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Synthesis and Structure of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$, a Highly Twisted [Tris(3,5-di-*tert*-butylpyrazolyl)hydroborato]indium(I) Complex: Comparison with the Re-Evaluated Ordered Structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$

Matthew C. Kuchta,[†] H. V. Rasika Dias,[‡] Simon G. Bott,[§] and Gerard Parkin*,[†]

Department of Chemistry, Columbia University, New York, New York 10027, Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, and Department of Chemistry, University of North Texas, Denton, Texas 76203

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The indium(I) complex $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$ ($[\mathrm{Tp}^{\mathrm{Bu^t}_2}]$ = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato), synthesized by the reaction of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Na}$ with InCl, exhibits a structure in which the $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]$ ligand adopts a highly twisted configuration due to steric interactions of the *tert*-butyl substituents in the 5-positions of the pyrazolyl groups. In contrast, the absence of 5-*tert*-butyl substituents allows the pyrazolyl groups in $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ to be coplanar with their respective In−N−N−B planes. The structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ has been previously reported but was noted to exhibit an unusual type of disorder in which a nitrogen atom of one molecule was coincident with the boron atom of its disordered configuration [Dias, H. V. R.; Huai, L.; Jin, W.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1973−1974]. In view of the unusual nature of the disorder, which involved both a 2-fold rotation and a canting of the molecule, the disordered structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ was re-evaluated. Significantly, an ordered structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ was obtained. The disorder present in the previously reported structure is a consequence of adopting a space group with unnecessarily high symmetry. Thus, $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ provides an example where the structure is much better described as ordered in a noncentrosymmetric space group, rather than disordered in the centrosymmetric alternative. $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$ is monoclinic, of space group $P2_1/c$ (No. 14), with $a = 18.781(9)$ Å, $b = 10.380(2)$ Å, $c = 20.849(6)$ Å, $\beta = 112.76(3)°$, and $Z = 4$. $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ is orthorhombic, of space group $Cmc2_1$ (No. 36), with $a = 16.193(3)$ Å, $b = 15.214(3)$ Å, $c = 9.963(3)$ Å, and $Z = 4$.

Introduction

As a consequence of the facile incorporation of a variety of substituents (R and R′) into the 3- and 5-positions, the tris(pyrazolyl)hydroborato $[\mathrm{Tp}^{\mathrm{R,R'}}]$ ligand system (Figure 1) continues to be one of the most popular in coordination chemistry.[1,2] For example, *tert*-butyl incorporation at the 3-position affords considerable steric protection about a metal center and $[\mathrm{Tp}^{\mathrm{Bu^t,R}}]$ ligands have been used extensively to support monomeric terminal alkyl, hydride, and hydroxide derivatives of the main group elements,[1b] as in $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{BeH}$,[3] $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{MgR}$,[4] $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{ZnH}$,[5,6] $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{ZnR}$[5,7] and $[\mathrm{Tp}^{\mathrm{Bu^t,Me}}]\mathrm{ZnOH}$.[8] More recently, we synthesized the related tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligand, $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]$, in which the 5-position of the pyrazolyl group is also occupied by the sterically demanding *tert*-butyl substituent.[9] Significantly, intraligand repulsive interactions between the 5-*tert*-butyl substituents result in the $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]$ ligand adopting a highly twisted, propeller-like, configuration, so that the local symmetry of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]$ is reduced to C_3, compared to the C_{3v} symmetry that is typical for the $[\mathrm{Tp}^{\mathrm{Bu^t}}]$ ligand. In this paper, we describe the synthesis and structure of the In(I) derivative $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$. As part of this study, we have also had course to re-evaluate the structure of the less substituted derivative, $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$, which was reported to exhibit an unusual type of 2-fold disorder.[10] Significantly, we have identified that the structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ is indeed ordered and that the unusual disorder originally proposed is a consequence of adopting a space group with unnecessarily high symmetry.

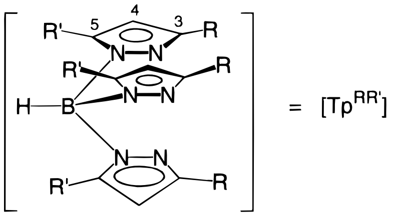

Figure 1. The $[\mathrm{Tp}^{\mathrm{R,R'}}]$ ligand system.

[†] Columbia University.

[‡] The University of Texas at Arlington.

[§] University of North Texas.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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(2) The abbreviations adopted here for tris(pyrazolyl)hydroborato ligands are based on those described by Trofimenko.[1a] Thus, the tris(pyrazolyl)hydroborato ligands are represented by the abbreviation Tp, with the 3- and 5-alkyl substituents listed respectively as superscripts.

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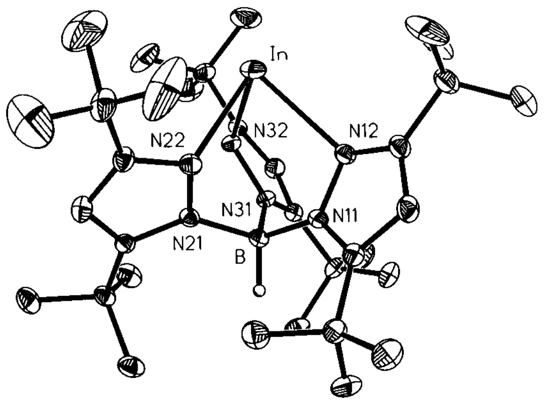
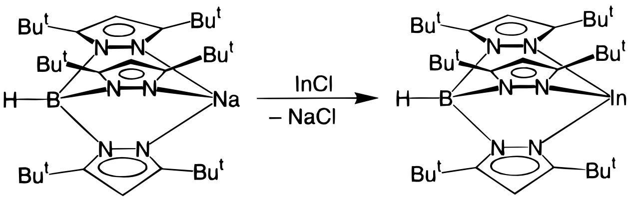


Figure 2. Molecular structure of [Tp$^{\mathrm{Bu^t_2}}$]In.

Scheme 1



Results and Discussion

Synthesis of [Tp$^{\mathrm{Bu^t_2}}$]In and Structural Comparisons with [Tp$^{\mathrm{Bu^t}}$]In. Although In(I) complexes are well-precedented,[11] many of these complexes are oligomeric. For example, (cyclopentadienyl)indium(I) derivatives [(C_5R_5)In] exhibit a varied degree of oligomerization, which includes monomeric,[12] dimeric,[13] hexameric,[14] and polymeric structures,[15] depending on the nature of the substituents of the cyclopentadienyl ligand. Recently, however, Piggott and Dias independently reported the use of bulky tris(pyrazolyl)hydroborato ligands to isolate the monomeric In(I) complexes [Tp$^{\mathrm{Ph}}$]In[16] and [Tp$^{\mathrm{Bu^t}}$]In.[10] In view of our interest in the structural and chemical ramifications of bulky *tert*-butyl substituents in the 5-positions of the pyrazolyl groups of tris(pyrazolyl)hydroborato ligands, *i.e.* in the vicinity of the boron, we have now synthesized the related In(I) complex [Tp$^{\mathrm{Bu^t_2}}$]In by the reaction of [Tp$^{\mathrm{Bu^t_2}}$]Na with InCl (Scheme 1).

The structure of [Tp$^{\mathrm{Bu^t_2}}$]In has been determined by X-ray diffraction, as illustrated in Figures 2 and 3. Selected bond lengths and angles for [Tp$^{\mathrm{Bu^t_2}}$]In are presented in Table 1. In comparison to the less substituted [Tp$^{\mathrm{Bu^t}}$]In derivative, the most interesting feature of the structure of [Tp$^{\mathrm{Bu^t_2}}$]In is the dramatically twisted [Tp$^{\mathrm{Bu^t_2}}$] ligand. Specifically, the pyrazolyl groups in [Tp$^{\mathrm{Bu^t_2}}$]In adopt a highly twisted, propeller-like, array with respect to the In···B axis. As noted previously, such twisting is a consequence of intraligand repulsive interactions between the 5-*tert*-butyl substituents, and similar structures have been observed for other [Tp$^{\mathrm{Bu^t_2}}$]M and [Tp$^{\mathrm{Bu^t_2}}$]MX derivatives.[9] For comparison, the average twist angle for [Tp$^{\mathrm{Bu^t_2}}$]In (22.4°) is comparable to that for the thallium analogue [Tp$^{\mathrm{Bu^t_2}}$]Tl (22.8°).[9]

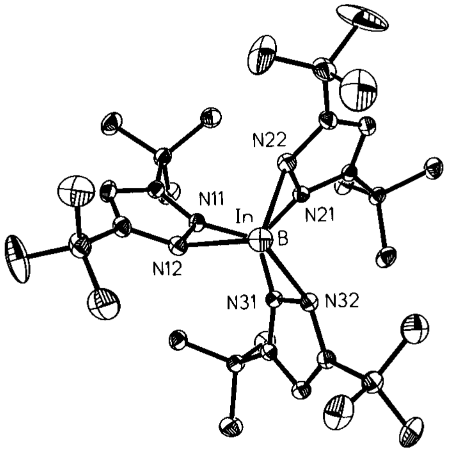


Figure 3. View of [Tp$^{\mathrm{Bu^t_2}}$]In down the In···B axis, emphasizing the twisted nature of the [Tp$^{\mathrm{Bu^t_2}}$] ligand.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Tp$^{\mathrm{Bu^t_2}}$]In

In−N(12)	2.471(4)	N(12)−In−N(22)	77.3(1)
In−N(22)	2.474(3)	N(12)−In−N(32)	81.9(1)
In−N(32)	2.458(4)	N(22)−In−N(32)	80.5(1)

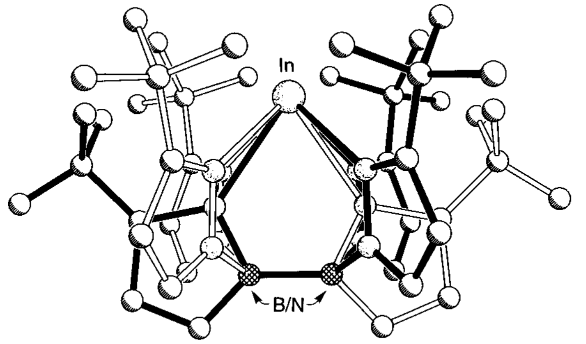


Figure 4. The two disordered configurations of [Tp$^{\mathrm{Bu^t}}$]In in *Cmcm*, emphasizing the canted nature of the disorder.

Although further comparisons between the structures of [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In were of interest, the reported structure of [Tp$^{\mathrm{Bu^t}}$]In was disordered,[10] so that more detailed comparisons with the published data were not appropriate. Curiously, however, the disorder model proposed for [Tp$^{\mathrm{Bu^t}}$]In was rather unusual, in the sense that the molecule exhibited a 2-fold disorder about an *m*2*m* site in such a manner that a nitrogen atom of one molecule was coincident with the boron atom of its disordered configuration, as illustrated in Figures 4 and 5. Thus, the disordered configurations are related by a 2-fold rotation about the In···B axis, coupled with a canting of the molecules. Such a disorder model is even more unusual when it is considered that the thallium analogue [Tp$^{\mathrm{Bu^t}}$]Tl[17] exhibits an ordered structure. Furthermore, disorder of this type has not (to our knowledge) been observed for any other tris(pyrazolyl)hydroborato complex. Therefore, in view of both the unprecedented nature of the disorder and our interest in making a detailed comparison between the structures of

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(11) Tuck, D. G. *Chem. Soc. Rev.* **1993**, *22*, 269−276.

(12) [η^5-$C_5Me_4(PPh_2)$]In is a monomer with an In···In separation of 5.929(1) Å. See: Schumann, H.; Ghodsi, T.; Esser, L. *Acta Crystallogr.* **1992**, *C48*, 618−620.

(13) {[η^5-$C_5(CH_2Ph)_5$]In}$_2$ exists as a dimer with an In···In separation of 3.631 Å. See: Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243−251.

(14) [(η^5-C_5Me_5)In]$_6$ exists as a hexamer. See: Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346−356.

(15) [(C_5H_5)In]$_x$,[15a,b] [(C_5H_4Me)In]$_x$,[15b] [($C_5H_4Bu^t$)In]$_x$,[15c] [($C_5H_4SiMe_3$)In]$_x$,[15d] and [(C_5Me_4H)In]$_x$[15e] are polymeric. (a) Frasson, E.; Menegus, F.; Panattoni, C. *Nature*, **1963**, *199*, 1087−1089. (b) Beachley, O. T., Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051−1059. (c) Beachley, O. T., Jr.; Lees, J. F.; Rogers, R. D. *J. Organomet. Chem.* **1991**, *418*, 165−171. (d) Beachley, O. T., Jr.; Lees, J. F.; Glassman, T. E.; Churchill, M. R.; Buttrey, L. A. *Organometallics* **1990**, *9*, 2488−2492. (e) Schumann, H.; Kucht, H.; Kucht, A.; Görlitz, F. H.; Dietrich, A. Z. *Naturforsch.* **1992**, *47B*, 1241−1248.

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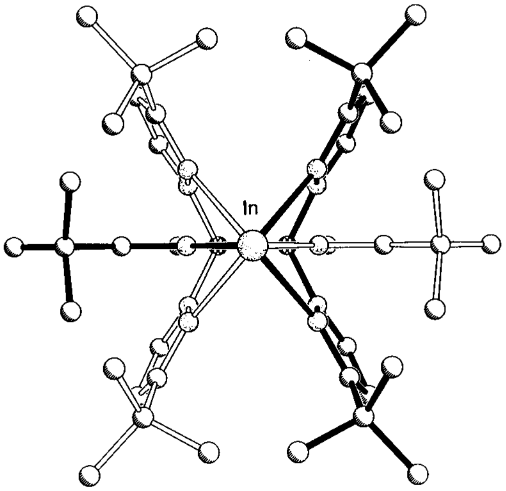

Figure 5. View orthogonal to that of Figure 4, illustrating the two disordered configurations of [Tp$^{\mathrm{Bu^t}}$]In in *Cmcm*.

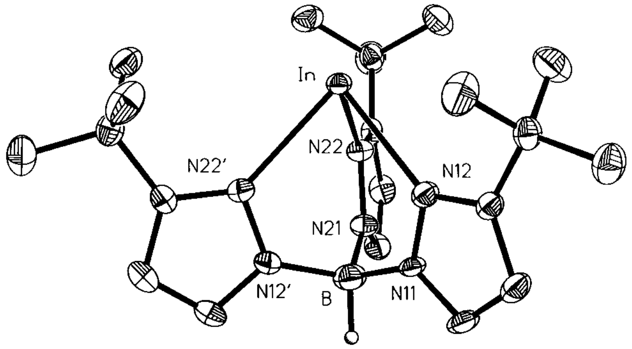

Figure 6. An ordered structure for [Tp$^{\mathrm{Bu^t}}$]In in $Cmc2_1$.

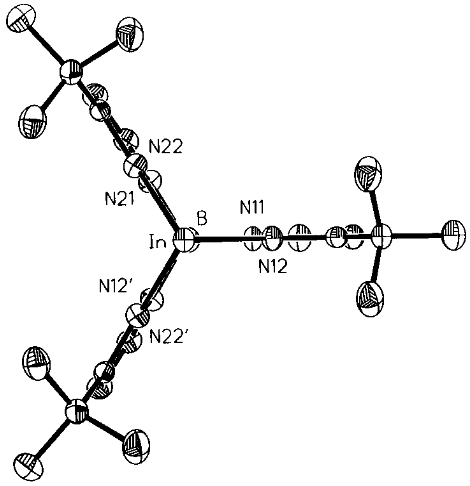

Figure 7. View of [Tp$^{\mathrm{Bu^t}}$]In down the In···B axis, illustrating the C_{3v} molecular symmetry.

[Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In, we decided to re-investigate the X-ray structure of [Tp$^{\mathrm{Bu^t}}$]In. Significantly, as will be described later in the text, an ordered structure was indeed obtained for [Tp$^{\mathrm{Bu^t}}$]In (Figures 6 and 7, Table 2), thereby allowing a more detailed comparison to be made with the structure of [Tp$^{\mathrm{Bu^t_2}}$]In. Thus, averaged metrical data for [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In are collated in Table 3, from which it is evident that, despite the pronounced twisting of the pyrazolyl groups, the local coordination environments about the indium centers in [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In are very similar. The closest In···In separation between adjacent molecules of [Tp$^{\mathrm{Bu^t_2}}$]In is 6.90 Å, comparable to that of 6.48 Å in [Tp$^{\mathrm{Bu^t}}$]In, and thereby attests to the monomeric nature of these In(I) complexes.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Tp$^{\mathrm{Bu^t}}$]In

	$Cmc2_1$[a]	*Cmcm*[a]	*Cmcm*[b]
In−N(12)	2.494(6)	2.43(3)	2.44(4)
In−N(22)	2.485(4)	2.56(2)	2.45(1)
N(12)−In−N(22)	80.4(1)	80.3(6)	81.3(5)
N(22)−In−N(22′)	77.1(2)	75.5(9)	78.6(5)

[a] This work. [b] Reference 10.

Table 3. Comparison of the Structures of [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In

	[Tp$^{\mathrm{Bu^t_2}}$]In	[Tp$^{\mathrm{Bu^t}}$]In
$d(\mathrm{In-N_{av}})$/Å	1.468[9]	2.488[6]
$d(\mathrm{B-N_{av}})$/Å	1.561[8]	1.55[1]
$\mathrm{N-In-N_{av}}$/deg	80[3]	79[2]
$d(\mathrm{In\cdots N_3})$/Å[a]	1.66	1.68
twist angles, τ/deg[b]	19.8, 23.5, 23.8	0, 2.4, 2.4
τ_{av}/deg[b]	22.4	1.6
$d(\mathrm{In\cdots In})$/Å[c]	6.90	6.48

[a] $d(\mathrm{In\cdots N_3})$ is the displacement of In from the coordinating N_3 plane. [b] The twist angle is defined as the N−In···B−N torsion angle. [c] $d(\mathrm{In\cdots In})$ is the closest separation between indium centers in adjacent molecules.

Table 4. Comparison of the Unit Cell Parameters of [Tp$^{\mathrm{Bu^t}}$]In

	[Tp$^{\mathrm{Bu^t}}$]In[a]	[Tp$^{\mathrm{Bu^t}}$]In[b]
a/Å	16.150(1)	16.193(3)
b/Å	15.1935(6)	15.214(3)
c/Å	9.9325(8)	9.963(3)
α, β, γ/deg	90, 90, 90	90, 90, 90

[a] Reference 10. [b] This work.

Re-Evaluation of the Structure of [Tp$^{\mathrm{Bu^t}}$]In. Crystals of [Tp$^{\mathrm{Bu^t}}$]In suitable for X-ray diffraction studies were grown from benzene at room temperature, and cell constant data identified that the crystal selected was isomorphous with that used in the previous determination (Table 4).[10] Systematic absences were consistent with three space groups, namely *Cmcm* (No. 63), $Cmc2_1$ (No. 36), and *C*2*cm* (No. 40), the latter being a nonstandard setting for *Ama*2. For a unit cell with $Z = 4$, space group *Cmcm* requires the molecule to be located on a site with either *m*2*m* or 2/*m* symmetry, both of which are inconsistent with the presumed molecular symmetry (which does not possess a 2-fold axis), whereas a site of only *m* symmetry is required by the other two space group alternatives. Since the space group originally reported for [Tp$^{\mathrm{Bu^t}}$]In is *Cmcm* (No. 63), we selected the related noncentrosymmetric alternative $Cmc2_1$ (No. 36), a space group which is consistent with the presumed molecular symmetry. Significantly, a well-defined ordered structure (Figures 6 and 7), with the molecule residing on a crystallographic mirror plane, was obtained following a series of least-squares refinements which converged to $R = 0.0304$ and $R_{\mathrm{w}} = 0.0359$. The final difference map was effectively featureless, furnishing no evidence for the presence of a disordered configuration. It is, therefore, apparent that the disordered structure previously reported for [Tp$^{\mathrm{Bu^t}}$]In is a consequence of the structure being solved in a space group of unnecessarily high symmetry.

An important issue that bears consideration is the question concerning why the noncentrosymmetric space group was not selected as the correct choice in the original publication. In this regard, since systematic absences do not distinguish between centrosymmetric and noncentrosymmetric space group alternatives, ambiguities between such space groups are quite common.[18] Fortunately, intensity statistics have been used with some success to distinguish between noncentrosymmetric and centrosymmetric alternatives.[18,19] In this respect, a value of 0.666 for $\langle |E^2 - 1| \rangle$ (based on all reflections) is observed for

$[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$, which is much more in accord with the theoretical value for a noncentrosymmetric (0.736) than centrosymmetric (0.968) space group.[18,19] However, since statistical tests based on the more intense reflections may be biased toward a noncentrosymmetric choice,[18] it is plausible that such a test may not be regarded as definitive, and thereby not influence one strongly in the selection of a space group. Furthermore, there are many examples where the noncentrosymmetric space group has been incorrectly selected in preference to the centrosymmetric alternative,[18] and it is possible that such a factor may prejudice one to favor erroneously the centrosymmetric space group.

Commonly, however, the correct selection of space group is judged by the success of the final solution. The natural conclusion is, therefore, that the solution for $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ in the centrosymmetric space group *Cmcm* was regarded as "successful", albeit disordered. We have also refined the structure of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ in *Cmcm* and obtained a structure similar to that described previously.[10,20] However, the refinement is not as well behaved and the R values ($R = 0.081$, $R_w = 0.1230$) and goodness-of-fit (3.19) are considerably worse than for the correct structure.

It still remains to be explained why the noncentrosymmetric space group was not selected for the final solution in the original publication,[10] especially since it was in fact considered as a possibility once it was recognized that the structure was (apparently) disordered. However, at that time, a successful solution giving an ordered structure was not obtained in the noncentrosymmetric space group, thus leading to the erroneous conclusion that the noncentrosymmetric space group was an incorrect selection.

The reason why the correct structure was not obtained when the structure was originally refined in the noncentrosymmetric space group is that electron density maps at early and middle stages of refinement suggested a disordered structure. In this regard, it is well-known that an electron density difference map based on the position of a single heavy atom in the noncentrosymmetric space group $Cmc2_1$ would necessarily exhibit mirror symmetry perpendicular to the polar z axis. In effect, such a difference map represents a superposition of the two polar configurations and therefore gives the *appearance* of a disordered structure. However, it would not necessarily be expected that electron density difference maps midway through the refinement procedure would also exhibit mirror symmetry. Thus, since the difference maps midway through the refinement appeared to indicate a disordered structure, it was assumed incorrectly that the centrosymmetric space group *Cmcm* was the correct choice.

The ability of a single heavy atom to impose effective mirror symmetry in the electron density difference maps in the final stages of refinement (as observed here) has been previously reported.[21,22] In fact, a rather extreme consequence of such an effect is that, in certain circumstances, groups of atoms may be incorrectly located in positions that are related to their true locations by reflection perpendicular to the polar axis; *i.e.*, a completely incorrect ordered molecular structure may be derived.[21] Thus, it is quite conceivable that if one were to be prejudiced by the appearance of the electron density difference maps in a noncentrosymmetric space group, one could incorrectly assume that the centrosymmetric space group should be selected in preference.

The effect of the imposed disorder on the derived metrical data of $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ is summarized in Table 2. Thus, it is evident that, as a result of the imposed disorder, the In-N bond lengths deviate from their true values and are accompanied by higher esd's.

As indicated above, ambiguities between noncentrosymmetric and centrosymmetric space groups have many precedents, with centrosymmetric structures often being incorrectly refined in noncentrosymmetric space groups.[18] Although attempts to refine a centrosymmetric structure in a noncentrosymmetric space group are normally accompanied by problems (*e.g.* structural distortions, significant variations in chemically equivalent bond lengths, ill-behaved displacement parameters, and large esd's), the ability to perform such a refinement with a "reasonable degree of success" is logical in the sense that the additional atoms which are required for the noncentrosymmetric space group are in positions effectively determined by the symmetry of the centrosymmetric alternative. The converse situation, however, *i.e.* one in which a noncentrosymmetric structure is refined in a centrosymmetric space group, is neither common[23] nor obvious, since the higher symmetry space group effectively requires atoms to be refined in sites that are not occupied. Such is the circumstance for refining $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ in *Cmcm*, and the ability to observe such an unusual effect in the present case is presumably related to the fact that the X-ray scattering is dominated by the indium atoms which themselves are described by the centrosymmetric space group, even though the molecules are not.

Summary

The In(I) complex $[\mathrm{Tp}^{\mathrm{Bu^t_2}}]\mathrm{In}$ has been synthesized by the reaction of $[\mathrm{Tp}^{\mathrm{Bu^t_2}}]\mathrm{Na}$ with InCl. Due to steric interactions derived from the presence of *tert*-butyl substituents in the 5-positions of the pyrazolyl groups, the $[\mathrm{Tp}^{\mathrm{Bu^t_2}}]$ ligand in this complex adopts a highly twisted configuration. For comparison purposes, the structure of the related complex $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$, which was previously reported to exhibit an unusual type of disorder, was re-evaluated. Significantly, an ordered structure was derived for $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$, and the origin of the disorder in the previous structure determination was identified as a consequence of incorrectly adopting a space group with unnecessarily high symmetry. Since it is not unprecedented for structures that are correctly described in a centrosymmetric space group to be incorrectly refined in the noncentrosymmetric alternative,[18] $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$ provides an interesting counterexample where the structure is much better described as ordered in the noncentrosymmetric space group, rather than disordered in the centrosymmetric alternative.[24]

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(18) For some leading references, see: (a) Marsh, R. E.; Bernal, I. *Acta Crystallogr.* **1995**, *B51*, 300−307. (b) Marsh, R. E. *Acta Crystallogr.* **1994**, *A50*, 450−455. (c) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1988**, *B44*, 77−78. (d) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280−287. (e) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331−2336. (f) Marsh, R. E. *Acta Crystallogr.* **1986**, *B42*, 193−198. (g) Marsh, R. E. *Acta Crystallogr.* **1981**, *B37*, 1985−1988. (h) Marsh, R. E. *Inorg. Chim. Acta* **1989**, *157*, 1−2. (i) Baur, W. H.; Tillmanns, E. *Acta Crystallogr.* **1986**, *B42*, 95−111.

(19) Karle, I. L.; Dragonette, K. S.; Brenner, S. A. *Acta Crystallogr.* **1965**, *19*, 713−716.

(20) The structure was also attempted in *Ama*2, but similar, and more extreme, problems were encountered compared to those for *Cmcm*.

(21) Murphy, V. J.; Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 9762−9763.

(22) Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608−7617.

(23) Obviously, it is plausible that small deviations from centrosymmetry may not be sufficient to prevent a strictly noncentrosymmetric structure from being refined in a centrosymmetric space group. In this specific instance, we are referring to a disorder in which there is a significant structural change.

Table 5. Crystal and Intensity Collection Data for $[\mathrm{Tp^{Bu^t_2}}]$In and $[\mathrm{Tp^{Bu^t}}]$In

	$[\mathrm{Tp^{Bu^t_2}}]$In	$[\mathrm{Tp^{Bu^t}}]$In
formula	$C_{33}H_{58}BN_6In$	$C_{21}H_{34}BN_6In$
fw	664.5	496.2
lattice	monoclinic	orthorhombic
a/Å	18.781(9)	16.193(3)
b/Å	10.380(2)	15.214(3)
c/Å	20.849(6)	9.963(3)
α/deg	90.0	90.0
β/deg	112.76(3)	90.0
γ/deg	90.0	90.0
V/Å^3	3760(2)	2454(1)
Z	4	4
radiation (λ/Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/c$ (No. 14)	$Cmc2_1$ (No. 36)
ρ(calcd)/g cm^{-3}	1.174	1.343
μ(Mo Kα)/cm^{-1}	6.56	9.81
R^a	0.0446	0.0304
$R_w{}^a$	0.0559	0.0359

[a] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$; $w = [\sigma^2(F) + gF^2]^{-1}$.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[25] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 spectrophotometer. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (CH_4) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $[\mathrm{Tp^{Bu^t_2}}]$Na was prepared as described previously for the potassium derivative $[\mathrm{Tp^{Bu^t_2}}]$K, with the exception of substituting KBH_4 by $NaBH_4$.[9] $[\mathrm{Tp^{Bu^t}}]$In was prepared as previously reported, with the exception that the reaction was carried out in benzene over a period of 2 days at room temperature.[10]

Synthesis of $[\mathrm{Tp^{Bu^t_2}}]$In. A mixture of $[\mathrm{Tp^{Bu^t_2}}]$Na (1.28 g , 2.24 mmol) and InCl (0.50 g, 3.36 mmol) in benzene (*ca.* 10 mL) was heated at *ca.* 85 °C for 4 days. After this period, the gray-green mixture was cooled to room temperature and an additional quantity of benzene (*ca.* 80 mL) was added. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure to give $[\mathrm{Tp^{Bu^t_2}}]$In as a white solid (1.10 g, 68% based on $\mathrm{Na[Tp^{Bu^t_2}]}$). Anal. Calcd for $[\mathrm{Tp^{Bu^t_2}}]$In: C, 59.7; H, 8.8; N, 12.7. Found: C, 60.6; H, 8.6; N, 12.6. MS: $m/z = 665$ (M^+). IR data: 2552 cm^{-1} (ν_{B-H}). ^{1}H NMR (C_6D_6): δ 1.36 [s, 27H, 3C(CH_3)$_3$], 1.40 [s, 27H, 3C(CH_3)$_3$], 6.10 [s, 3H, 3C*H*] (B$-$*H* not observed). ^{13}C NMR (C_6D_6): δ 30.3 [q, $^1J_{C-H} = 128$, 3C(CH_3)$_3$], 31.7 [q, $^1J_{C-H} = 128$, 3C(CH_3)$_3$], 32.5 [s, 3*C*(CH_3)$_3$], 32.6 [s, 3*C*(CH_3)$_3$], 101.9 [d, $^1J_{C-H} = 173$, 3*C*H], 158.0 [s, 3*C*C(CH_3)$_3$], 162.1 [s, 3*C*C(CH_3)$_3$].

X-ray Structure Determinations. Crystal data and data collection and refinement parameters for $[\mathrm{Tp^{Bu^t_2}}]$In and $[\mathrm{Tp^{Bu^t}}]$In are summarized in Table 5, while atomic coordinates are listed in Tables 6 and 7. A typical procedure is provided by the example of $[\mathrm{Tp^{Bu^t}}]$In. A single crystal of $[\mathrm{Tp^{Bu^t}}]$In was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\ 73$ Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods and standard difference map techniques on using SHELXTL PC. Systematic absences were consistent with *Cmcm* (No. 63), $Cmc2_1$ (No. 36), and *C*2*cm* (No. 40), of which the choice $Cmc2_1$ (No. 36) was selected for the reasons described above. Hydrogen atoms on carbon were

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[\mathrm{Tp^{Bu^t_2}}]$In

	x	y	z	U(eq)^a
In	8619(1)	1087(1)	582(1)	54(1)
N(11)	7570(2)	3594(3)	−31(2)	37(1)
N(12)	8219(2)	3361(4)	554(2)	41(1)
N(21)	7062(2)	1555(3)	−716(2)	35(1)
N(22)	7815(2)	1436(3)	−664(2)	42(1)
N(31)	6939(2)	1871(3)	441(2)	34(1)
N(32)	7333(2)	714(3)	598(2)	38(1)
C(11)	7644(2)	4733(4)	−327(2)	42(2)
C(12)	8357(3)	5239(5)	97(3)	52(2)
C(13)	8691(2)	4366(5)	634(2)	48(2)
C(21)	6588(2)	811(4)	−1251(2)	36(2)
C(22)	7048(3)	241(4)	−1555(2)	49(2)
C(23)	7797(3)	643(4)	−1180(2)	47(2)
C(31)	6578(2)	2066(4)	885(2)	38(2)
C(32)	6723(3)	999(4)	1311(2)	46(2)
C(33)	7189(2)	190(4)	1121(2)	40(2)
C(41)	7071(3)	5283(4)	−1007(2)	48(2)
C(42)	6926(3)	4324(5)	−1600(2)	63(2)
C(43)	7411(3)	6505(5)	−1180(3)	73(3)
C(44)	6300(3)	5680(5)	−964(3)	65(2)
C(51)	5723(2)	625(4)	−1451(2)	43(2)
C(52)	5269(3)	1843(5)	−1796(3)	58(2)
C(53)	5553(3)	269(5)	−818(3)	60(2)
C(54)	5450(3)	−477(5)	−1978(3)	61(2)
C(61)	6091(2)	3247(4)	882(2)	45(2)
C(62)	5929(3)	3220(5)	1556(3)	72(3)
C(63)	6525(3)	4494(4)	882(3)	56(2)
C(64)	5309(3)	3211(5)	263(3)	58(2)
C(71)	9464(3)	4494(5)	1238(3)	62(2)
C(72)	9582(4)	5842(7)	1510(4)	142(4)
C(73)	10098(3)	4129(8)	988(3)	1104(4)
C(74)	9520(4)	3602(8)	1834(3)	121(4)
C(81)	8515(3)	377(6)	−1315(3)	73(3)
C(82)	9048(5)	1425(8)	−1121(6)	192(9)
C(83)	8946(4)	−780(8)	−864(6)	160(7)
C(84)	8344(4)	−168(22)	−1985(4)	198(7)
C(91)	7491(3)	−1141(4)	1409(2)	52(2)
C(92)	7623(4)	−1954(5)	862(3)	96(4)
C(93)	6893(3)	−1806(5)	1629(3)	84(3)
C(94)	8231(4)	−998(6)	2047(3)	97(3)
B	6911(3)	2572(5)	−227(2)	25(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[\mathrm{Tp^{Bu^t}}]$In

	x	y	z	U(eq)^a
In	5000	3637(1)	2500	42(1)
N(11)	5000	1482(6)	1725(11)	44(4)
N(12)	5000	2282(4)	1091(6)	52(2)
N(21)	4212(3)	1817(3)	3888(4)	51(1)
N(22)	4044(3)	2710(3)	3842(4)	52(1)
C(11)	5000	832(5)	847(10)	63(3)
C(12)	5000	1195(5)	−415(9)	64(3)
C(13)	5000	2098(5)	−232(7)	50(2)
C(14)	5000	2818(6)	−1280(8)	57(3)
C(15)	5000	2421(6)	−2683(14)	80(4)
C(16)	4259(5)	3404(5)	−1119(8)	93(3)
C(21)	3629(4)	1409(4)	4581(6)	61(2)
C(22)	3063(4)	2023(4)	5005(6)	67(2)
C(23)	3334(3)	2827(3)	4531(5)	50(2)
C(24)	2940(4)	3726(4)	4706(5)	60(2)
C(25)	2561(5)	4013(5)	3373(7)	94(3)
C(26)	3580(4)	4388(4)	5180(7)	80(3)
C(27)	2253(5)	3670(5)	5775(8)	90(3)
B	5000	1394(10)	3263(27)	74(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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(24) For another example in which a structure that was initially refined in centrosymmetric $P\bar{1}$ is better described as noncentrosymmetric $P1$, see: Calabrese, J. C.; Gardner, K. H. Acta *Crystallogr.* **1985**, *C41*, 389−392.

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included in calculated positions. Data were collected for h, k, $\pm l$, and inversion of configuration allowed the correct polarity to be established. Systematic absences for [Tp$^{\mathrm{Bu^t_2}}$]In were consistent uniquely with the space group $P2_1/c$ (No. 14).

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Supporting Information Available: Additional ORTEP diagrams and tables of crystal and intensity collection data, hydrogen coordinates, bond distances and angles, and anisotropic displacement parameters for [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t}}$]In (14 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.

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