Isolation and Characterization of a Nucleophilic Allylic Indium Reagent

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Summary: Transmetalation between allylic stannanes and indium halides gave allylic indium dihalides. The bond length of In-C is 2.172 Å, which is close to the reported average indium-carbon bond length. The isolated allylic indium dibromide with two phthalan ligands showed nucleophilicity for a carbonyl compound.

Reactions of allylic indium species have been extensively studied in recent years, in particular for the alkylation of carbonyl compounds.1 A number of reports have appeared regarding stereoselective reactions and aqueous media reactions using allylic indium species.² The methods used to generate allylic indium can be classified into two types: (i) a reductive process using either allylic halides with low-valent indium^{3,4}

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or dienes with hydroindium;⁵ (ii) transmetalation of a parent allylic metal species with indium halides.⁶ Only a few reports have proffered a structural discussion of allylic indiums. Araki and Butsugan generated the allylic indium species using a reductive method and considered the species as allylindium sesquihalide^{3a,c} or allylindium dihalide,^{3b} by NMR spectroscopic analysis. Chan employed a reductive method and proved the formation of allylindium(I) in aqueous media and allylindium(I)/ allylindium dibromide in organic solvent or ionic liquid.3f,k In the reaction system using allylstannane and InCl₃, the generation of allylic indium species via transmetalation was assumed by observing the halostannane byproduct.^{6b} Despite extensive synthetic studies on allylic indium, the pure isolation and X-ray analysis of allylic indium⁷ with the potential for nucleophilic allylation have never been reported, as far as we know. Recently a reactive propargylic indium, a system related to the allylic indium, was investigated on the basis of X-ray crystallographic characterization.⁸ The establishment of a structural discussion of allylic indium is indispensable for the development of the chemistry of allylic indium and, furthermore, for other related organometallic nucleophiles. In this communication, introducing bulky substituents and external ligands realized the isolation of an allylic indium compound from the corresponding stannane with indium trihalide. Herein, we describe its structural analysis on the basis of X-ray crystallography and reactivity of the isolated allylic indium species.

We chose a transmetalation method to investigate an allylic indium species, because the method would simply give the desired allylic indium and a reductive method could generate two types of species.³ The mixture of allyltributylstannane (1a) with either InCl₃ or InBr₃ was examined in acetonitrile. The NMR spectra of the mixture showed halostannane but no allylic signals, perhaps because the generated allylindium species was unstable. Changing the solvent to THF, which was expected to stabilize the indium species by coordination, gave a reasonable NMR spectrum. The formation of halostannane and the appearance of allylic signals without satellites by ¹¹⁹Sn coupling indirectly proved the generation of an allylindium species (see the Supporting Information). The substituted allylic stannane

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cinnamyltributylstannane (1b) also showed similar results, even in an acetonitrile solvent. Although evaporation of the volatiles of the mixture unfortunately led to the decomposition of the allylic indium species, the addition of external ligands stabilized the active allylic indium species and enabled the isolation of a sample that, when solidified,⁹ was appropriate for X-ray analysis. After various combinations of allylic stannanes, indium halides, external ligands, and solvents were examined, the use of 1c, a new type of allylic stannane, and InBr3 and phthalan in acetonitrile successfully isolated the allylic indium species (Scheme 1). The allylic stannane 1c, bearing bulky substituents (tert-butylphenyl) at the γ -position, was mixed with InBr₃ in acetonitrile to quantitatively give Bu₃SnBr, as confirmed by NMR. Allylic signals corresponding to the allylic indium species 2 were also observed (2.20 ppm, $InCH_2$, CD_3CN). After the addition of 3 equiv of phthalan (1,3-dihydroisobenzofuran = L) to the mixture, removing the volatiles gave a yellow viscous oil, which was then mixed with hexane to give two layers. The upper layer (hexane layer) was pipetted out to remove the byproduct Bu₃SnBr. The yellow residue was cooled to -25 °C to be solidified. The obtained solid was washed with hexane to give a pale yellow solid, which was confirmed to be the allylic indium species 3 (29% isolated) without contamination by a tin residue. The NMR spectrum in CDCl₃ showed allylic protons at 2.53 ppm. The spectrum also showed that 2 equiv of phthalan was included as ligands, because the signals of its methylenes (8H) appeared at a lower chemical shift (5.20 ppm) as compared with that of free phthalan (5.10 ppm). It is noted that this pureisolation experiment first clarified the precise structure around indium, including ligand (or sometimes solvent) coordination that is often neglected.

A suitable crystal for X-ray analysis was obtained after recrystallization of **3** from acetonitrile at -25 °C to give **4**. The ORTEP drawing of **4** is shown in Figure 1. One of the ligands was exchanged from phthalan to acetonitrile after recrystallization. Indium has a trigonal-bipyramidal coordination sphere with two bromines and an allylic group in the equatorial plane and two ligands, phthalan and acetonitrile, in axial positions. The sum of the bond angles in the equatorial plane is 359.7° (Br(1)-In(1)-Br(2) = $112.64(5)^{\circ}$, Br(2)-In(1)-C(1) = $122.4(3)^{\circ}$, C(1)-In(1)-Br(1) = $124.7(3)^{\circ}$). Two axial ligands and indium are in a small bent line (O(1)-In(1)-N(1) = $169.7(3)^{\circ}$). The bond length of In-C(1) is 2.172(12) Å, which is close to the reported average indium-carbon bond length (2.184 Å).

The direct observation of compound **4** in solution by NMR studies was not successful because the obtained sample amount was too small. Instead, the isolated compound **3** in CD₃CN was investigated using ¹H NMR. The results showed chemical shifts that were almost the same as those of **2** in CD₃CN, as described in Scheme 1. Additionally, the signals of the phthalan moiety



Figure 1. ORTEP drawing of allylic indium dibromide 4 (all hydrogens and solvent are omitted for clarity). Selected bond lengths (Å): In(1)-C(1) = 2.172(12), C(1)-C(2) = 1.481(15), C(2)-C(3) = 1.299(14), C(3)-C(4) = 1.518(16), C(3)-C(14) = 1.502(14), In(1)-Br(1) = 2.5031(15), In(1)-Br(2) = 2.5179(14), In(1)-O(1) = 2.429(7), In(1)-N(1) = 2.362(9). Selected bond angles (deg): Br(1)-In(1)-Br(2) = 112.64(5), Br(2)-In(1)-C(1) = 122.4(3), C(1)-In(1)-Br(1) = 124.7(3), O(1)-In(1)-N(1) = 169.7(3).





L = phthalan, L' = acetonitrile

appeared at the chemical shifts corresponding to its free form (see the Supporting Information). These results suggest that the ligand exchange on indium readily occurred from phthalan to acetonitrile, giving the doubly acetonitrile coordinated allylic indium **2** as shown in Scheme 2. It was found that the species **2** observed in Scheme 1 was also the doubly acetonitrile coordinated one. During the recrystallization process, compound **4**, bearing phthalan and acetonitrile, was crystallized.

The isolated allylic indium **3** was mixed with benzaldehyde in dichloromethane at room temperature for 2 h and gave the homoallylic alcohol **5** in 15% yield through carbon–carbon bond formation in a S_E2' manner (eq 1). Surprisingly, complex **3** still has the potential for nucleophilic attack, in spite of the bulky substituents that should retard the addition of allylic indium **3** to a carbonyl compound. The use of acetonitrile as a solvent, in which acetonitrile coordinates to the indium center in situ, also gave the same level of yield. This fact indicates that phthalan provides minimal stabilization for the species. As a practical method, we also employed the reaction system starting from the allylic stannane **1c**/InBr₃/benzaldehyde in acetonitrile. It gave the product **5** in 12% yield, which was similar to the result of eq 1.



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In summary, the allylic indium dibromide complex was isolated in a pure form and analyzed by X-ray crystallography. The indium center has trigonal-bipyramidal coordination geometry with two external ligands. This study will help develop indium-mediated synthetic chemistry based on structural modification. A structural analysis of the allylic indium species generated by a reductive system³ is now under investigation.

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Supporting Information Available: Text, figures, tables, and a CIF file giving experimental procedures and X-ray data for 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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