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Structure and reactivity of derivatives of dihalogenomethyl indium(III) halides, X_2InCHX_2 (X = Cl, Br, I)

Clovis Peppe [a,*], Dennis G. Tuck [b,1], Fabiano M. de Andrade [a], José A. Nóbrega [c],
Martin A. Brown [b], Robert A. Burrow [a]

[a] *Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, Campus UFSM,
97105-900 Santa Maria-RS, Brazil*
[b] *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont., Canada N9B3P4*
[c] *Departamento de Química, CCT, Universidade Estadual da Paraíba-UEPb, R. Juvêncio Arruda s/n, 58109-790 Campina Grande-PB, Brazil*

Abstract

The reactions of indium monohalides, InX with haloforms, CHX_3, in 1,4-dioxane (diox), produce the dioxane adducts of dihalogeno–dihalogenomethyl–indium(III), $X_2In(diox)_nCHX_2$ (X = Cl, Br, $n = 1$; X = I, $n = 2$) compounds. The ionic derivative $[(C_2H_5)_4N] [Cl_3InCHCl_2]$ was prepared and its crystal structure determined by X-ray means. The reactions of the $X_2In(diox)_nCHX_2$ compounds are significantly different from those of the related X_2InCH_2X compounds. The dihalogenomethyl derivatives react with strong electrophiles suggesting dihalogenomethyl substituents of mild nucleophilic character, while the carbon atoms in the halogenomethyl derivatives are electrophilic.
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1. Introduction

Metal carbenoids such as the Simmons–Smith reagent, iodomethylzinc iodide, $IZnCH_2I$ have found extensive applications in olefin cyclopropanation [1]. More recently, it was determined that they are able to homologate copper(I) reagents, RCu by adding methylene units to produce new organocopper–zinc reagents of the type $R(CH_2)_nCu \cdot ZnI_2$ able to react with electrophiles [2]. The synthesis and structural investigation of related new metal carbenoids is therefore of great interest.

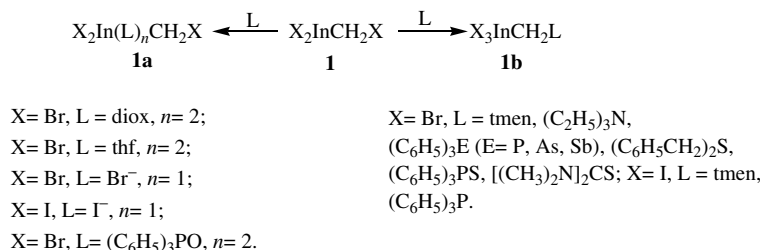Previous papers have investigated the preparation, crystal structure and reactivity of X_2InCH_2X (X = Br, I) compounds, **1** and their derivatives with anionic and neutral donors, L. Adduct formation may occur at either the metallic center, **1a** favored by hard ligands, or at the halogenomethyl carbon atom, in which case ylid complexes of InX_3, **1b** were identified (Scheme 1) [3].

Related work has shown that the analogous dihalogenomethyl compounds X_2InCHX_2 (X = Cl, Br, I) could also be prepared by the reaction of InX with CHX_3 in acetonitrile, although the only stable derivatives then obtained were the salts of the $[X_3InCHX_2]^-$ anions. All efforts to obtain adducts with neutral donors such as dimethylsulfoxide (dmso), triphenyl phosphine and 1,1,3,3-tetramethyl-2-thiourea (tmtu) resulted in the formation of adducts of the corresponding indium(III) halide, InX_3L_n(X = Cl, L = tmtu, $n = 2$; X = Cl, I, L = Ph_3P, $n = 2$; X = Cl, Br, L = dmso, $n = 3$; X = I, L = tmtu, $n = 1$) [4]. We now report the isolation of

* Corresponding author. Tel.: +55552208868; fax: +55552208031.
E-mail address: peppe@quimica.ufsm.br (C. Peppe).
[1] In memmorian.

$$X_2In(L)_nCH_2X \xleftarrow{\;L\;} X_2InCH_2X \xrightarrow{\;L\;} X_3InCH_2L$$
$$\mathbf{1a} \qquad\qquad \mathbf{1} \qquad\qquad \mathbf{1b}$$

X= Br, L = diox, n= 2;
X= Br, L = thf, n= 2;
X= Br, L= Br⁻, n= 1;
X= I, L= I⁻, n= 1;
X= Br, L= (C₆H₅)₃PO, n= 2.

X= Br, L = tmen, (C₂H₅)₃N,
(C₆H₅)₃E (E= P, As, Sb), (C₆H₅CH₂)₂S,
(C₆H₅)₃PS, [(CH₃)₂N]₂CS; X= I, L = tmen,
(C₆H₅)₃P.

Scheme 1. The coordination chemistry of X₂InCH₂X compounds, **1**.

the 1,4-dioxane (diox) adducts, $X_2In(diox)_nCHX_2$. The salts $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$ and $[(C_6H_5)_4P]$ $[Br_3InCHBr_2]$ were also prepared from $X_2In(diox)$-CHX_2, and the structure of the chlorine derivative determined by X-ray methods. Further, we have demonstrated that the dihalogenomethyl substituents on the $X_2In(diox)_nCHX_2$ compounds is of a mild nucleophilic character, reacting only with strong electrophiles, such as allyl bromide derivatives, carboxylic and mineral acids.

2. Experimental

2.1. General

The preparation of InX (X = Cl, Br, I) source and treatment of starting materials, methods of elemental analysis, and spectroscopic techniques were those described earlier [4]. Allyl bromide and 3-bromo-2-methyl-prop-1-ene were commercial reagents (Aldrich) and distilled before used. 1,4-Dioxane was dried over sodium/benzophenone and distilled before used. Other reagents and solvents (ACS grade) were used as supplied.

2.2. Preparation of $X_2In(diox)_nCHX_2(X = Cl, Br, n = 1; X = I, n = 2)$

InX (X = Cl, 0.40 g, 2.66 mmol; X = Br, 0.40 g, 2.05 mmol; X = I, 0.50 g, 2.07 mmol) was suspended in 20 mL of freshly distilled dry 1,4-dioxane (diox). Excess CHX₃ (X = Cl, 1.00 mL, 12.50 mmol; X = Br, 0.55 mL, 6.30 mmol; X = I, 1.63 g, 4.14 mmol) was added to the suspension and the mixture stirred to complete dissolution of InX (X = Cl, 6 h; X = Br, 4 h; X = I, 16 h). At this point, any small quantity of solid impurity was removed by filtration, the volatiles removed from the filtrate under high vacuum, and the solution held at low pressure for ca. 3 h. This procedure yields the chloro and bromo derivatives as white solids (X = Cl, 0.71 g, 2.00 mmol, 75%; X = Br, 0.90 g, 1.68 mmol, 82%). The iodine compound was isolated by adding toluene (10 mL) to the yellow solid obtained; this removes

excess CHI₃, leaving I₂In(diox)₂CHI₂ as a yellow powder (0.95 g, 1.32 mmol, 64%). All the $X_2In(diox)_nCHX_2$ compounds are air sensitive. Spectroscopic studies and handling for elemental analysis were conducted under dry nitrogen. Anal. Calc. for Cl₂In(diox)CHCl₂, C₅H₉O₂InCl₄: In 32.1%. Found: 31.1%. ¹H NMR (CD₃CN): δ = 5.60 (s, 1H), 3.60 (s, 8H); ¹³C NMR (CD₃CN): δ = 67.58, 46.65. Calc. for Br₂In(diox)CHBr₂, C₅H₉O₂InBr₄, In 21.5%. Found: 21.2%. ¹H NMR (CD₃CN): δ = 5.36 (s, 1H), 3.60 (s, 8H); ¹³C NMR (CD₃CN): δ = 67.77, 37.31. Calc. for I₂In(diox)₂CHI₂, C₉H₁₇O₄InI₄, In 14.1%, I 62.5. Found: 13.9%, 62.4%. ¹H NMR (CD₃CN): δ = 4.30 (s, 1H), 3.59 (s, 16H); ¹³C NMR (CD₃CN): δ = 67.50, −47.75.

2.3. Preparation of [Q] [X₃InCHX₂] [Q = (C₂H₅)₄N, X = Cl; Q = (C₆H₅)₄P, X = Br]

The salts [Q][X₃InCHX₂] were prepared from the corresponding X₂In(diox)CHX₂ compounds. Thus, to a solution of X₂In(diox)CHX₂ (X = Cl, 2.66 mmol; X = Br, 2.05 mmol) in 20 mL of dry acetonitrile was added an equimolar amount of QX [X = Cl, Q = (C₂H₅)₄N, 2.66 mmol; X = Br, Q = (C₆H₅)₄P, 2.05 mmol]. The mixture was stirred for ca. 2 h. At this point, any solid impurity was removed by filtration. The salts [Q] [X₃InCHX₂]were isolated as described below:

[(C₂H₅)₄N] [Cl₃InCHCl₂]: Removal of all the volatiles from the filtrate solution, gave an oil, which was redissolved in 20 mL of a mixture (1:1, v/v) of acetonitrile:ethanol (95%). Slow evaporation of the solvent in air deposited colorless crystals of [(C₂H₅)₄N] [Cl₃InCHCl₂] (0.70 g, 1.6 mmol, 60%). Anal. Calc. for C₉H₂₁NInCl₅: In 26.4%. Found: 25.9%. ¹H NMR [(CD₃)₂ CO]: δ = 5.63 (s, 1H), 3.47 (q, J = 7.5 Hz, 8H); 1.37 (tt, J = 7.5 Hz, J = 2.4 Hz, 12H); ¹³C NMR [(CD₃)₂ CO]: δ = 53.01, 46.65, 7.67.

[(C₆H₅)₄P] [Br₃InCHBr₂]: Addition of 20 mL of ethanol (95%) to the acetonitrile filtrate solution and slow concentration in air deposited colorless crystals of [(C₆H₅)₄P] [Br₃InCHBr₂] (1.45 g, 1.67 mmol, 82%). Anal. Calc. for C₂₅H₂₁PInBr₅: In 13.2%. Found: 13.2%. ¹H NMR [(CD₃)₂CO]: δ = 7.87–7.82 (m, 20H), 5.34 (s, 1H); ¹³C NMR [(CD₃)₂CO]: δ = 136.39, 135.60

(d, $J = 9.8$ Hz), 131.33 (d, $J = 12.1$ Hz), 118.86 (d, $J = 83.70$ Hz), 45.57.

2.4. The thermal decomposition of $Br_2In(diox)CHBr_2$

A solution of $Br_2In(diox)CHBr_2$ (2.2 g, 4.1 mmol) in dioxane (10 mL) was heated under reflux for 3 h. After this period, all the volatiles were removed under vacuum and condensed in a liquid nitrogen trap; a GC/MS analysis of the condensed liquid revealed only the solvent, 1,4-dioxane, and residual $CHBr_3$, used in the preparation of $Br_2In(diox)CHBr_2$. The brown solid residue left in the reaction flask, after pumping, was chromatographed on a silica gel column; initial eluent was *n*-hexane, then an *n*-hexane:ethyl acetate mixture with increasing proportion of the ester up to the pure ester was used; finally very polar solvents (acetone and ethanol) were employed as eluents; no organic derivative from the initial reagent, $Br_2In(diox)CHBr_2$, was detected.

In a parallel experiment, the brown solid residue, obtained by removal of the solvent was partitioned in a separation funnel with water and toluene; to the aqueous phase was added $(C_2H_5)_4NBr$ (0.86 g, 4.1 mmoles) leading to the precipitation of $[(C_2H_5)_4N](InBr_4)$ (1.69 g, 3.0 mmol, 73%). Anal. Calc. for $C_8H_{20}InBr_4$: In, 20.4%; Br, 56.4%. Found: In, 20.1%; Br, 56.6%. ^{1}H NMR [$(CD_3)_2CO$]: $\delta = 3.50$ (q, $J = 7.5$ Hz, 2H), 1.43 (tt, $J = 7.5$ Hz, $J = 2.4$ Hz, 3H).

2.5. The reaction of $Br_2In(diox)CHBr_2$ with benzoic acid

$Br_2In(diox)CHBr_2$ (1.65 g, 3.08 mmol) and benzoic acid (0.37 g, 3.08 mmol) were stirred in 1,4-dioxane (10 mL) for 16 h and then heated under reflux for additional 3 h. All the volatiles were removed under high vacuum and condensed in a trap cooled by liquid nitrogen; this solution revealed the presence of CH_2Br_2 by GC/MS. After pumping, a solid residue is left in the flask; this solid was re-dissolved in 20 mL of an ethanol:acetone (1:1, v/v) solution containing $(C_2H_5)_4NBr$ (0.64 g, 3.08 mmol); a tedious recrystallization process by reduction of the solution volume by slow evaporation open to the atmosphere leads first to the deposition of $[(C_2H_5)_4N](InBr_4)$ (0.76 g, 1.35 mmol), 44% based on initial $Br_2In(diox)CHBr_2$ as colorless needles. Anal. Calc. for $C_8H_{20}InBr_4$: In, 20.4%; Br, 56.4%. Found: In, 20.1%; Br, 56.5%. ^{1}H NMR [$(CD_3)_2CO$]: $\delta = 3.50$ (q, $J = 7.5$ Hz, 2H), 1.43 (tt, $J = 7.5$ Hz, $J = 2.4$ Hz, 3H). Ceased the deposition of $[(C_2H_5)_4N](InBr_4)$ occurred the precipitation of colorless plates of $[(C_2H_5)_4N][Br_2In(O_2CC_6H_5)_2]$ (0.78 g, 1.20 mmol), 39% based on initial $Br_2In(diox)CHBr_2$. Anal. Calc. for $C_{22}H_{30}NO_4InBr_2$: In, 17.8%; Br, 24.7%. Found: In, 17.3%; Br, 24.5%. ^{1}H NMR (CD_3CN): $\delta = 7.40$–8.10

(m, 10H), 3.16 (q, $J = 7.5$ Hz, 8H), 1.20 (tt, $J = 7.5$ Hz, $J = 2.4$ Hz, 12H).

2.6. The reaction of $X_2In(diox)_nCHX_2$ (X = Br, n = 1; X = I, n = 2) with HX in the presence of 1,1,3,3-tetramethyl-2-thiourea (tmtu), $[(CH_3)_2N]_2CS$, and InX_3

$X_2In(diox)_nCHX_2$ (X = Br, $n = 1$, 1.65 g, 3.08 mmol; X = I, 2.01 g, 2.48 mmol) and two molar equivalents of tmtu were stirred in 1,4-dioxane (10 mL) for 2 h. An excess of gaseous HX was passed through the solution, followed by addition of solid InX_3 (X = Br, 3.08 mmol; X = I, 2.48 mmol). After 1 h of continuous stirring, all the volatiles were removed under high vacuum. This treatment produced an oily material. Stirring this oil in ethanol 95% (10 mL) caused the precipitation of $[\{[(CH_3)_2N]_2CS\}_2CH_2][InX_4]_2$ [X = Br, 3.12 g (colorless crystals), 2.71 mmol, 88%; X = I, 3.42 g (yellow solid), 2.24 mmol, 90%]. Analytical and spectroscopic data for these compounds are as follows:

$[\{[(CH_3)_2N]_2CS\}_2CH_2][InBr_4]_2$: Anal. Calc. for $C_{11}H_{14}N_4S_2In_2Br_8$: In, 20.02%; Br, 55.72%; C, 11.49%; H, 2.26%; N, 4.87%. Found: In, 19.96%; Br, 55.52%; C, 11.36%; H, 2.21%; N, 4.72%. Molar conductivity (1 mmol L^{-1}, CH_3CN): 249 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 3.55$ (s, 12H), 5.15 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 38.29$, 44.72, 173.88.

$[\{[(CH_3)_2N]_2CS\}_2CH_2][InI_4]_2$: Anal. Calc. for $C_{11}H_{14}N_4S_2In_2I_8$: In, 15.11%; I, 66.64%; C, 8.66%; H, 1.70%; N, 3.67%. Found: In, 15.07%; I, 66.33%; C, 8.63%; H, 1.66%; N, 3.52%. Molar conductivity (1 mmol L^{-1}, CH_3CN): 258 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 3.55$ (s, 12H), 5.15 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 38.29$, 44.72, 173.88.

2.7. The reaction of $I_2In(diox)_2CHI_2$ with allyl bromide: the preparation of 4,4-diiodo-but-1-ene

To a solution of $I_2In(diox)_2CHI_2$ prepared from equimolar amounts (0.82 mmol) of InI (0.20 g) and CHI_3 (0.33 g) in 1,4-dioxane (10 mL) was added allyl bromide (0.14 mL, 1.64 mmol). The mixture stirred for 4 h. After this time, diethyl ether (40 mL) was added to the solution and the reaction was quenched with water (10 mL). The organic phase was extracted and washed with additional 10 mL of water. The organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum. The oily residue was purified in a silica gel column with hexane as eluent to yield 4,4-diiodo-but-1-ene (173 mg, 0.56 mmol, 68% based on initial $I_2In(diox)_2CHI_2$). It is important to note that the column chromatography must be carried out as quickly as possible to avoid light-induced decomposition of the product, 4,4-diiodo-but-1-ene. ^{1}H NMR ($CDCl_3$): $\delta = 3.12$ (triplet of multiplets, [3]$J = 6.6$Hz, [4]$J = 1.3$ Hz, [4]$J = 1.0$ Hz, 2H),

4.90 (t, $^3J = 6.6$ Hz, 1H), 5.18 (doublet of multiplets, $^3J = 16.9$ Hz, $^2J = 1.3$ Hz, $^4J = 1.3$ Hz, 1H), 5.28 (doublet of multiplets, $^3J = 10.2$ Hz, $^2J = 1.7$ Hz, $^4J = 1.0$ Hz, 1H), 5.68 (m, $^3J = 16.9$ Hz, $^3J = 10.2$ Hz, $^3J = 6.6$ Hz, 1H); ^{13}C NMR (CDCl$_3$): $\delta = -27.42$, 51.64, 119.29, 136.34; MS (70 eV, EI): m/z (%): 308 (M, 25), 267 (5), 183(100).

2.8. The reaction of I$_2$In(diox)$_2$CHI$_2$ with 3-bromo-2-methyl-prop-1-ene: the preparation of 4,4-diiodo-2-methyl-but-1-ene

To a solution of I$_2$In(diox)$_2$CHI$_2$ prepared from equimolar amounts of InI (0.20 g, 0.82 mmol) and CHI$_3$ (0.33 g, 0.82 mmol) in 1,4-dioxane (10 mL) was added 3-bromo-2-methyl-prop-1-ene (0.16 mL, 1.64 mmol). The mixture was kept under stirring for 1 h at room temperature and at 60 °C for one additional hour. An identical work up to that described for the reaction with allyl bromide (Section 2.7) afforded 4,4-diiodo-2-methyl-but-1-ene (143 mg, 0.44 mmol, 54% based on initial I$_2$In(diox)$_2$CHI$_2$). ^{1}H NMR (CDCl$_3$): $\delta = 1.73$ (s, 3H), 3.19 (d, $^3J = 7.6$ Hz, 2H), 4.87 (d, $^2J = 1.5$ Hz, 1 H), 5.05 (d, $^2J = 1.5$ Hz, 1 H), 5.10 (t, $^3J = 7.6$, 1H); MS (70 eV, EI): m/z (%): 322 (M, 4), 195 (47), 67(100).

2.9. Crystallographic measurements

A suitable crystal of [(C$_2$H$_5$)$_4$N][Cl$_3$InCHCl$_2$] was mounted on a glass fiber, and X-ray diffraction data was collected on a Rigaku AFC65 instrument with graphite monochromated Mo Kα radiation (0.71073 Å). Cell constants and orientation matrices for data collection were obtained using 25 reflections in the range $8.59 \leqslant 2\theta \leqslant 16.07$. The space group was identified from the systematic absences as $P2_1/c$, and this was subsequently confirmed by the successful structure refinement. Corrections were applied for decay, absorption (semi-empirical using psi-scans), Lorentz and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included initially in ideal positions, and subsequently refined isotropically. Other details of the data collection and structure refinement are given in Table 1. Programs used in solving the structure are in [5–10].

3. Results and discussion

We have demonstrated in previous papers that the molecule Br$_2$InCH$_2$Br contains two electron deficient sites, the metallic center and the halomethylic carbon atom [3]. Accordingly, it forms stable adducts with the ligand attached at either the In or C atoms (see Scheme 1). Hard ligands such as halides and oxygen donors coordinate to the metal atom, while soft ligands (phosphines, arsines, sulfides, selenides) were found bonded to the halomethylic carbon. The molecules X$_2$InCHX$_2$ demonstrate very different pattern of Lewis acid behavior, the essence of which is that they give stable adducts only with ligands such as halides by coordination at the indium atom, as described previously [4]. The dioxane adducts synthesized in this study also involve coordination at the metallic center, as revealed by NMR spectroscopic data displayed in Table 2, which summarizes the chemical shifts associated to the dihalomethyl substitu-

Table 1
Crystal data and structural refinement of [(C$_2$H$_5$)$_4$N][Cl$_2$CHInCl$_3$]

Empirical formula	C$_9$H$_{21}$Cl$_5$InN
Formula weight	435.36
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.421(19)
b (Å)	16.377(35)
c (Å)	16.289(17)
β (°)	92.045(10)
V (Å^3)	3578(9)
Z	8
D_{calc} (Mg/m^3)	1.62
Absorption coefficient (mm^{-1})	2.047
$F_{(000)}$	1728
Theta range for data collection (°)	2.0–25.0
Index ranges	$0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 19$
Reflections collected	6813
Independent reflections	6517 [$R_{int} = 0.12$]
Absorption correction	φ-scan
Max. and min. transmission	1.000 and 0.738
Refinement method	Full-matrix least-squares on F
Data/restraints/parameters	2765/0/290
Goodness-of-fit on F	1.92
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.050$, $wR_2 = 0.044$
Largest diff. peak and hole (e Å^{-3})	1.20 and −1.02

Table 2
^{1}H and ^{13}C Resonances of the dihalomethyl substituent on the X$_2$In(diox)$_n$CHX$_2$ compounds and related molecules

Compound	^{1}H	^{13}C
Cl$_2$In(diox)CHCl$_2$	5.60	46.6
Br$_2$In(diox)CHBr$_2$	5.36	37.3
I$_2$In(diox)$_2$CHI$_2$	4.30	−47.8
[Cl$_3$InCHCl$_2$]$^-$	5.63	46.6
[Br$_3$InCHBr$_2$]$^-$	5.34	45.6
[I$_3$InCHI$_2$]$^{-a}$	3.95	−23.2
CH$_2$Cl$_2$	5.32	54.0
CH$_2$Br$_2$	5.00	20.3
CH$_2$I$_2$	3.34	−62.5
CHCl$_3$	7.27	77.5
CHBr$_3$	6.84	12.1
CHI$_3$	5.00	−139.9

[a] Data from [4].

ent attached to indium together with the parent CHX_3 reagents and related molecules.
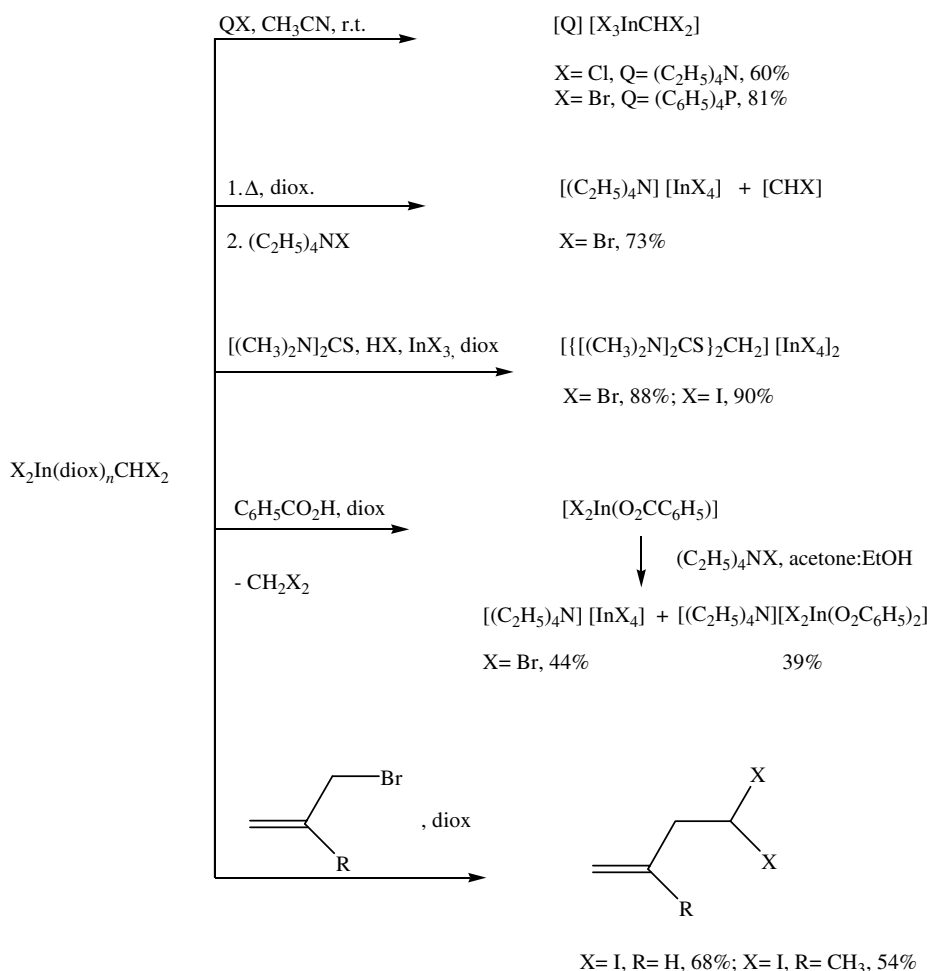
The most fundamental chemical properties of the $X_2In(diox)_nCHX_2$ compounds are depicted at Scheme 2. The compounds are of marginal stability. The bromine derivative decomposes in refluxing dioxane to $InBr_3$, the trihalide was isolated as the tetrabromoindate(III) following reaction with tetraethylammonium bromide; but we were not able to detect any identifiable product derived from the organyl substituent after careful GC/MS analysis; it is possible that gaseous products were formed and lost before product analysis.

The dioxane ligand attached to the metallic center is easily replaced by halide anions. Thus, crystalline $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$ and $[(C_6H_5)_4P]$ $[Br_3InCHBr_2]$ were prepared from the corresponding $X_2In(diox)_n$-CHX_2 compounds. Crystals of both compounds were examined by single crystal X-ray methods. In the case of the bromine derivative, the diffraction data were recorded satisfactorily but it proved impossible to refine the structure beyond $R < 15\%$, and the analysis was abandoned; disorder in the anion seems the most likely explanation for this failure. We successfully determined

the crystal structure of $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$. The refinement showed the presence of two independent ion pairs in the unit cell. The compound crystallizes in alternate layers of both types of anions, with the cations between these layers. Fig. 1 shows a cross-section of the layers; crystallographic symmetry generates equivalent ions stacked down the z-axis. The two corresponding anions are identical within the experimental error, and are so treated in this discussion. The two cations differ only by the conformation of the ethyl groups.

The structure of one anion is shown in Fig. 2. The other is identical as mentioned above and selected distances are listed in Table 3. The structure of the $[Cl_3In-CHCl_2]^-$ anion clearly establishes the four-coordinate indium(III) species. The stereochemistry around the indium atom is slightly distorted tetrahedral (sum of all angles at In 656(3)°).

The Cl(3,4,5)–In–C1 angles (mean value 111.6° for In1 and 111.3° for In2) are larger than the ideal value for a tetrahedron, and this is presumably imposed by the size of the $CHCl_2$ substituent. The In–Cl distances (mean value 2.371 Å for both anions) are slightly greater than those in $InCl_4^-$ for which the In–Cl distances are in the range

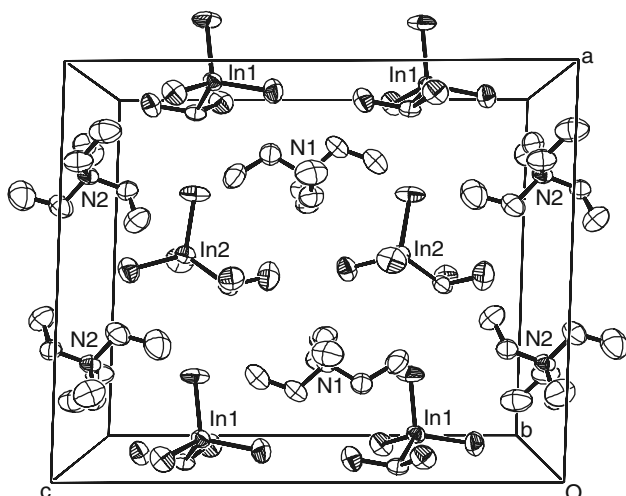Scheme 2. Fundamental chemical properties of $X_2In(diox)_nCHX_2$ compounds.

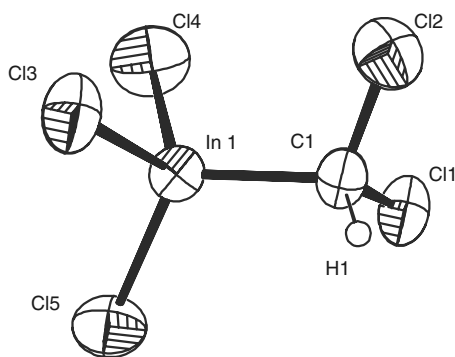Fig. 1. Layers arrangement in the crystal structure of [(C$_2$H$_5$)$_4$N] [Cl$_3$InCHCl$_2$].

Fig. 2. Molecular structure of the [Cl$_2$CHInCl$_3$]$^-$ anion and numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for the [Cl$_2$CHInCl$_3$]$^-$ anions

In1–Cl3	2.376(4)	In2–Cl8	2.372(4)
In1–Cl4	2.371(4)	In2–Cl9	2.368(4)
In1–Cl5	2.366(4)	In2–Cl10	2.374(3)
In1–C1	2.17(1)	In2–C2	2.17(1)
Cl1–C1	1.80(1)	Cl6–C2	1.77(1)
Cl2–C1	1.76(1)	Cl7–C2	1.76(1)
Cl3–In1–Cl4	107.0(1)	Cl8–In2–Cl9	108.7(2)
Cl3–In1–Cl5	107.9(1)	Cl8–In2–Cl10	107.2(1)
Cl3–In1–C1	110.2(3)	Cl8–In2–C2	114.8(4)
Cl4–In1–Cl5	106.9(1)	In2–C2–Cl6	110.8(6)
Cl4-In1–C1	109.7(3)	Cl9–In2–Cl10	106.6(1)
Cl5–In1–C1	114.8(3)	In2–C2–Cl7	110.2(6)
In1–C1–Cl1	110.8(6)	Cl9–In2–C2	108.9(3)
In1–C1–Cl2	110.1(6)	Cl6–C2–Cl7	110.1(7)
Cl1–C1–Cl2	109.9(6)	Cl10–In2–C2	110.3(3)

2.345–2.355 Å [11,12], and in the [CH$_3$InCl$_3$]$^-$ containing In–Cl distances in the range 2.394–2.409 Å [13]; this is ascribed by repulsion between the bulky CHCl$_2$ substituent and the chloride ligands bonded to the metal atom. This effect imposes a closing in the Cl–In–Cl angles followed by the increasing of the Cl–In–C angles at the anion. The constrained Cl–In–Cl angles forces the increasing "p" orbital contribution in the sp^3 hybrids direct toward the In–Cl bonds, and this effect is responsible for the slightly longer In–Cl distances. In consequence of this, the sp^{3}Hybrid toward the In–C bond contains a higher "s" character, causing a shorter In–C bond distance [2.17(1) Å for both In1 and In2] in [Cl$_3$InCHCl$_2$]$^-$ when compared to [CH$_3$InCl$_3$]$^-$ (2.213 Å) [13].

The X$_2$In(diox)$_n$CHX$_2$ compounds react with selected electrophiles. Both, mineral (HX, X = Br,I) and benzoic acid provoked the hydrolysis of the In–C bonds in the molecules. From the reaction of Br$_2$In(diox)CHBr$_2$ and benzoic acid, organic product analysis by GC/MS revealed the production of CH$_2$ Br$_2$ (M, 172/174/176). The inorganic products isolated after reaction with (C$_2$H$_5$)$_4$NBr were the salts [(C$_2$H$_5$)$_4$N] [InBr$_4$] and [(C$_2$H$_5$)$_4$N] [Br$_2$In(O$_2$CC$_6$H$_5$)$_2$], which come from ligand redistribution reaction of the primary Br$_2$In(O$_2$C$_6$H$_5$) formed by the hydrolysis (Eq. (1)). Ligand redistribution is a common process in indium(III) chemistry and in fact mixed bromide and benzoate ligands complexes of indium(III) are known to redistribute [14].

$$2Br_2In(O_2CC_6H_5) \rightarrow InBr_3 + BrIn(O_2CC_6H_5)_2 \qquad (1)$$
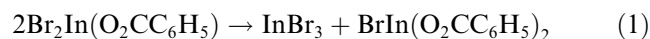
Hydrolysis of X$_2$In(diox)$_n$CHX$_2$ (X = Br, I) with the corresponding mineral HX acid follows a similar pathway. Hydrolysis in the presence of 1,1,3,3-tetramethyl-2-thiourea and InX$_3$ yields the ionic species [{[(CH$_3$)$_2$N]$_2$CS}$_2$CH$_2$][InX$_4$]$_2$, which we have reported before [15]. The reaction leading to these salts seems a double nucleophilic displacement at the CH$_2$ site of CH$_2$X$_2$, the primary product of hydrolysis.

The acid hydrolysis of the X$_2$In(diox)$_n$CHX$_2$ molecules suggests a nucleophilic electronic character of the dihalomethyl substituent attached to the metal. Accordingly, we attempted to react the X$_2$In(diox)$_n$CHX$_2$ species with selected organic electrophiles. They failed to react with carbonyl compounds, but they react with allyl bromide derivatives. Thus, 4,4-diiodo-but-1-ene and 4,4-diiodo-2-methyl-but-1-ene were prepared from allyl bromide and 3-bromo-2-methyl-prop-1-ene, respectively. The scope of this coupling reaction is limited, since reactions with 4-bromo-2-methyl-buten-2-ene, 2-bromo-1-phenyl-propen-1-ene and 3-bromo-cyclohexen-1-ene afforded a complex mixture of products. A plausible intermediate to accommodate these results is depicted at Fig. 3, that shows the interaction of the allylic substrate with the organoindium compound to produce a 6-membered ring intermediate, with the coupling of the CHX$_2^-$ nucleophile to the γ carbon following a S$'_N$ mechanism. Further, allyl halides containing substituents R^1 and R^2 different of hydrogen will inhibit the carbon–carbon coupling reaction, presumably by steric hindrance.
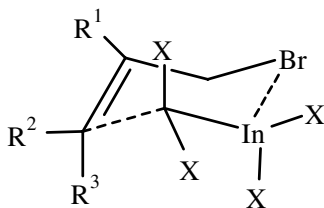
Fig. 3. Proposed intermediate for the reaction of $X_2In(diox)_nCHX_2$ with allyl bromide derivatives

4. Conclusion

The oxidative insertion of indium monohalides into the carbon–halogen bonds of methylene trihalides affords dihalogeno–dihalogenomethyl–indium(III) organometallics, which form adducts with hard ligands by coordination of the Lewis bases to the metallic center. Structural information about the organoindium compounds was obtained by solving the crystal structure of the ionic derivative $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$. The halogenomethylic substituents of the dioxane adducts of X_2InCHX_2 compounds are of a mild nucleophilic character, and react only with strong electrophiles such as allyl halides derivatives, mineral and carboxylic acids. The compounds remain inert upon reaction with milder electrophiles, such as carbonyl compounds. These findings indicates that it is possible to modulate the electronic character of the α-halogenoalkyl substituent attached to indium carbenoids of general formula $X_2InCR^1R^2X$, easily obtained by inserting InX into carbon–halogen bond of dialkyldihalides, $R^1R^2CX_2$, by the correct choice of the substituents R's. Electron withdrawing R's groups determine nucleophilic characteristics on the haloalkyl substituent, as indeed we have observed for the compounds derived from dibromoacetonitrile ($R^1 = CN$, $R^2 = H$) [16], trichloroacetonitrile ($R^1 = CN$, $R^2 = Cl$) [17], and dichloroketones [$R^1 = C(O)R$, $R^2 = H$] [18], which easily couple to carbonyl compounds to generate new carbon–carbon bonds. Carbenoids derived from CH_2X_2 substrates have the halogenomethyl group of considerable electrophilic character to the point to accept electron pair of suitable Lewis bases to generate organoindium ylids of general structure X_3InCH_2L, such as we have isolated in previous works [3].

5. Supporting material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC No. 248952. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or http://www.ccd.cam.ac.uk).

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