

THE INSERTION OF INDIUM(I) HALIDES INTO THE M–X BOND OF SOME MAIN GROUP ORGANOMETALLIC HALIDES *

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Summary

Indium(I) halides (InX) react with Ph_3SnX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in toluene/tmed mixtures to give $\text{Ph}_3\text{SnInX}_2 \cdot \text{tmed}$ compounds (tmed = *N,N,N',N'*-tetramethylethanediamine), and $\text{Ph}_3\text{Sn}(\text{OAc})$ yields $\text{Ph}_3\text{SnIn}(\text{OAc})\text{X}_2 \cdot \text{tmed}$. Vibrational spectra and conductivities of these compounds, and of the salt $\text{Et}_4\text{N}[\text{Ph}_3\text{SnInCl}_3]$, show that these are the first examples of Sn–In bonded molecules. With Me_3SnCl , Ph_3SnH , Ph_3GeCl , Ph_3PbCl and Ph_2PCl , no oxidative addition reaction was observed. The results are compatible with previous discussions of the mechanism of such reactions, based on the insertion of indium into the M–X bond.

Introduction

The investigation of the chemistry of the indium(I) halides has been much facilitated by the discovery of their significant solubility in mixture of aromatic hydrocarbons and neutral bases such as toluene plus *N,N,N',N'*-tetramethylethanediamine (tmed) [1]. The use of such solutions has led to the investigation of the reaction of InX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with InX_3 ($\text{X} = \text{Br}, \text{I}$) [2] with various homonuclear M–M bonded compounds [3], and with InCl_3 [4]. These reactions all appear to proceed via a common reaction pathway involving InX acting both as an electron pair donor and acceptor.

A related set of reactions are those of InX ($\text{X} = \text{Br}, \text{I}$) and In_2X_4 with organic halides RX to give the corresponding RInX_2 compounds [5–10]. We have now investigated the insertion of InX into various Main Group organometallic halides with varying degrees of success, which can be rationalized on the basis of the mechanism proposed earlier. One result of this work has been the first isolation of compounds with Sn–In bonds.

* This paper is dedicated to Prof. Geoffrey Coates on his seventieth birthday. All those who study the chemistry of Main Group metals are constantly in debt to Prof. Coates for his pioneering work in this area.

Experimental

General

Indium monohalides were prepared by treating the corresponding trihalide with indium metal [11]. Triphenyltin chloride, triphenyltin acetate, triphenyllead chloride, diphenylboron bromide (Alfa) and tetraethylammonium chloride (Aldrich) were used as supplied, *N,N,N',N'*-tetramethylethanediamine (tmed) (Aldrich) was dried over molecular sieves before use. Solvents were distilled and stored over drying agents before use.

Triphenyltin bromide was prepared by the reaction of the hydroxide with hydrobromic acid [12], and triphenyltin iodide by treating tetraphenyltin with iodine in carbon tetrachloride [13]. Triphenyltin hydride was obtained by reducing Ph_3SnCl with LiAlH_4 [14], and triphenylgermanium chloride from GeCl_4 and PhMgBr [15].

Spectroscopic methods were those described in earlier papers [1,2]. Tin analysis was by atomic absorption spectrophotometry. All preparative work was carried out under dry nitrogen.

Reaction of InX with triphenyltin compounds

The same experimental method was used throughout this part of the work. Equimolar quantities (ca. 2–3 mmol) of InX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and Ph_3SnX or Ph_3SnOAc were placed in a flask and 50 ml of toluene added. The suspension was cooled with stirring, to -20°C , at which point tmed (0.3 g, 2.6 mmol) was syringed into the mixture. Stirring was continued for about 1 h, after which the cooling bath was removed and the mixture allowed to reach room temperature (ca. 20°C) over a period of 1–2 h.

The mixture was filtered, and the suspended solid collected, washed with toluene and dried in vacuo at room temperature. This material was shown to be $\text{Ph}_3\text{SnInX}_2 \cdot \text{tmed}$ or $\text{Ph}_3\text{SnIn}(\text{OAc})\text{X} \cdot \text{tmed}$; Table 1 shows percentage yield, melting points and analytical results for these compounds. The products are insoluble in most

TABLE 1

YIELD, MELTING POINTS AND ANALYTICAL RESULTS FOR $\text{Ph}_3\text{SnIn}(\text{X})\text{Y} \cdot \text{tmed}$ COMPOUNDS

Compound	Yield (%)	M.p. ($^\circ\text{C}$)	Analyses (Found (calc)(%))					
			C	H	N	In	Sn	X
$\text{Ph}_3\text{SnInCl}_2 \cdot \text{tmed}$	96	> 150(dec)	44.10 (44.21)	4.66 (4.76)	4.19 (4.30)	17.6 (17.6)	18.1 (18.2)	10.5 (10.6)
$\text{Ph}_3\text{SnInBr}_2 \cdot \text{tmed}$	94	> 150(dec)	38.91 (38.90)	4.15 (4.18)	3.75 (3.78)	15.4 (15.5)	15.9 (16.0)	21.48 (21.6)
$\text{Ph}_3\text{SnInI}_2 \cdot \text{tmed}$	97	> 200(dec)	34.50 (34.52)	3.70 (3.72)	3.35 (3.36)	13.6 (13.7)	14.0 (14.2)	30.5 (30.4)
$\text{Ph}_3\text{Sn}(\text{OAc})\text{Cl} \cdot \text{tmed}$	94	90	—	—	—	17.0 (17.0)	17.4 (17.5)	5.4 (5.3)
$\text{Ph}_3\text{Sn}(\text{OAc})\text{Br} \cdot \text{tmed}$	98	95	—	—	—	15.9 (16.0)	16.3 (16.5)	11.2 (11.1)
$\text{Ph}_3\text{Sn}(\text{OAc})\text{I} \cdot \text{tmed}$	92	110	—	—	—	15.0 (15.0)	15.4 (15.5)	16.5 (16.6)

TABLE 2

¹H NMR SPECTRA OF Ph₃SnIn(X)Y COMPOUNDS (ppm from Me₄Si)

Compound	Solvent	Resonances (ppm) ^a	Assignment
Ph ₃ SnInCl ₂ · tmed	CD ₃ OD/CDCl ₃	7.4–7.8 (m, 15H) 2.9 (m, 15H) 2.6 (s, 12H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃
Ph ₃ SnInBr ₂ · tmed	CD ₃ OD/CDCl ₃	7.4–7.7 (m, 15H) 2.8 (s, 4H) 2.5 (s, 12H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃
Ph ₃ SnInI ₂ · tmed	CD ₃ OD/CDCl ₃	7.2–7.7 (m, 15H) 2.8 (s, 4H) 2.5 (s, 12H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃
Ph ₃ SnIn(OAc)Cl · tmed	CDCl ₃	7.2–7.7 (m, 15H) 2.8 (s, 4H) 2.65 (s, 12H) 2.10 (s, 3H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃ O ₂ C-CH ₃
Ph ₃ SnIn(OAc)Br · tmed	CDCl ₃	7.2–7.8 (m, 15H) 2.75 (s, 4H) 2.60 (s, 12H) 2.10 (s, 3H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃ O ₂ C-CH ₃
Ph ₃ SnIn(OAc)I · tmed	CDCl ₃	7.3–7.9 (m, 15H) 2.7 (s, 4H) 2.6 (s, 12H) 2.1 (s, 3H)	Sn-(C ₆ H ₅) ₃ N-CH ₂ N-CH ₃ O ₂ C-CH ₃

^a s = singlet, m = multiplet. Integrated intensities in parentheses.

common organic solvents, but Ph₃SnIn(OAc)I · tmed could be recrystallized from 1 : 1 mixtures of tetrahydrofuran and methanol.

The compounds were characterized by means of infrared and ¹H NMR spectra. The infrared spectra are discussed below; the details of the ¹H NMR spectra are listed in Table 2. Conductivities were also measured (see below).

Preparation of Et₄N[Ph₃SnInCl₃]

Equimolar quantities (approx. 0.5 mmol) of Et₄NCl and Ph₃SnInCl₂ · tmed were suspended in toluene and the mixture stirred together for 10 h. Filtration yielded a colourless product which was washed with toluene and dried in vacuo. Analysis: Found: Sn, 16.9; In, 16.5; Cl, 15.4. Et₄N[Ph₃SnInCl₃], C₂₆H₃₅N₂SnInCl₃ calc: Sn, 16.9; In 16.4; Cl 15.2%. Yield quantitative. The molar conductivity in nitromethane (4 × 10⁻⁴ mol l⁻¹) was 88 ohm⁻¹ cm², corresponding to the values reported for 1 : 1 electrolytes in this solvent [16]. The ¹H NMR spectrum in dms_o-d₆ had resonances at 7.9–7.4 m (15H), 3.2 q (8H) 1.3t (12H).

Reaction of Ph₃SnInBr₂ · tmed with 1,2-dibromoethane

Following the work of Burham, Glockling and Stobart [17], we treated Ph₃SnInBr₂ · tmed (0.3 g) with 1,2-C₂H₄Br₂ (20 ml). The resultant suspension was stirred at room temp. for 3 h, after which the solid was collected by filtration, washed with toluene and dried overnight in vacuo. This solid was InBr₃ · 1.5tmed.

Analysis: Found: In, 21.8; Br, 45.6. $C_9H_{24}N_3InBr_3$ calc: In, 21.7; Br, 45.3%. 1H NMR in $dmsO-d_6$ 2.6(s), 2.8 s ppm. Excess 1,2- $C_2H_4Br_2$ was removed from the filtrate by evaporation in vacuo to leave a colourless solid identified as Ph_3SnBr . (1H NMR and infrared spectra identical to those of sample prepared from $Ph_3SnOH + HBr$ (see above). Mass spectrum (FD mode), molecular ion at $m/e = 429$ (plus manifold of isotopic peaks), minor peaks at 352 ($M - 77$), 275 ($M - 144$). Analysis: Found: Br, 19.0. $C_{18}H_{15}SnBr$ calc: Br, 18.6%).

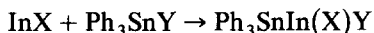
Other systems

We investigated the reaction of InX with the compounds Me_3SnCl , Ph_3SnH , Ph_3GeCl , and Ph_2PCl under essentially the same conditions as those used for InX/Ph_3SnX systems. In each case, the deposition of metallic indium occurred as the reaction mixture warmed up to room temperature, and it was not possible to isolate any product corresponding to the reaction of InX with the substrate. With Ph_3PbCl , the metallic deposit which formed as the reaction mixture reached room temperature contained both indium and lead.

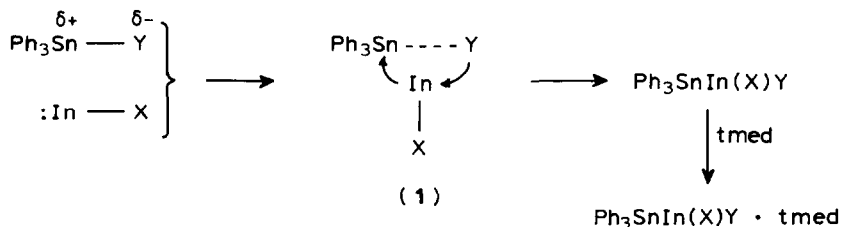
Results and discussion

Reaction pathway

The results demonstrate that there is an efficient reaction between InX and Ph_3SnY ($Y = Cl, Br, I, OAc$) to give the corresponding $Ph_3SnIn(X)Y$ compounds, which were isolated as their *tmed* adducts. We discuss the structure of these compounds below; the main conclusion at this point is that the reaction



corresponds formally to the oxidative addition of $In^I X$ across the $Sn-Y$ bond. Following the earlier discussions of such reactions with indium(I) halides, the postulated pathway is



The reaction proceeds smoothly for triphenyltin halides and acetate, for all of which the ligand Y has the required bridging properties, and the appropriate leaving group properties.

When Ph_3SnH is used, the insertion reaction does not occur, but rather indium metal is formed, and this has been previously taken as evidence of the disproportionation $3In^I \rightarrow In^{III} + 2In^0$, with the In^{III} eventually going to InX_3 , as the *tmed* adduct [1-3]. Clearly the $Sn-H$ bond cannot form the postulated intermediate **1** in the above scheme since the hydrido ligand lacks the necessary electrons for donation. The difference between the triphenyltin halides and Me_3SnCl , which does not yield $Me_3SnInCl_2$, presumably resides in the lower Lewis acidity of the alkyl

compound [18,19], with a consequent failure to form the intermediate **1**, and a similar argument can be applied to Ph_3GeCl , since tin compounds are much stronger acceptors than the corresponding germanium analogues [18]. In all of these systems then, the course of the reaction is explicable in terms of the mechanism proposed earlier [2–4], and outlined in the scheme above.

The reaction between InCl and Ph_3PbCl is anomalous, in that the Pb-In bonded compound is not recovered, and the decomposition produces a mixture of both metallic elements. It may be that the oxidizing properties of the lead(IV) compound result in the formation of Ph_3Pb^+ and InCl_2^+ ; the former could then go to Pb^0 , with the reaction of InCl_2^+ and unreacted InCl yielding In^0 . Further work on this system is planned.

The structure of $\text{Ph}_3\text{SnIn(X)Y} \cdot \text{tmed}$ compounds

It is clear that the products of the reaction of Ph_3SnX with InX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in toluene/tmed solution are the $\text{Ph}_3\text{SnInX}_2 \cdot \text{tmed}$ adducts, which are readily formulated as having an Sn-In bond. Although such species have been identified in the NMR spectra of $\text{Li}[\text{Me}_3\text{SnInMe}_3]$ solutions [19], no stable solids have been isolated. The present compounds can be regarded formally as intermediate between Ph_6Sn_2 and $\text{In}_2\text{X}_4 \cdot 2\text{tmed}$, both of which are M-M bonded, and the analysis of the vibrational spectra relies on published information of these systems [20–23].

In each of the $\text{Ph}_3\text{SnInX}_2 \cdot \text{tmed}$ compounds, there are weak bands in the $400\text{--}500\text{ cm}^{-1}$ region, assigned to $\nu(\text{In-N})$ modes, although exact identification is hindered by the dominating Sn-Ph bands at $\sim 445\text{ cm}^{-1}$ (vs). The $\nu(\text{In-X}_2)$ vibrations are then identified at $296\text{s} + 275\text{sh}$ (Cl), $212\text{s} + 195\text{sh}$ (213, 189 Ra) (Br) and $165\text{m} + 158\text{m cm}^{-1}$ (I), all in good agreement with the spectra of $\text{In}_2\text{X}_4 \cdot 2\text{tmed}$ [23]. In the salt $\text{Et}_4\text{N}[\text{Ph}_3\text{SnInCl}_3]$, the $\nu(\text{In-Cl})$ modes are identified at $330\text{m} + 302\text{m cm}^{-1}$, higher than in the $\text{In}_2\text{Cl}_6^{2-}$ anion [22], but close to the values reported [24] for InCl_3^- . The various Sn-Ph modes in these compounds are little changed from those in the parent Ph_3SnX compounds. Each compound shows a weak absorption in the $145\text{--}150\text{ cm}^{-1}$ region in which the $\nu(\text{Sn-In})$ mode might be expected; the Raman spectrum of $\text{Ph}_3\text{SnInBr}_2 \cdot \text{tmed}$ has a strong emission at 148 cm^{-1} , which can be assigned with confidence to $\nu(\text{Sn-In})$.

The molar conductivities of these compounds are close to zero, so that the formulation as neutral Sn-In bonded species is supported. Tin is four-coordinate, while indium is five-coordinate with a InSnX_2N_2 kernel, analogous to the coordination in $\text{In}_2\text{X}_4 \cdot 2\text{tmed}$ (InInX_2N_2). The compounds therefore formally involve tin(III) and indium(II). The reaction of $\text{Ph}_3\text{SnInBr}_2 \cdot \text{tmed}$ with $1,2\text{-C}_2\text{H}_4\text{Br}_2$ is then seen as the oxidation of the two moieties to tin(IV) and indium(III) respectively, with the elimination of C_2H_4 .

The spectra and structure of the acetato compounds $\text{Ph}_3\text{SnIn(X)OAc} \cdot \text{tmed}$ are best discussed in terms of Ph_3SnOAc and Me_2InOAc . The $\nu(\text{C-O})$ vibrations in these compounds are at $1544\text{vs} + 1428\text{vs cm}^{-1}$ and $1530\text{s} + 1445\text{s cm}^{-1}$, respectively, and in the latter case crystallographic studies have shown that acetate ligand is bidentate [25,26]. The present compounds typically show these same vibrations at $1550\text{vs} + 1430\text{vs}$, so that bidentate acetate is present. Weak bands at $300\text{--}320\text{ cm}^{-1}$ are then reasonably assigned to $\nu(\text{In-O})$ (cf. ref. 25). The $\nu(\text{In-X})$ modes are at 297w (Cl) and 205 cm^{-1} (Br; 209 cm^{-1} Ra); no $\nu(\text{In-I})$ mode could be detected. The remaining features of the spectra are essentially identical to those discussed

above, except that the $\nu(\text{In-N})$ region is effectively blanked by strong bands at 450 and 570 cm^{-1} . The molar conductivity of the iodo derivative in both dmf ($67\text{ ohm}^{-1}\text{ cm}^2$) and nitromethane ($79\text{ ohm}^{-1}\text{ cm}^2$) shows that the compound is a 1:1 electrolyte in these solvents. The absence of the $\nu(\text{In-I})$ band in the infrared spectrum suggests that the correct formulation for both solid and solution states is $[\text{Ph}_3\text{SnIn}(\text{OAc})\text{tmed}]^+\text{I}^-$. In contrast, the chloro compound is a non-conductor in dmf ($\Lambda_0\ 10\text{ ohm}^{-1}\text{ cm}^2$), while the bromo analogue undergoes some dissociation in polar solvents ($\Lambda_0\ 27\text{ ohm}^{-1}\text{ cm}^2$ in dmf, $34\text{ ohm}^{-1}\text{ cm}^2$ in MeNO_2) so that both these compounds can be formulated as neutral species in the solid state. The difference between the iodo compounds, and the chloro- or bromo-acetato species, probably lies in the difficulty of accomodating the larger iodine atom in the coordination kernel of $\text{InSnO}_2\text{N}_2\text{X}$.

General conclusion

The insertion of indium(I) into the M-X bonds of organometallic compounds is a useful route to M-In bonded species, and provides an extension of our knowledge of the metallic elements to which this element can bond (cf. ref. 27). Preliminary experiments show that the same methods can be used to prepare M-In derivatives of transition metal compounds, and of organoboron halides. In the latter case, the products contain In-B bonds, but the complexity of the products requires further investigations currently in progress.

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