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Low-Valent Gallium, Indium, and Tin Compounds That Contain a Highly Fluorinated Tris(pyrazolyl)borate Ligand: Syntheses and Characterization of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$, and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$

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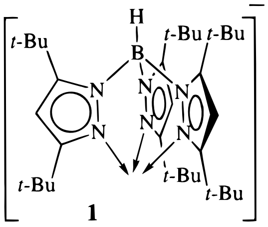
Syntheses and characterization of gallium(I), indium(I), and tin(II) complexes of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]^- =$ hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate)) are reported. X-ray crystal structures of $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$ show monomeric structures in the solid state. The In−N and Sn−N bond distances are longer than the corresponding bond distances of nonfluorinated analogues. NMR data of the gallium(I) adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$ are very similar to those of the indium(I) analogue suggesting similar solution structures.

Introduction

Tris(pyrazolyl)borate ligands play an important role in the study of low-valent, post-transition metal compounds.[1−3] Particularly noteworthy is their use in the isolation of monomeric, thermally and even air-stable compounds featuring gallium(I),[4] indium(I),[5−8] germanium(II),[9,10] and tin(II) ions.[11] Among these, tin(II) tris(pyrazolyl)borates[11−16] have attracted the most attention whereas only a very few examples of related germanium(II), gallium(I), or indium(I) derivatives presently known. Examples of indium(I) complexes synthesized using tris(pyrazolyl)borate ligands include $[HB(3\text{-}(Ph)Pz)_3]In$,[5] $[HB(3\text{-}(t\text{-}Bu)Pz)_3]In$,[7] and $[HB(3,5\text{-}(t\text{-}Bu)_2Pz)_3]In$.[6] A common trait in these compounds is the presence of bulky tris(pyrazolyl)borate ligands such as **1**. Products isolated using sterically less demanding ligands either show limited thermal stability or various degrees of aggregation.[5,17,18] With tin(II) however, even sterically less demanding ligands such as $[HB(Pz)_3]^-$ and $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$ are sufficient to generate thermally stable compounds, e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]SnCl$.[11,12] The first structurally characterized tris(pyrazolyl)borate featuring gallium(I), $[HB(3,5\text{-}(t\text{-}Bu)_2Pz)_3]Ga$, was reported by Parkin et al. in 1996.[4] A few germanium(II) derivatives $\{[HB(3,5\text{-}(CH_3)_2Pz)_3]Ge\}X$, where X = Cl, I, N_3, or PF_6, have also been reported recently.[9,10]



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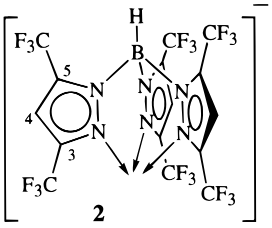

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An area of research focus in this laboratory is the chemistry of tris(pyrazolyl)borate ligands containing fluorinated substituents, e.g., $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**2**, where $[HB(3,5\text{-}(CF_3)_2Pz)_3]^- =$ hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate)).[8,19−27] These ligands are very different electronically compared to the analogous nonfluorinated systems. Considering the importance

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and current interest of low-valent main group species,[17,18,28−35] we have decided to investigate the use of these polyfluorinated tris(pyrazolyl)borates in group 13 and 14 chemistry. Our preliminary findings on this subject involving indium(I) was reported previously in a short communication.[8] Here we present full details of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ as well as the synthesis and characterization of closely related gallium(I) and tin(II) complexes, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources, distilled from conventional drying agents, and degassed twice prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz). Proton and carbon chemical shifts are reported in ppm vs Me_4Si. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$. Infrared spectra were recorded on a BioRad 40S spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Mass spectroscopic data were recorded on the Finnigan MAT TSQ 70 spectrometer. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer model 2400 CHN analyzer. Syntheses of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$, and "GaI" were carried out as reported previously.[8,22,36] InCl and $Sn(CF_3SO_3)_2$ were purchased from commercial sources.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$, 3: GaI (270 mg, 1.37 mmol) and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$ (560 mg, 0.62 mmol) were mixed in 20 mL of toluene and stirred overnight at room temperature. The resulting gray/black mixture was filtered through a bed of Celite. The precipitate was washed with hexane, and the filtrate and hexane washings were collected and combined. This mixture was concentrated under reduced pressure to obtain a white solid. The analytically pure product was obtained by extracting the solid into warm hexane followed by the removal of volatile materials under vacuum at room temperature. Yield: 56%. Mp: **3** slowly decomposes around 140 °C. ^1H NMR (C_6D_6): d 6.03 (s, CH). ^{19}F NMR (C_6D_6): δ −58.6 (s), −58.7 (d, $J = 3.2$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 107.1 (s, CH), 119.3 (q, $J = 269$ Hz, CF_3), 120.4 (q, $J = 273$ Hz, CF_3), 140.5 (br, CCF_3), 143.9 (q, $J = 38$ Hz, CCF_3). IR (Nujol), cm^{-1}: 2645 (BH). EI-MS: *m/z* 690. Anal. Calcd for $C_{15}H_4N_6BGaF_{18}$: C, 26.08; H, 0.58; N, 12.17. Found: C, 26.40; H, 0.69; N, 12.36.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]In$, 4. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (1.1 g, 1.37 mmol) in THF (30 mL) was treated with InCl (216 mg, 1.44 mmol) at −70 °C. The reaction mixture immediately became brown. After being stirred for 5 h at −70 °C, the mixture was brought to room temperature and stirred for a further 12 h. The solvent was removed under vacuum, and the residue was extracted into toluene. Filtration over Celite, followed by the removal of solvent from the filtrate, yielded $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ as a colorless solid (78% yield). The X-ray-quality crystals were grown from *n*-hexane at −25 °C. Mp: **4** turns opaque at 85 °C. ^1H NMR (C_6D_6): δ 6.16 (s, CH). ^{19}F NMR (C_6D_6): δ −58.4, −58.5 (d, $^5J = 3.5$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 107.1 (s, CH), 119.5 (q, $^1J(C,F) = 271$ Hz, CF_3), 120.9 (q, $^1J(C,F) = 271$ Hz, CF_3), 140.8 (q, $^2J(C,F) = 39$ Hz, CCF_3), 143.9 (q, $^2J(C,F) = 39$ Hz, CCF_3). IR (Nujol), cm^{-1}: 2636 (BH). MS: *m/z* 736. Anal. Calcd for $C_{15}H_4N_6BInF_{18}$: C, 24.48; H, 0.55; N, 11.42. Found: C, 24.68, H, 0.86, N, 11.04.

Table 1. Crystal Data and Structure Refinement Parameters for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)\cdot 3,5\text{-}(CF_3)_2PzH$

formula	$C_{21}H_6BF_{27}N_8O_3SSn$	fw	1092.9
a, Å	10.203(1)	space group	$P2_1/n$
b, Å	15.194(1)	T, K	193(2)
c, Å	22.096(2)	λ (Mo Kα), Å	0.710 73
α, deg	90	ρ(calc), g/cm^3	2.142
β, deg	98.299(6)	μ, mm^{-1}	1.008
γ, deg	90	R1, wR2 ($I > 2\sigma(I)$)[a]	0.0290, 0.0749
V, Å^3	3389.7(6)	R1, wR2 (all)[a]	0.0347, 0.0783
Z	4	GOF (on F^2)	1.068

[a] $R1 = \sum||F_o| - |F_c||/\sum |F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)\cdot 3,5\text{-}(CF_3)_2PzH$, 5. A CH_2Cl_2 solution (20 mL) of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(OH_2)$ (463 mg, 0.7 mmol) was treated with tin(II) triflate (291 mg, 0.7 mmol) in CH_2Cl_2 (20 mL) at −70 °C. After 30 min, this mixture was slowly brought to room temperature and stirred for a further 2 h. The solution was filtered through Celite, and the filtrate was concentrated under reduced pressure and stored at −20 °C to obtain colorless crystals of **5** (65% yield). Mp: **5** decomposes around 110 °C. ^1H NMR ($CDCl_3$): δ 6.89 (s, 1H, $3,5\text{-}(CF_3)_2PzH$), 7.08 (s, 3H, CH), 10.4 (br, NH). ^{19}F NMR ($CDCl_3$): δ −59.2 (s), −59.7 (d, $^5J(F,H) = 3.0$ Hz), −61.9 (br s; $3,5\text{-}(CF_3)_2PzH$), −78.8 (s, CF_3SO_3). IR (Nujol), cm^{-1}: 3655, 3221, 3169, 3128, 2653 (BH), 1659, 1498, 1460, 1049, 985, 846, 781, 739. MS: *m/z* 741 ($[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn^+$, 100%). Anal. Calcd for $C_{21}H_6N_8BF_{27}SO_3Sn$: C, 23.08; H, 0.55; N, 10.25. Found: C, 22.75; H, 0.25; N, 9.76.

Crystallographic Data Collection and Structure Determinations. A colorless crystal of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)\cdot 3,5\text{-}(CF_3)_2PzH$ (**5**) was mounted on a glass fiber with a small amount of Paratone-N oil/grease and placed in the dinitrogen cold stream of a Siemens P4 diffractometer equipped with a LT-2A device. Cell parameters were determined using 29 reflections. Data were corrected for Lorentz and polarization effects and for absorption correction (ψ scan). The space group determination was based upon a check of Laue symmetry and symmetric absences present and was confirmed by the structure solution. The structure was solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using Bruker SHELXTL 5.1 software package.[37] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on B and N were located from the difference map. The remaining hydrogens were included in the calculated positions.

Cell dimensions and structure refinement data are listed in Table 1. Selected bond lengths and angles are given in Table 2. Full crystallographic data, atomic coordinates, complete bond distances and angles, anisotropic thermal parameters, and the hydrogen coordinates of **5** are presented in the Supporting Information.

Results and Discussion

The ability to isolate thermally stable compounds such as $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Sn$,[38] $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Pb$,[39] and $[2,4,6\text{-}(CF_3)_3C_6H_2OIn]_2$[40] using fluoro-substituted ligands, and the successes we had in stabilizing low-valent transition metal adducts with fluorinated tris(pyrazolyl)borates, prompted us to investigate the use of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ in main group chemistry. In this paper, we describe the results of our study involving gallium(I), indium(I), and tin(II) ions.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$ was obtained by treating $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(toluene)$ with GaI in toluene. The analysis of the

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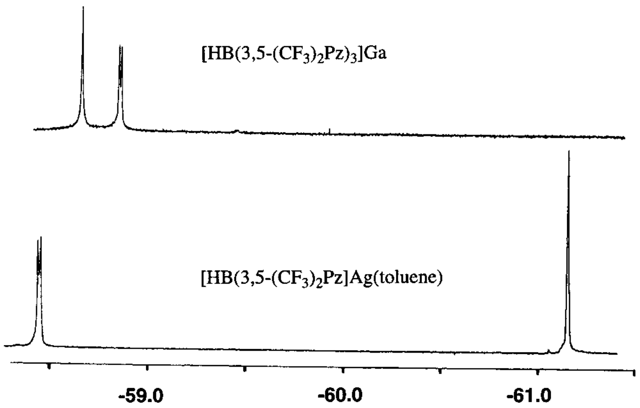

Figure 1. Room-temperature ^{19}F NMR spectra of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(toluene) in C$_6$D$_6$. Chemical shift values are given in ppm relative to CFCl$_3$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]In	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Sn(CF$_3$SO$_3$)
M−N	2.600(3)	2.288(3)
	2.600(3)	2.362(3)
	2.533(5)	2.436(3)
B−N	1.551(5)	1.561(5)
	1.551(5)	1.562(5)
	1.573(7)	1.547(5)
Sn−O		2.507(3)
S−O		1.460(3)
		1.420(3)
		1.435(3)
N−M-N	71.4(1)	82.67(10)
	71.4(1)	76.92(10)
	71.8(1)	72.82(10)
N−B−N	109.7(5)	109.4(3)
	109.4(3)	107.7(3)
	109.4(3)	110.0(3)

crude reaction mixture indicated the presence minor amounts of 3,5-(CF$_3$)$_2$PzH and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga•GaI$_3$ as well. The byproduct [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga•GaI$_3$ presumably arises from the reaction between [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga and "GaI" disproportionation product GaI$_3$. Similar adduct formation has been observed previously during the synthesis of [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]Ga using GaI as the starting material.[4] Nevertheless, analytically pure [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga could be isolated from the mixture by extracting into warm hexane followed by drying under reduced pressure. [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga was characterized by NMR, mass, and infrared spectroscopy. The mass spectrum showed a cluster at *m/z* 690 (with the expected isotope pattern) corresponding to the parent molecular ion {[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga}$^+$. The elemental analysis data are also consistent with the proposed formula. The ^{19}F NMR spectrum exhibited a singlet and a doublet at −58.6 and −58.7 ppm, respectively. These chemical shift values are in the expected region for CF$_3$ groups. We believe that the doublet structure of the signal at δ -58.7, which could be assigned to the trifluoromethyl substituents on the pyrazole 5 position, is a result of spin−spin coupling to the hydrogen on boron.[22,24]

Interestingly, in contrast to the starting material [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(toluene), the ^{19}F NMR resonance due to CF$_3$ groups on the pyrazole ring 3 position appears at a lower frequency relative to CF$_3$ groups on the 5 position (see Figure 1). A similar pattern was observed for indium(I) and tin(II) adducts; [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In (^{19}F NMR; δ −58.4 (s), −58.5 (d)) and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Sn$^+$ (^{19}F NMR; δ −59.2 (s), −59.7 (d)). In contrast, high-valent group 13 species such as [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In(CH$_3$)$_2$ (^{19}F NMR; δ −59.6 (d), −60.6 (s)) or [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Al(CH$_3$)$_2$ (^{19}F NMR; δ −58.4 (d), −61.1 (s)) show an opposite pattern where ^{19}F NMR signal of the CF$_3$ groups on pyrazole ring 3 position appears at a higher frequency relative to CF$_3$ groups on the 5 position.[41]

Despite repeated attempts, we have not been able to obtain suitable crystals of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga for an X-ray crystal structure analysis. However, we were able to obtain a few crystals of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga•GaI$_3$ from the crude reaction mixture suitable for an X-ray data collection. Unfortunately, it presented problems during the structure solution and refinement stage due to twinning and disordered toluene molecules. Although the metric parameters may not be very reliable for detailed analysis, the final structure clearly indicates the presence of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga•GaI$_3$ molecules in the crystal lattice (see the Supporting Information for the structure).[42] The Ga−Ga bond length is 2.494(2) Å, and Ga−N bond distances range from 2.073(11) to 2.097(12) Å. These values agree well with those observed for [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]Ga•GaI$_3$ (Ga−Ga = 2.506(3); Ga−N = 2.05(2) Å).[4]

The indium(I) analogue [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In was synthesized by treating [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) with InCl. Again the most notable change was observed in the ^{19}F NMR spectrum. The 3-CF$_3$ resonance in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In (δ −58.4) appeared at a significantly higher chemical shift value relative to [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) (δ −61.2). A byproduct InCl$_3$(THF)$_2$, presumably resulting from the InCl disproportionation, was also observed in the crude mixture.[43] The ^{1}H, ^{13}C, and ^{19}F NMR spectra of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In are very similar between the gallium(I) and indium(I) adducts suggesting similar solution structures. The infrared stretching frequencies corresponding to C−H and B−H were observed at 3167 and 2642 cm^{-1}, respectively. Corresponding bands for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga were observed at 3164 and 2645 cm^{-1}.

[HB(3,5-(CF$_3$)$_2$Pz)$_3$]In affords crystals suitable for an X-ray crystallographic study. The molecular structure is shown in Figure 2. It contains a crystallographically imposed mirror plane containing indium, boron, and one of the pyrazole rings. The indium center adopts a pyramidal geometry, and there are no close interactions between indium atoms of neighboring molecules. The In−N bond distances of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]In (2.600(3), 2.533(5) Å) are longer than the corresponding distances in [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]In (2.468(9) Å), [HB(3-*t*-BuPz)$_3$]In (2.488(6) Å), or [HB(3-PhPz)$_3$]In (2.430 (4) Å).[5,6] This is perhaps due the weak donor properties of the highly fluorinated [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ ligand. A similar trend in the metal−N bond distances has been observed between [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Tl (average Tl−N = 2.708 Å)[44] and nonfluorinated analogues such as [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]Tl (average Tl−N =

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(42) Crystallographic data for [HB(3, 5-(CF$_3$)$_2$Pz)$_2$]Ga•GaI$_3$; crystallizes with two toluene molecules, formula C$_{29}$H$_{20}$BF$_{18}$Ga$_2$I$_3$N$_6$; trigonal, $P\bar{3}$; temperature = 183(2) K; a = 19.159(3) Å, b = 19.159(3) Å, c = 20.717(4) Å, α = 90°, β = 90°, γ = 120°, V = 6585.6(18) Å^3, Z = 6; final R indices [$I > 2\sigma(I)$] R1 = 0.0624, wR2 = 0.1505, GOF = 1.068. Selected bond lengths (Å) and angles (deg): Ga−Ga 2.494(2), Ga−N 2.073(11), 2.083(13), 2.097(12), Ga−I 2.537(2), 2.543(2), 2.546(2); N−Ga−N 89.1(5), 87.3(5), 88.5(5).

(43) Disproportionation products have also been observed in the reaction of InCl with Cp*Li: Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K. J.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346−356.

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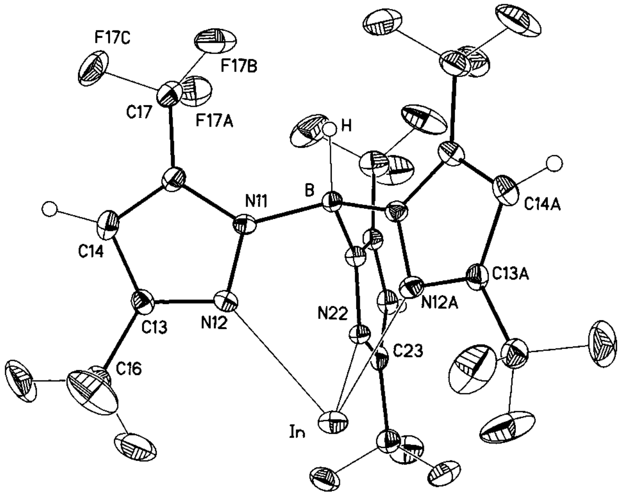

Figure 2. Structure and atom-numbering scheme of $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]In$.

2.573 Å).[45] The Tl−N bond distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Tl$ (2.724(7), 2.725(7), 2.675(10) Å) are longer than the In−N distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$. This is expected on the basis of the atomic radii of thallium and indium.[46] The closest intra- and intermolecular In···F distances for $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ are 3.157 and 3.250 Å, respectively.

The cationic group 14 species such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn^+$ (or $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ge^+$) are isoelectonic to neutral group 13 complexes such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ (or $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$). To compare the properties of these two groups, we have attempted the synthesis $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn^+$ containing a weakly coordinating anion $CF_3SO_3^-$. The reaction between $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$ and $Sn(CF_3SO_3)_2$ led to colorless, crystalline $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)\cdot 3,5\text{-}(CF_3)_2PzH$ in 65% yield. It shows poor solubility even in polar solvents such as CH_2Cl_2 or $CHCl_3$. The presence of $(CF_3)_2PzH$ (presumably arising from the decomposition of $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]^-$ ligand during the reaction) in the crystalline product is also evident from the analytical data.

The X-ray crystal structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$ is shown in Figure 3. The coordination about tin is derived from pseudo-trigonal bipyramidal geometry (Figure 4) with O1 and N32 occupying the axial sites (O1−Sn−N32 = 143.99(9)°) while N12, N22, and the tin lone pair occupying the equatorial sites (N12−Sn−N22 = 82.67(10)°). The average Sn−N distance in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$ (2.362 Å) is longer than the corresponding distance in $[HB(3,5\text{-}(CH_3)_2\text{-}Pz)_3]SnCl$ (average 2.307 Å).[11] The relatively long Sn−O bond distance of 2.507(3) Å (sum of covalent radii of tin and oxygen = 2.13 Å)[46] indicates a weakly bonded anion. However, this interaction is significant enough to affect the S−O distance as evident from relatively long S−O1 bond. There are three intramolecular Sn···F contacts (Sn···F16C, 2.867 Å; Sn···F26C, 2.966 Å; Sn···F36B, 3.054 Å) that are within the sum of the Sn and F van der Waals radii distance (3.64 Å). The Sn−N bond distances of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn^+$ are significantly shorter than In−N distances of the isoelectronic indium species $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ (see Table 2). A smaller covalent radius of tin (Sn, 1.41 Å; In, 1.44 Å) alone cannot account for this difference. It is perhaps a result of increased positive charge at the tin due to weakly coordinating triflate anion. A molecule of $3,5\text{-}(CF_3)_2PzH$ is also present in the asymmetric unit (Figure 4).[47] It shows weak hydrogen bonding to one of the triflate oxygen atoms (O3···H41 = 1.788 Å).[48]

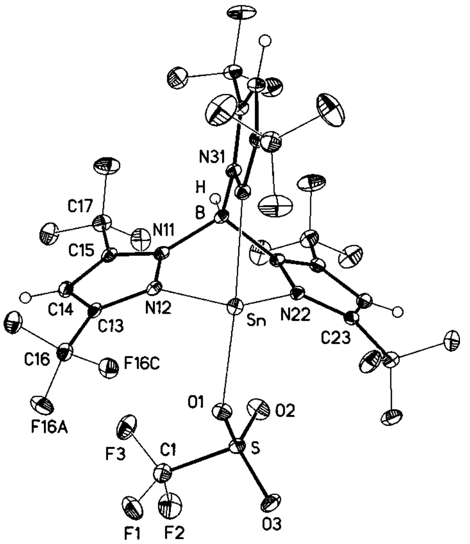

Figure 3. Structure and atom-numbering scheme of $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]Sn(CF_3SO_3)$.

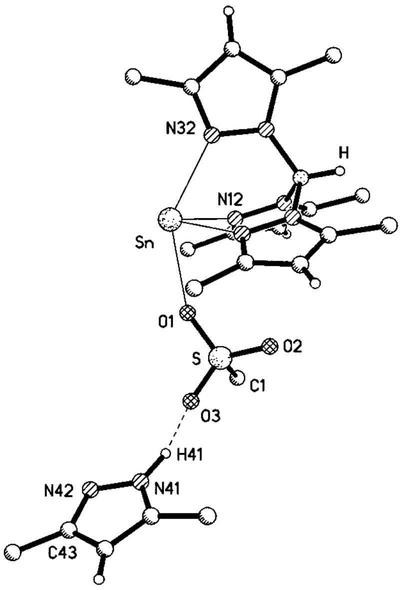

Figure 4. Diagram of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)\cdot 3,5\text{-}(CF_3)_2PzH$ showing the geometry at the tin center and weak O···H interaction between $CF_3SO_3^-$ and $3,5\text{-}(CF_3)_2PzH$. Fluorine atoms were omitted for clarity.

The ^1H and ^{19}F NMR spectra of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$ in $CDCl_3$ display resonances for three equivalent pyrazolyl groups. This suggests the presence of an ion separated species or a highly fluxional molecule. As in the case with the low-valent gallium(I) or indium(I) adduct described above, the ^{19}F NMR resonance due to CF_3 groups at the pyrazole ring 3-position appears at a lower frequency compared to the $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(H_2O)$. The signal due to $CF_3SO_3^-$ appears at the expected region.

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(47) The X-ray structure determination attempts of $3,5\text{-}(CF_3)_2PzH$ have not been successful due to its high volatility. See: Hargittai, I.; Brunvoll, J.; Foces-Foces, C.; Llamas-Saiz, A. L.; Elguero, J. *J. Mol. Struct.* **1993**, *291*, 211−217.

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Overall, this study shows that $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand allows the isolation of compounds which feature low-valent main group ions such as gallium(I), indium(I), and tin(II). Although several tin(II) complexes have been isolated using sterically less demanding tris(pyrazolyl)borate ligands such as $[HB(Pz)_3]^-$, the related gallium(I) and indium(I) tris(pyrazolyl)borates isolated thus far contain much bulkier ligands. There is a report of an attempt using $[HB(3,5-(CH_3)_2Pz)_3]K$ and indium(I) iodide to isolate $[HB(3,5-(CF_3)_2Pz)_3]In$, without a success.[5,49] $\{[HB(3,5-(CH_3)_2Pz)_3]_2In\}I$ was the final product from this reaction. It is not clear from that report whether $[HB(3,5-(CH_3)_2Pz)_3]In$ is formed during the reaction and later disproportionates to an indium(III) species or the In(III) product is formed directly from a disproportionation product of InI and $[HB(3,5-(CH_3)_2Pz)_3]K$ salt.

The CF_3 groups are often considered sterically equivalent or only slightly larger than the CH_3 groups.[38,50,51] Therefore, the stability of $[HB(3,5-(CF_3)_2Pz)_3]In$ and $[HB(3,5-(CF_3)_2Pz)_3]Ga$ suggest that the fluorinated $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand is a good choice to stabilize low-valent, low-coordinate main group species without overly protecting the metal site. This feature is desirable for the study of chemistry at the metal center. Interestingly, despite the presence of highly electron withdrawing $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand on the metal center, the metal sites of its complexes are nucleophilic enough to form adducts such as $[HB(3,5-(CF_3)_2Pz)_3]Ga{\cdot}GaI_3$.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for **5** and $[HB(3,5-(CF_3)_2Pz)_3]Ga{\cdot}GaI_3$, the molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]Ga{\cdot}GaI_3$, and two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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