



## Structural diversity of indium complexes containing a tetradentate (OSSO)-type bis(phenolate) ligand

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### ABSTRACT

Indium bis(phenolato) complexes  $[\{\text{In}(\text{CH}_3)_2(\text{THF})\}_2(\text{L})]$  ( $\text{L} = 1,4$ -dithiabutanediylbis(4,6-di-*tert*-butylphenolato) (etbbp), **2**) and  $[\text{In}(\text{cytp})(\text{CH}_3)_2]$  ( $\text{L} = (1,2$ -cyclohexanediyldithio)-2,2'-diphenolato (*rac*-cytp), **3**) were prepared from  $[\text{In}(\text{CH}_3)_3]$  and the tetradentate 1,2-dithiaalkanediyl-bridged bis(phenol)  $\text{LH}_2$ . The nature of the ligand bridging two indium centers was shown by X-ray diffraction studies of the complex  $[\{\text{In}(\text{CH}_3)_2(\text{THF})\}_2(\text{etbbp})]$  (**2**) that was synthesized from complex  $[\text{In}(\text{etbbp})(\text{CH}_3)(\text{THF})_n]$  (**1**) by reaction with a second equivalent of  $[\text{In}(\text{CH}_3)_3]$ . A related ligand without bulky substituents on the aromatic rings leads to the dimeric compound  $[\text{In}(\text{cytp})(\text{CH}_3)_2]$  (**3**) with distorted octahedral configuration in the solid state. It was converted into the cation  $[\text{In}(\text{cytp})]^+$  by methyl abstraction with  $[\text{B}(\text{C}_6\text{F}_5)_3]$ .

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## 1. Introduction

Indium reagents are becoming increasingly important in organic synthesis because of their new reactivity profile, low toxicity, and water tolerance [1]. Other catalytic applications include the use of indium alkoxides as initiators for the ring-opening polymerization of cyclic esters such as lactide [2]. Indium alkoxides are structurally related to aluminum complexes and lanthanide alkoxides [3,4]. Structurally defined indium-based initiators have recently been reported in the literature [5]. Reactions of  $[\text{In}(\text{CH}_3)_3]$  and  $[\text{In}(\text{CH}_3)_2(\text{OCH}_3)]$  with bulky bis(phenolates) have been described [6]. Tetradentate (OSSO)-type bis(phenols) (Chart 1) are known to act as highly versatile proligands in polymerization catalysts for group 3 and 4 metals in olefin and lactide polymerization [2,7]. We report here on the synthesis and structural characterization of indium methyl bis(phenolates) with two variants of this ligand type. The ethylene-bridged bis(phenol) ligand containing bulky <sup>t</sup>Bu substituents on the aromatic rings reacted with two equivalents of  $[\text{In}(\text{CH}_3)_3]$  to give a bimetallic complex bridged by one bis(phenolate) ligand. A *trans*-1,2-cyclohexanediylyl bridged ligand without any substituents at the aromatic rings led to a dimeric complex.

## 2. Results and discussion

Reacting  $[\text{In}(\text{CH}_3)_3]$  [22] with one equivalent of 1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenol) (etbbpH<sub>2</sub>) gave  $[\{\text{In}(\text{etbbp})(\text{CH}_3)(\text{THF})\}_n]$  (**1**) [2]. Further addition of a second equivalent of  $[\text{In}(\text{CH}_3)_3]$  to **1** gave the dinuclear compound  $[\{\text{In}(\text{CH}_3)_2(\text{THF})\}_2(\text{etbbp})]$  **2** that was isolated as colorless crystals from a toluene/THF solution (Scheme 1).

The crystal structure analysis of  $[\{\text{In}(\text{CH}_3)_2(\text{THF})\}_2(\text{etbbp})]$  (**2**) shows both indium centers in a distorted trigonal bipyramidal coordination geometry (Fig. 1). The two methyl groups and the oxygen atom O1 occupy the basal positions with the sulfur atom and the coordinated THF molecule situated in the axial position with an O2–In1–S1 angle of 161.91(18)°. The In1–S1 distance is 2.746(2) Å. The In–O bond length of 2.112(6) Å is slightly longer than the distances published previously [2]. This can be explained by the larger steric demand of the etbbp ligand or the bridging unit within this bis(phenol) ligand. A similar dinuclear lanthanum complex with two bridging (OSSO)-type ligands was reported [8].

Reacting (1,2-cyclohexanediyldithio)-2,2'-diphenol (cytpH<sub>2</sub>) with one equivalent of  $[\text{In}(\text{CH}_3)_3]$  gave  $[\text{In}(\text{cytp})(\text{CH}_3)_2]$  (**3**) that could be crystallized from a concentrated dichloromethane solution at –30 °C. The crystals of **3** revealed the structure in a *meso*-form with bridging phenoxy groups (Fig. 2). The indium oxygen bond lengths of In1–O1 [2.125(2) Å] and In1–O2 [2.255(2) Å] show that the coordinating bond is around 0.1 Å longer than the  $\sigma$ -bond.

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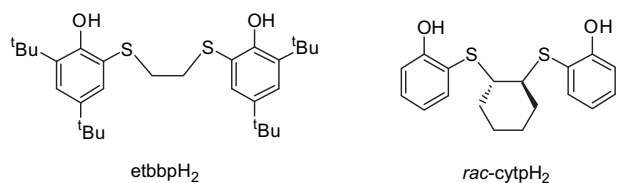


Chart 1.

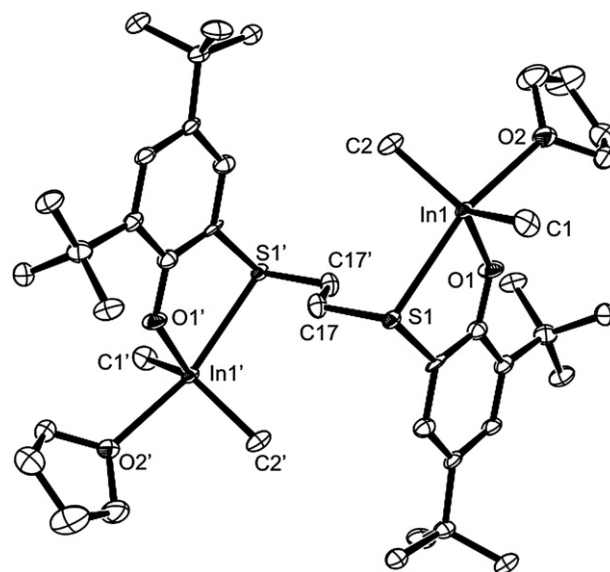
This unique *cis*- $\beta$  type structure of an indium complex crystallizes with the atoms O1, O2 and S2 atoms in the equatorial position and S1 as well as C19 atom in the axial position. The indium atoms are located in the center of the distorted octahedron with a nearly linear angle for C19–In1–S1 of 174.09(9)°. This is a rare example for a six-coordinated indium center that is bridged by a  $\mu^3$ -O(phenolate) [2,6]. The broad signals in the  $^1\text{H}$  NMR spectrum do not allow to distinguish between a monomeric or a dimeric structure in solution.

The Cambridge Structural Database (Version 5.31 updated Feb 2010) gives 14 results for phenolic oxygen bonded to two indium centers. These results include salicylaldehyde–aroylhydrazone, salicylaldehyde–ferrocenoyl hydrazone complexes [9], 2-methoxyphenolato [10], tripodal polydentate amine-phenolato [11], trifluorophenolato [12], salicylaldehyde [13], di-*t*-butyl-catecholato [14], *N,O*-bidentate oxazoline phenolato [15], *N*-phenyl-salicylideneaminato [16], *P,O*-bidentate phosphinophenolato [17], oxybenzoquinolato [18], methyl-salicylato [19], and benzene-1,2-diolato ligands [20]. The In–O bond lengths are in the range of 2.134–2.607 Å. In the structure described here, the In–O bond lengths are 2.125(2) and 2.255(2) Å. Similar bond lengths are found in published structures [10,17,20].

The reaction of **3** with one equivalent of the strong Lewis acid  $[\text{B}(\text{C}_6\text{F}_5)_3]$  gave the monocationic species **4** via methyl abstraction (Scheme 2). NMR spectroscopic data indicate the formation of an ion pair with an  $^{11}\text{B}$  chemical shift value of  $\delta = -14.91$  ppm for tetrahedrally coordinated boron in the anion  $[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_3)]^-$ . The methyl group attached to the boron center is shown by a signal in the  $^{13}\text{C}$  NMR spectrum at  $\delta = 14.03$  ppm.

### 3. Summary

As was previously found for group 3 and 4 metals, the coordination mode of the (OSSO)-type ligand depends on the nature of the bridging unit in the ligand backbone as well as on the *ortho*-substituents on the phenol rings. The indium centers in **2** show the typical penta-coordination of a trigonal bipyramid, whereas compound **3** shows the *cis*- $\beta$  type distorted octahedral coordination geometry around indium.



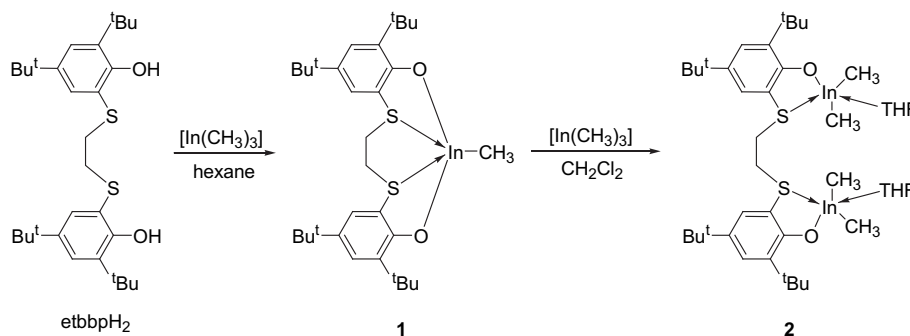
**Fig. 1.** ORTEP diagram of the molecular structure of  $[\text{In}_2(\text{etbbp})(\text{CH}_3)_2(\text{THF})_2]$  (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): In1–O1 2.112(6), In1–O2 2.452(7), In1–C1 2.141(10), In1–C2 2.152(9), In1–S1 2.746(2), S1–C17 1.823(10), O2–In1–S1 161.91(18).

## 4. Experimental

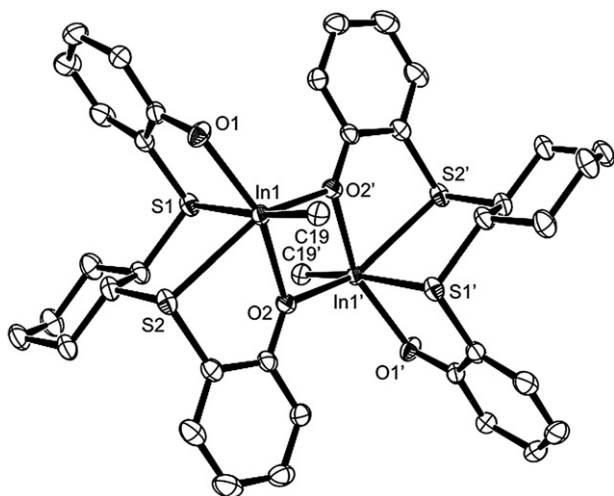
### 4.1. General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene and THF were distilled under argon from sodium/benzophenone ketyl prior to use. Dichloromethane was distilled from calcium hydride. Anhydrous indium trichloride (ABCR) was used as received. Benzene- $d_6$ , chloroform- $d_1$ , dichloromethane- $d_2$  and other reagents were carefully dried and stored in a glovebox. The bis(phenols) 1,4-dithiabutanediyl-bis(4,6-di-*tert*-butylphenol) (etbbpH<sub>2</sub>) [1 g, 8, 21], and (1,2-cyclohexanediylidithio)-2,2'-diphenol (cytpH<sub>2</sub>) [7e] were synthesized according to reported methods, as well as trimethylindium [22]. All other chemicals were commercially available and used after appropriate purification.

NMR spectra were recorded on Bruker DRX 400 or Varian 200 and 500 spectrometers at 25 °C ( $^1\text{H}$ : 200, 400, 500 MHz;  $^{13}\text{C}$ : 50, 100, 125 MHz) unless otherwise stated. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced internally using residual solvent resonances and are reported relative to tetramethylsilane. NMR assignments were confirmed by APT,  $^1\text{H}$ – $^1\text{H}$  (COSY), and  $^1\text{H}$ – $^{13}\text{C}$



Scheme 1.



**Fig. 2.** ORTEP diagram of the molecular structure of the heterochiral  $\Delta, \Delta$ -(*cis*- $\beta$ , *cis*- $\beta$ ) dimer  $[\text{In}(\text{cytp})(\text{CH}_3)_2]$  (**3**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles ( $^\circ$ ): In1–S1 2.7391(8), In1–S2 2.6911(8), In1–O1 2.125(2), In1–O2 2.255(2), In1–C19 2.147(3), In1'–O2 2.220(2), C19–In1–S1 174.09(9), O1–In1–S2 92.44(7), S1–In1–S2 79.91(2).

(HMQC) experiments where necessary. The spectroscopic analyses of polymers were performed in  $\text{CDCl}_3$ . Elemental analyses were performed by the microanalytical laboratory of this department.

#### 4.2. $[\{1,4\text{-Dithiabutenediylbis}(4,6\text{-di-}t\text{-butylphenolato})\}(\text{methyl})\text{indium}]$ (**1**)

This compound was synthesized in analogy to a published procedure [2] and isolated as a colorless solid in 47% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.46$  (s,  $1 \times 3\text{H}$ ,  $\text{InCH}_3$ ), 1.31 (s,  $2 \times 9\text{H}$ ,  $4\text{-C}(\text{CH}_3)_3$ ), 1.69 (s,  $2 \times 9\text{H}$ ,  $4\text{-C}(\text{CH}_3)_3$ ), 2.12 (m,  $1 \times 2\text{H}$ ,  $\text{SCH}_2$ ), 2.36 (m,  $1 \times 2\text{H}$ ,  $\text{CH}_2\text{S}$ ), 7.31 (s,  $2 \times 1\text{H}$ , Ph-3), 7.53 (s,  $2 \times 1\text{H}$ , Ph-5).  $^{13}\text{C}$  NMR ( $^{1}\text{H}$ ) (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 22.67$  ( $\text{InCH}_3$ ), 29.84 ( $4\text{-C}(\text{CH}_3)_3$ ), 31.80 ( $6\text{-C}(\text{CH}_3)_3$ ), 34.26 ( $4\text{-C}(\text{CH}_3)_3$ ), 36.25 ( $6\text{-C}(\text{CH}_3)_3$ ), 38.67 ( $\text{SCH}_2$ ), 113.88 (Ph-C2), 127.17 (Ph-C5), 128.13, (Ph-C3), 137.81 (Ph-C4), 140.01 (Ph-C6), 162.92 (Ph- $\text{C}_{\text{ipso}}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.05$  (s,  $1 \times 3\text{H}$ ,  $\text{InCH}_3$ ), 1.30 (s,  $2 \times 9\text{H}$ ,  $4\text{-C}(\text{CH}_3)_3$ ), 1.41 (s,  $2 \times 9\text{H}$ ,  $6\text{-C}(\text{CH}_3)_3$ ), 2.09 (m,  $1 \times 2\text{H}$ ,  $\text{SCH}_2$ ), 2.23 (m,  $1 \times 2\text{H}$ ,  $\text{CH}_2\text{S}$ ), 7.20 (s,  $2 \times 1\text{H}$ , Ph-3), 7.26 (s,  $2 \times 1\text{H}$ , Ph-5).

#### 4.3. $[\{1,4\text{-Dithiabutenediylbis}(4,6\text{-di-}t\text{-butylphenolato})\}\text{bis}(\text{dimethylindium})]$ (**2**)

To a suspension of  $[\{1,4\text{-dithiabutenediylbis}(4,6\text{-di-}t\text{-butylphenolato})\}(\text{methyl})\text{indium}]$  (**1**) (259 mg, 0.50 mmol) in 5 mL of

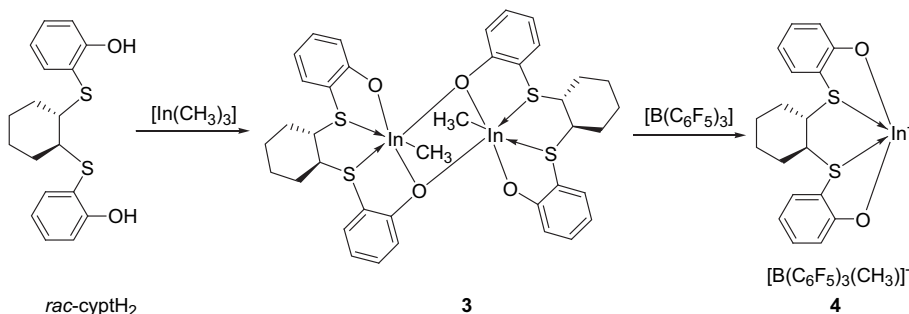
dichloromethane was slowly added a solution of  $[\text{In}(\text{CH}_3)_3]$  (80 mg, 0.50 mmol) in 5 mL of dichloromethane. The reaction mixture was stirred at  $-30^\circ\text{C}$  for 2 h, before the solvent was concentrated to a volume of ca. 2 mL under reduced pressure. A layer of ca. 0.5 mL of THF was added. Colorless crystals in 20% yield (70 mg, 0.110 mmol) were obtained at  $-30^\circ\text{C}$  overnight. The compound decomposes quickly above  $0^\circ\text{C}$ , hence microanalytical data could not be obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.13$  (br,  $4 \times 3\text{H}$ ,  $\text{InCH}_3$ ), 1.25 (s,  $2 \times 9\text{H}$ ,  $4\text{-C}(\text{CH}_3)_3$ ), 1.37 (s,  $2 \times 9\text{H}$ ,  $4\text{-C}(\text{CH}_3)_3$ ), 1.84 (m,  $2 \times 4\text{H}$ ,  $\beta\text{-THF}$ ), 3.49 (s,  $1 \times 4\text{H}$ ,  $\text{SCH}_2\text{CH}_2\text{S}$ ), 3.74 (m,  $2 \times 4\text{H}$ ,  $\alpha\text{-THF}$ ), 6.99 (br,  $2 \times 1\text{H}$ , Ph-3), 7.46 (br,  $2 \times 1\text{H}$ , Ph-5).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.06$  ( $\text{InCH}_3$ ), 25.60 ( $\alpha\text{-THF}$ ), 29.43 ( $4\text{-C}(\text{CH}_3)_3$ ), 31.45 ( $6\text{-C}(\text{CH}_3)_3$ ), 52.02 ( $\text{SCH}_2\text{CH}_2\text{S}$ ), 67.99 ( $\beta\text{-THF}$ ), 115.29 (Ph-C2), 123.80, (Ph-C3), 130.42 (Ph-C5), 136.98 (Ph-C4), 144.54 (Ph-C6), 157.43 (Ph- $\text{C}_{\text{ipso}}$ ).

#### 4.4. $[\{(1,2\text{-Cyclohexanediyldithio})\text{diphenolato}\}(\text{methyl})\text{indium}]$ (**3**)

To a suspension of (1,2-cyclohexanediyldithio)-2,2'-diphenol (222 mg, 0.70 mmol) in 5 mL of toluene was added a solution of  $[\text{In}(\text{CH}_3)_3]$  (107 mg, 0.70 mmol) in 5 mL of toluene. The solution was heated at  $60^\circ\text{C}$  for 24 h. After removal of all volatiles, the colorless precipitate was washed three times with *n*-pentane and dried under reduced pressure to give a colorless solid in 92% yield (283 mg, 0.644 mmol). Single crystals were obtained from a saturated dichloromethane solution overnight.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.07$  (s,  $1 \times 3\text{H}$ ,  $\text{InCH}_3$ ), 1.09 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_3\text{H}_2$ ), 1.55 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_2\text{H}_2$ ), 1.60 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_3\text{H}_2$ ), 2.19 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_2\text{H}_2$ ), 2.31 (br, 1H, S-cy- $\text{C}_1\text{H}_2$ ), 2.57 (br, 1H, S-cy- $\text{C}_1\text{H}$ ), 6.48–7.40 (broad area,  $2 \times 4\text{H}$ , Ph-*H*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.00$  ( $\text{InCH}_3$ ), 26.02 (S-cy- $\text{C}_3\text{H}_2$ ), 32.32 (S-cy- $\text{C}_2\text{H}_2$ ), 51.81 (S-cy- $\text{C}_1\text{H}$ ), 118.21 (Ph-C3), 120.56 (Ph-C1), 131.73 (Ph-C4), 132.85 (Ph-C5), 133.99 (Ph-C6). Anal. Calcd. for  $\text{C}_{19}\text{H}_{21}\text{InO}_2\text{S}_2$ : C, 49.58; H, 4.60. Found: C, 49.23; H, 4.51.

#### 4.5. $[\{(1,2\text{-Cyclohexanediyldithio})\text{diphenolato}\}\text{indium}][(\text{methyl})\text{tris}(\text{pentafluorophenyl})\text{borate}]$ (**4**)

To a solution of **3** (90 mg, 0.200 mmol) in 10 mL of dichloromethane, a solution of  $[\text{B}(\text{C}_6\text{F}_5)_3]$  (100 mg, 0.200 mmol) in 10 mL of dichloromethane was added during 15 min. The mixture was stirred at  $60^\circ\text{C}$  for 72 h. After concentrating the solution to a volume of ca. 2 mL under reduced pressure, the remaining solution was filtered. After removing all volatiles under reduced pressure, the remaining solid was washed with *n*-pentane ( $3 \times 5\text{ mL}$ ) and dried again under reduced pressure to give a colorless solid in 96% yield (184 mg, 0.192 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.06$  (s,  $1 \times 3\text{H}$ ,  $\text{BCH}_3$ ), 1.16 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_3\text{H}_2$ ), 1.73 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_3\text{H}_2$ ), 2.05 (br, 1H, S-cy- $\text{C}_1\text{H}$ ), 2.17 (t,  $1 \times 2\text{H}$ ,  $^3J_{\text{HH}} = 9.8\text{ Hz}$ , S-cy- $\text{C}_2\text{H}_2$ ), 2.56 (br,  $1 \times 2\text{H}$ , S-cy- $\text{C}_2\text{H}_2$ ), 2.81 (br, 1H, S-cy- $\text{C}_1\text{H}$ ), 6.59–7.57 (br m,  $2 \times 4\text{H}$ , Ph-*H*).



**Scheme 2.**

**Table 1**  
Crystallographic data for **2** and **3**.

Compound	2	3
Empirical formula	C <sub>42</sub> H <sub>72</sub> In <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>38</sub> H <sub>42</sub> In <sub>2</sub> O <sub>4</sub> S <sub>4</sub> ·3(CH <sub>2</sub> Cl <sub>2</sub> )
<i>M<sub>r</sub></i> (g mol <sup>-1</sup> )	934.80	1175.37
Crystal size (mm)	0.27 × 0.24 × 0.08	0.28 × 0.15 × 0.12
Crystal color and habit	Colorless plate	Colorless block
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	10.912(3)	10.4984(6)
<i>b</i> (Å)	10.388(3)	16.1310(9)
<i>c</i> (Å)	19.118(6)	13.6502(8)
α (°)	90.00	90.00
β (°)	94.258(5)	93.6460(10)
γ (°)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	2161.1(11)	2307.0(2)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.437	1.692
<i>T</i> (K)	100(2)	100(2)
μ (mm <sup>-1</sup> )	1.201	1.568
<i>F</i> (000)	972	1180
θ Range (°)	1.87–28.46	1.96–28.31
No. of refl. collected	20214	46941
No. of independent refl.	5376	5738
<i>R</i> <sub>int</sub>	0.0704	0.0535
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0964, 0.2607	0.0391, 0.1014
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1132, 0.2715	0.0420, 0.1038
Goodness of fit on <i>F</i> <sup>2</sup>	1.108	1.040
Δρ <sub>max, min</sub> /e Å <sup>-3</sup>	11.844, -2.137	2.857, -2.471

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 14.03 (BCH<sub>3</sub>), 22.31 (S-cy-C<sub>3</sub>H<sub>2</sub>), 31.62 (S-cy-C<sub>2</sub>H<sub>2</sub>), 54.28 (S-cy-C<sub>1</sub>H), 119.33 (Ph-C3), 121.37 (Ph-C1), 133.91 (Ph-C4), 134.35 (Ph-C5), 135.53 (Ph-C6), 136.81 (d, <sup>1</sup>J<sub>CF</sub> = 250.6 Hz, BPh-C3), 137.10 (d, <sup>1</sup>J<sub>CF</sub> = 251.4 Hz, BPh-C4), 141.53 (Ph-C6), 148.12 (d, <sup>1</sup>J<sub>CF</sub> = 240.2 Hz, BPh-C2), 160.58 (Ph-C<sub>ipso</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>): δ = -14.91 (s, [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)<sup>-</sup>]. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>): δ = -163.91 (*ortho*-F), -158.14 (*para*-F), -133.22 (*meta*-F). Anal. Calcd. for C<sub>37</sub>H<sub>21</sub>BF<sub>15</sub>InO<sub>2</sub>S<sub>2</sub>: C, 45.71; H, 2.18. Found: C, 46.08; H, 2.49.

#### 4.5.1. Single crystal X-ray diffraction studies

X-ray diffraction measurements were performed on a Bruker AXS diffractometer with Mo-Kα radiation using ω-scans. Crystal parameters and results of the structure refinements are given in Table 1. Absorption corrections were carried out with the multi-scan method using Mulabs as implemented in the program system PLATON [23]. All structures were solved by direct methods (SIR-92) [24] and refined (SHELXS-97) [25] against all *F*<sup>2</sup> data. For the graphical representation, the program ORTEP-3 was used as implied in the program system WinGX [26].

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#### Appendix A. Supporting information

CCDC 771252 (**2**) and 771253 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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