Monomeric Indium(I) and Silver(I) Complexes of a Polyfluorinated Tris(pyrazolyl)borate

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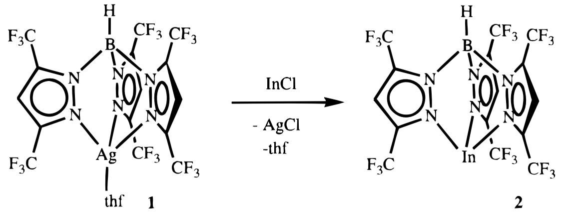
There has been considerable interest in the study of low valent indium compounds.[1] However, most of the structurally well-characterized neutral In(I) systems are limited to their cyclopentadienyl compounds. Depending on the substituents on the cyclopentadienyl ring system, they display different degrees of aggregation ranging from polymers, hexamers to dimers, in the solid state.[1,2] Recently, we and others reported the synthesis of monomeric, indium(I) compounds using sterically demanding tris(pyrazolyl)borate ligands, $[HB(3\text{-}tert\text{-}BuPz)_3]^-$ and $[HB(3\text{-}PhPz)_3]^-$.[3,4] The stability of these compounds was mainly attributed to the steric effects of the *tert*-butyl or phenyl substituents on the tris(pyrazolyl)borate ligand.[3,4] Use of the sterically less demanding methylated ligand $[HB(3,5\text{-}(CH_3)_2\text{-}Pz)_3]^-$ with In(I) resulted in slow disproportionation leading to an In(III) product.[5] Here, we show an alternative approach in which a polyfluorinated tris(pyrazolyl)borate ligand,[6] $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (which is sterically somewhat similar but electronically very different from the methylated analog, $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$),[7,8] has been utilized to obtain an In(I) compound.[9]



(1)

Compound **1**, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(thf)$ (**1**) was prepared in good yield from $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na$ and AgOTf in tetrahydrofuran.[10] Interestingly, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ was isolated as the thf adduct. This tendency to form adducts with neutral oxygen donors has not been observed in the corresponding non-fluorinated analogs. For example, $[HB(Pz)_3]Ag$ or $[HB(3,5\text{-}(CH_3)_2Pz)_3]Ag$ has been synthesized in aqueous solution and isolated as a solid, free of any coordinated solvent.[11] The presence of thf in **1** was clearly evident from the elemental analysis and ^1H and ^{13}C NMR spectroscopic data. The ^{19}F NMR spectrum of **1** shows two signals as expected for the CF_3 groups on the 3- and 5-positions of the pyrazole ring. One of the peaks corresponding to the trifluoromethyl groups on the pyrazole ring 5-position appears as a doublet. We believe this is due to long range coupling to the H on boron.[12,13] Although, we could not observe the signal corresponding to B−*H* in the ^1H NMR spectrum, the ^{19}F-NMR spectrum of the deuteriated analog, $[DB(3,5\text{-}(CF_3)_2Pz)_3]Ag(thf)$, displayed only a singlet for 5-CF_3, suggesting that the splitting is indeed a result of spin−spin coupling due to a B−H proton.

The treatment of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(thf)$ (**1**) with InCl in thf at −78 °C followed by slow warming to room temperature led to the precipitation of AgCl. After overnight stirring, the solvent was removed, and the residue was extracted into toluene. Filtration, followed by removal of the solvent from the filtrate yielded $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ (**2**) as a colorless solid in 78% yield (eq 1).[14] A notable change was observed in the ^{19}F-NMR spectrum. The 3-CF_3 resonance in **2** (δ −58.42) appeared at a significantly higher chemical shift value relative to **1** (δ −61.16).[15]

The structures of **1** and **2** were confirmed by X-ray crystallography. Figures 1 and 2 illustrate their ORTEP diagrams along with some of the important bond distances and angles.[16] Compound **1** crystallizes as well-separated molecules with pseudotetrahedral geometry about the silver atom. The Ag−N distances of 2.381(4), 2.344(4), and 2.365(5) Å are slightly longer than the Ag−O distance (2.234(4) Å). Structurally characterized complexes of Ag(I) with oxygen donors are

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(9) Fluorinated aryloxide has been used previously to obtain a dimeric In(I) species, Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383.

(10) Synthesis of **1**: AgOTf (0.463 g, 1.8 mmol) was treated with $HB(3,5\text{-}(CF_3)_2Pz)_3Na$ (1.16 g, 1.8 mmol) in thf at room temperature. The mixture was stirred overnight, and the solvent was removed under reduced pressure. The residue was extracted into hexane and filtered through Celite, and the hexane was removed from the filtrate to obtain **1** as a white solid: 92% yield: mp >60 °C dec; ^1H NMR (C_6D_6, TMS) δ 1.43 (m, 4 H, thf), 3.58 (m, 4 H, thf), 6.34 (s, 3 H, Pz); ^{19}F NMR (C_6D_6, external reference $CFCl_3$) δ −58.45 (d, J = 2.9 Hz), −61.16 (s); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS) δ 25.84 (s, CH_2), 68.15 (s, CH_2), 106.81 (s, *C*H), 119.83 (q, CF_3, ^1J = 270.5 Hz), 120.86 (q, CF_3, ^1J = 269.4 Hz), 140.73 (q, CCF_3, ^2J = 44.3 Hz), 143.73 (q, CCF_3, ^2J = 38.1 Hz); IR, cm^{-1}, 2612 (BH). Anal. Calcd for $C_{19}H_{12}N_6AgOB$: C, 28.49; H, 1.51; N, 10.49. Found: C, 28.69; H, 1.23; N, 10.18.

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(14) Analytical data for **2**: turns opaque at 85 °C, ^1H NMR (C_6D_6, TMS) δ 6.16 (s, C*H*); ^{19}F NMR (C_6D_6, external reference $CFCl_3$) δ −58.42 (s), −58.50 (d, J = 3.5 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS) δ 107.09 (s, *C*H), 119.49 (q, ^1J = 271 Hz, CF_3), 120.87 (q, ^1J = 271 Hz, CF_3), 140.83 (q, ^2J = 39 Hz, CCF_3), 143.91 (q, ^2J = 39 Hz, CCF_3); IR, cm^{-1}, 2636 (BH); MS *m/z* 736. Anal. Calcd for $C_{15}H_4BInF_{18}N_6$: C, 24.48; H, 0.55; N, 11.42. Found: C, 24.68; H, 0.86; N, 11.04. A minor byproduct, $InCl_3(thf)_2$, resulting from the disproportionation of InCl was also observed in some of the runs. See Supporting Information for the X-ray structural data for this molecule.

(15) A similar pattern was observed for the closely related $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]Sn^+OTf^-$ (^{19}F NMR: δ −59.31 (s), −59.76 (d)): Dias, H. V. R.; Jin, W. Unpublished data.

(16) Crystal data for **1**: monoclinic $C2/c$, with $a = 16.236(2)$ Å, $b = 21.658(2)$ Å, $c = 17.180(2)$ Å, $\beta = 114.710(6)$, $V = 5488.4(11)$ Å^3, $Z = 8$, and $D_{calc} = 1.939$ g cm^{-3}. Data were collected on a Siemens P4 diffractometer at $T = 193$ K with Mo Kα ($\lambda = 0.710\,73$ Å) radiation using ω scan technique up to $2\theta_{max} = 45°$. Of the 4317 reflections measured, 3599 ($R_i = 3.10\%$) were unique. $R = 3.84\%$, $R_w = 4.22\%$ for 2785 reflections with $F > 4\sigma(F)$, and 439 parameters. Crystal data for **2**: monoclinic $P2_1/m$ with $a = 8.203(1)$ Å, $b = 15.155(2)$ Å, $c = 9.256(1)$ Å, $\beta = 100.427(5)$, $V = 1131.6(3)$ Å^3, $Z = 2$, and $D_{calc} = 2.160$ g cm^{-3}. Data were collected on a Siemens P4 diffractometer at $T = 193$ K with Mo Kα ($\lambda = 0.710\,73$ Å) radiation using $\theta-2\theta$ scan technique up to $2\theta_{max} = 45°$. Of the 2152 reflections measured, 1542 ($R_i = 1.25\%$) were unique. $R = 3.06\%$, $R_w = 3.06\%$ for 1470 reflections with $F > 4\sigma(F)$, and 202 parameters.

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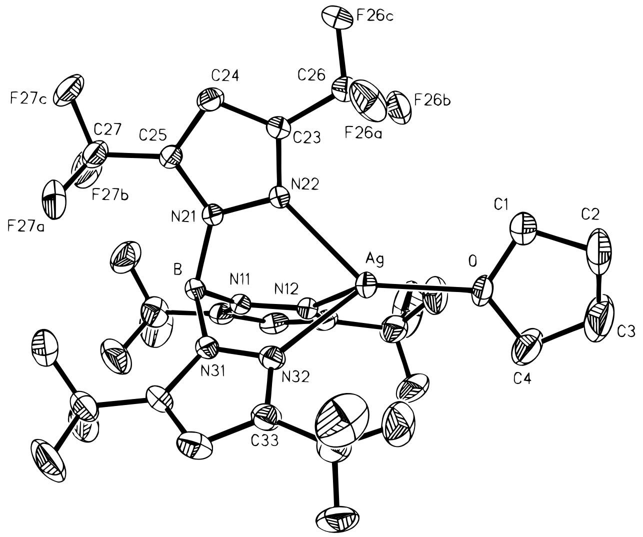

Figure 1. Molecular structure of compound **1** (ellipsoids are shown at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag−O 2.234(4), Ag−N12 2.381(4), Ag−N22 2.344(4), Ag−N32 2.365(5), B−N11 1.539(6), B−N21 1.569(8), B−N31 1.560(8); N12−Ag−N22 81.0(1), N12−Ag−N32 80.2(1), N22−Ag−N32 82.2(2), N12−Ag−O 131.7(1), N22−Ag−O 134.6(2), N32−Ag−O 127.4(2).

rare,[17,18] and to the best of our knowledge, they have not been reported in the poly(pyrazolyl)borate family.[19] However, the Ag−O distance can be compared with that in the $BaAg[OC(CF_3)_3]_3(thf)_4$ (2.209(12) Å), $[Ag(12\text{-crown-}4)_2][AsF_6]$ (average 2.57 Å) or $[Pt_2AgCl_2(C_6F_5)_4OEt_2]^-$ (2.299(10) Å).[20−22] The Ag−N separation in **1** is within the corresponding values observed for $Ph_2B(Pz)_2AgP(4\text{-}MeC_6H_4)_3$ (2.194(4), 2.411(4) Å).[23]

Compound **2** crystallizes in the $P2_1/m$ space group with a crystallographically imposed plane of symmetry containing one of the pyrazole rings, B and In. The indium center adopts a pyramidal geometry and there are no close interactions between In atoms of neighboring molecules. The In−N bond distances of **2** (2.600(3), 2.600(3), 2.533(5) Å) are longer than the corresponding distances in $[HB(3\text{-}PhPz)_3]In$ (2.430 (4) Å).[4] The N−In−N angles of **2** (average 71.3°) are smaller compared to those in $[HB(3\text{-}PhPz)_3]In$ (78.2(2)°). Similar trends are observed between **2** and **1** where the metal−N bond lengths are relatively longer and the N−metal−N angles are significantly smaller in **2**. The closest intra- and intermolecular In···F distances for **2** are 3.157 and 3.250 Å, respectively.

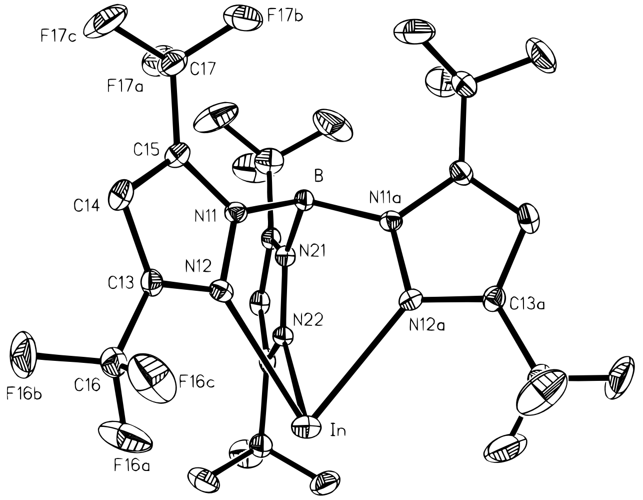

Figure 2. Molecular structure of compound **2** (ellipsoids are shown at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): In−N12 2.600(3), In−N22 2.533(5), In−N12A 2.600(3), B−N11 1.551(5), B−N21 1.573(7), B−N11A 1.551(5); N12−In−N22 71.4(1), N12−In−N12A 71.8(1), N22−In−N12A 71.4(1).

The CF_3 groups are often considered sterically equivalent or only slightly larger than the CH_3 groups.[7] Therefore, the stability of $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$ relative to $[HB(3,5\text{-}(CH_3)_2Pz)_3]In$ can be attributed mainly to the electronic effects of the fluorinated ligand. The isolation of **2** suggests that the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand is particularly suitable for the stabilization of low valent metal species.[9] Furthermore, the indium center in **2** is not overly protected by the ligand as in [HB(3-*tert*-BuPz)$_3$]In. This feature is desirable for the study of chemistry at the indium center. We are currently studying the chemistry of **2** and the use of **1** in the synthesis of various other low valent metal species.

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Supporting Information Available: Text and a table giving crystallographic data and details of the structure determination, figures giving the structures of **1** (with disorder) and $InCl_3(thf)_2$ and tables of atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1**, **2**, and $InCl_3(thf)_2$ (14 pages). Ordering information is given on any current masthead page.

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