

α,α' -*m*-Xylenediylbis(indium dichloride). A Novel Bifunctional Lewis Acid

Martin Tschinkl, Annette Schier, Jürgen Riede, and François P. Gabbaï*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Reaction of the di-Grignard compound 1,3-(ClMgCH₂)₂C₆H₄ with HgCl₂ yields 1,3-(ClHgCH₂)₂C₆H₄ (**1**), which crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *a* = 8.494(1), *b* = 10.859(1), and *c* = 10.906(1) Å, *V* = 1005.9(2) Å³, and *Z* = 4 (*R* values: *R*₁ = 0.0354, *wR*₂ = 0.0942). Treatment of **1** with InCl results in a transmetalation reaction and affords the tetrakis(tetrahydrofuran) adduct of 1,3-(Cl₂InCH₂)₂C₆H₄ (**2**), which crystallizes in the monoclinic space group *I*2/a with *a* = 15.230(1), *b* = 13.125(1), and *c* = 15.299(1) Å, β = 92.14(1)°, *V* = 3056.0(4) Å³, and *Z* = 4 (*R* values: *R*₁ = 0.0411, *wR*₂ = 0.1003). As indicated by ¹⁹⁹Hg NMR spectroscopy, compound **1** does not form any stable anionic complexes in the presence of chlorides. In contrast, compound **2** readily complexes chloride anions. According to a VT ¹H NMR investigation, the species present in an equimolar mixture of **2** and Ph₄PCl is the monoanionic complex [1-(Cl₃InCH₂)-3-((THF)₂Cl₂InCH₂)C₆H₄]⁻ (**3**), whose structure is fluxional at room temperature. From this mixture, the salt [1,3-(Cl₃InCH₂)₂C₆H₄]²⁻[Ph₄P⁺]₂ (**4**) can be isolated by precipitation. Compound **4** crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *a* = 14.632(1), *b* = 17.080(1), and *c* = 21.384(1) Å, *V* = 5344.2(5) Å³, and *Z* = 4 (*R* values: *R*₁ = 0.0346, *wR*₂ = 0.0649).

Introduction

The cooperative binding of nucleophilic substrates by neutral polydentate Lewis acids¹ is a rapidly emerging area of research which is gaining importance in many fields of chemistry. A series of recent reports demonstrates that the cooperative binding of keto or thioketo functions by aluminum-² or mercury- based³ bidentate Lewis acid catalysts results in an increased or double-electrophilic activation. Furthermore, polyfunctional systems containing electrophilic elements such as copper,⁴ silver,⁴ uranium,⁵ mercury,⁶ boron,⁷ aluminum,⁸ silicon,⁹ or tin¹⁰ are well-established anion receptors. Their strong complexing character results from their ability to chelate the incoming anionic guest which ends up concomitantly ligated to the

different electrophilic centers of the host. Most of the efforts made in the latter area have been motivated by the key role that anions play in many biological systems.¹¹ It should be pointed out that this type of system could also prove useful in environmental chemistry as agents for the sensing and trapping of anionic pollutants.¹²

Interestingly, the systems containing weakly Lewis acidic elements like mercury^{3,6} constitute the most developed and elaborated class of neutral anion receptors. In contrast, the study of polyfunctional Lewis acids containing the strongly Lewis acidic group 13 elements is far less advanced and is limited to the case of a few boron⁷ and aluminum² systems. We recently reported that polyfunctional indium-based Lewis acids are in some cases able to chelate nucleophiles such as THF molecules.^{13a} These results prompted us to further investigate related systems in the hope of discovering new anion receptors or catalysts.

Our previous efforts were focused on molecules in which the indium centers are linked by the rigid *o*-phenylene backbone.¹³ Since molecules with semirigid or even flexible backbones should have properties which differ from those of their rigid congeners, we have directed our attention toward the synthesis of bifunctional organoindium derivatives in which the indium centers reside in a molecular framework capable of moderate structural variations. In this respect, the α,α' -*m*-xylenediyl motif appears interesting since only rotation about the C_{aryl}–CH₂ single bonds is allowed. It should also be noted that this backbone has been successfully used for the elaboration of bidentate nitrogen- and phosphorus-based ligands.¹⁴ In the present report, we describe the synthesis of α,α' -*m*-xylenediyl-

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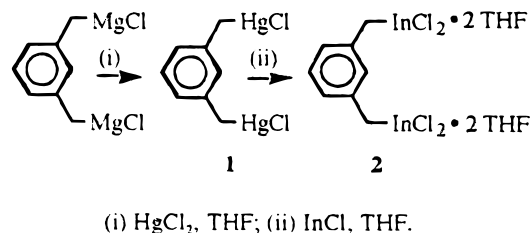
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Table 1. Crystal Data and Data Collection and Structure Refinement Details for Compounds **1**, **2**, and **4**

	1	2	4
formula	C ₈ H ₈ Cl ₂ Hg ₂	C ₂₄ H ₄₀ Cl ₄ In ₂ O ₄	C ₅₆ H ₄₈ Cl ₆ In ₂ P ₂
<i>M_r</i>	576.22	764.00	1225.22
crystal system	orthorhombic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	8.494(1)	15.230(1)	14.632(1)
<i>b</i> (Å)	10.895(1)	13.125(1)	17.080(1)
<i>c</i> (Å)	10.906(1)	15.299(1)	21.384(1)
α (deg)	90	90	90
β (deg)	90	92.14(1)	90
γ (deg)	90	90	90
<i>V</i> (Å ³)	1005.9(2)	3056.0(4)	5344.2(5)
ρ_{calc} (g cm ⁻³)	3.805	1.661	1.523
<i>Z</i>	4	4	4
<i>F</i> (000) (e)	1000	1528	2456
μ (Mo K α) (cm ⁻¹)	309.58	18.85	12.59
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (λ (Å))	Mo K α (0.710 73)	Mo K α (0.710 73)	Mo K α (0.710 73)
<i>T</i> (°C)	-74	-74	-74
scan mode	ω	ω - θ	ω
<i>hkl</i> range	-10 \rightarrow +10	-16 \rightarrow +19	0 \rightarrow +17
	0 \rightarrow 13	-16 \rightarrow 0	-21 \rightarrow +21
	0 \rightarrow 12	-16 \rightarrow 19	0 \rightarrow 26
$((\sin \theta)/\lambda)_{\text{max}}$ (Å ⁻¹)	0.64	0.64	0.62
no. of measd reflns	2325	4112	10208
no. of unique reflns	2113 (<i>R</i> _{int} = 0.0335)	3199 (<i>R</i> _{int} = 0.0206)	9651 (<i>R</i> _{int} = 0.0224)
no. of obsd reflns	2111	3129	9649
no. of refined params	109	182	595
no. of H atoms (found/calcd)	0/8	0/21	0/48
<i>R</i> 1 ^a	0.0354	0.0411	0.0346
w <i>R</i> 2 ^b	0.0942	0.1003	0.0649
GOF	1.075	1.222	1.056
Flack param	0.00(2)		-0.03(2)
(shift/error) _{max}	<0.001	<0.001	<0.001
ρ_{fin} (max/min) (e Å ⁻³)	1.633/-1.959	0.760/-0.836	0.424/-0.593

^a *R*1 = $\sum(|F_o| - |F_c|)/\sum|F_o|$. ^b w*R*2 = $\{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.773$ (**1**), 0.335 (**2**), 0.0294 (**4**); $b = 0.80$ (**1**), 12.59 (**2**), 1.47 (**4**).

Scheme 1



bis(mercury chloride) (**1**) and of α,α' -*m*-xylenediylbis(bis-(tetrahydrofuran)indium dichloride) (**2**). Both compounds have been fully characterized, and their ligative behavior toward chloride anions has been investigated.

Results and Discussion

Synthesis of the Bifunctional Mercury and Indium Lewis Acids. The di-Grignard compound 1,3-(ClMgCH₂)₂C₆H₄ was synthesized according to the literature procedure¹⁵ and was allowed to react with HgCl₂ to afford a 33% yield of the corresponding organomercury compound 1,3-(ClHgCH₂)₂C₆H₄ (**1**), which can be recrystallized from DMSO or DMF (Scheme 1). The ¹H NMR spectrum of **1** exhibits as expected a single methylene resonance together with three distinct arene signals. Its ¹⁹⁹Hg chemical shift (-1170 ppm in DMSO-*d*₆) is characteristic of mercury chloride moieties in benzylic positions and can be compared to that of benzylmercury chloride (-1184 ppm in DMSO-*d*₆).¹⁶ Although compound **1** is only sparingly soluble

in THF, it undergoes rapid transmetalation in this solvent upon addition of 2 equiv of InCl. The resulting organoindium compound (**2**) can be crystallized by cooling the filtered reaction mixture. Compound **2** is air and moisture sensitive and insoluble in aromatic and aliphatic hydrocarbons. According to its ¹H NMR spectrum, the molecule is highly symmetrical in solution, since only one methylene resonance and three arene resonances are detected. Furthermore, the ¹H NMR spectrum reveals the presence of two coordinated THF molecules per indium center, which is in agreement with the elemental analysis data obtained for **2**.

X-ray Crystal Structure of Compounds 1 and 2. Single crystals of compound **1** suitable for an X-ray analysis slowly formed in a DMSO solution of **1** containing an equimolar amount of tetraphenylphosphonium chloride. It is interesting to note that solutions of pure **1** in DMSO or DMF yielded only polycrystalline material from which no single crystals of sufficient quality could be isolated. Crystals of **1** belong to the orthorhombic space group *P*2₁2₁2₁ with four molecules in the unit cell (Table 1). As shown in Figure 1, the molecules approach a C₂ symmetry with all carbon atoms being in the same plane and the two mercury chloride moieties pointing in opposite directions (dihedral angles C(2)-C(1)-C(7)-Hg(1) = 73.4° and C(2)-C(3)-C(8)-Hg(2) = 98.1°). There are no unusual features in the structure of **1** which merit comments, with the exception of the angles C(7)-Hg(1)-Cl(1) and C(8)-Hg(2)-Cl(2) (177.9 and 173.3°, respectively), which deviate slightly from the ideal linear coordination usually encountered at divalent mercury centers. This deviation is in fact due to the participation of the mercury centers in secondary interac-

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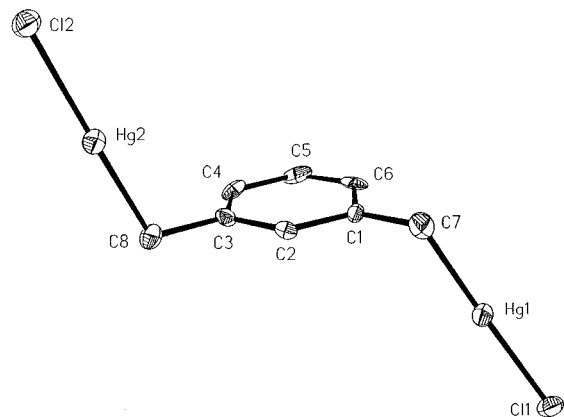


Figure 1. Structure of **1** in the crystal shown by an ORTEP drawing with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg(1)–C(7) 2.110(13), Hg(2)–C(8) 2.101(12), Hg(1)–Cl(1) 2.345(3), Hg(2)–Cl(2) 2.353(3), C(1)–C(7) 1.43(2), C(3)–C(8) 1.50(2); C(7)–Hg(1)–Cl(1) 177.9(4), C(8)–Hg(2)–Cl(2) 173.3(4).

Table 2. Intermolecular Hg⋯Cl Interaction Distances in the Supramolecular Structure of **1**^a

Hg(2)⋯Cl(1') ⁱ	3.223	Hg(1')⋯Cl(2) ⁱⁱⁱ	3.295
Hg(2)⋯Cl(1b) ⁱⁱ	3.350	Hg(1')⋯Cl(2d) ^{iv}	3.211

^a Symmetry position of the chlorine atom with respect of the position of mercury atom: (i) $x, y - 1, z$; (ii) $x - 1/2, -y - 1/2, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x - 1/2, -y - 1/2, z + 1/2$.

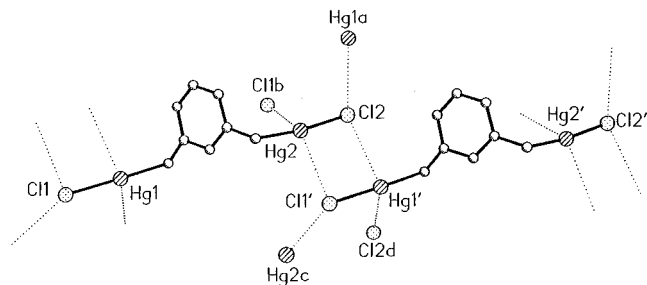


Figure 2. View of a portion of a polymeric chain parallel to the y axis. The formation of the head-to-tail Hg₂Cl₂ bridge is evident from this view. The contacts between the central chain and four atoms belonging to neighboring chains are also depicted.

tions. Indeed, as a result of the presence of intermolecular subvan der Waals Hg⋯Cl contacts (Table 2),¹⁷ compound **1** forms a very intricate and compact three-dimensional molecular network. Although the overall supramolecular structure is rather complex, the formation of a chain along the y axis can easily be recognized (Figure 2). In this chain, the individual molecules are connected through head-to-tail Hg₂Cl₂ bridges.¹⁸ In addition, each mercury/chlorine atom of a given chain interacts with a chlorine/mercury atom of neighboring chains.

X-ray-quality crystals of **2** were obtained upon slow diffusion of hexane in a THF solution of **2**. They belong to the monoclinic space group $I2/a$ with four molecules in the unit cell (Table 1). The individual molecules (Figure 3) have a crystallographically imposed C₂ symmetry with the C₂ axis passing through C(1) and C(4). The InCl₂(THF)₂ moieties are positioned above and below the plane containing the aryl and methylene carbon atoms (dihedral angle C(1)–C(2)–C(5)–In = 110.6°), thus leading to a molecular arrangement in which

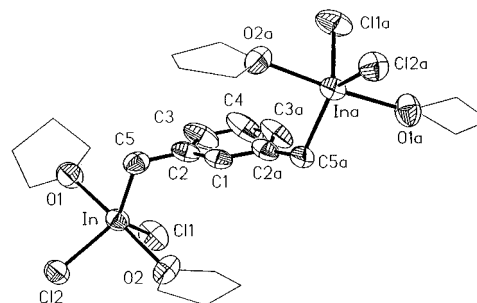


Figure 3. Structure of **2** in the crystal shown by an ORTEP drawing with 50% probability ellipsoids. H atoms are omitted for clarity; the carbon backbones of the disordered THF molecules are represented by thin lines. Selected bond lengths (Å) and angles (deg): In–C(5) 2.159(4), In–Cl(1) 2.3838(14), In–Cl(2) 2.3796(12), In–O(1) 2.363(4), In–O(2) 2.341(4); C(5)–In–Cl(1) 123.3(2), In–C(5)–Cl(2) 126.7(2), C(5)–In–O(1) 91.7(2), C(5)–In–O(2) 92.3(2), O(2)–In–O(1) 175.90(14).

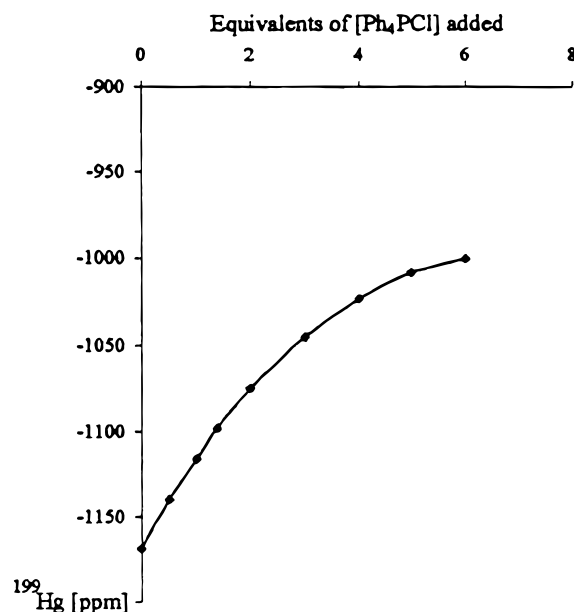


Figure 4. ¹⁹⁹Hg chemical shift of **1** versus the equivalents of Ph₄PCl added.

the steric constraints are minimized. The indium centers are in a trigonal bipyramidal environment with the THF molecules in axial positions and two chloride ligands as well as the methylene carbon atom in equatorial positions. Altogether, the coordination sphere of the indium center in **2** is very similar to that encountered in the structure of PhCH₂InBr₂(THF)₂, which was described previously.¹⁹

Anion Coordination Studies. Since compounds **1** and **2** can be regarded as electrophilic “pincer” ligands, the study of their ligative behavior toward anions became an obvious target.

Bifunctional mercury systems with rigid backbones such as *o*-C₆H₄(HgCl)₂ readily chelate chloride anions.^{6b} In order to determine if **1** would exhibit a similar complexing ability, a chloride titration experiment monitored by ¹⁹⁹Hg NMR spectroscopy was carried out. As shown in Figure 4, incremental addition of Ph₄PCl results in dramatic changes of the chemical shift of the mercury centers of **1**. However, the resulting curve, which does not exhibit any plateau, resembles that previously reported for the system [MeHgCl/*n*Cl[−]]²⁰ and differs markedly

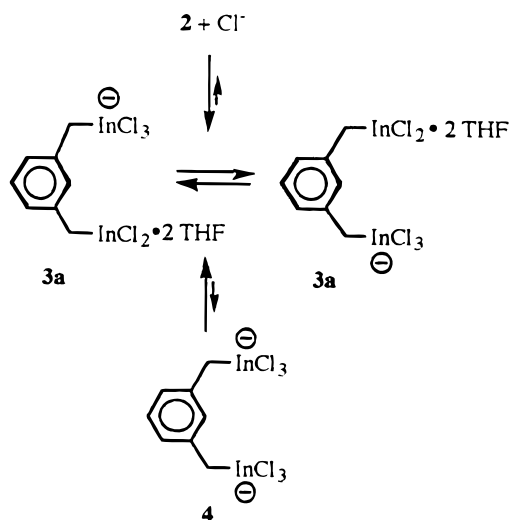
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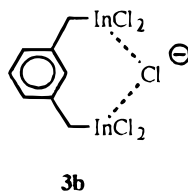
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Scheme 2



from that obtained for the system $[o\text{-C}_6\text{H}_4(\text{HgCl})_2/n\text{Cl}^-]$.^{6b} Altogether, the data indicate that **1** behaves as a monofunctional organomercury derivative and does not form stable anionic halide complexes.²¹ This conclusion is consistent with the observation that crystals of pure **1** spontaneously formed in a DMSO solution containing 1 equiv of Ph_4PCl .

In contrast to **1**, compound **2** readily complexes chloride anions. The ^1H NMR spectrum of an equimolar mixture of **2** and Ph_4PCl in $\text{THF-}d_8$ corresponds to that of a symmetrical species (**3**) different from pure **2**, as indicated by the different chemical shift of the methylene protons. While it is tempting to suggest that this species is in fact the anionic chelate complex **3b**, the existence of a fluxional complex cannot be ruled out.



In order to distinguish between these two possibilities, a VT ^1H NMR experiment was carried out. At $-25\text{ }^\circ\text{C}$, the methylene signal decoalesces and splits into two distinct sharp signals of equal intensity at temperature below $-50\text{ }^\circ\text{C}$. Using the Eyring equation,²² an activation energy of $49 (\pm 2)$ kJ/mol can be obtained for this dynamic process. These results suggest that the low-temperature solution structure of the complex is that of an unsymmetrical species containing a trichloroindate center and a neutral dichloroindium center (**3a**). At room temperature, there is rapid exchange of the chloride between the indium centers, thus leading to the detection of a time-averaged signal (Scheme 2). The possibility that the low-temperature ^1H NMR spectrum corresponds to that of an equimolar mixture of **2** and **4** could be ruled out since the chemical shifts of the methylene protons measured for **3a** (δ 2.19 and 2.41 ppm) do not correspond to those of the methylene protons of pure **2** (δ 2.46 ppm) and pure **4** (δ 2.94 ppm) at $-60\text{ }^\circ\text{C}$.

(21) Monofunctional organomercury derivatives do not usually form anionic complexes with halides, unless perfluorinated electron-withdrawing substituents are employed. See: Korpar-Colig, B.; Popovic, Z.; Bruvo, M.; Vickovic, I. *Inorg. Chim. Acta* **1988**, *150*, 113 and references cited therein.

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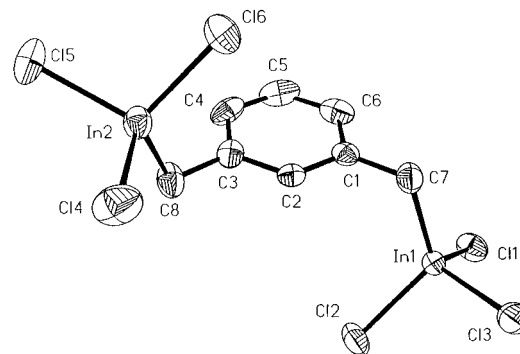
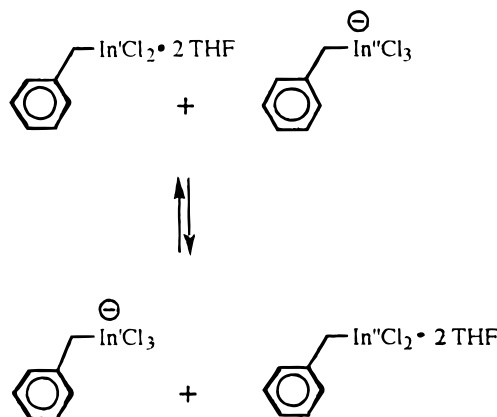


Figure 5. Structure of the dianion of **4** in the crystal shown by an ORTEP drawing with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): In(1)–C(7) 2.162(4), In(2)–C(8) 2.164(5), In(1)–Cl(2) 2.3911(13), In(1)–Cl(1) 2.3731(12), In(1)–Cl(3) 2.4060(13), In(2)–Cl(4) 2.4015(12), In(2)–Cl(5) 2.3778(12), In(2)–Cl(6) 2.3802(13); Cl(1)–In(1)–Cl(2) 104.44(5), Cl(1)–In(1)–Cl(3) 108.87(5), Cl(2)–In(1)–Cl(3) 103.90(5), C(7)–In(1)–Cl(3) 103.94(14), Cl(5)–In(2)–Cl(6) 105.16(5), Cl(5)–In(2)–Cl(4) 105.04(5), Cl(6)–In(2)–Cl(4) 106.15(6), C(8)–In(2)–Cl(4) 110.1(2).

Scheme 3



In order to provide complementary data, an additional experiment with a monofunctional species was undertaken. The ^1H NMR spectrum of a 2:1 mixture of $\text{PhCH}_2\text{InCl}_2$ ²³ and Ph_4PCl in $\text{THF-}d_8$ exhibits a single methylene signal. This methylene signal was found to decoalesce at $-29\text{ }^\circ\text{C}$ and to split into two distinct sharp signals of equal intensity at temperature below $-60\text{ }^\circ\text{C}$. These two sharp methylene signals, respectively, correspond to those detected at $-60\text{ }^\circ\text{C}$ for pure $\text{PhCH}_2\text{InCl}_2$ and pure $[\text{PhCH}_2\text{InCl}_3]^-$, thus clearly indicating that intermolecular chloride anion exchange is occurring (Scheme 3). Using the Eyring equation, an activation energy of $47 (\pm 2)$ kJ/mol can be calculated for this process. This value is equal within experimental error to that derived for the chloride exchange process in the system $2/\text{Cl}^-$. While intramolecular chloride exchange can take place in the system $2/\text{Cl}^-$, the above observations indicate that there is no effect of the organoindium functionality number (mono- vs bifunctional) on the activation energy. It is in fact very likely that both intra- and intermolecular exchanges have analogous activation energies and occur concomitantly in the system $2/\text{Cl}^-$.

In order to investigate the solid state structure of **3**, several crystallization attempts were made. To our surprise, slow diffusion of a hexane layer in a THF solution containing an equimolar amount of **2** and Ph_4PCl led to the crystallization of the salt $[\text{1,3-(Cl}_3\text{InCH}_2)_2\text{C}_6\text{H}_4]^{2-}[\text{Ph}_4\text{P}^+]_2$ (**4**). The formation

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of **4** indicates that intermolecular chloride exchange occurs (Scheme 2). Although low-temperature ^1H NMR spectroscopy shows that an equimolar THF solution of **2** and Ph_4PCl mainly contains **3a**, the poor solubility of **4** in the given solvent mixture leads to its precipitation. Compound **4** is an air-stable solid. It crystallizes in the $P2_12_12_1$ space group with four molecules in the cell (Table 1, Figure 5). Examination of the cell packing diagram indicates that there are no anion-cation contacts. The structure of the dianion approaches C_2 symmetry and resembles that of compound **2**. All aryl and methylene carbon atoms lie in the same plane, with the trichloroindate moieties pointing in opposite directions (dihedral angles $\text{C}(2)-\text{C}(1)-\text{C}(7)-\text{In}(1) = 87.3^\circ$ and $\text{C}(2)-\text{C}(3)-\text{C}(8)-\text{In}(2) = 92.3^\circ$). The geometry at each indium center is close to tetrahedral with $\text{In}-\text{Cl}$ bonds ranging from 2.373 to 2.406 Å.

Conclusion

The present results indicate that polyfunctional Lewis acids containing indium as electrophilic sites can be conveniently prepared through transmetalation reactions, starting from the corresponding polyfunctional organomercury compounds. The observation that **1** does not complex chloride anions contrasts strongly with the results previously obtained for $o\text{-C}_6\text{H}_4(\text{HgCl})_2$, which was found to have a strong affinity for this anion.^{6b} Most probably, this difference results from the fact that the mercury centers in **1** are not fixed in a position allowing them to cooperatively interact with the incoming chloride anions. In other words, due to the flexibility of the organic backbone, the cooperative binding of the chloride by **1** is entropically too costly. In contrast to **1**, compound **2** readily complexes chloride anions. As suggested by VT ^1H NMR, the structure of the monoanionic complex **3** in solution is fluxional and corresponds to that of an unsymmetric complex (**3a**) in which the chloride anion undergoes a dynamic exchange between the indium centers. These results indicate that chloride chelation with **2** as a Lewis acidic ligand is difficult to achieve. The competitive ligation of THF molecules to the electrophilic indium centers is most certainly the limiting factor hindering the cooperative binding of the chloride anion.

Experimental Section

General Considerations. Nuclear magnetic resonance spectra were obtained on a JEOL-GX 400 instrument. Neat HgMe_2 was used as an external standard for the ^{199}Hg NMR spectra. The proton and carbon signals of the deuterated solvent were used as internal standards for the ^1H and ^{13}C NMR spectra, respectively. All NMR measurements were carried out at 25°C unless otherwise noted. Elemental analyses were performed by the Laboratory for Microanalysis at the Technischen Universität München. When necessary, the experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk techniques or a glovebox (Labmaster 130, Fa. M. Braun). All melting points were measured on samples in sealed capillaries and are uncorrected. THF and $\text{THF-}d_8$ were dried over Na/K and distilled prior to use. Hexane was dried over CaH_2 prior distillation and use. All other solvents were used without further purification. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. $\text{PhCH}_2\text{InCl}_2$ was prepared according to the published procedure.²³

Synthesis of α,α' -*m*-Xylenediylbis(mercury chloride) (1**).** A solution of 1,3-(ClMgCH_2) $_2\text{C}_6\text{H}_4$ was prepared according to the literature procedure¹⁵ from a THF solution (23 mL) of α,α' -dichloro-*m*-xylene (3.0 g, 0.017 mmol) and a suspension of magnesium (5.5 g, 0.225 mol) in THF (200 mL). The resulting mixture was filtered, and the filtrate was slowly added to a cooled (0°C) THF solution (25 mL) containing an excess of HgCl_2 (9.2 g, 0.034 mol). The reaction proceeded immediately, as indicated by the formation of a white precipitate. The resulting mixture was stirred for 12 h at room

temperature and refluxed for 90 min. The precipitate was isolated by filtration, washed three times with 40 mL portions of water, one time with 20 mL of THF, and finally on time with 20 mL of Et_2O before being dried under vacuum to afford a 33% yield (3.2g) of colorless powdery **1** (mp 217°C). Anal. Calc for $\text{C}_8\text{H}_8\text{Cl}_2\text{Hg}_2$: C, 16.66; H, 1.39; Cl, 12.31; Hg, 69.63. Found: C, 17.22; H, 1.64; Cl, 12.71; Hg, 67.4. ^1H NMR ($\text{DMSO-}d_6$): δ 2.91 (s, 4 H, CH_2), 6.87 (d, 3J 7.3 Hz, 2 H, $H\text{-}4/6$), 7.02 (t, 3J 7.3 Hz, 1 H, $H\text{-}5$), 7.06 (s, 1 H, $H\text{-}2$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}d_6$): δ 34.7 (CH_2), 124.3 ($C\text{-}4/6$), 128.0 ($C\text{-}2$), 128.3 ($C\text{-}5$), 141.7 ($C\text{-}1/3$). $^{199}\text{Hg}\{^1\text{H}\}$ NMR ($\text{DMSO-}d_6$): δ -1170.

Synthesis of α,α' -*m*-Xylenediylbis(bis(tetrahydrofuran)indium dichloride) (2**).** InCl (0.188 g, 1.25 mmol) and **1** (0.288 g, 0.5 mmol) were stirred together in THF (5 mL) for 12 h. The reaction mixture was then filtered to remove the metallic precipitate. Concentration of the filtrate followed by cooling to -25°C afforded a 26% yield (0.1 g) of crystalline **2** (mp 94°C dec). Anal. Calc for $\text{C}_{24}\text{H}_{40}\text{Cl}_4\text{In}_2\text{O}_4$: C, 37.72; H, 5.24. Found: C, 36.90; H, 5.19. ^1H NMR ($\text{THF-}d_8$): δ 1.77 (br, 16 H, OCH_2CH_2), 2.44 (s, 4 H, CH_2), 3.61 (br, 16 H, OCH_2), 6.79 (d, 3J 7.3 Hz, 2 H, $H\text{-}4/6$), 6.94 (t, 3J 7.3 Hz, 1 H, $H\text{-}5$), 6.98 (s, 1 H, $H\text{-}2$). ^1H NMR ($\text{THF-}d_8$, -60°C): δ 1.77 (br, 16 H, OCH_2CH_2), 2.46 (s, 4 H, CH_2), 3.61 (br, 16 H, OCH_2), 6.77 (d, 3J 7.7 Hz, 2 H, $H\text{-}4/6$), 6.96 (t, 3J 7.3 Hz, 1 H, $H\text{-}5$), 6.98 (s, 1 H, $H\text{-}2$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$): δ 26.4 (OCH_2CH_2), 68.2 (OCH_2CH_2), 124.0 ($C\text{-}4/6$), 128.1 ($C\text{-}2$), 128.9 ($C\text{-}5$), 143.0 ($C\text{-}1/3$), C_{in} not detected.

Synthesis of Bis(tetraphenylphosphonium) α,α' -*m*-Xylenediylbis(trichloroindate) (4**).** A layer of hexane (1 mL) was slowly allowed to diffuse into a THF solution (1 mL) containing **2** (0.03 mmol, 23.5 mg) and tetraphenylphosphonium chloride (0.03 mmol, 11.2 mg). After a period of 1 week, needlelike crystals of **4** (mp 172°C) could be recovered in a 82% yield (based on Ph_4PCl). Anal. Calc for $\text{C}_{56}\text{H}_{48}\text{Cl}_6\text{In}_2\text{P}_2$: C, 54.89; H, 3.92. Found: C, 54.11; H, 3.86. ^1H NMR ($\text{THF-}d_8$): δ 2.48 (s, 4 H, CH_2), 6.54 (d, 3J 7.9 Hz, 2 H, $H\text{-}4/6$), 6.60 (t, 3J 7.9 Hz, 1 H, $H\text{-}5$), 6.67 (s, 1 H, $H\text{-}2$), 7.70–7.91 (m, 40 H, $\text{P}(\text{C}_6\text{H}_5)$). ^1H NMR ($\text{THF-}d_8$, -60°C): δ 2.94 (s, 4 H, CH_2), 6.47 (d, 3J 7.7 Hz, 2 H, $H\text{-}4/6$), 6.59 (t, 3J 7.7 Hz, 1 H, $H\text{-}5$), 6.62 (s, 1 H, $H\text{-}2$), 7.70–7.94 (m, 40 H, $\text{P}(\text{C}_6\text{H}_5)$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$): [1,3-(Cl_3InCH_2) $_2\text{C}_6\text{H}_4$] $^{2-}$ δ 123.2 ($C\text{-}4/6$), 127.7 ($C\text{-}2$), 128.0 ($C\text{-}5$), 143.5 ($C\text{-}1/3$); [Ph_4P^+] δ 119.0 (d, $^1J_{\text{CP}}$ 15.7 Hz, $C\text{-ipso}$), 131.4 (d, $^2J_{\text{CP}}$ 12.8 Hz, $C\text{-meta}$), 135.6 (d, $^3J_{\text{CP}}$ 10.1 Hz, $C\text{-ortho}$), 136.4 ($C\text{-para}$).

^{199}Hg NMR Investigation of the Ligative Behavior of **1 toward Chloride Anions.** An NMR sample was prepared by dissolving **1** (14.4 mg, 25 μmol) in $\text{DMSO-}d_6$ (0.5 mL). Between each measurement, an incremental amount of solid Ph_4PCl was added to the solution. This procedure was continued until no further change of the ^{199}Hg chemical shift was observed.

VT ^1H NMR Investigation of 2-Cl^- (3**).** A sample of **3** was prepared by mixing **2** (9.2 mg, 12 μmol) and Ph_4PCl (4.4 mg, 12 μmol) in 0.4 mL of $\text{THF-}d_8$. The resulting solution was transferred into a 5 mm NMR tube. The measurements were carried out between $+25$ and -80°C . ^1H NMR ($\text{THF-}d_8$, 25°C): δ 2.29 (s, 4 H, CH_2), 6.71 (d, 3J 7.9 Hz, 2 H, $C_{4/6}H$), 6.83 (t, 3J 7.9 Hz, 1 H, C_5H), 6.89 (s, 1 H, C_2H), 7.70–7.91 (m, 20 H, $\text{P}(\text{C}_6\text{H}_5)$). Coalescence of the methylene signal took place at -25°C . Below -50°C , the two new methylene signals were detected at δ 2.19 and 2.41 ppm. Note that these values do not correspond to those recorded for the methylene resonance of pure **2** (δ 2.46) and pure **4** (δ 2.94) at -60°C .

VT ^1H NMR Investigation of $\text{PhCH}_2\text{InCl}_2/\text{Cl}^-_{0.5}$ (3**).** A sample was prepared by mixing $\text{PhCH}_2\text{InCl}_2$ (6.6 mg, 24 μmol) and Ph_4PCl (4.4 mg, 12 μmol) in 0.4 mL of $\text{THF-}d_8$. The resulting solution was transferred into a 5 mm NMR tube. The measurements were carried out between $+25$ and -80°C . ^1H NMR ($\text{THF-}d_8$, 25°C): δ 2.40 (s, 2 H, CH_2), 6.80–7.15 (m, 5H, aryl- CH), 7.70–7.91 (m, 20 H, $\text{P}(\text{C}_6\text{H}_5)$). Coalescence of the methylene signal took place at -29°C . Below -60°C , the two new methylene signals were detected at δ 2.23 and 2.54 ppm.

$\text{PhCH}_2\text{InCl}_2$ (3.3 mg, 12 μmol) was dissolved in in 0.4 mL of $\text{THF-}d_8$. The low-temperature ^1H NMR spectrum of this solution was recorded at -60°C : ^1H NMR ($\text{THF-}d_8$, -60°C): δ 2.54 (s, 2 H, CH_2), 6.80–7.15 (m, 5H, aryl- CH).

A sample of $[\text{PhCH}_2\text{InCl}_3]^- [\text{PPH}_4]^+$ was prepared by mixing $\text{PhCH}_2\text{InCl}_2$ (3.3 mg, 12 μmol) and Ph_4PCl (4.4 mg, 12 μmol) in 0.4 mL of $\text{THF-}d_8$. The low-temperature ^1H NMR spectrum of this mixture was

recorded at $-60\text{ }^{\circ}\text{C}$: ^1H NMR ($\text{THF-}d_6$, $-60\text{ }^{\circ}\text{C}$): δ 2.23 (s, 2 H, CH_2), 6.80–7.15 (m, 5H, aryl- CH), 7.70–7.91 (m, 20 H, $\text{P}(\text{C}_6\text{H}_5)$).

Crystal Structure Determinations. Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all compounds. L_p corrections were applied, and intensity data of compounds **1** and **4** were corrected for absorption effects (DIFABS and ψ -scans, respectively). The structures were solved by Patterson methods and completed by full-matrix least-squares techniques against F^2 . The thermal motion of all non-hydrogen atoms was treated anisotropically. One THF molecule of compound **2** was disordered and refined in split positions. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{\text{iso}(\text{fix})} = 1.5 \times U_{\text{eq}}$ of the attached C atom), with the exception of the H

atoms of the disordered THF molecule of compound **2**, which were partly neglected. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

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Supporting Information Available: Tables listing experimental crystallographic details, atomic positional parameters, thermal parameters, and bond lengths and angles (22 pages). Ordering information is given on any current masthead page.

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