ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 6893–6901 6893
DOI: 10.1021/om9007967

Synthesis and Structure of Polynuclear Indoxanes and Thalloxanes Containing Bulky *m*-Terphenyl Substituents

S. Usman Ahmad and Jens Beckmann*

Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany

Received September 11, 2009

Depending on the reaction conditions, the base hydrolysis of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}Cl)_2Cl_2$ (**1**) in a two-layer system of aqueous NaOH/diethyl ether or toluene afforded $2,6\text{-}Mes_2C_6H_3InCl_2\cdot H_2O$ (**2**), $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}OH)_2Cl_2$ (**3**), $(2,6\text{-}Mes_2C_6H_3In)_3(\mu\text{-}OH)_4Cl_2$ (**4**), and $(2,6\text{-}Mes_2C_6H_3In)_4(\mu\text{-}OH)_8$ (**5**), respectively, in high yields. The indoxane **5** can be regarded as a heavier and aggregated congener of arylboronic acids. An attempt at preparing $(2,6\text{-}Mes_2C_6H_3Tl)_2(\mu\text{-}Cl)_2Cl_2$ (**6**) by the chlorination of $2,6\text{-}Mes_2C_6H_3Tl$ (prepared in situ from $2,6\text{-}Mes_2C_6H_3Li$ and TlCl) using SO_2Cl_2 provided the isomeric diarylthallium cation $[(2,6\text{-}Mes_2C_6H_3)_2Tl]TlCl_4$ (**7**). The exposure of crude reaction mixture consisting of $2,6\text{-}Mes_2C_6H_3Tl$ and LiCl to moist air surprisingly produced $(2,6\text{-}Mes_2C_6H_3Tl)_2(\mu\text{-}OH)_2Cl_2$ (**8**), which reacted with hydrochloric acid to give **6**. Base hydrolysis of **8** in a two-layer system of aqueous NaOH/$CHCl_3$ proceeded with partial cleavage of the *m*-terphenyl substituents and yielded the thalloxane cluster $(2,6\text{-}Mes_2C_6H_3Tl)_4Tl_2(\mu_3\text{-}O)_4(\mu\text{-}OH)_6$ (**9**) in moderate yield. Compounds **1**−**9** were characterized by X-ray crystallography.

Introduction

The importance of boronic acids, $RB(OH)_2$, and the related boroxine rings, $[RB(\mu\text{-}O)]_3$, for many branches of chemistry cannot be overstated. Arguably, the most prominent application involves the use as reagents for transition metal catalyzed cross-coupling reactions,[1] but boronic acids are also of current interest as building blocks in supramolecular chemistry[2] and for applications in carbohydrate sensing.[3] The chemistry of the heavier aluminoxanes and galloxanes also progresses at a rapid pace, as highlighted by a recent review.[4] This research is stimulated by the industrial use of polymeric methylaluminoxane (MAO) as cocatalyst for the polymerization of ethylene. While the exact structure of MAO is unknown, a number of discrete molecular aluminoxane and galloxane clusters were obtained by the controlled hydrolysis of sterically encumbered triorganoallanes and -gallanes. Well-defined examples include the aluminoxane clusters $(t\text{-}BuAl)_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_4$, $[t\text{-}BuAl(\mu_3\text{-}O)]_n$ (n = 6, 7, 9, 12), $[(2,4,6\text{-}t\text{-}Bu_3C_6H_2Al)_4(\mu\text{-}O)]_4$, and $[(Me_3Si)_3CAl]_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$ and the galloxane clusters $(t\text{-}BuGa)_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_2(\mu\text{-}OH)_4$, $(t\text{-}BuGa)_9(\mu_3\text{-}O)_9$, $[(MesGa)_6(\mu_3\text{-}O_4)(\mu\text{-}OH)_4\cdot THF]$, $(MesGa)_9(\mu_3\text{-}O)_6(\mu\text{-}O)_3$, and $[(Me_3Si)_3CGa]_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$, respectively.[5] The degree of condensation and aggregation within these clusters depends on the method of preparation and most importantly the nature of the organic substituents, which provide the kinetic stabilization. In the same review it was pointed out that there are surprisingly few studies dealing with the heavier group 13 congeners, which was attributed to the reduced oxophilicity and lower Lewis acidity of In and Tl.[4] We are aware of only two well-defined indoxane clusters, $[(Me_3Si)_3CIn]_4(\mu_4\text{-}O)(\mu\text{-}OH)_6$[6] and $[(Me_3Si)_3CIn(\mu_3\text{-}O)]_4$,[7] which adopt an oxygen-centered adamantane structure and a cubane-like structure, respectively. During the course of this work two asymmetric four-membered galloxane and indoxane rings, $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3E(\mu\text{-}O)]_2$ (E = Ga, In), were also reported in which further aggregation is prevented by a bulky *m*-terphenyl substituent.[8] Herein, we report a number of complementary polynuclear indoxanes

*Corresponding author. E-mail: beckmann@chemie.fu-berlin.de.

(1) Hall, D. G., Ed. *Boronic Acids*; Wiley-VCH: Weinheim, 2005; and references therein.

(2) (a) Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Sturba, L.; Grepioni, F. *Organometallics* **2003**, *22*, 2142. (b) Fournier, J.-H.; Maris, T.; Wuest, J. D.; Guo, W.; Galoppini, E. *J. Am. Chem. Soc.* **2003**, *125*, 1002. (c) Pedireddi, V. R.; Lekshmi, N. S. *Tetrahedron Lett.* **2004**, *45*, 1903. (d) Fujita, N.; Shinkai, S.; James, T. D. *Chem. Asian J.* **2008**, *3*, 1076. (e) Mastalerz, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 445. (f) Severin, K. *Dalton Trans.* **2009**, 5254, and references therein.

(3) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1910. (b) James, T. D.; Shinkai, S. *Top. Curr. Chem.* **2002**, *218*, 159, and references therein.

(4) Roesky, H. W.; Walawalkar, M. G.; Murugavel, R. *Acc. Chem. Res.* **2001**, *34*, 201, and references therein.

(5) (a) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M.; Atwood, J. L.; Bott, S. G. *Organometallics* **1993**, *12*, 24. (b) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971. (c) Landry, C. C.; Harlan, C. J.; Bott, S. G.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1201. (d) Harlan, C. J.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479. (e) Storre, S.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 1380. (f) Storre, S.; Schnitter, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1997**, *119*, 7505. (g) Storre, J.; Klemp, A.; Roesky, H. W.; Fleischer, R.; Stalke, D. *Organometallics* **1997**, *16*, 3074. (h) Schnitter, C.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Riipken, C.; Parisini, E.; Sheldrick, G. M. *Chem.—Eur. J.* **1997**, *3*, 1783. (i) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387.

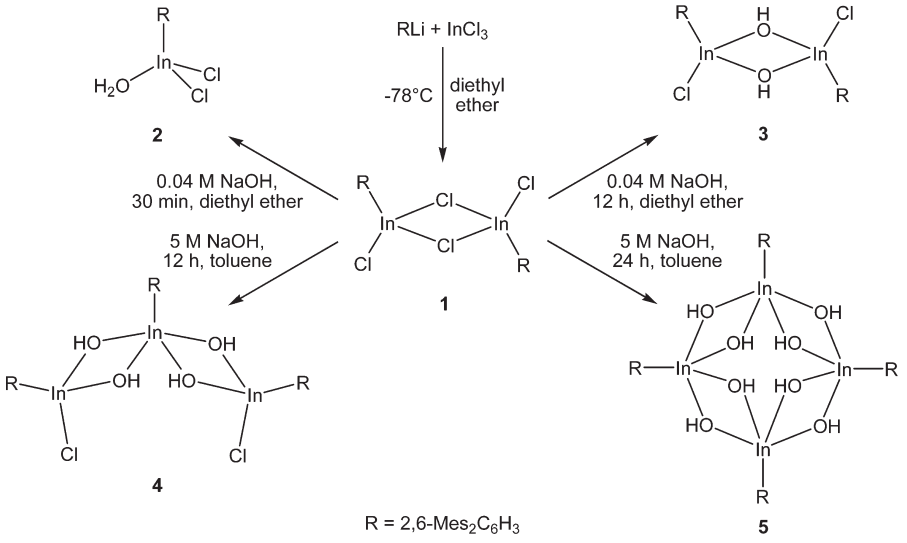
(6) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908.

(7) Uhl, W.; Pohlmann, M. *Chem. Commun.* **1998**, 451.

(8) Zhu, Z.; Wright, R. J.; Brown, Z. D.; Fox, A. R.; Phillips, A. D.; Richards, A. F.; Olstead, M. M.; Power, P. P. *Organometallics* **2009**, *28*, 2512.

Published on Web 10/29/2009

Scheme 1



and thalloxanes containing hydroxy groups and chlorine atoms, which were obtained by the controlled hydrolysis of arylindium and arylthallium dichlorides containing a similar *m*-terphenyl substituent.

Discussion

The arylindium dichloride $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}Cl)_2Cl_2$ (**1**)[9] was obtained by the reaction of $2,6\text{-}Mes_2C_6H_3Li$[10] with $InCl_3$ similar to a procedure already published by Robinson et al. (Scheme 1). While these authors used a benzene/toluene mixture for the extraction and isolated the solvate $\mathbf{1}\cdot C_6H_6$, we avoided the use of aromatic solvents and obtained a solvent-free crystalline product **1**.

The molecular structure of **1** is shown in Figure 1, and selected bond parameters are collected in the caption of the figure. The solvent-free orthorhombic modification of **1** measured at 150 K adopts a four-membered $In_2(\mu\text{-}Cl)_2$ ring structure very similar to that of the monoclinic pseudo polymorph $\mathbf{1}\cdot C_6H_6$ measured at room temperature.[9] While the exocylic In−Cl bond lengths are identical within the experimental error (2.346(4) and 2.344(3) Å), the endocylic In−Cl bond lengths are slightly shorter in **1** (2.482(4) and 2.491 Å) than in $\mathbf{1}\cdot C_6H_6$ (2.519(2) and 2.514(2) Å).[9] The slightly shorter bond lengths can be attributed to the lower temperature during the X-ray data collection and is not due to the "contamination of the μ-Cl sites by μ-OH groups", as it was discussed for the related $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)\text{-}C_6H_3In]_2(\mu\text{-}Cl)_2Cl_2$ (see below).[11]

The base hydrolysis of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}Cl)_2Cl_2$ (**1**) in a two-layer system of aqueous NaOH/diethyl ether or toluene afforded $2,6\text{-}Mes_2C_6H_3InCl_2\cdot H_2O$ (**2**), $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}OH)_2Cl_2$ (**3**), $(2,6\text{-}Mes_2C_6H_3In)_3(\mu\text{-}OH)_4Cl_2$ (**4**), and $(2,6\text{-}Mes_2C_6H_3In)_4(\mu\text{-}OH)_8$ (**5**), depending on the reaction conditions (NaOH concentration and reaction time) applied (Scheme 1). Compounds **2**−**5** were isolated in high yields as single crystalline materials and can be distinguished easily by their melting points. The molecular structures of **2**−**5** are shown in Figures 2−5, and selected bond parameters are collected in the captions of the figures. The structure of $2,6\text{-}Mes_2C_6H_3InCl_2\cdot H_2O$ (**2**) comprises a simple Lewis acid−base pair (Figure 2). The spatial arrangement of the In atom is distorted tetrahedral and defined by a CCl_2O donor set. The In−Cl bond lengths of **2** (2.374(2) and 2.408(2) Å) are somewhat longer than the exocyclic In−Cl bond lengths of **1**, and the In−O bond length of **2** (2.207(5) Å) falls within the range of In-μ-OH groups being observed for **3**−**5** (see below). In the crystal lattice, the water molecule is involved in weak hydrogen bonding with chlorine atoms of adjacent molecules (O···Cl 3.173(6) and 3.256(6) Å). The IR spectrum of **2** shows two absorptions at $\tilde{\nu}$ (OH) = 3611 and 3587 cm^{-1} that were assigned to OH stretching vibrations. The molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}OH)_2Cl_2$ (**3**) consists of a four-membered $In_2(\mu\text{-}OH)_2$ ring featuring tetrahedral In atoms defined by CO_2Cl donor sets. It is noteworthy that similar four-membered $In_2(\mu\text{-}OR)_2$ ring structures were also observed in methylindium(III) alkoxides (R = alkyl, aryl).[12]

The molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_3(\mu\text{-}OH)_4Cl_2$ (**4**) contains two of these $In_2(\mu\text{-}OH)_2$ rings that are linked by a central spirocylic In atom that adopts a square-pyramidal arrangement defined by a CO_4 donor set. The spatial arrangement of the two terminal In atoms resembles those of **3**. The structure of $(2,6\text{-}Mes_2C_6H_3In)_4(\mu\text{-}OH)_8$ (**5**) possesses C_2 symmetry and contains four of these spirocylic In atoms that are involved in four $In_2(\mu\text{-}OH)_2$ rings, two of which are crystallographically independent. Compound **5** can be regarded as a heavier and aggregated analogue of arylboronic acids. It is worth mentioning that the central $(L_nM)_4(\mu\text{-}O)_8$ structural motif of **5** is unprecedented in metalloxane chemistry, whereas similar motifs, such as $(L_nM)_3(\mu\text{-}O)_6$ and $(L_nM)_6(\mu\text{-}O)_{12}$, are already known.[13] The In−O bond lengths of **3**−**5** vary within the range 2.093(6) to 2.224(3) Å

(9) Robinson, G. H.; Li, X.-W.; Pennington, W. T. *J. Organomet. Chem.* **1995**, *501*, 399.
(10) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353.
(11) (a) Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1998**, 2015. (b) Twamley, B.; Power, P. P. *Chem. Commun.* **1999**, 1805.
(12) (a) Veith, M.; Hill, S.; Huch, V. *Eur. J. Inorg. Chem.* **1999**, 1343. (b) Hecht, E.; Gelbrich, T.; Thiele, K.-H.; Sieler, J. *Main Group. Chem.* **2000**, *3*, 109. (c) Chitsaz, S.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2451. (d) Chamazi, N. N.; Heravi, M. M.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2006**, *632*, 2043.
(13) Roesky, H. W.; Haiduc, I.; Hosmane, N. S. *Organometallics* **2003**, *103*, 2579, and references therein.

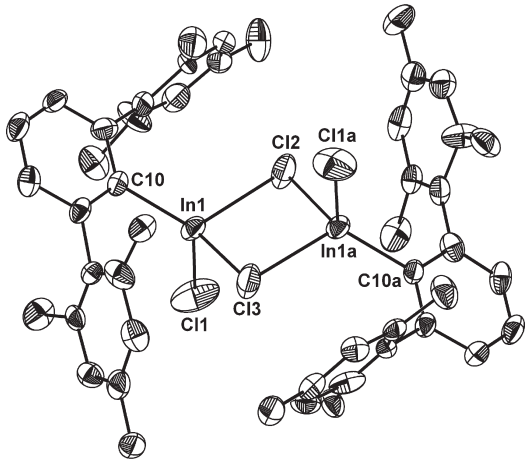


Figure 1. Molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}Cl)_2Cl_2$ (**1**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: In1−Cl1 2.346(4), In1−Cl2 2.482(4), In1−Cl3 2.491(4), In1−C10 2.118(8), Cl1−In1−Cl2 103.7(2), Cl1−In1−Cl3 100.0(2), Cl2−In1−Cl3 85.0(1), Cl1−In1−C10 121.7(3), Cl2−In1−C10 120.9(4), Cl3−In1−C10 118.2(4).

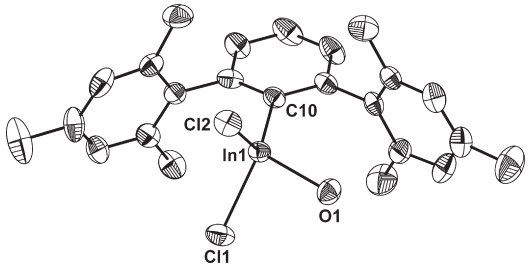


Figure 2. Molecular structure of $2,6\text{-}Mes_2C_6H_3InCl_2\cdot H_2O$ (**2**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: In1−O1 2.207(5), In1−Cl1 2.374(2), In1−Cl2 2.408(2), In1−C10 2.130(8), O1−In1−Cl1 91.4(2), O1−In1−Cl2 91.5(2), O1−In1−C10 117.4(3), Cl1−In1−Cl2 109.70(9), Cl1−In1−C10 117.3(2), Cl2−In1−C10 122.5(2).

(average 2.159(6) Å). None of the hydroxy groups of **3**−**5** are involved in hydrogen bonding. This is confirmed by the IR spectra, which show absorptions at $\tilde{\nu}$(OH) = 3617 and 3534 cm^{-1} (**3**), 3633, 3598, 3568, 3529, and 3484 cm^{-1} (**4**), and 3646, 3632, and 3599 cm^{-1} (**5**), respectively, which were assigned to OH stretching vibrations. The endocylic In−Cl bond lengths of **4** (2.455(3) and 2.5207(3) Å) are somewhat longer than the related values of **1** and **3**. In light of established molecular structures and bond parameters, we support the hypothesis of Twamley and Power that the crystal of $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}Cl)_2Cl_2$ originally investigated by Robinson et al. was in fact a mixture of the related hydrolysis products $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}OH)_2Cl_2$ and $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}OH)_2(OH)_2$.[11] It is interesting to compare the (average) In···In separation, which is significantly larger in the chlorine-bridged compounds **1** (3.896(9) Å) and $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}Cl)_2Cl$ (3.7765(4) Å)[11] than in the hydroxy-bridged compounds **3** (3.345(1) Å), **4** (3.401(2) Å), and **5** (3.350(2) Å). Notably, the latter values are also in good agreement with the In···In separation observed in the mixture of $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}OH)_2Cl_2$ and

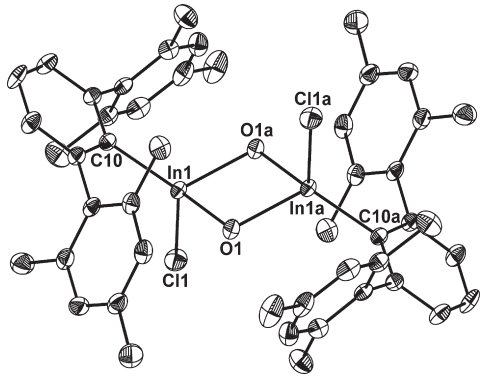


Figure 3. Molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}OH)_2Cl_2$ (**3**) showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a = $-x$, $-y$, $-z$). Selected bond parameters [Å, deg]: In1−O1 2.130(3), In1−O1a 2.131(3), In1−Cl1 2.368(2), In1−C10 2.138(4), O1−In1−O1a 76.6(1), O1−In1−Cl1 101.72(9), O1a−In1−Cl1 103.53(9), O1−In1−C10 122.5(2), O1a−In1−C10 120.3(1), C10−In1−Cl1 122.3(1).

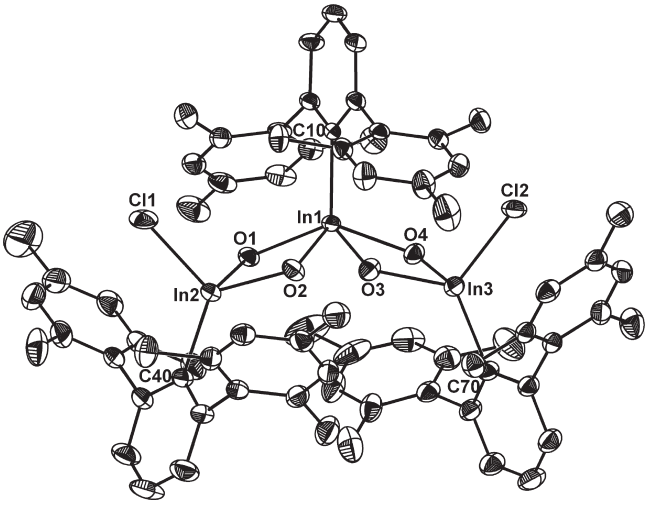


Figure 4. Molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_3(\mu\text{-}OH)_4Cl_2$ (**4**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: In1−O1 2.211(5), In1−O2 2.142(6), In1−O3 2.138(4), In1−O4 2.200(5), In1−C10 2.164(6), In2−O1 2.093(6), In2−O2 2.107(5), In2−Cl1 2.455(3), In2−C40 2.122(7), In3−O3 2.1152(5), In3−O4 2.0999(5), In3−Cl2 2.5207(3), In3−C70 2.1420(7), O1−In1−O2 72.5(2), O1−In1−O3 87.0(2), O1−In1−O4 140.2(2), O2−In1−O3 118.7(2), O2−In1−O4 87.3(2), O3−In1−O4 72.9(2), O1−In1−C10 111.1(2), O2−In1−C10 121.9(2), O3−In1−C10 119.5(2), O4−In1−C10 108.7(2), O1−In2−O2 75.6(2), O1−In2−Cl1 104.0(2), O1−In2−C40 124.4(2), O2−In2−Cl1 108.9(2), O2−In2−C40 120.6(3), Cl1−In2−C40 116.3(2), O3−In3−O4 75.4(2), O3−In3−Cl2 105.7(2), O3−In3−C70 121.4(2), O4−In3−Cl2 108.5(2), O4−In3−C70 121.3(2), Cl2−In3−C70 117.1(2), In1−O1−In2 104.6(2), In1−O2−In2 106.5(2), In1−O3−In3 106.0(2), In1−O4−In3 104.4(2).

$[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In]_2(\mu\text{-}OH)_2(OH)_2$ (3.38(2) Å)[11] and the four-membered asymmetric indoxane ring $[2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)C_6H_3In(\mu\text{-}O)]_2$ (3.598 Å).[8] Compounds **1**−**5** are readily soluble in most organic solvents. The ^1H and ^{13}C NMR spectra show one (**1**, **2**, **3**, **5**) and two sets (**4**) of signals for the *m*-terphenyl substituents.

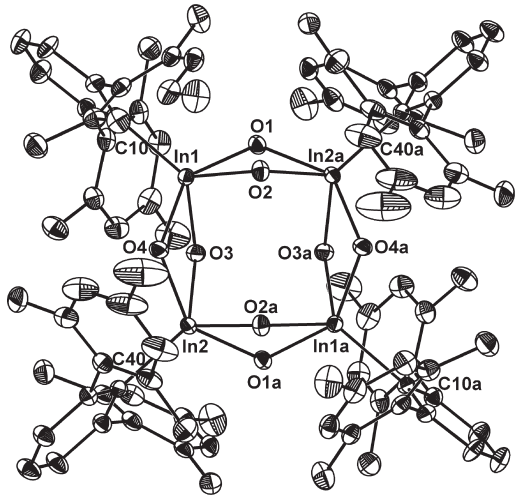


Figure 5. Molecular structure of $(2,6\text{-}Mes_2C_6H_3In)_4(\mu\text{-}OH)_8$ (**5**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: In1−O1 2.189(3), In1−O2 2.137(3), In1−O3 2.163(3), In1−O4 2.190(3), In2−O1a 2.198(3), In1−C10 2.198(5), In2−O2a 2.141(3), In2−O3 2.136(3), In2−O4 2.224(3), In2a−O1 2.198(3), In2a−O2 2.141(3), In2−C40 2.192(4), O1−In1−O2 71.5(1), O1−In1−O3 84.0(1), O1−In1−O4 142.6(1), O2−In1−O3 106.9(1), O2−In1−O4 87.8(1), O3−In1−O4 72.3(1), O1−In1−C10 108.7(2), O2−In1−C10 127.0(2), O3−In1−C10 126.1(2), O4−In1−C10 108.6(2), O1−In2a−O2 71.3(1), O1a−In2−O3 86.1(1), O1a−In2−O4 142.1(1), O2a−In2−O3 107.4(1), O2a−In2−O4 85.8(1), O3−In2−O4 72.2(1), O1a−In2−C40 110.4(2), O2a−In2−C40 125.2(2), O3−In2−C40 127.4(2), O4−In2−C40 107.4-(2), In1−O1−In2a 102.1(1), In1−O2−In2a 105.8(1), In1−O3−In2 108.5(1), In1−O4−In2 104.4(1).

The *m*-terphenyllithium $2,6\text{-}Mes_2C_6H_3Li$[10] was reacted with TlCl to produce $2,6\text{-}Mes_2C_6H_3Tl$ in analogy with a procedure published for similar *m*-terphenylthallium(I) compounds.[14] It is noted that the structure of these compounds is very sensitive to the steric demand of the organic substituent; for example, $2,6\text{-}(2',4',6'\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3Tl$ is a monomer, $2,6\text{-}(2',6'\text{-}i\text{-}Pr_2C_6H_3)_2C_6H_3Tl$ is a dimer, and $2,6\text{-}(2',6'\text{-}Me_2C_6H_3)_2C_6H_3Tl$ is a trimer, respectively. Despite several attempts, we failed to separate $2,6\text{-}Mes_2C_6H_3Tl$ from the byproduct LiCl by recrystallization from inert solvents, such as toluene and diethyl ether. Consequently, the crude mixture of $2,6\text{-}Mes_2C_6H_3Tl$ and LiCl was chlorinated using SO_2Cl_2, upon which the color changed from purple to yellow. To our surprise, the extraction of the crude reaction mixture with $CHCl_3$ did not afford the expected $(2,6\text{-}Mes_2C_6H_3Tl)_2(\mu\text{-}Cl)_2Cl_2$ (**6**), but the isomeric diarylthallium cation $[(2,6\text{-}Mes_2C_6H_3)_2Tl]TlCl_4$ (**7**) as a colorless crystalline solid in good yield (Scheme 2), which implies that a migration of *m*-terphenyl groups occurred. The molecular structure of **7** is shown in Figure 6, and selected bond parameters are collected in the caption of the figure. Crystals of **7** contain essentially separated $[(2,6\text{-}Mes_2C_6H_3)_2Tl]^+$ cations and $TlCl_4^-$ anions. By contrast, the closely related compounds $[Mes_2Tl][MesTlCl_3]$[15] and $[Mes_2Tl]BF_4$[16] comprise

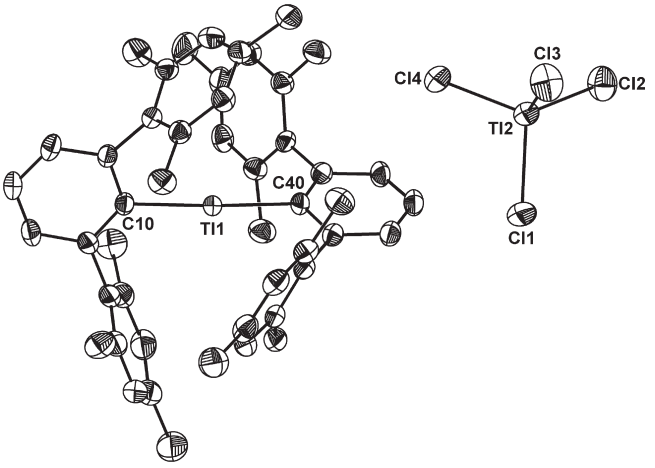
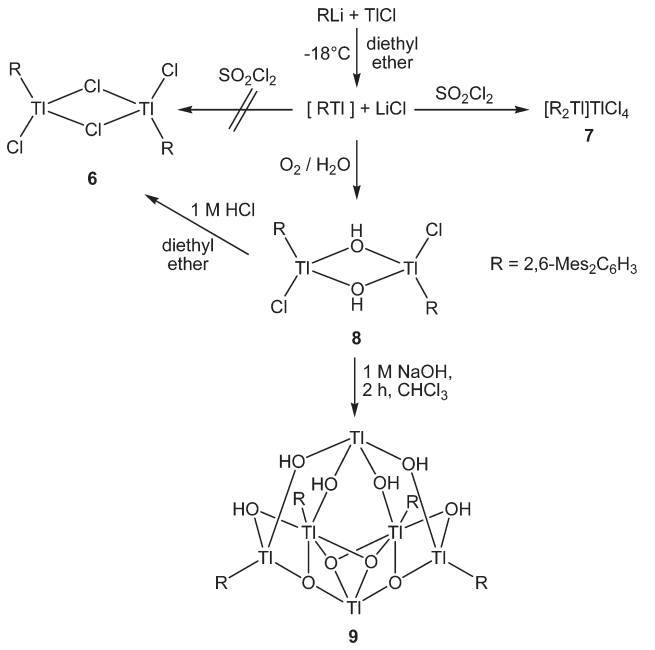


Figure 6. Molecular structure of $[2,6\text{-}Mes_2C_6H_3)_2Tl]TlCl_4$ (**7**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: Tl1−C10 2.126(9), Tl1−C40 2.127(9), Tl2−Cl1 2.412(4), Tl2−Cl2 2.394(4), Tl2−Cl3 2.413(6), Tl2−Cl4 2.398(5), C10−Tl1−C40 177.4(3), Cl1−Tl2−Cl2 108.2(2), Cl1−Tl2−Cl3 111.0(2), Cl1−Tl2−Cl4 107.1(2), Cl2−Tl2−Cl3 106.9(2), Cl2−Tl2−Cl4 112.7-(2), Cl3−Tl2−Cl4 110.9(2).

Scheme 2



organothallium cations that are involved in significant secondary Tl···Cl (3.046(3) and (3.119(3) Å) and Tl···F (2.796-(8) Å) interactions, which can be attributed to the smaller size of the mesityl groups. Like the isoelectronic $[(2,6\text{-}Mes_2C_6H_3)_2Hg]$[17] and the cation of $[(2,6\text{-}Mes_2C_6H_3)_2Ga]Li\{Al[OCH(CF_3)_2]_4\}_2$,[18] the $[(2,6\text{-}Mes_2C_6H_3)_2Tl]^+$ cation of **7** possesses an almost linear C−M−C linkage (178.6(3)°, M = Hg; 175.69-(7)°, M = Ga; 177.4(3)°, M = Tl). By contrast, the more Lewis acidic cation of $[(2,6\text{-}Mes_2C_6H_3)_2Al][B(C_6F_5)_4]$[19] reveals an

(14) (a) Niemeyer, M.; Power, P. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1277. (b) Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 4794.

(15) Laguna, A.; Fernandez, E. J.; Mendia, A.; Ruiz-Romero, M. E.; Jones, P. G. *J. Organomet. Chem.* **1989**, *365*, 201.

(16) Kuzu, I.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2007**, *633*, 941.

(17) Niemeyer, M.; Power, P. P. *Organometallics* **1997**, *16*, 3258.

(18) Wehmschulte, R. J.; Steele, J. M.; Young, J. D.; Khan, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 1470.

(19) Young, J. D.; Khan, M. A.; Wehmschulte, R. J. *Organometallics* **2004**, *23*, 1965.

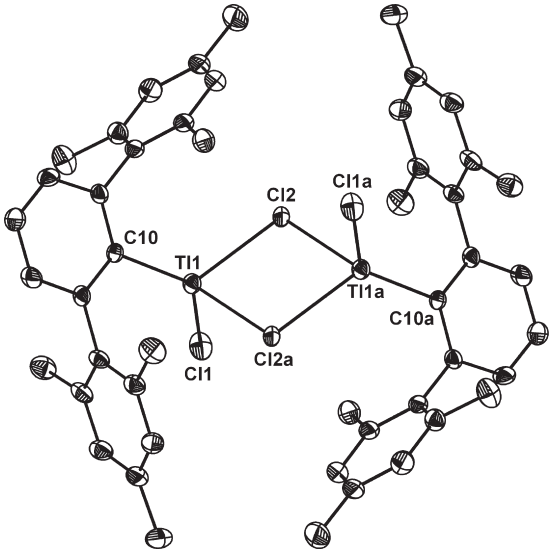


Figure 7. Molecular structure of (2,6-$Mes_2C_6H_3Tl)_2(\mu$-Cl)$_2$Cl$_2$ (**6**) showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a = $-x$, $-y$, $-z$). Selected bond parameters [Å, deg]: Tl1−Cl1 2.427(3), Tl1−Cl2 2.633(2), Tl1−Cl2a 2.681(2), Tl1−C10 2.159(7), Cl1−Tl1−Cl2 93.08(7), Cl1−Tl1−Cl2a 99.05(8), Cl2−Tl1−Cl2a 84.37(7), Cl1−Tl1−C10 130.7(2), Cl2−Tl1−C10 124.6(2), Cl2a−Tl1−C10 113.8(2).

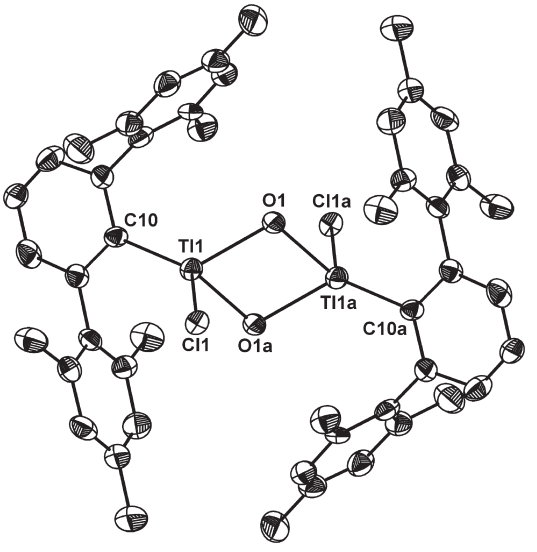


Figure 8. Molecular structure of (2,6-$Mes_2C_6H_3Tl)_2(\mu$-OH)$_2$Cl$_2$ (**8**) showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a = $-x$, $-y$, $-z$). Selected bond parameters [Å, deg]: Tl1−O1 2.202(9), Tl1−O1a 2.25(1), Tl1−Cl1 2.546(4), Tl1−C10 2.10-(1), O1−Tl1−O1a 76.1(3), O1−Tl1−Cl1 96.6(3), O1a−Tl1-Cl1 97.2(3), O1−Tl1−C10 125.4(4), O1a−Tl1−C10 121.4(4), Cl1−Tl1−C10 126.8(3).

C−Al−C angle (159.17(5)°) that is distorted from linearity, due to significant Al$\cdots\pi$ interaction with the ipso-C atoms of the *o*-mesityl groups. Similar M$\cdots\pi$ interactions appear to be absent in the heavier compounds with M = Hg, Ga, Tl.

The Tl−Cl bond lengths (average 2.404(4) Å) of the tetrahedral $TlCl_4^-$ anion of **7** resemble those with other counterions (e.g., Bu_4N^+).[20] The electrospray ionization time-of-flight mass (ESI-TOF-MS) spectrum of **7** (MeOH, positive mode) shows only one mass cluster at m/z = 831.4 g mol^{-1}, which was assigned to the [(2,6-$Mes_2C_6H_3)_2Tl]^+$ cation.

When a crude reaction mixture consisting of 2,6-$Mes_2C_6H_3Tl$ and LiCl was exposed to moist air, the color faded immediately. Extraction with chloroform surprisingly afforded (2,6-$Mes_2C_6H_3Tl)_2Cl_2(\mu$-OH)$_2$ (**8**), the Tl analogue of **3**, in reasonable yields (Scheme 2). Treatment of **8** with hydrochloric acid provided (2,6-$Mes_2C_6H_3Tl)_2(\mu$-Cl)$_2$Cl$_2$ (**6**), the elusive analogue of **1**. The molecular structures of **6** and **8** are shown in Figures 7 and 8, and selected bond parameters are collected in the captions of the figures. Not surprising, the structures of **6** and **8** closely resemble those of the lighter homologues **1** and **3**. The spatial arrangement of the Tl atoms is tetrahedral and defined by CCl_3 and CO_2Cl donor sets, respectively. Again, the endocyclic Tl−Cl bond lengths (2.681(2) and 2.633(2) Å for **6** and 2.546(4) Å for **8**) are slightly longer than the related exocyclic value (2.427(3) Å for **6**). Interestingly, the Tl−O bond lengths of **8** (2.202(9) and 2.25(1) Å) are only marginally longer than the In−O bond lengths of **3**−**5** (average 2.159(6) Å), which is presumably due to the fact that Tl is only marginally larger than In (as the result of the lanthanide contraction). The IR spectrum of **8** shows two absorptions at $\tilde{\nu}$(OH) = 3574 and 3551 cm^{-1}, which were unambiguously assigned to OH stretching vibrations of hydroxy groups that are not involved in hydrogen bonding. Similarly to the In$\cdots$In separation of **1** (3.896(9) Å) and **3** (3.345(1) Å), the Tl$\cdots$Tl separation of **6** (3.937(2) Å) and **8** (3.502(4) Å) is distinctively different.

The base hydrolysis of (2,6-$Mes_2C_6H_3Tl)_2(\mu$-OH)$_2$Cl$_2$ (**8**) in a two-layer system of aqueous NaOH/$CHCl_3$ afforded only a single product, the thalloxane cluster (2,6-$Mes_2C_6H_3Tl)_4Tl_2(\mu_3$-O)$_4(\mu$-OH)$_6$ (**9**), which was isolated as colorless crystals in moderate yield (Scheme 2). The formation of **9** can be rationalized by the partial hydrolytic cleavage of Tl−C bonds. All attempts to prepare a chlorine-free thalloxane without the concomitant cleavage of Tl−C bonds failed. The molecular structure of **9** is shown in Figure 9, and selected bond parameters are collected in the caption of the figure. We critically note that with the exception of Tl1 and Tl2 all atoms of the inorganic core are disordered over two positions (see Supporting Information), which can be attributed to the shielding of the *m*-terphenyl substituents dominating the crystal packing. We already made a similar observation for the molecular structure of the mixed-valent antimony oxo cluster (2,6-$Mes_2C_6H_3Sb)_2$-$(ClSb)_4(\mu_3$-O)$_8$, which contains the same *m*-terphenyl substituent.[21] The spatial arrangement of the organometallic Tl atoms of **9** is distorted tetradedral, whereas the inorganic Tl atoms are best described as distorted square pyramidal. The Tl−O bond lengths of **9** vary between 2.00(2) and 2.69(2) Å and are not discussed in more detail due to the disorder (see Supporting Information). The hydroxy groups were tentatively assigned on the basis of the coordination numbers of the O atoms. The presence of hydroxy groups is confirmed by IR spectroscopy. The IR spectrum of **9** shows only one absorption at $\tilde{\nu}$(OH) = 3596 cm^{-1} that arose from OH stretching vibrations. Attempts to independently confirm the

(20) Rudawska-Frackiewicz, K.; Siekierski, S. *J. Coord. Chem.* **2004**, *57*, 777.

(21) Beckmann, J.; Heek, T.; Takahashi, M. *Organometallics* **2007**, *26*, 3633.

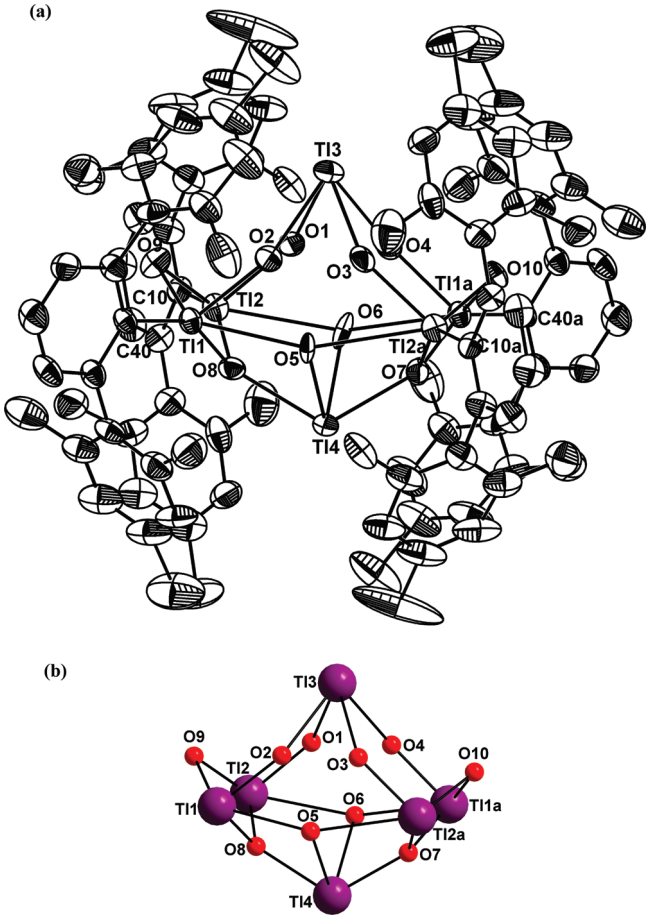


Figure 9. (a) Molecular structure of $(2,6\text{-}Mes_2C_6H_3Tl)_4Tl_2(\mu_3\text{-}O)_4(\mu\text{-}OH)_6$ (**9**) showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a = $-x, -y, -z$). (b) Inorganic core of **9**. Selected bond parameters [Å, deg]: Tl1−O2 2.24(2), Tl1a−O4 2.19(2), Tl1a−O7 2.14(2), Tl1−O8 2.11(2), Tl1−O9 2.25(2), Tl1a−O10 2.29(2), Tl1−C40 2.14(1), Tl2−O1 2.27(2), Tl2a−O3 2.21(2), Tl2a−O7 2.08(2), Tl2−O8 2.18(2), Tl2−O9 2.29(2), Tl2a−O10 2.24(1), Tl2−C10 2.14(1), Tl3−O1 2.66(2), Tl3−O2 2.59(2), Tl3−O3 2.69(2), Tl3−O4 2.59(2), Tl4−O1 2.00(2), Tl4−O2 2.12(2), Tl4−O7 2.40(2), Tl−O8 2.45(2).

molecular mass of **9** using electron impact mass (EI-MS) spectroscopy at ambient conditions failed, as no reasonable spectrum could be obtained. At 200 °C, the only mass cluster observed was at m/z = 831.4 g mol^{-1} and unambiguously assigned to the $[(2,6\text{-}Mes_2C_6H_3)_2Tl]^+$ cation, which apparently formed by migration of the *m*-terphenyl substituent under MS conditions. Compounds **6**−**9** are readily soluble in most organic solvents. The ^{1}H and ^{13}C NMR spectra show one set of signals for the *m*-terphenyl substituents.

Conclusion

The family of group 13 element oxide hydroxides has been extended to a new series of well-defined indoxanes and thalloxanes that are kinetically stabilized by a bulky *m*-terphenyl substituent. These air-stable compounds are easy accessible on a multigram scale via a simple hydrolysis route. Studies are underway to investigate the reactivity of these compounds.

Experimental Section

General Procedures. The *m*-terphenyl lithium $2,6\text{-}Mes_2C_6H_3Li$ was prepared according to a literature procedure.[10] The starting materials $InCl_3$, TlCl, and SO_2Cl_2 were obtained from commercial sources and used as received. The ^{1}H and ^{13}C NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$. Microanalyses were obtained from a Vario EL elemental analyzer. Infrared spectra were recorded using a Nexus FT-IR spectrometer with a Smart DuraSamplIR. Electron impact mass (EI-MS) spectra were measured using a Varian MAT 711 mass spectrometer. The electron energy was set to 80 eV. The electrospray ionization time-of-flight mass (ESI-TOF-MS) spectrum was obtained using an Agilent 6210 ESI-TOF mass spectrometer. The solvent flow rate was adjusted to 4 μL min^{-1} and the spray voltage set to 4 kV.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}Cl)_2Cl_2$ (1).[9] To a suspension of $InCl_3$ (1.50 g, 6.77 mmol) in Et_2O (20 mL) cooled to −78 °C was slowly added a solution of $2,6\text{-}Mes_2C_6H_3Li$ (2.16 g, 6.77 mmol) in Et_2O (40 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the product was extracted with warm hexane (100 mL) and filtered. The solvent was reduced in vacuum to almost one-third, and the precipitates were redissolved by heating. Crystallization afforded **1** as colorless crystals (2.57 g, 2.57 mmol, 76%; mp dec at 270 °C).

^{1}H NMR ($CDCl_3$): δ 7.51 (t, 1H; p-C_6H_3), 7.14 (d, 2H; m-C_6H_3), 6.94 (s, 4H; m-Mes), 2.34 (s, 6H; p-CH_3), 2.03 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 148.7, 146.5, 140.2, 137.6, 136.6, 130.4, 128.7, 127.3, (Ar-C) 21.2, 20.9 (Me-C). Anal. Calcd for $C_{48}H_{50}Cl_4In_2$ (998.30): C, 57.75; H, 5.05. Found: C, 57.77; H, 5.21.

Synthesis of $2,6\text{-}Mes_2C_6H_3InCl_2\cdot H_2O$ (2). A solution of **1** (300 mg, 0.3 mmol) in diethyl ether (30 mL) was hydrolyzed with a solution of NaOH (48 mg, 1.20 mmol) in water (30 mL). The mixture was vigorously stirred for 30 min at room temperature before the layers were separated. The solvent was dried over Na_2SO_4 and removed under vacuum. Recrystallization of the solid residue from CH_2Cl_2/hexane (1:3) provided **2** as colorless crystals (280 mg, 0.275 mmol, 92%; mp dec at 300 °C).

^{1}H NMR ($CDCl_3$): δ 7.49 (t, 1H; p-C_6H_3), 7.12 (d, 2H; m-C_6H_3), 6.93 (s, 4H; m-Mes), 2.33 (s, 6H; p-CH_3), 2.02 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 148.3, 140.5, 138.0, 136.6, 130.3, 128.7, 128.0, 127.1 (Ar-C), 21.2, 20.8 (Me-C). IR $\tilde{\nu}$(OH): 3611, 3587 cm^{-1}. Anal. Calcd for $C_{24}H_{27}Cl_2InO$ (517.19): C, 55.73; H, 5.26. Found: C, 55.30; H, 5.43.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)_2(\mu\text{-}OH)_2Cl_2$ (3). A solution of **1** (300 mg, 0.3 mmol) in diethyl ether (30 mL) was hydrolyzed with a solution of NaOH (48 mg, 1.2 mmol) in water (30 mL). The mixture was vigorously stirred for 12 h at room temperature before the layers were separated. The solvent was dried over Na_2SO_4 and removed under vacuum. Recrystallization of the solid residue from CH_2Cl_2/hexane (1:3) provided **3** as colorless crystals (230 mg, 0.25 mmol, 83%; mp 300−302 °C).

^{1}H NMR ($CDCl_3$): δ 7.30 (t, 1H; p-C_6H_3), 7.02 (d, 2H; m-C_6H_3), 6.86 (s, 4H; m-Mes), 2.43 (s, 6H; p-CH_3), 1.91 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 149.2, 142.5, 136.3, 136.2, 135.5, 128.2, 127.8, 126.8 (Ar-C), 21.5, 21.4 (Me-C). IR $\tilde{\nu}$(OH): 3617, 3534 cm^{-1}. Anal. Calcd for $C_{48}H_{52}Cl_2In_2O_2$ (961.46): C, 59.96; H, 5.45. Found: C, 60.13; H, 5.32.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)_3(\mu\text{-}OH)_4Cl_2$ (4). A solution of **1** (500 mg, 0.5 mmol) in toluene (35 mL) was hydrolyzed with a solution of NaOH (7.0 g, 175 mmol) in water (35 mL). The mixture was vigorously stirred overnight at room temperature before the layers were separated. The solvent was dried over Na_2SO_4 and removed under vacuum. Recrystallization of the solid residue from $CHCl_3$/hexane (1:3) provided **5** as colorless crystals (380 mg, 0.27 mmol; 80%; mp 342−348 °C).

Table 1. Crystal Data and Structure Refinement for 1−9

	1	**2**	**3**·$2CH_2Cl_2$
formula	$C_{48}H_{50}Cl_4In_2$	$C_{24}H_{25}Cl_2InO$	$C_{49}H_{50}Cl_4In_2O_2$
fw, g mol^{-1}	998.32	515.16	1042.33
cryst syst	orthorhombic	orthorhombic	monoclinic
cryst size, mm	0.18 × 0.17 × 0.15	0.25 × 0.25 × 0.11	0.17 × 0.16 × 0.13
space group	*Fdd*2	$P2_12_12_1$	$P2_1/n$
a, Å	27.593(6)	8.292(4)	10.874(5)
b, Å	14.179(3)	15.249(8)	16.852(7)
c, Å	23.793(5)	19.409(9)	13.180(4)
α, deg	90	90	90
β, deg	90	90	91.89(3)
γ, deg	90	90	90
V, $Å^3$	9309(3)	2454(2)	2413(2)
Z	8	4	2
D_{calcd}, Mg m^{-3}	1.425	1.394	1.434
T, K	150	150	150
μ, mm^{-1}	1.251	1.191	1.212
F(000)	4032	1040	1052
θ range, deg	0.99 to 25.25	0.99 to 25.25	1.96 to 25.25
index ranges	$-32 \le h \le 31$	$-9 \le h \le 9$	$-13 \le h \le 12$
	$-19 \le k \le 17$	$-17 \le k \le 18$	$-20 \le k \le 18$
	$-37 \le l \le 36$	$-23 \le l \le 19$	$-15 \le l \le 15$
no. of reflns collcd	16 640	9466	11 285
completeness to θ_{max}	99.8	99.3%	99.2%
no. of indep reflns/R_{int}	2162	4280	4321
no. of reflns obsd with ($I > 2\sigma(I)$)	1767	3519	3045
no. refined params	250	253	262
GooF (F^2)	1.033	0.956	0.938
$R_1(F)$ ($I > 2\sigma(I)$)	0.0543	0.0528	0.0343
$wR_2(F^2)$ (all data)	0.1389	0.1304	0.0910
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	< 0.001
largest diff peak/hole, e $Å^{-3}$	0.970/−0.743	0.533/−1.017	1.015/−0.922

	4	**5**·H_2O·$2CHCl_3$	**6**·$1/2CH_2Cl_2$
formula	$C_{72}H_{75}Cl_2In_3O_4$	$C_{98}H_{100}Cl_6In_4O_9$	$C_{49}H_{50}Cl_6Tl_2$
fw, g mol^{-1}	1419.68	2093.76	1260.33
cryst syst	triclinic	monoclinic	monoclinic
cryst size, mm	0.50 × 0.50 × 0.14	0.48 × 0.20 × 0.06	0.21 × 0.10 × 0.09
space group	$P\bar{1}$	*C*2/*c*	$P2_1/n$
a, Å	13.300(8)	24.77(1)	10.615(6)
b, Å	16.108(9)	15.353(5)	16.90(1)
c, Å	18.934(7)	27.74(1)	13.685(9)
α, deg	89.87(4)	90	90.00
β, deg	105.87(4)	115.91(3)	94.10(5)
γ, deg	90.73(5)	90	90.00
V, $Å^3$	3901(3)	9488(6)	2448(3)
Z	2	4	2
D_{calcd}, Mg m^{-3}	1.208	1.466	1.710
T, K	150	150	150
μ, mm^{-1}	0.987	1.183	6.933
F(000)	1440	4232	1216
θ range, deg	1.69 to 25.25	0.99 to 25.25	1.92 to 25.25
index ranges	$-13 \le h \le 15$	$-29 \le h \le 29$	$-12 \le h \le 12$
	$-19 \le k \le 19$	$-18 \le k \le 17$	$-20 \le k \le 20$
	$-22 \le l \le 22$	$-23 \le l \le 33$	$-16 \le l \le 16$
no. of reflns collcd	28823	21866	13128
completeness to θ_{max}	99.3%	99.1%	99.5%
no. of indep reflns/R_{int}	14 021	8538	4413
no. of reflns obsd with ($I > 2\sigma(I)$)	9660	5172	3298
no. refined params	730	532	262
GooF (F^2)	1.040	0.890	0.995
$R_1(F)$ ($I > 2\sigma(I)$)	0.0581	0.0397	0.0375
$wR_2(F^2)$ (all data)	0.1943	0.0836	0.0973
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	< 0.001
largest diff peak/hole, e $Å^{-3}$	1.916/−1.025	0.894/−0.751	1.569/−1.579

Table 1. Continued

	7·2CHCl$_3$	**8**·2H$_2$O	**9**
formula	$C_{50}H_{52}Cl_{10}Tl_2$	$C_{48}H_{54}Cl_2O_4Tl_2$	$C_{96}H_{100}O_{10}Tl_6$
fw, g mol^{-1}	1416.16	1174.55	2639.98
cryst syst	triclinic	Monoclinic	Monoclinic
cryst size, mm	0.50 × 0.50 × 0.43	0.50 × 0.28 × 0.27	0.50 × 0.17 × 0.16
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	10.46(1)	10.84(2)	14.30(1)
b, Å	15.55(3)	17.12(2)	20.80(2)
c, Å	18.04(2)	13.36(2)	18.082(2)
α, deg	87.7(1)	90.00	90.00
β, deg	75.30(9)	92.52(10)	108.26(6)
γ, deg	74.5(1)	90.00	90.00
V, Å^3	2733(7)	2477(5)	5108(8)
Z	2	1	2
D_{calcd}, Mg m^{-3}	1.721	1.575	1.716
T, K	150	150	150
μ, mm^{-1}	6.411	6.642	9.478
F(000)	1368	1140	2484
θ range, deg	1.77 to 25.25	2.37 to 25.25	2.37 to 25.25
index ranges	$-12 \le h \le 11$	$-13 \le h \le 13$	$-17 \le h \le 14$
	$-18 \le k \le 18$	$-20 \le k \le 18$	$-24 \le k \le 24$
	$-21 \le l \le 21$	$-13 \le l \le 16$	$-21 \le l \le 21$
no. of reflns collcd	21358	11063	25482
completeness to θ_{max}	99.3%	99.4%	99.1%
no. of indep reflns/R_{int}	9827	4450	9159
no. of reflns obsd with ($I > 2\sigma(I)$)	7923	3342	5464
no. refined params	554	261	568
GooF (F^2)	1.029	1.072	1.006
$R_1(F)$ ($I > 2\sigma(I)$)	0.0567	0.0649	0.0723
$wR_2(F^2)$ (all data)	0.1687	0.2045	0.1782
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	< 0.001
largest diff peak/hole, e Å^{-3}	1.590/−2.341	3.258/−1.789	3.542/−1.723

^{1}H NMR ($CDCl_3$): δ 7.46, 7.40 (t, 1H; p-C_6H_3) 7.10, 7.00 (d, 2H; m-C_6H_3) 6.93, 6.88 (s, 4H; m-Mes) 2.45, 2.41 (s, 6H; p-CH_3)1.94, 1.92 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 148.6, 148.5, 141.3, 141.0, 137.3, 137.2, 136.8, 136.7, 136.6, 136.5, 128.5, 128.4, 128.2, 128.1, 126.6 126.5 (Ar-C) 21.5, 21.0, 20.9, 20.7 (Me-C). IR $\tilde{\nu}$(OH): 3633, 3598, 3568, 3529, 3484 cm^{-1}. Anal. Calcd for $C_{72}H_{79}Cl_2In_3O_4$ (1423.75): C, 60.74; H, 5.59. Found: C, 60.79; H, 5.41.

Synthesis of (2,6-Mes$_2$C$_6$H$_3$In)$_4$(μ-OH)$_8$ (5). A solution of **1** (500 mg, 0.5 mmol) in toluene (35 mL) was hydrolyzed with a solution of NaOH (7.0 g, 175 mmol) in water (35 mL). The mixture was vigorously stirred for 12 h at room temperature before the layers were separated. A fresh solution of NaOH (7.0 g, 175 mmol) in water (35 mL) was added, and the mixture stirred again for 12 h. The solvent was dried over Na_2SO_4 and removed under vacuum. Recrystallization of the solid residue from $CHCl_3$/hexane (1:3) provided **4** as colorless crystals (340 mg, 0.18 mmol, 74%; mp 354−360 °C).

^{1}H NMR ($CDCl_3$): δ 7.30 (t, 1H; p-C_6H_3), 6.87 (d, 2H; m-C_6H_3), 6.85 (s, 4H; m-Mes), 2.43(s, 6H; p-CH_3), 1.90 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 149.1, 142.5, 136.3, 135.8, 135.4, 128.2, 127.8, 126.8 (Ar-C) 21.5, 21.4 (Me-C). IR $\tilde{\nu}$(OH): 3646, 3632, 3599 cm^{-1}. Anal. Calcd for $C_{96}H_{108}In_4O_8$ (1849.2): C, 62.35; H, 5.89. Found: C, 62.29; H, 5.87.

Synthesis of (2,6-Mes$_2$C$_6$H$_3$Tl)$_2$(μ-Cl)$_2$Cl$_2$ (6). A solution of **8** (500 mg, 0.43 mmol) in diethyl ether was treated with 1 M HCl (10 mL). The mixture was stirred for 2 h before the layers were separated. The organic layer was dried over Na_2SO_4 and the solvent removed under vacuum. Recrystallization from $CHCl_3$/hexane (1:3) furnished **6** as colorless crystals (470 mg, 0.37 mmol, 92%; mp 132−134 °C).

^{1}H NMR ($CDCl_3$): δ 7.45 (t, 1H, p-C_6H_3), 7.11 (d, 2H, m-C_6H_3), 6.94 (s, 4H, m-Mes), 2.32 (s, 6H, p-CH_3), 2.05 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 141.1, 139.0, 136.4, 135.8, 130.2, 128.4, 128.0, 127.5 (Ar-C) 21.0, 20.7 (Me-C). Anal. Calcd for $C_{48}H_{50}Cl_4Tl_2$ (1177.48): C, 48.96; H, 4.28. Found: C, 48.92; H, 4.59.

Synthesis of [(2,6-Mes$_2$C$_6$H$_3$)$_2$Tl]TlCl$_4$ (7). In the absence of light, a stirred suspension of TlCl (1.55 g, 6.46 mmol) in Et_2O (75 mL) was cooled to −18 °C, and a solution of 2,6-$Mes_2C_6H_3Li$ (2.07 g, 6.46 mmol) in Et_2O (30 mL) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for 4 h. Then, the solution was cooled to 0 °C, and SO_2Cl_2 (2.11 g, 15.65 mmol) was slowly added via syringe. The reaction mixture was stirred at room temperature for 2 h before the precipitate of LiCl was filtered off. The solvent was removed under reduced pressure and the crude solid recrystallized from $CHCl_3$/hexane to give colorless crystals of **7**·2 $CHCl_3$. The crystals were dried at 50 °C under high vacuum to give an analytical sample of **7** (yield 2.58 g, 2.20 mmol, 68%; mp 120−124 °C).

^{1}H NMR ($CDCl_3$): δ 7.46 (t, 3H; p-C_6H_3), 7.09 (d, 2H, m-C_6H_3), 6.94 (s, 8H; Ar), 2.33 (s, 12H; Me), 2.05 (s, 24H; Me). ^{13}C NMR ($CDCl_3$): δ 141.0, 138.9, 136.4, 135.8, 130.2, 128.3, 127.9, 127.4 (Ar), 21.0, 20.7 (Me). Anal. Calcd for $C_{48}H_{50}Cl_4Tl_2$ (1177.48): C, 48.96; H, 4.28. Found: C, 48.73; H, 4.15. ESI-TOF-MS (MeOH, positive mode): m/z 831.4 ([$C_{48}H_{50}Tl$]$^+$).

Synthesis of (2,6-Mes$_2$C$_6$H$_3$Tl)$_2$(μ-OH)$_2$Cl$_2$ (8). In the absence of light, a stirred suspension of TlCl (1.55 g, 6.46 mmol) in 75 mL of Et_2O was cooled to −18 °C, and a solution of 2,6-$Mes_2C_6H_3Li$ (2.07 g, 6.46 mmol) in 25 mL of Et_2O was added dropwise to the suspension. The reaction mixture was then allowed to warm to room temperature and stirred for over 4 h. The solvent was removed under vacuum. The solid residue was extracted with $CHCl_3$ in the air. After filtration the solvent was again removed under vacuum. Recrystallization of the colorless residue from $CHCl_3$/hexane (1:3) yielded **8** as colorless crystals (2.57 g, 2.25 mmol, 69.8%; mp dec at 270 °C).

^{1}H NMR ($CDCl_3$): δ 7.46 (t, 1H; p-C_6H_3), 7.11 (d, 2H; m-C_6H_3), 6.95 (s, 4H; m-Mes), 2.33 (s, 6H; p-CH_3), 2.05 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 141.2, 139.1, 136.6, 136.0, 130.3, 128.5, 128.2, 127.6 (Ar-C) 21.2, 21.0 (Me-C). IR $\tilde{\nu}$(OH): 3574, 3551 cm^{-1}. Anal. Calcd for $C_{48}H_{52}Cl_2O_2Tl_2$ (1140.59): C, 50.54; H, 4.60. Found: C, 50.50; H, 4.48.

Synthesis of $(2,6\text{-}Mes_2C_6H_3Tl)_4Tl_2(\mu_3\text{-}O)_4(\mu\text{-}OH)_6$ (9). A solution of **8** (500 mg, 0.43 mmol) in $CHCl_3$ (30 mL) was hydrolyzed with a solution of NaOH (1.2 g, 30 mmol) in water (30 mL). The mixture was vigorously stirred for 2 h at room temperature before the layers were separated. The solvent was dried over Na_2SO_4 and removed under vacuum. Recrystallization of the solid residue from $CHCl_3$/hexane (1:3) provided **9** as colorless crystals (300 mg, 0.11 mmol, 79%; mp 120−124 °C).

^{1}H NMR ($CDCl_3$): δ 7.45 (t, 1H; p-C_6H_3), 7.11 (d, 2H; m-C_6H_3), 6.94 (s, 4H; m-Mes), 2.33 (s, 6H; p-CH_3), 2.05 (s, 12H; o-CH_3). ^{13}C NMR ($CDCl_3$): δ 141.1, 139.0, 136.4, 135.8, 130.2, 128.4, 128.0, 127.5 (Ar-C), 21.0, 20.7 (Me-C). IR $\tilde{\nu}$(OH): 3596 cm^{-1}. Anal. Calcd for $C_{96}H_{106}Tl_6O_{10}$ (2644.2): C, 43.56; H, 4.00. Found: C, 43.49; H, 4.06.

X-ray Crystallography. Intensity data were collected on a STOE IPDS 2T area detector with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the program Stoe X-Area.[22] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[23] Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Carbon-bonded hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Disorder was resolved for the In atom of **1** and refined with split occupancies of 0.9 (In1) and 0.1 (In′). Disorder was also resolved for one Tl atom and five O atoms of **9** and refined with split occupancies of 0.45 (Tl3), 0.05 (Tl3′), and 0.5 (Tl4) as well as 0.5 (O1−O10), respectively. Crystal and refinement data are collected in Table 1. The absolute structures of **1** and **2** were determined by refinement of the Flack parameters 0.0(4) and 0.0(3) and comparison of the *R*-values of the enantiomeric space groups. Figures were created using the program DIAMOND.[24] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 751065 (**1**), 751066 (**2**), 751067 (**3**), 751068 (**4**), 751069 (**5**), 751070 (**6**), 751071 (**7**), 751072 (**8**), and 751073 (**9**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

Acknowledgment. Dr. Malte Hesse (Freie Universität Berlin) is thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting Information Available: Cif files of **1**−**9** and figures of the disordered structure of **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

(22) *STOE X-Area* and *X-Red*; Stoe & Cie GmbH: Darmstadt, Germany, 2004.
(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(24) Brandenburg, K.; Putz, H. *DIAMOND* V3.1d; Crystal Impact GbR, **2006**.