Reactions of Some Main Group Metals with Diphenyl Disulphide and Diphenyl Diselenide

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Indium reacts with both Ph_2S_2 and Ph_2Se_2 in refluxing toluene to give the compounds $In(EPh)_3$ (E = S or Se) in high yield. Under similar conditions tin gives $Sn(EPh)_4$. Thallium reacts with Ph_2Se_2 to form Tl(SePh), but does not react with Ph_2S_2. Neither zinc nor gallium reacts with Ph_2S_2 or Ph_2Se_2. With mixtures of Ph_2E_2 and I_2, indium yields the previously unreported $InI(EPh)_2$ compounds. The reactions of $In(SePh)_3$ are those of a typical indium(III) Lewis acid. Possible factors affecting the reactions of metals with Ph_2S_2 or Ph_2Se_2 are briefly discussed.

In a recent paper we described the synthesis of $In(SPh)_3$ by the metathetical reaction of $InCl_3$ with Na(SPh), and showed that the compound is a Lewis acid, forming adducts with neutral and anionic donors.[1] An alternative electrochemical route to this, and other $In(SR)_3$, species involves the anodic oxidation of indium metal in non-aqueous solutions of RSH or R_2S_2.[2] We now report a high-yield one-step route to $In(SPh)_3$ involving a direct reaction between Ph_2S_2 and indium metal in refluxing toluene. Subsequent investigation showed that $In(SePh)_3$ can be prepared by a similar method, as can $Sn(EPh)_4$ (E = S or Se). Thallium reacts with Ph_2Se_2 to give Tl(SePh); gallium and zinc do not react with either Ph_2E_2 compounds under these conditions.

Experimental

Toluene was dried by refluxing over calcium hydride before use. All metals, disulphides, diselenides, and ligands were used as supplied. Products were characterized by analysis, by comparison with information in the literature, and by i.r., ^1H n.m.r., and mass spectroscopy using spectroscopic and analytical methods described in earlier work.[1]

Table. Analytical and related results. Calculated values are given in parentheses

Compound	Colour	M.p. (°C)	Analysis (%)	
			M	Halogen
$In(SPh)_3$	White	245[a]	26.2 (26.0)	
$InI(SPh)_2$	Yellow	190	24.8 (25.0)	27.4 (27.6)
$NBu_4[InI_2(SPh)_2]$	White	85—87	13.8 (13.9)	30.5 (30.6)
$In(SePh)_3$	Yellow	150	19.7 (19.7)	*b*
$In(SePh)_3\cdot bipy$	Yellow	100	15.5 (15.5)	
$In(SePh)_3\cdot phen$	Yellow	135	15.2 (15.0)	
$In(SePh)_3\cdot 2PPh_3$	White	123	10.5 (10.4)	
$PPh_4[InBr(SePh)_3]$	White	147	11.6 (11.5)	8.1 (8.0)
$InI(SePh)_2$	Yellow	155	20.4 (20.7)	23.0 (22.9)
Tl(SPh)	Yellow	253[c]	65.0 (65.2)	
Tl(SePh)	Orange	242	56.7 (56.8)	
$Sn(SPh)_4$	Pale yellow	67[d]	21.6 (21.4)	
$Sn(SePh)_4$	Gold-yellow	80—83[e]	16.1 (16.0)	

[a] *cf.* 240—245 °C.[1] [b] Found: C, 37.1; H, 2.60: Calc. C, 37.2; H, 2.50%. [c] *cf.* 258 °C.[11] [d] *cf.* 67 °C.[5] [e] *cf.* 83.5 °C.[6]

Direct Syntheses.—(*i*) $In(SPh)_3$. In a typical experiment, small pieces of indium metal (1.5 g, 13 mmol) were refluxed vigorously with Ph_2S_2 (4.27 g, 19.6 mmol) in toluene (60 cm^3) for 6 h, during which time the metal gradually dissolved and a white solid pecipitated. At the end of the refluxing, the mixture was allowed to cool to room temperature, and the solid collected, washed with pentane (2 × 10 cm^3), and dried *in vacuo*. Yield 5.2 g, 11.9 mmol, 91% based on indium metal. Analytical results for this and other products are given in the Table. The properties of $In(SPh)_3$ prepared by this route were identical in all respects with those reported earlier.[1]

(*ii*) $InI(SPh)_2$ *and* $NBu_4[InI_2(SPh)_2]$. A mixture of indium metal chips (0.6 g, 5.2 mmol), Ph_2S_2 (1.14 g, 5.2 mmol), and iodine (0.66 g, 2.6 mmol I_2) was refluxed vigorously for 6 h. The colour of iodine was completely discharged after about 1 h. The final yellow solution was filtered hot to remove traces of unreacted metal, and then cooled to precipitate a pale yellow powder, which was collected, washed with n-pentane (2 × 10 cm^3), and dried *in vacuo*. Yield of $InI(SPh)_2$ 2.25 g, 4.7 mmol, 90% based on indium metal. The electron impact (e.i.) mass spectrum showed no molecular ion peak; significant ions at $m/e > 100$ were at 115 (In^+), 218 ($Ph_2S_2^{\cdot +}$), and 369 ($InI_2^{\cdot +}$), and minor intensity ions at 478 [$InI_2(SPh)^{\cdot +}$] and 351 [$InI(SPh)^{\cdot +}$]. The field desorption (f.d.) spectrum had essentially no ions above m/e 115.

The compound $InI(SPh_2)_2$, which is air stable over a few days, is soluble in dimethyl sulphoxide (dmso) and dimethylformamide, but insoluble in MeCN, methanol, benzene, and carbon tetrachloride.

When $InI(SPh)_2$ (0.46 g, 1 mmol) in MeCN (30 cm^3) was treated with $NBu^n{}_4I$ (0.37 g, 1 mmol) in the same solvent a white precipitate immediately formed. After 4 h, during which the mixture was stirred at room temperature, this solid was collected, washed twice with n-pentane, and dried *in vacuo*. Yield of $NBu^n{}_4[InI_2(SPh)_2]$ 0.71 g (86%). The compound is an electrolyte in dimethyl sulphoxide (molar conductivity 59 $ohm^{-1}\ cm^2\ mol^{-1}$; *cf.* typical values of 30—50 $ohm^{-1}\ cm^2\ mol^{-1}$ quoted[3] for such salts in this solvent). This anionic indium(III) complex had been prepared earlier[4] by the reaction of InI + Ph_2S_2 in CH_2Cl_2–pyridine, followed by subsequent treatment with NPr_4I to give $NPr_4[InI_2(SPh)_2]$.

(*iii*) $In(SePh)_3$. Indium metal chips (1.16 g, 10.1 mmol) and Ph_2Se_2 (4.73 g, 15.2 mmol) were refluxed in toluene for 3 h, by which time the metal was completely consumed. During the reaction, the initially yellow solution became orange, and finally light yellow. After filtration to remove metal particles, the solution was slowly evaporated to give a yellow powder which was collected, washed with n-pentane, and dried *in vacuo*. Yield 5.46 g, 9.4 mmol, 93%.

The ^1H n.m.r. spectrum in $(CD_3)_2SO$ consisted of a complex multiplet in the aromatic region (6.6—7.2 p.p.m. with reference to $SiMe_4$; *cf.* 7.2—7.4 p.p.m. for Ph_2Se_2 in the same solvent). The compound $In(SePh)_3$ is an air-stable yellow solid, m.p. 150 °C, soluble in most common polar organic solvents, but insoluble in diethyl ether, light petroleum (b.p. 30—60 °C), or n-pentane. The f.d. mass spectrum had a molecular ion (*m/e* 586), and ions identified as $InPh(SePh)_2^{\cdot +}$ and $Ph_2Se_2^{\cdot +}$, all of very low intensity. The e.i. spectrum had the highest *m/e* value at 314 ($Ph_2Se_2^{\cdot +}$), and other prominent ions at 234 ($Ph_2Se^{\cdot +}$), 157 ($PhSe^{\cdot +}$), and $Ph_2^{\cdot +}$ (154).

(*iv*) $InI(SePh)_2$. Indium metal chips (0.89 g, 7.7 mmol) was treated with a solution of I_2(0.98 g, 3.85 mmol) and Ph_2Se_2 (2.41 g, 7.7 mmol) in refluxing toluene (100 cm^3). The iodine colour was discharged within 15 min, and the indium was completely consumed after 5 h. The solution was filtered and the filtrate evaporated *in vacuo* to give $InI(SePh)_2$ as a yellow solid which was collected, washed with toluene, and then n-pentane, and dried *in vacuo*. Yield 3.92 g, 92%. M.p. 155 °C; solubilities apparently the same as for $InI(SPh)_2$. The e.i. mass spectrum showed a weak group of ions from the parent (*m/e* 556), a large number of ions showing the loss of ligand fragments, and a group of heavy ions (*m/e ca.* 980, 944, 906, 870, and 847) which cannot be assigned because of uncertainty in the mass measurement, but which indicate the presence of dimeric species. As with $InI(SPh)_2$, the f.d. mass spectrum had no significant ions beyond *m/e* 115.

(*v*) $Sn(SPh)_4$ *and* $Sn(SePh)_4$. Tin metal chips (0.76 g, 6.39 mmol) were treated with Ph_2S_2 (2.79 g, 12.8 mmol) in toluene (40 cm^3) under vigorous reflux. The metal dissolved over a period of 5 h, during which time the colour of the solution phase changed from yellow to yellow-green. The mixture was filtered and the filtrate evaporated *in vacuo* to give a yellow-green residue which was triturated with n-pentane (10 cm^3) to give a pale yellow solid, which was collected and dried *in vacuo*. Yield 3.2 g, 90%. The product is identical with the literature description of $Sn(SPh)_4$.[5] The f.d. mass spectrum contained only one manifold of ions from $Sn(SPh)_4$ (most intense, *m/e* 556), whose isotopic composition was essentially identical with that obtained by computer simulation. The e.i. spectrum had low-intensity ions corresponding to $Sn(SPh)_4^{\cdot +}$ and $Sn(SPh)_3^{\cdot +}$, and strong lines at *m/e* 229 [$Sn(SPh)^{\cdot +}$] and 218 ($Ph_2S_2^{\cdot +}$).

A similar reaction involving tin (0.4 g, 3.4 mmol), Ph_2Se_2 (2.13 g, 6.8 mmol), and toluene (30 cm^3) eventually (3 h) produced a deep green-yellow solution which on evaporation gave a golden yellow solid identified as $Sn(SePh)_4$ (*cf.* ref. 6). Yield 2.2 g, 2.96 mmol, 87%. The f.d. mass spectrum was again essentially a complex manifold of $Sn(SePh)_4^{\cdot +}$ ions (most intense, *m/e* 744). The predominant ions in the e.i. spectrum were at *m/e* 314 ($Ph_2Se_2^{\cdot +}$), 234 ($Ph_2Se^{\cdot +}$), and 157 ($SePh^{\cdot +}$), with very low-intensity species from $Sn(SePh)_3^{\cdot +}$, and a vanishingly small contribution from $Sn(SePh)_4^{\cdot +}$.

(*vi*) Tl(SePh). A mixture of thallium metal chips (1.47 g, 6.7 mmol) and Ph_2Se_2 (1.05 g, 3.34 mmol) was refluxed in toluene (50 cm^3) for 5 h. An orange solid began to precipitate during the first hour, and the metal had completely dissolved by the end of the reaction period. The orange solid was collected, washed with diethyl ether, and dried *in vacuo*. Yield of Tl(SePh) 2.1 g, 5.8 mmol, 87%. This compound is insoluble in all common organic solvents, hot or cold.

Derivatives of $In(SePh)_3$.—(*i*) $In(SePh)_3\cdot$bipy. The compound $In(SePh)_3$ (0.58 g, 1 mmol) was treated with 2,2′-bipyridine (bipy) (0.16 g, 1 mmol) in benzene (total volume 30 cm^3). A golden-yellow oil immediately formed. After stirring for 2 h, the colourless solution phase was decanted off, and the oil triturated overnight with diethyl ether (30 cm^3). The resultant yellow solid was washed with diethyl ether and dried *in vacuo*. The 1:1 adduct is soluble in dmso, but insoluble in other common organic solvents. Yield 9.62 g, 84%.

(*ii*) $In(SePh)_3\cdot$phen. The reaction of $In(SePh)_3$ (0.71 g, 1.2 mmol) and 1,10-phenanthroline (phen) (0.22 g, 1.2 mmol) in methanol (10 cm^3) yielded a yellow oil, which became a solid on stirring overnight. This solid was collected, washed with methanol (3 × 5 cm^3) and dried *in vacuo*. Yield of $In(SePh)_3\cdot$phen 0.84 g, 90%. Soluble in polar organic solvents (dmso, MeCN, $CHCl_3$, or CH_2Cl_2), insoluble in diethyl ether and n-pentane.

(*iii*) $In(SePh)_3\cdot 2PPh_3$. On addition of $In(SePh)_3$ (0.59 g, 1 mmol) to a solution of PPh_3 (0.52 g, 2 mmol) in n-pentane (20 cm^3) a white precipitate immediately formed. The mixture was stirred overnight, and the solid collected, washed with n-pentane, and dried *in vacuo*. Yield of $In(SePh)_3\cdot 2PPh_3$ 1.05 g, 95%. Soluble in polar organic solvents.

(*iv*) $PPh_4[InBr(SePh)_3]$. A mixture of $In(SePh)_3$ (0.53 g, 0.91 mmol) and PPh_4Br (0.38 g, 0.91 mmol) was stirred at room temperature in methanol (20 cm^3) for 2 d. The resultant suspended solid was collected, washed with diethyl ether, and dried *in vacuo*. Yield of $PPh_4[InBr(SePh)_3]$ 0.76 g, 84%. The compound is insoluble in common organic solvents. The conductivity of a 1 mmol dm^{-3} solution in dimethyl sulphoxide was 49 ohm^{-1} cm^2 mol^{-1}.

Unsuccessful Reactions.—(*i*) Tl + Ph_2S_2. After an extended period of refluxing in toluene, there was no sign of any reaction between thallium metal chips (0.4 g, 1.96 mmol) and Ph_2S_2 (0.21 g, 0.98 mmol); after 30 h, 0.398 g of metal was recovered.

(*ii*) In + $Bu^n{}_2S_2$ or $(p\text{-}O_2NC_6H_4)_2S_2$. When indium metal was refluxed for 20 h with a solution of $Bu^n{}_2S_2$ in toluene in the usual way, no evidence of reaction was seen, and the metal was recovered *in toto*. A similar result was found when the solution was of $(p\text{-}O_2NC_6H_4)_2S_2$ in toluene, with a refluxing period of 48 h, although in this case the indium metal surface became black. Tin metal likewise did not react with $(p\text{-}O_2NC_6H_4)_2S_2$ under these conditions over 40 h.

(*iii*) In + Ph_2S_2 *in the presence of sodium*. Indium metal (0.21 g, 1.85 mmol) was refluxed in a solution of Ph_2S_2 (0.60 g, 2.71 mmol) in toluene (50 cm^3) to which freshly cut sodium (15 mg) was added. After 3 h, the indium metal surface remained bright and shining, and 0.21 g of indium metal was subsequently recovered from the cooled reaction mixture.

(*iv*) Zn + Ph_2S_2. Zinc metal ('mossy'; 0.54 g, 8.2 mmol) and Ph_2S_2 (1.98 g, 9.1 mmol) were refluxed vigorously in toluene for 10 d. Although some black material appeared in suspension during this period, the mass of unreacted metal collected at the end of this period was 0.52 g, showing the essential absence of reaction.

(*v*) Ga + Ph_2S_2 *and* Ph_2Se_2. The reaction mixture, consisting of gallium metal (0.125 g, 1.8 mmol), Ph_2S_2 (0.59 g, 2.7 mmol), and toluene (50 cm^3), was refluxed for 3 d. The gallium metal collected at the end of the reaction weighed 0.124 g. The same result emerged from an identical reaction with Ga + Ph_2Se_2.

(*vi*) In + Ph_4P_2. Indium metal (0.11 g, 0.96 mmol) and Ph_4P_2 (0.53 g, 1.4 mmol) were refluxed together in toluene (50 cm^3) for 16 h; 0.11 g of indium metal was recovered at the end of the procedure, showing the absence of reaction.

Electrochemical Synthesis of Tl(SPh) *and* Tl(SePh).—Thallium metal formed the anode of an electrochemical cell in which the solution phase consisted of Ph_2S_2 (0.17 g) and NEt_4ClO_4 (15 mg) in acetonitrile (50 cm^3). The cathode was a platinum foil, and the procedure followed the methods used in other electrochemical syntheses of metal thiolates in this laboratory.[7—10] During electrolysis for 2 h with an initial voltage of 25 V and a current of 20 mA, 289 mg thallium dissolved from the anode. The yellow material which precipitated in the cell was collected, washed (acetonitrile, then diethyl ether), and dried *in vacuo*. Yield 0.45 g. The product, Tl(SPh), had identical properties to those described in the literature.[11]

A similar procedure with a solution of Ph_2Se_2 (0.16 g), NEt_4ClO_4 (20 mg) in acetonitrile (50 cm^3), and the electrical conditions 15 V, 15 mA, gave an orange precipitate identified as Tl(SePh). Yield 0.13 g, 81% based on 107 mg metal dissolved. The properties were identical to those of the chemically prepared material.

Results and Discussion

Preparative.—The techniques described clearly represent simple and efficient 'one-pot' syntheses of a number of $M(EPh)_n$ compounds by methods which are noticeably simpler than those used in the past for the preparation of $M(EPh)_n$ compounds of Main Group elements, involving metathetical reactions of MCl_n with Na(EPh), Li(EPh), or $Mg(EPh)_2$.[1,5,6,11] The present work has also provided the first synthesis of $In(SePh)_3$, and in the brief investigations reported we have established that this compound closely resembles $In(SPh)_3$ in its Lewis-acid properties, giving both neutral and anionic 1:1 adducts, as does its sulphur analogue. In addition, the direct syntheses give rise to the compounds $InI(EPh)_2$ (E = S or Se), which have not been previously reported, and which should be useful starting materials for other syntheses.

Reaction Pathway.—The selectivity noted in the Experimental section is intriguing, in that while indium and tin react with both Ph_2S_2 and Ph_2Se_2, gallium and zinc do not react with either, and thallium reacts only with Ph_2Se_2. It is worth noting immediately that the thermal reactions are clearly different from those involving the electrochemical oxidation of metal anodes in non-aqueous media, since the latter method is known to give the benzenethiolates of zinc, tin, and thallium.[8,9]

$$2\,M + R_2E_2 \longrightarrow 2\,M(ER) \qquad (1)$$

$$2\,M(ER) + (n-1)R_2E_2 \longrightarrow 2\,M(ER)_n \qquad (2)$$

Given that thallium reacts with Ph_2Se_2 to give the corresponding +I oxidation-state species, the most likely primary reaction can be written as in equation (1) and in the case of indium and tin this would be followed by reaction (2) (M = In, $n = 3$; M = Sn, $n = 4$). The oxidative-insertion process (2) is clearly analogous to other known reactions which convert $\mathrm{In^{I}} \longrightarrow \mathrm{In^{III}}$ or $\mathrm{Sn^{II}} \longrightarrow \mathrm{Sn^{IV}}$. Two questions then arise. The first is whether the observed results with various R_2E_2 compounds are compatible with this mechanism. The known E–E bond-dissociation energies are in the order Se < S < P, which is in keeping with the results for R = Ph; Ph_2Se_2 reacts with tin, indium, and thallium, Ph_2S_2 with tin and indium, and Ph_4P_2 does not react with indium. The effect of changing the group attached to sulphur is that neither Bu_2S_2 nor $(p\text{-}O_2NC_6H_4)_2S_2$ reacts with tin or indium. The contrast between Bu_2S_2 and Ph_2S_2 has been observed in reaction with InI in basic media[4] and in other reactions involving insertions into S–S bonds.[12]

The second point, the differences in the behaviour of the various metals investigated, cannot readily be rationalized in terms of any simple parameter such as ionization energy (I_1 order Zn > Sn > Tl > Ga > In), and the fact that addition of sodium metal to the reaction mixture inhibits the reaction of indium with Ph_2S_2 suggests that the removal of one electron from the metal surface is not a dominant factor. One final observation underlines the difficulties in explaining the mechanism of these systems. The compound $Hg(SePh)_2$ can be prepared by the reaction of mercury metal with Ph_2Se_2 under nitrogen in dioxane at room temperature, but decomposes in refluxing dioxane;[13] it follows that the thermal stability of M(EPh) or $M(EPh)_n$ species may be an important factor governing the reaction pathway in the present experiments.

In these circumstances, the safest conclusion is that the methods are useful for the preparation of some Main Group metal derivatives of PhS and PhSe, proceeding by a mechanism in which cleavage of the S–S or Se–Se bond is the first, but not the only, important step.

Acknowledgements

This work was supported by Operating Grants (to D. G. T.) from the Natural Sciences and Engineering Research Council of Canada.

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Received 30*th March* 1987; *Paper* 7/558