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Coordination Chemistry of Br_2InCH_2Br: Coordination at the Metal Center

Antonio B. de Carvalho, Maria A. M. A. de Maurera, José A. Nobrega, and Clovis Peppe*

Departamento de Quimíca, CCEN, Universidade Federal da Paraíba, Campus I, João Pessoa-PB, Brazil 58059-900

Martyn A. Brown and Dennis G. Tuck

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Marcelo Z. Hernandes, Elson Longo, and Fabricio R. Sensato

Departamento de Quimíca, Universidade Federal de São Carlos, São Carlos-SP, Brazil 13565-905

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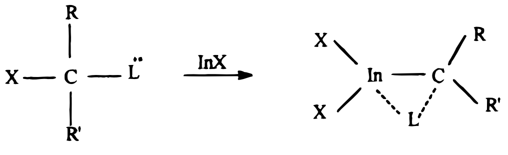
(Bromomethyl)dibromoindium(III), Br_2InCH_2Br, reacts with tetraethylammonium bromide, 1,4-dioxane (diox), or tetrahydrofuran (thf) to produce addition compounds of the general formula $Br_2In(L)_nCH_2Br$ ($L = $ diox, thf, $n = 2$; $L = Br^-$, $n = 1$) in which the ligand is directly attached to the indium atom. The crystal structure of the ionic derivative $[(C_2H_5)_4N][Br_3InCH_2Br]$ has been solved by X-ray diffraction methods: cell constants $a = 10.1710(1)$ Å, $b = 10.1710(1)$ Å, and $c = 35.1745(4)$ Å, space group $P4_12_12$, $V = 3638.78(7)$ Å^3, $Z = 8$, $R = 0.0519$, $R_w = 0.0543$ for 2374 independent reflections. Quantum mechanical calculations, by the PM3 method, on the parent molecule confirm the postulated strong intramolecular interaction between the bromomethylic bromine and the metal center. Complete intramolecular bromide transfer gives the tautomeric structure $Br_3In^{\delta-}CH_2^{\delta+}$. The calculations also satisfactorily predict the bond distances and angles in the $Br_3InCH_2Br^-$ anion. Preliminary investigations of the energetics and chemical properties of $Br_2In(diox)_2CH_2Br$ show that the molecule can decompose via elimination of methylene, which can be trapped by a suitable substrate (carboxylic acid, iodine), demonstrating the potential use of the compound as a methylene-transfer reagent.

Introduction

In the past few years, some important organic transformations mediated by indium compounds have been reported.[1] Relevant examples include the Barbier allylation,[2] the Reformatsky reaction,[2] and the epoxidation of carbonyl compounds.[3] A common feature of these three processes is the presence of a donor group, directly attached to the haloalkyl carbon atom of the corresponding reagent, and a probable initial step in these transformations is that shown in Scheme 1, involving the oxidative insertion of the indium(I) halide, InX ($X = Cl$, Br), at the carbon−halogen bond of the organic reagent. This is in keeping with our earlier finding that InX inserts into the carbon−halogen bonds of alkyl halides,[4,5] dihalides,[6] and trihalides.[7,8] The key step in all these reactions is a strong interaction between the α-donor groups and the metal center, giving an intermediate which reacts readily with carbonyl compounds.

Scheme 1



During the past few years, we have also examined the interactions of α-donor groups with the metal center of organoindium(III) compounds. We have demonstrated[6] that the bromomethyl compound Br_2InCH_2Br can be prepared by the oxidative insertion of indium(I) bromide into the carbon−bromine bond of methylene dibromide, and the coordination chemistry of Br_2InCH_2Br is being extensively explored. The addition of a neutral ligand L ($L = N,N,N',N'$-tetramethylethanedi-

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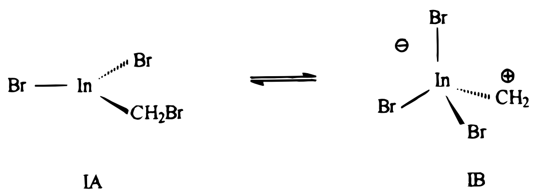
Scheme 2



amine,[6] $P(C_6H_5)_3$,[6] $As(C_6H_5)_3$,[9] $Sb(C_6H_5)_3$,[9] 1,1,3,3-tetramethyl-2-thiourea (tmtu),[10] or dibenzyl sulfide[11]) to Br_2InCH_2Br yields the corresponding X_3InCH_2L adduct, in which the ligand L is directly attached to the methylene carbon atom. These results led to an interpretation of the reactivity of the Br_2InCH_2Br parent molecule in terms of the tautomeric relationship shown in Scheme 2, which can be seen as the consequence of the presence of an empty acceptor orbital on indium in **IA**, strongly favoring intramolecular bromide transfer.

The present paper reports an extension of these studies of the coordination chemistry of Br_2InCH_2Br. The addition of ethers, or bromide, to Br_2InCH_2Br leads to adducts in which the new ligand is attached to the indium atom. We also present semiempirical quantum chemistry calculations using the PM3 method on the parent Br_2InCH_2Br molecule, and its dioxane and bromide adducts, and compare the results with experimental data, which include the X-ray structure of the $[Br_3InCH_2Br]^-$ anion. The calculations suggest that Br_2InCH_2X may act as a methylene transfer reagent with the CH_2 group as an electrophile, and preliminary results on the reactions of the Br_2InCH_2Br with iodine and benzoic acid show that methylene is indeed transferring from the organoindium reagent to the substrate.

Experimental Section

General Data. Indium(I) bromide was prepared by heating the metal with $InBr_3$ in a sealed tube for 24 h at 350 °C. Methylene dibromide (Aldrich) was stored over Linde 4A molecular sieves. Diethyl ether (Merck), tetrahydrofuran (thf), and 1,4-dioxane (diox) (Aldrich) were refluxed over sodium in the presence of benzophenone and distilled before use from the blue ketyl form. Acetonitrile was dried over calcium hydride and distilled before use. Acetone was dried over calcium chloride and distilled before use. Tetraethylammonium bromide (Aldrich) was dried under high vacuum at 70° C; after drying, it was handled under dry nitrogen. Iodine (Merck) was purified by sublimation at normal pressure minutes before use. Benzoic acid (Merck) was sublimed at low pressure.

Indium analysis was carried out by back-titration of excess EDTA by thorium nitrate, and bromine analysis was accomplished by the Volhard method, using the techniques described elsewhere.[7] Microanalysis was performed by the Canadian Microanalytical Services Ltd.

^1H and ^{13}C NMR spectra were recorded on Bruker AC-300L and Varian Unity Plus 300 instruments. Mass spectra were recorded on a Hewlett-Packard HP5890-II GC-MS spectrometer, using a column of methyl silicone.

All preparative work was carried out under dry nitrogen, using standard vacuum line techniques, up to the isolation of the final products. The thf and dioxane adducts of Br_2InCH_2Br are very sensitive to moisture and must be handled under dry nitrogen.

Preparative Details. (i) Br_2InCH_2Br. Indium(I) bromide (1.00 g, 5.13 mmol) and excess CH_2Br_2 (1.80 mL, 4.46 g, 25.6 mmol) were stirred together in acetonitrile (15 mL) until the indium(I) bromide had completely dissolved (ca. 2 h). Removal of the volatiles under high vacuum gave an oil, which was redissolved in diethyl ether; removal of the solvent gave $Br_2InCH_2Br{\cdot}0.5Et_2O$ as a colorless oil (cf. ref 6).

(ii) $Br_2In(diox)_2CH_2Br$. Indium(I) bromide (1.00 g, 5.1 mmol) was suspended in 1,4-dioxane (15 mL), and CH_2Br_2 (4.46 g, 25.6 mmol) was added to the stirred mixture. Stirring was continued until all InBr dissolved (ca. 4−6 h), and the mixture was then filtered to remove any solid residue. The volatiles were removed from the filtrate in vacuo over 2−3 h, giving a colorless crystalline solid identified as $Br_2In(diox)_2CH_2Br$ (yield 2.49 g, 4.54 mmol, 89% based on indium(I) bromide). Anal. Calcd for $C_9H_{18}O_4Br_3In$: In, 21.1; Br, 44.0. Found: In, 22.0; Br, 44.5. ^1H NMR (thf-d_8), δ: 2.60 s, 1H, CH_2; 3.40 s, 8H, dioxane. ^1H NMR (acetonitrile-d_3), δ: 2.77 s, 1H, CH_2; 3.61 s, 8H, dioxane. ^{13}C NMR (acetonitrile-d_3), δ: 18.96, CH_2; 67.53, dioxane.

(iii) $Br_2In(thf)_2CH_2Br$. A suspension of indium(I) bromide (0.50 g, 2.56 mmol) in thf (15 mL) was treated with CH_2Br_2 (2.23 g, 12.8 mmol), and the mixture was stirred until all the solid dissolved (ca. 1−2 h). Small quantities of residue were removed by filtration, and volatile compounds were removed from the filtrate in vacuo to give $Br_2In(thf)_2CH_2Br$ (0.85 g, 1.66 mmol, 65% yield based on indium(I) bromide) as a colorless oil. Anal. Calcd for $C_9H_{18}O_2Br_3In$: In, 22.4; Br, 46.8. Found: In, 23.0; Br, 47.4.

(iv) $[(C_2H_5)_4N][Br_3InCH_2Br]$. A solution of Br_2InCH_2Br in acetonitrile was prepared as in (i) above from 0.50 g (2.56 mmol) of indium(I) bromide. After dissolution of indium(I) bromide, $[(C_2H_5)_4N]Br$ (0.54 g, 2.56 mmol) was added to the solution, and the mixture was stirred for 30 min. All the volatiles were removed under vacuo, and the white solid obtained was washed with ethanol (95%) to yield $[(C_2H_5)_4N][Br_3InCH_2Br]$ (1.24 g, 2.15 mmol, 84%). This compound can be handled in air. Crystals for X-ray determination were grown from an acetonitrile/ethanol solution (1:1, v:v).

Chemical Properties of $Br_2In(L)_2CH_2Br$ (L = diox, thf). (i) Thermal Decomposition. (a) $Br_2In(diox)_2CH_2Br$ (0.41 g, 0.75 mmol) prepared according to the procedure described above was redissolved in 1,4-dioxane (20 mL). The solution was refluxed for 2 h, after which the mixture was taken to dryness under vacuum. The resultant residue was dissolved in ethanol (3 mL); the addition of an equimolar amount of $(C_2H_5)_4NBr$ (0.16 g, 0.75 mmol, in 5 mL of ethanol) led to the precipitation of $[(C_2H_5)_4N][InBr_4]$ (0.36 g, 0.64 mmol, 85%), which was recrystallized in ethanol by heating the suspension to the point of complete dissolution of the precipitate; slow cooling produced colorless needles of the product. Anal. Calcd for $C_8H_{20}NBr_4In$: In, 20.3; Br, 56.6. Found: In, 20.3; Br, 56.6. ^1H NMR (C_2D_6CO), δ: 3.50 q, 2H, CH_2; 1.43 triplet of triplets, 3H, CH_3. Analogous procedures involving $Br_2In(thf)_2CH_2Br$ also led to $[(C_2H_5)_4N][InBr_4]$ in 82% yield.

(b) $Br_2In(thf)_2CH_2Br$ was redissolved in thf (10 mL). The solution was refluxed for 2 h; GC-MS analysis of this solution showed only the presence of thf.

(ii) Reaction with Iodine. Br_2InCH_2Br (1.54 mmol) prepared from indium(I) bromide (1.54 mmol) and CH_2Br_2 in acetonitrile was dissolved in diethyl ether (10 mL); iodine (0.31 g, 1.20 mmol) was added to the ethereal solution, followed by stirring (1 h) and the extraction of $InBr_3$ into water. GC-MS analysis (m/z units) of the ether phase showed the presence of CH_2I_2 ($CH_2I_2^+ = 268$; $CH_2I^+ = 141$) and CH_2BrI ($CH_2BrI^+ = 220{-}222$; $CH_2I^+ = 141$; $CH_2Br^+ = 93{-}95$) with CH_2Br_2 and $CHBr_3$ as minor components.

(iii) Reaction with Benzoic Acid. $Br_2In(thf)_2CH_2Br$ (1.50 mmol) and benzoic acid (0.18 g, 1.50 mmol) were stirred in

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Table 1. Summary of Crystal Data, Intensity Collection, and Structural Refinement for $[(C_2H_5)_4N][Br_3InCH_2Br]$

empirical formula	$C_9H_{22}NBr_4In$
fw	578.74
temp, K	298(2)
wavelength, Å	0.710 73
crystal system	tetragonal
space group	$P4_12_12$
unit cell dimens, Å	$a = 10.1710(1)$ $b = 10.1710(1)$ $c = 35.1745(4)$
volume, Å^3	3638.78(7)
Z	8
d_c, g cm^{-3}	2.113
abs coeff, cm^{-1}	100.62
F(000)	2176
cryst dimens, mm	0.20 × 0.20 × 0.20
θ range for data collcn, deg	2.08−22.48
no. of reflns collected	15 162
no. of indep reflns	2374 [R(int) = 0.0408]
max and min transm	0.324 43 and 0.164 21
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2366/0/156
goodness-of-fit on F^2	1.141
final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0543$, $R_w = 0.1448$
R indices (all data)	$R = 0.0618$, $R_w = 0.1531$
absolute structure parameter	0.06(3)
largest diff peak and hole, e Å^{-3}	2.545 and −0.519

thf (10 mL) at room temperature for 12 h; GC-MS analysis (m/z units) of this solution showed the presence of methyl benzoate ($C_8H_8O_2^+ = 136$; $C_6H_5CO^+ = 105$; $C_6H_5^+ = 77$) and unreacted benzoic acid. Removal of the thf under vacuum, followed by dissolution of the residue in ethanol (5 mL) and addition of $(C_2H_5)_4NBr$ (1.50 mmol), led to the precipitation of $[(C_2H_5)_4N][InBr_4]$.

Crystallographic Measurements. The diffraction data for $[(C_2H_5)_4N][Br_3InCH_2Br]$ **(1)** were collected at the University of Windsor. A single crystal of **1**, dimensions 0.20 × 0.20 × 0.20 mm, was attached to a quartz fiber mounted on a Siemens SMART three-circle diffractometer equipped with graphite-monochromatized Mo Kα radiation and a CCD area detector and controlled by a Pentium-based PC running the SMART software package.[12] ω scans were used in such a way that an initial 180° scan range consisting of 0.3° intervals was followed by three further 120, 180, and 120° scans with ϕ offsets of 88, 180, and 268°, respectively. This strategy samples the sphere of reciprocal space up to $2\theta = 56.62°$. Cell parameters were refined using the centroid values of 300 reflections with 2θ angles up to 56.62°. Raw frame data were integrated using the SAINT program.[13] The structure was solved by direct methods.[14] An empirical absorption correction was applied to the data using the program SADABS.[15] Convergence was achieved at final values of $R = 0.0543$ and $R_w = 0.0618$ for 2366 unique observed reflections. Details of the crystal structure refinement are given in Table 1, and bond distances and angles for the anion, in Table 2. The structure of the anion is shown in Figure 1. Tables of thermal parameters, atomic coordinates, and a complete set of bond distances and angles are available as Supporting Information.

Calculation Methods and Models. The PM3 semiempirical method,[16] implemented in the MOPAC (version 5.0) program package,[17,18] was used with the standard indium

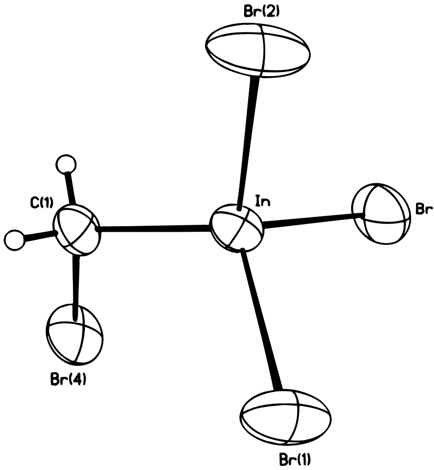

Figure 1. Molecular structure of the $[Br_3InCH_2Br]^-$ anion in **1**, with atoms shown as 30% probability ellipsoids.

Table 2. Interatomic Distances (Å) and Angles (deg) for $Br_3InCH_2Br^-$

Distances			
In−C(1)	2.127(12)	In−Br(1)	2.521(2)
Br(4)−C(1)	1.942(14)	In−Br(2)	2.539(2)
		In−Br(3)	2.494(2)

Angles			
C(1)−In−Br(1)	113.2(4)	Br(1)−In−Br(3)	105.68(8)
C(1)−In−Br(2)	110.3(4)	Br(2)−In−Br(3)	107.62(8)
C(1)−In−Br(3)	114.0(4)	Br(4)−In−C(1)	111.1(7)
Br(1)−In−Br(2)	105.62(7)		

parameters. The geometry optimization of the molecules via gradients and minimization of energy were carried out using the BFGS[18] algorithm, which makes use of first and second derivatives. The Br_2InCH_2Br molecule was assumed to have trigonal planar geometry around the indium atom. The intramolecular bromide-transfer reaction relating structures **IA** and **IB** was modeled via a three-membered-ring In−C−Br intermediate; the indium−bromine (−CH_2Br) distance was gradually decreased from the calculated value for the Br_2InCH_2Br structure to that of Br_3InCH_2.

The $[Br_3InCH_2Br]^-$ anion was modeled using the stereochemistry established by X-ray crystallography (see above). The mono(dioxane) adduct, $Br_2In(diox)CH_2Br$, was modeled in two different ways; the first assumed coordination of the ether at the metal forming a molecule with a tetrahedral $Br_2In(O)C$ kernel, while the second assumed interaction of the ligand with the carbon atom leading to the structure $Br_3InCH_2(diox)$. For the bis(dioxane) adduct, $Br_2In(diox)_2CH_2Br$, both ligands were assumed to be attached to the indium center in a trans configuration. Other isomeric forms were also generated, but all were found to have total energies higher than that of the trans isomer, and the final results discussed in this paper are for this last species.

In all the calculated structures, the indium−bromine bond distances are considerably shorter than the corresponding experimental values. Such differences are inherent in the PM3 method, as has been observed earlier,[18] and possible reasons are outlined elsewhere.[19]

Results and Discussion

Preparations. The insertion of indium(I) bromide into the carbon−bromine bond of dibromomethane,

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reported earlier

$$InBr + CH_2Br_2 \rightarrow Br_2InCH_2Br \qquad (1)$$

occurs in donor solvents such as 1,4-dioxane, tetrahydrofuran, or acetonitrile, and the final products are the corresponding solvates of Br_2InCH_2Br. No reaction was observed in benzene, toluene, or *n*-hexane, so that the donor solvent apparently has an important role in the activation of the monohalide toward oxidative insertion. This is in keeping with an earlier finding[4] that the intractable and insoluble indium(I) halides are soluble in organic solvents in the presence of bases such as *N*,*N*,*N′*,*N′*-tetramethylethanediamine, dimethyl sulfoxide, or 2,2′-bipyridine and that the solvated indium(I) species in such solutions undergo oxidative insertion with substrates containing carbon−halogen[4,5] and metal−halogen bonds.[20,21]

The addition of the bromide anion, as the tetraethylammonium salt, to an acetonitrile solution of Br_2InCH_2Br leads to the air-stable solid $[(C_2H_5)_4N][Br_3InCH_2Br]$, whose crystal structure is discussed below. The adducts $Br_2In(L)_2CH_2Br$ (L = thf, diox) can be obtained by reacting indium(I) bromide and CH_2Br_2 in thf and diox, respectively. The thf adduct is an oily material, but the dioxane derivative is a solid; both are very unstable toward moisture.

The observed chemical ^1H shifts for the CH_2 unit are in the range 2.75−3.07 ppm; ^{13}C resonances appear between 17.6 and 19.0 ppm. The ^1H resonances are comparable to those for the analogous Simmons−Smith reagents, observed at 2.1−2.3 ppm for $BrCH_2ZnBr$,[22] which slowly rearranges to $(BrCH_2)_2Zn$, for which the ^1H resonance is at 3.1 ppm. With the mercury analogues $BrCH_2HgBr$ and $(BrCH_2)_2Hg$,[23,24] the corresponding proton resonances were observed at 2.17 and 3.18 ppm, respectively. The large downfield shift relative to the zinc and mercury analogues indicates a lower electron density at the methylene group; presumably the more acidic character of the indium atom leads to a strong α-interaction with the bromine of the $-CH_2Br$ substituent, as is suggested by the quantum mechanical calculations (see below).

Crystallographic Results. The features of the structure of the anion $Br_3InCH_2Br^-$ (Table 2) are in good agreement with those reported for the neutral adducts Br_3InCH_2L (L = Ph_3P, tmtu).[6,10] The average indium−bromine bond distance is 2.518 Å, close to that for L = Ph_3 P (2.512 Å) or tmtu (2.517 Å), although the range of bond distances is greater in the anion (2.539(2)−2.494(2) Å) than in the neutral species (2.514(2)−2.510(2) Å for L = Ph_3P, 2.525(6)−2.504(6) Å for L = tmtu). These values are all lower than those reported recently[25] for the neutral adduct $Br_2(thf)_2In(CH_2)_4In(thf)_2Br_2$ (*r*(In−Br) = 2.517(1), 2.544(1) Å) and the analogous anion $[Br_3In(CH_2)_4InBr_3]^{2-}$, for which *r* (In−Br)(av) = 2.543(3) Å. Similarly, the In−C bond distance agrees with those in the neutral adducts (2.18(4) Å in both cases) but is lower than that in the diindium compounds,[25] for which *r*(In−C) = 2.154(4) (dioxane adduct) and 2.146(5) (anion) Å. The *r*(C−Br) value in **1**, 1.945(13) Å, is in the normal range for aliphatic C−Br bonds. The sum of the bond angles at indium is 656.3°, as it is in the adducts studied, providing further confirmation of the identical stereochemistry at the metal in all three cases. The In−C−Br(4) angle (111.2(6)°) establishes the quasi-tetrahedral stereochemistry at the carbon atom of the anion. There appears to be some disorder in one of the tetraethylammonium cations, but in view of the interest in the structure of the anion, no attempt was made to resolve this.

Table 3. Calculated Total Energies (eV) for Br_2InCH_2Br, Its Derivatives, and Related Molecules

Br_2InCH_2Br	−1266.807 43	$Br_2In(diox)_2CH_2Br$	−3636.461 43
Br_3InCH_2	−1265.900 56	$InBr_3$	−1118.186 24
$[Br_3InCH_2Br]^-$	−1626.512 26	H_2CCH_2	−297.889 94
$Br_2In(diox)CH_2Br$	−2452.053 86	1,4-dioxane	−1184.680 94
$Br_3InCH_2(diox)$	−2450.702 42		

Table 4. Calculated HOMO and LUMO Energy Levels (eV) for Br_2InCH_2Br and Derivatives

structure	HOMO	LUMO
Br_2InCH_2Br	−11.590	−3.630
Br_3InCH_2	−13.556	−5.155
$[Br_3InCH_2Br]^-$	−6.897	2.626
$Br_2In(diox)CH_2Br$	−10.632	−2.802
$Br_2In(diox)_2CH_2Br$	−10.435	−2.148

Quantum Mechanical Calculations. Table 3 gives the total energies for all calculated structures, and the HOMO and LUMO orbital energies of the organoindium species are listed in Table 4. Calculated bond lengths and angles, net atomic charges, bond orders, and atomic orbital populations for the parent Br_2InCH_2Br compound and its bromide and dioxane adducts are given in Tables 5−7, respectively.

(i) The Br_2InCH_2Br Molecule. The initial modeling of the Br_2InCH_2Br molecule assumed a trigonal planar arrangement around the indium atom. The most significant feature of the calculations is a strong interaction between the indium atom and the bromine of the $-CH_2Br$ group, related to the empty p orbital on indium, perpendicular to the Br_2InC plane. The interaction corresponds to 0.29 au of a formal indium−bromine bond (see Table 6), and on the basis of the low electron population at the p_z orbital of the CH_2Br bromine atom (1.17 au—Table 8), this can be described as a $p_\pi - p_\pi$ bond involving the p_z orbital of each atom. The flow of electron density from CH_2Br to the indium center leaves the CH_2Br group electron deficient, with an excess of +0.19 au. Such a strong interaction indicates a structure in which intramolecular bromide ligand transfer to give tautomer **IB** is inherently probable. The calculated geometrical arrangement around the carbon atom in structure **IA** is quasi-trigonal-planar, with In−C−H and H−C−H angles of 123.5 and 113°, respectively, in keeping with an sp^2 hybridization model in which the carbon atom is electron deficient (+0.57 au) and the least populated orbital is p_z of carbon. The calculated total energies of structures **IA** and **IB** (Table 3) lead to ΔE = 0.907 eV (87 kJ mol^{-1}) for the intraconversion. The intramolecular bromide ligand transfer reaction is

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Table 5. Calculated Bond Lengths (Å) and Angles (deg) for Br_2InCH_2Br and Derivatives

	Br_2InCH_2Br	Br_3InCH_2	$[Br_3InCH_2Br]^-$ [a]	$Br_2In(diox)CH_2Br$	$Br_3InCH_2(diox)$	$Br_2In(diox)_2CH_2Br$
			Distances			
In−Br[b]	2.15	2.15	2.20	2.18	2.15	2.34
In−C	2.17	2.15	2.14	2.13	2.17	2.14
C−H	1.08	1.09	1.09	1.09	1.08	1.09
C−Br		1.99	1.95	1.96		1.94
In−O				2.18		2.23
In−Br($-CH_2Br$)	2.83		3.37	2.88		2.91
C−O					3.19	
			Angles			
Br−In−C[b]	123.3	106.0	112.8	117.1	106.2	118.9
In−C−Br($-CH_2Br$)			111.2	89.4		90.5
In−C−O					176.1	

[a] Experimental values given in Table 3. [b] Average value.

Table 6. Net Atomic Charges (au) and Bond Orders for Br_2InCH_2Br and Derivatives

	Br_2InCH_2Br	Br_3InCH_2	$[Br_3InCH_2Br]^-$	$Br_2In(diox)CH_2Br$	$Br_3InCH_2(diox)$	$Br_2In(diox)_2CH_2Br$
			Atomic Charges			
Br[a]	−0.23	−0.27	−0.32	−0.29	−0.27	−0.34
In	0.26	0.15	−0.03	0.10	0.14	0.04
C	−0.01	0.57	−0.01	−0.04	0.57	−0.07
$H(CH_2)$[a]	0.10	0.04	0.08	0.10	0.05	0.09
Br($-CH_2Br$)	0.00		0.13	−0.01	−0.05	
O(−In)				−0.10		−0.09
O($-CH_2$)					−0.31	
O(free)				−0.24	−0.25	−0.25
C(diox)[a]				0.00	0.03	−0.03
H(diox)[a]				0.08	0.06	0.08
			Bond Orders			
In−Br[a]	1.00	0.93	0.88	0.91	0.93	0.83
In−C	0.99	0.82	0.97	0.98	0.83	0.95
C−Br	0.92		0.95	0.95		0.96
In−Br($-CH_2Br$)	0.29		0.03	0.15		0.08
In−O[a]				0.45		0.39
O−CH_2					0.00	

[a] Average value.

Table 7. Atomic Orbital Populations for Br_2InCH_2 Br and Derivatives

atom (orbital)	Br_2InCH_2Br	Br_3InCH_2	$[Br_3InCH_2Br]^-$	$Br_2In(diox)CH_2Br$	$Br_3InCH_2(diox)$	$Br_2In(diox)_2CH_2Br$
In (s)	1.035	0.878	0.947	1.002	0.881	0.990
In (p_x)	0.660	0.642	0.661	0.662	0.661	0.697
In (p_y)	0.713	0.660	0.686	0.724	0.649	0.772
In (p_z)	0.330	0.667	0.749	0.508	0.664	0.504
C (s)	1.207	1.325	1.195	1.200	1.324	1.206
C (p_x)	1.034	1.104	0.815	1.013	0.878	0.941
C (p_y)	0.993	0.983	1.010	0.953	1.069	0.974
C (p_z)	0.781	0.014	0.990	0.874	0.155	0.945
Br(−In) (s)[a]	1.617	1.584	1.603	1.607	1.583	1.704
Br(−In) (p_x)[a]	1.812	1.956	1.897	1.848	1.876	1.759
Br(−In) (p_y)[a]	1.866	1.868	1.899	1.918	1.949	1.908
Br(−In) (p_z)[a]	1.928	1.863	1.925	1.919	1.865	1.967
Br(−C) (s)	1.948		1.954	1.951		1.954
Br(−C) (p_x)	1.960		1.302	1.878		1.698
Br(−C) (p_y)	1.916		1.957	1.919		1.850
Br(−C) (p_z)	1.175		1.905	1.259		1.547
O(−In, C) (s)[a]				1.789	1.857	1.798
O(−In,C) (p_x)[a]				1.608	1.311	1.534
O(−In,C) (p_y)[a]				1.268	1.307	1.175
O(−In, C) (p_z)[a]				1.443	1.836	1.586

Table 8. Total Energies (eV) for the Br_2InCH_2Br Molecule as a Function of the Carbon−Bromine Bond Distance

r(C−Br), Å	−total energy	ΔE, 10^{-2} eV	r(C−Br), Å	−total energy	ΔE, 10^{-2} eV
1.99	1266.807 43	0	3.10	1265.799 28	100.8
2.10	1266.739 79	6.80	3.20	1265.800 65	100.7
2.50	1266.225 11	58.2	3.30	1265.803 35	100.4
2.80	1265.893 15	91.4	3.40	1265.802 70	100.5
3.00	1265.803 80	100.4	3.60	1265.900 56	90.7

depicted in Figure 2, in which r(C−Br) is taken as the reaction coordinate; the total energies were calculated with C−In−Br, Br−In−C, and all dihedral angles allowed to move freely, with all other internal coordinates constrained. The total energies, calculated as a function of r(C−Br), are given in Table 8, and the possible transition state based on a three-membered In−C−Br ring, was detected at r(C−Br) = 3.1 Å. This transition state and the important parameters are illustrated in Figure 3.

Complete transfer of bromide to the metal center gives tautomer **IB**, in which the In−C bond order is 0.82, compared with 0.99 in **IA**. The thermodynamic instability of **IB**, together with the weakening of the In−C bond, will drive the elimination of the methylene group, leaving $InBr_3$ as final product, as found when Br_2InCH_2Br is heated in dioxane, thf, or acetonitrile. From the values in Table 3, the calculated ΔE for the process

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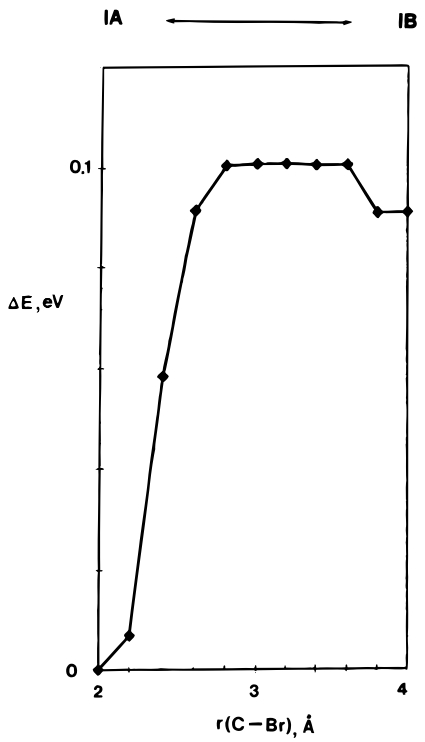


Figure 2. Energetics of the intramolecular bromide-transfer reaction in Br_2InCH_2Br.

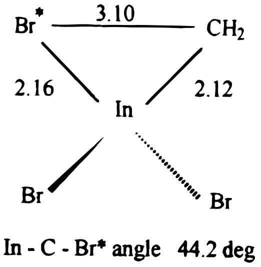


Figure 3. Transition state of the bromide-transfer reaction.

$$Br_3InCH_2 \rightarrow InBr_3 + {}^1/_2H_2C{=}CH_2 \qquad (2)$$

is −1.231 eV (−119 kJ mol^{-1}). Taken with the calculated ΔE for the tautomeric change **IA** → **IB** (see above), the complete decomposition of Br_2InCH_2Br

$$Br_2InCH_2Br \rightarrow InBr_3 + {}^1/_2C_2H_4 \qquad (3)$$

is exoenergetic ($\Delta E = -0.324$ eV, or −31 kJ mol^{-1}).

(ii) Coordination Chemistry of Br_2InCH_2Br. The calculated net atomic charges for the tautomeric structures **IA** and **IB** reveal the existence of two electron deficient sites in the molecule, namely the indium and carbon atoms. Coordination may therefore occur at either of these two sites, depending on the ligand in question, as is observed experimentally.

(iii) The $[Br_3InCH_2Br]^-$ Anion. The structure of the salt $[(C_2H_5)_4N][Br_3InCH_2Br]$ is described above, and the calculations predict the observed tetrahedral environment of the Br_3InC kernel of the anion. The bond orders for the three In−Br bonds vary from 0.86 to 0.88; and the value for In−C is 0.97. A major consequence of the coordination of bromide to indium is a decrease in the $In-Br(CH_2)$ interaction, whose bond order drops from 0.29 in Br_2InCH_2Br to 0.06 in the anion.

(iv) The Dioxane Adducts of Br_2InCH_2Br. The parent compound forms a 1:2 adduct with 1,4-dioxane. Since the Br_2InCH_2Br molecule has two electron-deficient sites, we began the calculations by considering a 1:1 adduct in which the different modes of coordination were possible. The first involves $Br_2In(diox)CH_2Br$ with a distorted tetrahedral $Br_2In(O)C$ kernel, while in the second the dioxane is attached to the carbon atom to produce the organoindium ylide $Br_3InCH_2(diox)$, analogous to the Br_3InCH_2L compounds reported earlier.[6,10] The calculated total energies (Table 3) are −2452.054 eV for $Br_2In(diox)CH_2Br$ and −2450.702 eV for $Br_3InCH_2(diox)$, implying a preferred coordination of the ether to the metal. Furthermore, the $Br_3InCH_2(diox)$ model gives a large calculated C−O bond distance (3.19 Å), indicating zero bond formation (see Table 3; bond order C−O = 0). The In−O interaction is only moderate, judging by the calculated bond order of 0.45, but the establishment of this new bond expands the coordination sphere of the indium center and so contributes sensibly to a decrease in the interaction between the metal and the bromomethylic bromine atom; the calculated bond order drops from 0.29 in Br_2InCH_2Br to 0.15 in the mono(dioxane) adduct. Finally, dioxane coordination at the metal center increases the electron density at the bromomethylic carbon atom from −0.01 to −0.04 in the mono(dioxane) adduct.

The bis(dioxane) adduct, $Br_2In(diox)_2CH_2Br$, shows the same general trends. The indium−oxygen interaction is even weaker (bond order 0.39), and the bond order for the $In-Br(CH_2)$ bromine interaction is only 0.08. The calculated charge at the carbon atom is now −0.07 au. The calculated bond distance for r(In−C) is in good agreement with the value in $Br_2(diox)_2In(CH_2)_4In(diox)_2Br_2$ (2.145(4) Å),[25] but the values for r(In−Br) and r(In−O) are both smaller than the experimented values; such differences have been noted earlier in the case of r(In−Br).[18,19]

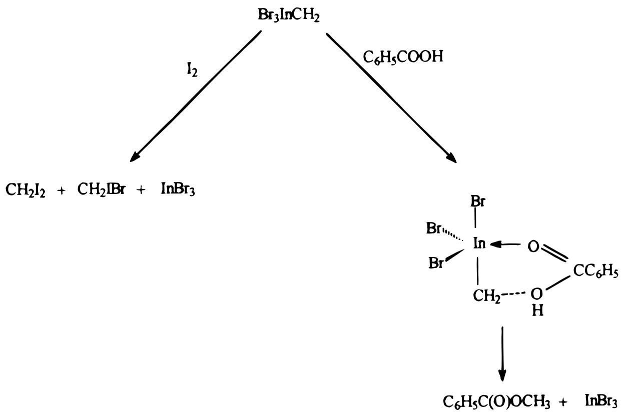
The major difference between $[Br_3InCH_2Br]^-{}_4$ and the bis(dioxane) adduct is in the strength of the new indium−ligand interaction. In the anionic complex, the In−Br bond has a bond order of 0.87, whereas the new In−O bonds in the neutral adduct are considerably weaker (bond order 0.39), and these differences are illustrated by the differing stabilities of these substances. No sign of decomposition of $[(C_2H_5)_4N][Br_3InCH_2Br]$ was detected for aqueous ethanol or acetone solutions, whereas $Br_2In(diox)_2CH_2Br$ decomposed in acetone, releasing CH_2 (see Experimental Section). The weaker the indium−ligand interaction, the easier is intramolecular bromide transfer from the bromomethylic ligand to the metal center

$$Br_2In(L)CH_2Br \rightarrow Br_2InCH_2Br + L \qquad (4)$$

followed by the tautomerization **IA** → **IB** to give the reactive carbonium-containing structure Br_3InCH_2.

Preliminary Studies on the Reactivity of Br_2InCH_2Br. The adducts $Br_2In(L)_2CH_2Br$ (L = thf, diox) decompose in refluxing thf (bp 65 °C) or dioxane (bp 100 °C), giving an ~85% yield of $(C_2H_5)_4][InBr_4]$ in

Scheme 3



such reactions. The postulated overall sequence is

$$\mathrm{Br_2In(L)CH_2Br} \rightarrow [\mathrm{:CH_2}] + \mathrm{InBr_3} \xrightarrow{\mathrm{Br^-}} \mathrm{InBr_4}^- \qquad (5)$$

with CH_2 being lost as some gaseous derivative. In keeping with this scheme, reaction with I_2 gives CH_2I_2 and CH_2IBr as the main products. Cleavage of the In−C bond leads directly to CH_2I_2, while intramolecular halogen exchange in the intermediate prior to cleavage gives $BrCH_2I$. Further ligand exchange may lead to the minor products CH_2Br_2 and $CHBr_3$. Finally, the addition of benzoic acid to Br_2InCH_2Br, followed by intramolecular ligand exchange, yields methyl benzoate. These reactions are summarized in Scheme 3.

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Supporting Information Available: Listings of nonhydrogen coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **1** (5 pages). Ordering information is given on any current masthead page.

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