Indium as an Electrophilic Center in Polyfunctional Lewis Acids

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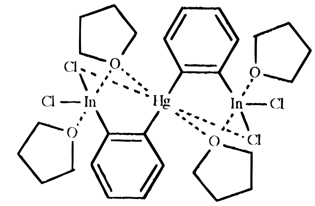
*Summary: The reaction of indium(I) bromide with ortho-phenylenemercury and 1,2-bis(bromomercurio)benzene leads to the isolation of the polyfunctional Lewis acid−Lewis base adducts (o-$C_6H_4(InBr(THF)_2))_2$ (**2**) and Hg-(o-$C_6H_4(InBr_2(THF)))_2$ (**3**), respectively.*

Heavier group 13 based polyfunctional organo-Lewis acid systems remain a rarity and are limited to a few aluminum[1] and indium[2] systems. While most of the research in this area of chemistry has been motivated by its relevance to material science, potential applications in the fields of anion recognition and molecular catalysis also are of interest.[3] As already illustrated in a few recent contributions, molecular systems containing more than one electrophilic center bind anions with different degrees of selectivity,[4] or activate[5] and catalyze[6] organic reactions. One of the main difficulties associated with this theme is the fact that the anions or the nucleophilic substrates are generally coordinatively saturated and therefore bind only weakly.[7] Conceptually, such a problem could be circumvented by the use of strongly Lewis acidic elements. Taking this as an incentive, we have investigated the synthesis of potential polyfunctional Lewis acids in which the Lewis acid centers are heavier group 13 elements. We report here the synthesis of novel homobi- and heterotrifunctional Lewis acids which have been isolated as Lewis base adducts.

We have recently reported that the reaction of indium(I) chloride with *ortho*-phenylenemercury affords the mixed-metal system Hg(*o*-$C_6H_4(InCl_2(THF)_2))_2$ (**1**).[8] The reaction of indium(I) bromide with *ortho*-phenylenemercury in THF takes a different course (Scheme 1) since it results in a clean transmetalation and yields dimeric *ortho*-phenyleneindium bromide (**2**) and metallic mercury.[9] The NMR spectroscopic features of **2** are in accordance with a symmetrical *ortho*-substitution of the phenylene ring.[10] The aromatic region of the ^{1}H spectrum shows two resonances whose multiplicity can be best understood as resulting from the existence of a higher order AA′BB′ spin system; only three aromatic carbon resonances are detected in the ^{13}C spectrum. As indicated by NMR[10] and elemental analysis,[9] **2** coordinates THF molecules. Definitive structural insight (i.e., molecularity of the complex, THF content) were gained from a low-temperature, single-crystal X-ray diffraction study.[11]



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Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. Both molecules are centrosymmetric and consist of dimeric *ortho*-phenyleneindium bromide−tetrakis(tetrahydrofuran) adducts (Figure 1). The median core of one of the two independent molecules is planar within experimental error, the bromine atoms being displaced by only 0.012 Å out of the plane containing the phenylene rings

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(9) Synthesis of **2**: InBr (1.31 g, 7.1 mmol) and *o*-phenylenemercury[14] (1.83 g, 6.6 mmol) are stirred together in THF (15 mL) under nitrogen for 7 h, after which time the reaction mixture is filtered to remove the metallic precipitate. Concentration of the filtrate followed by cooling to −25 °C affords crystals of **2**. These crystals become instantaneously brittle when the solvent is removed to give a 68% yield (1.54 g) of **2**·2THF (mp 230 °C, dec). Anal. Calc for $C_{20}H_{24}Br_2In_2O_2$: C, 34.9; H, 3.5; Br, 23.3. Found: C, 35.1; H, 3.9; Br, 23.1. Synthesis of **3**: InBr (0.20 g, 1.0 mmol) and 1,2-bis(bromomercurio)benzene[15] (0.31 g, 0.49 mmol) are stirred together in THF (5 mL) under nitrogen for 3 h, after which time the reaction mixture is filtered to remove the metallic precipitate. Concentration of the filtrate followed by cooling to −25 °C affords a 19% yield (0.1 g) of crystalline **3** (mp 68 °C, dec). Anal. Calc for $C_{20}H_{24}Br_4HgIn_2O_2$: C, 22.9; H, 2.3. Found: C, 23.4; H, 2.7.

(10) NMR data are as follows. ^{1}H NMR (400 MHz, THF-d_8): **2**, δ 1.77 (br, 16H, OCH_2CH_2), 3.61 (br, 16H, OCH_2), 7.12 (dd, J 5.2 Hz, J 3.3 Hz, 4H, AA′), 7.56 (dd, J 5.2 Hz, J 3.3 Hz, 4H, BB′); **3**, δ 1.77 (br, 8H, OCH_2CH_2), 3.61 (br, 8H, OCH_2), 7.09 (*pseudo* td, ^3J 7.3 Hz, ^4J 1.2 Hz, 2H, B), 7.27 (*pseudo* td, ^3J 7.3 Hz, ^4J 1.2 Hz, 2H, C), 7.49 (dd, ^3J 7.3 Hz, ^4J 1.2 Hz, 2H, A), 7.71 (dd, ^3J 7.3 Hz, ^4J 1.2 Hz, 2H, D). ^{13}C NMR (100.5 MHz, THF-d_8): **2**, δ 26.4 (s, OCH_2CH_2), 68.2 (s, OCH_2-CH_2), 127.7, 137.7 (s, *aryl*-CH), 170.2 (*s*, CIn); **3**, δ 26.4 (s, OCH_2CH_2), 68.2 (s, OCH_2CH_2), 127.9, 129.0, 137.8, 140.5 (s, *aryl*-CH), 182.9 (*s*, CHg), CIn not detected. ^{199}Hg NMR (71.56 MHz, THF-d_8, $HgMe_2$ ext.): **3**, δ −879.

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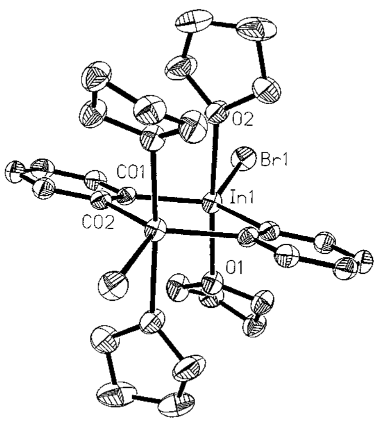
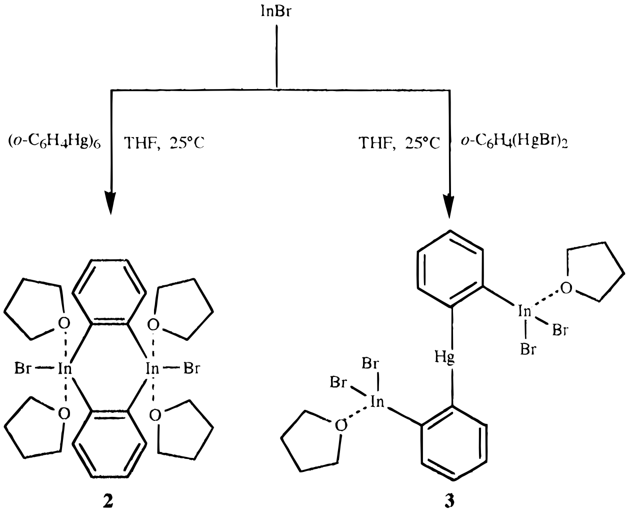


Figure 1. Molecular structure of **2** in the crystal. Selected bond lengths (Å) and angles (deg), with the corresponding metrical parameters of the second independent molecule given in brackets, In(1)−C(01) 2.153(4) [2.156(4)], In(1)−C(02a) 2.157(4) [2.162(5)], In(1)−Br(1) 2.547(1) [2.533(1)], In(1)−O(1) 2.407(3) [2.428(4)], In(1)−O(2) 2.492(3) [2.488-(4)]; O(1)−In(1)−O(2) 176.0(1) [176.3(1)], Br(1)−In(1)−C(01) 112.7(1) [112.2(1)], Br(1)−In(1)−C(02a) 121.4(1) [124.2(1)], C(01)−In(1)−C(02a) 124.7(2) [123.5(2)].

Scheme 1



and the indium atoms. Each indium atom is pentacoordinate in a trigonal bipyramidal fashion, the equatorial sites being occupied by the two phenylene rings and the bromine atom while two molecules of THF occupy the axial positions. As a result, the approximate symmetry of this molecule is D_{2h}. The second independent molecule does not approach such a high symmetry since the bromine atoms are displaced by 0.807 Å out of the plane containing the phenylene rings and the indium atoms. This peculiar feature is the only major structural difference existing between both molecules and probably results from packing interactions, thus indicating that the out of plane motion of the bromine ligands is a low-energy process. In both molecules there is a relatively strong dissymmetry in the In−O bond distances around a unique indium center which indicates that one THF is more strongly coordinated than its counterpart. This structural feature can be correlated with the observation that when exposed to a dry inert atmosphere, crystals of **2** become instantaneously brittle through loss of exactly half of the THF component as indicated by elemental analysis.

Because of the clean transmetalation observed in the synthesis of **2** the reaction of 1,2-bis(bromomercurio)-benzene with indium(I) bromide was investigated. The NMR data collected on the product of this reaction clearly indicated that rather than 1,2-bis(dibromoindio)-benzene, an unexpected product (**3**) had formed (Scheme 1).[9] As indicated by the ^{1}H and ^{13}C NMR data, the phenylene rings in **3** are unsymmetrically substituted (existence of an ABCD spin system in the ^{1}H NMR spectrum and detection of five ^{13}C resonances).[10] Additional information was gained from a ^{199}Hg NMR study carried out on a THF solution of **3** which allowed the detection of one resonance at −879 ppm thus indicating the presence of mercury in **3**.[10] Altogether, the NMR data of **3** are very similar to those obtained for **1**[8] and indicate that **3** is the bromo analog of **1**. It must however be noted that **3** forms an adduct which contains only one THF molecule per indium center as indicated by ^{1}H NMR[10] and elemental analysis[9] while **1** was found to have a higher THF content (two molecules per indium center). This difference in THF content observed between **1** and **3** most probably results from a difference in the Lewis acidity of the indium centers which is directly influenced by the electron-withdrawing ability of the halide ligands. The formation of **3** can be rationalized by a mechanism involving transmetalation of only one mercury center of 1,2-bis-(bromomercurio)benzene, followed by an exchange of the ligands at mercury, leading to symmetrization.

The present results indicate that the course of the reactions of indium(I) halide with polyfunctional organomercuric compounds is hard to predict but allow the synthesis of highly novel poly-Lewis acidic systems. Compound **2** is the first indacycle to be structurally characterized.[12] While it readily hydrolyzes in the presence of water, no reaction is observed with bulky phenols such as 2,4,6-trimethylphenol. It also survives thermal treatment in refluxing THF, thus indicating the substantial robustness of the indacycle. The respective arrangement of the indium centers places the potentially vacant indium p-orbitals in a parallel rather than convergent direction. As a result, compound **2** is able to coordinate four Lewis base molecules rather than acting as a chelating system. Present studies are focused on the use of **2** as a catalyst for the anionic

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(11) Crystal and structure determination data for **2**: $C_{28}H_{40}Br_2In_2O_4$, $M = 830.06$; triclinic, space group $P\bar{1}$; $a = 9.430(2)$, $b = 9.765(2)$, $c = 17.130(3)$ Å; $\alpha = 85.23(2)$, $\beta = 84.91(1)$, $\gamma = 79.40(2)$°; $V = 1540.7(5)$ Å^3; $Z = 2$; $D_c = 1.789$ g/cm^3; $F(000) = 816$; Enraf Nonius CAD4 diffractometer; Mo Kα radiation ($\lambda = 0.710\ 73$ Å); $T = -62$ °C. A total of 6032 data were collected and corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELXTL-PLUS, SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All H atoms were calculated in idealized geometry and allowed to ride on their corresponding C atom with $U_{iso} = 1.5U_{eq}$ of the attached C atom. The structure converged for 325 refined parameters to $R1$ (w$R2$) = 0.0325 (0.0710) for 4564 reflections with $F > 4\sigma(F)$.

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polymerization of epoxides, a process in which the two Lewis acidic centers would work in a cooperative manner.[13]

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters and ORTEP diagrams (8 pages). Ordering information is given on any current masthead page.

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