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Crown Ether Ligation: An Approach to Low-Oxidation-State Indium Compounds**

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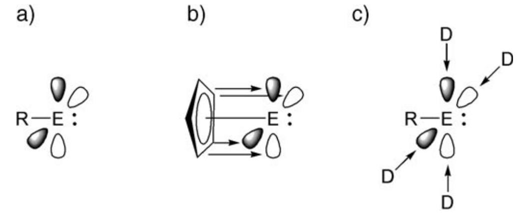
In memory of Dennis G. Tuck

The chemistry of Group 13 elements in oxidation states lower than +3 has been a subject of increasing importance in main-group chemistry over the last 20 years. Particular attention has focused on the chemistry of compounds containing Group 13 elements in the +1 oxidation state (E^I) for both fundamental and practical purposes.[1–3] The presence of the "lone pair" of electrons on E^I (Scheme 1a) often makes the normally Lewis acidic Group 13 center behave as a Lewis base instead. Such altered reactivity means that compounds containing E^I centers can be used as ligands for main-group[4] and transition-metal acceptors;[5,6] some of the coordination complexes thus obtained have proven to be useful precursors for the formation of intermetallic and other materials.[6]



Scheme 1. a) The "lone pair" of electrons on E^I. b) Electron donation to the formally vacant p orbitals on the E^I center resulting in stabalization. The postulated use of an appropriately shaped auxiliary donor to stabilize the vacant orbitals.

Although sterically demanding substituents such as terphenyl[7,8] and β-diketiminate[9–13] ligands have been used to obtain some examples, the vast majority of stable monomeric compounds containing E^I centers (apart from thallium[14]) have the Group 13 element bound to either a cyclopentadienyl (Cp) substituent[15] or to an isolobal tris(pyrazolyl)borate group.[16] These σ- and π-donating substituents stabilize

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the low-oxidation-state center by providing sufficient electron density to fill the formally vacant p orbitals on the E^{I} center, as illustrated for a Cp group in Scheme 1 b. We postulated that monomeric E^{I} species containing nonbulky, poorly or non-π-donating ligands could be stabilized by using an appropriately shaped auxiliary donor to stabilize the vacant orbitals (Scheme 1 c). The shape and properties of the polydentate donor ligand are important in this context because, although coordination to E^{I} centers may appear to be trivial in theory, all previous attempts to coordinate donors to potentially monomeric E^{I} centers have resulted in the disproportionation of the Group 13 compound and the isolation of higher-oxidation-state products.[17–19]

Herein, we demonstrate that properly sized crown ethers are suitable ligands for this task; this approach has allowed us to isolate the first example of a monomeric adduct of a true $R-E^{I}$ compound with a Lewis base. Furthermore, the presence of the crown ether modifies the reactivity of the $R-E^{I}$ species. Lastly, we show that appropriate crown ethers can even be used to favor the formation of an $R-E^{I}$ environment from higher-oxidation-state precursors.

Recently, we reported syntheses for the salt $InSO_3CF_3$ (InOTf, **1**),[20] which is unusually soluble for an inorganic In^{I} salt. The solubility of this reagent in organic and particularly aromatic solvents has allowed us to conduct experiments using homogeneous solutions and to avoid the heterogeneous conditions often caused by the insolubility of In^{I} halides. Thus the reaction of **1** with 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6; compounds labeled **a**) or 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadecane (dibenzo[18]crown-6; compounds labeled **b**) in toluene resulted in the formation of a colorless solution. Concentration of the solution produced crystals of the 1:1 coordination complex **2a** or **2b**, as confirmed by spectroscopic and analytical methods. The colorless crystals of **2a** were subjected to a single-crystal X-ray diffraction experiment;[21] the molecular structure of **2a** is depicted in Figure 1, and there are no unusually short intermolecular contacts. There are three important features in the structure of **2a**. Most noticeably, the complex still contains an In^{I} center, and **2a** is thus the only example of an intact monomeric In^{I} compound acting as a Lewis acid; every previous attempt to ligate bases to In^{I} salts has resulted in the disproportionation of the In^{I} compound.[18,19] Secondly, the In atom is situated essentially on the centroid of the O_6 ring, in marked contrast to the cationic In^{III} center in $[InI_2([18]crown\text{-}6)][InI_4]$.[22] Of further note is the relatively short In–O(11) distance of 2.370(2) Å, which is considerably shorter than the shortest distance of 2.579(6) Å found in **1**. Moreover, the crystallographic equivalence of the S–O bond lengths (1.435(2), 1.432(2), and 1.426(2) Å) is consistent with an ionic trifluoromethansulfonate (triflate) anion, thus, the data suggest that **2a** is best considered as an isolated contact ion pair in the solid state. Such an interpretation is also consistent with the ionic radii suggested for In^{I} (1.04 Å) and O^{2-} ions (1.40 Å).[23] All other metrical parameters are as one would predict, given the components of the adduct, and require no further comment.

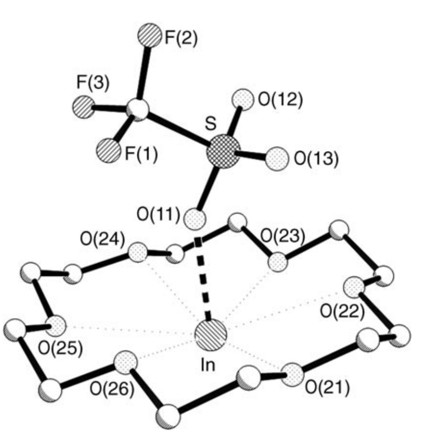
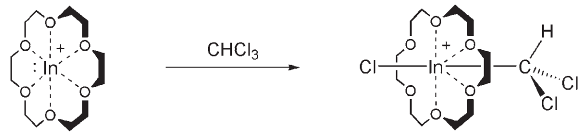


Figure 1. Molecular structure of **2a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: O(11)-S 1.435(2), O(11)-In 2.370(2), O(12)-S 1.431(2), O(13)-S 1.426(2), O(21)-In 2.8690(18), O(22)-In 2.8492(18), O(23)-In 2.8299(18), O(24)-In 2.8513(18), O(25)-In 2.9292(18), O(26)-In 2.9167(19); S-O(11)-In 151.39(13).

Perhaps surprisingly, the analogous reactions of indium(I) chloride with [18]crown-6 or dibenzo[18]crown-6 result in the immediate deposition of In metal and the formation of products with In in a higher oxidation state. The disproportionation of $In^{I}Cl$ clearly contrasts with the behavior of **1** and suggests that the triflate anion confers benefits other than merely increased solubility to such low-oxidation-state reagents.

As well as providing monomeric compounds, the crown ethers appear to alter the reactivity of **1**. In particular, **1** is soluble in dichloromethane and chloroform but does not appear to react with the solvents at an appreciable rate. In contrast, **2a** and **2b** react rapidly with such chlorinated solvents through formal oxidative insertions into C–Cl bonds to form the compounds **3a** and **3b**, respectively, as outlined in Scheme 2. In the case of **3b**, crystalline material suitable for analysis by X-ray diffraction was obtained and the molecular structure obtained from the experiment is displayed in Figure 2.



Scheme 2. Oxidative addition of a C–Cl bond in chloroform to the In^{I} cation in **2** to produce the cation in **3**. Note: the crown ether is [18]crown-6 for **a** and dibenzo[18]crown-6 for **b**.

The molecular structure of **3b** consists of distinct cations of the form $[In(CHCl_2)Cl(dibenzo[18]crown\text{-}6)]^{+}$ and triflate anions. There are no unusually short interionic distances and the metrical parameters of the anion are consistent with it being noncoordinating and ionic. The structural features of the cation, although unique, are predictable. For example, the smaller In^{III} ion is offset from the center of the O_6 ring to allow for four shorter In–O contacts (2.517(5) to 2.550(5) Å) and thus leaves two much longer In···O contacts (2.738(5) and 2.756(5) Å). The In–Cl bond length of 2.304(2) Å is one of the

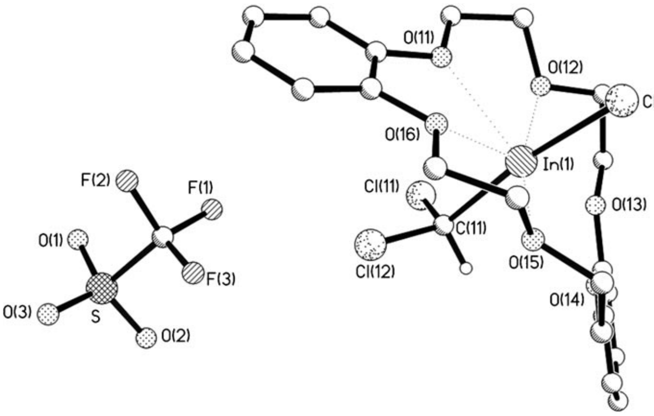


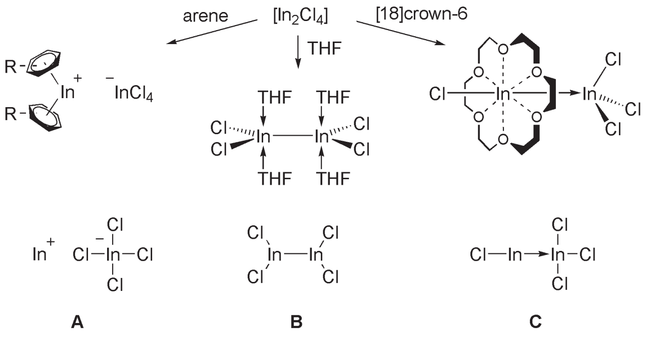
Figure 2. Molecular structure of **3b**. Most of the hydrogen atoms are omitted for clarity and two additional molecules of chloroform are not shown. Selected bond lengths [Å] and angles [°]: C(11)-In(1) 2.174(7), Cl(1)-In(1) 2.304(2), C(11)-Cl(11) 1.717(8), C(11)-Cl(12) 1.747(7), O(11)-In(1) 2.528(5), 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), O(1)-S 1.438(6), O(2)-S 1.424(7), O(3)-S 1.425(7); C(11)-In(1)-Cl(1) 171.81(19).

shortest such distances so far reported;[24] however, the In–C bond length of 2.174(7) Å is typical of such bonds[25,26] reported in the Cambridge Structural Database (CSD).[27] The minor deviation of the Cl-In-C angle from linearity (171.82(19)°) is consistent with the asymmetric ligation of the In center by the crown ether. All the other bond lengths and angles are typical and require no further comment.

Whereas the structural details of **3b** are unambiguous, the mechanism through which the oxidative addition occurs remains to be elucidated. Overall, we postulate that the enhanced reactivity of **2** with chlorocarbons relative to **1** may be attributable to the crown ether limiting the degree of agglomeration of **1** in solution. In this context, ligation of $\mathrm{In^I}$ species by crown ethers may possibly be used to significantly alter the reactivity of this important class of catalysts for certain organic transformations.[28]

Finally, crown ethers have provided us with a new method to generate $\mathrm{In^I}$ centers from $\mathrm{In^{II}}$ reagents. It is well-known that $[\mathrm{In_2Cl_4}]$ disproportionates to form the $\mathrm{In^I/In^{III}}$ salt $[\mathrm{In}][\mathrm{InCl_4}]$ in the presence of certain arenes (Scheme 3, **A**);[29,30] however, the reactions of such salts with ethers or other donors yield complexes containing $\mathrm{In^{II}}$ (Scheme 3, **B**).[31] In contrast, the reaction of $[\mathrm{In_2Cl_4}]$ with dibenzo[18]-crown-6 produces the $\mathrm{In^I/In^{III}}$ donor–acceptor complex **4b** (Scheme 3, **C**).[32]

Crystals of **4b** were obtained by slowly concentrating a solution of the reaction mixture in toluene; the molecular structure of the adduct is depicted in Figure 3. The structure of **4b** consists of a mixed-valent dinuclear indium core of the form $\mathrm{Cl{-}In{-}InCl_3}$ that is symmetrically coordinated about the $\mathrm{In^I}$ center by the crown ether. Predictably, the In–In bond length of 2.7020(12) Å lies at the short end of the range of In–In bond lengths[33] compiled in the CSD and is shorter than the distance of 2.748(4) Å observed in the only other In–In donor–acceptor complex reported.[34] The $\mathrm{In^I{-}Cl}$ bond length of 2.324(3) Å is somewhat shorter than the $\mathrm{In^{III}{-}Cl}$ bond but still falls within the range typical for terminal bonds.[35] As observed in the structure of **2a**, the $\mathrm{In^I}$ center sits essentially at the centroid of the $\mathrm{O_6}$ ring and the $\mathrm{Cl{-}In^I{-}In^{III}}$ angle of 177.12(9)° is consistent with the expected linear geometry.



Scheme 3. Valence isomers of $[\mathrm{In_2Cl_4}]$ (postulated or observed structures above and parent structure below): **A** is the mixed-valent ionic form ($\mathrm{In^I/In^{III}}$); **B** is the isovalent, covalent form ($\mathrm{In^{II}{-}In^{II}}$); and **C** is the mixed-valent donor–acceptor form ($\mathrm{In^I{-}In^{III}}$) adopted by **4b**.

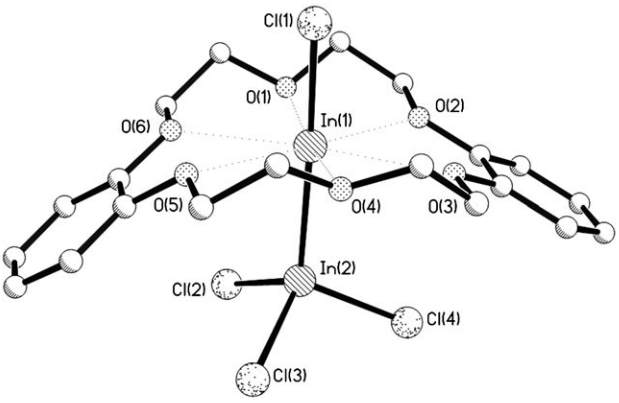


Figure 3. Molecular structure of **4b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: In(1)-In(2) 2.7020(12), Cl(1)-In(1) 2.324(3), Cl(2)-In(2) 2.408(3), Cl(3)-In(2) 2.372(3), Cl(4)-In(2) 2.377(3), In(1)-O(1) 2.548(8), In(1)-O(2) 2.652(8), In(1)-O(3) 2.691(8), In(1)-O(4) 2.650(9), In(1)-O(5) 2.754(8), In(1)-O(6) 2.696(8); Cl(1)-In(1)-In(2) 177.12(9), Cl(3)-In(2)-Cl(4) 104.82(14), Cl(3)-In(2)-Cl(2) 102.52(12), Cl(4)-In(2)-Cl(2) 103.19(13), Cl(3)-In(2)-In(1) 116.77(9), Cl(4)-In(2)-In(1) 113.50(9), Cl(2)-In(2)-In(1) 114.47(9).

We believe that the adoption of the donor–acceptor structure **4b** over the more common valence isomers (**A** and **B** depicted in Scheme 3) must be attributable to the size and shape of the crown ether. Overall, the crown ether alters the thermodynamic preference for the covalent $\mathrm{In^{II}{-}In^{II}}$ form[36] and has allowed us to isolate a homoleptic donor–acceptor isomer for the first time. Although the reaction of $[\mathrm{In_2Cl_4}]$ with [18]crown-6 likely produces the analogous compound **4a**, we have not yet been able to obtain material suitable for single-crystal experiments.

In conclusion, we have discovered that crown ether ligation is a new, convenient, and mild method for the preparation and stabilization of $\mathrm{In^I}$ compounds. This approach has allowed for the first observation of two unprecedented structural types, and it is our hope that the stabilization or activation of low-oxidation-state centers by cyclic, polydentate donors will increase the availability and practicality of such reagents for use by the larger chemical community. We are currently investigating the application of compounds such as **2** as ligands for main-group and transition-metal complexes and we are examining the use of the methods outlined herein to gain access to analogous compounds containing the lighter Group 13 elements.[37]

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[21] Crystallographic data: Each crystal was covered in nujol and placed rapidly into the cold N_2 stream of a Kryo-Flex low-temperature device. The data were collected on a Bruker APEX CCD diffractometer employing a graphite monochromator with MoKα radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected by using a counting time of 30 s per frame. The data were collected at −100 or −150 °C. Details of crystal data, data collection, and structure refinement are listed below. Data reductions were performed by using the SAINT software and the data were corrected for absorption with SADABS. The structures were solved by direct methods by using SIR97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms by using SHELXL-97. **2a**: $C_{13}H_{24}F_3InO_9S$, monoclinic, space group $P2_1/n$, $a = 9.3622(5)$, $b = 11.9469(7)$, $c = 18.4097(10)$ Å, $\beta = 101.8380(10)°$, $V = 2015.32(19)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.741\ \mathrm{g\,cm^{-3}}$, $\mu = 1.344\ \mathrm{mm^{-1}}$, $F(000) = 1064$, crystal size $0.5 \times 0.5 \times 0.3\ \mathrm{mm^3}$. A total of 17568 reflections ($2.05 \leq \theta \leq 27.54°$) were collected of which 4631 were unique ($R(\mathrm{int}) = 0.0250$); 256 parameters; $R1 = 0.0287$; $wR2 = 0.0677$; GOF = 1.218. **3b**: $C_{24}H_{27}Cl_9F_3InO_9S$, monoclinic, space group $P2_1/n$, $a = 8.8651(13)$, $b = 17.844(3)$, $c = 23.039(3)$ Å, $\beta = 90.327(2)°$, $V = 3644.5(9)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.790\ \mathrm{g\,cm^{-3}}$, $\mu = 1.427\ \mathrm{mm^{-1}}$, $F(000) = 1952$, crystal size $0.8 \times 0.3 \times 0.1\ \mathrm{mm^3}$. A total of 33811 reflections ($1.44 \leq \theta \leq 25.00°$) were collected of which 6424 were unique ($R(\mathrm{int}) = 0.0808$); $R1 = 0.0826$; $wR2 = 0.1948$; GOF = 1.156. **4b**: $C_{20}H_{24}Cl_4In_2O_6$, monoclinic, space group $P2_1/c$, $a = 10.3560(15)$, $b = 15.261(2)$, $c = 16.348(2)$ Å, $\beta = 104.234(2)°$, $V = 2504.5(6)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.941\ \mathrm{g\,cm^{-3}}$, $\mu = 2.302\ \mathrm{mm^{-1}}$, $F(000) = 1432$, crystal size $0.8 \times 0.3 \times 0.3\ \mathrm{mm^3}$. A total of 23053 reflections ($1.85 \leq \theta \leq 25.00°$) were collected of which 4413 were unique ($R(\mathrm{int}) = 0.0699$); $R1 = 0.0930$; $wR2 = 0.1704$; GOF = 1.385; CCDC-280061–280063 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[37] Details of the synthesis and characterization of the products presented in this work are located in the Supporting Information.