

Preparation, crystal structure determination, and properties of adducts of halogenomethyl compounds of indium with Group 16 donors

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Abstract

The bis-1,4-dioxane (diox) adduct of bromomethyl-dibromo-indium(III), $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$, reacts with triphenylphosphine oxide, triphenylphosphine sulfide and benzyl sulfide to produce the compounds $\text{Br}_2\text{In}[\text{OP}(\text{C}_6\text{H}_5)_3]_2\text{CH}_2\text{Br}$ and $\text{Br}_3\text{InCH}_2\text{L}$ (L = benzyl sulfide, triphenylphosphine sulfide). The crystal structures of these new organoindium compounds have been solved by X-ray diffraction methods. The structural results are compared with those for related organoindium compounds. Quantum mechanical calculations, by the PM3 method, satisfactorily predict the measured bond distances and angles in all compounds, and hence furnish reliable net atomic charge maps, which demonstrate the presence of a sulfur ylid ligand, $\text{H}_2\text{C}^{\delta-}-\text{S}^{\delta+}(\text{CH}_2\text{C}_6\text{H}_5)_2$, and a triphenylphosphonium-sulfur methylide ligand, $^{\delta-}\text{CH}_2\text{S}-^{\delta+}\text{P}(\text{C}_6\text{H}_5)_3$, in the $\text{Br}_3\text{InCH}_2\text{L}$ compounds. Mass spectra and thermal decomposition studies establish that $\text{Br}_3\text{InCH}_2\text{S}(\text{CH}_2\text{C}_6\text{H}_5)_2$ decomposes via an intramolecular nucleophilic attack of a bromide ligand, either to the InCH_2 carbon atom to produce benzyl sulfide, or to the $\text{C}_6\text{H}_5\text{CH}_2$ carbon to yield benzyl bromide and benzyl-methyl-sulfide. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent work has shown that α -halogeno-organoinidium reagents promote carbon–carbon bond formation. This class of reagents, readily obtained [1] from indium metal and Br_2CR_2 ($\text{R} = -\text{CN}$, $-\text{CO}_2\text{Et}$), has been successfully employed in the cyclopropanation of electron-deficient alkenes, and in the epoxidation of carbonyl compounds ($\text{R} = -\text{CO}_2\text{Et}$). More recently [2], it was found that bromocyanomethylation of a variety of carbonyl compounds to produce the corresponding 2-bromo-3-hydroxynitriles can be carried out by the action of dibromoacetonitrile and indium(I) bromide. Indium(III) compounds of the general structure $\text{X}_2\text{InCR}^1\text{R}^2\text{X}$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$, Cl , Br , I ; $\text{X} = \text{Cl}$, Br , I)

are believed to be structurally related to the active organoindium intermediates in these reactions, and the preparation of these has allowed us to study the properties of these compounds in detail [3–5]. The $\text{X}_2\text{InCR}^1\text{R}^2\text{X}$ molecules have been shown to have two electron deficient sites, namely the indium atom and the halogenomethylic carbon. Addition of halide anions to $\text{X}_2\text{InCR}^1\text{R}^2\text{X}$ leads to the corresponding salts of $[\text{X}_3\text{InCR}^1\text{R}^2\text{X}]^-$ which were fully characterized by X-ray methods ($\text{X} = \text{Br}$, $\text{R}^1 = \text{R}^2 = \text{H}$ [3]; $\text{X} = \text{Cl}$, Br , $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{X}$ [6]). A series of Group 15 adducts of general structure $\text{X}_3\text{InCH}_2\text{L}$ ($\text{X} = \text{Br}$, $\text{L} = (\text{C}_2\text{H}_5)_3\text{N}$ [7], $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ [5], $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$ [5], $(\text{C}_6\text{H}_5)_3\text{As}$ [7], $(\text{C}_6\text{H}_5)_3\text{Sb}$ [7]; $\text{X} = \text{I}$, $\text{L} = (\text{C}_6\text{H}_5)_3\text{As}$ [7]) has also been synthesized and fully characterized.

The potential application of main group metal ylids in organic synthesis as storable precursors of Wittig and other ylids has lead us to extend this work by

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preparing adducts of $\text{Br}_2\text{InCH}_2\text{Br}$ with Group 16 ligands, namely triphenylphosphine oxide, triphenylphosphine sulfide and benzyl sulfide. The structures and some properties of these species are discussed in the light of quantum mechanical semi-empirical calculations.

2. Experimental

2.1. General

Indium monobromide was prepared [8] by heating metal and indium tribromide in a vacuum sealed tube at 450°C. Methylene bromide (Aldrich) was dried over Linde 4 Å molecular sieves. $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$ was prepared from InBr and CH_2Br_2 as described earlier [3]. Triphenylphosphine oxide, triphenyl phosphine sulfide and benzyl sulfide were used as supplied (Aldrich). 1,4-dioxane (diox) was dried over sodium and benzophenone, and distilled just before use from the blue ketyl form.

Indium and bromine analysis were as described previously [9]. Proton and carbon NMR were recorded on a Varian Unity Plus 300 instrument; phosphorus NMR on a Bruker DPX-400 instrument. Thermogravimetric analysis were carried out on a Shimadzu TGA-50 instrument (flow rate 50 ml min⁻¹); the sample (ca. 5 mg) contained in an alumina cell, was heated from 30–800°C. Mass spectra were recorded on a Finnigan GC-MS spectrometer operating at 70 eV.

All preparative work was carried out under dry nitrogen, using standard vacuum line techniques, up to the isolation of the final products. The $\text{Br}_3\text{InCH}_2\text{S}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**) compound is sensitive to air and must be handled under nitrogen.

2.2. Preparative details

2.2.1. $\text{Br}_2\text{In}[\text{OP}(\text{C}_6\text{H}_5)_3]_2\text{CH}_2\text{Br}$ (**1**)

A solution of $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$ was prepared from 400 mg (2.05 mmol) of InBr and 0.72 ml (10.3 mmol) of CH_2Br_2 in 1,4-dioxane (20 ml); after which all volatiles were removed under vacuum, until complete removal of excess CH_2Br_2 . The white $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$ solid was redissolved in dioxane (20 ml) and solid triphenylphosphine oxide (1.14 g, 4.10 mmol) added to the solution. This mixture was stirred for 4 h; on concentration, 1.35 g (1.46 mmol, 71%) of **1** was deposited. This solid was collected by filtration, and dried under vacuum. Colorless single crystals were obtained by recrystallization from ethanol (95%) in an open vessel. Anal. Calc. for $\text{C}_{37}\text{H}_{32}\text{Br}_3\text{InO}_2\text{P}_2$: In, 12.4; Br, 25.9. Found. In, 12.4; Br, 25.9%. ¹H-NMR (CDCl_3), δ 7.50–7.75 m, 15H, $\text{OP}(\text{C}_6\text{H}_5)_3$; δ 2.63 s, 1H, InCH_2Br . ¹³C-NMR ($\text{DMSO}-d_6$), δ 132.7, $J_{\text{C-P}} = 102.1$ Hz, aromatic *ipso*; δ 132.04,

$J_{\text{C-P}} = 2.3$ Hz, aromatic *para*; δ 131.48, $J_{\text{C-P}} = 9.9$ Hz, aromatic *ortho*; δ 128.76, $J_{\text{C-P}} = 12.1$, aromatic *meta*; InCH_2Br not detected. ³¹P-NMR ($\text{DMSO}-d_6$), δ 26.28 (from H_3PO_4).

2.2.2. $\text{Br}_3\text{InCH}_2\text{S}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**)

To a solution of $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$, prepared as above from 2.05 mmol of InBr , was added solid benzyl sulfide (439 mg, 2.05 mmol). Colorless crystals suitable for X-ray analysis precipitated from the undisturbed solution on gradual concentration. If the rate of concentration is increased, a white powder precipitates (932 mg, 1.60 mmol, 78% yield). Both products are the dibenzyl sulfide adduct of $\text{Br}_2\text{InCH}_2\text{Br}$. Anal. Calc. for $\text{C}_{15}\text{H}_{16}\text{Br}_3\text{InS}$: In, 19.7; Br, 41.1. Found. In, 19.5; Br, 41.1%. ¹H-NMR ($\text{THF}-d_8$), δ 7.25 s, 5H, $\text{C}_6\text{H}_5\text{CH}_2\text{S}$; δ 4.33, dd, 2 H $\text{C}_6\text{H}_5\text{CH}_2\text{S}$; δ 2.05 s, 1H, InCH_2S . ¹³C-NMR ($\text{DMSO}-d_6$), δ 130.54, 129.25, 129.03, $\text{C}_6\text{H}_5\text{CH}_2\text{S}$; δ 67.13, $\text{C}_6\text{H}_5\text{CH}_2\text{S}$; InCH_2S not detected.

2.2.3. $\text{Br}_3\text{InCH}_2\text{SP}(\text{C}_6\text{H}_5)_3$ (**3**)

Procedures identical to those described for **1** above, produced 1.02 g (1.54 mmol, 75% yield) of **3**. Colorless single crystals for X-ray analysis were grown from acetone–ethanol (2:1, v/v). Anal. Calc. for $\text{C}_{19}\text{H}_{17}\text{Br}_3\text{InPS}$: In, 17.3; Br, 36.2. Found. In, 17.0; Br, 36.1%. ¹H-NMR (acetone- d_6), δ 7.80–8.03 m, 15H, $\text{SP}(\text{C}_6\text{H}_5)_3$; δ 2.00 d, $J_{\text{P-H}} = 8.6$ Hz, 2H, InCH_2S . ¹³C-NMR (acetone- d_6), δ 119.92, $J_{\text{C-P}} = 83.1$ Hz, aromatic *ipso*; δ 136.39, $J_{\text{C-P}} = 3.0$ Hz, aromatic *para*; δ 134.69, $J_{\text{C-P}} = 10.7$ Hz, aromatic *ortho*; δ 131.39, $J_{\text{C-P}} = 13.0$ Hz, aromatic *meta*; InCH_2S not detected. ³¹P-NMR (acetone, C_6D_6 as internal locker), δ 50.78 (from H_3PO_4).

2.3. Thermal decomposition of **2**

2.3.1. In the solid state

A sample of **2** (500 mg) was sealed in a glass tube under vacuum. The tube was heated for 24 h at 110–120°C, after which the residue was partitioned in a silica-gel chromatographic column in hexane–ethyl acetate (4:1, v/v), and the hexane–acetate solution analyzed by GC-MS. The compounds which were identified included benzyl bromide: m/z (70 eV) 170–172 (M^+ , 3%), 91 (100%), 65 (27%), benzyl-methyl-sulfide: m/z 138 (M^+ , 38%), 91 (100%), 65 (14%), and benzyl sulfide: m/z 214 (M^+ , 43%), 122 (100%), 91 (95%).

2.3.2. In solution

A solution of **2** (500 mg, 0.86 mmol) in dioxane (25 ml) was refluxed for 8 h, after which all volatiles were removed under vacuum, and the residue re-dissolved in ethanol (95%, 20 ml). Addition of tetraethylammonium bromide (181 mg, 0.86 mmol) produced a white precipitate, which was collected by filtration, dried and iden-

tified as $[(C_2H_5)_4N][InBr_4]$ (233 mg, 0.41 mmol). Anal. Calc. for $C_8H_{20}NBr_4In$: In, 20.3; Br, 56.6. Found. In, 20.0; Br, 55.9%. The ethanol solution was submitted to GC-MS analysis and the products detected were benzyl bromide, benzyl-methyl-sulfide and benzyl sulfide (MS as above).

2.4. Reaction of $Br_3InCH_2S(CH_2C_6H_5)_2$ (**2**) with carbonyl compounds

Compound **2** (1 mmol) and an equimolar amount of benzaldehyde (or acetophenone) were refluxed in dioxane (5 ml) for 8 h. GC-MS analysis on the resultant solution showed benzyl bromide, benzyl-methyl-sulfide and benzyl sulfide (MS as above) as the prod-

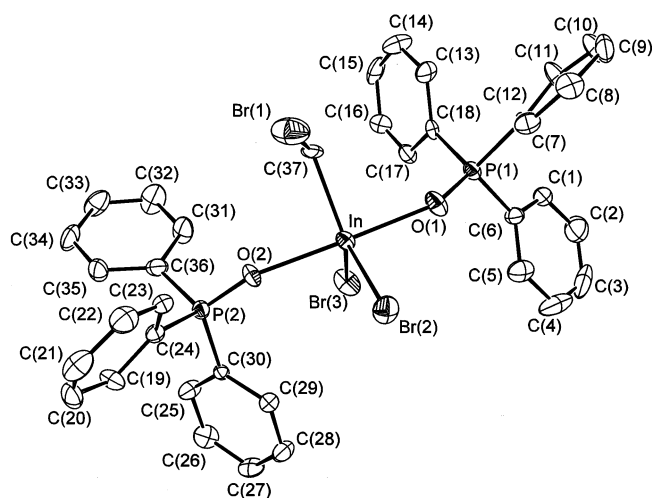


Fig. 1. The molecular structure of $Br_2In[OP(C_6H_5)_3]CH_2Br$ (**1**), (ORTEP diagram), with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

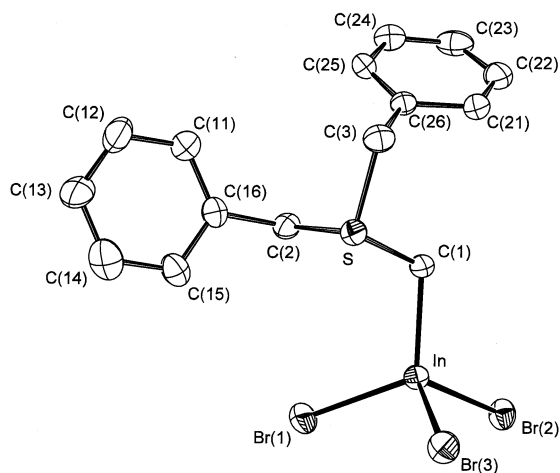


Fig. 2. The molecular structure of $Br_3InCH_2S(CH_2C_6H_5)_2$ (**2**), (ORTEP diagram), with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

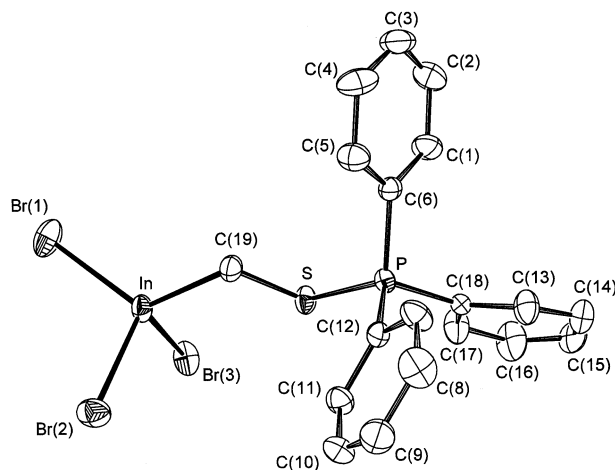


Fig. 3. The molecular structure of $Br_3InCH_2SP(C_6H_5)_3$ (**3**), (ORTEP diagram), with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

ucts, together with unreacted benzaldehyde (or acetophenone).

2.5. Crystallographic studies

Suitable crystals of **1**, **2** and **3** were mounted on glass fiber on a Siemens SMART three-circle diffractometer with graphite-monochromated Mo- K_α radiation and a CCD area detector, controlled by a Pentium-based PC. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were initially introduced in ideal positions and subsequently refined isotropically. The software package, data collection strategy, methodology for structural solutions, and corrections, were as described in an earlier paper [7]. Figs. 1–3 show the molecular structures of **1**, **2**, and **3**, respectively, and Table 1 summarizes crystal and structural refinement data. Those structural results relevant to the present paper are given at Table 2.

2.6. Calculations: methods and models

The PM3 semi-empirical Hamiltonian [10–12], implemented in the GAUSSIAN 98 package [13], was used in all calculations, employing the standard parameters. Molecular geometry was optimized with default convergence criteria, starting from the X-ray structure. For compound **1**, the angles Br–C–In, O–In–O and P–O–In were constrained to their experimental values; only the S–C–In angle was constrained for compound **2**, while S–C–In and P–S–C angles were fixed during geometry optimization of **3**.

Table 1
Crystal data and structural refinement for **1–3**

	1	2	3
Empirical formula	C ₃₇ H ₃₂ Br ₃ InO ₂ P ₂	C ₁₅ H ₁₆ Br ₃ InS	C ₁₉ H ₁₇ Br ₃ InPS
Formula weight	925.12	582.89	662.91
Temperature (K)	296(2)	298(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.0637(5)	9.4196(7)	14.5623(6)
<i>b</i> (Å)	14.5682(5)	11.4496(8)	10.8675(6)
<i>c</i> (Å)	17.4788(5)	17.798(1)	16.1124(8)
β (°)	109.868(2)	102.757(1)	114.805(2)
<i>V</i> (Å ³)	3607.4(2)	1872.1(2)	2314.6(2)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g cm ^{−3})	1.703	2.068	1.902
Absorption coefficient (mm ^{−1})	4.098	7.765	6.360
Crystal size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.40 × 0.40	0.40 × 0.20 × 0.20
2 θ collection range (°)	1.44–22.50	2.13–23.24	1.54–22.50
Total number of reflections	12373	7012	8487
Unique data/parameters	4597/406	2662/181	2994/227
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0624	0.0269	0.0401
<i>R</i> _w [<i>I</i> > 2 σ (<i>I</i>)]	0.1174	0.1129	0.0757
ρ_{max} difference peak and hole (e Å ^{−3})	0.667/−1.002	0.586/−0.615	0.630/−0.610

3. Results and discussion

3.1. Structural results

The general features of the structures **1**, **2** and **3** are in good agreement with those reported for the anion Br₃InCH₂Br[−] [3], and for the neutral adducts of Group 15 ligands, Br₃InCH₂L. The average indium–bromine bond distances of 2.507(1) for **1**, 2.5150(7) for **2** and 2.534 Å for **3**, are close to that for the anion of 2.518(2) Å and for the neutral species, Br₃InCH₂L {L = (C₆H₅)₃N, 2.529(1) [7]; (C₆H₅)₃P, 2.512(2) [5]; (C₆H₅)₃As, 2.508(6) [7]; (C₆H₅)₃Sb, 2.509(5) Å [7]}. Similarly, the In–C bond distances in **1** [2.183(9)], **2** [2.189(5)] and **3** [2.177(6) Å] agree well with the value of 2.13(1) Å in the anion, and with the corresponding values for the neutral compounds, [(C₆H₅)₃N, 2.185(5) Å; (C₆H₅)₃P, 2.18(1) Å; (C₆H₅)₃As, 2.17(5) Å; (C₆H₅)₃Sb, 2.16(3) Å].

The structural difference between **1**, **2** and **3** can be understood in terms of the tautomeric relationship, and hence reactivity, of the parent Br₂InCH₂Br molecule [3] Scheme 1.

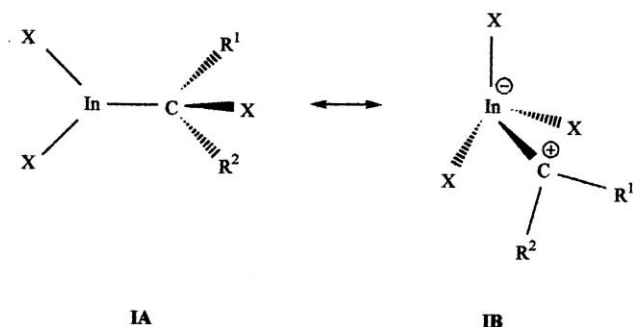
It was shown earlier [3] that this behavior is the consequence of the presence of an indium empty acceptor orbital in **IA**, which strongly favors intramolecular bromide transfer. The net atomic charges calculated for **IA** and **IB** confirmed the existence of two electron deficient sites in the molecule, namely the indium and carbon atoms. The nucleophilicity of an incoming ligand, and its ability to support positive charges at either of these sites, will determine the coordination mode in the resultant organoindium compound.

Triphenylphosphine oxide was found to coordinate at the indium center leading to **1** (Fig. 1) giving a trigonal bipyramidal structure with the two

Table 2
Important bond distances (Å) and angles (°) for **1–3**

	1	2	3
<i>Bond distances</i>			
In–Br ^a	2.507(1), [0.026]	2.5150(7), [0.0175]	2.534(1), [0.075]
In–CH ₂	2.183(9)	2.189(5)	2.177(6)
In–O ^a	2.281(6), [0.007]		
CH ₂ –Br	1.89(1)		
O–P ^a	1.493(7), [0.008]		
P–C _{ar} ^a	1.79(1), [0.02]		1.806(7), [0.018]
C _{ar} –C _{ar} ^a	1.37(2), [0.06]	1.38(1), [0.04]	1.381(1), [0.04]
InCH ₂ –S		1.759(5)	1.815(7)
S–CH ₂ C _{ar} ^a		1.840(5), [0.020]	
CH ₂ –C _{ar} ^a		1.497(5), [0.011]	
S–P			2.068(2)
<i>Bond angles</i>			
Br–In–Br ^a	113.84(5)	106.63(3), [3.72]	105.84(4), [4.84]
Br–In–CH ₂ ^a	123.1(3), [5.0]	112.1(1), [7.2]	112.5(2), [17.1]
O–In–O	178.4(2)		
Br–In–O ^a	90.5(2), [0.3]		
O–In–C ^a	89.2(3), [0.6]		
In–O–P ^a	149.8(5), [7.8]		
In–C–Br	112.8(5)		
In–C–S		113.6(3)	109.3(3)
C–S–C ^a		103.7(3), [3.2]	
C–S–P			101.5(2)
S–P–C _{ar} ^a			109.7(2)

^a Mean value; parentheses indicate experimental uncertainty; square brackets is the difference between highest and lowest values.



Scheme 1.

Table 3

Final heat of formation (in kJ mol⁻¹) of 1–3 and related structures

Molecule	Energy
Br ₂ InCH ₂ Br	–184.74
(C ₆ H ₅) ₃ PO	141.14
1	41.75
(C ₆ H ₅ CH ₂) ₂ S	188.91
2	–204.12
(C ₆ H ₅) ₃ PS	417.28
3	–16.79
InBr ₃	–250.72
(C ₆ H ₅ CH ₂) ₂ S=CH ₂	362.48
Br ₂ InCH ₂ SCH ₂ C ₆ H ₅	–65.87
C ₆ H ₅ CH ₂ Br	90.30

Table 4

Calculated HOMO and LUMO energy levels (in kJ mol⁻¹) for 1–3

Compound	HOMO	LUMO
1	–871.351	–43.268
2	–1032.294	–235.008
3	–997.270	–275.651

triphenylphosphine oxide ligands in apical positions, with an average In–O bond distance of 2.281(6) Å. This is significantly greater than the values of 2.164(1) and 2.171(7) Å reported for the six-coordinate adduct of trimethylphosphine oxide and indium trichloride, and in the more closely related bis-adduct of InCl₃ and Me₂PhPO, for which the In–O distance is 2.196(7) Å [14].

The P=O distances in these adducts are 1.493(12), 1.507(7) for the six-coordinate molecule, and 1.507(10) Å for the five coordinate case, in reasonably good agreement with the present results.

Benzyl sulfide and triphenylphosphine sulfide, on the other hand, are found to coordinate to the methylenic carbon atom leading to the sulfur ylid **2** (Fig. 2) and the triphenylphosphonium-sulfur-methylide **3** (Fig. 3) derivatives. The stereochemistry at the indium atom of **2** and **3** is essentially tetrahedral in both cases, and are

very similar to the situation in the analogous complexes with Group 15 ligands discussed above.

The structure of InX₃(Me₃MS) (X = Cl, Br; M = P, As) are pseudo-tetrahedral [15], which shows that such S donors can coordinate to In under suitable conditions, and hence emphasizes that the presence of a positive charge on the carbon is important in determining the coordination in these organoindium compounds. Another way of rationalizing the interactions of these ligands with Br₂InCH₂Br is in terms of hard and soft acid-bases. The harder phosphine oxide coordinates at the hard indium acid site, whereas the softer sulfur ligands prefer the carbon atom.

3.2. Quantum mechanical calculations

Table 3 gives the calculated final heat of formation of 1–3, and of various related molecules, and Table 4 shows the appropriate energy levels for the HOMO and LUMO orbitals in 1–3. The data in Table 3 allow the Δ*E* for the processes



to be derived. We find, for L=(C₆H₅)₃P=O (*n* = 2), Δ*E* = –55.79 kJ mol⁻¹; for L=(C₆H₅CH₂)₂S (*n* = 1), Δ*E* = –208.29 kJ mol⁻¹; and for L=(C₆H₅)₃P=S (*n* = 1), Δ*E* = –249.33 kJ mol⁻¹, suggesting that adduct formation is energetically favorable in keeping with the ready reaction observed under the mild conditions described in Section 2.

Table 5 shows the calculated bond distances, angles, and bond orders for compounds 1–3. These values agree well with the experimentally determined X-ray results. The relative difference between calculated and crystallographic parameters is always less than ca. 7% except for the In–Br distances, which seems to be an inherent difficulty in this method that produces In–Br bond lengths considerably shorter than experimental values [12,16]. The good fit establishes the reliability of the calculations. Another useful set of data listed in Table 6 gives the net atomic charges on the molecules, and these confirm the ylid and the methylide ligands in compounds **2** and **3**, for which the calculated net atomic charge on the methylene carbon atoms is –0.58 and –0.50 a.u., respectively.

3.3. Spectroscopic results

The calculated charges on the methylene carbon atoms of the compounds prepared in this work and their parent molecule, Br₂In(diox)₂CH₂Br [3], are correlated with their ¹H-NMR spectra in Table 7. There is a clear relationship between the observed ¹H chemical shift and the calculated charge; compounds **2** and **3** with high negative electron density at the methylene carbon atom absorb at a higher fields than compound

Table 5
Important calculated bond distances (Å), angles (°) and orders for **1–3**^a

	1	2	3
<i>Bond distances</i>			
In–Br ^b	2.51(0), [0.73] ^b	2.17(13.72), [0.91] ^b	2.17(14.36), [0.91] ^b
In–CH ₂	2.13(2.43), [0.93]	2.14(2.23), [0.88]	2.13(2.16), [0.85]
In–O ^b	2.12(7.04), [0.49] ^b		
CH ₂ –Br	1.94(2.43), [0.94]		
O–P ^b	1.55(3.33), [1.11] ^b		
P–C _{ar} ^b	1.81(1.12), [0.75] ^b		1.80(0.33), [0.85] ^b
C _{ar} –C _{ar} ^b	1.39(1.46), [1.42] ^b	1.39(0.72), [1.41] ^b	1.39(0.72), [1.41] ^b
InCH ₂ –S		1.74(1.14), [0.99]	1.72(5.23), [1.05]
S–CH ₂ C _{ar} ^b		1.86(1.09), [0.90]	
CH ₂ –C _{ar} ^b		1.48(0.67), [1.01] ^b	
S–P			2.12(2.51), [0.85]
<i>Bond angles</i>			
Br–In–Br ^b	114.3(0.40)	109.6(2.84)	108.8(2.84)
Br–In–CH ₂ ^b	122.9(0.16)	109.3(2.50)	110.1(2.13)
O–In–O	178.4 ^c		
Br–In–O ^b	89.6(0.97)		
O–In–C ^b	90.8(1.79)		
In–O–P ^b	149.8 ^c		
In–C–Br	112.8 ^c		
In–C–S		113.9 ^c	109.3 ^c
C–S–C ^b		104.7(0.96)	
C–S–P			101.5 ^c
S–CH ₂ –C _{ar} ^b		114.3(1.42)	
S–P–C _{ar} ^b			111.6(1.73)

^a Parentheses indicate relative error between calculated and crystallographic measured parameters and values in square brackets correspond to bond orders.

^b Mean value.

^c Constrained parameter during calculations.

Table 6
Net atomic charges (a.u.) in **1–3**

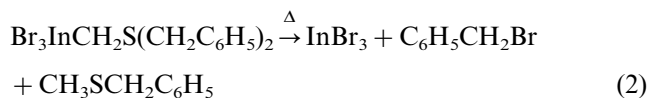
Atom	1	2	3
In	0.44	0.44	0.43
Br(–InBr) ^a	–0.51	–0.37	–0.38
Br(–CH ₂ Br)	–0.15	—	—
C(–InCH ₂)	–0.22	–0.58	–0.50
H(–InCH ₂) ^a	0.13	0.21	0.19
O ^a	–0.70		
S		0.68	–0.10
P	2.36		1.84
C _{ar} ^a	–0.63	–0.17	–0.23
C(ArCH ₂ S–)		–0.36	

^a Mean value.

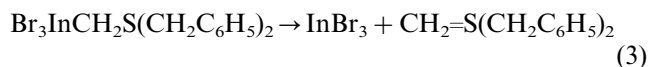
1, whose charge is closer to the parent molecule. Unfortunately, we were not able to detect the corresponding ¹³C resonances for compounds **1–3**, even after long accumulation times, due to the high quadrupolar moment of indium. This problem has been observed in our previous studies [7,17] of organoindium compounds. The decoupled ³¹P-NMR spectra of **1** and **3** (see Section 2) show, in both cases, the expected single line pattern. The observed chemical shift for **1** (δ 26.28 ppm), is readily comparable with the corresponding value measured [18] for the free ligand, (C₆H₅)₃PO (δ 27 ppm). For compound **3**, the observed ³¹P resonance signal (δ 50.78 ppm) is shifted downfield from the corresponding signal [19] of the free ligand, (C₆H₅)₃PS (δ 39.9–43.5 ppm), and this is, again, in keeping with the presence of a triphenylphosphonium-sulfur methyllide ligand, ^δ–CH₂S–^δ+P(C₆H₅)₃.

3.4. Thermal decomposition studies

We have examined the thermal decomposition of compounds **1–3** by TGA analysis. The temperature dependence–weight loss curves for compounds **1** and **3** exhibit a single stage weight loss over the temperature ranges 204–430°C (for **1**) and 230–515°C (for **3**), leaving final residues of 5 and 10% of the initial mass, respectively. The sulfur ylid, **2**, lost weight in four different range of temperatures: ca. 100–200°C (16.3%), 207–274°C (26.2%), 275–429°C (22.6%) and 430–460°C (5.0%). It was not possible to derive any simple decomposition pathway from these results, and we therefore carried out two further experiments in attempts to induce thermal decomposition on compound **2**, under vacuum in a sealed tube at 120°C and in refluxing dioxane. Product analysis, by GC-MS, in both cases, revealed, inter alia, the production of benzyl bromide, benzyl-methyl-sulfide and benzyl sulfide (Eq. (2)).



These results demonstrate that fission of the indium carbon bond in **2** to generate the sulfur ylid (Eq. (3)) is more difficult than



the intramolecular nucleophilic substitutions (Eqs. (4) and (5))

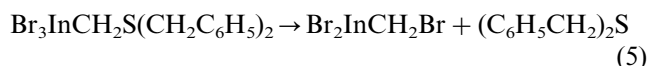


Table 7

¹H-NMR chemical shifts (ppm from TMS) and net atomic charges (a.u.) of the methylene groups in **1–3** and their parent molecules

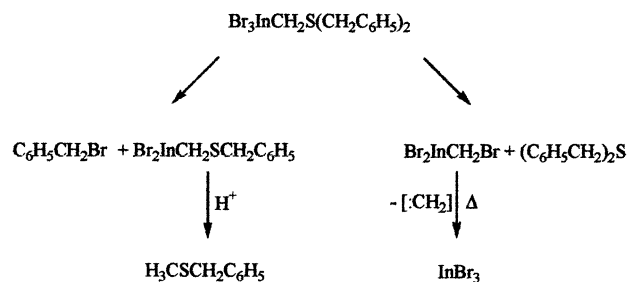
Compound	Net atomic charge	¹ H (δ)
Br ₃ In(diox) ₂ CH ₂ Br ^a	−0.07	2.77
Br ₂ In[(C ₆ H ₅ PO) ₂ CH ₂ Br (1) ^b	−0.22	2.63
Br ₃ InCH ₂ S(CH ₂ C ₆ H ₅) (2) ^c	−0.58	2.05
Br ₃ InCH ₂ SP(C ₆ H ₅) ₃ (3) ^d	−0.50	2.00

^a In CD₃CN.

^b In CDCl₃.

^c In THF-*d*₈.

^d In acetone-*d*₆.

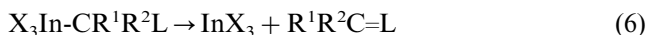


Scheme 2.

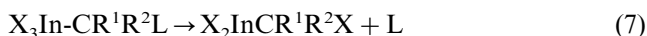
and, therefore, a reasonable pathway for the decomposition is depicted in Scheme 2.

These experimental results are in agreement with the heats of reaction calculated from the data in Table 3, which give $\Delta E = 315.9 \text{ kJ mol}^{-1}$ for Eq. (3), compared with 228.6 for Eq. (4) and 208.3 kJ mol^{-1} for Eq. (5), so that intramolecular substitution is the favored route for these thermal decomposition processes.

In fact, generation of free ylids by the route of Eq. (6) proved to be impractical, as predicted [7] by the highly positive calculated ΔE for this process for a series of adducts (X = Br; R¹ = R² = H; L = P: 241, As: 243, Sb: 276 and S: 316 kJ mol^{-1}).



Furthermore, these values are, in every case, considerably more endothermic than for the reverse reaction (Eq. (7)) leading to the Br₂InCH₂Br starting material (L = P: 199, As: 50, Sb: −58, S: 208 kJ mol^{-1})



and this explains the lack of reactivity of **2** and other related organoindium ylids toward carbonyl compounds.

4. Conclusions

We have postulated previously [3] that the structure and reactivity of halogenomethylic compound of in-

dium, X₂InCR¹R²X reflects the presence of two electron deficient sites, namely the metal center and the halogenomethylic carbon. This concept also explains the results reported in the present paper. Given a ligand capable of accommodating a positive charge, coordination will occur at the carbon atom generating organometallic ylids of the general structure X₃InCR¹R²L, as isolated for the sulfur ligands used in this work. On the other hand, the harder base triphenylphosphine oxide was found to coordinate to the indium center leading to organoindium species of general structure X₂In(L)_nCR¹R²X. These have proved to be useful starting materials for the synthesis of di-indium, [Br₃InCH₂InX₃]^{2−}, [20] and tri-indium, [(Br₃In)₃CH]^{3−}, [21] methane derivatives, by the oxidative insertion of indium bromide into the C–Br bond of [Br₃InCH₂Br][−] and [Br₃InCHBr₂][−], respectively.

Semi-empirical calculations in this and earlier work, again, provide a rationale for the spectroscopic properties, for the thermal decomposition pathway, and for the lack of reactivity of the X₃InCR¹R²L compounds as ylid carriers.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 148 838 for compound **1**, CCDC No. 148 839 for **2** and CCDC No. 148 840 for **3**. 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 www: <http://www.ccdc.cam.ac.uk>).

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