A heteronuclear trifunctional Lewis acid

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Indium(I) chloride reacts with *ortho*-phenylenemercury to afford the mixed-metal system $Hg\{o\text{-}C_6H_4[InCl_2(thf)_2]\}_2$ 1, a novel heteronuclear trifunctional Lewis acid which is characterized by single crystal X-ray diffraction, elemental analysis, and NMR.

Chemical recognition processes are essential to the functioning of biological systems. This fact has for many decades been recognized and has stimulated a tremendous amount of research at the interface of biology and chemistry aiming at the mimicry and understanding of those processes. On the chemistry side, the surge of activity has first been directed toward the synthesis and behaviour of macromolecular nucleophilic systems as ligands or molecular receptors for electrophiles.[1] More recently, the reverse-charge analogues have attracted attention and many macromolecules containing ionic or neutral electrophilic centres have been prepared.[2,3] Highly important behaviour such as catalysis of organic reactions[4,5] or anion recognition[6,7] have already been observed. The selectivity necessary for the recognition process or for the catalytic properties have been shown to depend both on the nature and on the stereospecific arrangement of the electrophilic sites in the molecular architecture. In an innovative approach, we have investigated the use of indium as an electrophilic element and herein wish to report the synthesis and characterization of an unusual mixed-metal trifunctional Lewis acid.

The reaction of indium(I) halides with organomercury compounds has been known for a long time and is a well established method for the preparation of organoindium(III) halides. The equimolar reaction of indium(I) chloride with hexameric *ortho*-phenylenemercury takes an unexpected course and results in the precipitation of an indium amalgam and production of a colourless moderately air-sensitive compound (**1**).† Preliminary information on the nature of **1** was derived from its ^1H NMR spectrum.‡ The aromatic region can be best interpreted as resulting from an ABCD spin system thus implying an asymmetrical substitution of the *ortho*-phenylene nucleus. This conclusion is consistent with the presence of 5 independent aromatic resonances in the ^{13}C NMR spectrum of **1**.‡ Another valuable piece of information was gained from ^{199}Hg NMR spectroscopy carried out on a thf solution of **1** which allowed the detection of a resonance at δ −894 thus indicating that **1** contains mercury.‡ It is noteworthy that the ^{199}Hg chemical shift of **1** is comparable to that of diphenylmercury [δ −820 in $(CD_3)_2SO$] thus suggesting that the molecular structure of **1** comprises a diphenylene–mercury moiety. The CI mass spectrum of **1** which exhibits peaks corresponding to Hg^+ and $PhInCl^+$ as fragments indicates that **1** is indeed a mixed-metal system. Definitive identification of **1** was derived from a low-temperature single-crystal X-ray diffraction study.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell. The molecular structure consists of two *ortho*-phenyleneindium dichloride moieties linked through a central Hg atom, giving rise to a pseudo-centric core (Fig. 1). The mercury atom is, as expected, linearly coordinated [C(1)–Hg–C(7) 178.7(3) °]. Each indium atom is five-coordinate in a trigonal-bipyramidal fashion with two thf molecules at the axial positions and two chloride ligands as well as a phenylene ring at the equatorial sites; it is interesting that the two phenylene rings are coplanar. An additional feature which merits comment concerns the out of plane rotation of the $InCl_2(thf)_2$ moieties (with respect to the plane containing the two phenylene rings, the Hg and In atoms). At first examination, there is no obvious explanation for this peculiar geometric arrangement. However, examination of the secondary coordination sphere of the mercury atom reveals that two of the chloride ligands [Cl(2), Cl(4)] as well as the oxygen atoms of two of the thf molecules [O(2), O(3)] are positioned in such a manner that the resulting Cl(2)–Hg, Cl(4)–Hg, O(2)–Hg and O(3)–Hg vectors are close to being perpendicular to the C(1)–Hg–C(7) sequence, the mercury atom being therefore in a distorted octahedral environment [O(2)–Hg–Cl(4) 160.7, O(3)–Hg–Cl(2) 162.2, O(2)–Hg–Cl(2) 53.9, O(3)–Hg–Cl(4) 52.9, C(1)–Hg–O(2) 78.4, C(1)–Hg–O(3) 99.0, C(1)–Hg–Cl(2) 92.2, C(1)–Hg–Cl(4) 88.7, C(7)–Hg–O(2) 102.0, C(7)–Hg–O(3) 79.7, C(7)–Hg–Cl(2) 89.1, C(7)–Hg–Cl(4) 90.6 °]. In other words, two of the chloride ligands and two thf molecules occupy a position in space where the Lewis acidity of the mercury atom is expected to be maximal. While the Hg···Cl and Hg···O distances are long [Hg–Cl(2) 3.729, Hg–Cl(4) 3.914, Hg–O(2) 3.405, Hg–O(3) 3.302 Å], they are within the upper range for the implication of van der Waals forces[8] and are respectively comparable to the intermolecular associative interactions observed in the solid state of the 2 : 1 adduct of 1,2-phenylenedimercury dichloride with tetraphenylphosphonium chloride[9] (Hg···Cl 3.998 Å) and

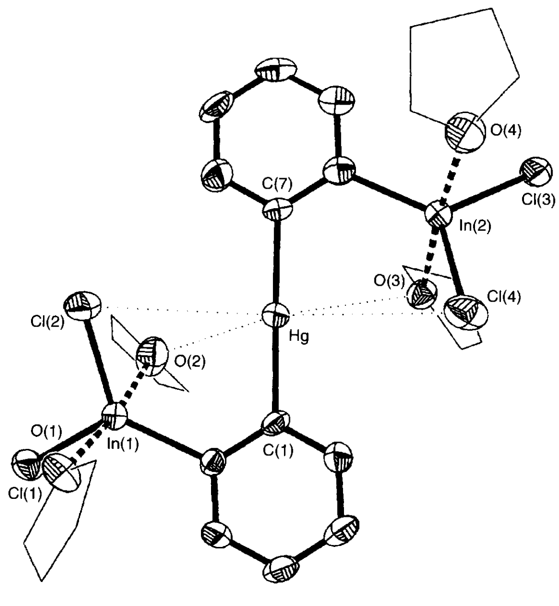

Fig.1 Structure of **1** in the crystal showing the secondary coordination sphere of the Hg atom. The representation of the thf molecules has been simplified (thin lines) for clarity. Selected bond lengths (Å) and angles (°): Hg–C(1) 2.090(6), Hg–C(7) 2.086(6), In(1)–C(2) 2.122(6), In(1)–Cl(1) 2.379(2), In(1)–Cl(2) 2.368(2), In(1)–O(1) 2.342(5), In(1)–O(2) 2.360(6), In(2)–C(8) 2.128(8), In(2)–Cl(3) 2.377(2), In(2)–Cl(4) 2.369(2), In(2)–O(3) 2.376(5), In(2)–O(4) 2.339(6); C(1)–Hg–C(7) 178.7(3), O(1)–In(1)–O(2) 173.4(2), Cl(1)–In(1)–Cl(2) 113.18(8), Cl(1)–In(1)–C(2) 123.4(2), Cl(2)–In(1)–C(2) 123.4(2), O(3)–In(2)–O(4) 175.3(2), Cl(3)–In(2)–Cl(4) 112.58(9), Cl(3)–In(2)–C(8) 120.5(2), Cl(4)–In(2)–C(8) 126.9(2).

phenylmercuryoxinate[10] (Hg···O 3.34 Å). It is therefore very likely that these weak Hg–Cl and/or Hg–O interactions are responsible for the out-of-plane rotation of the $InCl_2(thf)_2$ moieties as well as for the coplanar arrangement of the two phenylene rings. While all In–Cl bond distances are equal within experimental error, there is a detectable lengthening of the In–O(2) and In–O(3) bonds when compared to the In–O(1) and In–O(4) linkages which indicates that two of the thf molecules are in a bridging situation. As a result, the structure of **1** can be regarded as containing weakly and asymmetrically chelated thf molecules [thf at O(2) and O(3)].

It is quite remarkable that even after prolonged exposure to a dry inert atmosphere, crystals of **1** do not become brittle through loss of part of the thf component as indicated by elemental analysis.† This fact contrasts strongly with the observed low stability of the isovalent complex $[In(thf)_2Cl_2]_2$ (rapid decomposition at 25 °C by loss of thf) which contains $InCl_2(thf)_2$ moieties analogous to that of **1**[11] and is suggestive of the existence of a chelate effect in **1**.

Compound **1** is a trifunctional heteronuclear Lewis-acid system with an open-chain framework. The presence of the NMR active mercury atom as one of the Lewis-acidic sites will facilitate the probing of its ligative behaviour toward nucleophiles. Anion complexation studies are presently underway.

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Footnotes

† *Synthesis* of **1**: InCl (0.15 g, 1.0 mmol) and *o*-phenylenemercury (0.28 g, 1.0 mmol) were stirred together in thf (5 ml) under nitrogen for 3 h, after which time the reaction mixture was filtered to remove the metallic grey precipitate. Concentration of the filtrate followed by cooling to −25 °C afforded a 22% yield (based on indium, 0.11 g) of crystalline **1** (mp 95–97, decomp.). Elemental analysis. Calc. for $C_{28}H_{40}Cl_4HgIn_2O_4$: C, 33.21; H, 3.95; Cl, 14.00. Found C, 33.05; H, 4.26; Cl, 13.88%.

‡ *NMR data* for **1**: ^{1}H NMR (270 MHz, [^{2}H$_8$]thf): δ 7.07 (pseudo td, ^3J 7.32, ^4J = 1.5 Hz, 2 H, B), 7.27 (pseudo td, ^3J 7.45, ^4J 1.5 Hz, 2 H, C), 7.48 (dd, ^3J 7.08, ^4J 1.5 Hz, 2 H, A), 7.73 (dd, ^3J 7.30, ^4J 1.5 Hz, 2 H, D). ^{13}C NMR (67.9 MHz, [^{2}H$_8$]thf): δ 128.0, 129.1, 138.1, 140.7 (s, aryl*C*H), 183.2 (*s*, *C*Hg), *C*In not detected. ^{199}Hg NMR (71.56 MHz, [^{2}H$_8$]thf, $HgMe_2$ ext.): δ −894 ($\omega_{1/2}$ 82 Hz).

§ *Crystal and structure determination data* for **1**: $C_{28}H_{40}Cl_4HgIn_2O_4$, M = 1012.63, monoclinic, space group $P2_1/n$, a = 14.530(2), b = 14.411(2), c = 17.518(2) Å, β = 107.56(1) °, U = 3497.2(8) Å^3, Z = 4, D_c = 1.923 g cm^{-3}, $F(000)$ = 1944, Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71069 Å), T = −62 °C. Data were corrected for Lorentz, polarization, and absorption effects (ψ-scans, $T_{min,max}$ = 37.84, 99.80%). The structure was solved by direct methods and refined by full-matrix least squares methods against F^2 (SHELXTL-PLUS, SHELXL-93).[12] Of 6823 measured reflections [$(\sin\theta/\lambda)_{max}$ = 0.64 Å^{-1}], 6600 were used for refinement with all data. The thermal motion of all non-hydrogen atoms was treated anisotropically without resolving a slight disorder of the ligand thf C atoms. All H atoms were calculated in idealized geometry and allowed to ride on their corresponding C atom with U_{iso} = 1.5 U_{eq} of the attached C atom. The structure converged for 352 refined parameters to $R1$ = 0.0387 for 5327 reflections with $F > 4\sigma(F)$ and $wR2$ = 0.0837. Residual electron densities: +1.623 and −1.216 e Å^{-3} located at the Hg atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/54.

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