

## Direct Electrochemical Synthesis of Alkane- and Arenethiolato Derivatives of Indium and Thallium

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The electrochemical oxidation of anodic indium in acetonitrile solutions of thiols RSH ( $R = C_2H_5$ ,  $n-C_4H_9$ ,  $C(CH_3)_2C_2H_5$ ,  $C_6H_5$ ,  $2-C_{10}H_7$ ,  $C_6F_5$ ) has been shown to give thiolato derivatives of indium(I), -(II), or -(III), depending on R and on the experimental conditions. With  $R = C_2H_5$  or  $n-C_4H_9$ , electrolysis in the absence of oxygen gives the hitherto unreported InSR compounds, while, with  $R = C_5H_{11}$  or  $2-C_{10}H_7$ , the products are  $In(SR)_2$ , formulated as the In-In-bonded  $In_2(SR)_4$ . Arenethiols yield  $In(SR)_3$ , and products of this stoichiometry are always obtained in the presence of oxygen. The structures of these compounds are discussed, as are the reactions of the indium(I) and -(II) species with iodine and certain other oxidizing agents. Corresponding reactions with thallium anodes gave TISR for all R studied ( $C_6H_5$ ,  $C_6H_4CH_3-o$ ,  $C_6H_4CH_3-m$ ,  $2-C_{10}H_7$ ).

### Introduction

Despite the interest in ligands containing sulfur donor atoms, the alkane- or arenethiolato derivatives of the main-group metals have received much less attention than has been given to the corresponding transition-metal compounds. The tin(IV) and tin(II) species have been known for many years,<sup>1-3</sup> as have lead(II) compounds,<sup>4</sup> while in group III the thallium(I) thiolates are also long established.<sup>5,6</sup> With indium, only  $In(SC_6H_5)_3$  has been prepared, either by metathesis of  $InCl_3$  and  $NaSC_6H_5$ ,<sup>7</sup> or more simply by a direct thermal reaction between indium metal and  $(C_6H_5)_2S_2$  in refluxing toluene.<sup>8</sup> In keeping with the known chemistry of indium(III),  $In(SC_6H_5)_3$  and its selenium analogue are Lewis acids, and both neutral and anionic complexes can be prepared.<sup>7,8</sup>

We now report that a series of indium-thiolato compounds can be prepared by the direct electrochemical techniques successfully used for the synthesis of thiolates of a number of d<sup>10</sup> metal ions.<sup>9-12</sup> These experiments yield products in which indium is in the +1, +2, or +3 oxidation state, depending on the nature of the thiol and on the experimental conditions used in the electrochemistry. By comparison, thallium gave TISR products in all the systems investigated in this work.

### Experimental Section

**General Data.** Solvents were distilled from calcium hydride and stored over molecular sieves. Indium metal rod (o.d. 5 mm) (Alfa Inorganics) was washed with nitric acid and then water and dried; thallium was in the form of wire, 3-mm diameter (Alfa). These and all other reagents were used as supplied.

Metal analysis was by atomic absorption spectrophotometry, and microanalysis on selected compounds was carried out by Guelph Chemical Laboratories Ltd. Infrared spectra were recorded on a Nicolet 5DX instrument, and Raman spectra on a Spex 1403 double monochromator, with a Ramanov U-1000 detector for backscattering and a Spectraphysics Model 2000 Ar laser for excitation. <sup>1</sup>H NMR spectroscopy involved a Perkin-Elmer EM 360 instrument operating at 60 MHz. Mass spectra were obtained with a Varian MAT CH-5 instrument.

**Electrochemical Procedures.** The initial electrochemical syntheses followed the methods described elsewhere.<sup>9,10,13</sup> A 100-mL tall-form

beaker contained solutions whose compositions are summarized in Table I in the case of indium, and the cells were of the general form  $Pt_{(-)}/RSH + CH_3CN/M_{(+)}$  ( $M = In, Tl$ ) with the anode suspended in the solution phase on a platinum wire. The high applied voltage required to ensure current flow in the low-conductivity solution was supplied by a Coutant LQ 50/50 power supply. Unless otherwise noted, all preparative work was carried out under dry nitrogen. Specific procedures and reactions are discussed below.

**Thallium.** The electrochemical oxidation of thallium was carried out in a 100-mL tall-form beaker with solutions of RSH ( $R = C_6H_5$ ,  $o-CH_3C_6H_4$ ,  $m-CH_3C_6H_4$ ,  $2-C_{10}H_7$ ) in acetone (1 g of RSH in 35 mL of acetone containing ca. 50 mg of  $Et_4NClO_4$ ), with an initial voltage of 40 V and a current of 35 mA. Hydrogen gas evolved at the cathode. A yellow insoluble substance began to form at the anode as soon as the current flowed; at the end of the 2-h electrolysis, this material was collected, washed with acetone, and dried in vacuo. The TISR products were characterized by analysis, by <sup>1</sup>H NMR spectroscopy in  $CF_3COOH$ , and by melting point (Table II). The product yields were typically >90%, based on the mass of metal dissolved, and the electrochemical efficiency,  $E_F$ , defined as moles of metal dissolved per faraday of charge, was  $1.0 \pm 0.05$  mol faraday<sup>-1</sup>. No deposition of metal occurred at the cathode (cf. indium below), and there was no evidence of any decomposition of the product.

**Indium-Ethanethiol.** Electrolysis under nitrogen with the conditions summarized in Table I led to the evolution of hydrogen at the cathode and to the formation of a yellow precipitate at the anode. This material gradually changed color over about 5 min, becoming red-violet. At the end of the electrolysis, this material was collected, washed with  $CH_3CN$  (15 mL), and dried in vacuo. Analytical and <sup>1</sup>H NMR results for this and other products are given in Table III.  $InSC_2H_5$  is insoluble in toluene, dimethyl sulfoxide, acetonitrile, or *N,N*-dimethylformamide, and reacts with methylene dibromide (see below).

The preparation was repeated under oxidizing conditions. Oxygen was bubbled through the solution for 3 min to saturate it prior to electrolysis; during the experiment the cell was open to the atmosphere, and the contents of the cell were stirred magnetically during the electrolysis. A yellow precipitate formed immediately at the anode when current began to flow, and as before, this turned red-violet during preparation. In addition, a white product appeared; at the end of the electrolysis, the contents of the cell were stirred for approximately 12 h, during which time the precipitate became uniformly colorless. The final solid, which was collected by filtration, washed (acetonitrile, 15 mL), and then petroleum ether, 15 mL), and dried in vacuo, was identified as  $In(SC_2H_5)_3$ .

**Indium-Butanethiol.** The formation of a yellow precipitate was evident as soon as electrolysis started (see Table I), but this material became red-violet within 5-10 min. The quantity of this material grew as the electrolysis continued; the final red solid product was collected, washed with acetonitrile (15 mL), and dried in vacuo and identified as  $InSC_4H_9-n$ .

The reaction was repeated by using a solution of *n*- $C_4H_9SH$  in acetonitrile presaturated with oxygen and open to the atmosphere (cf.  $C_2H_5SH$  above). At the end of the electrolysis, the mixture was stirred overnight and the resultant white precipitate of  $In(SC_4H_9-n)_3$  collected, washed with acetonitrile (10 mL) and then diethyl ether, and dried in vacuo. The <sup>1</sup>H NMR spectrum of this substance in pyridine-*d*<sub>5</sub> changes on the addition of a drop of  $CS_2$  (see Table III), suggesting a reaction between  $CS_2$  and  $In(SC_4H_9-n)_3$ .

**Indium-2-Methylbutane-2-thiol.** With the conditions summarized in Table I, a yellow solid began to precipitate near the anode within the first

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**Table I.** Experimental Conditions for the Electrochemical Synthesis of Indium Thiolates

thiol	vol, mL <sup>a</sup>	init voltage, V <sup>b</sup>	time of electrolysis, h	amt of In dissolved, mg	product	% yield <sup>c</sup>	E <sub>F</sub> <sup>d</sup>
C <sub>2</sub> H <sub>5</sub> SH	3	15	1.0	221	InSR	90	1.03
C <sub>2</sub> H <sub>5</sub> SH/O <sub>2</sub>	4	15	1.0	222	In(SR) <sub>3</sub>	98	1.03
<i>n</i> -C <sub>4</sub> H <sub>9</sub> SH	2	15	1.0	222	InSR	90	1.03
<i>n</i> -C <sub>4</sub> H <sub>9</sub> SH/O <sub>2</sub>	1	15	1.0	210	In(SR) <sub>3</sub>	72	0.98
C <sub>5</sub> H <sub>11</sub> SH <sup>e</sup>	0.5	20	0.75	133	In(SR) <sub>2</sub>	30	1.03
C <sub>5</sub> H <sub>11</sub> SH/O <sub>2</sub>	1.0	20	1.75	300	In(SR) <sub>3</sub>	80	1.0
C <sub>6</sub> H <sub>5</sub> SH	0.5	15	1.0	214	In(SR) <sub>3</sub>	30	1.0
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH	1.0 g	30	5.0	640	In(SR) <sub>3</sub>	nr <sup>f</sup>	nr <sup>f</sup>
2-C <sub>10</sub> H <sub>7</sub> SH	1.52 g	20	0.6	118	In(SR) <sub>2</sub>	35	0.94
2-C <sub>10</sub> H <sub>7</sub> SH/O <sub>2</sub>	1.52 g	15	0.20	46	In(SR) <sub>3</sub>	42	1.06
C <sub>6</sub> F <sub>5</sub> SH	0.5	20	1.0	226	In(SR) <sub>3</sub>	30	1.05

<sup>a</sup> Dissolved in 60 mL of CH<sub>3</sub>CN containing ca. 50 mg of Et<sub>4</sub>NClO<sub>4</sub>. <sup>b</sup> Voltage required to give an initial current of 50 mA. <sup>c</sup> Based on metal dissolved. <sup>d</sup> Moles of metal dissolved per faraday. <sup>e</sup> C<sub>5</sub>H<sub>11</sub> = -C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>. <sup>f</sup> nr = not recorded.

**Table II.** Analytical and <sup>1</sup>H NMR Results for Thallium(I) Thiolates

product	mp, °C <sup>a</sup>	% Tl		<sup>1</sup> H NMR in CF <sub>3</sub> COOD <sup>b</sup>
		found	calcd	
TlSC <sub>6</sub> H <sub>5</sub>	260 (258)	64.4	65.2	7.18 s
TlSC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	214 (dec)	61.8	62.4	6.59 br (4), 1.68 s (3)
TlSC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i>	167 (178)	64.0 <sup>c</sup>	62.4	6.55 br (4), 1.65 s (3)
TlSC <sub>10</sub> H <sub>7</sub> -2	166 (165)	57.6	56.2	7.0 m

<sup>a</sup> Literature values<sup>5,6</sup> in parentheses. <sup>b</sup> ppm from the 0 ppm resonance of Me<sub>4</sub>Si; relative intensities in parentheses. <sup>c</sup> Calcd: C, 25.7; H, 2.16. Found: C, 25.8; H, 2.01.

10 min of the electrolysis. The quantity of this material continued to increase with time, but after about 40 min, buildup of a deposit on the anode caused the current to drop significantly. An increase in the voltage at this point resulted in the disintegration of this deposit, with an accompanying spark discharge (cf. 2-C<sub>10</sub>H<sub>7</sub>SH below), and we therefore chose to use short and repeated electrolyses in this preparation. The yellow precipitate was collected by filtration, washed with acetonitrile, and dried in vacuo. Analysis (Table III) identified this product as In(SC<sub>3</sub>H<sub>11</sub>)<sub>2</sub>. The mass spectrum (EI mode) included peaks at *m/e* = 642 (molecular ion, 28%), 571 (In<sub>2</sub>(SR)<sub>3</sub>S<sup>+</sup>, 6%), 501 (In<sub>2</sub>(SR)<sub>2</sub>S<sub>2</sub><sup>+</sup>, 14%), 469 (In<sub>2</sub>(SR)<sub>2</sub>S<sup>+</sup>, 16%), 431 (In<sub>2</sub>(SR)S<sub>3</sub><sup>+</sup>, 24%), 399 (In<sub>2</sub>(SR)S<sub>2</sub><sup>+</sup>, 20%), 361 (In<sub>2</sub>S<sub>4</sub><sup>+</sup>, 26%), 329 (In<sub>2</sub>S<sub>3</sub><sup>+</sup>, 16%), and 295 (In<sub>2</sub>S<sub>2</sub><sup>+</sup>, 10%). The *m/e* values are for the most abundant ion in a given manifold, and the intensities are relative to *m/e* = 206 ((C<sub>5</sub>H<sub>11</sub>S)<sub>2</sub><sup>+</sup>, 100%).

A later electrolysis was carried out in an oxygen atmosphere, with the gas bubbling through the reaction mixture for 5 min before beginning the current flow and throughout the experiment. The white solid produced at the anode during the electrolysis was collected, washed with cold acetonitrile (5 mL), and dried in vacuo; this product is In(SC<sub>5</sub>H<sub>11</sub>)<sub>3</sub>.

A third experiment involved a solution containing C<sub>5</sub>H<sub>11</sub>SH (0.5 mL, 0.72 g, 6.94 mmol) and (C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub> (0.70 g, 3.70 mmol) in acetonitrile (60

mL). After 1 h of electrolysis at 15 V and 40 mA, the solution was filtered to remove traces of indium metal, and the filtrate was evaporated to give a white solid, which was washed with acetonitrile and identified as In(SC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, identical with the previously reported substance.<sup>7</sup> The NMR spectrum was free of any resonance in the alkane region.

**Indium-Benzenethiol.** As soon as electrolysis of a solution of C<sub>6</sub>H<sub>5</sub>SH in acetonitrile began, gas evolved at the cathode and a yellow coloration developed at the anode; with continuing electrolysis, a yellow precipitate appeared in the cell, the anode became black, and the region around the cathode showed a brown coloration. As the quantity of the yellow precipitate increased, we noted a change in the nature of this solid, with finely divided indium metal being formed. At the end of the electrolysis, the metal was collected by filtration, washed with acetonitrile (10 mL), and weighed. The amount of indium dissolved from the anode was 214 mg (1.86 mmol), and that collected 128 mg (1.11 mmol; 60% of that dissolved). The filtrate was evaporated until a white solid appeared; this was collected, washed, and dried in vacuo and identified as In(SC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

The experiment was repeated with a solution of C<sub>6</sub>H<sub>5</sub>SH (0.5 mL, 5.5 mmol) and (C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub> (0.85 g, 3.91 mmol) in acetonitrile (60 mL), with a voltage of 15 V and a current of 50 mA. Under these conditions, we observed the deposition of a white solid upon the anode, and after about 1 h the presence of this adhering material caused the current to drop significantly. No red coloration was seen near the cathode (cf. above). The final solution was filtered and evaporated to give a white-yellow residue of In(SC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

Electrolysis (30 V, 35 mA) using acetone solutions of C<sub>6</sub>H<sub>5</sub>SH (1.0 g in 35 mL) produced a yellow coloration near the anode, but no precipitate appeared. After 2–3 h, indium metal began to deposit in the cell. After 5 h, the electrolysis was stopped, the solution filtered, and the filtrate reduced in volume (~10 mL), after which petroleum ether was added to precipitate In(SC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, which was collected and dried in vacuo.

**Indium-*o*-Toluenethiol.** Electrochemical oxidation of indium under the conditions shown in Table I gave In(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*o*)<sub>3</sub>. The color changes observed, and the isolation methods used, were essentially those

**Table III.** Analytical and <sup>1</sup>H NMR Results for Indium-Thiolato Compounds

compd	% In		% halogen		<sup>1</sup> H NMR <sup>a</sup>	solvent
	found	calcd	found	calcd		
InSC <sub>2</sub> H <sub>5</sub>	64.8	65.3			2.51 q (2), 1.17 t (3)	CF <sub>3</sub> COOH/dms <sub>o</sub> -d <sub>6</sub>
In(SC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	38.9	38.6			2.61 q (2), 1.31 t (3)	py-d <sub>5</sub>
InSC <sub>4</sub> H <sub>9</sub> - <i>n</i> <sup>b</sup>	55.8	56.4			2.54 t (2), 1.44 m (4), 0.90 t (3)	CF <sub>3</sub> COOH/dms <sub>o</sub> -d <sub>6</sub>
In(SC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	29.8	30.1			2.62 t (2), 1.45 m (4), 0.77 t (3)	py-d <sub>5</sub>
					2.95 m (2), 1.40 m (4), 0.71 m (3)	py-d <sub>5</sub> /CS <sub>2</sub>
In(SC <sub>3</sub> H <sub>11</sub> ) <sub>2</sub> <sup>c</sup>	35.3	35.7			1.9–0.9 m	acetone-d <sub>6</sub>
In(SC <sub>5</sub> H <sub>11</sub> ) <sub>3</sub>	26.7	27.1			1.42 q (2), 1.35 s (6)	dms <sub>o</sub> -d <sub>6</sub>
In(SC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	26.5	26.0			7.6–6.7 m	dms <sub>o</sub> -d <sub>6</sub>
In(SC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> ) <sub>3</sub>	23.7	23.7			7.14 m (4), 2.31 s (3)	CF <sub>3</sub> COOD
In(SC <sub>10</sub> H <sub>7</sub> ) <sub>2</sub> <sup>d</sup>	26.2	26.5			see text	
In(SC <sub>10</sub> H <sub>7</sub> ) <sub>3</sub>	19.3	19.4			7.8 br m, 7.4 br m	CDCl <sub>3</sub> /dms <sub>o</sub> -d <sub>6</sub>
In(SC <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	17.0	16.2			see text	
InI <sub>2</sub> (SC <sub>2</sub> H <sub>5</sub> )-bpy	18.8	19.6	42.7	43.3	8.37 m (8), 2.60 q (2), 1.27 t (3)	dms <sub>o</sub> -d <sub>6</sub>
InI(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN	27.8	28.4	31.8	31.4	2.55 q (4), 1.20 t (6), 2.07 s (3), (CH <sub>3</sub> CN)	dms <sub>o</sub> -d <sub>6</sub>
InI(SC <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	28.0	27.3	31.1	30.2	3.1 t, 1.42 m, 0.81 t	dms <sub>o</sub> -d <sub>6</sub>
InI <sub>2</sub> (SC <sub>4</sub> H <sub>9</sub> )-phen	17.5	18.0	39.0	39.8	8.1–9.7 m (8), 3.03 t (2), 1.46 m (4), 0.83 t (3)	dms <sub>o</sub> -d <sub>6</sub>
[(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N][In(SC <sub>5</sub> H <sub>11</sub> ) <sub>4</sub> ] <sup>e</sup>	14.5	14.9			insoluble	
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> P][InBr(SC <sub>10</sub> H <sub>7</sub> ) <sub>3</sub> ]	10.9	11.4	7.48	7.91	8.0–6.7 m	CDCl <sub>3</sub>

<sup>a</sup> ppm from the 0 ppm resonance of Me<sub>4</sub>Si; relative intensities in parentheses. <sup>b</sup> Calcd: C, 23.6; H, 4.42. Found: C, 24.8; H, 4.95. <sup>c</sup> Calcd: C, 37.4; H, 6.9. Found: C, 36.8; H, 6.9. <sup>d</sup> Calcd: C, 55.5; H, 3.3. Found: C, 56.4; H, 3.7. <sup>e</sup> Calcd: C, 56.1; H, 10.5; N, 1.82. Found: C, 56.5; H, 10.6; N, 2.07.

described above for the  $\text{In}/\text{C}_6\text{H}_5\text{SH}/\text{acetone}$  system.

**Indium-Naphthalene-2-thiol.** As with other aromatic thiols in acetone solution, electrolysis with a solution of  $2\text{-C}_{10}\text{H}_7\text{SH}$  (0.5 g) in acetone (35 mL) at 40 V and 30 mA for 1 h yielded  $\text{In}(\text{SC}_{10}\text{H}_7)_3$ . This compound is soluble in dmsO, pyridine, and dimethylformamide and slightly soluble in acetonitrile.

When the electrolysis was performed in acetonitrile (see Table I), a yellow precipitate was seen at the anode within a few minutes; after about 40 min, deposition on the anode was such that the current fell sharply. The solid products were collected, washed with acetonitrile (15 mL), and dried in vacuo. We found that if the product was allowed to accumulate on the anode, it tended to flake off with an accompanying spark discharge. Apart from any inherent danger, the reaction mixture is then contaminated with gray-black particles of indium metal from the anode. As with  $\text{In}(\text{SC}_5\text{H}_{11})_3$ , short preparative runs lasting 40 min were used for subsequent studies. The product,  $\text{In}(\text{SC}_{10}\text{H}_7)_2$ , is insoluble in all organic solvents. In order to record the  $^1\text{H}$  NMR spectrum,  $\text{In}(\text{SC}_{10}\text{H}_7)_2$  was digested in  $\text{CF}_3\text{COOD}$  (0.5 mL), the resultant mixture taken to dryness, and the residue dissolved in either  $\text{CDCl}_3$  or  $\text{dmsO}-d_6$ ; the only broad resonance observed, 7.85–7.33 ppm from that of  $\text{Me}_2\text{Si}$ , was almost identical with the  $2\text{-C}_{10}\text{H}_7\text{SH}$  resonance. The vibrational spectrum of  $\text{In}(\text{SC}_{10}\text{H}_7)_2$  is discussed below.

When the electrolytic oxidation of indium was carried with solutions of  $\text{C}_{10}\text{H}_7\text{SH}$  in  $\text{CH}_3\text{CN}$  presaturated with oxygen, the product was a white solid, which was collected and identified as  $\text{In}(\text{SC}_{10}\text{H}_7\text{-}2)_3$ , mp 265–270 °C. Yield: 42%, based on indium dissolved.

**Indium-Pentafluorobenzenethiol.** During the first 10 min of electrolysis, we observed only gas evolution at the cathode, with neither precipitation nor coloration in the solution. At the end of this period, a cloudiness in the solution was followed by the precipitation of finely divided indium metal throughout the solution phase. As the electrolysis proceeded, deposition of indium on the cathode occurred. The conductivity of the solution also increased markedly during this period. The indium metal was collected by filtration (33 mg), and the metal on the cathode was also removed and weighed (78 mg). The filtrate from the electrolysis was evaporated to dryness. The resultant residue was extracted with tetrahydrofuran ( $2 \times 25$  mL); after filtration, the thf was removed by evaporation in vacuo to give a solid identified as  $\text{In}(\text{SC}_6\text{F}_5)_3$ . The infrared spectrum (KBr disk) is essentially identical with that of  $\text{C}_6\text{F}_5\text{SH}$ , apart from the absence of S–H vibrations. The  $^{19}\text{F}$  NMR spectrum (dmsO solution; frequencies measured relative to  $\text{CF}_3\text{COOD}$  and recalculated to the frequency of  $\text{CFCl}_3 = 0$  ppm) of  $\text{C}_6\text{F}_5\text{SH}$  has resonances centered at  $-139.2$  t (F2, F6),  $-160.6$  q (F4), and  $-163.8$  m ppm (F3, F5) (cf. the frequency of  $\text{C}_6\text{F}_6 = -163$  ppm). The spectrum of  $\text{In}(\text{SC}_6\text{F}_5)_3$  has resonances at  $-130.6$  t, br,  $-160.5$  q, br, and  $-164.5$  m, br ppm. The broadening may be the result of the presence of  $^{115}\text{In}$  (spin  $9/2$ ). The changes in chemical shift on complexing are most obvious at those fluorine atoms closest to the sulfur atom.

**Reactions of Indium(I) and Indium(II) Compounds.** In order to investigate the reactions of the air-sensitive  $\text{InSR}$  and  $\text{In}(\text{SR})_2$  compounds prepared, electrolyses were carried out in a cell whose base was a fine glass sinter. At the end of the electrolysis, the solution phase could be run off through this sinter, allowing the solid to be collected. The quantity of this solid was calculated from the weight loss of the anode, which was removed from the cell at this stage. Reagents could then be added to the residue in situ, and the products of these secondary reactions were collected and characterized in the usual way. All procedures were carried out under an atmosphere of dry nitrogen.

**Reactions of  $\text{InSC}_2\text{H}_5$ .** (i) Following the preparation and collection of  $\text{InSC}_2\text{H}_5$  by the dissolution of 212 mg of indium (1.84 mmol), the solid product was washed with acetonitrile (15 mL) and treated with a solution of  $\text{I}_2$  (468 mg, 1.84 mmol) plus 2,2'-bipyridine (bpy; 288 mg, 1.84 mol) in acetonitrile (30 mL). During a reaction period of  $\sim 16$  h at room temperature, the red-violet solid dissolved to give a yellow solution, which was evaporated to dryness in vacuo. The resultant yellow solid was triturated with diethyl ether (15 mL) and dried in vacuo. The final yellow powder is  $\text{InI}_2(\text{SC}_2\text{H}_5)\cdot\text{bpy}$ ; yield 90%.

(ii) After isolation as above,  $\text{InSC}_2\text{H}_5$  (1.92 mmol) was oxidized with an equimolar quantity of  $\text{I}_2$  in acetonitrile. Under these conditions, the red solid quickly became colorless. After 15 h, the color of iodine had been discharged, and the reaction mixture was filtered and the colorless solid identified as  $\text{InI}(\text{SC}_2\text{H}_5)_2\cdot\text{CH}_3\text{CN}$ . The filtrate was treated with bpy (400 mg, 2.56 mmol), which resulted in the slow precipitation of yellow crystalline  $\text{InI}_3\cdot\text{bpy}$ , which was collected and dried in the usual way.

(iii) Freshly prepared and isolated  $\text{InSC}_2\text{H}_5$  was treated with excess  $\text{CH}_2\text{Br}_2$  (5 mL) in acetonitrile (50 mL). The reaction mixture was stirred overnight under nitrogen; the white precipitate which formed during this period was collected, washed with acetonitrile (15 mL), and dried and identified as  $\text{InBr}(\text{SC}_2\text{H}_5)_2\cdot\text{CH}_3\text{CN}$ .

**Reactions of  $\text{InSC}_4\text{H}_9\text{-}n$ .** (i) Following the procedure just described,  $\text{InSC}_4\text{H}_9\text{-}n$  (calcd 1.91 mmol) was treated with a solution of  $\text{I}_2$  (485 mg, 1.91 mmol) in acetonitrile (15 mL). The color of  $\text{I}_2$  discharged, and the red-violet solid became colorless over 3–4 h. This solid was collected, washed, and dried and identified as  $\text{InI}(\text{SC}_4\text{H}_9)_2$ . The filtrate from this reaction was treated with bpy, which precipitated  $\text{InI}_3\cdot\text{bpy}$ . [Anal. Calcd: In, 17.6; I, 58.4. Found: In, 17.0; I, 58.4.  $^1\text{H}$  NMR: 9.30–7.20 m ppm.]

(ii) When  $\text{InSC}_4\text{H}_9\text{-}n$  was treated with equimolar quantities of  $\text{I}_2$  and 1,10-phenanthroline in acetonitrile, the red solid became yellow. This material was collected, triturated with acetonitrile, and dried and identified as  $\text{InI}_2(\text{SC}_4\text{H}_9)\cdot\text{phen}$ .

(iii)  $\text{InSC}_4\text{H}_9$  (1.99 mmol) was treated with  $\text{I}_2$  (0.50 g, 1.99 mmol) and  $(\text{C}_6\text{H}_5)_3\text{PI}$  (0.925 g, 1.99 mmol), and the mixture was stirred for 1 h, during which the red color of  $\text{InSC}_4\text{H}_9$  discharged and a clear solution was obtained. After further stirring, the mixture was filtered to remove traces of gray material, and the filtrate was evaporated to dryness. The resultant white solid was triturated for 15 min with methanol (25 mL) and then dried in vacuo; the residual solid was identified as  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{I}_2\text{In}(\text{SC}_4\text{H}_9)_2]$ . The methanol extract deposited colorless acicular crystals on standing, and these were identified as  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{InI}_4]$ . [Anal. Calcd: In, 12.0; I, 52.8. Found: In, 11.8; I, 52.85.] The infrared spectrum confirmed the absence of *n*-butyl groups in this material.

(iv) There was no reaction when  $\text{InSC}_4\text{H}_9$  was treated with triethylamine or *N,N,N',N'*-tetramethylethanediamine.

**Reactions of  $\text{In}(\text{SC}_5\text{H}_{11})_2$ .** (i) Electrolytically prepared  $\text{In}(\text{SC}_5\text{H}_{11})_2$  (calcd 351 mg, 1.09 mmol) was treated with  $\text{I}_2$  (139 mg, 1.09 mmol) in acetonitrile (20 mL). The iodine reacted completely as judged by the color change, leaving a pale yellow solid, which was collected and dried and identified as  $\text{InI}_3$  [Anal. Calcd: In, 23.2; I, 76.8. Found: In, 21.2; I, 74.0.  $^1\text{H}$  NMR (dmsO- $d_6$ ) spectroscopy showed absence of organic groups, as did the infrared spectrum (KBr disk).] When evaporated in vacuo, the filtrate gave no solid deposit.

(ii)  $\text{In}(\text{SC}_5\text{H}_{11})_2$  was prepared electrochemically as described above, with the amount of product, as calculated from the electrochemical efficiency and anode weight loss, being 0.622 g (1.94 mmol). At the end of the electrolysis,  $(\text{C}_2\text{H}_5)_3\text{N}$  (0.5 mL, 0.70 g, 6.92 mmol) was syringed into the reaction mixture without separating the product, and the mixture was stirred overnight. The suspended  $\text{In}(\text{SC}_5\text{H}_{11})_2$  dissolved, leaving a gray suspension, which was removed by filtration. The filtrate was taken to dryness, the resultant solid extracted with acetonitrile (10 mL), and the residue dried in vacuo. Analysis and  $^1\text{H}$  NMR spectroscopy identified this residue as  $\text{In}(\text{SC}_5\text{H}_{11})_3$ .

(iii)  $\text{In}(\text{SC}_5\text{H}_{11})_2$  (0.46 g, 1.42 mmol), prepared electrochemically and suspended in the reaction mixture, was treated with  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$  in methanol (4 mL of 25% w/v solution; 3.9 mmol). The precipitate dissolved immediately to give a colorless solution. After filtration to remove a gray cloudy material, the solution was slowly evaporated in vacuo to give colorless needles, which were collected, washed with cold acetonitrile, and dried in vacuo and identified as  $[(\text{C}_4\text{H}_9)_4\text{N}][\text{In}(\text{SC}_5\text{H}_{11})_4]$ .

**Reactions of  $\text{In}(\text{SC}_{10}\text{H}_7)_2$ .** (i) Freshly prepared and separated  $\text{In}(\text{SC}_{10}\text{H}_7)_2$  (0.31 g, 0.72 mmol) suspended in acetonitrile (20 mL) was treated with 0.27 g of  $\text{I}_2$  (1.06 mmol). The solid dissolved, and the iodine color was discharged over 10–15 min as the mixture was stirred at room temperature. After 3 h, the colorless mixture was filtered to remove any traces of unreacted solid, and the filtrate was evaporated in vacuo until a colorless crystalline product was obtained. This was collected, washed with  $\text{CH}_3\text{CN}$  (5 mL), and dried in vacuo. Yield: 0.21 g. The compound was shown to contain  $-\text{SC}_{10}\text{H}_7$  by infrared and  $^1\text{H}$  NMR spectroscopy (comparison with  $2\text{-C}_{10}\text{H}_7\text{SH}$ ). Mp: 145 °C; lit. value<sup>14</sup> for  $(\text{C}_{10}\text{H}_7\text{S})_2$  137 °C. Mass spectrum (EI):  $m/e = 318$  (molecular ion), 159 ( $\text{C}_{10}\text{H}_7\text{S}^+$ ).

(ii) Repetition of the above experiment with the reagents in the molar ratio  $\text{In}(\text{SR})_2:\text{I}_2 = 2:1$  (0.25 g, 0.58 mmol:0.073 g, 0.29 mmol) showed the same sequence of dissolution and color change. The final solution was worked up as above to give a white flaky solid, mp 144–148 °C, again identified spectroscopically as  $(\text{C}_{10}\text{H}_7\text{S})_2$ .

(iii) When 0.35 g (0.81 mmol) of  $\text{In}(\text{SC}_{10}\text{H}_7)_2$  suspended in  $\text{CH}_3\text{CN}$  (15 mL) was treated with  $(\text{C}_6\text{H}_5)_4\text{PBr}$  (0.34 g, 0.81 mmol), the yellow solid immediately dissolved to give a green cloudy solution. After the solution was stirred for 2 h, gray suspended material (indium metal, ca. 15 mg) was removed by filtration and the filtrate taken to dryness in vacuo. The resultant solid was triturated with methanol (5 mL); evaporation of the methanol extract gave a solid identified as  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{InBr}(\text{SC}_{10}\text{H}_7)_3]$ . Yield: 40%.

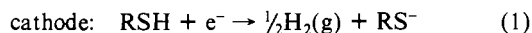
(iv) A 0.35-g amount of  $\text{In}(\text{SC}_{10}\text{H}_7)_2$  (0.81 mmol) was suspended in benzene (20 mL) and treated with *N,N,N',N'*-tetramethylethanediamine

(14) Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1984**, *117*, 3388.

(tmen) (0.5 mL, 0.71 g, 6.1 mmol). The solid immediately went into solution, and a colorless oil separated. After further stirring (2 h), the solvent was evaporated, leading to the precipitation of further oil. We were unable to solidify this material, but  $^1\text{H}$  NMR spectroscopy confirmed the presence of both  $\text{C}_{10}\text{H}_7$  and tmen, in the ratio 1:6.

## Results and Discussion

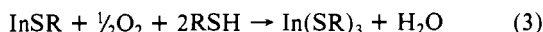
**Electrochemical Preparation.** For each of the systems studied, we determined the electrochemical efficiency,  $E_F$ , defined as moles of metal dissolved per faraday of charge, and found a constant value of  $1.00 \pm 0.03$  mol faraday $^{-1}$  irrespective of metal, solvent, thiol, or presence or absence of oxygen. Together with the evolution of hydrogen at the cathode, this identifies the electrochemical reactions as



It also follows that the formation of products identified as derivatives of indium in the +2 or +3 state is the consequence of the subsequent reaction of  $\text{In}^{\text{I}}\text{SR}$  produced via reaction 2. In this respect, the indium systems behave like those of tin,<sup>10</sup> in that the low-oxidation-state species is the electrochemical product which reacts in situ; thallium and lead<sup>10</sup> in contrast give stable MSR or  $\text{M}(\text{SR})_2$  products which resist further oxidation.

The studies of the electrochemical synthesis of thallium thiolate show clearly that only  $\text{Tl}^{\text{I}}\text{SR}$  species are produced and that these products are stable against further reaction in situ. This is in keeping with the known chemistry of thallium(I) with sulfur-donor ligands, although a systematic study of these TISR compounds appears to be lacking. Attempts to prepare thallium(III) derivatives of monodentate sulfur-donor ligands have been unsuccessful,<sup>15</sup> emphasizing the stability of thallium(I) in such systems.

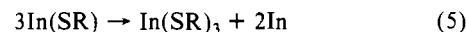
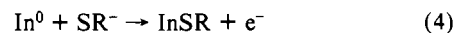
With indium, the electrochemical evidence clearly identifies the initial formation of  $\text{In}^{\text{I}}\text{SR}$  at the anode, but only in the case of  $\text{R} = \text{C}_2\text{H}_5$  or  $n\text{-C}_4\text{H}_9$  is this product sufficiently stable to resist oxidation or disproportionation in situ. The synthesis of these substances increases the small number of indium(I) species known<sup>15</sup> and opens a new field of group III (13) chemistry, especially since the stability of  $\text{InSR}$  for  $\text{R} = \text{C}_2\text{H}_5$  or  $n\text{-C}_4\text{H}_9$  suggests that other indium(I) alkanethiolates could be prepared electrochemically and that there will be an oxidative-addition chemistry paralleling that of other indium(I) species.<sup>17-19</sup> The compounds are air and moisture sensitive and react readily with mild oxidizing agents such as  $\text{I}_2$  or  $\text{R}_2\text{S}_2$  (see below). The synthetic evidence also shows that in the presence of dissolved oxygen, the product is  $\text{In}(\text{SR})_3$ , demonstrating the in situ oxidation of  $\text{InSR}$ . The simplest description of this process would be



although the detailed mechanism is no doubt more complex. The substitution of acetone for acetonitrile as the reaction solvent also results in the formation of  $\text{In}(\text{SR})_3$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ -*o*,  $\text{C}_{10}\text{H}_7$ ), and presumably the oxidizing properties of this solvent, discussed elsewhere,<sup>16</sup> again explain this result. We have also shown that the presence of  $\text{R}_2\text{S}_2$  in the solution leads to the formation of  $\text{In}(\text{SR})_3$  for  $\text{R} = \text{C}_6\text{H}_5$ , and similarly the electrochemical oxidation of indium metal in the presence of  $\text{C}_5\text{H}_{11}\text{SH}$  and  $(\text{C}_6\text{H}_5\text{S})_2$  gave  $\text{In}(\text{SC}_6\text{H}_5)_3$  as the only product, a result that is compatible with the in situ oxidation of  $\text{InSC}_5\text{H}_{11}$  by diphenyl disulfide, followed by disproportionation of  $\text{In}(\text{SC}_5\text{H}_{11})(\text{SC}_6\text{H}_5)_2$  to the tris(arenethiolato) product. These reactions parallel the oxidative addition reported earlier between  $\text{InX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{R}_2\text{S}_2$  to give  $\text{InX}(\text{SR})_2$  derivatives.<sup>17</sup>

With  $\text{R} = \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2$ , the anode product  $\text{InSC}_5\text{H}_{11}$  is unstable in the presence of the other components of the solution with respect to the formation of  $\text{In}(\text{SC}_5\text{H}_{11})_2$ . When  $\text{O}_2$  is present

during the electrolysis, the product is again  $\text{In}(\text{SC}_5\text{H}_{11})_3$ , although the  $E_F$  value remains at unity. Similarly, with  $\text{R} = \text{C}_{10}\text{H}_7$ -2, the product in acetonitrile is  $\text{In}(\text{SR})_2$ , while  $\text{In}(\text{SR})_3$  is obtained in acetone. In this latter case, acetone is the likely oxidant (cf. discussion above). The synthesis of these two  $\text{In}(\text{SR})_2$  compounds again expands the known range of indium(II) species. We return to the question of their structure below. Their formation in solution may be the result of the sequence



which involves the disproportionation of  $\text{InSR}$  (see below) and the subsequent reaction of indium(I) and -(III) species. This last process would parallel that identified between  $\text{InX}$  and  $\text{InX}_3$  to give  $\text{InX}_2$ .<sup>18</sup>

With benzenethiol or other arenethiols,  $\text{In}(\text{SR})_3$  is the only product recovered, irrespective of the solvent used, although  $E_F$  is again unity, so that the products result from the oxidation of  $\text{In}^{\text{I}}\text{SR}$ . This disproportionation reaction (5) has been confirmed in the case of  $\text{R} = \text{C}_6\text{H}_5$ , since indium metal corresponding to 60% of that dissolved was recovered (cf. 66% required for eq 5).

In general, it is clear that the electrochemical oxidation of indium in the presence of alkanethiols is a simple route to some hitherto unknown  $\text{In}^{\text{I}}\text{SR}$  compounds. A simple variant on the procedure yields  $\text{In}(\text{SR})_3$  species, and the redox reactions of  $\text{In}^{\text{I}}\text{SR}$  ( $\text{R} = \text{alkyl}, \text{aryl}$ ) can be utilized in the synthesis of other indium(III) derivatives. Thallium(I) compounds can also conveniently be prepared by the electrochemical route.

**Structure of  $\text{In}(\text{SR})_n$  Compounds.** The properties of  $\text{In}(\text{SC}_6\text{H}_5)_3$  as described elsewhere<sup>7</sup> are those of a typical  $\text{MX}_3$  acceptor, which gives rise to both neutral  $\text{In}(\text{SR})_3\text{L}$  and anionic  $[\text{In}(\text{SR})_4]^-$  derivatives. The  $\text{In}(\text{SR})_3$  compounds prepared in the present work appear to be similar, in that the anionic derivatives  $[\text{BrIn}(\text{S-C}_{10}\text{H}_7)_3]^-$  and  $[\text{In}(\text{SC}_5\text{H}_{11})_4]^-$  were obtained in secondary reactions. The solubility in acetonitrile and acetone is in keeping with the acceptor properties of  $\text{In}(\text{SR})_3$ , and the mixed  $\text{InX}(\text{SR})_2$  and  $\text{InX}_2(\text{SR})$  complexes obtained by the oxidation of  $\text{InSR}$  or  $\text{In}(\text{SR})_2$  are also typical of known indium(III) chemistry.<sup>7,8,15</sup>

Indium(II) compounds known thus far are of two dimeric forms, either the ionic  $[\text{InX}_4]$  ( $\text{X} = \text{Br}, \text{I}$ )<sup>19-21</sup> or  $\text{In-In}$ -bonded species, as in the anionic  $\text{In}_2\text{X}_6^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>22</sup> or neutral adducts  $\text{In}_2\text{X}_4\text{L}_2$ .<sup>23-25</sup> No monomeric indium(II) species have been prepared. We believe that the two compounds identified as  $\text{In}(\text{SR})_2$  ( $\text{R} = \text{C}_{10}\text{H}_7$ ,  $\text{C}_5\text{H}_{11}$ ) are in fact the neutral  $(\text{RS})_2\text{InIn}(\text{SR})_2$  species, since the ionic form  $[\text{In}(\text{SR})_4]^-$  would lack the stabilizing coordination of  $\text{In}^+$  observed in  $[\text{InI}_4]^-$ , but the only physical evidence presently available is that the Raman spectrum of the naphthyl compound has an emission at  $142\text{ cm}^{-1}$ , close to that observed for  $\nu(\text{In-In})$  in other systems.<sup>17,23,24</sup> Strong fluorescence prevented Raman examination of the analogous  $\text{C}_5\text{H}_{11}$  compound.

The spectroscopic evidence available on the indium(I) thiolates isolated in this work is limited to that from  $^1\text{H}$  NMR spectroscopy, which confirmed the presence of the ligand after decomposition with  $\text{CF}_3\text{COOH}$ . There is an interesting comparison to be made, related to the stabilization of  $\text{InSR}$  species. As noted earlier, the  $E_F$  value of  $1.0$  mol faraday $^{-1}$  found in each system studied shows that the anodic oxidation of  $\text{In}$  by  $\text{SR}^-$  produces  $\text{InSR}$ , and therefore the subsequent reactions of this molecule determine the nature of the final product. In the limiting case, arenethiols yield  $\text{In}(\text{SR})_3$ , whereas straight-chain alkanethiolate ligands stabilize  $\text{InSR}$  against disproportionation in situ, although these substances do react with various oxidizing agents. The stability of  $\text{InSR}$  therefore depends in part on the nature of  $\text{R}$ , and we suggest that

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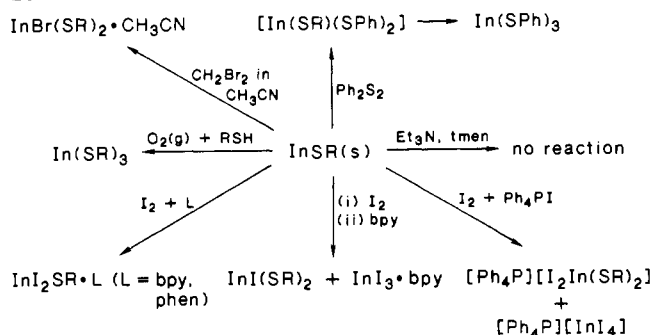
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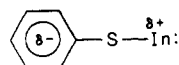
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(25) Khan, M. A.; Peppe, C.; Tuck, D. G. *Can. J. Chem.* **1984**, *62*, 601.

## Scheme I



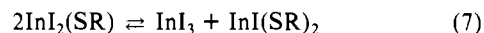
the differing behavior of  $\text{InSR}$  for  $\text{R} = \text{alkyl}$  or  $\text{aryl}$  can be understood in the following way. First, any indium(I) molecule presumably has a lone pair of electrons available for reaction, and this has been demonstrated in a number of studies of indium(I) halides<sup>17,18</sup> and cyclopentadienylindium(I).<sup>26,27</sup> Second, we are dealing with  $\text{InSR}$  compounds, which precipitate in the reaction medium (except for  $\text{R} = \text{C}_6\text{F}_5$  discussed below), and by analogy with other metal thiolates, homopolymerization by  $\text{M}-\text{S}$  cross-linking is critical in determining the solubility and reactivity of such substances. In this context, there is a significant difference in the charge delocalization between alkane- and arenethiolato ligands; for an alkyl derivative, the polarization  $\text{H}_3\text{C}-\text{S}^\delta-\text{In}^{\delta+}-\text{In}^{\delta+}$  must reduce the availability of the lone pair on indium, while for  $\text{InSC}_6\text{H}_5$  there will be contributions from



and as pointed out elsewhere,<sup>28</sup> this can weaken the cross-linking. These arguments suggest that, in the solid state, aryl  $\text{InSR}$  compounds will be more prone to depolymerize, and hence to react or disproportionate, than the alkyl analogues.

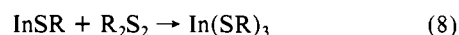
The nonprecipitation of  $\text{InSC}_6\text{F}_5$  and its rapid decomposition in solution (see Experimental Section) represent an extreme case of the effect of an electron-withdrawing group on the stability of the  $-\text{S}-\text{In}$  system.

**Reactions of  $\text{In}(\text{SR})$  and  $\text{In}_2(\text{SR})_4$  Compounds.** The two  $\text{In}(\text{SR})$  compounds prepared ( $\text{R} = \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$ ) are moisture and air sensitive and react readily with mild oxidizing agents as shown in Scheme I. With iodine, we suggest that the initial product is  $\text{InI}_2(\text{SR})$ , which in the presence of strong neutral donors is stabilized as (e.g.)  $\text{InI}_2(\text{SR}) \cdot \text{bpy}$ , a typical indium(III) reaction. In the absence of such donors, the product is  $\text{InI}(\text{SR})_2$ , or a solvate, and subsequent treatment of the solution remaining after the removal of this compound yields an adduct of  $\text{InI}_3$ . These results indicate that the typical redistribution reaction



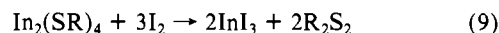
is established in solution, with different species (or their derivatives) being precipitated under different conditions. The formation of  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{I}_2\text{In}(\text{SC}_6\text{H}_5)_2]$  and  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{InI}_4]$  is equally evidence for eq 7, with the products stabilized as the anionic complexes identified in previous work.<sup>18,29</sup>

The other oxidation reaction identified in this work is



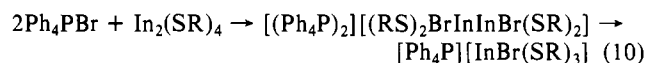
( $\text{R} = \text{C}_6\text{H}_5$ ), which is clearly parallel to that observed between  $\text{InX}$  ( $\text{X} = \text{Cl, Br, I}$ ) and  $(\text{C}_6\text{H}_5)_2\text{S}_2$ .<sup>18</sup> In the case of the reaction between  $\text{InSC}_5\text{H}_{11}$  and  $(\text{C}_6\text{H}_5)_2\text{S}_2$ , the final isolated product was  $\text{In}(\text{SC}_5\text{H}_{11})_3$ , which points to a rearrangement reaction similar to eq 7 involving the presumed initial product  $\text{In}(\text{SC}_5\text{H}_{11})(\text{SC}_6\text{H}_5)_2$ . The reaction of  $\text{InSC}_2\text{H}_5$  with  $\text{CH}_2\text{Br}_2$  also produces the oxidation product  $\text{InBr}(\text{SC}_2\text{H}_5)_2$ . The mechanism of this process has yet to be elucidated, as has that for the conversion of  $\text{InSR}$  to  $\text{In}(\text{SR})_3$  by oxygen.

The oxidation of  $\text{In}_2(\text{SR})_4$  by  $\text{I}_2$  follows a pathway different from that of  $\text{InSR}$ . With  $\text{R} = \text{C}_5\text{H}_{11}$ , we identified  $\text{InI}_3$  as the only product; if the other product is  $\text{R}_2\text{S}_2$ , as shown for  $\text{R} = \text{C}_{10}\text{H}_7$ , it would have been lost in the final workup since it is highly volatile. The preparative evidence is that the overall process is



The mechanism of this reaction has not been investigated, but it is clear that the oxidation of  $\text{In}_2(\text{SR})_4$  by  $\text{I}_2$  involves a pathway different from the formally simpler reaction of  $\text{InSR}$  with the same oxidant. The formation of  $\text{R}_2\text{S}_2$  itself implies oxidation of the anionic ligand, as well as oxidation of the metal, but here, as in the other reactions reported, the mechanism can only be a matter of speculation. Any kinetic or spectroscopic study is hindered by the insolubility of  $\text{In}_2(\text{SR})_4$  compounds in common organic solvents.

The addition of  $(\text{C}_6\text{H}_5)_4\text{PBr}$  to  $\text{In}_2(\text{SC}_{10}\text{H}_7)_4$  yields the corresponding salt of  $[\text{BrIn}(\text{SR})_3]^-$ , together with other unidentified products. The suggested sequence here is



with the anionic intermediate being the analogue of the previously identified  $\text{In}_2\text{X}_6^{2-}$  anions. Treatment with  $(\text{C}_2\text{H}_5)_3\text{N}$  in the presence of  $\text{RSH}$  ( $\text{R} = \text{C}_5\text{H}_{11}$ ), equivalent to  $(\text{C}_2\text{H}_5)_3\text{NH}^+\text{SR}^-$ , gives  $\text{In}(\text{SR})_3$ , presumably following formation and decomposition of  $[\text{In}_2(\text{SR})_6]^{2-}$ . Finally, the reaction between  $\text{R}'_4\text{NOH}$  ( $\text{R}' = n\text{-C}_4\text{H}_9$ ) and  $\text{In}_2(\text{SR})_4$  ( $\text{R} = \text{C}_5\text{H}_{11}$ ) in the presence of  $\text{RSH}$  yields  $\text{R}'_4\text{N}[\text{In}(\text{SR})_4]$ , again via the decomposition of the presumed  $[\text{In}_2(\text{SR})_6]^{2-}$  anion. Further work on these systems is planned.

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