Synthesis and Crystal and Molecular Structure of [{Hydroboratotris(3′-phenylpyrazolyl)}indium]: An Air-Stable Monomeric Indium(I) Complex

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As part of our work on the chemistry of the heavier members of group 13, we recently synthesized and structurally characterized [bis{hydroboratotris(3,5-dimethylpyrazolyl)}indium(III)]-iodide (**2**) and [bis{methylgallatotris(pyrazolyl)}indium(III)]-$[InI_4]$ (**3**).[1] Recognizing the formal analogy between the hydroboratotrispyrazolyl anion $HB(Pz)_3^-$ (and its pyrazolyl-substituted derivatives) and the cyclopentadienyl anions $C_5R_5^-$ (R = H, CH_3),[2] we were led to claim **2** and **3** as analogues of the unknown "indocene" cations $[\eta^5\text{-}(C_5R_5)_2In]^+$. A characteristic of the cyclopentadienyl anions is their ability to stabilize metals in low oxidation states, e.g., $In(C_5H_5)$[3] and the recently synthesized $Ga(C_5H_5)$[4] and $Al_4(C_5R_5)_4$.[5] It seemed to us that synthesis of an In^I complex with $HB(Pz'')_3^-$ (Pz″ = a substituted pyrazole) would strengthen the analogy between hydroboratotris(pyrazolyl) anions and cyclopentadienyl anions and also significantly extend the chemistry of In^I.[6] In a previous study, we observed the gradual disproportionation of In^I to In^{III} and In in the presence of $HB(Pz^*)_3^-$ (Pz* = 3,5-dimethylpyrazole) on slowly raising the temperature of the reactants from −30 °C to ambient.[1] We argued that use of a more sterically hindered pyrazole than Pz* might facilitate the isolation of a stable In^I species. On reacting indium iodide with $HB(Pz^{**})_3^-$ (Pz** = 3-phenylpyrazole) in tetrahydrofuran at −50 °C, we were able to isolate colorless, blocklike crystals. The mass spectra, ^1H and ^{13}C NMR spectra, and elemental analyses indicated these crystals to be $[In\text{-}\{HB(Pz^{**})_3\}]$ (**1**). This was confirmed by an X-ray structural study.[7]

The structure of **1** is shown in Figure 1a and b, and comparisons between it and related compounds are shown in Table 1. Whereas the geometry about the metal in **2** and particularly **3** is very close to octahedral, in **1** the In adopts a pyramidal geometry with respect to the coordinated nitrogen atoms. This arrangement is also seen in **5**. The In–N distance in **1** is longer than the corresponding distances in **2** and **3**, as expected, and exceeds the sum of the covalent radii by about 8%. There is no In–In interaction in **1**, the closest contacts being 6.5 Å. The In–In distance in $In(C_5H_5)$ is 3.99 Å,[10] whereas in In_2X_4 (X = 2,4,6–$(CF_3)_3C_6H_2$), the In–In bond distance is 2.744(2) Å.[11] The mean plane of each pyrazole ring makes an angle of 48° 59′ with that of its phenyl substituent and results in an In–H4 distance of 3.388 Å. An explanation for

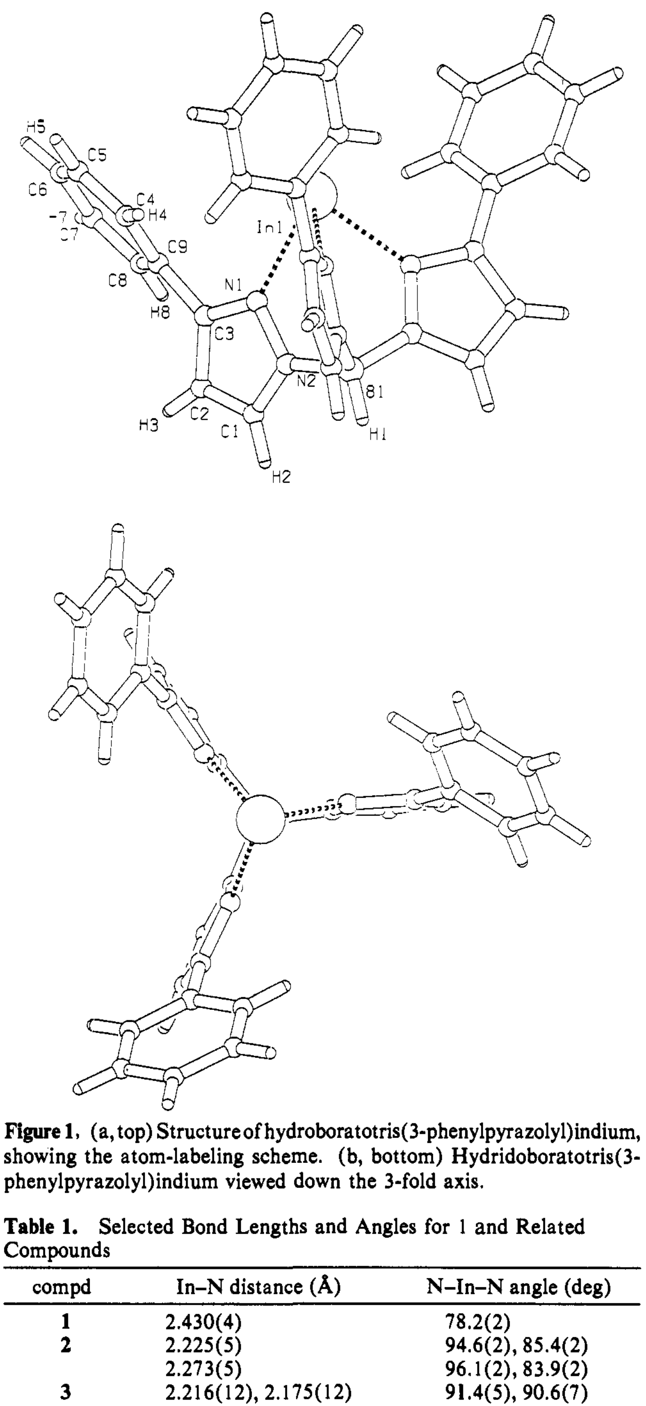

Figure 1. (a, top) Structure of hydroboratotris(3-phenylpyrazolyl)indium, showing the atom-labeling scheme. (b, bottom) Hydridoboratotris(3-phenylpyrazolyl)indium viewed down the 3-fold axis.

Table 1. Selected Bond Lengths and Angles for 1 and Related Compounds

compd	In–N distance (Å)	N–In–N angle (deg)
1	2.430(4)	78.2(2)
2	2.225(5)	94.6(2), 85.4(2)
	2.273(5)	96.1(2), 83.9(2)
3	2.216(12), 2.175(12)	91.4(5), 90.6(7)
	2.207(12), 2.177(22)	91.4(5), 90.7(9)
	2.228(13), 2.167(29)	88.7(5), 90.8(13)
4[a]	2.268(4)	
	2.233(6)	not reported
	2.249(5)	
5[b]	2.582(6)	79.3(2)
	2.587(9)	75.2(2)

[a] **4** ≡ $[\{hydroboratotris(3,5\text{-}dimethylpyrazolyl)\}InCl_2{\cdot}CH_3CN]$.[8] [b] **5** ≡ [{hydroboratotris(3-*tert*-butylpyrazolyl)}thallium(I)].[9]

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(7) **1**: trigonal, space group *P*3 (No. 147) with a = 11.472(1) Å, b = 11.471(1) Å, c = 7.203(1) Å, $\alpha = \beta = 90°$; $\gamma = 120°$, V = 1255.66 Å^3, and $Z = 2$ (d_{calcd} = 1.471 gm cm^{-3}), μ (Mo Kα) = 9.353 cm^{-1}; absorption correction DIFABS; 5963 reflections, 1910 unique; 1837 with $F_o > 3\sigma(F_o)$ were used in the refinement; R = 2.6, R_w = 3.5.

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this observation is being sought. This arrangement of phenyl rings forms a "pocket" about the indium ion as seen in Figure 1a and b. Whether the stabilization of In^I in this complex is due solely to the steric properties of this "pocket" or to concomitant electronic effects is currently being investigated.

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Supplementary Material Available: Synthesis of **1**; tables of fractional atomic coordinates, anisotropic thermal parameters, hydrogen atom coordinates, bond lengths and bond angles, and selected intramolecular and intermolecular nonbonded distances (5 pages); tables of observed and calculated structure factors (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.