

Articles

Synthesis of Dihalomethyl Compounds of Indium, X_2InCHX_2 , and a Study of Their Coordination Chemistry

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Indium(I) halides, InX ($X = Cl, Br, I$), react with haloforms, CHX_3 , to give X_2InCHX_2 derivatives. Treatment of the latter with $(C_2H_5)_4N^+X^-$ gives the 1:1 electrolytes $[(C_2H_5)_4N][X_3InCHX_2]$, but with neutral ligands L ($L =$ dimethylsulfoxide (dmsu), 1,1,3,3-tetramethyl-2-thiourea (tmtu), triphenylphosphine), the products were the adducts of the corresponding indium trihalide, InX_3L_n ($X = Cl, L = tmtu, n = 2$; $X = Cl, L = Ph_3P, n = 2$; $X = Cl, L = dmsu, n = 3$; $X = Br, L = dmsu, n = 3$; $X = I, L = Ph_3P, n = 2$; $X = I, L = tmtu, n = 1$). $[(C_2H_5)_4N][X_3InCHX_2]$ ($X = Br, I$) reacts with InX to give, after the addition of $(C_2H_5)_4NX$, the salts $[(C_2H_5)_4N]_2[X_3InCHXInX_3]$.

Introduction

We have demonstrated that halomethyl complexes of indium(III), X_2InCH_2X ($X = Br, I$), can be prepared by the oxidative insertion of an indium monohalide, InX , into the carbon–halogen bond of the appropriate methylene dihalide.¹ The addition of halide anions X^- to these species yields the corresponding salt of $[X_3InCH_2X]^-$, but on treatment with neutral ligands, L ($L = Ph_3P$,¹ tmen,¹ or tmtu²), the corresponding phosphorus, nitrogen, or sulfur ylides X_3InCH_2L were obtained. We now report the reactions of indium monohalides, InX , with haloforms, CHX_3 ($X = Cl, Br, I$), and again we find that InX inserts oxidatively into one carbon–halogen bond of CHX_3 to give X_2InCHX_2 derivatives. Some of chemical properties of these compounds have been investigated, especially their coordination chemistry with anionic and neutral ligands and their reaction with InX leading to halo–dimetallo–methane derivatives $X_2InCHXInX_2$, isolated and structurally characterized as the salts $[(C_2H_5)_4N]_2[X_3InCHXInX_3]$ ($X = Br, I$).

Experimental Section

General Data. Indium monohalides were prepared by heating metal and trihalide together in a sealed tube.³ $CHCl_3$ (Merck) was refluxed over anhydrous calcium chloride and distilled before used; $CHBr_3$, CHI_3 , N,N,N',N' -tetramethylethanediamine (tmen), and 1,1,3,3-tetramethyl-2-thiourea (tmtu)

(Aldrich) were used as supplied. $(C_2H_5)_4N^+X^-$ salts ($X = Cl, Br, I$) (Aldrich) were dried over P_2O_5 ; dimethylsulfoxide (dmsu) (Merck) was dried over Linde 4A molecular sieves; triphenylphosphine (Aldrich) was recrystallized from anhydrous diethyl ether. Acetonitrile and CH_2Cl_2 (ACS grade; Merck) were refluxed over calcium hydride and distilled before use. Acetone (ACS grade; Merck) was refluxed over anhydrous calcium chloride and distilled before use. Toluene (ACS grade; Merck), diethyl ether (ACS grade; Merck), n -hexane (ACS grade Merck), and petroleum ether (ACS grade; Merck) were dried over sodium and distilled before use.

Indium analysis involved back-titration of excess EDTA with thorium nitrate. In a typical analysis, ca. 50 mg of the compound was destroyed in nitric acid, the resultant solution neutralized with sodium hydroxide, and the pH adjusted to 3 using a buffer of potassium hydrogen phthalate (0.1 M) and HCl (0.1 M). Excess EDTA (10^{-2} M) was then added, and the mixture was titrated with a standard solution (10^{-2} M) of thorium(IV) nitrate, using xylenol orange as indicator. Halide analysis was by the Volhard method, involving silver halide precipitation and back-titration with potassium thiocyanate solution. Microanalysis was by Canadian Microanalytical Services Ltd. Conductivities were measured in a standard platinum electrode cell, standardized with 1 M aqueous KNO_3 . Proton NMR were recorded on a Varian EM 360 spectrometer, and ^{13}C NMR on a Bruker AC300L Instrument.

All preparative work was conducted under a dry nitrogen atmosphere, using standard vacuum line techniques up to the isolation of the products, which are air stable.

Preparation of $[(C_2H_5)_4N][Cl_3InCHCl_2]$. Indium monochloride (0.30 g, 2.00 mmol) and $CHCl_3$ (3.00 mL, 4.38 g, 37.5 mmol) were stirred together in acetonitrile (15 mL) until the monochloride was consumed (ca. 48 h). A white precipitate, an impurity resulting from the oxidation of $InCl$, was filtered off and discarded. All the volatiles were removed from the solution under vacuum to give an oil, which was redissolved in acetonitrile (15 mL); tetraethylammonium chloride (0.33 g, 2.0 mmol) was added, and volatiles again were removed under

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(1) Annan, T. A.; Tuck, D. G.; Khan, M. A.; Peppe, C. *Organometallics* 1991, 10, 2159.

(2) Souza, A. C.; Peppe, C.; Tian, Z.; Tuck, D. G. *Organometallics* 1993, 12, 3354.

(3) Contreras, J. G. Ph.D. Thesis, Simon Fraser University, 1972.

(4) Weast, R. C. *Handbook of Chemistry and Physics*, 57th ed.; CRC Press: Boca Raton, FL, 1976.

Table 1. Analytical Results

| compd | indium, % | | halogen, % | |
|----------------------------------------------------------------------------------------------------------------------|-----------|-------|-------------------|-------|
| | found | calcd | found | calcd |
| (C ₂ H ₅) ₄ N[Cl ₃ InCHCl ₂] | 26.2 | 26.4 | 28.5 ^a | 40.8 |
| (C ₂ H ₅) ₄ N[Br ₃ InCHBr ₂] ^b | 17.2 | 17.5 | 55.3 ^a | 60.8 |
| (C ₂ H ₅) ₄ N[I ₃ InCHI ₂] | 12.8 | 12.9 | 70.0 | 71.1 |
| InCl ₃ (tmtu) ₂ | 22.8 | 23.7 | 21.5 | 21.9 |
| InCl ₃ (Ph ₃ P) ₂ | 15.7 | 15.4 | 14.8 | 14.3 |
| InCl ₃ (dmsO) ₃ | 25.0 | 25.2 | 23.0 | 23.6 |
| InBr ₃ (dmsO) ₃ | 18.7 | 19.5 | 40.2 | 40.7 |
| InI ₃ (Ph ₃ P) ₂ | 11.1 | 11.3 | 38.0 | 37.3 |
| InI ₃ (tmtu) | 18.3 | 18.3 | 62.0 | 60.6 |
| [(C ₂ H ₅) ₄ N] ₂ [(Br ₃ In) ₂ CHBr] ^c | 21.4 | 21.7 | 52.0 | 52.6 |
| [(C ₂ H ₅) ₄ N] ₂ [(I ₃ In) ₂ CHI] | 16.4 | 16.5 | 63.5 | 63.8 |

^a Halide bonded to carbon may not be completely detected by the Volhard method. ^b Found: C, 6.56; H, 3.35; N, 2.13. Calcd: C, 16.44; H, 3.22; N, 3.13. ^c Found: C, 18.60; H, 3.77; N, 2.69. Calcd: C, 19.20; H, 3.89; N, 2.64.

vacuum. Addition of 10 mL of ethanol caused the precipitation of [(C₂H₅)₄N][Cl₃InCHCl₂] as colorless crystals (0.60 g, 1.38 mmol, 69% based on InCl). Analytical results for this and other compounds are collected in Table 1.

Preparation of [(C₂H₅)₄N][Br₃InCHBr₂]. Indium monobromide (1.03 g, 5.28 mmol) and CHBr₃ (2.0 mL, 5.79 g, 22.9 mmol) were stirred in acetonitrile (15 mL) until all the monobromide dissolved (ca. 2 h). Small traces of residual solid were removed by filtration, and tetraethylammonium bromide (1.11 g, 5.29 mmol) was added to the filtrate. All the volatile materials were removed from the solution to give an oil, which was redissolved in 20 mL of acetone/ethanol (1:1, v/v); on standing, this solution deposited colorless crystals of [(C₂H₅)₄N][Br₃InCHBr₂] (2.74 g, 4.16 mmol, 79% based on InBr).

Preparation of [(C₂H₅)₄N][I₃InCHI₂]. Indium monoiodide (0.51 g, 2.10 mmol) and CHI₃ (0.83 g, 2.10 mmol) were stirred in acetonitrile (10 mL) until the monoiodide dissolved (ca. 4 h). Small traces of residual solid were removed by filtration, and tetraethylammonium iodide (0.54 g, 2.10 mmol) was added to the filtrate. The solution was reduced in volume by ca. 30% in vacuo, at which point yellow crystals of CHI₃ (0.38 g, 0.96 mmol) (¹H NMR in CDCl₃: 5.00 ppm) precipitated and were removed by filtration. Additional concentration of the solution led to by precipitation of [(C₂H₅)₄N][I₃InCHI₂] as yellow crystals (0.90 g, 1.00 mmol, 48% based on InI).

Reactions of Cl₂InCHCl₂ with Neutral Ligands. Indium monochloride (0.30 g, 2.00 mmol) and CHCl₃ (3.00 mL, 4.48 g, 37.5 mmol) were stirred in acetonitrile (15 mL) until the monochloride dissolved (ca. 48–72 h). A white precipitate was filtered off and discarded, the volatiles were removed from the solution under vacuum, and the residue so obtained was redissolved in acetonitrile (15 mL). The ligand L (L = Ph₃P, dmsO, tmtu) was added to the solution, and the reactions were worked up as follows:

1,1,3,3-Tetramethyl-2-thiourea. tmtu (0.53 g, 4.02 mmol) was added and the mixture stirred for 30 min; all the volatiles were removed under vacuum to leave an oil, which on treatment with toluene (10 mL) precipitated InCl₃(tmtu)₂ (0.44 g, 0.91 mmol, 45% based on InCl) as a white powder, which was filtered off and dried under vacuum.

Triphenylphosphine. Triphenylphosphine (0.52 g, 2.00 mmol) was added and the solution concentrated to 50% of its initial volume. The colorless crystals which precipitated, and which were removed, were shown to be Ph₃P (0.29 g, 1.11 mmol; mp = 81–82 °C, lit.³ mp 80 °C). Volatiles were removed under vacuum to yield an oil; addition of *n*-hexane (10 mL) led to the precipitation of InCl₃(Ph₃P)₂ (0.34 g, 0.46 mmol, 34% based on InCl) as a white powder, which was collected and dried.

Dimethyl Sulfoxide. In the case of X = Cl, dmsO (0.43 mL, 0.47 g, 6 mmol) was added to the solution, which was concentrated to half its initial volume, when InCl₃(dmsO)₃ (0.30

g, 0.66 mmol, 33.1% based on InCl) deposited as a white powder, which was collected and dried.

Reaction of Br₂InCHBr₂ with dmsO. This reaction was investigated in two different ways:

Method i. Reaction with Equimolar Quantities of InBr and CHBr₃. Indium monobromide (0.89 g, 4.56 mmol) and CHBr₃ (0.40 mL, 1.16 g, 4.58 mmol) were stirred in acetonitrile (15 mL) until the monobromide dissolved (ca. 1 h). Small traces of residual solids were removed, and dmsO (0.98 mL, 1.07 g, 13.7 mmol) was added to the filtrate. The solution was pumped under vacuum to yield an oil, which was redissolved in hot ethanol (40 mL); after storage at –18 °C, InBr₃(dmsO)₃ (1.53 g, 2.60 mmol, 57% based on InBr) precipitated and was collected by filtration and dried.

Method ii. Reaction with Excess CHBr₃. Indium monobromide (0.51 g, 2.62 mmol) and CHBr₃ (2.00 mL, 5.78 g, 22.9 mmol) were stirred in acetonitrile (15 mL) until the monobromide dissolved. Small traces of residual solids were removed, and dmsO (2.40 mL, 2.64 g, 33.8 mmol) was added to the filtrate. The solution was pumped under vacuum to yield an oil; addition of diethyl ether again led to the precipitation of InBr₃(dmsO)₃ (0.90 g, 1.53 mmol, 58% based on InBr) as a white powder.

Reaction of I₂InCHI₂ with tmtu. Indium monoiodide (0.36 g, 1.49 mmol) and CHI₃ (0.58 g, 1.49 mmol) were stirred in acetonitrile (15 mL) until the monoiodide dissolved (ca. 4 h). Small traces of residual solids were removed by filtration, and tmtu (0.40 g, 3.03 mmol) was added to the filtrate; evaporation to 50% of the initial volume led to the deposition of 0.40 g of a solid, which was filtered off and dried under vacuum. It was shown by GC/MS to be a mixture of CHI₃ and tmtu. The volatiles were removed from the filtrate to leave an oil; addition of petroleum ether (10 mL) led to the precipitation of InI₃(tmtu) (0.33 g, 0.53 mmol, 35% based on InI) as a white powder, which was collected and dried.

Reaction of I₂InCHI₂ with Ph₃P. Indium monoiodide (0.51 g, 2.10 mmol) and CHI₃ (0.83 g, 2.10 mmol) were stirred in acetonitrile (15 mL) until the monoiodide dissolved (ca. 4 h), and small traces of residual solids were removed by filtration. Ph₃P (1.10 g, 4.20 mmol) was added to the filtrate, which was concentrated to 50% of its initial volume. The yellow solid (0.24 g) which deposited was discarded since it contained no indium. When the filtrate was kept at –18 °C, InI₃(Ph₃P)₂ precipitated as a white powder, which was collected and dried (1.10 g, 1.10 mmol, 52% based on InI).

Reaction of I₂InCHI₂ with dmsO. Indium monoiodide (0.30 g, 1.24 mmol) and CHI₃ (0.49 g, 1.24 mmol) were stirred in acetonitrile (15 mL) until the monoiodide dissolved (ca. 4 h), traces of residual solids were removed, and dmsO (0.30 mL, 0.33 g, 4.23 mmol) was added to the filtrate. The filtrate was concentrated under vacuum to 50% and cooled to –18 °C, which led to the precipitation of yellow crystals (0.60 g), which were filtered off and dried under vacuum. The analytical results for this material (C, 8.66; H, 2.02; In, 13.2; 159.0) are not those for InI₃(dmsO)₂ or I₂InCHI₂(dmsO)_{*n*}, and the formulation of this product is not possible at this point (see below).

Preparation of [(C₂H₅)₄N]₂[Br₃InCHBrInBr₃]. [(C₂H₅)₄N][Br₃InCHBr₂] (0.53 g, 0.80 mmol) and InBr (0.16 g, 0.80 mmol) were stirred in acetonitrile (15 mL) until the monobromide dissolved (ca. 2 h); (C₂H₅)₄NBr (0.17 g, 0.80 mmol) was added to the solution, and residual solids were removed. The filtrate was pumped to dryness to yield an oil, which was redissolved in 20 mL of acetone/ethanol (1:1 v/v); on standing, this solution yielded [(C₂H₅)₄N]₂[Br₃InCHBrInBr₃] (0.61 g, 0.57 mmol, 71.1% based on InBr) as colorless crystals, which were filtered off and dried.

Preparation of [(C₂H₅)₄N]₂[I₃InCHIInI₃]. [(C₂H₅)₄N][I₃InCHI₂] (1.02 g, 1.14 mmol) and InI (0.28 g, 1.14 mmol) were stirred in acetonitrile (15 mL) until the monoiodide dissolved; (C₂H₅)₄NI (0.29 g, 1.14 mmol) was added to the solution, residual solids were removed, and the filtrate was concentrated

Table 2. Molar Conductivities^a

| compd | molar conductivity (Ω ⁻¹ cm ² mol ⁻¹) |
|---------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| (C ₂ H ₅) ₄ N[Cl ₃ InCHCl ₂] | 138 |
| (C ₂ H ₅) ₄ N[Br ₃ InCHBr ₂] | 166 |
| (C ₂ H ₅) ₄ N[I ₃ InCHI ₂] | 157 |

^a All measurements in CH₃CN solution at concentrations of ca. 1mM; standard value¹⁰ for 1:1 electrolytes in CH₃CN 120–160 Ω⁻¹ cm² mol⁻¹.

Table 3. ¹H and ¹³C NMR Spectra of X₂InCHX₂ Derivatives

| compd | ¹ H ^a | ¹³ C ^a | assgnt |
|------------------------------------------------------------------------------------------------------|-----------------------------|------------------------------|-----------------------------------------------------|
| [(C ₂ H ₅) ₄ N][Cl ₃ InCHCl ₂] ^b | 5.63, s (1) | <i>c</i> | InCHCl ₂ |
| | 3.13, q (8) | 51.4 | NCH ₂ CH ₃ |
| | 1.20, tt (12) | 7.2 | NCH ₂ CH ₃ |
| [(C ₂ H ₅) ₄ N][Br ₃ InCHBr ₂] ^d | 5.41, s (1) | 36.3 | InCHBr ₂ |
| | 3.51, q (8) | 52.9 | NCH ₂ CH ₃ |
| | 1.39, tt (12) | 7.7 | NCH ₂ CH ₃ |
| [(C ₂ H ₅) ₄][I ₃ InCHI ₂] ^c | 3.95, s (1) | -23.2 | InCHI ₂ |
| | 3.17 q, (8) | 51.6 | NCH ₂ CH ₃ |
| | 1.15, tt (12) | 7.3 | NCH ₂ CH ₃ |
| InCl ₃ (tmtu) ₂ ^d | 3.20, s | | S=C[N(CH ₃) ₂] ₂ |
| InCl ₃ (Ph ₃ P) ₂ ^c | 7.44, s, br | | PC ₆ H ₅ |
| InCl ₃ (dmsO) ₃ | <i>f</i> | | |
| InBr ₃ (dmsO) ₃ ^d | 2.70, s | | OS(CH ₃) ₂ |
| InI ₃ (Ph ₃ P) ₂ ^e | 7.5, m | | PC ₆ H ₅ |
| InI ₃ (tmtu) ^d | 3.44, s | | S=C[N(CH ₃) ₂] ₂ |
| CHCl ₃ | 7.27 | 77.5 | |
| CHBr ₃ | 6.84 | 12.1 | |
| CHI ₃ | 5.00 | -139.9 | |

^a ppm from δ(Me₄Si) = 0. s = singlet, t = triplet, q = quartet, m = multiplet, br = broad, tt = triplet of triplets. Numbers in parentheses show relative integrated intensities. ^b In CD₃CN. ^c Not recorded. ^d In (CD₃)₂CO. ^e In (CD₃)₂SO. ^f Too insoluble for NMR studies. ^g In CDCl₃.

to 50%, when yellow crystals of [(C₂H₅)₄N]₂[I₃InCHIInI₃] (1.12 g, 0.81 mmol, 71%) precipitated.

Reaction of (C₂H₅)₄N[Cl₃InCHCl₂] with InCl. When [(C₂H₅)₄N][Cl₃InCHCl₂] (0.40 g, 0.92 mmol) and InCl (0.14 g, 0.92 mmol) were stirred in acetonitrile (15 mL), disproportionation led to deposition of indium metal. This was collected, and volatiles were removed from the filtrate under vacuum to leave an oil, which on treatment with ethanol (10 mL) gave a white solid shown to be unreacted [(C₂H₅)₄N][Cl₃InCHCl₂] (0.26 g, 0.58 mmol).

Results and Discussion

Preparation of X₂InCHX₂ Species and Their Reactions with Halide. The reaction of InX (X = Cl, Br, I) with CHX₃, which involves the oxidative addition to one C–X bond of the haloform to give X₂InCHX₂ species, is very similar to that between InX and CH₂X₂, which yielded the halomethyl complexes of indium X₂InCH₂X (X = Br, I).¹ Attempts to isolate the X₂InCHX₂ compounds formed in acetonitrile gave oily materials, probably because of solvation of the indium center by the donor solvent, but addition of (C₂H₅)₄NX (X = Cl, Br, I) to these solutions caused precipitation of the crystalline [(C₂H₅)₄N][X₃InCHX₂] salts. Elemental analysis (Table 1), and the molar conductivities (Table 2), show that these compounds are 1:1 electrolytes in acetonitrile. Additional structural information can be obtained from their NMR spectra (Table 3). We first note significant changes between CHX₃ and the [X₃InCHX₂]⁻ anions, corresponding to increased shielding of protons relative to those in CHX₃. The ¹³C resonances of the InCHX₂ group were difficult to detect; in fact, it

proved impossible to detect the resonance of the chloride compound in a 200 MHz instrument, due to the breadth of the resonance signal, and it was necessary to use an unusually large line-sharpening parameter in recording the spectra. This is no doubt the result in part of the presence of neighboring atoms with high nuclear spin (¹¹⁵In, *I* = 9/2; ^{35,37}Cl, *I* = 3/2; ^{79,81}Br, *I* = 3/2; ¹²⁷I, *I* = 9/2). We also note significant deshielding of the carbon resonances of the InCHX₂ compounds relative to CHX₃, which is probably due to the higher polar character of the In^{δ+}–C^{δ-} bond in the organoindium relative to the parent CHX₃ compounds.

Reaction of the X₂InCHX₂ Species with Neutral Donors. The reactions of acetonitrile solutions of X₂InCHX₂ species with neutral ligands were investigated. In almost every case, the product was an adduct of corresponding indium(III) halide; the individual compounds isolated are as follows: X = Cl, L = tmtu, *n* = 2; X = Cl, L = Ph₃P, *n* = 2; X = Cl, L = dmsO, *n* = 3; X = Br, L = dmsO, *n* = 3; X = I, L = Ph₃P, *n* = 2; X = I, L = tmtu, *n* = 1. The formation of adducts of InX₃ adducts is apparent from both the analytical results (Table 1) and from NMR studies (Table 3). The products are in general conventional neutral derivatives of the trihalides, which have been discussed elsewhere.^{5,6}

The product of the reaction between dmsO and I₂InCHI₂ is clearly different from those identified above. The ¹H and ¹³C NMR spectra (in CDCl₃) confirm the presence of dmsO (¹H, 2.57 ppm, s; ¹³C, 40.4 ppm), but the analytical results do not correspond to the adduct InI₃(dmsO)₂ (calc: C, 7.37; H, 1.86; In, 17.6). Resonances at 4.84, s (¹H), and -39.3 ppm (¹³C) may indicate the presence of a CH group (cf results for I₃InCHI₂⁻, Table 3), but again no sensible formula can be written on the basis of the analytical data. The crystals were not suitable for X-ray crystallography. The tentative conclusion is that the product is the result of attack by a halomethylene group (see eq 1 below) on dmsO, but we have at present no structural data on which to formulate the processes involved.

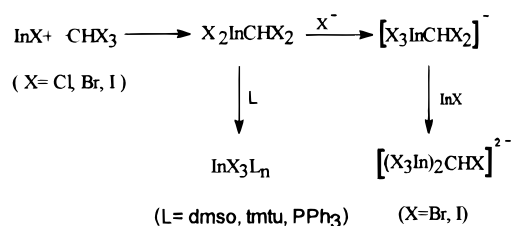
Reaction of [X₃InCHX₂]⁻ Species with InX. Tetraethylammonium salts of [X₃InCHX₂]⁻ react with equimolar quantities of InX (X = Br, I) by dissolution of the monohalides, and subsequent addition of equimolar quantities of (C₂H₅)₄NX allowed the isolation of [(C₂H₅)₄N]₂[X₃InCHXInX₃]. The analytical results obtained (Table 1) are in good agreement with the molecular formulae. The solution chemistry of these compounds suggests that complex and interesting decomposition processes occur in basic solvents, and this aspect of the problem will be discussed elsewhere.⁷

Mechanistic Aspects. The dihalomethyl compounds of indium(III), X₂InCHX₂, synthesized by the insertion of InX into the carbon–halogen bond of the corresponding haloform, are close analogues of the halomethyl compounds reported recently.¹ A study of the coordination chemistry of the latter showed that there are two electron acceptor sites in such molecules, namely the indium atom and the CH₂ group, and that coordination may occur at either or both of these. Anionic ligands coordinate to the metal center, while neutral ligands (L),

(5) Carty, A. J.; Tuck, D. G. *Prog. Inorg. Chem.* **1975**, *19*, 143.

(6) Carty, A. J.; Tuck, D. G. *J. Chem. Soc. A* **1966**, 1081.

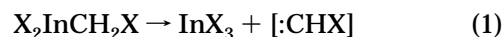
(7) Santos, J. D.; Maurera, M. A. M. A.; Longo, E.; Peppe, C. Unpublished results.

Scheme 1

such as Ph_3P , tmen, tmtu,² and dmsO,⁸ prefer to attack the CH_2 group yielding nonelectrolyte adducts whose structure (e.g. $\text{Br}_3\text{InCH}_2\text{L}$) indicates that the reaction results in nucleophilic substitution of the halide at the CH_2X group by the corresponding ligand, accompanied by halide transfer to the indium atom.

The new X_2InCHX_2 compounds behave analogously only in their reactions with anionic ligands, where the corresponding salts of $[\text{X}_3\text{InCHX}_2]^-$ were isolated. In contrast, reaction with neutral ligands leads to isolation of the corresponding adduct of InX_3 (Scheme 1). The adduct formation implies decomposition of the dihalo-

methyl complex of indium and carbene elimination:



This process has been verified in the case of the bromomethyl analogue, $\text{Br}_2\text{InCH}_2\text{Br}$, and we have been able to identify methylene transfer reactions such as olefination of acetone⁸ and the esterification of benzoic acid.⁹ These reactions clearly show the possibility of using halomethyl compounds of indium as methylene transfer reagents. The use of the new dihalomethyl complexes, X_2InCHX_2 , as reagents for transference of halomethylene is also being investigated, and we will deal with these results elsewhere.

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(8) Maurera, M. A. M. A. M.Sc. Thesis, Universidade Federal da Paraíba, 1993.

(9) Ferreira, J. M. M.Sc. Thesis, Universidade Federal de Paraíba, 1994.

(10) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.