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The insertion reactions of "crowned" indium(I) trifluoromethanesulfonate into carbon–chlorine bonds

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Abstract

Whereas the soluble reagent indium(I) trifluoromethanesulfonate, InOTf, does not appear to react rapidly with chlorinated solvents, the crown ether ligated compounds [In(18-crown-6)][OTf] and [In(dibenzo-18-crown-6)][OTf] react rapidly with CH_2Cl_2 and $CHCl_3$ to produce the corresponding C–Cl insertion products. The structural features and the formation of the new indium-containing products are rationalized.

Keywords: Indium; Low oxidation state; Main group; Oxidative addition; Redox chemistry; Insertion chemistry; Chlorocarbon solvents; Crown ether chemistry

1. Introduction

The concept of an element existing in a particular oxidation state is a fundamental and simple tool that may be used to understand or rationalize the structural and chemical characteristics of a molecule in which the element is located. By definition, an element in a lower oxidation state has a greater number of electrons associated with it than it would in a higher oxidation state; the presence of additional electrons has the potential to drastically alter the chemistry of compounds containing such centers [1]. In the case of the lighter members of the group 13 elements ($E = B$, Al, Ga, In), the +3 oxidation state (E^{III}) is the most stable which causes the electron-deficient neutral molecules containing such elements to behave as the prototypical Lewis acids. In contrast, the less common compounds that contain group 13 elements in the +1 oxidation state (E^{I}) can behave either as Lewis bases or Lewis acids, as illustrated in Scheme 1. Given their electron-rich nature, the use of E^{I} compounds, particularly cyclopentadienyl (C_5R_5, Cp′) compounds of the type Cp′E [2], as ligands for transition metal and main group acceptors has been exploited significantly since the late 1990's for the synthesis of new catalysts or materials precursors [3,4]. For indium, the unique behavior and redox properties of In^{I} compounds (often generated in situ) have proven to be particularly useful for the catalysis of several types of organic transformations [5–9].

One significant drawback to the exploitation of the chemistry of +1 oxidation state group 13 chemistry has been the lack of convenient starting materials [10]. For example, whereas well-characterized oligomeric E^{I} halides for $E = B$, Al and Ga are known, these materials have only been prepared in gas-phase reactions using special equipment that is not readily available. Furthermore, the metastable materials obtained using that protocol tend to decompose or disproportionate at ambient temperature [11,12]. The gallium reagent known as "$Ga^{I}I$" [13], which is often used as source of Ga^{I} centers, has neither the structure nor the composition suggested by the indicated formula [14,15]. In contrast to the lighter congeners, thallium(I) salts are often more stable than the corresponding thallium(III) analogues because of inert pair effects.

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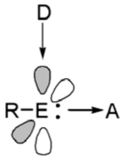


Scheme 1.

For indium, simple halide salts of both +1 and +3 oxidation states are well-known and commercially available, however such In^I salts are insoluble in most common organic solvents [10]. To allay the situation, we synthesized the unusually soluble indium(I) trifluoromethanesulfonate salt (indium(I) triflate, $InOSO_2CF_3$, InOTf, **1**) as an improved starting material for the study of low oxidation state group 13 chemistry [16].

Because of their electron-rich nature, it is not surprising that oxidative addition chemistry is typical of In^I reagents [10]. Several research groups have reported that In^I halides will readily insert into, e.g. elemental halogens; the Ch–Ch bonds in some peroxy-acids (Ch = O), organo-dithiolates (Ch = S), or organo-diselenides (Ch = Se); and certain other reactive heteronuclear bonds [10]. Of particular import to the work presented herein is the reported insertion of In^I halides into dihalomethanes (CH_2X_2; X = Br, I) to yield In^{III} compounds of the type X_2InCH_2X [17,18] or into haloforms (CHX_3; X = Cl, Br, I) to provide In^{III} compounds of the form X_2InCHX_2 [19,20]. These products were generally isolated as Lewis base adducts or as phosphonium ylides.

Recently, we have shown that the ligation of **1** with cyclic polyethers 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, indicated by the label "**a**" in the text) or 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadecane (dibenzo-18-crown-6, indicated by the label "**b**" in the text) allows for the isolation of unambiguously monomeric indium(I) compounds and alters the reactivity of the reagent significantly [21]. In this report, we present some of our findings regarding the reaction of [In(18-crown-6)][OTf] (**2a**[OTf]) and [In(dibenzo-18-crown-6)][OTf] (**2b**[OTf]) with solvents containing carbon–chlorine bonds.

2. Results and discussion

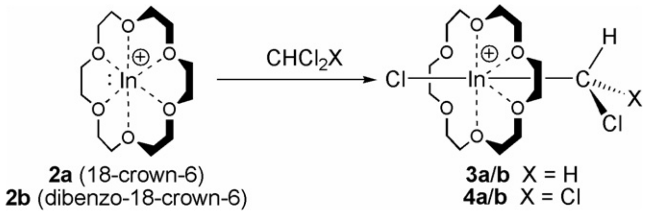
Given that insertion chemistry is typical of In^I halides and is employed for many organic transformations, we were surprised that the uncomplexed indium(+1) reagent InOTf [16] appears to be stable and unreactive toward chlorinated solvents, as evidenced by multi-nuclear NMR experiments, IR spectroscopy, physical characteristics (appearance, melting point) and X-ray crystallography. In contrast, when the crown ether ligated complexes of InOTf, **2a**[OTf] or **2b**[OTf], are subjected to chlorinated solvents, we had noticed that the reagent behaves quite differently. We have observed that whereas the dissolution of **1** in chlorinated solvents appears to occur slowly, samples of **2a**[OTf] or **2b**[OTf] are taken up rapidly in either dichloromethane or chloroform. More importantly, multinuclear NMR spectroscopic investigations and other characterization techniques reveal that the crowned indium triflate compound is not simply dissolved in the process but that the reagent actually reacts with the solvent. The results of the experiments with dichloromethane and chloroform (illustrated in Scheme 2) are summarized in the following sections.

2.1. Dichloromethane

The attempted dissolution of **2a**[OTf] (**2b**[OTf]) in dichloromethane results in the rapid uptake of the solid into the solution without any observable change in color or signs of decomposition. Upon removal of all volatile compounds from the reaction mixture, a colorless microcrystalline solid, characterized as **3a**[OTf] (**3b**[OTf]), is obtained in good yield. The melting points of the resultant materials (ca. 220° for **3a**[OTf] and 140° for **3b**[OTf]) are considerably different than the melting points of the corresponding crowned triflate reagents. The ^1H NMR spectra of **3a**[OTf] and **3b**[OTf] display peaks at 3.47 and 4.37 ppm, respectively, which are comparable to the chemical shifts reported by Tuck et al. [17] for the unstable adduct $Cl–In–CH_2Cl \cdot tmeda$ and are consistent with the presence of the CH_2Cl fragment on the In center in each case. Finally, positive ion mass spectra of each of the salts exhibit peak manifolds with isotopic ratios that are clearly indicative of the presence of two chlorine atoms in the cation of each salt.

While attempts to obtain pure crystalline samples of either **3a**[OTf] or **3b**[OTf] suitable for examination by single-crystal X-ray diffraction were unsuccessful, we were able to obtain some extremely-low-quality crystals of a related by-product of **3b** containing a different anion [22]. The crystallographic data were of such poor quality that the investigation of the sample (space group $P\bar{1}$: *a* 10.837(5), *b* 13.422(6), *c* 14.783(7), α 110.829(5), β 97.986(6), γ 109.970(5)) is only able to establish the connectivity of the cation, which is depicted in Fig. 1. Although the values of the metrical parameters in this model are not reliable, the presence of the observed C–Cl moiety and the Cl atom attached to the indium atom are consistent with the insertion of the In^I center into a carbon–chlorine bond of dichloromethane.

It is perhaps interesting to note that whereas the attempted reaction of InCl with CH_2Cl_2 did not provide for the isolation of the expected C–Cl insertion product



Scheme 2.