Alternative syntheses of univalent indium salts including a direct route from indium metal†‡

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Protonolysis of indium(I) reagents using an [18]crown-6 poly-ether pre-treated with trifluoromethanesulfonic acid (HOTf) provides an efficient route to the known salt [In([18]-crown-6)][OTf] in excellent yield. The analogous reaction employing trifluoroacetic acid (HTFA) allows for the isolation of [In([18]crown-6)][TFA], a monovalent indium complex for which the uncrowned salt is not stable at ambient conditions. The direct treatment of indium metal with HOTf, either in the presence or absence of [18]crown-6, provides a high-yield synthetic approach to univalent indium salts that does not require the use of a pre-existing indium(I) reagent.

Low valent, low oxidation state[1] indium species have received increased attention in recent years in terms of their fundamental chemistry[2,3] and for their use as stoichiometric reagents and catalysts.[4–9] In 2004, we described the preparation and isolation of a new source of monovalent indium in the form of a trifluoromethane (triflate) salt: InOTf, **1**.[10] This triflate salt is considerably more soluble and more stable at ambient temperature in a variety of organic solvents than are the comparable halide salts and thus allows for its reactions to be conducted under homogenous conditions. A selection of the reactions that have been reported employing this reagent are illustrated in Fig. 1. While some of the reactivity of **1** clearly mimics that of the related halide salts, such as its use in the metathetical preparation of In^I clusters,[11] its ability to function as a catalyst for organic allylation reactions[8] and its use as a reagent for the generation of mixed-valent species,[12] other chemical behaviour of the triflate reagent is distinct. For example, indium(I) halide salts typically disproportionate rapidly in the presence of coordinating solvents or other Lewis bases[2,3] and structural analyses of preparations that have been employed synthetically as soluble indium(I) halide sources reveal that they do not have the proposed composition;[13] the isolation of a genuine example of a Lewis base adduct of an In^I halide has only proven possible through careful handling at low temperature.[14] In sharp contrast to the halides, the treatment of **1** with crown ethers[15,16] or bis(iminopyridyl) ligands[17] produce stable, monomeric adducts that are even more soluble than the parent salt, as also illustrated in Fig. 1.[15]

In the case of the ligand [18]crown-6, we have found that there are significant changes in the behaviour of **1** in the presence or absence of the ligand. For example, while **1** decomposes upon prolonged exposure to THF, the "crowned" salt [In([18]crown-6)[OTf], **2**, appears to be stable indefinitely in that solvent. Furthermore, whereas **1** does not appear to react with chlorinated solvents at an appreciable rate, the "crowned" indium(I) salt **2** rapidly inserts into the carbon–chlorine bonds of dichloromethane and chloroform.[15,18] The differing reactivity of the ligated species as compared to its parent salt, **1**, illustrates the potential versatility and tunability of these monovalent indium reagents.

As illustrated in Scheme 1, the preparative routes to **1** that we reported previously involve the protonolytic removal of C_5Me_5H (Cp*H) or HCl from the corresponding indium(I) starting materials C_5Me_5In (Cp*In)[19] or InCl with the strong non-oxidizing triflic acid. In both cases, the resultant protonated by-product is readily removed under reduced pressure and with washing; the use of indium(I) chloride is somewhat more convenient given the commercial availability and lower cost of the reagent, however subsequent reactivity studies reveal that the salt prepared in this manner contains minor amounts of chloride ion contamination. In this work, we present a new synthetic approach to **1**, **2** and related species that eliminates the possibility of chloride ion contamination and, more importantly, eliminates the need for a pre-existing indium(I) reagent.

Before describing our new synthetic protocol, we wish to note that we have also discovered a perhaps predictable

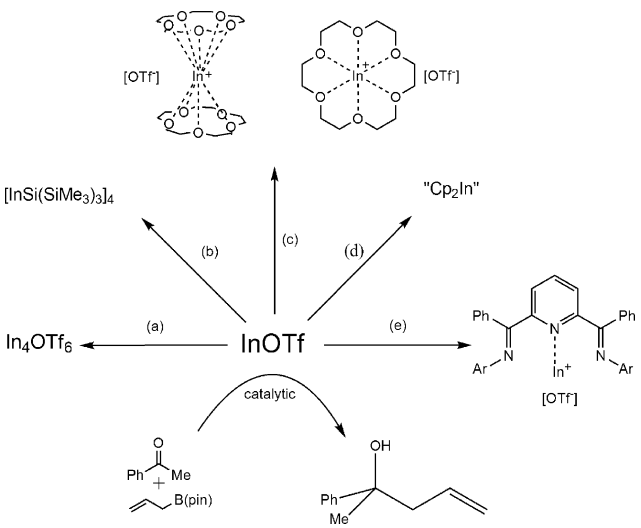

Fig. 1 Some examples of indium(I) triflate, **1**, as a reagent. (a) $[Cp_2Fe][PF_6]$, – by-products;[12] (b) $LiSi(SiMe_3)_3{\cdot}3thf$, – by-products;[11] (c) L = 2 [15]crown-5 or [18]crown-6;[15,16] (d) Cp_2Mn, – by-products;[12] (e) $[\{2,4\text{-}^tBu_2C_6H_3NCPh\}_2(NC_5H_3)]$.[17]

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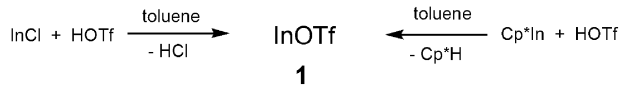


Scheme 1 Preparation of InOTf *via* protonolysis of In^{I}-containing precursors.

modification of the synthetic approach outlined in Scheme 1 that can be used to generate **2** in a "one-pot" reaction. Given that we had already found that protonated diethylether (present in the etherial solution of HBF_4) is sufficiently acidic to effect such protonolysis reactions,[10] we reasoned that a protonated crown ether may also be a suitable acid for the reaction. As anticipated, the treatment of either InCl or Cp*In with an equimolar solution of [18]crown-6 and HOTf in toluene results in the formation of **2** in essentially quantitative yield. As one might anticipate, it is also possible to treat [18]crown-6 with HOTf prior to the reaction in order to obtain a "crowned-acid" reagent of the form HOTf·[18]crown-6 *in situ* that may be more convenient for some applications; the treatment of either of the indium(I) reagents in Scheme 1 with toluene solutions of this acid complex also produces **2**.

While the one-pot "crowned-acid" approach may appear to be a trivial development in the case of triflic acid, we wish to note that this protocol appears to be applicable to other acids. Importantly, we have found that such an *in situ* approach can be employed to generate and isolate stable crown ether adducts of salts that are *not stable in the absence of the crown ether*. For example, whereas the protonolysis of InCl or Cp*In with trifluoroacetic acid results in the formation of a material that rapidly decomposes, if the same reactions are conducted in the presence of [18]crown-6, one is able to isolate a stable colorless crystalline material characterized as [In([18]crown-6)-[TFA], **3** (TFA = trifluoroacetate), on the basis of spectroscopic methods and X-ray diffraction.

The salt **3** crystallizes in the space group $P2_1/m$ with the molecule bisected by a mirror plane; the molecular structure is illustrated in Fig. 2 and some relevant metrical parameters are included in the figure caption. The In–O(1) distance of 2.272(5) Å is considerably shorter than the corresponding In–OTf distance of 2.370(2) Å found in **2**,[15] which we describe as a contact ion pair, and is well within the sum of the ionic radii for In(+1) and O(−2) (1.04 Å + 1.40 Å = 2.44 Å).[20] The closer approach may suggest a stronger interaction between the indium(I) center and the anion however the C–O distances in the TFA anion (1.218(8) and 1.221(8) Å) are indistinguishable from each other and are again consistent with the complex being described as a contact ion pair. All of the other metrical parameters are consistent with those reported for **2** and require no additional comment.

As indicated above, during investigations into the reactivity of salts **1** and **2** it was observed that a chloride contaminant was sometimes present in indium(I) triflate prepared from InCl. Furthermore, both of the protonolytic routes described in Scheme 1 rely upon the use of expensive or inconvenient reagents that already contain indium(I). Given the potential of these and related salts as reagents, an alternative synthetic route to such compounds appeared desirable. Herein, we report a facile, clean synthetic approach to making univalent salts starting from indium metal.

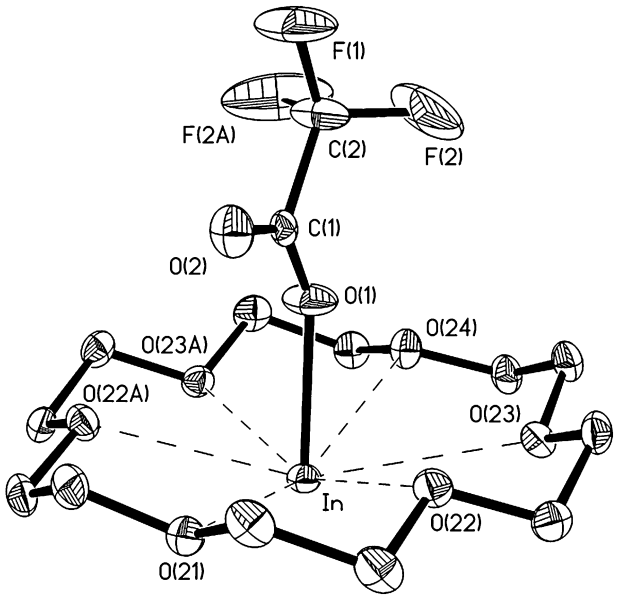


Fig. 2 Solid-state molecular structure of [In([18]crown-6)][TFA], **3**, with 30% probability ellipsoids (hydrogen atoms are omitted for clarity; the symmetry-related atoms labelled with "A" are generated by the presence of the mirror plane (x, $\frac{1}{2} - y$, z)). Selected metrical parameters including bond distances (Å) and angles (°): C(1)–O(1) 1.218(8), C(1)–O(2) 1.221(8), In–O(1) 2.272(5), In–O(21) 2.785(5), In–O(22) 2.825(4), In–O(23) 2.951(4), In–O(24) 2.985(5), In–O(1)–C(1) 144.0(5), O(1)–C(1)–O(2) 132.4(7).

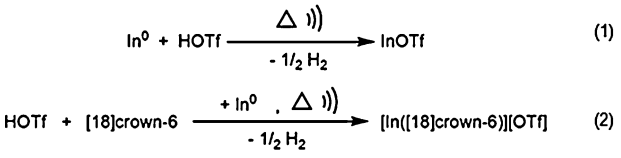
The ability to synthesize indium(I) species starting from metallic indium has been reported previously. For example, the electrochemical oxidation of indium metal has been used to prepare some monovalent indium species[21,22] and, in a related fashion, the redox reaction of silver(I) salts with metallic indium has been used to generate solutions of In^{I} that were used *in situ*.[23] More pertinently to the present work, the reaction of indium with boron trifluoride in anhydrous HF generates $InBF_4$[24] whereas attempts to prepare $InPnF_6$ (Pn = P, As, Sb) using a similar approach employing PnF_5 in HF only worked partially in the case of Pn = P and generated InF_3 derivatives for Pn = As and Sb.[25] In spite of the last observation and in light of the preparation of monovalent indium compounds from phenolic quinone derivatives and indium metal reported by Tuck and co-workers[26,27] (and the well-known behaviour of indium's group 14 neighbour tin[28]), we reasoned that it might be possible to obtain indium(I) salts by the treatment of indium metal with a stoichiometric quantity of an appropriate acid. Our discoveries in this regard are presented below.

The reaction of equimolar amounts of triflic acid and metallic indium in toluene in a heated ultrasonic bath affords **1** in high yields (Scheme 2) after prolonged treatment. The progress of the reaction can be followed using ^{115}In NMR spectroscopy. Aliquots of the reaction mixture were taken at several intervals, all volatile components were removed and the remaining solid was dissolved in MeCN. Analysis of the resultant spectra suggests that the reaction proceeds through the initial formation of $InOTf_3$ (δ −188 ppm) which subsequently reacts with the remaining indium metal to provide

the stoichiometric product, InOTf (δ −1053 ppm); signals for each of these species are the only resonances present in the ^{115}In NMR spectra of incomplete reaction mixtures. It should be noted that test reactions starting with commercial $InOTf_3$ and two equivalents of indium metal in toluene do indeed produce **1** and thus corroborate the NMR spectroscopy observations. The amount of time required for completion of the reaction can vary considerably (up to a month in certain instances) and the progress of the reaction can be conveniently estimated visually on the basis of the amount of metal remaining in the flask. We wish to emphasize that the solvent employed in this reaction appears to be of critical importance: test reactions reveal that the use of acetonitrile appears to block the reaction of $InOTf_3$ with In^0 (perhaps by filling the vacant coordination site(s) on the In^{III} center) and, although it is the solvent we use for the preparation, the very low solubility of $InOTf_3$ in toluene may be responsible for the slow rate of the reaction.

Perhaps not surprisingly, the presence of a crown ether ligand in the metal–acid synthesis alters the reaction dramatically and also decreases the time for the reaction to proceed to completion. The reaction of triflic acid with [18]crown-6 and indium metal shows no evidence of the formation of $InOTf_3$ at any point in the reaction and ^{115}In NMR studies of samples of the incomplete reaction feature only the signal at *ca.* −1050 ppm attributable to the In^I cation. This observation suggests the presence of the crown ether hinders the complete oxidation to In^{III}, either by trapping the In^I center and/or by rendering the trivalent alternative relatively unfavourable. The purity of the bulk sample for of **2** produced in using this method was confirmed by powder X-ray diffraction (pXRD) studies. Fig. 3 shows the agreement between the predicted pXRD pattern and the experimentally obtained pattern for the metal synthesized product, and confirms that the only observable crystalline material is the desired product. It should be noted that similar pXRD studies of **1** are hindered by significant absorption of the CuKα radiation by the salt.

Given that triflic acid in the presence of [18]crown-6 can successfully oxidize indium metal to produce monovalent indium salts, and the ability of that same crown ether to stabilize In^I salts that are otherwise unstable, we wished to probe the reaction of indium metal with other "crowned" acids. Thus, the reactions of metallic indium with *p*-toluenesulfonic acid, methanesulfonic acid, and trifluoroacetic acid were conducted under conditions identical to those employed for triflic acid. In each case, the reactions featured the characteristic In^I resonance in the ^{115}In NMR spectra at −1062, −1070, and −1085 ppm, respectively. However, it must be emphasized that, in contrast to the reaction employing triflic acid, these reactions were not complete even after 2 months of reaction time, and the low intensity of the signals in their ^{115}In NMR spectra suggests only limited product formation. Attempts to optimize the reaction conditions for these experiments are ongoing.



Scheme 2 Metal–acid syntheses of indium(I) salts.

In closing, we wish to emphasize that reaction of a mixture of acid and [18]crown-6 can be employed to synthesize unusually-stable complexed In^I salts and, more generally, that the direct reaction of triflic acid with indium metal, either in the presence or absence of [18]crown-6, provides a reliable method for the generation of soluble monovalent indium reagents.

Experimental

General methods

All work was carried out using standard inert-atmosphere techniques as indium(I) compounds tend to be somewhat air- or moisture-sensitive. All reagents and solvents were obtained from Aldrich and were used without further purification. Solvents were dried on a series of Grubbs'-type columns and were degassed prior to use.[29] Unless otherwise noted in the text, NMR spectra were recorded at room temperature on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards ($SiMe_4$ for ^{1}H and ^{13}C, $In^{+3}(OH_2)_6$ for ^{115}In, $CFCl_3$ for ^{19}F), please note that the ^{115}In spectra were referenced using a solution of $[NEt_4][InCl_4]$ (δ 365 ppm) because it has a much smaller line-width than the indium(III) hexahydrate standard. Melting points were obtained using an Electrothermal® melting point apparatus on samples sealed in glass capillaries under dry nitrogen. Each of the reactions reported below appears to occur in a nearly quantitative fashion; the somewhat smaller isolated yields are attributable to mechanical losses during the workup.

X-Ray crystallography‡

The subject crystal was covered in Nujol®, mounted on a goniometer head and rapidly placed in the dry N_2 cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the SMART[30] software on a Bruker APEX CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10 s per frame at −100 °C. Data reduction was performed using the SAINT-Plus[31] software and the data were corrected for absorption using SADABS.[32] The structure was solved by direct methods using SIR97[33] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97[34,35] and the WinGX[36] software package and thermal ellipsoid plots were produced using SHELXTL.[37] Please note that the use of alternative models to describe the disorder of the fluorine atoms did not improve the solution significantly and attempts to solve the crystal in the space group $P2_1$ produce models containing numerous non-positive definite thermal ellipsoids (Table 1).

Powder X-ray diffraction (pXRD) experiments were performed with a Bruker D8 Discover diffractometer equipped

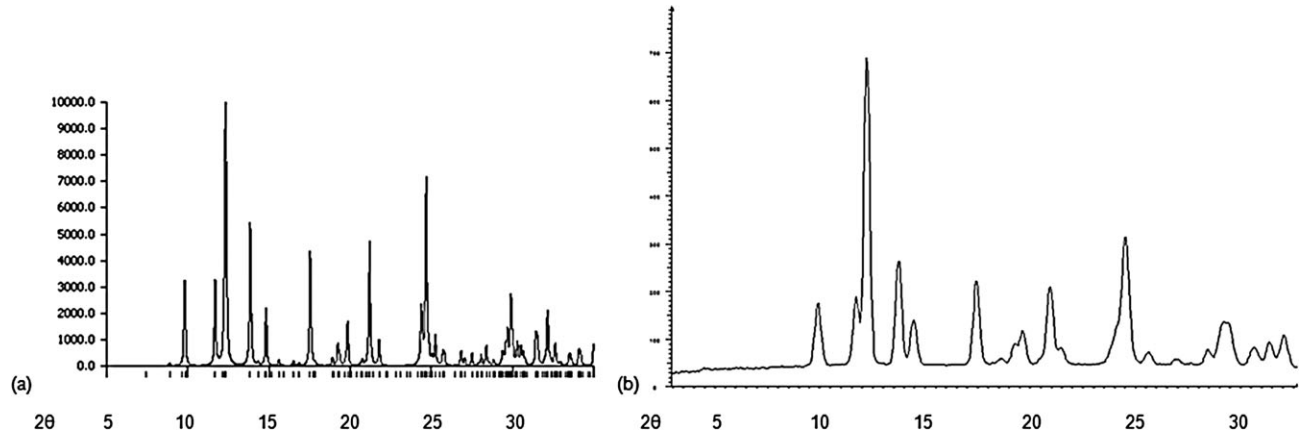


Fig. 3 (a) Calculated powder pattern for **2** on the basis of the single crystal structure;[15] (b) experimentally observed pattern for **2** prepared by the metal–"crowned-acid" protocol.

with a Hi-Star area detector using CuKα radiation (λ = 1.54186 Å). Powder XRD pattern simulations were performed using Mercury CSD 2.2.[38] For known compounds, these patterns were simulated on the basis of relevant data contained in the Cambridge Structural Database (CSD).[39]

Protonolysis synthesis of [In([18]crown-6)][OTf], 2

Cp*In (88 mg, 0.333 mmol) was added to a solution of triflic acid (50 mg, 0.333 mmol) and [18]crown-6 (83 mg, 0.333 mmol) in toluene (25 mL). The reaction mixture was then allowed to stir for 12 h. Volatile components were then removed under reduced pressure and the product was obtained as a colorless powder (137 mg, 78% yield).

Protonolysis synthesis of [In([18]crown-6)][TFA], 3

Cp*In (131 mg, 0.524 mmol) was added to a solution of trifluoroacetic acid (60 mg, 0.526 mmol) and [18]crown-6 (139 mg, 0.526 mmol) in toluene (25 mL). The reaction was stirred at ambient conditions for 12 h and then volatile components were then removed under reduced pressure, and

Table 1 Crystal data and structure refinement for [In([18]crown-6)][TFA]

Compound	[In([18]crown-6)][TFA]
Empirical formula	$C_{14}H_{24}F_3InO_8$
Formula weight	492.15
Temperature/K	173(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 9.100(3) Å; α = 90°
	b = 11.571(3) Å; β = 105.692(3)°
	c = 9.634(3) Å; γ = 90°
Volume/Å^3	976.7(5)
Z	2
Density (calculated)/g cm^{-3}	1.674
Absorption coefficient/mm^{-1}	1.274
F(000)	496
Crystal size/mm^3	0.20 × 0.10 × 0.10
θ range for data collection	2.20° to 27.50°
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-12 \leq l \leq 12$
Reflections collected	10 655
Independent reflections	2303
R_{int}	0.1133
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.880 and 0.702
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2303/0/130
Goodness-of-fit on F^2	0.989
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0552
	wR_2 = 0.0917
R indices (all data)	R_1 = 0.1060
	wR_2 = 0.1040
Largest diff. peak and hole/e Å^{-3}	1.130 and −1.214

[a] $R_1(F)$: $\{\sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sum(F_o))$. w$R_2(F^2)$: $\{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2\}^{1/2}$ where w is the weight given each reflection.

the product was obtained as a colorless powder. While the reaction appears quantitative, the isolated yield is diminished by loss of product during work up (285 mg, 58% yield). Found: C, 28.60; H, 4.26%. $C_{14}H_{24}F_3O_8In$ requires: C, 34.14; H, 4.92% (partially decomposed in transit). Mp 96–103 °C; ^{1}H NMR (MeCN-d_3): δ = 3.607 (CH_2); ^{13}C NMR (MeCN-d_3): δ = 70.917 (CH_2); ^{115}In NMR (MeCN): δ = −1085 ppm; ^{19}F NMR (MeCN): δ = −75.3 ppm.

Metal–acid synthesis of InOTf, 1

Indium metal (1.00 g, 8.71 mmol) was added to a solution of triflic acid (1.31 g, 8.71 mmol) in toluene (25 mL). The reaction mixture was then allowed to sonicate at 40 °C until no traces of indium metal remained in the reaction vessel (this can take up to one month). Volatile components were then removed under reduced pressure, the resultant solid was washed with pentane and the product was obtained as a colorless powder (2.12 g, 92% yield). ^{115}In NMR (MeCN): δ = −1053 ppm. All other physical and spectroscopic features of the product are identical to those of material obtained using the Cp* protonolysis approach.

Metal–acid synthesis of [In([18]crown-6)][OTf], 2

Indium metal (1.00 g, 8.71 mmol) was added to a solution of triflic acid (1.31 g, 8.71 mmol) and [18]crown-6 (2.30 g, 8.71 mmol) in toluene (25 mL). The reaction mixture was then allowed to sonicate at 40 °C for two weeks, or until no traces of indium metal remained in the reaction vessel. Volatile components were then removed under reduced pressure, the resultant solid was washed with pentane and the product was obtained as a colorless powder (4.360 g, 95% yield). ^{115}In NMR (MeCN): δ = −1054 ppm. All other physical and spectroscopic features of the product are identical to those of material obtained using the Cp* protonolysis approach.

Acknowledgements

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