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Unusual Ring Systems Containing Indium. Synthesis and Structure of the First Mercuraindacycles

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The mercuraindacycles bis(μ-1,8-naphthalenediyl)mercury(II)(bis(tetrahydrofuran)chloroindium(III)) (**5**) and bis(μ-1,8-naphthalenediyl)mercury(II)(bis(tetrahydrofuran)bromoindium(III)) (**7**) are the products of the reaction of indium(I) halides with 1,8-naphthalenediylbis(mercury(II) halides). Their formation involves a partial transmetalation followed by a spontaneous ring closure. Compounds **5** and **7** have been characterized by ^{1}H, ^{13}C, and ^{199}Hg NMR spectroscopy. The X-ray crystal structures of **5**$\cdot$($InCl_3(THF)_3$) and **7** have been determined. Compound **5** crystallizes as an $InCl_3(THF)_3$ adduct in the monoclinic space group $P2_1/c$ with $a = 17.529(2)$ Å, $b = 8.954(1)$ Å, $c = 27.704(1)$ Å, $\beta = 107.02(1)°$, $V = 4157.8(7)$ Å^3, and $Z = 4$. Compound **7** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 8.368(1)$ Å, $b = 15.357(1)$ Å, $c = 19.446(1)$ Å, $V = 2499.0(4)$ Å^3, and $Z = 4$. In both structures, the eight-membered dimetallacycles adopt a twisted conformation with conspicuously short In$\cdots$Hg transannular distances. Finally, the X-ray crystal structure of the diindacycle bis(μ-1,8-naphthalenediyl)bis(bis(tetrahydrofuran)chloroindium(III)) (**8**) is reported. This compound is isolated as a low-yield side product in the synthesis of **5**. Compound **8** crystallizes in the tetragonal space group $P4/n$ with $a = 19.492(1)$ Å, $c = 10.432$ Å, $V = 3963.5(5)$ Å^3, and $Z = 4$.

Introduction

Trimeric *o*-phenylenemercury (**1**) is well-known to undergo transmetalation reactions with a variety of main-group elements.[1] *o*-Dilithiobenzene,[1a] tetrameric *o*-phenylenemagnesium,[1c] and dimeric *o*-phenylenezinc[1d] are representative examples, the preparation of which demonstrates the importance of this synthetic method. We have recently reported that the reaction of **1** with indium(I) halides also results in transmetalation but that the nature of the halide governs the outcome of the reaction (Scheme 1).[2] In the case of the bromide, a complete transmetalation occurs and dimeric *o*-phenyleneindium bromide (**2**) is formed.[2a] On the other hand, the analogous reaction with InCl leads to a heteronuclear trifunctional system (**3**), indicating that only a partial transmetalation takes place.[2b] Because of the unpredictable character of these reactions, we decided to further investigate the interaction of indium(I) halides with bifunctional arylmercury derivatives and report herein that the reaction of *peri*-dimercurated naphthalene compounds with indium(I) halides leads to the synthesis of novel indium-containing ring systems.

Results and Discussion

Synthesis. The reaction of the dimercuracycle **4**[3] with InCl or InBr in THF (Scheme 2) was attempted first. However, even after prolonged stirring, no reaction was observed. Contrarily, 1,8-naphthalenediylbis(mercury(II) chloride)[3] reacts with InCl (Scheme 2) to yield a compound (**5**) with spectroscopic characteristics consistent with the presence of an unsymmetrically *peri*-substituted naphthalene moiety (^{1}H and ^{13}C NMR) and of a mercury center (^{199}Hg NMR). In order to study the influence of the halide on the course of this reaction, 1,8-naphthalenediylbis(mercury(II) bromide) (**6**) was prepared.[4] InBr reacts with compound **6** to afford compound **7** (Scheme 2). The NMR data obtained for **7** are almost identical to those of **5**, thus indicating that these two compounds are closely related and probably have analogous structures. Especially noteworthy are the almost identical ^{199}Hg NMR chemical shifts of −280 and −283 ppm measured for compounds **5** and **7**, respectively. While pure **5** could not be obtained (*vide infra*), the elemental analysis data as well as the integrated ^{1}H NMR spectrum of **7** clearly indicated the presence of one coordinated THF molecule per naphthalene ring. Single-crystal X-ray analysis of compounds **5**$\cdot$($InCl_3(THF)_3$) and **7** revealed that the products of these reactions are in fact mercuraindacycles. To our knowledge, the synthesis of such bimetallic heterocycles has no precedent.

The elemental analysis data collected on the microcrystalline precipitate containing **5** revealed the presence of inorganic impurities since unexpectedly low carbon and hydrogen contents were obtained. Moreover, addition of hexane to the mother liquor from which impure **5** was obtained resulted in the precipitation of $InCl_3(THF)_2$ (see Experimental Section). These observations indicate that disproportionation of InCl takes place ($3InCl \rightarrow 2In(0) + InCl_3$) and allow one to rationalize the fact that crystals of **5**$\cdot$($InCl_3(THF)_3$) could be grown from the mixture. The complexity of this reaction is further reflected by the serendipitous isolation of an additional side product.

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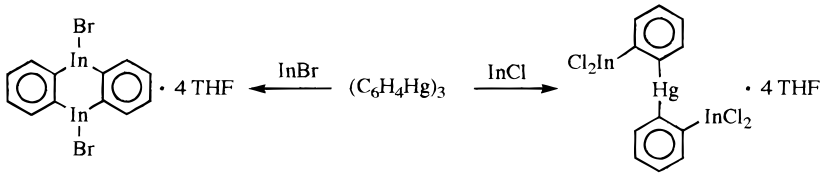
(4) Compound **6** crystallizes as a DMSO adduct upon cooling of a saturated DMSO solution. **6**$\cdot$DMSO (space group $P2_1/n$ with $a = 7.376(1)$ Å, $b = 9.434(2)$ Å, $c = 23.010(3)$ Å, and $\beta = 92.050°$) is isomorphous to the analogous chloride complex.[3]

Scheme 1



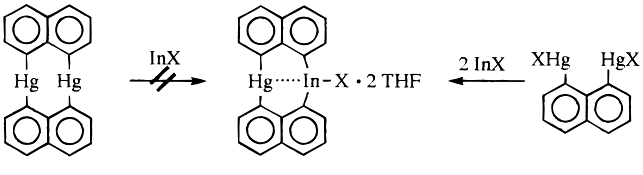
2 **1** **3**

Table 1. Crystal Data, Data Collection, and Structure Refinement for Compounds **5**·InCl$_3$(THF)$_3$, **7**, and **8**·0.5THF

	5·InCl$_3$(THF)$_3$	**7**	**8**·0.5THF
	Crystal Data		
formula	$C_{40}H_{52}O_5In_2HgCl_4$	$C_{28}H_{28}O_2InBrHg$	$C_{38}H_{48}Cl_2In_2O_{4.5}$
M_r	1184.85	791.82	877.30
cryst system	monoclinic	orthorhombic	tetragonal
space group	$P2_1/c$	$P2_12_12_1$	$P4/n$
a (Å)	17.529(2)	8.368(1)	19.492(1)
b (Å)	8.954(1)	15.357(1)	19.492(1)
c (Å)	27.704(2)	19.446(1)	10.432(1)
α (deg)	90	90	90
β (deg)	107.02(1)	90	90
γ (deg)	90	90	90
V (Å^3)	4157.8(7)	2499.0(4)	3963.5(5)
ρ_{calc} (g cm^{-3})	1.893	2.105	1.470
Z	4	4	4
F(000) (e)	2312	1504	1776
μ(Mo Kα) (cm^{-1})	50.82	86.81	133.5
	Data Collection		
T (°C)	−74	−68	−74
scan mode	$\omega-\theta$	ω	ω
hkl range	0 → +21	−10 → +10	−24 → 0
	0 → +11	0 → +19	0 → +24
	−34 → +32	0 → +24	0 → +13
$\sin(\theta/\lambda)_{max}$ (Å^{-1})	0.62	0.62	0.62
measd reflns	7984	5600	4096
unique reflns	7753 (R_{int} = 0.0205)	5281 (R_{int} = 0.0174)	3873 (R_{int} = 0.0268)
reflns used for refinement	7728	5279	3851
abs corr	ψ-scans	ψ-scans	ψ-scans
T_{min}/T_{max}	0.847/0.999	0.663/0.999	0.885/0.999
	Refinement		
refined params	469	298	215
final R values [$I > 2\sigma(I)$]:			
R1^a	0.0272	0.0202	0.0572
wR2^b	0.0632	0.0462	0.1312
(shift/error)$_{max}$	<0.001	<0.001	<0.001
ρ_{fin}(max/min) (e Å^{-3})	+0.758/−1.004	+0.616/−1.183	1.518/−0.592

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0239$ (**5**·InCl$_3$(THF)$_3$), 0.0273 (**7**), 0.0375 (**8**·0.5THF); $b = 18.33$ (**5**·InCl$_3$(THF)$_3$), 0.85 (**7**), 17.17 (**8**·0.5THF).

Scheme 2



4

5 (X = Cl)
7 (X = Br)

Indeed in one of the numerous crystallization attempts which were made to purify **5**, a few cubic crystals of a new compound (**8**) were obtained. While the small number of these crystals did not allow their bulk characterization, one of them was found to be suitable for an X-ray analysis, which revealed that **8** is the bis(μ-1,8-naphthalenediyl)bis(indium(III) chloride) tetrakis(tetrahydrofuran) adduct (Figure 4), a naphthalenediyl analog of compound **2**. In contrast to the formation of **5**, which is accompanied by numerous side reactions, the reaction yielding **7** is cleaner, which substantiates the higher stability of InBr over InCl toward disproportionation in donor solvents such as THF.

Structures of the Mercuraindacycles 5 and 7. Compound **5** crystallizes as an InCl$_3$(THF)$_3$ adduct in the monoclinic space group $P2_1/c$ (Table 1). As shown in Figure 1, the InCl$_3$(THF)$_3$ and the mercuraindacycle are associated via Hg···Cl, whose lengths (Hg···Cl(2) = 3.254 Å, Hg···Cl(3) = 3.478 Å) are smaller than the sum of the van der Waals radii (r_{vdw}(Cl) = 1.8 Å,[5] r_{vdw}(Hg) = 1.73 Å)[6] and can be compared to the intramolecular associative Hg···Cl contact present in the structure of organomercury chloride derivatives such as $PhCH_2HgCl$ (3.176(5)−3.337(5) Å).[7] As a result, the mixture **5**·(InCl$_3$(THF)$_3$) is best regarded as an adduct rather than a cocrystallizate, with the InCl$_3$ moiety acting as a chelating ligand of the mercury center (Cl(2)···Hg···Cl(3) = 63.6°). The respective

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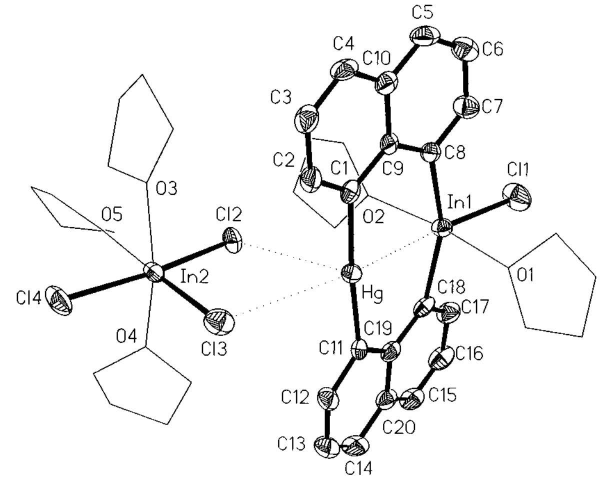

Figure 1. Molecular structure of **5**·($InCl_3(THF)_3$) in the crystal. The representation of the THF molecules has been simplified (thin lines) for clarity. Selected bond lengths (Å) and angles (deg): Hg−C(1) 2.048(4), Hg−C(11) 2.055(4), Hg···In(1) 3.0110(4), In(1)−C(8) 2.167(4), In(1)−C(18) 2.173(5), In(1)−Cl(1) 2.446(1), In(1)−O(1) 2.427(3), In(1)−O(2) 2.450(3), C(7)−C(8) 1.374(6), C(17)−C(18) 1.378(7), C(8)−C(9) 1.441(6), C(18)−C(19) 1.432(7); C(1)−Hg−C(11) 175.4(2), Hg···In(1)−Cl(1) 174.01(4), C(8)−In(1)−C(18) 157.2(2), C(8)−In(1)−Cl(1) 101.1(1), C(18)−In(1)−Cl(1) 101.48(1), O(1)−In(1)−O(2) 168.8(1), C(7)−C(8)−In(1) 113.7(3), C(17)−C(18)−In(1) 113.5(4), C(9)−C(8)−In(1) 127.8(3), C(19)−C(18)−In(1) 127.8(3).

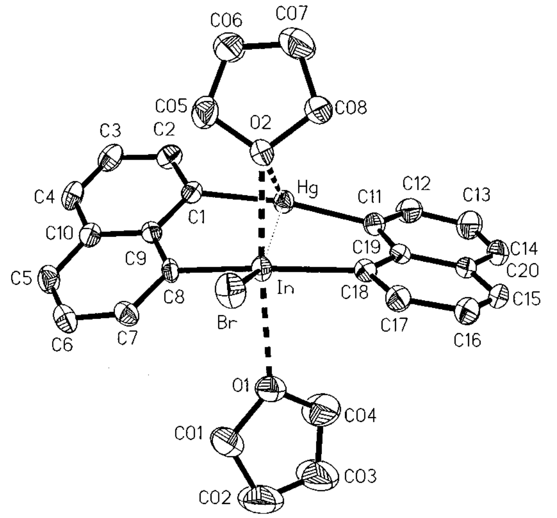

Figure 2. Molecular structure of **7** in the crystal. Selected bond lengths (Å) and angles (deg). Hg−C(1) 2.082(4), Hg−C(11) 2.080(4), Hg···In 3.0305(5), Hg−O(2) 3.106(3), In−C(8) 2.171(4), In−C(18) 2.165(4), In−Br 2.596(1), In−O(1) 2.579(3), In−O(2) 2.395(3), C(7)−C(8) 1.384(5), C(17)−C(18) 1.379(6), C(8)−C(9) 1.422(6), C(18)−C(19) 1.436(6); C(1)−Hg−C(11) 171.7(2), Hg···In−Br 159.77(2), C(8)−In−C(18) 150.9(2), C(8)−In−Br 102.5(1), C(18)−In−Br 105.7(1), O(1)−In−O(2) 175.0(1), C(7)−C(8)−In 113.4(3), C(17)−C(18)−In 113.4(3), C(9)−C(8)−In 127.8(3), C(19)−C(18)−In 126.9(3), In−O(2)−Hg 65.4(1).

arrangement of the two components confers to the whole adduct an approximate C_s symmetry with a mirror plane containing the three metallic centers. The structure of the $InCl_3(THF)_3$ entity is similar to that reported for the pure complex,[8] and the existing geometrical differences are essentially negligible.

The eight-membered ring containing the mercury and indium atoms has a slightly twisted conformation. The mercury atom is almost linearly coordinated (C(1)−Hg−C(11) = 175.4(2)°) to the two planar naphthalene moieties which form a dihedral angle of 11.0°. The indium center is pentacoordinated in a distorted trigonal bipyramidal fashion. Its coordination sphere comprises two THF molecules at the axial positions and two *peri*-carbon atoms as well as a chloride ligand at the equatorial sites. The main deviation from an ideal geometry occurs in the equatorial plane as indicated by the large C(8)−In(1)−C(18) angle (157.2(2)°), which is comparable to the wide C-*ipso*−In−C-*ipso* angles observed in the structure of sterically crowded diarylindium systems.[9] The naphthalenediyl backbones exhibit also some unusual geometrical features. Specially noteworthy are the values of the C(1)−C(9)−C(8) (123.0(4)°), C(9)−C(8)−In(1) (127.8(3)°), C(11)−C(19)−C(18) (122.2(2)°), and C(19)−C(18)−In(1) (127.8(3)°) angles, which are substantially larger than the ideal value of 120°. Similar distortions are encountered in the structure of sterically hindered *peri*-substituted naphthalene systems such as 1,8-dimethyl-[10] or 1,8-disilylnaphthalene[11] and indicate that sterical/geometrical constraints are also present in the structure of **5**.

Compound **7** crystallizes in the orthorhombic chiral space group $P2_12_12_1$ (Table 1). The structure of the complex is very similar to that of **5** (Figure 2). However, a few structural differences merit comment. The eight-membered dimetallacycle exhibits a stronger twist. The coordination of the mercury center remains close to linear (C(1)−Hg−C(11) = 171.7(2)°), but the two naphthalene rings form a more acute dihedral angle (30.9°) than in the case of **5**. As a result, the mercurybis(naphthalenediyl) backbone of **7** has an approximate C_2 symmetry. As in **5**, the indium coordination sphere is distorted (C(8)−In−C(18) = 150.9(2)°) and the C(1)−C(9)−C(8) (123.8(3)°), C(9)−C(8)−In (127.8(3)°), C(11)−C(19)−C(18) (124.2(4)°), and C(19)−C(18)−In (126.9(3)°) angles are larger than 120°. Hence, as in **5**, consequential geometrical constraints are affecting the structure of the dimetallacycle. Interestingly, in the structure of **7** there is a detectable difference in the In−O distances, which indicates an unsymmetrical coordination of the axial THF molecules. The oxygen atom O(2) (r_{vdw}(O) = 1.4 Å)[5] is rather close to the mercury center (Hg−O(2) = 3.106 Å), which suggests the presence of a moderate interaction between those two atoms. The THF molecule at O(2) can therefore be regarded as being unsymmetrically chelated by the indium and mercury centers. The secondary coordination sphere of the mercury atom in **7** also comprises a bromine atom (r_{vdw}(Br) = 2.0 Å)[5] belonging to a neighboring molecule ($Hg_a···Br_b$ = 3.368 Å) (Figure 3). Consequently, the supramolecular structure of **7** consists of zigzagging ($Hg_a···Br_b−In_b$ = 128.1°) polymeric chains.

The most striking feature in the structures of **5** and **7** is the very short transannular Hg···In distances of 3.0110(4) and 3.0305(5) Å, respectively. There are no data available for a discrete Hg−In linkage. However, these distances are clearly shorter than the sum of the van der Waals radii of the two metals (3.6 Å),[6,12] close to the sum of the metallic radii (3.12 Å), and just slightly above the sum of the Pauling covalent radii (2.94 Å). Hence, a Hg−In bond order close to unity could be proposed, still keeping in mind that both metals have a d^{10} closed-shell electronic configuration and are therefore not expected to form a classical bond. Moreover, it is interesting

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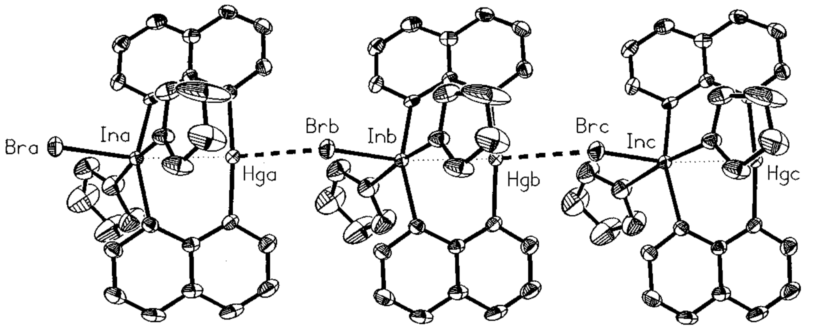
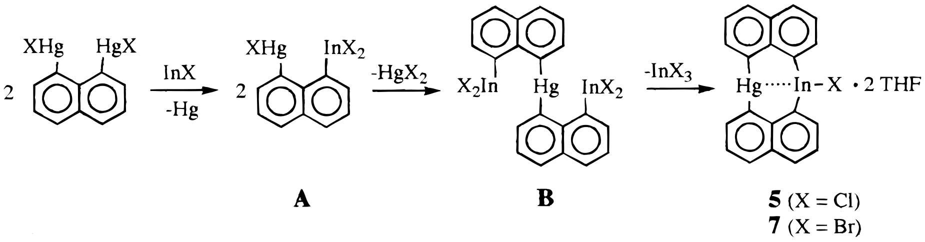


Figure 3. View of a portion of a polymeric chain of **7** in the crystal.

Scheme 3



to note that the C(1)−Hg−C(11) vector is bowed away from the indium center in the structures of both **5** and **7**. This deformation suggests the presence of a repulsive interaction between the two metals. On the other hand, examination of the literature indicates that associative interactions between d^{10} closed-shell elements occurs, especially in the case of gold(I) ($5d^{10}$)[13,14] but also in the case of silver(I) ($4d^{10}$)[14,15] and mercury(II) ($5d^{10}$).[3,16] Therefore, the presence of such an interaction (usually referred to as a nonbonded interaction) between the mercury(II) and indium(III) ($4d^{10}$) centers of the mercuraindacycles cannot be totally ruled out.

Structure of the Diindacycle 8. Compound **8** crystallizes in the tetragonal space group *P*4/*n* with half of an interstitial, strongly disordered solvate THF molecule (Table 1). The solid state structure consists of individual molecules of **8** with a center of inversion in the center of the eight-membered diindacycle (Figure 4). The indium atoms are respectively displaced 0.340 Å above and below the coplanar naphthalene moieties. The indium centers are pentacoordinated in an approximate trigonal bipyramidal fashion resembling that encountered in **5** and **7**, with a large C(1)−In−C(7) angle (154.2(3)°). The naphthalenediyl backbone of **8** is also distorted as indicated by the large C(1)−C(6)−C(7a) (124.7(6)°), C(1)−C(6)−In (127.5(5)°), and C(6a)−C(7)−In (128.1(4)°) angles. Despite the strong geometrical constraints present in **8**, the attachment of the naphthalenediyl moieties to the indium centers is covalent. In that respect, compound **8** is comparable to the mercury analog **4** but differs from the 1,8-naphthalenediylmagnesium, which forms a tetrameric cluster.

Mechanistic Considerations on the Formation of 5 and 7. The formation of **5** and **7** in the reaction depicted in Scheme 2 most probably involves transmetalation of only one mercury center followed by a series of ligand exchange processes as shown in Scheme 3. Considering the sterical and geometrical constraints in **5** and **7**, such a ring closure reaction is very surprising but constitutes the most valid hypothesis allowing rationalization of the formation of these mercuraindacycles. Indeed, since **4** does not react with InCl and InBr, a mechanism involving symmetrization of the 1,8-naphthalenediylbis(mercury(II) halide) into **4**,[3] followed by transmetalation of one mercury center, can be ruled out. Note that the reaction of 1,2-bis(bromomercurio)benzene with InBr produces an isolable phenylene analog of the proposed intermediate **B**.[2a]

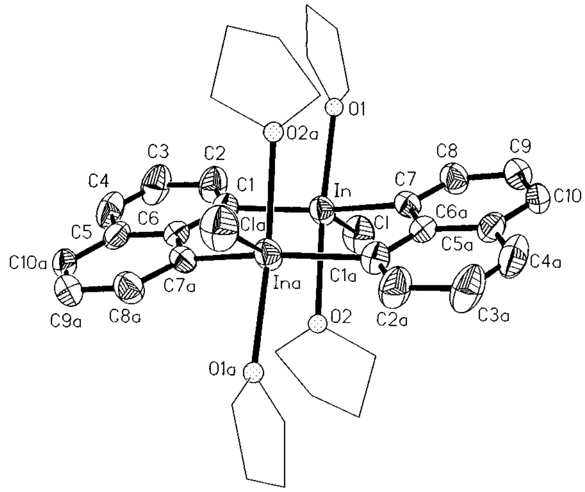


Figure 4. Molecular structure of **8** in the crystal. The representation of the THF molecules has been simplified (thin lines) for clarity. Selected bond lengths (Å) and angles (deg): In−C(1) 2.154(6), In−C(7) 2.148(6), In−Cl 2.463(2), In−O(1) 2.423(5), In−O(2) 2.467(4), C(1)−C(2) 1.364(9), C(7)−C(8) 1.383(8), C(1)−C(6) 1.434(9), C(7)−C(6a) 1.430(9); C(1)−In−C(7) 154.2(3), C(1)−In−Cl 103.5(2), C(7)−In−Cl 102.3(2), O(1)−In−O(2) 166.6(2), C(2)−C(1)−In 112.1(1), C(8)−C(7)−In 112.2(2), C(6)−C(1)−In 127.2(5), C(6a)−C(7)−In 128.1(4).

Conclusion

The present synthetic results indicate that the course of the reaction of polyfunctional organomercuric compounds with indium(I) halides is hard to predict but allows the synthesis of novel systems. The duplication of the synthesis of mercurain-

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dacycles in two different reactions substantiates the thermodynamical stability of such ring systems. The most important structural finding herein reported concerns the short transannular Hg$\cdots$In distances present in the structures of **5** and **7**. Attempts to synthesize systems with unsupported Hg(II)$\cdots$In(III) contacts as well as theoretical calculations might allow elucidation of the cause of this short distance.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra were obtained on a JEOL-GX 400 instrument (400 MHz for ^{1}H, 100.5 MHz for ^{13}C, 71.56 MHz for ^{199}Hg). 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 ^{1}H and ^{13}C NMR spectra, respectively. All NMR measurements were carried out at 25 °C. Elemental analyses were performed by the Laboratory for Microanalysis at Technische Universität München. All 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 THF-d_8 were dried over Na/K and distilled prior to use. Hexane was dried over CaH_2 prior to distillation and use. All other solvents were used without further purification. All commercially available starting materials were purchased from Aldrich Chemicals and used without further purification. InBr was prepared by fusing $InBr_3$ and 2 equiv of In(0) at 375 °C under vacuum and was purified through sublimation under those conditions. 1,8-Naphthalenediylbis(mercury(II) chloride) and **4** were synthesized according to the literature procedure.[3]

Synthesis of 1,8-Naphthalenediylbis(mercury(II) bromide) (6). A 1,8-dilithionaphthalene solution was prepared by adding a 1.6 M hexane solution of *n*-butyllithium (8.5 mL, 13.7 mmol) to a cooled (0 °C) Et_2O solution (15 mL) of 1,8-diiodonaphthalene (2.00 g, 5.26 mmol). After 2 h of stirring, a THF solution (15 mL) of $HgBr_2$ (10.24 g, 28.4 mmol) was added dropwise. The resulting reaction mixture was stirred for 15 h and refluxed for 6 h, after which time all volatiles were removed under vacuum. The resulting residue was washed twice with H_2O (25 mL) and twice with THF (25 mL) and dried under vacuum to afford compound **6** (mp 350 °C dec) in 42% yield (1.51 g). Elemental anal. Calcd for $C_{10}H_6Br_2Hg_2$: C, 17.5; H, 0.88; Br, 23.3. Found: C, 16.9; H, 1.00; Br, 22.42. Poor analysis due to Hg(0) contamination. ^{1}H NMR (DMSO-d_6): δ 7.46 (dd, $J = 7.5$ Hz, $J = 6.3$ Hz, 2H, *H*-3/6), 7.80 (d, $J = 6.3$ Hz, 2H, *H*-2/7), 7.88 (d, $J = 7.5$ Hz, 2H, *H*-4/5). ^{13}C NMR (DMSO-d_6): δ 125.1 (s, *aryl*-*C*H-3/6), 128.8 (s, *aryl*-*C*H-4/5), 135.9 (s, *aryl*-*C*H-2/7), 160.7 (*s*, *aryl*-*C*Hg), *C*H-9 and -10 not detected. ^{199}Hg NMR (DMSO-d_6): δ −1094.

Reaction of 1,8-Naphthalenediylbis(mercury(II) chloride) with InCl. InCl (0.18 g, 1.20 mmol) and 1,8-naphthalenediylbis(mercury(II) chloride) (0.30 g, 0.50 mmol) were stirred together in THF (5 mL) under nitrogen for 4 h, after which time the reaction mixture was filtered to remove the metallic precipitate. Concentration of the filtrate followed by cooling to −25 °C afforded a microcrystalline precipitate of impure **5**. Estimated yield of **5**: 20%. Addition of hexane to the supernatant solution followed by cooling to −25 °C resulted in the precipitation of $InCl_3(THF)_2$. (Anal. Calcd for $C_8H_{16}Cl_3InO_2$: C, 26.3; H, 4.4; Cl, 29.1. Found: C, 25.5; H, 4.3; Cl, 28.0.) Despite several crystallization attempts, **5** could not be obtained pure. In one of those attempts a few cubic crystals of compound **8** were formed and isolated. Crystals of **8** become slowly brittle at 25 °C through loss of the interstitial THF. A few crystals of **5**$\cdot$($InCl_3(THF)_3$) (mp 85−87 °C) were obtained by cooling a solution of impure **5**. The NMR data for **5** are as follows. ^{1}H NMR (THF-d_8): δ 1.77 (br, 8H, OCH_2CH_2), 3.61 (br, 8H, OCH_2), 7.46 (dd, $J = 7.9$ Hz, $J = 6.7$ Hz, 2H, *H*-6/6′ or -3/3′), 7.51 (dd, $J = 7.9$ Hz, $J = 6.7$ Hz, 2H, *H*-3/3′ or -6/6′), 7.71 (dd, $J = 6.7$ Hz, $J = 1.2$ Hz, 2H, *H*-7/7′ or -2/2′), 7.77 (dd, $J = 7.9$ Hz, $J = 1.2$ Hz, 2H, *H*-5/5′ or -4/4′), 7.86 (dd, $J = 7.9$ Hz, $J = 1.2$ Hz, 2H, *H*-4/4′ or -5/5′), 8.74 (dd, $J = 6.7$ Hz, $J = 1.2$ Hz, 2H, *H*-2/2′ or -7/7′). ^{13}C NMR (THF-d_8): δ 26.4 (s, OCH_2CH_2), 68.2 (s, OCH_2CH_2), 125.3 (s, *aryl*-*C*H-6/6′ or -3/3′), 125.5 (s, *aryl*-*C*H-3/3′ or -6/6′), 129.0 (s, *aryl*-*C*H-5/5′ or -4/4′), 129.7 (s, *aryl*-*C*H-4/4′ or -5/5′), 135.2 (s, *aryl*-*C*H-7/7′ or -2/2′), 139.5 (s, *aryl*-*C*H-2/2′ or -7/7′), 175.7 (*s*, *C*Hg), *C*In, *C*H-9/9′, and *C*H-10/10′ not detected. ^{199}Hg NMR (THF-d_8): δ −280.

Synthesis of Bis(μ-1,8-naphthalenediyl)mercury(II)(bis(tetrahydrofuran)bromoindium(III)) (7). InBr (0.10 g, 0.51 mmol) and **6** (0.17 g, 0.25 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 precipitate. Concentration of the filtrate followed by cooling to −25 °C afforded crystals of **7** (mp 90−100 °C, dec) in 31% yield (56 mg). Further purification can be achieved by vapor diffusion of hexane into a THF solution of **7**. Elemental anal. Calcd for $C_{28}H_{28}BrHgInO_2$: C, 42.4; H, 3.5. Found: C, 42.1; H, 3.6. ^{1}H NMR (THF-d_8): δ 1.77 (br, 8H, OCH_2CH_2), 3.61 (br, 8H, OCH_2), 7.46 (dd, $J = 7.9$ Hz, $J = 6.7$ Hz, 2H, *H*-6/6′ or -3/3′), 7.51 (dd, $J = 7.9$ Hz, $J = 6.7$ Hz, 2H, *H*-3/3′ or -6/6′), 7.71 (dd, $J = 6.7$ Hz, $J = 1.2$ Hz, 2H, *H*-7/7′ or -2/2′), 7.77 (dd, $J = 7.9$ Hz, $J = 1.2$ Hz, 2H, *H*-5/5′ or -4/4′), 7.86 (dd, $J = 7.9$ Hz, $J = 1.2$ Hz, 2H, *H*-4/4′ or -5/5′), 8.66 (dd, $J = 6.7$ Hz, $J = 1.2$ Hz, 2H, *H*-2/2′ or -7/7′). ^{13}C NMR (THF-d_8): δ 26.4 (s, OCH_2CH_2), 68.2 (s, OCH_2CH_2), 125.3 (s, *aryl*-*C*H-6/6′ or -3/3′), 125.5 (s, *aryl*-*C*H-3/3′ or -6/6′), 129.0 (s, *aryl*-*C*H-5/5′ or -4/4′), 129.6 (s, *aryl*-*C*H-4/4′ or -5/5′), 135.2 (s, *aryl*-*C*H-7/7′ or -2/2′), 138.6 (s, *aryl*-*C*H-2/2′ or -7/7′), 175.8 (*s*, *C*Hg), *C*In, *C*H-9/9′, and *C*H-10/10′ not detected. ^{199}Hg NMR (THF-d_8): δ −283.

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **5**$\cdot InCl_3(THF)_3$, **7**, and **8**$\cdot$0.5THF were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer (Mo $K\alpha$ radiation, λ(Mo $K\alpha$) = 0.710 73 Å). 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. Lp correction was applied and intensity data were corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the disordered solvent THF molecule in the compound **8**$\cdot$0.5THF. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom). The hydrogen atoms of the solvent molecule in **8**$\cdot$0.5THF were 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: Three X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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