



## Dihalogen–halogenomethyl complexes of indium(III) $X_2InCH_2X$ ( $X = Br, I$ ): Simultaneous coordination of soft and hard ligands

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### ABSTRACT

Halogenomethyl–dihalogen–indium(III) compounds  $X_2InCH_2X$  ( $X = Br, I$ ) obtained from indium monohalides and methylene dihalides were reacted with the soft donor ligands dialkylsulfides,  $R_2S$  ( $R = CH_3, CH_2Ph$ ) to afford the corresponding dialkylsulfonium methylene complexes of  $InX_3$ ,  $X_3InCH_2SR_2$  ( $X = Br, R = CH_3$ , **1**;  $X = I, R = CH_3$ , **2**;  $X = I, R = CH_2Ph$ , **3**). Compound **1** was reacted with the hard donor ligands dimethylsulfoxide or triphenylphosphine oxide to give the corresponding 1:1 adduct,  $Br_3(L)InCH_2S(CH_3)_2$  ( $L = (CH_3)_2SO$ , **4**;  $L = (C_6H_5)_3PO$ , **5**). Compounds **1–5** were fully characterized in solution by NMR spectroscopy and in the solid state by X-ray methods.

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### 1. Introduction

Oxidation of indium monohalides,  $InX$  with alkylhalides,  $R-X$  to produce organoindium(III) compounds of general structure  $RInX_2$  is a well-established process [1,2]. Similarly, oxidative insertions of  $InX$  into the carbon–halogen bonds of organyl dihalides,  $RR^1CX_2$  ( $R = R^1 = H, X = Br, I$  [3,4];  $R = H, R^1 = CN, X = Br$  [5];  $R = H, R^1 = PhCO, X = Cl$  [6,7]) and trihalides,  $RCX_3$  ( $R = H, X = Cl, Br, I$  [8–10];  $R = CN, X = Cl$  [11]) lead to the corresponding halogenoalkyl,  $X_2InC-RR^1X$  and the dihalogenoalkyl,  $X_2InCRX_2$  compounds of indium(III). While some of these compounds contain nucleophilic alkyl substituents capable of coupling to electrophiles [5–7,10,11], the methylene dihalide derivatives have been used mainly as models for coordination chemistry studies. Independently, we have determined that ligands with the hard donor atom oxygen,  $L^H$ , such as ethers, dimethylsulfoxide and triphenylphosphine oxide coordinate to the metallic center of the  $Br_2In(L^H)_nCH_2Br$  complex [12], while bases with soft donor atoms,  $L^S$ , displace the bromine atom of the bromomethyl substituent to form corresponding ylides of  $InBr_3$  of general structure  $Br_3InCH_2L^S$  [13–17].

The  $X_2InCH_2X$  compounds are structurally related to  $IzNCH_2I$ , firstly prepared by Emschwiller from metallic zinc and diiodomethane [18]. The zinc carbenoid is used in the Simmons–Smith reaction [19,20] for the stereospecific conversion of alkenes into cyclopropanes, which is one of the most important methods leading to three-membered rings. After the pioneer work of Simmons and Smith, other zinc compounds bearing the  $Zn-CH_2I$  unit were intro-

duced [21]; further effective halogenomethyl–metal complexes of samarium [22,23] and aluminium [24] were developed for cyclopropanations. A “butterfly-type” transition state structure containing an electrophilic carbene was proposed during the stereospecific cyclopropanation of alkenes with  $IzNCH_2I$  [18,25–27] (Scheme 1).

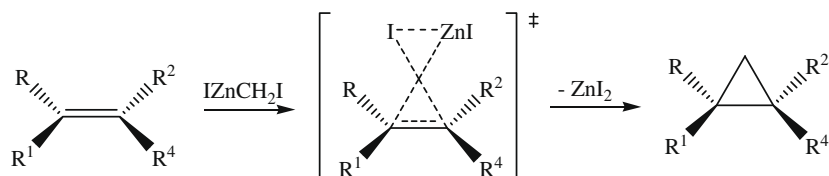
Despite the structural and electronic similarities between the  $X_2InCH_2X$  ( $X = Br, I$ ) compounds with the Simmons–Smith reagent,  $IzNCH_2I$  and its analogues, we were disappointed to verify that the indium complexes were not able to act as methylene carriers in cyclopropanations. The remarkable stability of the  $X_2InCH_2X$  compounds allied with their ability to coordinate to hard and soft bases through their two different electrophilic sites suggest that the halogenomethyl complexes of indium are, on the other hand, potential starting materials to obtain novel metal organic frameworks (MOFs) which have been extensively studied in the past few years due to their application in catalysis, fuel storage, ion and molecular recognition [28]. To acquire a deeper knowledge on the coordination chemistry of the indium organometallics to design novel MOF's, we now set to investigate the conditions to prepare adducts of  $X_2InCH_2X$  of general structure  $X_3(L^H)_nInCH_2L^S$  using dialkylsulfides  $R_2S$  ( $R = CH_3, CH_2Ph$ ) as soft ligands ( $L^S$ ) and dimethylsulfoxide and triphenylphosphine oxide acting as hard ones ( $L^H$ ).

### 2. Results and discussion

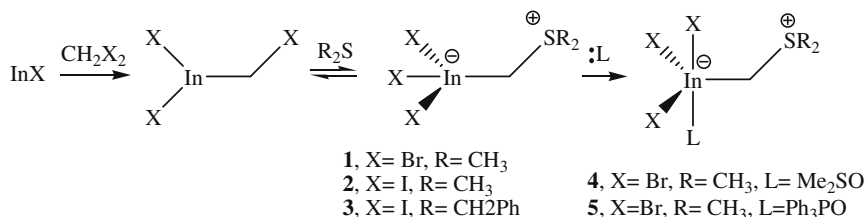
#### 2.1. Preparative work

Three new sulfonium methylene complexes  $X_3InCH_2SR_2$  ( $X = Br, R = CH_3$ , **1**;  $X = I, R = CH_3$ , **2**;  $X = I, R = CH_2Ph$ , **3**) were prepared by adding the sulfide ligands to solutions of the corresponding

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**Scheme 1.** Proposed transition state for the Simmons–Smith reaction.



**Scheme 2.** Preparation of sulfonium methylide complexes of indium(III).

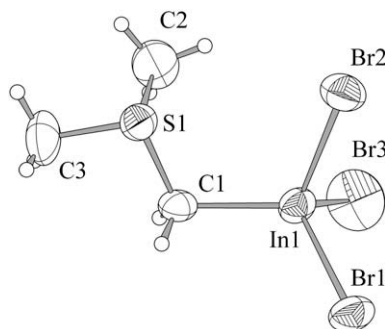
$X_2InCH_2X$  compounds generated from  $InX$  and  $CH_2X_2$  (Scheme 2). Analytically pure single crystals of **1–3** were grown from acetone–ethanol solutions in yields varying from 70% to 84%. Addition of dimethyl sulfoxide and triphenylphosphine oxide to solutions of **1** in cyclic ethers (THF or 1,4-dioxane) gave  $Br_3(L)InCH_2S(CH_3)_2$  ( $L = (CH_3)_2SO$ , **4**;  $L = Ph_3PO$ , **5**) in 60% and 92% of yield, respectively, after recrystallization from acetone–chloroform mixtures. The analogous adducts of **2** and **3** were not formed through similar procedure.

The molecular formulae of compounds **1–5** were established by indium and halide analysis. NMR spectroscopy unequivocally revealed the sulfonium methylide ligands attached to the indium(III) centers according to the singlets corresponding to the methylide groups observed from 2.60 to 2.86 ppm, which are in the typical range observed for other indium(III) ylides [13–17].

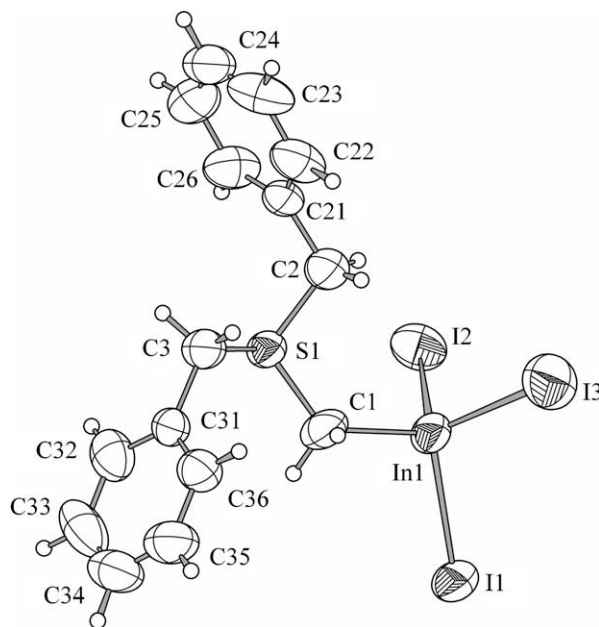
## 2.2. Molecular structure determinations

X-ray single crystal studies allowed to determine the structures of compounds **1–5** depicted in Figs. 1–4, respectively, and in which the thermal ellipsoids are drawn at 50% probability level. Only the figure corresponding to compound **1** is showing because compound **2** is isostructural. In every case, the structures consist of discrete molecules, with no significant intermolecular interactions. In compounds **1–3** the indium atoms are coordinated by three halogen atoms and one sulfonium methylide ligands. The coordination geometry around the indium atom of **1–3** is distorted tetrahedral.

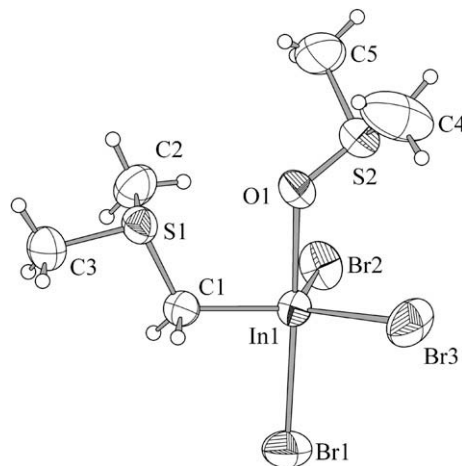
Compound **1** reacts with dimethylsulfoxide and triphenylphosphine oxide to produce the mono-adducts **4** and **5**, respectively. In



**Fig. 1.** Molecular structure of dimethylsulfoniummethylide-tribromo-indium(III), **1**.



**Fig. 2.** Molecular structure of dibenzylsulfoniummethylide-triiodo-indium(III), **3**.



**Fig. 3.** Molecular structure of dimethylsulfoniummethylide-dimethylsulfoxide-tribromo-indium(III), **4**.

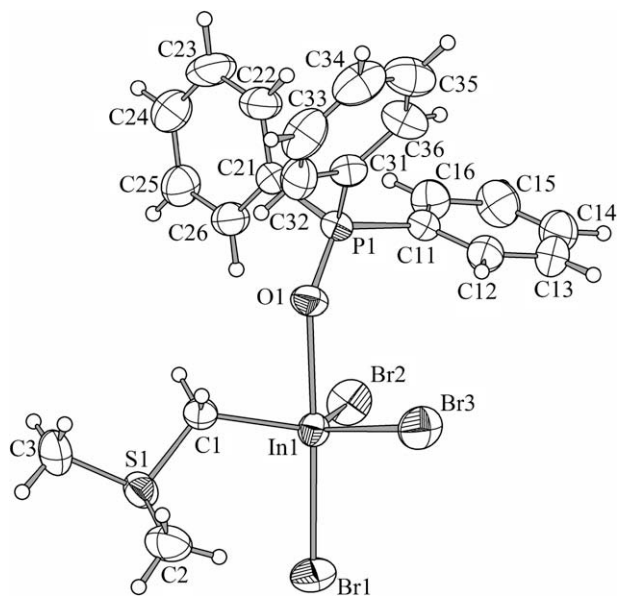


Fig. 4. Molecular structure of dimethylsulfoniummethylide-tribromo-triphenylphosphineoxide-indium(III), **5**.

both cases, the coordination geometry around the indium is distorted trigonal bipyramidal. The equatorial positions are occupied by two bromine atoms and one sulfonium methylide ligand, while the apical ligands are one bromine atom and the hard sulfoxide or phosphine oxide ligands. Perhaps the most interesting difference between structures **4** and **5** is the orientation relating the sulfonium methylide and the hard sulfoxide and phosphine oxide ligands. In compound **4** the dimethylsulfonium moiety of the sulfonium methylide and the dmso ligands are in the same side of the equatorial plane, while in compound **5** the dimethylsulfonium moiety and the  $\text{Ph}_3\text{PO}$  are in opposite planes. The torsion angles  $\text{S1-C1-In1-O1}$  are  $14.1(3)$  and  $173.1(2)^\circ$  in **4** and **5**, respectively; no doubt the bulky  $\text{Ph}_3\text{PO}$  ligand imposes such stereochemistry.

Table 1 compares the relevant bond distances in compounds **1–5**. There are no significant differences in the  $\text{In-C1}$  bond lengths for tetra (in **1**) or penta-coordinated (**4** and **5**) sulfonium methylide complexes of  $\text{InBr}_3$ . One significant feature is the difference between the equatorial and axial indium–bromine bonds in compounds **4** and **5**, with the axial bonds  $0.125 \text{ \AA}$  and  $0.150 \text{ \AA}$  longer in **4** and **5**, respectively.

Table 1  
Important bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1–5**.

Length ( $\text{\AA}$ )	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
$\text{In-X}^a$	2.504(1)	2.7107(9)	2.7097(6)	–	–
$\text{In-Br}_{\text{eq}}^{a,b}$	–	–	–	2.5228(6)	2.5178(6)
$\text{In-Br}_{\text{ax}}^{a,c}$	–	–	–	2.6482(7)	2.6677(9)
$\text{In-C1}$	2.17(1)	2.210(9)	2.209(5)	2.1695(5)	2.180(4)
$\text{S-C1}$	1.75(1)	1.73 (1)	1.737(5)	1.750(4)	1.764(4)
$\text{S-C}^a$	1.78(1)	1.76(1)	1.803(6)	1.771(5)	1.791(6)
$\text{In-O}$	–	–	–	2.302(3)	2.372(3)
Angle ( $^\circ$ )					
$\text{X1-In1-X2}$	107.29(6)	109.67(3)	109.46(2)	97.11(2)	93.69(2)
$\text{X1-In1-X3}$	106.17(8)	111.02(3)	109.78(2)	92.85(2)	96.03(2)
$\text{X2-In1-X3}$	104.84(7)	108.36(3)	109.13(2)	111.24(3)	113.86(3)
$\text{X1-In1-C1}$	112.6 (3)	108.8(2)	107.3(1)	90.5 (1)	99.9(1)
$\text{X2-In1-C1}$	108.7(3)	110.0 (3)	110.9(2)	116.9(1)	120.0(1)
$\text{X3-In1-C1}$	116.7(3)	109.0(3)	110.3(2)	130.9(1)	122.1(1)
$\text{In1-C1-S1}$	114.4(5)	114.7(4)	118.1(3)	118.2(2)	117.6(2)
$\text{O1-In1-C1}$	–	–	–	86.3(1)	77.9 (1)

<sup>a</sup> Mean value.

<sup>b</sup> Equatorial bromine.

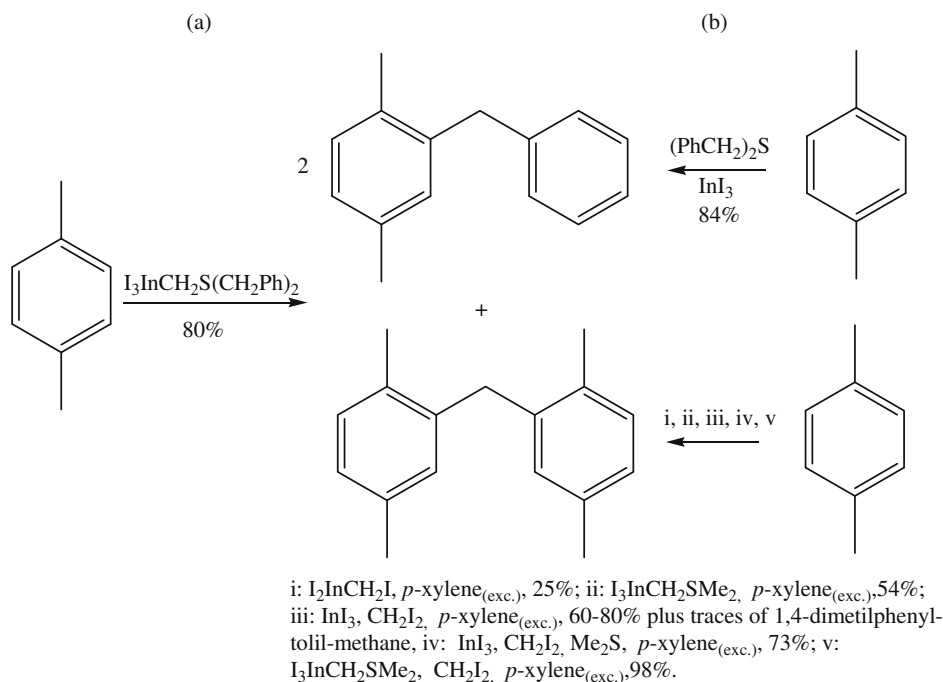
<sup>c</sup> Axial bromine.

The averaged indium–halogen and indium–carbon distances for compounds **1–5** are close to other ylide complexes of  $\text{InBr}_3$  of general structure  $\text{Br}_3\text{InCH}_2\text{L}$  ( $\text{L} = \text{Et}_3\text{N}$ ,  $\text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$ ,  $\text{Bn}_2\text{S}$ ) [13–17]. On the other hand, compounds **4** and **5** show abnormal longer indium–oxygen bond distances when compared with the values of  $2.20(1)$ ,  $2.14(1)$  and  $2.281(6) \text{ \AA}$  measured in the *fac* octahedral  $\text{InX}_3(\text{dmso})_3$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) [29], in the ionic  $[\text{InCl}_2(\text{Ph}_3\text{PO})_4][\text{InCl}_4]$  [29] and in the closely related  $\text{Br}_2\text{In}(\text{Ph}_3\text{PO})_2\text{CH}_2\text{Br}$  [16] compounds, respectively. These tenuous indium–oxygen bonds observed in **4** and **5** probably explain the failure to prepare stable dmso or  $\text{Ph}_3\text{PO}$  adducts of the iodide derivatives  $\text{I}_3\text{InCH}_2\text{SR}_2$  ( $\text{R} = \text{Me}$ ,  $\text{Bn}$ ).

### 2.3. The chemical properties of $\text{X}_3\text{InCH}_2\text{SR}_2$ compounds

Sulfonium ylides are reactive species containing nucleophilic carbon atoms directed bonded to leaving groups. Their most typical reactions include coupling with carbonyl compounds (Darzens-type) and alkenes bearing electron withdrawing groups (Michael Induced Ring Closure – MIRC) and consecutive ring closures leading to epoxides and cyclopropanes, respectively. None of the new indium compounds **1–5** promote these processes. To acquire a better knowledge about the chemical properties of these compounds, we have examined the thermal decomposition of compound **3** by TGA analysis. The temperature dependence-weight loss curve shows lost weight in two different range of temperatures: ca.  $190\text{--}200^\circ\text{C}$  (ca. 15%) and  $205\text{--}600^\circ\text{C}$  (ca. 70%). We were unable to derive any simple decomposition pathway from the experiment. We therefore induced the decomposition (Scheme 3 – part a) of compound **3** in boiling 1,4-dimethylbenzene ( $138^\circ\text{C}$ ). We were pleased to verify that, after standard work up (see Section 3), two products were isolated: 2,5-dimethylphenyl-phenylmethane and bis(2,4-dimethylphenyl)methane in 80% of yield. 2,5-Dimethylphenyl-phenylmethane was produced in similar yield (84%) refluxing equimolar amounts of dibenzylsulfide and indium triiodide in *p*-xylene (Scheme 3 – part b). Bis(2,4-dimethylphenyl)methane was produced from reactions involving  $\text{I}_3\text{InCH}_2\text{I}$ ,  $\text{InI}_3$  and  $\text{CH}_2\text{I}_2$  in yields varying from 25% to 98% (Scheme 2 – part b) in refluxing *p*-xylene. An interesting observation related to this last reaction is that in some cases we have detected simultaneous production of trace amounts of 2,5-dimethylphenyl-4-methylphenylmethane. Friedel–Crafts alkylations for the synthesis of diarylmethanes using alkyl halides as alkylating agents and traditional Lewis acid catalysts are known for long time [30]. Recent literature introduced indium trihalides as efficient catalysts for Friedel–Crafts reactions using both alkyl halides [31] and benzyl alcohols [32] as alkylating agents, but to the best of our knowledge there is no report on Friedel–Crafts alkylation catalyzed by indium salts using thioethers as the alkyl group source. Despite the novelty, the reaction has little practical value because thioethers are normally prepared from alkyl halides or alcohols [33]. The relevance of this reaction in the present context is that it allows one to understand the lack of reactivity of the  $\text{X}_3\text{InCH}_2\text{SR}_2$  compounds as methylene carriers. Upon heating, it is reasonable to postulate that the sulfonium methylide complexes of  $\text{InX}_3$  decompose to their precursors (see Scheme 1),  $\text{R}_2\text{S}$  and  $\text{X}_2\text{InCH}_2\text{X}$  [16], and that the halogenomethyl compound of indium(III) also decomposes to  $\text{InX}_3$  (and/or  $\text{InX}$  plus  $\text{CH}_2\text{X}_2$ ) [12] which catalyzed the Friedel–Crafts alkylations of *p*-xylene.

To conclude, we have synthesized three new dialkylsulfonium methylide complexes of indium trihalides,  $\text{X}_3\text{InCH}_2\text{SR}_2$  from halogenomethyl complexes,  $\text{X}_2\text{InCH}_2\text{X}$  and determined the characteristics of the ligands capable to coordinate to the metallic site of the ylide complexes to produce compounds of general structure  $\text{X}_3\text{In}(\text{L})\text{CH}_2\text{SR}_2$ . We expect to use the full coordinating ability of the  $\text{X}_2\text{InCH}_2\text{X}$ , in reactions with bidentate ligands, to synthesize



**Scheme 3.** Friedel–Crafts alkylation of 1,4-dimethylbenzene with **3** (a) and with  $(PhCH_2)_2S$  or  $CH_2I_2$  catalyzed by indium(III) compounds.

some new one and two-dimensional metal organic frameworks (MOF's) of indium, which we shall report briefly. Further, we have determined that the most important reactivity trend of the  $X_3InCH_2SR_2$  compounds is their decomposition into their precursors instead of acting as ylide carriers.

### 3. Experimental

#### 3.1. General

Indium monobromide and monoiodide were prepared by heating indium metal and the corresponding indium trihalide in a vacuum sealed tube at 450 °C. Methylene bromide and iodide (Aldrich) were dried over Linde 4°Å molecular sieves.  $X_2In(diox)_2CH_2X$  ( $X = Br, I$ ) was prepared from  $InX$  and  $CH_2X_2$  as described earlier [12]. 1,4-Dioxane (diox) was dried over sodium and benzophenone, and distilled just before use from the blue ketyl form. Chloroform (ACS grade) was used as supplied. All preparative work was carried out under dry nitrogen atmosphere, up to the isolation of final products. Proton, carbon and NMR spectra were recorded on the Bruker DPX-200 and DPX-400 instruments. Thermogravimetric analysis was carried out on a Shimadzu DTG-60 instrument (nitrogen flow rate 50 mL min<sup>-1</sup>); the sample (ca. 10 mg) contained in a platinum cell was heated from 25 to 600 °C at heating rate of 10 °C min<sup>-1</sup>. Indium and halogen analysis were as described previously [15].

#### 3.2. Preparative chemistry

##### 3.2.1. Preparation of $Br_3InCH_2S(CH_3)_2$ (**1**)

$InBr$  (978 mg, 5 mmol) and  $CH_2Br_2$  (4350 mg, 1.75 mL, 25 mmol) in 25 mL of dried (sodium) 1,4-dioxane were stirred in a Schlenk round bottomed flask at room temperature (25 °C) under a dry nitrogen atmosphere until all the red solid monobromide dissolved (about 2 h) and a clear colourless solution obtained. At this point, all the solvents were removed under high vacuo to remove the dihalide excess. The white solid obtained was redissolved in 25 mL of 1,4-dioxane and to this solution  $(CH_3)_2S$  (253 mg, 0.43 mL, 5.7 mmol) was added via syringe. The solution was kept

under stirring for 24 h. After this time, all the volatiles were removed under vacuo and the residue obtained recrystallized in acetone:ethanol (95%) (1:1, v/v) under the laboratory atmosphere. This treatment leads to deposition of 1.57 g (3.65 mmol, 73%, m.p. dec. 105 °C) of  $Br_3InCH_2S(CH_3)_2$  as colourless single crystals. Anal. Calc. for  $C_3H_8Br_3InS$ : In, 26.6; Br, 55.7. Found: In, 26.5; Br, 55.8%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>),  $\delta$  2.72 s, 2H,  $InCH_2S$ ; 3.14 s, 6H,  $S(CH_3)_2$ . <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>),  $\delta$  31.55,  $S(CH_3)_2$ ;  $InCH_2S$  not detected (due to the high quadrupolar moment of indium,  $I = 9/2$ ).

##### 3.2.2. Preparation of $I_3InCH_2S(CH_3)_2$ (**2**)

$InI$  (0.73 g, 3.0 mmol) and  $CH_2I_2$  (224  $\mu$ L, 0.80 g, 3.0 mmol) were stirred together in acetonitrile (5 mL) until the indium(I) iodide had completely dissolved (ca. 0.5 h). After dissolution of indium(I) iodide,  $(CH_3)_2S$  (198  $\mu$ L, 0.22 g, 3.5 mmol) was added to the solution, and the mixture was stirred for 3 h. All the volatiles were removed under vacuo, and the white solid obtained was recrystallized in acetone/ethanol (1:3), giving a colourless crystalline solid identified as  $I_3InCH_2S(CH_3)_2$  (yield 1.30 g, 2.1 mmol, 70% based on  $InI$ , m.p. dec. 114–118 °C). Anal. Calc. for  $I_3InCH_2S(CH_3)_2$ : In, 20.1; Br, 66.9. Found: In, 20.5; Br, 66.6%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>),  $\delta$ : 2.86 s, 1H,  $CH_2$ ; 3.15 s, 3H,  $CH_3$ . <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>),  $\delta$ : 30.90,  $InCH_2S$  not detected.

##### 3.2.3. Preparation of $I_3InCH_2S(CH_2C_6H_5)_2$ (**3**)

$InI$  (484 mg, 2 mmol) and  $CH_2I_2$  (536 mg, 0.16 mL, 2 mmol) in 2 mL of dried acetonitrile ( $CaH_2$ ) were stirred in a Schlenk flask round bottomed flask at room temperature (25 °C), under a dry nitrogen atmosphere until all the violet solid monoiodide dissolved (around 30 min) and a clear colourless solution obtained. At this point, solid dibenzyl sulfide (428 mg, 2 mmol) was added and the reaction kept under magnetic stirring for 4 h until all the white solid adduct precipitated. The solid is redissolved upon addition of acetone and slow removal of solvents coupled with freezing gave  $I_3InCH_2S(CH_2C_6H_5)_2$  as colourless single crystals (1.22 g, 84%, m.p. dec. 179–180 °C). Anal. Calc. for  $C_{15}H_{16}I_3InS$ : In, 15.8; I, 52.6. Found: In, 16.3; I, 53.0%. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>),  $\delta$  2.61 s, 2H,  $InCH_2S$ ; 4.73, d,  $J = 12.9$  Hz, 2H,  $SCH_2Ph$ ; 4.82, d,  $J = 12.9$  Hz, 2H,  $SCH_2Ph$ ;

7.50, m, 10H.  $^{13}\text{C}$  NMR (acetone- $d_6$ ),  $\delta$  49.26,  $\text{SCH}_2\text{Ph}$ , 129.77, 131.31, 131.68, 132.65;  $\text{InCH}_2\text{S}$  not detected.

### 3.2.4. Preparation of $\text{Br}_3[\text{OS}(\text{CH}_3)_2]\text{InCH}_2\text{S}(\text{CH}_3)_2$ (4)

$\text{Br}_3\text{InCH}_2\text{S}(\text{CH}_3)_2$  (1) (431 mg, 1 mmol) was dissolved in 1,4-dioxane (7 mL), under a nitrogen atmosphere, and to this solution was added dimethyl sulfoxide (234 mg, 0.21 mL, 3 mmol) via syringe. After 2 h of continuous stirring the white solid formed was filtered, dried under vacuo and recrystallized in acetone:chloroform (1:1, v/v) to produce  $\text{Br}_3[\text{OS}(\text{CH}_3)_2]\text{InCH}_2\text{S}(\text{CH}_3)_2$  (305 mg, 0.6 mmol, 60%, m.p. 109–111 °C). Anal. Calc. for  $\text{C}_5\text{H}_{14}\text{Br}_3\text{InOS}$ : In, 22.6; Br, 47.1%. Found: In, 22.2; Br, 47.1%.  $^1\text{H}$  NMR (acetone- $d_6$ ),  $\delta$  2.60 s, 6H,  $\text{OS}(\text{CH}_3)_2$ ;  $\delta$  2.66 s, 2H,  $\text{InCH}_2\text{S}$ ; 3.11 s, 6H,  $\text{S}(\text{CH}_3)_2$ .  $^{13}\text{C}$  NMR poor solubility prevented reliable spectrum.

### 3.2.5. Preparation of $\text{Br}_3[\text{OP}(\text{C}_6\text{H}_5)_3]\text{InCH}_2\text{S}(\text{CH}_3)_2$ (5)

The compound was prepared as  $\text{Br}_3[\text{OS}(\text{CH}_3)_2]\text{InCH}_2\text{S}(\text{CH}_3)_2$ , except that THF was used as the solvent.  $\text{Br}_3[\text{OP}(\text{C}_6\text{H}_5)_3]\text{InCH}_2\text{S}(\text{CH}_3)_2$  was obtained in 92% of yield (m.p. dec. 180 °C). Colourless single crystals were grown from acetone:chloroform (1:1, v/v) solution. Anal. Calc. for  $\text{C}_{21}\text{H}_{23}\text{Br}_3\text{InOPS}$ : In, 16.2; Br, 33.8. Found: In, 15.9; Br, 33.5%.  $^1\text{H}$  NMR (acetone- $d_6$ );  $\delta$  2.71 s, 2H,  $\text{InCH}_2\text{S}$ ; 3.13 s, 6H,  $\text{S}(\text{CH}_3)_2$ ;  $\delta$  7.68 m, 15H,  $\text{OP}(\text{C}_6\text{H}_5)_3$ .  $^{13}\text{C}$  NMR poor solubility prevented reliable spectrum.

### 3.2.6. Reactions of $\text{I}_3\text{InCH}_2\text{SR}_2$ ( $R = \text{Me}, \text{Bn}$ ) with $(\text{CH}_3)_2\text{SO}$ and $(\text{C}_6\text{H}_5)_3\text{PO}$

Solutions of  $\text{I}_3\text{InCH}_2\text{SR}_2$  and dimethylsulfoxide or  $\text{I}_3\text{InCH}_2\text{SR}_2$  and triphenylphosphine oxide in acetone always deposited unreacted  $\text{I}_3\text{InCH}_2\text{SR}_2$  upon addition of ethanol 95%, and no sign of adduct formation was observed.

## 3.3. The chemical properties of $\text{X}_3\text{InCH}_2\text{SR}_2$ compounds

### 3.3.1. The thermal decomposition of $\text{I}_3\text{InCH}_2\text{SBn}_2$ in 1,4-dimethylbenzene

$\text{I}_3\text{InCH}_2\text{SBn}_2$  (179.4 mg, 0.25 mmol) and freshly distilled 1,4-dimethylbenzene (1.5 mL) were heated under reflux in a Schlenk tube, under dry  $\text{N}_2$ , for 20 h. At the end of this period, the reaction was quenched with a saturated NaCl solution and the organic components extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL); this solution was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and pumped to dryness under vacuum. The oil obtained was purified by column chromatography (gradient ethyl acetate:hexanes, 2:98 up to 5:95%). This procedure gave (2,5-dimethylphenyl)phenylmethane (77 mg, 0.39 mmol, 80%) and *bis*(2,5-dimethylphenyl)methane (44.6 mg, 0.20 mmol, 80%).

(2,5-Dimethylphenyl)phenylmethane [32]: colourless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  2.19, s, 3H; 2.29, s, 3H; 3.95, s, 2H; 6.93–7.30, m, 8H.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  19.13; 20.93; 39.39; 125.81; 127.07; 128.31; 128.66; 130.16; 130.74; 133.38; 135.30; 138.62; 140.51. GCMS (% rel. intens.) 196 (M, 72), 181 (100), 165 (50), 118 (35), 91 (33).

*Bis*(2,5-dimethylphenyl)methane [34]: m.p. 53.5–54.5 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  2.22, s, 6H; 2.23 s, 6H; 3.83, s, 2H; 6.71, s, 2H; 6.94, d,  $J = 7.6$  Hz, 2H; 7.06, d,  $J = 7.6$  Hz, 2H.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  19.11, 21.01, 36.57, 126.92, 130.03, 133.52, 135.52, 138.26, 138.45. GCMS (% rel. intens.) 224 (M, 86), 209 (57), 194 (24), 179 (30) 118 (100), 91 (31).

(2,5-Dimethylphenyl)phenylmethane was also prepared (164 mg; 0.84 mmol; 84%) by refluxing  $\text{InI}_3$  (0.5 mmol) and dibenzylsulfide (0.5 mmol) in 1,4-dimethyl benzene (1 mL), under dry  $\text{N}_2$ .

*Bis*(2,5-dimethylphenyl)methane was prepared by heating the following mixtures under refluxing 1,4-dimethyl benzene (1 mL):

- $\text{I}_2\text{InCH}_2\text{I}$  (0.5 mmol) produced 28 mg (0.125 mmol, 25%) of *bis*(2,5-dimethylphenyl)methane,
- $\text{I}_3\text{InCH}_2\text{SMe}_2$  (0.5 mmol) produced 60.5 mg (0.27 mmol, 54%) of *bis*(2,5-dimethylphenyl)methane,
- $\text{InI}_3$  (0.5 mmol),  $\text{CH}_2\text{I}_2$  (0.5 mmol) produced 78.4 mg (0.35 mmol, 70%) of *bis*(2,5-dimethylphenyl)methane together with trace amounts of 2,5-dimethylphenyl-4-methylphenylmethane,
- $\text{InI}_3$  (0.5 mmol) and  $\text{CH}_2\text{I}_2$  (0.5 mmol) and  $\text{Me}_2\text{S}$  (0.5 mmol) produced 78.4 mg (0.36 mmol, 73%) of *bis*(2,5-dimethylphenyl)methane,
- $\text{I}_3\text{InCH}_2\text{SMe}_2$  (0.5 mmol) and  $\text{CH}_2\text{I}_2$  (0.5 mmol) produced 78.4 mg (0.49 mmol, 98%) of *bis*(2,5-dimethylphenyl)methane.

## 4. Supplementary material

CCDC 711962, 711963, 711964, 711965 and 711966 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. 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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