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Synthesis and Chemistry of [Hydridotris(3-*tert*-butylpyrazolyl)borato]indium(I)

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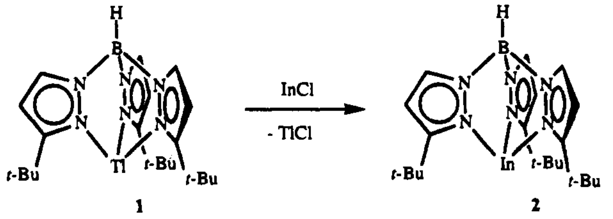
There has been considerable interest in the study of low-valent indium compounds.[1] However, most of the structurally well-characterized neutral In(I) systems are limited to their cyclopentadienyl compounds. Depending on the substituents on the cyclopentadienyl ring system, they display different degrees of aggregation in the solid state. For example $(C_5H_5)In$, $(C_5H_4Me)In$, $(C_5H_4\text{-}t\text{-}Bu)In$, and $(C_5H_4SiMe_3)In$ show polymeric structures in the solid state.[2–4] $(C_5Me_5)In$ forms a hexamer,[5,6] and the much bulkier cyclopentadienyl ligand $C_5(CH_2Ph)_5$ leads to a dimeric solid.[7] We were interested in exploring the stability of In(I) species derived from bulky tris(pyrazolyl)borate ligands. On the basis of the formal analogy between the cyclopentadienyl and tris(pyrazolyl)borate (Tp) systems[8] and because of their even higher steric demand,[9,10] one would expect to see In(I) compounds similar to those above with various Tp ligands. Recently, Piggott *et al.* reported one such indium(I) compound using the hydridotris(3-phenylpyrazolyl)borato ligand.[11] Here we report the synthesis of a monomeric In(I) compound of the hydridotris(3-*tert*-butyl-1-pyrazolyl)borato ligand, $[HB(3\text{-}t\text{-}Bupz)_3]^-$, and some preliminary reactivity studies.

The treatment of $HB(3\text{-}t\text{-}Bupz)_3Tl$ (**1**)[10] with InCl in THF led to the title compound as a colorless, air-stable solid (eq 1). $HB(3\text{-}t\text{-}Bupz)_3In$ (**2**) was characterized by NMR (^1H and ^{13}C) spectroscopy and elemental analysis.[12] The progress of the reaction is very clear from the ^1H NMR because, unlike **2**, the starting material **1** shows ^{205}Tl coupling in both ^1H and ^{13}C NMR spectra.[13] Compound **2** crystallized easily from a toluene/hexane mixture at −20 °C. The melting point of **2** is lower than that of **1**.



(1)

The identity of **2** was confirmed by X-ray crystallography. Figure 1 illustrates the structure of **2** and some important bond distances and angles.[14] It shows the presence of well-separated monomeric units in the crystal lattice. The indium adopts a pyramidal geometry, and there are no close interactions between

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(12) **1** (4.32 g, 7.4 mmol) and InCl (1.11 g, 7.4 mmol) were mixed in a Schlenk tube, and THF (30 mL) was added at −78 °C. The mixture was allowed to warm to room temperature very slowly and stirred overnight to obtain a cloudy solution. The mixture was filtered, and the volatiles were removed under reduced pressure. The residue was extracted with toluene, the extract was filtered, and the filtrate was concentrated. Hexane was added to the solution, and the resulting mixture was cooled at −20 °C to obtain colorless crystals of **2.** The product was recrystallized from warm hexane (2.15 g, 59%): mp 178–179 °C; NMR (C_6D_6) ^1H δ 1.42 (s, *t*-Bu), 5.90 (d, $J = 1.9$ Hz, 4-C*H*), 7.46 (d, $J = 1.9$ Hz, 5-C*H*); $^{13}C\{^1H\}$ δ 32.0 (s, *C*H_3), 32.5 (s, *C*Me_3), 101.9 (s, 4-*C*), 135.9 (s, 5-*C*), 164.1(s, 3-*C*). Anal. Calcd for $C_{21}H_{34}N_6BIn$: C, 50.84; H, 6.91; N, 16.94. Found: C, 50.60; H, 6.63; N, 16.74.

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(14) Crystal data for **2** are as follows: $C_{21}H_{34}BInN_6$, MW = 496.18, orthorhombic space group *Cmcm* with $a = 16.150(1)$ Å, $b = 15.1935(6)$ Å, $c = 9.9325(8)$ Å, $V = 2437.2(3)$ Å^3, $Z = 4$, and $D_{calc} = 1.352$ g cm^{-3}. The structure was solved by Patterson methods and refined using MolEN; 756 unique reflections ($F > 6\sigma(F)$) were used; absorption correction factors 0.79/1.21. $R = 0.0555$, $R_w = 0.0688$ ($w = [0.04F^2 + (\sigma F)^2]^{-1}$). Data were collected on an Enraf-Nonius CAD-4 diffractometer at $T = 298$ K with Mo Kα ($\lambda = 0.710\,73$ Å) radiation using the $\theta/2\theta$ scan technique up to $2\theta = 44°$. The molecule is disordered about an *m2m* site such that a nitrogen atom is coincident with the boron and each pyrazolyl ring has 50% occupancy. The disorder resolved exactly with the exception of a methyl group in *tert*-butyl for which the two positions less than 0.2 Å could not be resolved.

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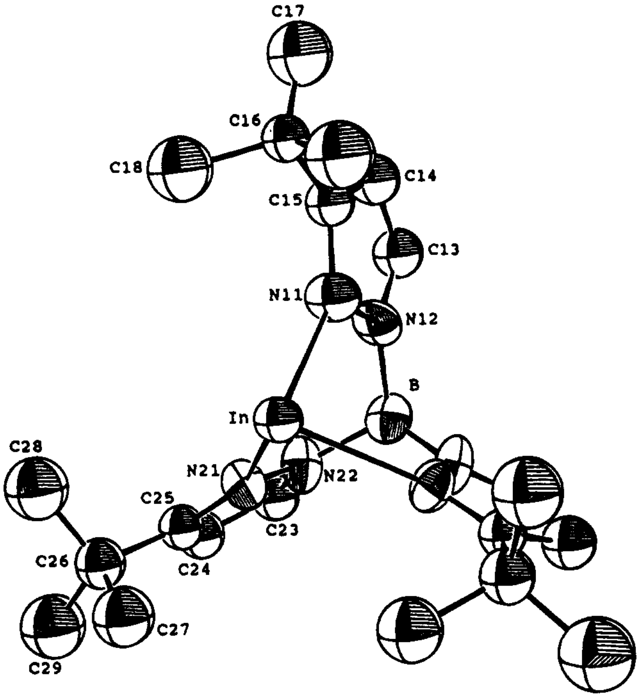

Figure 1. ORTEP view of **2**. Selected bond distances (Å) and angles (deg): In−N11 2.44(2), In−N21 2.45(1), B−N12 1.52(4), B−N22 1.53(4); N11−In−N21 81.3(5), N21−In−N21′ 78.6(5).

In atoms of neighboring molecules. The In−N bond distances of **2** (2.44(4), 2.45(1) Å) are similar to the values observed for HB(3-Phpz)$_3$In and are shorter than those in the analogous Tl(I) compound **1**. Unfortunately, the disorder observed in **2** prevents much detailed comparison of structural parameters.

The treatment of the compound **2** with ZnEt$_2$ lead to the formation of **3** (eq 2). This behavior of **2** is very similar to

$$\underset{\mathbf{2}}{\mathrm{HB(3\text{-}}t\mathrm{\text{-}Bupz)_3In}} \xrightarrow{\mathrm{ZnEt_2}} \underset{\mathbf{3}}{\mathrm{HB(3\text{-}}t\mathrm{\text{-}Bupz)_3ZnEt}} \tag{2}$$

that observed for **1**. Compound **3** has been previously prepared from the metathesis reaction of ZnEt$_2$ with **1**.[15] The identity of the zinc-containing product was confirmed by comparing the NMR data of the product to the reported values.

In summary, we have synthesized a monomeric [tris(pyrazolyl)borato]indium(I) compound using HB(3-*t*-Bupz)$_3$Tl. The stability of **2** could be attributed to the steric effects of the *tert*-butyl substitutents because the use of the sterically less demanding methylated ligand HB(3,5-Me$_2$pz)$_3$ with In(I) has resulted in slow dispropotionation leading to an In(III) product.[16] Compound **2** represents the first well-characterized monomeric In(I) species involving an alkylated Tp ligand.

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Supplementary Material Available: Text giving crystallographic data and details of the structure determination and tables of atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** (8 pages). Ordering information is given on any current masthead page.

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