Co-ordination Compounds of Indium. Part 40.[1] Reactions of non-aqueous Solutions of Indium(I) Halides

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Indium(I) halides can be dissolved in toluene containing certain neutral donor ligands below *ca.* 0 °C. The simplest solute species in InBr–toluene–*NNN'N'*-tetramethylethylenediamine (tmen) is InBr·3tmen which slowly precipitates solid InBr·0.5tmen. Disproportionation of InX occurs above 0 °C, yielding indium metal and In^{II} or In^{III} halide complexes, depending on X and the neutral ligand. Solutions of InX (X = Br or I) can oxidatively insert C–X bonds producing organoindium(III) halides.

One of the difficulties which has hindered the development of the chemistry of indium(I) is the absence of suitable reactive starting materials for the synthesis of complexes. In our previous publications the use of cyclopentadienylindium(I) has been advocated because of its solubility in organic solvents, and both neutral [2] and anionic [3,4] indium(I) species have been prepared. Unfortunately, $[In(C_5H_5)]$ itself is not readily available. Another possible route is *via* the dihalides, which can react as $In^{I}In^{III}X_4$ species, and cationic indium(I) complexes have been prepared from these compounds with crown ether and polydentate nitrogen donors.[5]

The indium(I) halides represent obvious sources of indium(I) species, but the general intractability and insolubility of these materials have been barriers to any investigation of their chemistry, although in a recent publication [6] we reported the ready reaction of suspensions of InCl with $Li(C_5H_5)$ to give $[In(\eta-C_5H_5)]$. We have now found that indium(I) halides are soluble in either toluene or CH_2Cl_2 containing neutral organic bases. The stability of such solutions depends on the temperature, halide concerned, and base. Disproportionation of InX occurs above *ca.* 0 °C, and the nature of the products of this reaction also depends on the halide and base. These InX solutions are useful precursors for In_2X_4 adducts and can be used for the insertion of InX into C–X bonds. Here we report investigations of such reactions using organic halides as substrate.

Results and Discussion

Solubility Studies.—We have investigated a variety of solution systems involving some six basic ligands (see below). Of these, the InX (X = Br or I)–toluene–*NNN'N'*-tetramethylethylenediamine (tmen) system proved to be the most suitable for a detailed study of solubility. The resultant solutions are unstable with respect to disproportionation, but show no signs of decomposition at −20 °C. The Figure shows the solubility of indium(I) bromide in toluene as a function of increasing quantities of tmen at this temperature. The solubility in toluene itself at −20 °C is negligible, and the quantity of indium in solution in toluene–tmen is obviously dependent on the tmen : In mol ratio reaching a maximum in the region of a mol ratio of 10 : 1. The limiting solubility under these conditions is 15.7 ± 0.2 mmol dm^{-3} (3.06 ± 0.02 mg cm^{-3}). The initial slope of the curve corresponds to the formation of InBr·3tmen in solution and presumably higher solvates are present in the saturated solution. When a mixture of InBr, tmen, and toluene was held at −20 °C for 30 min, the undissolved solid had the composition InBr·0.5tmen, and this was also precipitated on adding cold light petroleum to the solution. A solid of similar composition was obtained with indium(I) iodide, although the analysis is poor. The presence of tmen in these solids, and the absence of toluene, was confirmed in each case by ^{1}H n.m.r. spectroscopy.

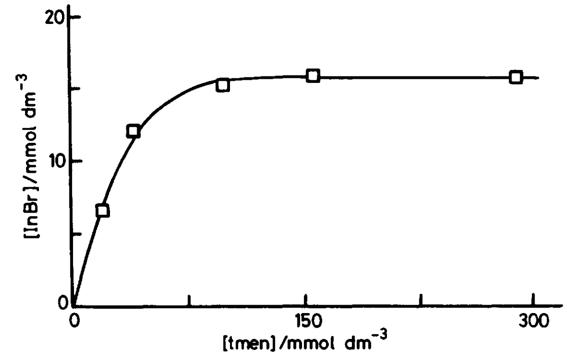

Figure. The solubility of InBr in a toluene–tmen mixture as a function of tmen concentration at −20 °C

The nature of these solid and solution phase species must remain a matter of speculation, since crystalline material was not available for *X*-ray studies. The species could not be deduced from Raman or ^{115}In n.m.r. studies. The solubility results imply that the solute species are InX molecules loosely co-ordinated by at least 2—3 molecules of tmen, but the precise nature of this co-ordination is unclear, as is the degree of association (if any) of these InX solvates. The solid compounds InX·0.5tmen (X = Br or I) are apparently the first stable indium(I) halide adducts to be isolated. The compounds $InX{\cdot}NH_3$ and $InX{\cdot}2NH_3$ (X = Cl or Br) have been reported,[7] but these black materials disproportionate in the presence of air or moisture to In, $InX_3{\cdot}5NH_3$, and NH_3; no structural or spectroscopic results have been reported. In this context, we note that our InBr·0.5tmen compound turns grey-black when kept under nitrogen at room temperature for *ca.* 24 h, suggesting that In is being formed under these conditions. It may be that the ammines also involve weak co-ordination of InX, but that this does not convey the same degree of stabilisation found with tmen.

Other systems proved much less satisfactory for solubility studies than those just described. Indium(I) chloride dissolves in toluene–tmen, but the solutions are unstable to decomposition even at −20 °C. Indium(I) bromide has a very low solubility in pyridine–toluene at −20 °C, and decomposition is rapid at those temperatures at which the solubility is measurable. This combination of factors appears to be the general case, with tmen–toluene a welcome exception.

Decomposition Reactions in Solution.—In all the systems studied, deposition of In begins at *ca.* 0 °C, and accelerates

Table 1. Outline of isolation procedures, and analysis for the products of disproportionation of InX in toluene–base solution

	Analysis Found (calc.)/%		
Product	In	halogen	Isolation [a]
$InCl_3 \cdot 3dmso$	25.3 (25.3)	23.2 (23.4)	Insoluble in toluene; extracted into hot MeCN
$InCl_3 \cdot NEt_3$	35.3 (35.7)	33.1 (33.0)	Insoluble in toluene; recrystallized from CH_2Cl_2–light petroleum
$InCl_3 \cdot 2PEt_3$	25.0 (25.1)	23.3 (23.3)	Precipitated by addition of light petroleum after removal of some toluene *in vacuo*
$InBr_3 \cdot 3C_5H_5N$	20.0 (19.4)	40.2 (40.5)	As for $InCl_3 \cdot 3dmso$
$InBr_3 \cdot bipy$ [b]	22.1 (22.5)	44.0 (47.0)	As for $InCl_3 \cdot 3dmso$
$InBr_3 \cdot 2PEt_3$	19.5 (19.5)	40.4 (40.6)	Solution concentrated, and light petroleum added
$InBr_3 \cdot 3PBu^n_3$	12.0 (12.0)	24.9 (25.0)	Solution pumped to dryness, compound recrystallized from MeOH
$In_2Br_4 \cdot 2tmen \cdot C_6H_5Me$	26.4 (26.2)	36.4 (36.5)	Precipitated by addition of Et_2O
$In_2I_4 \cdot 2tmen$	23.7 (23.7)	52.0 (52.3)	Precipitated by addition of light petroleum
$In_2I_4 \cdot 2PEt_3$ [c]	23.2 (23.6)	50.0 (52.2)	Precipitated by addition of Et_2O
$In_2Cl_5 \cdot 3tmen$ [d]	30.4 (30.4)	23.5 (23.5)	Insoluble in toluene; recrystallized from CH_2Cl_2–light petroleum
$In_2Cl_5 \cdot 3tmen \cdot 0.5C_6H_5Me$ [d]	29.1 (28.7)	22.2 (22.1)	Precipitated when toluene solution was concentrated
$In_2Br_5 \cdot 8dmso$ [d]	18.3 (18.3)	32.3 (31.9)	Insoluble in toluene; extracted into hot $CHCl_3$

[a] For light petroleum the b.p. range = 30—60 °C throughout this paper. [b] bipy = 2,2′-bipyridine. [c] Visible loss of iodine on dissolving (Found: C, 14.75; H, 3.10. $C_{12}H_{30}I_4In_2P_2$ requires C, 14.90; H, 3.10%). [d] These products are believed to be mixtures of as yet unidentified substances.

with temperature by pathways (1)—(3). The stoicheiometry of

$$InX\text{–}L \longrightarrow \tfrac{2}{3}In^0 + \tfrac{1}{3}InX_3 \cdot nL \qquad (1)$$

$$InX\text{–}L \longrightarrow In^0 + In_2X_4 \cdot 2L \qquad (2)$$

$$InX\text{–}L \longrightarrow In^0 + In_2X_5 \cdot nL \qquad (3)$$

reactions (1) and (2) has been established experimentally in a number of cases. The individual compounds isolated from these reactions are as follows.

(1) $InX_3 \cdot nL$. When X = Cl, L = dimethyl sulphoxide (dmso) (n = 3), NEt_3 (n = 1), and PEt_3 (n = 2); when X = Br, L = pyridine (n = 3), 2,2′-bipyridine (n = 1), PEt_3 (n = 2), and PBu^n_3 (n = 3). See Table 1 for analysis and procedures. In addition to elemental analysis, the compounds were characterised by i.r. and n.m.r. spectroscopy. The products are in general the conventional neutral adducts of the trihalides which have been discussed elsewhere,[8,9] although the stoicheiometry is not always that of previous reports. This may be another illustration of the well established effects of reaction conditions upon the composition of such adducts.[8]

(2) $In_2X_4 \cdot 2L$. When X = Br, L = tmen (+toluene); when X = I, L = tmen and PEt_3. Neutral adducts of In_2Br_4 and In_2I_4 with these ligands have been reported elsewhere.[1,10] The vibrational spectra identify such molecules as $X_2(L)In\text{–}In(L)X_2$ species, similar in structure to the $Cl_2(L)Ga\text{–}Ga(L)Cl_2$ compounds reported by Worrall and co-workers,[11] who established the presence of a metal–metal bond. The vibrational spectra of the present compounds were identical to those of compounds prepared by other routes.[1]

(3) $In_2X_5 \cdot nL$. When X = Cl, L = tmen (n = 3); when X = Br, L = dmso (n = 8). The composition of these products were determined by elemental analysis, n.m.r., and i.r. spectroscopy. Both materials have high conductivities in acetonitrile (~350 Ω^{-1} cm^2 mol^{-1}). Other evidence suggests that these are in fact mixtures of two or more species resulting from the reaction of indium(II) species with solvent. Further work on this problem is underway.[12]

The Mechanism of the Disproportionation Reactions.—The results described show that solutions of $InX \cdot nL$ undergo disproportionation above *ca.* −20 °C, to give In and either indium(II) or indium(III) products, depending on X and L. We have observed that the rate of disproportionation in the InBr–tmen system, as evidenced by the appearance of In in the solution, is lowered by the presence of excess tmen (relative to the 1 : 3 mol ratio). Using the same criterion, we find that the stability decreases in the order I > Br > Cl for comparable conditions. We suggest that the first reaction is the disproportionation shown by equation (4), and that in many

$$3InX \cdot nL \longrightarrow 2In^0 + InX_3 \cdot mL \qquad (4)$$

cases the reaction does not proceed beyond this point because the stable InX_3 adduct is thrown out of solution [pathway (1) above].

In those few cases where this precipitation does not occur, formation of adducts of In_2X_4 must depend on a process involving unreacted InX and InX_3 in solution [equation (5)].

$$InX_3 \cdot mL + InX \cdot nL \rightleftharpoons In_2X_4 \cdot 2L + pL \qquad (5)$$

This equilibrium is similar to that postulated in earlier studies of indium(II) anionic species,[13] where the existence of $[In_2X_6]^{2-}$ anions in non-aqueous solution was confirmed by ^{115}In n.m.r. studies.[14] Repeated attempts to extend the present investigations by this technique were uniformly unsuccessful. In terms of equation (5), it is worth pointing out that In_2X_4 adducts are recovered when L = tmen or PPh_3, ligands which we found to stabilise In_2X_4 in earlier preparative studies;[10] in that work, as here, complexes with other neutral ligands underwent disproportionation in solution. Equation (5) involves the formal insertion of In^IX into the $In^{III}\text{–}X$ bond of $InX_3 \cdot mL$, and further experiments on this problem are underway.

Insertion of InX *into* C–X *Bonds.*—The insertion of In^IX into C–X bonds has been extensively studied by Worrall and co-workers,[15] and in this laboratory.[16] We have now examined similar reactions with solutions of indium(I) halides. One immediate experimental difficulty is the quaternisation which may occur between alkyl halides and nitrogen or phosphorus donor ligands, so that such bases cannot always be used to stabilise the InX solution. We have been successful in using tmen–CH_2Cl_2 mixtures, since both InBr–EtBr and InI–EtI reactions proceed without difficulty in this medium. Of the available oxygen donors, 1,4-dioxan and tetrahydrofuran do not induce sufficient solubility, while dmso leads to the rapid formation of $InX_3 \cdot 3dmso$ for X = Cl or Br, and we have therefore confined our investigations with InI to dmso–toluene solutions.

The reactions between EtX and InX (X = Br or I) in CH_2Cl_2–tmen proceed smoothly to give $InEtX_2\cdot$tmen in quantitative yield. With all the other alkyl bromides (RBr) examined (R = Pr^n, Pr^i, or Bu^n) the products were oils which could not be recrystallised; nor was it possible to obtain crystalline derivatives as the ionic complex $[NR_4][InR'Br_3]$ as achieved successfully in the case of the iodo-compounds (see below). The mechanism of InBr–RBr reactions has been discussed in terms of the formation of various intermediate sub-halides.[15d] In view of the disproportionation reactions noted above, it seems probable that competing processes draw off indium(I) bromide and so prevent reaction with alkyl bromide. We cannot at present explain the difference between EtBr and the other compounds studied.

With InI and methyl iodide in toluene–dmso, the reaction product is $In_2MeI_5\cdot$4dmso, in contrast to the $InMe_2\cdot InI_4$ obtained in almost quantitative yield from the solvent-free reaction of InI and MeI.[15] The vibrational spectrum in the ν(In–I) region is very similar to those for the $[InEtI_3]^-$ and $[InBu^nI_3]^-$ anions, and on that basis we formulate the product as $[InI_2(dmso)_4]$ $[InMeI_3]$. The $[InI_2(dmso)_4]^+$ cation has been identified previously in the adduct $InI_3\cdot$2dmso.[17] With InI and EtI, the initial product is $InEtI_2\cdot$2dmso, which may be the neutral five-co-ordinate adduct or the ionic dimer $[InI_2(dmso)_4][InEtI_3]$. The yield was low (35%) and the compound is a powder which resisted attempted crystallisation, but the addition of Ph_4PI in dichloromethane yielded $[PPh_4][InEtI_3]$ whose structure has been confirmed by *X*-ray crystallography.[18] Similar procedures with InI and Bu^nI yielded $[PPh_4][InBu^nI_3]$ (52% yield).

We conclude that solutions of indium(I)-bromide or -iodide can indeed serve as the starting point for the synthesis of certain organoindium(III) halide species, but that the usefulness is somewhat constrained by the experimental restrictions noted above. Thus the EtBr–InBr system gives yields higher than those reported previously, whereas with solutions of InI yields are in general lower than in syntheses using the solid halide.

Experimental

Indium(I) halides were prepared by heating metal and trihalide together in a sealed tube.[16] Solvents were distilled under nitrogen before use; all other materials, including neutral ligands, were used as supplied. All experimental work was carried out in an atmosphere of dry nitrogen.

Infrared spectra were recorded with Beckman IR-12 or IR-180 instruments; n.m.r. spectra were run on Varian EM-360 or Jeolco spectrometers.

Indium analysis was by atomic absorption spectrophotometry, and halide analysis by Volhard titration.

Solubility of InBr *and Preparation of* $InX\cdot$0.5tmen.—Quantities of indium(I) bromide (0.2 g, 1.03 mmol) were shaken with toluene (50 cm^3) and differing quantities of tmen (0.12—1.8 g, 1.03—15.5 mmol) at −20 °C for 30 min. The undissolved material was allowed to settle, and samples of the solution phase withdrawn for indium analysis. Even when tmen was in large excess over InBr or InI, the undissolved solid recovered from such experiments was $InX\cdot$0.5tmen (Found: In, 45.4; Br, 32.3. C_3H_8BrInN requires In, 45.5; Br, 31.6%. Found: In, 36.0; I, 41.1. C_3H_8IInN requires In, 38.3; I, 42.3%). The InBr adduct was also obtained by adding excess, cold light petroleum to a solution of InBr in toluene–tmen at −20 °C.

Preparation of Adducts of InX_2 *and* InX_3.—The standard procedure used in all these experiments involved stirring InX (*ca.* 5 mmol) and a four-fold excess of the neutral ligand in toluene (50 cm^3) at −20 °C for 2 h. The cooling-bath was then slowly removed and the solution held at room temperature for *ca.* 20 h. The subsequent isolation procedures and the analytical results are given in Table 1. The presence of the neutral ligand was confirmed in each case by i.r. and n.m.r. spectroscopy (Table 2).

Table 2. Proton n.m.r. spectra of indium halide adducts

Compound	Solvent	Ligand resonances */p.p.m.
$InCl_3\cdot$3dmso	C_5D_5N	2.4 (s)
$InCl_3\cdot NEt_3$	CD_2Cl_2	3.3 (q, br) (2), 1.4 (t) (3)
$InCl_3\cdot 2PEt_3$	CD_2Cl_2	1.84 (m, complex), 1.1 (m, complex)
$InBr_3\cdot$bipy	$(CD_3)_2SO$	8.7 (m), 7.8 (m), 7.4 (m)
$InBr_3\cdot 2PEt_3$	CD_2Cl_2	1.8 (m, complex), 1.2 (m, complex)
$InBr_3\cdot PBu^n_3$	CD_2Cl_2	1.6 (m, complex), 0.9 (m), 0.12 (s)
$In_2Br_2\cdot$tmen	CD_3CN	2.7 (s) (1), 2.54 (s) (3)
$In_2Br_4\cdot$2tmen$\cdot C_6H_5Me$	CD_2Cl_2	7.2 (s) (5), 2.83 (s) (8), 2.72 (s) (24), 2.37 (s) (3)
$In_2I_4\cdot$2tmen	CD_2Cl_2	2.90 (s) (1), 2.82 (s) (3)
$In_2I_4\cdot 2PEt_3$	CD_2Cl_2	2.12 (m) (2), 1.33 (m) (3)
$In_2Cl_5\cdot$3tmen	CD_2Cl_2	2.88 (s), 2.64 (s)
$In_2Cl_5\cdot$3tmen$\cdot 0.5C_6H_5Me$	CD_2Cl_2	7.2 (s), 2.73 (s), 2.6 (s), 2.3 (s)
$In_2Br_5\cdot$8dmso	C_5D_5N	2.73 (s)

* s = Singlet, t = triplet, q = quartet, m = multiplet, br = broad. Numbers in parentheses show relative integrated intensities.

InX–RX *Reactions.*—(*a*) InBr–EtBr. The compound InBr (2.0 g, 10.3 mmol) was suspended in CH_2Cl_2 (50 cm^3) cooled in dry ice–acetone. The addition of tmen (3 cm^3) through a syringe produced a deep red solution, which gradually changed through yellow to a final colourless solution. The cold-bath was slowly removed and the solution finally stirred for 30 min at room temperature (total reaction time 3.5 h). Addition of diethyl ether to this final solution gave colourless crystals of $InEtBr_2\cdot$tmen in quantitative yield (Found: C, 22.90; H, 4.95; Br, 38.3; In, 27.5; N, 6.70. $C_8H_{21}Br_2InN_2$ requires C, 22.5; H, 5.00; Br, 38.1; In, 27.4; N, 6.65%).

(*b*) InI–MeI. The compound InI (1 g, 4.1 mmol) was suspended in a mixture of toluene (50 cm^3) and methyl iodide (1 cm^3, 16.2 mmol) in an ice-salt cooling bath, and dmso (10 cm^3) syringed into the mixture, after which the cooling-bath was removed. After *ca.* 2—3 h the InI had dissolved, and the excess liquid phase was removed by pumping *in vacuo* at 100 °C. The resultant oil was recrystallized from dichloromethane to form small colourless needles (yield 0.9 g, 37%) (Found: In, 19.2; I, 52.5. $CH_3I_5In_2\cdot 4C_2H_6OS$ requires In, 19.3; I, 53.3%).

(*c*) InI–EtI. This reaction has been investigated in two different media, CH_2Cl_2–tmen and toluene–dmso. Indium iodide (1.27 g, 5.25 mmol) and EtI (0.82 g, 5.25 mmol) were suspended in CH_2Cl_2 (40 cm^3), cooled in dry ice-acetone, and tmen (3 cm^3) added. A clear yellow solution was obtained after 20 min. The cold-bath was removed, and diethyl ether added; $InEtI_2\cdot$tmen was obtained in quantitative yield (Found: In, 22.6; I, 49.2. $C_8H_{21}I_2InN$ requires In, 22.4; I, 49.4%).

A procedure similar to that described for InI–MeI gave $InEtI_2\cdot 2C_2H_6SO$ (0.8 g, 35%) as a solid, from InI (1 g) and EtI (2 cm^3) (Found: In, 21.1; I, 46.8. $C_6H_{17}I_2InO_2S_2$ requires In, 20.7; I, 45.8%). In a second experiment, the oily product was dissolved in dichloromethane and Ph_4PI (1.5 g) in the same solvent added; subsequent removal of solvent and addition of diethyl ether yielded colourless crystals of [PPh_4]-[$InEtI_3$] (yield 2.4 g, 67%) (Found: In, 13.3. $C_{26}H_{25}I_3InP$ requires In, 13.3%).

(*d*) InI–Bu^{n}I. Identical procedures gave [PPh_4][$InBu^nI_3$] (yield 1.9 g, 52%) (Found: In, 13.2. $C_{28}H_{29}I_3InP$ requires In, 12.9%).

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