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.
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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 "GaI" [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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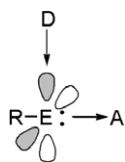
Scheme 1.

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 dichlo-

romethane 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

2a (18-crown-6)
2b (dibenzo-18-crown-6)
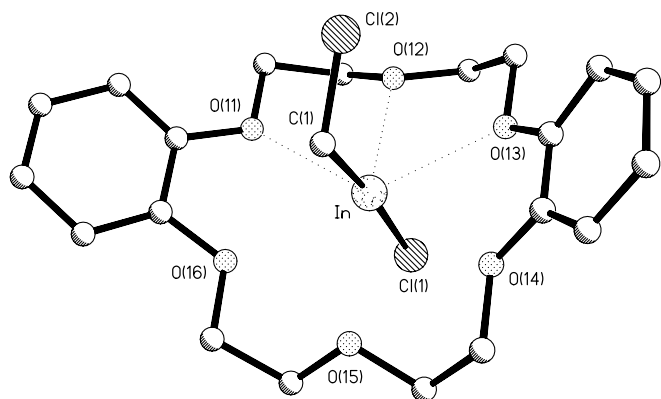
3a/b X = H
4a/b X = Cl
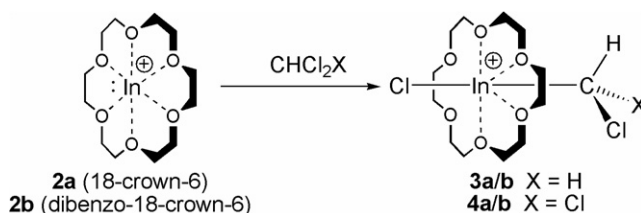
Scheme 2.

Fig. 1. Ball and stick representation of the connectivity in the cation **3b** from a diffraction experiment on a crystal of very poor quality.

in almost every instance because of a competing disproportionation process [17,18], in the cases of the crowned In^I reagents, the insertion reaction occurs as anticipated and no comparable disproportionation reactions are evident.

2.2. Chloroform

The reaction of **2a**[OTf] (**2b**[OTf]) with chloroform proceeds in a similar manner to that with dichloromethane. Thus the immersion of solid **2a**[OTf] (**2b**[OTf]) with chloroform results in the rapid disappearance of the solid and does not produce any obvious color changes. Removal of volatile materials under reduced pressure provides a colorless solid characterized as **4a**[OTf] (**4b**[OTf]) in very high yield. In one NMR scale reaction, large crystals rapidly precipitated from the as-prepared reaction mixture, however this behavior appears to have been a fortuitous consequence of the particular concentration; in most instances, crystalline material is obtained by the slow concentration of a solution of the salt in chloroform. As with the insertion products described above, every manner of characterization we employed indicates the formation of the insertion products. For example, the melting point of ca. 194 °C for **4a**[OTf] is clearly different than that of ca. 137 °C for **2a**[OTf]; the difference in temperatures between the melting points of 135 °C for **4b**[OTf] and 128 °C for **2b**[OTf] is considerably smaller, but the behavior is quite distinctive. Similarly, the new signals in the multinuclear NMR spectra are suggestive of the presence of the dichloromethyl substitutent in **4a**[OTf] and **4b**[OTf] and the isotope ratios in mass spectrometric investigations are consistent with the presence of three chlorine atoms in the cations of the salts.

For **4a**[OTf], the slow evaporation of a chloroform solution of the material yielded crystals suitable for examination by single-crystal X-ray diffraction. Details of the structure solution and refinement are located in Section 3 and in Table 1; a rendering of the salt components is provided in Fig. 2 and the values for important metrical parameters are listed in the figure caption. The salt crystallizes in the spacegroup $P2_1/m$ with half a cation and

half an anion in the asymmetric unit. There are no unusually short contacts between the cation and the anion and the triflate anion is (not surprisingly) very disordered; only the arrangement with the highest occupancy is shown in the figure. Of most import is the structure of the cation, which clearly shows the presence of a dichoromethyl fragment and a chloride substituent directly attached to the In center. The bond distances for the In–C bond (2.182(15) Å) and the In–Cl bond (2.329(4) Å) are consistent with the values that have been reported previously for the anion in the related salt [NEt$_4$][Cl$_3$In–CHCl$_2$] (In–C, 2.17(1) Å; In–Cl range from 2.366(4) to 2.376(4) Å) [20]. Consequently, the observed values fall within the range of values for such bonds [23] that have been collected in the Cambridge Structural Database (CSD) [24]. The most interesting features of the structure involve the arrangement of the crown ether about the cationic indium fragment. The 18-crown-6 ligand in **4a** adopts a conformation that allows for five close "equatorial" contacts (In-O distances range from 2.409(9) to 2.531(8) Å) between oxygen atoms on crown ether. The five-fold-coordination is in stark contrast to the symmetric 6-fold coordinated structure (with In-O distances from 2.8299(18) to 2.9292(18) Å) observed for the identical crown ether in **2a**[OTf] and emphasizes the difference in the sizes of In^{III} and In^I centers. A final observation concerning the conformation of the 18-crown-6 ligand in **4a** is that the 5-coordinate ligation of the indium center leaves one oxygen atom available to form a non-traditional hydrogen bond to the hydrogen atom situated on the dichloromethyl substituent. In fact, the importance of the putative hydrogen bonding interaction in determining the conformation adopted by the crown ether is illustrated by the structure of [InI$_2$ · 18-crown-6][InI$_4$], in which none of the oxygen atoms in the crown ether is distorted significantly away from the equatorial plane of the In atom [25].

In the case of **4b**[OTf], colorless crystals suitable for examination by single crystal X-ray diffraction experiments were obtained by the slow concentration of a solution of the salt in chloroform. Details regarding the solution and refinement of the structure are located in the Experimental section and in Table 1. The molecular structures of the cation and anion in the asymmetric unit are depicted in Fig. 3 (two molecules of chloroform that are also located in the asymmetric unit are not shown) and the values of important metrical parameters for the cation are listed in the figure caption. The bond distances and angle for the Cl–In–CHCl$_2$ fragment in **4b**[OTf] (In–C 2.174(7) Å; In–Cl 2.304(2) Å; C–In–Cl 171.81(19)°) are very similar to those described above for **4a**[OTf] and do not warrant further discussion. The indium atom in the cation **4b** is offset from the centroid of the six oxygen atoms in the ring toward one of the arene rings such that there are four close contacts (In-O from 2.517(5) to 2.550(5) Å) and two significantly longer contacts (2.738(5) and 2.756(5) Å).

Table 1
Summary of collection and refinement data for the X-ray diffraction investigations of **3a** and **3b**

Compound	[Cl–In–CHCl$_2$@18-cr-6][OTf] (**3a**[OTf])	[Cl–In–CHCl$_2$@db-18-cr-6][OTf] (**3b**[OTf])
Empirical formula	C$_{14}$H$_{25}$Cl$_3$F$_3$InO$_9$S	C$_{24}$H$_{27}$Cl$_9$F$_3$InO$_9$S
Formula weight	647.57	982.39
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/n$
Unit cell dimensions		
a (Å)	8.209(2)	8.8651(13)
b (Å)	11.010(3)	17.844(3)
c (Å)	13.018(3)	23.039(3)
α (°)	90	90
β (°)	101.763(3)	90.327(2)
γ (°)	90	90
Volume (Å^3)	1151.9(5)	3644.5(9)
Z	2	4
D_{calc} (g cm^{-3})	1.867	1.790
Absorption coefficient (mm^{-1})	1.531	1.427
$F(000)$	648	1952
θ Range for data collection (°)	1.60–25.00	1.44–25.00
Limiting indices	$-9 \leqslant h \leqslant 9$,	$-10 \leqslant h \leqslant 10$,
	$-13 \leqslant k \leqslant 13$,	$-21 \leqslant k \leqslant 21$,
	$-15 \leqslant l \leqslant 15$	$-27 \leqslant l \leqslant 27$
Reflections collected	10622	33811
Independent reflections	2136	6424
R_{int}	0.0609	0.0808
Data/restraints/parameters	2136/24/151	6424/6/437
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0959$, $wR_2 = 0.2303$	$R_1 = 0.0826$, $wR_2 = 0.1767$
R indices (all data)	$R_1 = 0.1223$, $wR_2 = 0.2499$	$R_1 = 0.1126$, $wR_2 = 0.1948$
Goodness-of-fit (S)[b] on F^2	1.133	1.156
Largest difference peak and hole (e Å^{-3})	4.749 and -1.542	1.399 and -0.838

[a] $R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $wR_2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2\}^{1/2}$, where w is the weight given each reflection.

[b] $S = \left[\sum w(|F_o|^2 - |F_c|^2)^2\right]/(n-p)^{1/2}$, where n is the number of reflections and p is the number of parameters used.
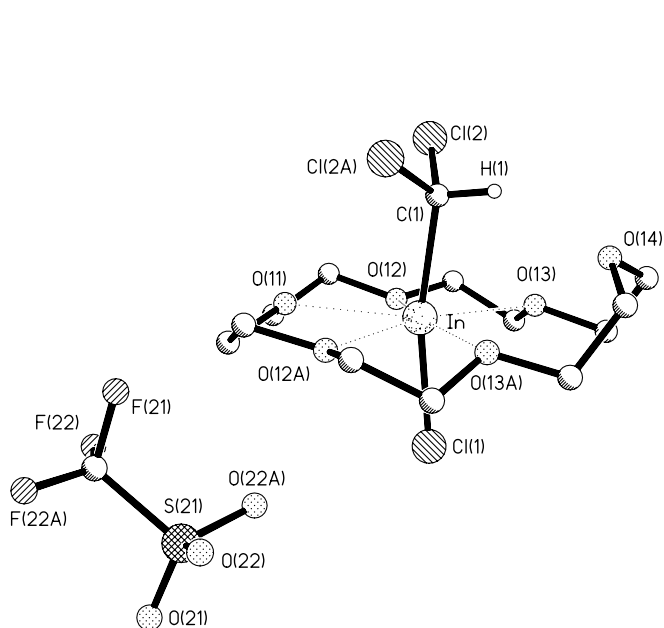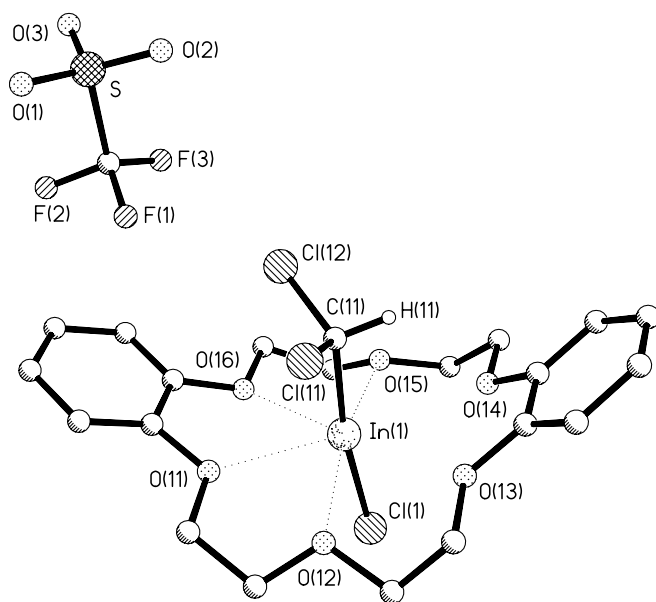

Fig. 2. Ball and stick representation of the salt **4a**[OTf] from a low-quality crystal; most of the hydrogen atoms have been omitted. Important bond distances (Å) and angles (°): In–C(1) 2.182(15), In–Cl(1) 2.329(4), In–O(11) 2.492(12), In–O(12) 2.409(9), In–O(13) 2.531(8), H(1)···O(14) 2.25(2), C(1)···O(14) 3.13(2), C(1)–In–Cl(1) 167.8(4).

Fig. 3. Ball and stick representation of the salt **4b**[OTf] from a low-quality crystal; most of the hydrogen atoms have been omitted. Important bond distances (Å) and angles (°): C(11)–In(1) 2.174(7), Cl(1)–In(1) 2.304(2), O(11)–In(1) 2.528(5), O(12)–In(1) 2.517(5), O(13)–In(1) 2.738(5), O(14)–In(1) 2.756(5), O(15)–In(1) 2.533(5), O(16)–In(1) 2.550(5), C(11)–In(1)–Cl(1) 171.81(19).

Perhaps the most interesting difference between the structures of **4a**[OTf] and **4b**[OTf] is the conformations adopted by the parent and benzannelated crown ethers. Whereas the parent 18-crown-6 polyether ligates the indium cation using five oxygen atoms at roughly similar distances and is contorted to engage in hydrogen bonding, the benzannelated analogue exhibits a structure that is virtually identical in conformation to that which is adopted in most of the structures in which the ligand is found in the CSD. It appears as if the rigidity imposed by the presence of the aromatic rings in dibenzo-18-crown-6 prevents the contortions that are possible for the more flexible polyether. In both cases, however, it is clear that the reduction in the size of the indium cation upon oxidation of the In^I centers (ionic radius 1.04 Å [26]) in the starting materials to In^{III} (ionic radius 0.81 Å [26]) requires an alteration in the arrangement of the crown ether to maximize the ligation of the metal.

2.3. Commentary

The reaction of the crown-ether-ligated In^I salts **2a**[OTf] and **2b**[OTf] with dichloromethane and chloroform proceeds rapidly to yield products derived from the formal insertion of the In^I center into a C–Cl bond of the solvent molecule. The observed reactivity is in contrast to the relatively inert behavior observed for the unligated salt InOTf, which does not appear to react with chlorocarbons at an appreciable rate. We surmise that the apparent non-reactivity of **1** is a kinetic effect that is likely attributable the agglomeration of the salt into clusters containing numerous In–O contacts, as observed in the crystal structure of **1** [16]. Because the ligation of **1** by the appropriately-sized crown ethers results in the formation of monomeric species, the increased reactivity of salts **2a**[OTf] and **2b**[OTf] is thus understandable.

We wish to note that our preliminary investigations of the interaction of salts **2a**[OTf] and **2b**[OTf] with carbon tetrachloride suggest that, while a reaction certainly occurs, the nature of the resultant products is ambiguous; mass spectrometric data suggest that the major cationic components are the chlorination products [InCl$_2$(18-crown-6)]$^+$ and [InCl$_2$(dibenzo-18-crown-6)]$^+$, respectively. More detailed studies of this system and studies of the insertion chemistry of **2a**[OTf] and **2b**[OTf] with more complex organo-chlorine compounds are currently underway.

Finally, we wish to note that, while the In^{III} products obtained from the reactions described above appear to be completely analogous to those that one would obtain from a traditional oxidative addition of a transition metal fragment, the mechanism for the actual process is unclear. If the crown ether remains attached to the In center during the reaction, it would seem unlikely that the reaction could occur by way of a concerted addition into the bond given that the Cl atom and CHClX fragments are *trans* to one another in the products. A more likely scenario would likely involve a step-wise addition; a computational investigation of this process is in progress.

3. Experimental

3.1. General methods

3.2. Specific procedures

3.2.1. Synthesis of 3a[OTf]

Dichloromethane (20 mL) was added to InOTf · C$_{12}$H$_{24}$O$_6$ (105 mg, 0.198 mmol) in a 100 mL Schlenk flask and stirred overnight. Volatiles were removed in vacuo and the product was obtained as a white powder (60 mg, 0.097 mmol) in 49% yield. m.p. 220–225 °C; ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 3.84$ (s; 24H; CH$_2$), 3.47 (s; 2H; CH$_2$Cl) ppm; ^{13}C NMR (CD$_2$Cl$_2$): $\delta = 70.5$ (s; CH$_2$) ppm. HRMS (ESI-TOF): m/z calculated for InC$_{13}$H$_{26}$O$_6$Cl$_2$: 463.0145, found: 463.0166 (4.5 ppm).

3.2.2. Synthesis of 3b[OTf]

Dichloromethane (20 mL) was added to InOTf · C$_{20}$H$_{24}$O$_6$ (101 mg, 0.162 mmol) in a 100 mL Schlenk flask and stirred overnight. Volatiles were removed in vacuo and the product was obtained as a white powder (72 mg, 0.102 mmol) in 63% yield. m.p. 140–144 °C; ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 4.03$ (s; 8H; CH$_2$), 4.13 (s; 8H; CH$_2$), 6.91 (m; 8H; Ar–H), 4.37 (m; 2H; CH$_2$Cl) ppm; ^{13}C NMR (CD$_2$Cl$_2$) $\delta = 67.7$ (s, CH$_2$), 69.6 (s, CH$_2$), 112.7 (s; β-Ar), 122.2 (s; α-Ar), 147.2 (s, O–C$_{Ar}$) ppm. HRMS (ESI-TOF): m/z calculated for InC$_{21}$H$_{26}$O$_6$Cl$_2$: 559.0145, found: 559.0153 (1.4 ppm).

3.2.3. Synthesis of 4a[OTf]

Chloroform (20 mL) was added to InOTf · C$_{12}$H$_{24}$O$_6$ (104 mg, 0.196 mmol) in a 100 mL Schlenk flask and stirred overnight. Volatiles were removed in vacuo and the product was obtained as a white powder (72 mg, 0.112 mmol) in 57% yield. m.p. 193–198 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.89$ (s; 24H; CH$_2$), 5.87 (s; 1H; CHCl$_2$) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 70.2$ (s; CH$_2$) ppm. HRMS (ESI-TOF):

m/z calculated for $InC_{13}H_{25}O_6Cl_3$: 496.9755, found: 496.9743 (-2.5 ppm).

3.2.4. Synthesis of **4b[OTf]**

Chloroform (20 mL) was added to $InOTf \cdot C_{20}H_{24}O_6$ (103 mg, 0.165 mmol) in a 100 mL Schlenk flask and stirred overnight. Volatiles were removed in vacuo and the product was obtained as a white powder (75 mg, 0.100 mmol) in 61% yield. m.p. 129–135 °C; ^1H NMR (CDCl$_3$): $\delta =$ 4.12 (m; 16H; CH$_2$), $\delta = 7.06$ (m; 8H; Ar–H), $\delta = 5.65$ (m; 1H; CHCl$_2$) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 67.9$ (s; CH$_2$), 69.0 (s; CH$_2$), 111.7 (s; β-Ar), 123.8 (s; α-Ar), 149.0 (s; O–C$_{Ar}$) ppm. HRMS (ESI-TOF): m/z calculated for $InC_{21}H_{25}O_6Cl_3$: 592.9755, found: 592.9745 (-1.8 ppm).

3.3. Crystallography

In the dry N$_2$ atmosphere of a VAC glovebox, each crystal was selected and mounted in thin-walled glass capillary tubes. These were subsequently flame-sealed and glued to brass pins suitable for attachment to a goniometer head. The data were collected using the SMART [28] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 10 s per frame at 25 °C. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reductions were performed using the SAINT [29] software and the data were corrected for absorption using SADABS [30]. The structures were solved by direct methods using SIR97 [31] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97 [32] and the WINGX [33] software package and thermal ellipsoid plots were produced using SHELXTL [34]. Considerable disorder in either anions or solvent molecules was manifested in each of the structures reported below; various restraints, constraints and partial occupancy models were employed in the solutions.

Acknowledgments

Appendix A. Supplementary material

CCDC 280062 and 623766 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.006.

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[22] The anion is very disordered and sits on an inversion center but appears to be primarily $[In(OTf)_4Cl]^{-2}$.
[23] CSD range for non-bridging In–C bonds: 2.044–2.453 Å, average 2.177 Å. CSD range for terminal In–Cl bonds: 2.266–2.893 Å, average 2.428 Å.
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