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

THEODORE A. ANNAN and DENNIS G. TUCK*

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

(Received October 9th, 1986)

Summary

Indium(I) halides (InX) react with Ph_3SnX (X = Cl, Br, I) in toluene/tmed mixtures to give $Ph_3SnInX_2 \cdot$ tmed compounds (tmed = N,N,N',N'-tetramethyl-ethanediamine), and $Ph_3Sn(OAc)$ yields $Ph_3SnIn(OAc)X_2 \cdot$ tmed. Vibrational spectra and conductivities of these compounds, and of the salt $Et_4N[Ph_3SnInCl_3]$, 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'-tetramethyl-ethanediamine (tmed) [1]. The use of such solutions has lead to the investigation of the reaction of InX (X = Cl, Br, I) with InX_3 (X = Br, 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 (X = Br, 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 (X = Cl, Br, 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 Ph_3SnInX_2 · tmed or $Ph_3SnIn(OAc)X$ · 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 $Ph_3SnIn(X)Y$·tmed COMPOUNDS

Compound	Yield (%)	M.p. (°C)	Analyses (Found (calc)(%))					
			C	H	N	In	Sn	X
$Ph_3SnInCl_2$·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)
$Ph_3SnInBr_2$·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)
Ph_3SnInI_2·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)
$Ph_3Sn(OAc)Cl$·tmed	94	90	–	–	–	17.0 (17.0)	17.4 (17.5)	5.4 (5.3)
$Ph_3Sn(OAc)Br$·tmed	98	95	–	–	–	15.9 (16.0)	16.3 (16.5)	11.2 (11.1)
$Ph_3Sn(OAc)I$·tmed	92	110	–	–	–	15.0 (15.0)	15.4 (15.5)	16.5 (16.6)

TABLE 2

^{1}H NMR SPECTRA OF Ph$_3$SnIn(X)Y COMPOUNDS (ppm from Me$_4$Si)

Compound	Solvent	Resonances (ppm) ^{a}		Assignment
Ph$_3$SnInCl$_2$·tmed	CD$_3$OD/CDCl$_3$	7.4–7.8	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.9	(m, 15H)	N-CH$_2$
		2.6	(s, 12H)	N-CH$_3$
Ph$_3$SnInBr$_2$·tmed	CD$_3$OD/CDCl$_3$	7.4–7.7	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.8	(s, 4H)	N-CH$_2$
		2.5	(s, 12H)	N-CH$_3$
Ph$_3$SnInI$_2$·tmed	CD$_3$OD/CDCl$_3$	7.2–7.7	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.8	(s, 4H)	N-CH$_2$
		2.5	(s, 12H)	N-CH$_3$
Ph$_3$SnIn(OAc)Cl·tmed	CDCl	7.2–7.7	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.8	(s, 4H)	N-CH$_2$
		2.65	(s, 12H)	N-CH$_3$
		2.10	(s, 3H)	O$_2$C-CH$_3$
Ph$_3$SnIn(OAc)Br·tmed	CDCl$_3$	7.2–7.8	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.75	(s, 4H)	N-CH$_2$
		2.60	(s, 12H)	N-CH$_3$
		2.10	(s, 3H)	O$_2$C-CH$_3$
Ph$_3$SnIn(OAC)I·tmed	CDCl$_3$	7.3–7.9	(m, 15H)	Sn-(C$_6$H$_5$)$_3$
		2.7	(s, 4H)	N-CH$_2$
		2.6	(s, 12H)	N-CH$_3$
		2.1	(s, 3H)	O$_2$C-CH$_3$

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

common organic solvents, but Ph$_3$SnIn(OAc)I · tmed could be recrystallized from 1 : 1 mixtures of tetrahydrofuran and methanol.

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

Preparation of Et$_4$N[Ph$_3$SnInCl$_3$]

Equimolar quantities (approx. 0.5 mmol) of Et$_4$NCl and Ph$_3$SnInCl$_2$ · 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. Et$_4$N[Ph$_3$SnInCl$_3$], C$_{26}$H$_{35}$NSnInCl$_3$ 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} cm^2, corresponding to the values reported for 1 : 1 electrolytes in this solvent [16]. The ^{1}H NMR spectrum in dmso-d_6 had resonances at 7.9–7.4 m (15H), 3.2 q (8H) 1.3t (12H).

Reaction of Ph$_3$SnInBr$_2$ · tmed with 1,2-dibromoethane

Following the work of Burham, Glockling and Stobart [17], we treated Ph$_3$SnInBr$_2$ · tmed (0.3 g) with 1,2-C$_2$H$_4$Br$_2$ (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 InBr$_3$ · 1.5tmed.

Analysis: Found: In, 21.8; Br, 45.6. $C_9H_{24}N_3InBr_3$ calc: In, 21.7; Br, 45.3%. ^{1}H 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. (^{1}H 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

$$InX + Ph_3SnY \rightarrow Ph_3SnIn(X)Y$$
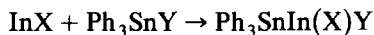
corresponds formally to the oxidative addition of In^IX across the Sn–Y bond. Following the earlier discussions of such reactions with indium(I) halides, the postulated pathway is
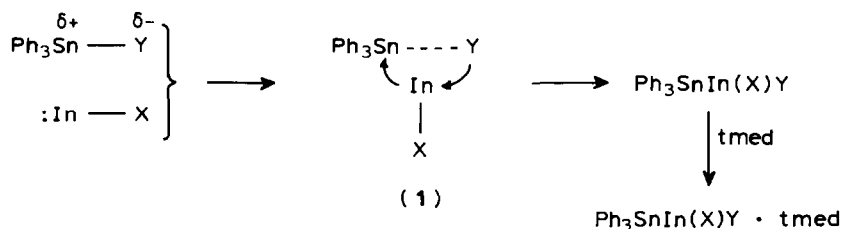
The reaction proceeds smoothly for triphenyltin halides and acetate, for all of which the ligand Y has the required bridging properties, and the appropriate leaving group properties.

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 $Ph_3SnIn(X)Y \cdot tmed$ compounds

It is clear that the products of the reaction of Ph_3SnX with InX (X = Cl, Br, I) in toluene/tmed solution are the $Ph_3SnInX_2 \cdot tmed$ adducts, which are readily formulated as having an Sn–In bond. Although such species have been identified in the NMR spectra of $Li[Me_3SnInMe_3]$ solutions [19], no stable solids have been isolated. The present compounds can be regarded formally as intermediate between Ph_6Sn_2 and $In_2X_4 \cdot 2tmed$, 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 $Ph_3SnInX_2 \cdot tmed$ compounds, there are weak bands in the 400–500 cm^{-1} region, assigned to ν(In–N) modes, although exact identification is hindered by the dominating Sn–Ph bands at ~ 445 cm^{-1} (vs). The ν(In–X_2) vibrations are then identified at 296s + 275sh (Cl), 212s + 195 sh (213, 189 Ra) (Br) and 165m + 158m cm^{-1} (I), all in good agreement with the spectra of $In_2X_4 \cdot 2tmed$ [23]. In the salt $Et_4N[Ph_3SnInCl_3]$, the ν(In–Cl) modes are identified at 330m + 302m cm^{-1}, higher than in the $In_2Cl_6^{2-}$ 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 145–150 cm^{-1} region in which the ν(Sn–In) mode might be expected; the Raman spectrum of $Ph_3SnInBr_2 \cdot tmed$ has a strong emission at 148 cm^{-1}, which can be assigned with confidence to ν(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 $In_2X_4 \cdot 2tmed$ ($InIn'X_2N_2$). The compounds therefore formally involve tin(III) and indium(II). The reaction of $Ph_3SnInBr_2 \cdot tmed$ with $1,2$-$C_2H_4Br_2$ 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 $Ph_3SnIn(X)OAc \cdot tmed$ are best discussed in terms of Ph_3SnOAc and Me_2InOAc. The ν(C–O) vibrations in these compounds are at 1544vs + 1428vs cm^{-1} and 1530s + 1445s 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 1550vs + 1430vs, so that bidentate acetate is present. Weak bands at 300–320 cm^{-1} are then reasonably assigned to ν(In–O) (cf. ref. 25). The ν(In–X) modes are at 297w (Cl) and 205 cm^{-1} (Br; 209 cm^{-1} Ra); no ν(In–I) mode could be detected. The remaining features of the spectra are essentially identical to those discussed

above, except that the ν(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 ohm^{-1} cm^2) and nitromethane (79 ohm^{-1} cm^2) shows that the compound is a 1:1 electrolyte in these solvents. The absence of the ν(In–I) band in the infrared spectrum suggests that the correct formulation for both solid and solution states is [Ph$_3$SnIn(OAc)tmed]$^+$I$^-$. In contrast, the chloro compound is a non-conductor in dmf (Λ_0 10 ohm^{-1} cm^2), while the bromo analogue undergoes some dissociation in polar solvents (Λ_0 27 ohm^{-1} cm^2 in dmf, 34 ohm^{-1} 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 InSnO$_2$N$_2$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.

Acknowledgement

References

1 C. Peppe, L. Victoriano and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1982) 2165.
2 C. Peppe and D.G. Tuck, Can. J. Chem., 62 (1984) 2793.
3 C. Peppe and D.G. Tuck, Can. J. Chem., 62 (1984) 2798.
4 M.A. Khan, C. Peppe and D.G. Tuck, Organometallics, 5 (1986) 525.
5 L.G. Waterworth and I.J. Worrall, Chem. Commun., (1971) 569.
6 M.J.S. Gynane and I.J. Worrall, Inorg. Nucl. Chem. Lett., 8 (1972) 547.
7 M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, J. Organomet. Chem., 43 (1972) 257.
8 L.G. Waterworth and I.J. Worrall, J. Organomet. Chem., 81 (1974) 23.
9 M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, Inorg. Nucl. Chem. Lett., 9 (1973) 543.
10 J.S. Poland and D.G. Tuck, J. Organomet. Chem., 42 (1972) 315.
11 J.J. Habeeb and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1976) 866.
12 R.H. Bullard and W.B. Robinson, J. Am. Chem. Soc., 49 (1927) 1368.
13 R.F. Chambers and P.C. Scherer, J. Am. Chem. Soc., 48 (1926) 1055.
14 H. Gilman and J.J. Eisch, J. Org. Chem., 20 (1955) 763.
15 J.J. Eisch and R.B. King, Organometallic Syntheses, Academic Press, New York, Vol. 2, 1981, p. 164.
16 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
17 R.A. Burnham, F. Glockling and S.R. Stobart, J. Chem. Soc., Dalton Trans., (1972) 1991.
18 G.P. van der Kelen, E.P. van den Berghe and L. Verdonck in A.S. Sawyer (Ed.), Organotin Compounds, Marcel Dekker, New York, 1971, Vol. 1, p. 118.
19 A.T. Weibel and J.P. Oliver, J. Am. Chem. Soc., 94 (1972) 8590.
20 R.C. Poller, Spectrochim. Acta, 22 (1966) 935.
21 M.J. Taylor, Metal-to-Metal Bonded States of the Main Group Elements, Academic Press, London, 1975, p. 87.

22 M.J. Taylor, D.G. Tuck and L. Victoriano, Can. J. Chem., 60 (1982) 690.

23 M.A. Khan, C. Peppe and D.G. Tuck, Can. J. Chem., 62 (1984) 601.

24 J.E. Drake, J.L. Hencher, L.N. Khasrou, D.G. Tuck and L. Victoriano, Inorg. Chem., 19 (1980) 34.

25 J.J. Habeeb and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1973) 243.

26 F.W.B. Einstein, M.M. Gilbert and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1973) 248.

27 S.G. Shore, K.B. Gilbert and S.K. Booeock in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 6, p. 879.