_2B(pz)_2]_2GaCl$.

relatively rare example of neutral five-coordinate gallium(III), especially with ligands containing nitrogen donor atoms [11].

The reaction of one equivalent of $[H_2B(pz)_2]^-$ with $GaCl_3$ yields the ionic compound $\{[H_2B(pz)_2]_2Ga\}GaCl_4$ [12]:

$$2GaCl_3 + 2K[H_2B(pz)_2] \rightarrow \underset{\mathbf{8}}{\{[H_2B(pz)_2]_2Ga\}GaCl_4} + 2KCl \qquad (1)$$

Formation of an ionic product is prevented by using $Ga(CH_3)Cl_2$ as the starting material in a similar reaction:

$$CH_3GaCl_2 + K[H_2B(pz)_2] \rightarrow \underset{\mathbf{9}}{[H_2B(pz)_2]Ga(CH_3)Cl} + KCl \qquad (2)$$

Complex **9** also forms in the exchange reaction of $[H_2B(pz)_2]_2GaCl$ and $(CH_3)_2GaCl$ [12]:

$$[H_2B(pz)_2]_2GaCl + (CH_3)_2GaCl \rightarrow 2[H_2B(pz)_2]Ga(CH_3)Cl \qquad (3)$$

In this reaction, a bis(pyrazolyl)borate ligand as well as a methyl group must undergo transmetallation. Molecular weight studies show that **9** is monomeric in benzene solution. The analogous complex with the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand, $[H_2B(3,5\text{-}Me_2pz)_2]Ga(CH_3)Cl$, has also been prepared [13].

The dimethyl complex, $[H_2B(pz)_2]Ga(CH_3)_2$, is prepared from $(CH_3)_2GaCl$ as shown in Eq. (4) [12,14]:

$$(CH_3)_2GaCl + K[H_2B(pz)_2] \rightarrow \underset{\mathbf{10}}{[H_2B(pz)_2]Ga(CH_3)_2} + KCl \qquad (4)$$

$[H_2B(3,5\text{-}Me_2pz)_2]Ga(CH_3)_2$ forms in an analogous reaction of the substituted ligand [13]. Complex **10** can be also be prepared by the reaction of **9** with CH_3Li.

Starting with $[(CH_3)_2B(pz)_2]^-$, the complex $[(CH_3)_2B(pz)_2]Ga(CH_3)_2$ (**11**) has been prepared and structurally characterized [14]. As shown in Fig. 3, the molecule adopts an asymmetric boat configuration with the boron atom located considerably above the N_4 plane of the nitrogen atoms in the six-member ring.

Also reported was the very similar structure of $[(CH_3)_2B(pz)_2]Ga(CH_3)(OH)$, a hydrolysis product of **11** [14]. The complexes $[R_2B(pz)_2]Ga(CH_2CH_3)_2$ ($R = C_2H_5$, C_6H_5, pz) have also been reported [15].

The reaction of two equivalents of $[H_2B(pz)_2]^-$ with $Ga(CH_3)Cl_2$ yields $[H_2B(pz)_2]_2GaCH_3$:

$$CH_3GaCl_2 + 2K[H_2B(pz)_2] \rightarrow \underset{\mathbf{12}}{[H_2B(pz)_2]_2GaCH_3} + 2KCl \qquad (5)$$

Complex **12** can also be prepared from the reaction of a variety of alkylation reagents, such as CH_3Li and CH_3MgBr, with **6**, but the reactions produce a number of by-products, mainly **10** [12].

The reaction of the ionic compound **8** with one equivalent of CH_3Li gave the expected product **12** in only low yield. The main product of the reaction was **10**. In a reaction of four equivalents of CH_3Li and **8**, complex **10** is isolated in high yield *based on both gallium atoms in* **8** [12]:

$$\{[H_2B(pz)_2]_2Ga\}GaCl_4 + 4CH_3Li \rightarrow 2[H_2B(pz)_2]Ga(CH_3)_2 + 4LiCl \qquad (6)$$

As in the exchange reaction shown in Eq. (3), a bis(pyrazolyl)borate ligand undergoes transmetallation in reaction (6).

The dihydrobis(pyrazolyl)borate ligand imparts considerable stability to these

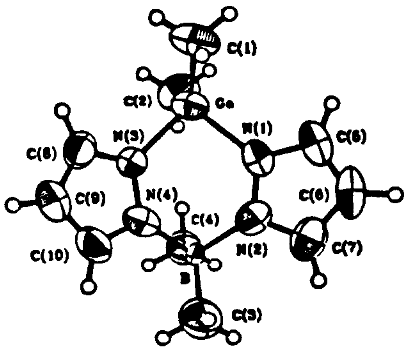


Fig. 3. Solid-state structure of $[(CH_3)_2B(pz)_2]Ga(CH_3)_2$.

complexes. The three organometallic complexes **9**, **10** and **12** are stable in air both as solids and in solution. In contrast, the CH_3GaCl_2 and $(CH_3)_2GaCl$ starting materials flame in air. Because of the high reactivity of these two compounds, they were generated in situ in the syntheses discussed above.

The dimethyl derivative **10** reacts with one equivalent of CH_3CO_2H, even when the acid is present in excess:

$$[H_2B(pz)_2]Ga(CH_3)_2 + CH_3CO_2H \rightarrow \underset{\mathbf{13}}{[H_2B(pz)_2](CH_3)Ga(O_2CCH_3)} + CH_4 \qquad (7)$$

Compound **13** can also be prepared from CH_3GaCl_2 and stoichiometric amounts of the two ligand salts. Molecular weight studies in benzene show that this air-stable complex is a monomer in solution [12].

As observed with **13**, the five-coordinate organometallic complex **12** does not react with acetic acid. Thus, it is possible to eliminate one methyl ligand from the dimethyl complex **10** with acetic acid, but it is not possible to eliminate a methyl ligand with acetic acid from the organometallics **12** or **13**, containing two chelate ligands. It has been shown previously that acetic acid will cleave either one or two methyl ligands from $(CH_3)_3Ga$, but not the third [16].

The expected product of the reaction of **12** with acetic acid, $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ forms in the reaction of $GaCl_3$ and stoichiometric amounts of the two ligand salts. It also forms in the exchange of one of the bis(pyrazolyl)borate ligands in **7** with acetic acid [12]:

$$[H_2B(pz)_2]_3Ga + CH_3CO_2H \rightarrow \underset{\mathbf{14}}{[H_2B(pz)_2]_2Ga(O_2CCH_3)} + H[H_2B(pz)_2] \qquad (8)$$

Molecular weight studies indicate that **14** is partially associated in benzene solution, but X-ray crystallography shows that the compound is monomeric, with a distorted-octahedral structure, in the solid phase [12].

4. Tris- and tetrakis(pyrazolyl)borate complexes of gallium

The reaction of equimolar amounts of $GaCl_3$ and $K[HB(3,5\text{-}Me_2pz)_3]$ yields $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}\{GaCl_4\}$ [17]. The complex was characterized in the solid state by X-ray crystallography, Fig. 4. The cation contains a nearly octahedral arrangement of the nitrogen donor atoms. The two planes formed by each of the three nitrogen atom donor atoms of each ligand are parallel. Given the formal analogy between hydrotris(pyrazolyl)borate and cyclopentadienyl ligands, the $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}^+$ cation corresponds to the unknown "gallocene" cations.

The reactions of $[B(pz)_4]^-$ or $[HB(pz)_3]^-$ and $GaCl_3$ yield the analogous products, $\{[B(pz)_4]_2Ga\}\{GaCl_4\}$ and $\{[HB(pz)_3]_2Ga\}\{GaCl_4\}$, respectively [18]. Surprisingly, the $\{[HB(pz)_3]_2Ga\}^+$ cation, with $[Ga(CH_3)Cl_3]^-$ as the counter-ion,

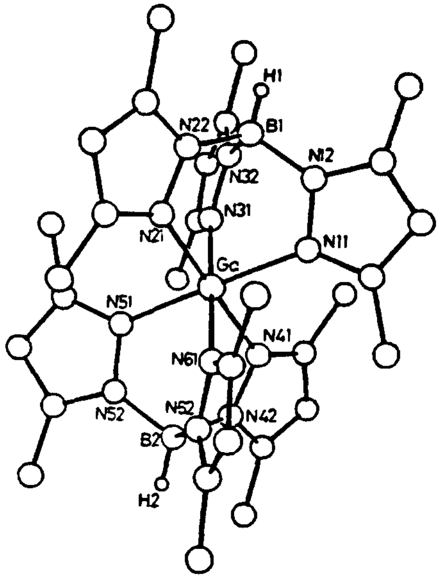


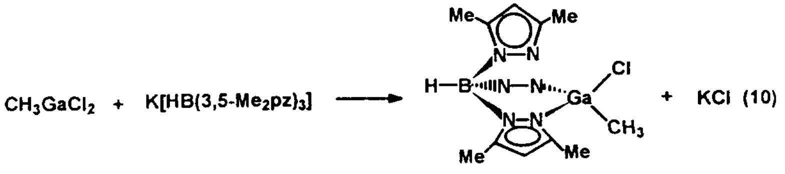
Fig. 4. Solid-state structure of the cation in $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}\{GaCl_4\}$.

is also formed in the reaction of one equivalent of $[HB(pz)_3]^-$ and $GaCH_3Cl_2$:

$$CH_3GaCl_2 \xrightarrow{K[HB(pz)_3]} \{[HB(pz)_3]_2Ga\}\{Ga(CH_3)Cl_3\} \tag{9}$$

In this case a methyl group, as well as the chlorides, is displaced by the $[HB(pz)_3]^-$ ligands. The driving force for this unusual reaction must be the formation of the extremely stable, octahedral gallium cations.

In contrast to reaction (9), one equivalent of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand reacts with $GaCH_3Cl_2$ to yield $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$:



15

The NMR spectra of **15** show the pyrazolyl rings as equivalent, even at −90 °C. As there is no geometry for which the rings are equivalent, the molecule must be dynamic in solution. The solid-state structure (Fig. 5) shows that the molecule is four-coordinate, with a distorted tetrahedral geometry about the gallium atom. The N12–Ga–N22 angle is restricted by the chelate ring to 97.3(3)° and the Cl–Ga–Cl angle trans to it is 107.9(3)°. The chloride ligand is rotated toward the nitrogen donor atoms, reducing the Cl–Ga–N angles to an average of 99.3° and the methyl

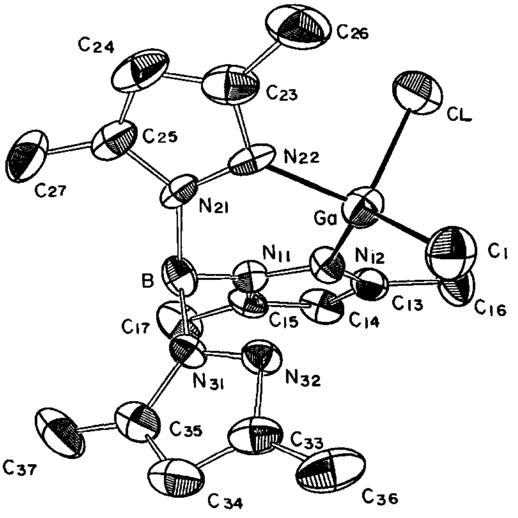
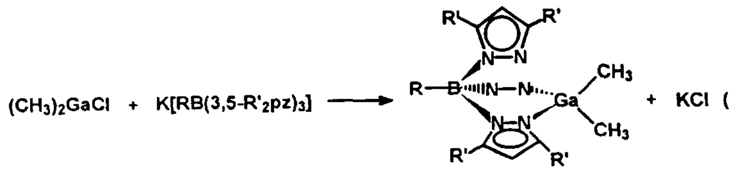


Fig. 5. Solid-state structure of [HB(3,5-$Me_2pz)_3$]Ga(CH_3)Cl.

ligand is rotated away from the nitrogen donor atoms giving an average C1–Ga–N angle of 124.0°.

The bidentate hydrotris(3,5-dimethylpyrazolyl)borate ligand retains its "umbrella" shape, with the long pyrazolyl ring Ga–N32 distance of 2.897(7) Å, nearly 1 Å longer than the normal bonding interactions. The proximity of this donor atom to the metal appears to be the reason for the asymmetric arrangement of methyl and the chloride ligands. The asymmetry can be explained by either the presence of a weak bonding interaction with the lone pair on N32 or simply non-bonding steric effects. If the long interaction is considered as a weak bond, the geometry about the gallium atom can be viewed as trigonal bipyramidal, with the long bond and the chlorine atom in the axial positions [18].

The ligands $[HB(pz)_3]^-$, $[HB(3,5\text{-}Me_2pz)_3]^-$ and $[B(pz)_4]^-$ all react with $Ga(CH_3)_2Cl$ to yield the respective (ligand)$Ga(CH_3)_2$ complex:



(11)

R = H, R' = H, CH_3; R = pz, R' = H

The solid-state structure of [HB(3,5-$Me_2pz)_3$]Ga$(CH_3)_2$ (**16**, Fig. 6) shows it is four-coordinate at gallium [18]. One of the pyrazolyl rings is clearly not bonded to the gallium, with a Ga–N32 distance of 3.420(8) Å. As with **15**, the methyl ligands are rotated away from the non-coordinated pyrazolyl ring, with average C1–Ga–N

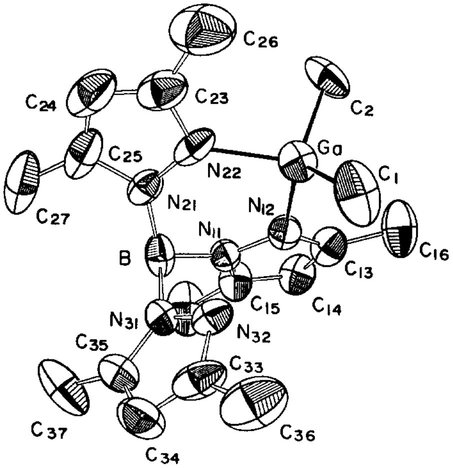


Fig. 6. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$.

angles of 115.1(5)° and C2–Ga–N angles of 105.3(4)°, but the distortion is considerably less in this case.

At ambient temperature, **16** shows single resonances in ^1H NMR spectra for each of the three types of hydrogen atoms in the pyrazolyl rings, and a single resonance for the two methyl groups on gallium. At low temperatures the resonance types for the pyrazolyl rings are in a 2:1 ratio, and the methyl groups on gallium become non-equivalent. This is the spectrum expected from the solid-state structure. The barrier to the dynamic process for **16** is 13.7 kcal mol^{-1}, as measured for the methyl ligand resonances at 6 °C [18].

The differences in the observed NMR behavior of **15** and **16** are surprising. In both cases the most reasonable dynamic process to explain the equilibration of the resonances for the ring hydrogen atoms at ambient temperatures is an intramolecular rearrangement involving an association–dissociation mechanism of the pyrazolyl rings going through a five-coordinate intermediate. The proximity of the third pyrazolyl ring to the gallium for **15** may considerably lower the barrier to such a process for this molecule in comparison to **16**, leading to the observed lower rearrangement barrier.

The reaction of two equivalents of $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ with $GaCH_3Cl_2$ yields the respective $(ligand)_2GaCH_3$ complexes:

$$GaCH_3Cl_2 + 2K[RB(pz)_3] \rightarrow [RB(pz)_3]_2GaCH_3 + 2KCl \qquad (12)$$

where R = H, pz. In contrast, a similar reaction with two equivalents of $[HB(3,5\text{-}Me_2pz)_3]^-$ yields $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ [18].

The solid-state structure of $[B(pz)_4]_2GaCH_3$ (**17**, Fig. 7) shows that the gallium is six-coordinate, and the molecule contains *both tridentate and bidentate* $[B(pz)_4]^-$ *ligands*. The arrangement of the donor atoms is nearly octahedral. The orientation of the boat-shaped BN_4Ga ring of the bidentate ligand places the boron "up" on

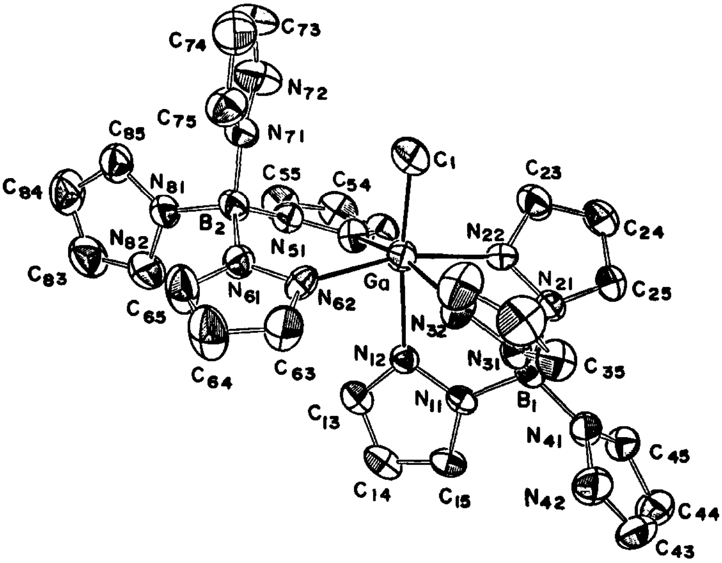


Fig. 7. Solid-state structure of $[B(pz)_4]_2GaCH_3$.

the same side of the octahedron as the methyl ligand. This arrangement allows the coordinated pyrazolyl ring trans to the methyl ligand to bisect the two coordinated rings of the bidentate ligand [18].

5. Bis(pyrazolyl)borate complexes of indium

The reaction of three equivalents of $[H_2B(pz)_2]^-$ with $In(NO_3)_3$ in water [19] or with $InCl_3$ in THF [20] yields $[H_2B(pz)_2]_3In$. The compound is distorted octahedral in the solid state (Fig. 8), with the distortion caused by the intraligand bite angle, which averages 86.5°. As expected, the three BN_4In rings are in boat configurations, but surprisingly the puckering is not in the same sense for all three ligands, with B1 puckered in the opposite sense from B2 and B3.

By appropriate control of starting material and stoichiometry, the complete series of complexes of the general formula $[H_2B(pz)_2]_mInCl_n(CH_3)_p$ $(m+n+p=3)$ has been prepared [20]. In contrast to the chemistry of gallium, the 1:1 reaction of the ligand and $InCl_3$ yields the neutral complex $[H_2B(pz)_2]InCl_2$ (**18**) rather than an ionic compound analogous to **8**. Although **18** does form, the yield of the reaction is low, and it is the only complex of the series that is not air and thermally stable. The complexes $[H_2B(3,5\text{-}Me_2pz)_2]In(CH_3)Cl$, $[H_2B(3,5\text{-}Me_2pz)_2]In(CH_3)_2$ and $[H_2B(3,5\text{-}Me_2pz)_2]_2InCH_3$ have also been prepared [13].

In addition to the direct reaction, the complex $[H_2B(pz)_2]In(CH_3)Cl$ (**19**) can also be prepared by the exchange reaction of $[H_2B(pz)_2]_2InCl$ and $(CH_3)_2InCl$. It is monomeric in benzene solution. In the solid state (Fig. 9), **19** is a weakly associated

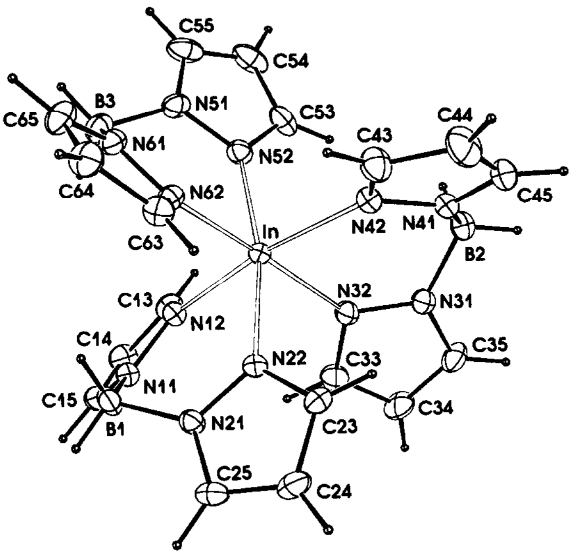


Fig. 8. Solid-state structure of $[H_2B(pz)_2]_3In$.

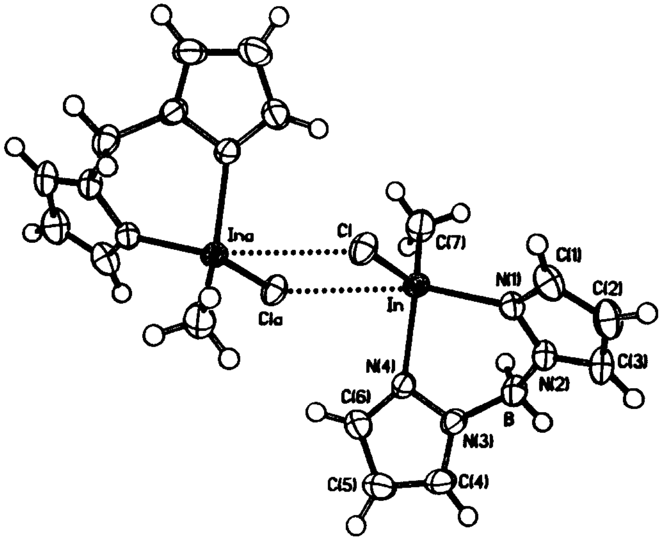


Fig. 9. Solid-state structure of $[H_2B(pz)_2]In(CH_3)Cl$.

dimer held together by a pair of very asymmetrically bonded chlorine atoms [20]. The shorter In–Cl bond distance is 2.410(1) Å and the long In–Cl bond distance is 3.203(1) Å.

The geometry about the indium atom is best described as a distorted trigonal bipyramid with the axial positions occupied by the bridging chlorine atom with the long In–Cl bond and the N(1) nitrogen atom of the bis(pyrazolyl)borate ligand. The axial N(1)–In–Cl(a) bond angle of 162.9(1)° is fairly close to the 180° angle expected for a trigonal bipyramid. The three equatorial bond angles (119.2(1), 128.0(1) and 104.7(1)°) are also close to the expected angle of 120°. The largest distortion is the C(7)–In–N(1) bond angle of 113.6(2)°, considerably different from the expected 90° axial-equatorial angle.

The solid-state structure of $[H_2B(pz)_2]In(CH_3)_2$ (**20**) has also been determined crystallographically (Fig. 10) [18]. The molecule is clearly a four-coordinate monomer with no close intermolecular contacts. The donor atoms are in a distorted tetrahedral arrangement. The natural bite angle of the bis(pyrazolyl)borate ligand restricts the N(1)–In–N(3) angle to 85.2(1)°. The C–In–N angles are fairly close to the tetrahedral angle, but the C(7)–In–C(8) angle is extremely large at 141.1(1)°. While it is reasonable to expect that this angle would open up somewhat in response to the low N(1)–In–N(3) angle opposite to it, the distortion is greater than would be expected from this alone. Large C–In–C angles are a feature that seems to be general for four-coordinate $In(CH_3)_2$-structures, where a range of values from 126.1(2) to 152.2(6)° has been observed previously [21]. Even in the anion $[In(CH_3)_2Br_2]^-$, which does not have any geometrical restraints imposed by chelate rings, the C–In–C angle is 135.0(6)° [21b]. Although this large bond angle is a common feature in $In(CH_3)_2$ compounds, the C–Ga–C bond angle in **16** is only 117.9(4)° [18].

The five-coordinate complexes, $[H_2B(pz)_2]_2InCl$, $[H_2B(pz)_2]_2InCH_3$ [20] and $[H_2B(3,5\text{-}Me_2pz)_2]_2InCH_3$ [13] are believed to have a trigonal bipyramidal structure with the Cl or CH_3 group in an equatorial site, similar to that observed for the gallium analog **6**. For the two methyl derivatives this structure is supported by ^1H NMR. At high temperatures, the molecules are fluxional, with only one resonance

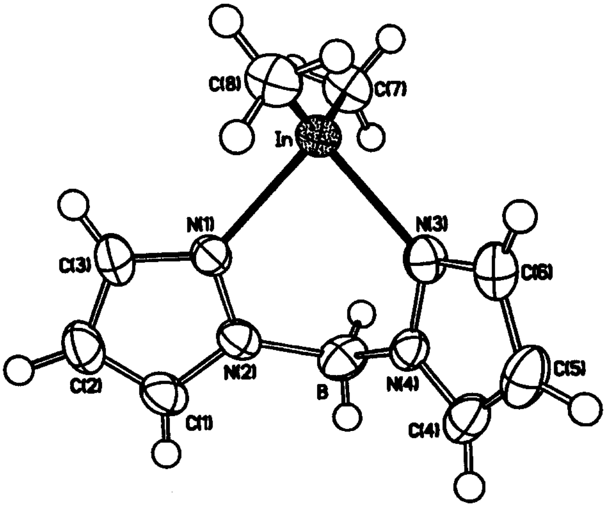


Fig. 10. Solid-state structure of $[H_2B(pz)_2]In(CH_3)_2$.

being observed for each of the three types of hydrogen atoms in the pyrazolyl rings. At low temperatures, each resonance type is split into two equal intensity resonances, as expected for axial and equatorial pyrazolyl rings. There is no change observed in the methyl resonances.

The complex $[H_2B(pz)_2]_2In(O_2CCH_3)$ forms in the reaction of $InCl_3$ with the ligand salts in appropriate proportions, from the reaction of $[H_2B(pz)_2]_3In$ or $[H_2B(pz)_2]_2InCH_3$ and CH_3CO_2H and from $[H_2B(pz)_2]_2InCl$ and the NaO_2CCH_3 [20]. The reaction of $[H_2B(pz)_2]_2InCH_3$ and CH_3CO_2H is particularly interesting, as the gallium analog **12** does not react with CH_3CO_2H under the same conditions. The mixed ligand complex $[H_2B(pz)_2]In(CH_3)(O_2CCH_3)$ (**21**) is prepared from the reaction of CH_3InCl_2 with the two ligand salts or from **20** and CH_3CO_2H. Molecular-weight studies indicate that **21** is dimeric in benzene solution [20]. In contrast, the analogous gallium compound is a monomer in solution [12].

6. Tris- and tetrakis(pyrazolyl)borate complexes of indium

The unusual indium(I) complex $[HB(3\text{-}Phpz)_3]In$ forms in the reaction of InI and $[HB(3\text{-}Phpz)_3]^-$ [22]. The structure was determined crystallographically (Fig. 11) and shows the indium in a pyramidal geometry. There are no close In–In contacts.

The reaction of $InCl_3$ and $[HB(3,5\text{-}Me_2pz)_3]^-$ yields, after recrystallization from CH_3CN, $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot CH_3CN$ (**22**) [17]. In contrast, the same reaction with $GaCl_3$ or $AlCl_3$ yields $\{[HB(3,5\text{-}Me_2pz)_3]_2M\}^+$ cations. The structure of **22** shows indium in an unsymmetrical, octahedral environment, Fig. 12 [17].

The THF adduct $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot THF$ (**23**) has also been isolated [23].

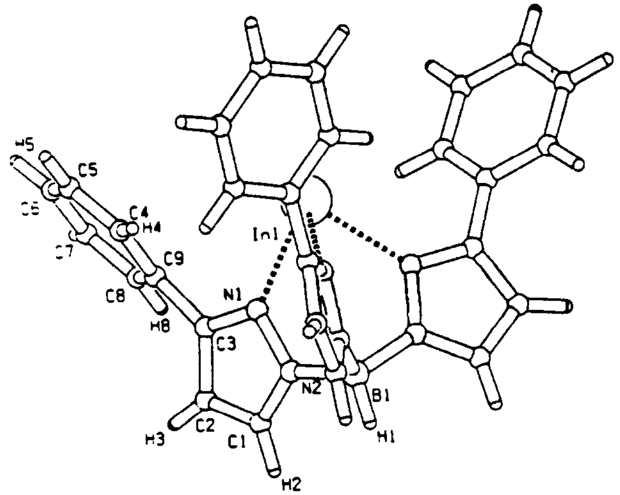


Fig. 11. Solid-state structure of $[HB(3\text{-}Phpz)_3]In$.

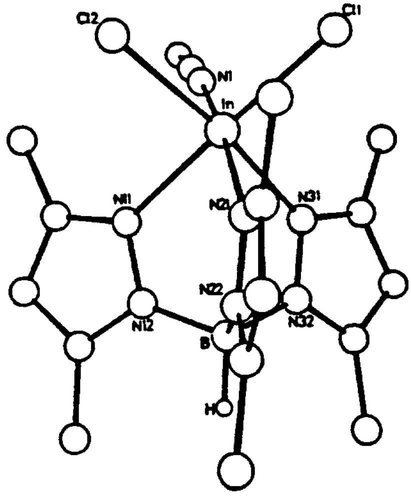


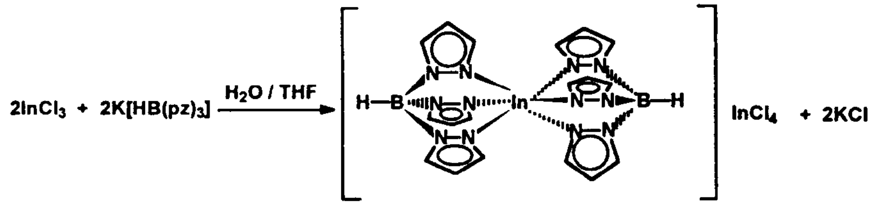
Fig. 12. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot CH_3CN$.

This compound is also the product isolated from the reaction of two equivalents 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 one equivalent of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCl_3$ in toluene. The product of this reaction is $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot H(3,5\text{-}Me_2pz)$ [23]. The only source of the $H(3,5\text{-}Me_2pz)$ ligand is decomposition of $[HB(3,5\text{-}Me_2pz)_3]^-$, apparently favored over the formation of five-coordinate $[HB(3,5\text{-}Me_2pz)_3]InCl_2$.

Cationic, six-coordinate complexes with two hydrotris(pyrazolyl)borate ligands about indium(III) form in the reactions of less bulky ligands than $[HB(3\text{-}Phpz)_3]^-$ with In(I) [24]. Thus, InI reacts with two equivalents of $K[HB(3,5\text{-}Me_2pz)_3]$ to yield $\{[HB(3,5\text{-}Me_2pz)_3]_2In\}I$. The structure of this complex is octahedral, with the planes of the two coordinating N_3 intraligand planes parallel. The analogous gallate cation, $\{[HGa(3,5\text{-}Me_2pz)_3]_2In\}^+$, was also prepared and structurally characterized [24].

The cation $\{[HB(pz)_3]_2In\}^+$ forms in a reaction of $K[HB(pz)_3]$ with InCl, and has also been prepared by halide abstraction from $[HB(pz)_3]_2InCl$ with $AgBF_4$, and by protonation of $[HB(pz)_3]_2InCH_3$ with $[HNEt_3][BPh_4]$ [23]. The $\{[HB(pz)_3]_2In\}^+$ cation is best prepared as the $InCl_4^-$ compound from the reaction of one equivalent of $[HB(pz)_3]^-$ and $InCl_3$ in a THF/H_2O solvent system [23].



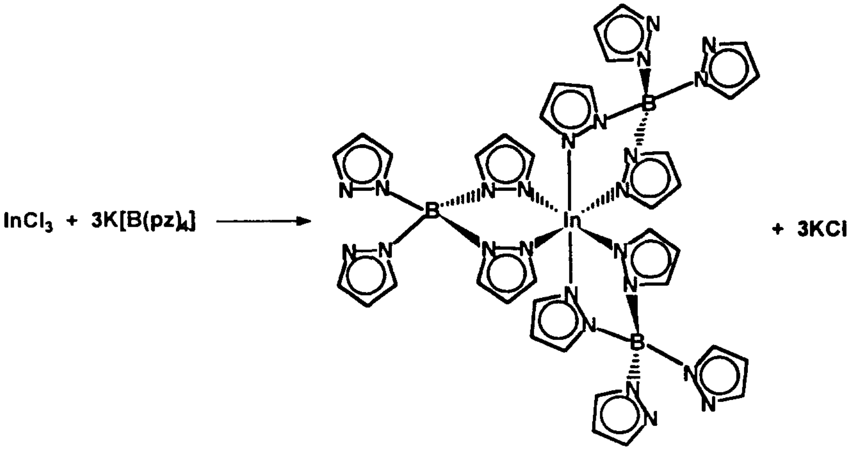
(13)

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

$$2InCl_3 + 3K[HB(pz)_3] \rightarrow \{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\} + 3KCl \qquad (14)$$

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 by crystallography (Fig. 13). The cation and anion show approximately octahedral coordination about the indium atoms [23].

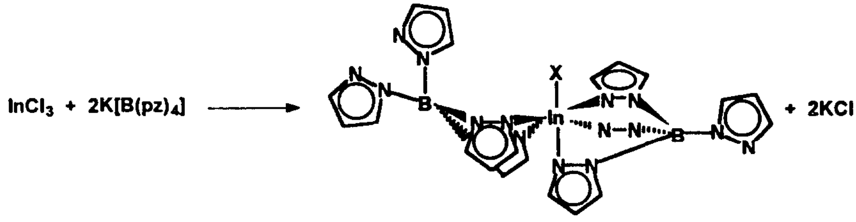
The reaction of three equivalents of $[B(pz)_4]^-$ with $InCl_3$ in either THF or THF/H_2O results in the formation of $[B(pz)_4]_3In$ in good yield [23]:



(15)

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 [19], $[H_2B(pz)_2]_3In$, is reasonable.

The reaction of $InCl_3$ and $In(CH_3)Cl_2$ with two equivalents of $K[B(pz)_4]$ yields the complexes $[B(pz)_4]_2InCl$ (**24**) and $[B(pz)_4]_2InCH_3$ (**25**), respectively:



(16)

X = Cl, CH$_3$

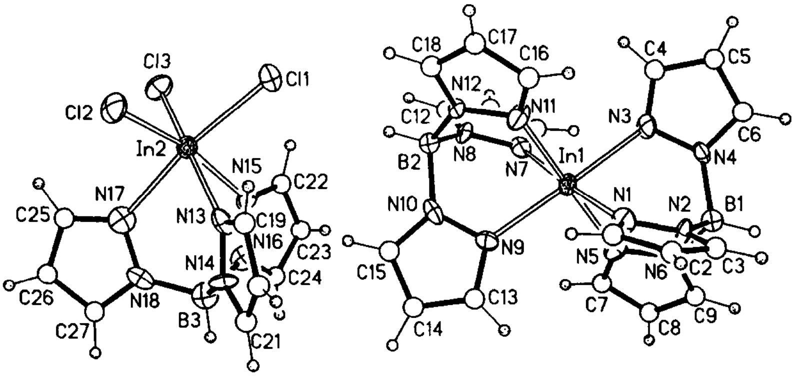
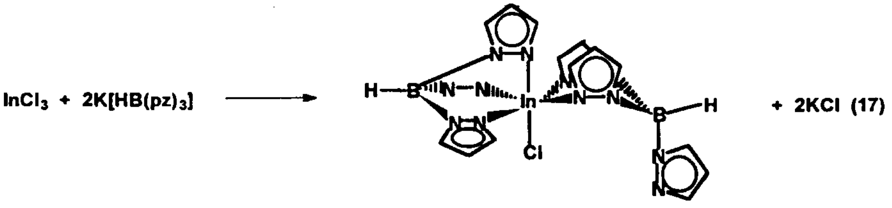


Fig. 13. Solid-state structure of $\{[HB(pz)_3]_2In\}\{[HB(pz)_3]InCl_3\}$.

The ambient-temperature ^1H NMR spectrum of **24** 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. These data are best explained by an octahedral structure with one bidentate and one tridentate ligand as pictured in the equation.

This structure in the solid state was confirmed for **25** by X-ray crystallography, Fig. 14 [23]. As observed in the gallium analog **17**, the bidentate ligand is oriented with the boron "up" on the same side of the octahedron as the methyl ligand. This arrangement places the hydrogen atom on C(4) between the coordinated pyrazolyl rings of the bidentate ligand. In all of the complexes with a bidentate and a tridentate poly(pyrazolyl)borate ligand, an unusually shielded hydrogen atom resonance, arising from the 3-position on a pyrazolyl ring, is observed. This shielding arises from the proximity of the 3-position hydrogen atom on the tridentate ligand that is oriented close to the aromatic ring currents in the coordinated pyrazolyl rings of the bidentate ligand.

The reaction of two equivalents of $[HB(pz)_3]^-$ with $InCl_3$ in THF results in the formation of $[HB(pz)_3]_2InCl$ (**26**) [23]:



This compound also forms in a reaction with three equivalents of $[HB(pz)_3]^-$, rather than $[HB(pz)_3]_3In$, the expected product given the analogous chemistry observed for ligands **A** and **C**. The ^1H NMR spectra of **26** in toluene-d_8 are as expected for a six-coordinate structure containing one bidentate and one tridentate

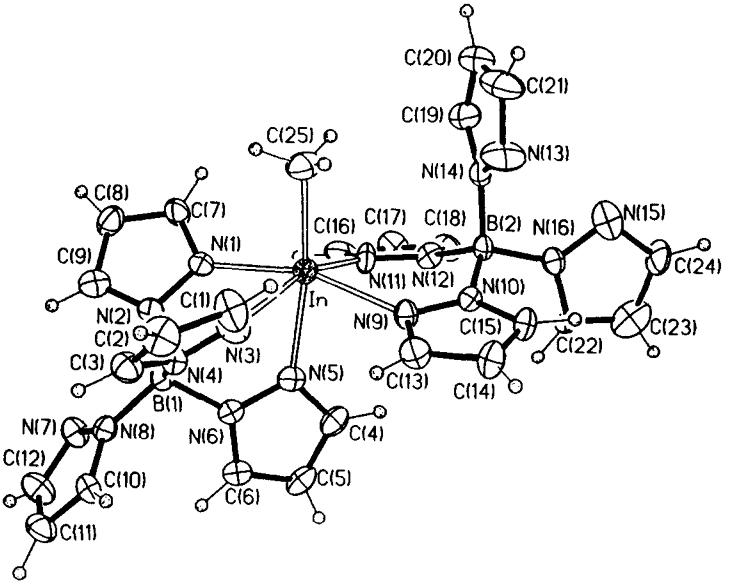
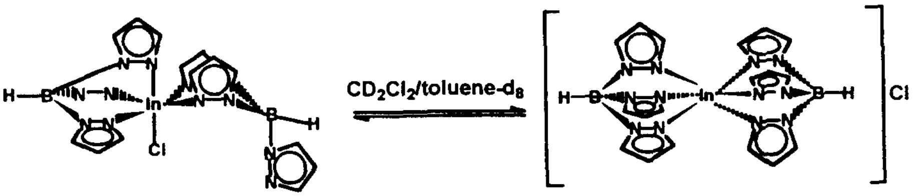


Fig. 14. Solid-state structure of $[B(pz)_4]_2InCH_3$.

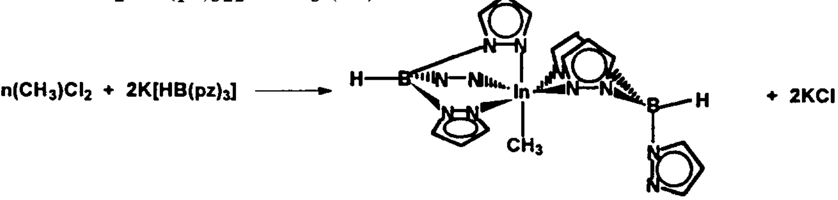
ligand, analogous to other $[\text{ligand}]_2MX$ (M = Ga, In; X = CH_3, Cl) complexes of these ligands. At low temperatures, each type of hydrogen atom shows resonances in a 2:2:1:1 ratio. An unusually shielded 3-position resonance at δ 6.29 is assigned to the hydrogen atom on the ring of the tridentate ligand in proximity to the pyrazolyl rings of the bidentate ligand, as discussed above [23].

In contrast, both ambient- and low-temperature spectra of **26** run in CD_2Cl_2 show just three sharp resonances, one for each type of hydrogen atom in the pyrazolyl rings. From the chemical shifts of the resonances in CD_2Cl_2, they clearly arise *not from* $[HB(pz)_3]_2InCl$, *but from cationic* $\{[HB(pz)_3]_2In\}^+$. 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*. In a 1:1 mixture of toluene-d_8 and CD_2Cl_2, resonances for both compounds are clearly observed at low temperatures. These resonances for the two compounds coalesce at higher temperatures. Thus dissolving $[HB(pz)_3]_2InCl$ in a 1:1 mixture of toluene-d_8 and 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:



(18)

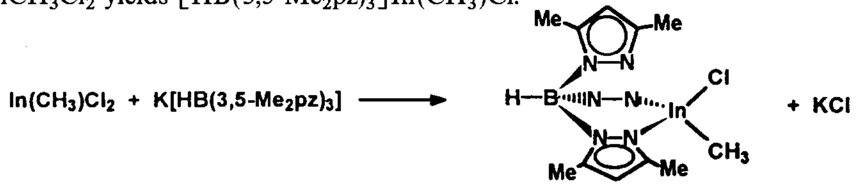
The reaction of $In(CH_3)Cl_2$ with two equivalents of $[HB(pz)_3]^-$ leads to the formation of $[HB(pz)_3]_2InCH_3$ (**27**):



(19)

Compound **27** can also be prepared from the reaction of CH_3Li with $[HB(pz)_3]_2InCl$ at −78 °C. This compound, rather than $[HB(pz)_3]In(CH_3)Cl$, is also isolated from the reaction of one equivalent of $[HB(pz)_3]^-$ with $In(CH_3)Cl_2$. The low-temperature NMR spectra, which include an unusually shielded resonance for a 3-position hydrogen atom, indicate the structure shown in the equation is correct [23].

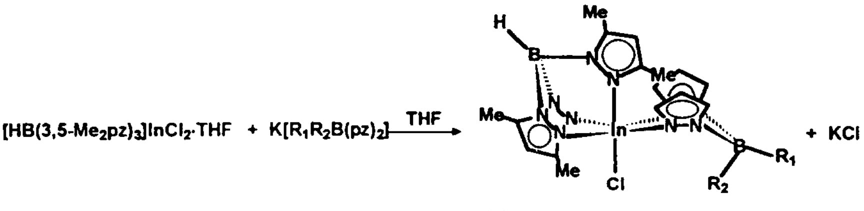
The reaction of either one or two equivalents of $[HB(3,5\text{-}Me_2pz)_3]^-$ with $InCH_3Cl_2$ yields $[HB(3,5\text{-}Me_2pz)_3]In(CH_3)Cl$:



(20)

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 $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(3,5\text{-}Me_2pz)_2]Cl$ has been prepared [25]. Although it is fluxional at ambient temperatures, the low-temperature ^1H NMR spectrum 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 $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)Cl$ 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, indicating a similar structure for $[HB(3,5\text{-}Me_2pz)_3]In(CH_3)Cl$. The reaction of $K[B(pz)_4]$ and $In(CH_3)_2Cl$ yields $[B(pz)_4]In(CH_3)_2$, which also has a similar four-coordinate structure [23].

Four mixed-ligand $[HB(3,5\text{-}Me_2pz)_3]In[poly(pyrazolyl)borato]Cl$ compounds have been prepared by the reaction of the THF adduct of $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ with an equivalent of the respective poly(pyrazolyl)borate ligand salts [25]:

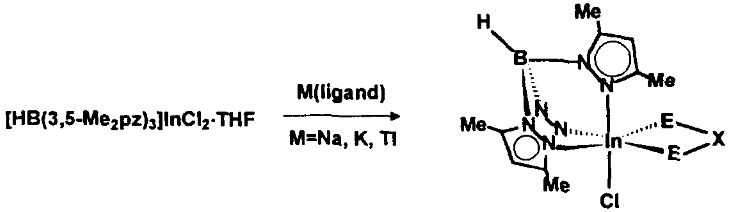


(21)

$R_1 = R_2 = H$, pz = 1-pyrazolyl
$R_1 = R_2 = H$, pz = 3,5-Me_2-1-pyrazolyl
$R_1 = H$, $R_2 = pz = 1$-pyrazolyl
$R_1 = R_2 = pz = 1$-pyrazolyl

The structure of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ has been determined crystallographically (Fig. 15). The complex is six-coordinate, and the geometry about the indium atom is a distorted octahedron. The arrangement of the ligands causes one 3-position methyl group (C6) of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand to be located between the aromatic rings of the bidentate ligand. Fig. 16 shows the ^1H NMR spectrum of this complex. The complex shows two types of 3,5-pyrazolyl rings in a 2:1 ratio, as expected from the solid-state structure. The ring currents of the two pyrazolyl rings of the bidentate ligand cause the 3-position methyl resonance of lower integration to be significantly shielded (the resonance at 0.15 δ).

Four complexes containing other types of uninegative, bidentate ligands have been prepared [25]:



(22)

E=S, X=CN(Et)$_2$
E=O, X=CCH$_3$
E=O, X=CH[CC(CH$_3$)$_3$]$_2$
E=O, X=CH[CCF$_3$]$_2$

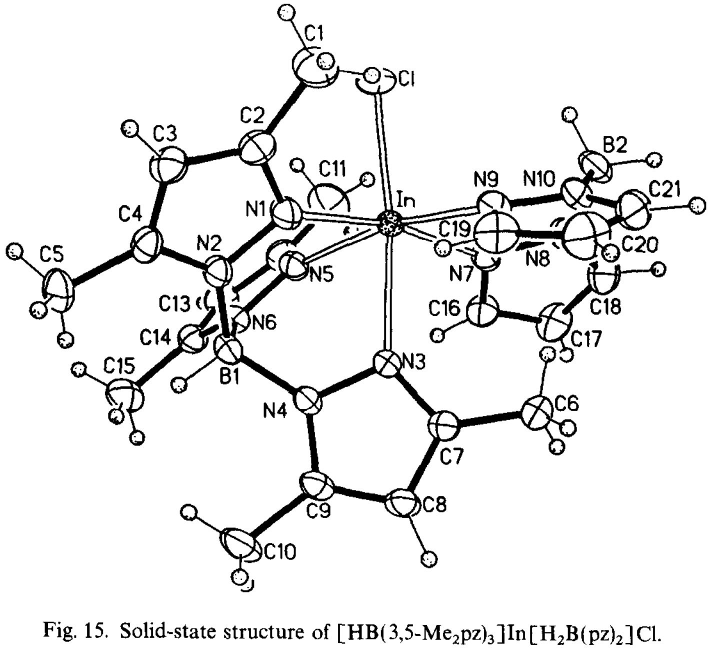


Fig. 15. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$.

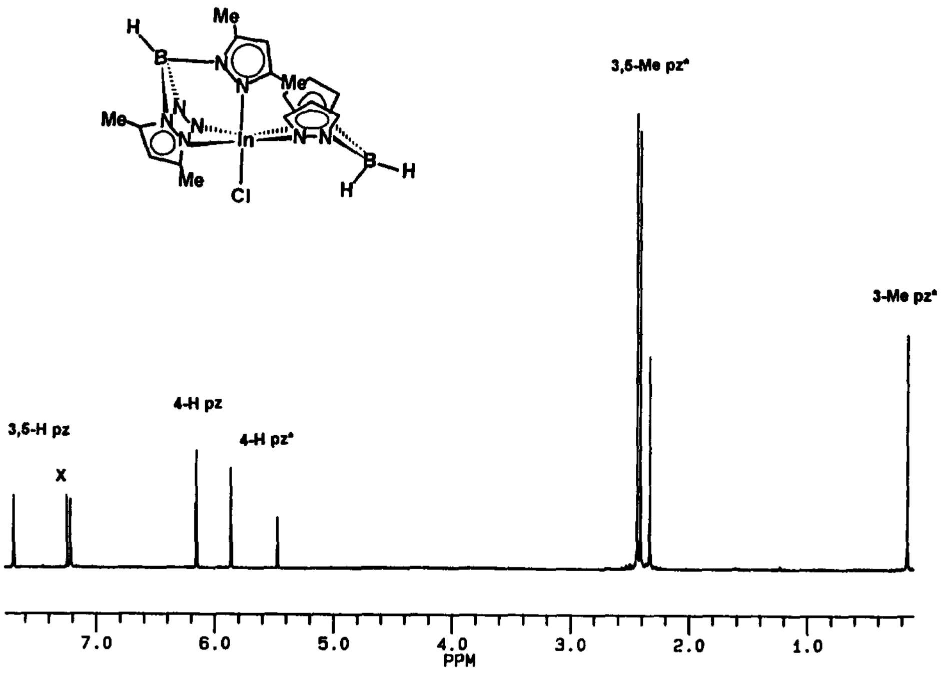
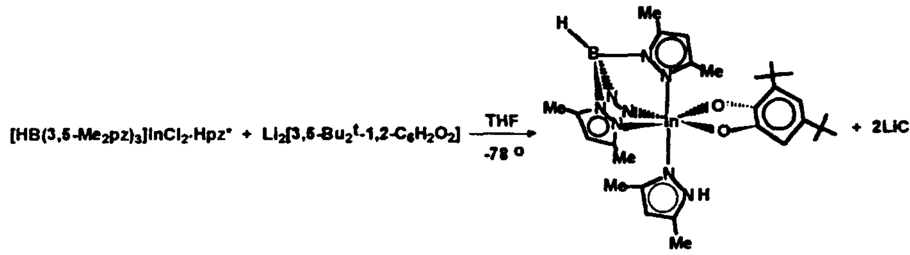


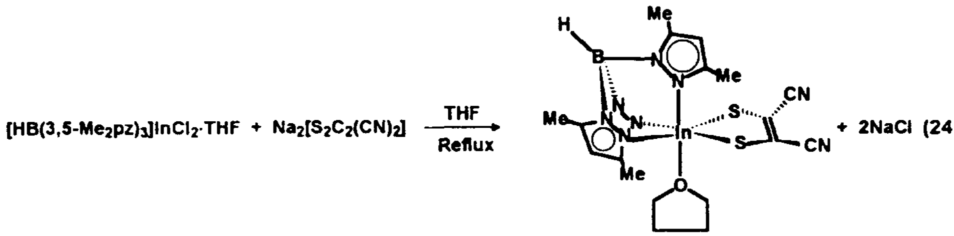
Fig. 16. ^1H NMR spectrum of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$. In the assignments, pz = pyrazolyl ring; pz* = 3,5-pyrazolyl ring.

Compounds of the dianionic ligands 3,5-di*tert*-butylcatecholate and maleonitriledithiolate were also prepared in THF, but at conditions other than ambient temperature. The complex $[HB(3,5\text{-}Me_2pz)_3]In[3,5\text{-}{}^tBu_2C_6H_2O_2]\cdot H(3,5\text{-}Me_2pz)$ was prepared by adding the dilithium salt of the ligand to the dimethyl pyrazolyl (pz*) adduct of $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ at −78 °C and slowly warming the solution to room temperature:



(23)

The complex $[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In\cdot THF$ was prepared by heating a THF solution of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ and $Na_2[S_2C_2(CN)_2]$ at reflux:



Both the catecholate and maleonitriledithiolate complexes retain the adduct of their starting material to remain six-coordinate. The solid-state structure of $[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In \cdot THF$ (Fig. 17) shows this compound is again six-coordinate, with the geometry around the indium a distorted octahedron. The bond distances indicate that the maleonitriledithiolate ligand clearly has a -2 charge, with the indium in the $3+$ oxidation state.

It is important to note that the success of the reactions in Eqs. (21)–(24) is based on the fact that it has not proven possible to prepare $[HB(3,5\text{-}Me_2pz)_3]_2InX$ complexes, a likely impurity in these types of reaction. Trofimenko has pointed out that for poly(pyrazolyl)borate complexes of metals in the $2+$ oxidation state, to prepare mixed ligand complexes it is important to use a poly(pyrazolyl)borate ligand with enough steric bulk (ligands with an isopropyl group or larger in the 3-position) to block formation of L_2M complexes, complexes that readily form with less bulky ligands [26]. In the case of indium in the $3+$ oxidation state, the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand appears bulky enough to prevent formation of L_2MX complexes.

The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ with K_2S_5 yields the first *neutral*

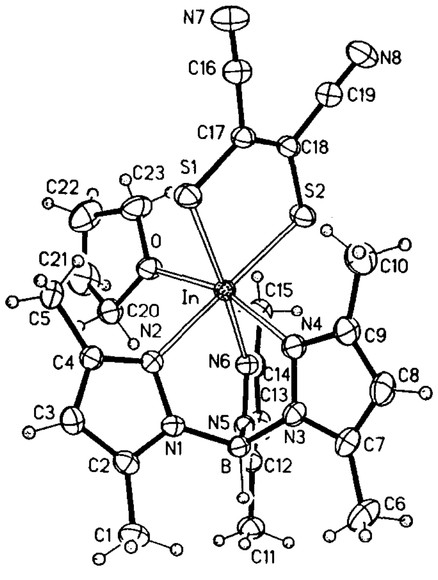


Fig. 17. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In \cdot THF$.

group-13 metal polysulfide complex $[HB(3,5\text{-}Me_2pz)_3]In(S_4)[3,5\text{-}Me_2pzH]$ (**28**) [27]. The coordinated 3,5-Me_2pzH ligand is apparently derived from the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand. Employing $[HB(3,5\text{-}Me_2pz)_3]InCl_2(3,5\text{-}Me_2pzH)$ as the indium starting material suppresses the destruction of the poly(pyrazolyl)borate ligand and results in an increased yield of the product. The solid-state structure of **28** (Fig. 18) reveals a distorted octahedral geometry about indium.

The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot THF$ with $Na_2Fe(CO)_4$ in THF yields $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ (**29**) [28]. The solid-state structure (Fig. 19) shows that the geometry about the iron atom is a trigonal bipyramid with the indium located at an axial position. The indium atom has pseudo-tetrahedral geometry, and the two metal halves of the molecule are oriented such that the pyrazolyl rings are staggered relative to the equatorial CO ligands on iron. The most important structural feature is the In–Fe bond length of 2.463(2) Å, the shortest In–Fe bond reported to date [29].

The short In–Fe bond can be explained by two alternative bonding descriptions. Given that **29** forms from displacement of two Cl^- ligands from $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ by $[Fe(CO)_4]^{2-}$, it can be considered as containing an In=Fe double bond. Alternatively, it can be viewed as containing an indium(I), $[HB(3,5\text{-}Me_2pz)_3]In$ group acting as a Lewis base to the Lewis acid $Fe(CO)_4(In \rightarrow Fe)$. Molecular orbital calculations indicate that little charge polarization exists in the iron–indium bond. Given the stability of the indium(I) complex $[HB(3\text{-}Phpz)_3]In$ [20], the latter bonding description is favored.

The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot THF$ with $Na_2W(CO)_5$ in THF yields

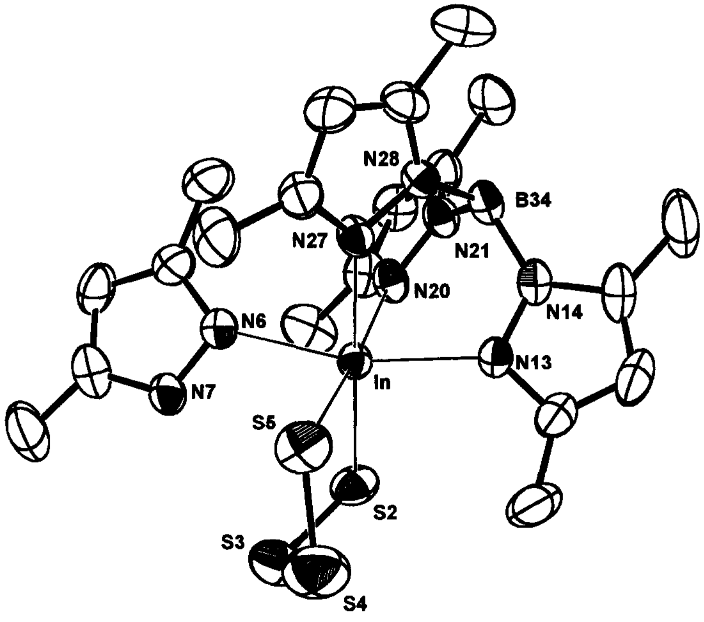


Fig. 18. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]In(S_4)[3,5\text{-}Me_2pzH]$.

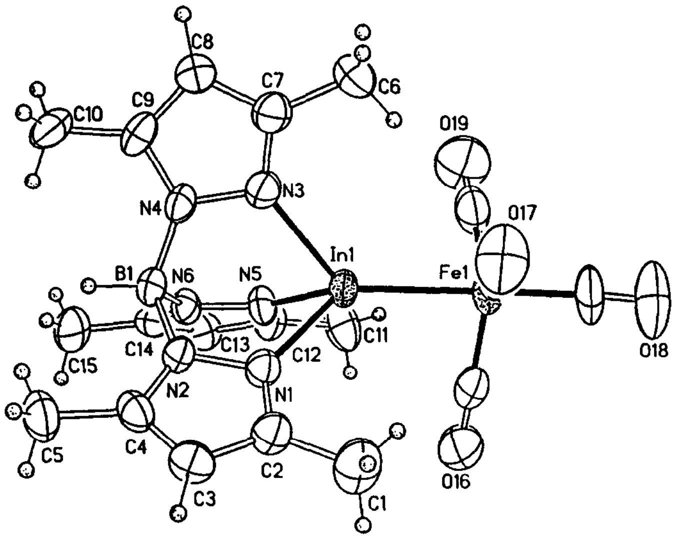


Fig. 19. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$.

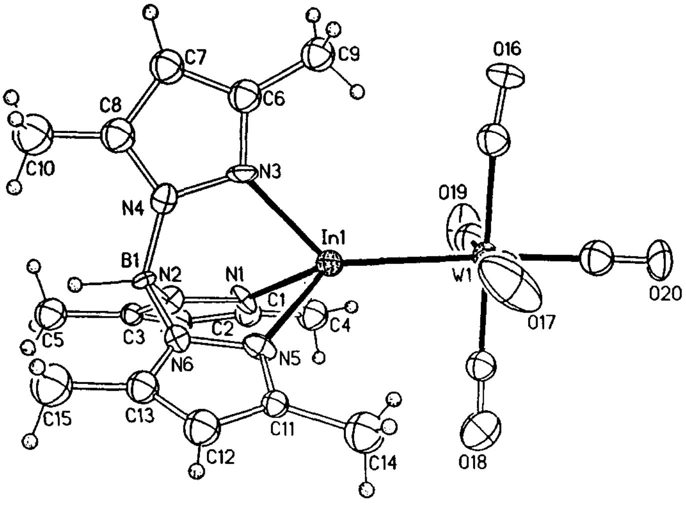


Fig. 20. Solid-state structure of $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$.

$[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$(**30**) [28]. This complex, with a In–W bond distance of 2.783(2) Å, is the first complex with an In–W bond to be structurally characterized (Fig. 20). The geometry about the tungsten atom is octahedral, and, as in the iron structure, the indium atom has pseudo-tetrahedral geometry. The structure is distorted somewhat by a close intramolecular contact between the methyl group from C9 and the O16 carbonyl oxygen atom. As with **29**, the bonding in **30** is best described as a dative bond arising from donation of a lone pair of electrons on indium(I) to the $W(CO)_5$ group.

7. Summary

A variety of stable coordination and organometallic complexes of gallium and indium have been prepared using poly(pyrazolyl)borate ligands. An important result of these studies is that in complexes of potentially multidentate poly(pyrazolyl)borate ligands these two metals prefer four- or six-coordination. The only five-coordinate complexes, $[H_2B(pz)_2]_2MX$, that have been prepared contain the dihydrobis(pyrazolyl)borate ligands. Six-coordinate $(ligand)_2MX$ complexes form readily with the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ligands, analogous complexes containing two of the bulkier $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand do not form. The $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand will form six-coordinate complexes of the type $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ (Lewis base), where the Lewis base is tightly bonded to indium. It is not possible to form the analogous gallium complex because 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 covalent as a solid and in non-polar solvents, but ionizes the chloride ligand to form the $\{[HB(pz)_3]_2In\}^+$ cation in CD_2Cl_2 solution. The complex $[B(pz)_4]_2InCl$ does not ionize in CD_2Cl_2. The complex $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ is an excellent starting material for the formation of complexes containing one poly(pyrazolyl)borate ligand and a second chelate ligand, either a second poly(pyrazolyl)borate or another type of ligand. It also reacts with main group and transition-metal dianions to form interesting types of complexes with indium–main group or indium–transition-metal bonds. A bulky poly(pyrazolyl)borate ligand stabilizes indium(I) in the complex $[HB(3\text{-}Phpz)_3]In$.

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