

# Substituent Effects on Indium–Phosphorus Bonding in $(4-RC_6H_4S)_3In\cdot PR'_3$ Adducts (R = H, Me, F; R' = Et, Cy, Ph): A Spectroscopic, Structural, and Thermal Decomposition Study

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The tris(arylthiolate)indium(III) complexes (4-RC<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>In [R = H (5), Me (6), F (7)] were prepared from the 2:3 reaction of elemental indium and the corresponding aryl disulfide in methanol. Reaction of 5–7 with 2 equiv of the appropriate triorganylphosphine in benzene or toluene resulted in isolation of the indium–phosphine adduct series (4-RC<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>In•PR'<sub>3</sub> [R = H, R' = Et (5a), Cy (5b), Ph (5c); R = Me, R' = Et (6a), Cy (6b), Ph (6c); R = F, R' = Et (7a), Cy (7b), Ph (7c)]. These compounds were characterized via elemental analysis, FT-IR, FT-Raman, solution <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F (7a–c) NMR spectroscopy, and X-ray crystallography (5c, 6a, 6c, and 7a). NMR spectra show retention of the In–P bond in benzene-*d*<sub>6</sub> solution, with phosphine <sup>31</sup>P{<sup>1</sup>H} signals shifted downfield compared to the uncoordinated ligand. The X-ray structures show monomeric 1:1 adduct complexes in all cases. The In–P bond distance [2.5863(5)–2.6493(12) Å] is influenced significantly by the phosphine substituents but is unaffected by the substituted phenylthiolate ligand. Relatively low melting points (88–130 °C) are observed for all adducts, while high-temperature thermal decomposition process, involving an initial loss of the phosphine moiety followed by loss of thiolate ligand.

# Introduction

Trialkyl indium compounds have been of considerable interest in recent years as reactants for the metal-organic chemical vapor deposition (MOCVD) of III-V semiconductor materials.<sup>1</sup> In particular, 1:1 adducts with tertiary phosphines have been studied as potential single-source precursors to indium phosphide (InP).<sup>2</sup> Complexes which incorporate both elements connected by a chemical bond may provide improved processes for the preparation of thin films due to the controlled stoichiometric introduction of the elements, simplified fabrication equipment, and deposition of desired phases at lower temperatures compared to multisource processes.<sup>3</sup>

9914 Inorganic Chemistry, Vol. 44, No. 26, 2005

Despite their potential utility, there has been an absence of systematic studies in the literature that examine the effect of the substituent variation on the bonding and physical (e.g., thermal stability) properties of indium—phosphine adducts. Compounds of the type (RS)<sub>3</sub>In•PR'<sub>3</sub> are ideal candidates for these investigations, as the requisite homoleptic alkyland arylindium thiolates (RS)<sub>3</sub>In [R = Et; *i*-Pr; *n*-Bu; *t*-Bu; C<sub>5</sub>H<sub>11</sub>; Ph; C<sub>6</sub>F<sub>5</sub>; 2-MeC<sub>6</sub>H<sub>4</sub>; 2,4,6-(CF<sub>3</sub>)C<sub>6</sub>H<sub>2</sub>; 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; C<sub>10</sub>H<sub>7</sub>] have been prepared in high yield via metathesis,<sup>4.5</sup> redox,<sup>6.7</sup> or electrochemical<sup>8</sup> routes. However, the alkyl- and unsubstituted phenylthiolate derivatives have

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### Substituent Effects on Indium-Phosphorus Bonding

not been structurally characterized due to limited solubility in organic solvents. This is presumably a result of extensive intermolecular In···S interactions and polymeric structures in the solid state.<sup>4,6</sup> The introduction of sterically encumbered arylthiolate ligands has facilitated an increased solubility and the structural characterization of the monomeric species  $(2,4,6-t-Bu_3C_6H_2S)_3In$  (1), which exhibits a distorted trigonal planar geometry at indium.5a The Lewis acidic nature of (RS)<sub>3</sub>In species has also allowed for the isolation of monomeric 1:1 [(t-BuS)<sub>3</sub>In(py) (2)<sup>4b</sup>] and 1:2 [(PhS)<sub>3</sub>In(py)<sub>2</sub> (3),<sup>6</sup> (*i*-PrS)<sub>3</sub>In(dmap)<sub>2</sub> (4)<sup>4b</sup>] adducts [py = pyridine, dmap = 4-(dimethylamino)pyridine] from reactions with excess amine ligand. Structural investigations show the former to display distorted tetrahedral geometries at indium in the solid state, while the latter exhibit trigonal bipyramidal coordination environments, with the amine nitrogen atoms occupying axial positions. Interestingly, the formation of both 1:1 (2) and 1:2 (3) adducts from excess pyridine suggests a varying Lewis acidity for indium, which is presumably an effect of altering the thiolate ligand.

Extensive studies into phosphine adducts of the related indium(III) halides have yielded similar 1:19,10 and 1:2,10,11 complexes, while 1:3 adducts have only been characterized spectroscopically.<sup>10g</sup> With regard to indium thiolate-phosphine adducts, only the 1:1 complex (PhS)<sub>3</sub>In·PCy<sub>3</sub> (5b) has been structurally characterized and was prepared in moderate yield from the reaction of the 1:2 hydride intermediate H<sub>3</sub>- $In \cdot (PCy_3)_2$  with  $Ph_2S_2$ .<sup>12</sup> Although little physical data were reported, the monomeric structure and relatively low melting point of **5b** suggest potential for the preparation of volatile indium thiolate-phosphine complexes, prerequisite for MOCVD materials. In this context, we report the facile synthesis of a series of 1:1 indium thiolate-phosphine adducts  $(4-RC_6H_4S)In\cdot PR'_3$  [R = H, R' = Et (5a), Cy (5b), Ph (5c); R = Me, R' = Et (6a), Cy (6b), Ph (6c); R = F, R' = Et (7a), Cy (7b), Ph (7c)], and the effect of the thiolate and phosphine substituents on the spectroscopic and structural characteristics, as well as the thermal decomposition properties, of these compounds.

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## **Experimental Section**

**General Considerations.** Melting points were recorded on an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. Infrared spectra were recorded as Nujol mulls on a Mattson Genesis II FT-IR spectrometer in the range  $4000-400 \text{ cm}^{-1}$ . FT-Ramam spectra were obtained on a Bruker RFS 100 spectrometer. Solution <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 23 °C on a JEOL GMX 270 MHz spectrometer (270.2, 67.9, 254.2, and 109.4 MHz, respectively) or a Varian Mercury 200 MHz+ spectrometer (200.0, 50.3, 188.2, and 81.0 MHz, respectively) and are calibrated to the residual solvent signal. Elemental analyses were provided by Chemisar Laboratories, Inc., Guelph, Ontario, Canada.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were collected simultaneously on a TA Instruments SDT Q600. Samples were held at 30 °C for 5 min, then heated at a rate of 10 °C/min to 600 °C. All analyses were carried out in aluminum sample cups under dinitrogen atmosphere.

Electron impact mass spectrometry (EI-MS) data were collected after direct insertion of the solid sample from a 1177 injection port on the Varian 3800 GC using a Varian Saturn MS/MS. An initial temperature of 40 °C was held for 3 min, ramped at a rate of 20 °C/min to 300 °C, and held for 4 min for a total of 20 min. Spectra were collected in the range of m/z 50–650.

**Synthetic Procedures.** Benzenethiol 97%, 4-methylbenzenethiol 98%, 4-fluorobenzenethiol 98%, triphenylphosphine 99%, triethylphosphine 99%, tricyclohexylphosphine, indium powder 99.99%, methanol anhydrous 99.8%, toluene anhydrous 99.8%, benzene anhydrous 99.8%, and hexane anhydrous 95+% were used as received from Aldrich. Hydrogen peroxide 30% solution was used as received from ACP.

Aryl disulfides  $(4\text{-RC}_6\text{H}_4\text{S})_2$  were prepared from reaction of the appropriate arylthiol ligand (5.51 mmol) with a 30% hydrogen peroxide solution (0.25 g, 7.35 mmol) in methanol (5 mL; R = H, Me) or water (5 mL; R = F). The reaction mixture was stirred for 3 h then allowed to evaporate slowly at 23 °C to yield colorless crystals. After 1 day, the reaction mixture was filtered, washed with MeOH (5 mL), and dried in vacuo to yield the aryl disulfide as colorless crystals (81–95%).

The compounds described herein were prepared by general procedures as indicated below. Specific details regarding reactant quantities and product isolation are presented in Table 1. The preparation of  $(C_6H_5S)_3$ In (5) is a modification of a previously reported procedure.<sup>7</sup> All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques.

**Preparation of**  $(4\text{-RC}_6\text{H}_4\text{S})_3$ **In** [ $\mathbf{R} = \mathbf{H}$  (5), **Me** (6), **F** (7)]. A solution of  $(4\text{-RC}_6\text{H}_4\text{S})_2$  in methanol (5 mL) was added dropwise to a slurry of indium powder in methanol (5 mL) at 23 °C and heated under reflux for 3 h. After cooling to 23 °C, the reaction was filtered to remove a white precipitate. The residual solvent removed under vacuum to yield a white powder of 5–7.

Table 1. Reaction Conditions, Yields, Elemental Analyses, and Melting Points

| compound | reagents (g. mmol)  | isolation conditions                | yield<br>(g. mmol, %) | elemental analysis<br>[% calcd (found)] <sup>a</sup>       | mp<br>(°C) |
|----------|---|-------------------------------------|-----------------------|--|------------|
| 5        | In(0.25, 2.1)   | pumped to dryness                   | 0.44, 2.0, 95         | C: [48.87 (48.46)]   | 208 (dec)  |
| 6        | $(C_6H_5S)_2$ (0.70, 3.3)<br>In(0.25, 2.1)<br>(4-MeC_6H_4)_2S_2 (0.80, 3.3)   | pumped to dryness                   | 0.48, 1.9, 90         | H: [3.42 (2.96)]<br>C: [52.06 (51.97)]<br>H: [4.38 (4.22)] | 210 (dec)  |
| 7        | In $(0.25, 2.1)$<br>(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> (0.83, 3.3)   | pumped to dryness                   | 0.45, 1.8, 82         | C: [43.56 (43.25)]<br>H: [2.44 (2.06)]                     | 220 (dec)  |
| 5a       | PEt <sub>3</sub> $(0.11, 0.90)$<br>(C <sub>6</sub> H <sub>5</sub> S) <sub>3</sub> In $(0.20, 0.45)$   | 1 day at 23 °C                      | 0.16, 0.28, 63        | C: [51.52 (51.93)]<br>H: [5.54 (5.93)]                     | 103        |
| 5b       | rotuene<br>$P(C_6H_{11})_3 (0.11, 0.90)$<br>$(C_6H_5S)_3In (0.20, 0.45)$<br>toluene   | 2 day at 23 °C                      | 0.21, 0.30, 66        | C: [59.82 (59.97)]<br>H: [6.71 (7.07)]                     | 130        |
| 5c       | PPh <sub>3</sub> $(0.24, 0.90)$<br>$(C_6H_5S)_3In (0.20, 0.45)$<br>toluene  | 12 h at 23 °C                       | 0.089, 0.13, 28       | C: [61.44 (61.52)]<br>H: [4.30 (4.21)]                     | 88         |
| 6a       | PEt <sub>3</sub> (0.10, 0.83)<br>(4-MeC <sub>6</sub> H <sub>4</sub> S) <sub>3</sub> In (0.20, 0.41)<br>benzene                                | layered with hexane<br>1 h at 23 °C | 0.092, 0.16, 38       | C: [53.80 (53.72)]<br>H: [6.03 (6.11)]                     | 118        |
| 6b       | P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> (0.18, 0.83)<br>(4-MeC <sub>6</sub> H <sub>4</sub> S) <sub>3</sub> In (0.20, 0.41)<br>benzene | layered with hexane 2 d at 23 °C    | 0.19, 0.24, 59        | C: [61.20 (61.70)]<br>H: [7.13 (7.31)]                     | 110        |
| 6c       | PPh <sub>3</sub> $(0.22, 0.83)$<br>$(4-MeC_6H_4S)_3In (0.20, 0.41)$   | 2 d at 23 °C                        | 0.11, 0.15, 36        | C: [62.70 (62.55)]<br>H: [4.87 (4.53)]                     | 122        |
| 7a       | PEt <sub>3</sub> (0.095, 0.81)<br>(4-FC <sub>6</sub> H <sub>4</sub> S) <sub>3</sub> In (0.20, 0.40)   | layered with hexane<br>1 h at 23 °C | 0.13, 0.20, 51        |  | 111        |
| 7b       | P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> (0.11, 0.40)<br>(4-FC <sub>6</sub> H <sub>4</sub> S) <sub>3</sub> In (0.20, 0.40)             | pumped to dryness                   | 0.27, 0.36, 89        |  | 104        |
| 7c       | PPh <sub>3</sub> (0.11, 0.40)<br>( $4$ -FC <sub>6</sub> H <sub>4</sub> S) <sub>3</sub> In (0.20, 0.40)<br>toluene                             | pumped to dryness                   | 0.28, 0.37, 93        |  | 123        |

<sup>*a*</sup> N < 0.5% for all compounds.

Preparation of  $(4\text{-RC}_6\text{H}_4\text{S})\text{In}\cdot\text{PR}'_3$  [ $\mathbf{R} = \mathbf{H}$ ,  $\mathbf{R}' = \text{Et}$  (5a), Cy (5b), Ph (5c);  $\mathbf{R} = \mathbf{Me}$ ,  $\mathbf{R}' = \text{Et}$  (6a), Cy (6b), Ph (6c);  $\mathbf{R} = \mathbf{F}$ ,  $\mathbf{R}' = \text{Et}$  (7a), Cy (7b), Ph (7c)]. A solution of PR'<sub>3</sub> in benzene, toluene, or methanol (2 mL) was added dropwise to a mixture of 5–7 in the same solvent (3 mL) at 23 °C. After 2 h, the clear solution was decanted and the volume decreased to 0.5 mL. The product was then layered with hexane (0.5 mL) or allowed to slowly evaporate to yield colorless crystals. For the preparation of compounds 7b and 7c, the reaction mixture was pumped to dryness to yield a white powder of the desired product. Despite several attempts, satisfactory elemental analysis could not be obtained for 7a-c.

**X-Ray Structural Analyses.** Crystals of **5c**, **6a**, and **7a** were isolated from the reaction mixtures as indicated above. Crystals of **6c**·MeOH·H<sub>2</sub>O were isolated from the 1:2 reaction of  $(4-\text{MeC}_{d}\text{H}_{4}\text{S})_{3}$ -In and PPh<sub>3</sub> in methanol in air. Single crystals of **5c**, **6a**, **6c**·MeOH·H<sub>2</sub>O, and **7a** were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\theta$  scans with a scan width of 0.3° and exposure times of 10 (**5c**, **7a**), 30 (**6a**), or 40 s (**6c**·MeOH·H<sub>2</sub>O). The detector distance was 5 cm. The data were reduced (SAINT)<sup>13</sup> and corrected for absorption (SADABS).<sup>14</sup> The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  (SHELXTL).<sup>15</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in Fourier difference maps and refined isotropically (**7a**) or were included in calculated

positions and refined using a riding model (**5c**, **6a**, and **6c**·MeOH· H<sub>2</sub>O). Due to a disorder in the phenylthiolate groups in **5a**, a satisfactory refinement of the structure could not be obtained. [Crystal data for **5a**: C<sub>24</sub>H<sub>30</sub>InPS<sub>3</sub>, fw = 560.45, trigonal, space group *P*31*c*, *a* = 13.9347(18) Å, *c* = 7.7828(12) Å, *V* = 1308.8-(3) Å<sup>3</sup>, *Z* = 2].

# **Results and Discussion**

**Syntheses.** The aryl disulfides  $(4\text{-RC}_6\text{H}_4\text{S})_2$  (R = H, Me, F) were prepared in high yield by oxidation of the corresponding aryl thiol with 30% H<sub>2</sub>O<sub>2</sub> in methanol or water. The 2:3 reaction of indium powder with the corresponding aryl disulfide in methanol under reflux gives  $(4\text{-RC}_6\text{H}_4\text{S})_3\text{In}$  [R = H (5), Me (6), F (7)] in high yield (82-95%) after removal of the solvent in vacuo. A slight modification of this synthetic method has been employed previously to prepare 5.<sup>7</sup>

Reaction of **5**–**7** with the tertiary phosphines  $PR'_3 [R' = Et (a), Cy (b), Ph (c)]$  in benzene or toluene resulted in the formation of the 1:1 adducts (4-RC<sub>6</sub>H<sub>4</sub>S)In·PR'<sub>3</sub> (**5a**–**c**, **6a**–**c**, **7a**–**c**) in moderate yields (see Table 1). Addition of the phosphine solution to a slurry of the insoluble indium thiolate gave a clear solution after stirring for a few minutes at room temperature, indicating the adduct is readily formed. Interestingly, a 1:2 reaction stoichiometry results in isolation of crystals of the 1:1 adducts only (**5a**–**c**, **6a**–**c**, **7a**). As **7b** and **7c** were isolated as powders after the removal of solvent from the reaction mixture, a 1:1 reaction stoichiometry was

<sup>(13)</sup> SAINT 6.02; Bruker AXS, Inc.: Madison, WI, 1997-1999.

<sup>(14)</sup> Sheldrick, G. SADABS; Bruker AXS, Inc.: Madison, WI, 1999.

<sup>(15)</sup> Sheldrick, G. SHELXTL 5.1; Bruker AXS, Inc.: Madison, WI, 1997.

| <b>Table 2.</b> Vibrational Bands and NMR Da | able 2. | le 2. Vibration | nal Bands | and | NMR | Dat |
|--|---------|-----------------|-----------|-----|-----|-----|
|--|---------|-----------------|-----------|-----|-----|-----|

|          |   |   | NMR $(ppm)^b$   |                     |  |
|----------|---|---|---|---------------------|--|
| compound | $FT-IR (cm^{-1})^a$                           | FT-Raman (cm <sup>-1</sup> ) <sup>a</sup>     | <sup>1</sup> H  | ${}^{31}P{}^{1}H{}$ |  |
| 5        | 669m, 731m, 825w,                             | 119m, 161s, 281w, 325w,                       | $6.99 (m, 9H, H_5C_6S)$   |                     |  |
|          | 877s, 1099w, 1252m,                           | 392m, 491w, 628s, 638w                        | $7.28 \text{ (m, 6H, } H_5 \text{C}_6 \text{S})$  |                     |  |
|          | 1643m, 2359s                                  |   |   |                     |  |
| 6        | 721s, 798vs, 877w,                            | 97m, 134w, 177vs, 253m,                       | 2.22 (s, 9H, 4- <i>Me</i> H <sub>4</sub> C <sub>6</sub> S)  |                     |  |
|          | 1016s, 1084m, 1184w,                          | 314m, 426s, 616m, 694m                        | $6.82 (d, {}^{3}J_{H,H} = 8 Hz, 6H, 4-MeH_4C_6S)$   |                     |  |
|          | 1633m   |   | 7.17 (d, ${}^{3}J_{H,H} = 8$ Hz, 6H, 4-MeH <sub>4</sub> C <sub>6</sub> S)   |                     |  |
| 7        | 513s, 625s, 762s, 827vs,                      | 116s, 160s, 208w, 229m,                       | $6.51 (m, 6H, 4-FH_4C_6S)$  |                     |  |
|          | 877m, 1159s, 1234vs,                          | 292s, 319w, 352m, 389s,                       | $6.71 \text{ (m, 6H, 4-F}H_4C_6S)$  |                     |  |
| _        | 1296w, 1587s                                  | 420w, 511w, 626s                              |   |                     |  |
| 5a       | 692vs, 739vs, 769s,                           | 110s, 226w, 285m, 335m,                       | $0.56-1.00 \text{ (m, 15H, PEt_3)}$   | -5.3                |  |
|          | 1022m, 1082m,                                 | 388m, 628m                                    | $6.84 - 7.00 \text{ (m, 9H, } H_5 \text{C}_6 \text{S})$   |                     |  |
|          | 1261m, 1574s                                  |   | $7.76-7.79$ (m, 6H, $H_5C_6S$ )   |                     |  |
| 5b       | 850m, 1020m, 1114m,                           | 105s, 247w, 285w                              | 1.00–1.93 (m, 33H, PCy)   | 19.8                |  |
|          | 1261m, 1296m, 1572w                           |   | 6.89 (t, ${}^{5}J_{H,H} = 9$ Hz, 3H, $H_{5}C_{6}S$ )  |                     |  |
|          |   |   | $7.01 \text{ (m, 6H, } H_5 \text{C}_6 \text{S)}$  |                     |  |
| -        |   | 102 107 214 252                               | $7.81 (d, {}^{3}J_{H,H} = 7 Hz, 6H, H_{5}C_{6}S)$   | 1.2                 |  |
| 5c       | 694vs, 742vs, 877w,                           | 103s, 196w, 214w, 253m                        | $6.85-6.88$ (m, 9H, $H_5C_6S$ )   | -4.2                |  |
|          | 1024s, 1080s, 1153m,                          |   | $6.96 - 7.02 \text{ (m, 9H, PPh_3)}$  |                     |  |
|          | 15768   |   | 7.26 - 7.33 (m, 6H, PPh <sub>3</sub> )  |                     |  |
| 60       | 408a 627m 812ma                               | 116a 160ma 200m 220m                          | $/.48 - /.51$ (m, 6H, $H_5 C_6 S$ )   | 2.0                 |  |
| 08       | 4985, 02/111, 812V8,                          | 202a 210vv 252m 280a                          | $0.56 - 1.10$ (III, 15 $\Pi$ , PE13)  | -2.0                |  |
|          | 8/0W, 1045111, 1088VS,<br>1210W, 1267m, 1505W | 2928, 319W, 532III, 5898,<br>421w, 510w, 626c | 2.01 (8, 9 $\pi$ , 4- <i>M</i> eH <sub>4</sub> C <sub>6</sub> S)<br>6.21 (4.31 - 2.47 6H 4 MaH C S)                   |                     |  |
|          | 1210w, 120/III, 1393w                         | 421w, 510w, 020s                              | $7.72 (d_{31} - 8 H_{7} - 6 H_{4} M_{6} + M_{6} + C_{6})$   |                     |  |
| 6h       | 721s 808s 877m                                | 145w 245m 273m 341m                           | $1.02 - 1.96 \text{ (m} 33 \text{H} \text{PC}_{32})$  | 10.7                |  |
| 00       | 1020s 1086m 1261m                             | 384m 687w                                     | $2.03 (s. 9H A M_{e}H_{e}C_{e}S)$   | 19.7                |  |
|          | 1620s, 1000m, 1201m,                          | 504m, 007w                                    | $6.85 (d^{-3}L_{WW} = 8 Hz 6H 4-MeH_{4}C_{4}S)$   |                     |  |
|          | 10213, 2727 w                                 |   | $7.77 (d^{-3}L_{HH} = 8 Hz, 6H, 4-MeH_4C_6S)$   |                     |  |
| 60       | 694s 721s 741m                                | 93m 111m 189m 262m                            | $1.96 (s. 9H 4-MeH_4C_6S)$  | -42                 |  |
| 00       | 800s 1026s 1086s                              | 322m 421w                                     | $6.72 \text{ (d}^{-3}I_{\text{H},\text{H}} = 8 \text{ Hz} 6 \text{H} 4-M_{\text{P}}\text{H}_{4}\text{C}_{2}\text{S})$ | 7.2                 |  |
|          | 1261s 1621m                                   | 522m, 121W                                    | $6.72$ (d, $3_{H,H}$ = 8 Hz, 6H, $4-MeH_4C_6S$ )  |                     |  |
|          | 12013, 102111                                 |   | $7.00-7.06 (m. 9H, PPh_3)$  |                     |  |
|          |   |   | 7.32-7.42 (m 6H PPh <sub>3</sub> )  |                     |  |
| 7a       | 723s, 804m, 876w,                             | 1138, 1888, 2628, 3248,                       | 0.51 - 0.67 (m, 9H, PEt <sub>3</sub> )  | -0.46               |  |
|          | 1018m, 1084m,                                 | 420m, 616m, 695m                              | 0.88-0.94 (m, 6H, PEt <sub>3</sub> )  |                     |  |
|          | 1153w, 1223w,                                 |   | $6.63 (m, 6H, 4-FH_4C_6S)$  |                     |  |
|          | 1261m, 1601m                                  |   | 7.49 (m, 6H, $4$ -FH <sub>4</sub> C <sub>6</sub> S)   |                     |  |
| 7b       | 509m, 627s, 721m,                             | 94w, 142m, 180w, 228m,                        | 0.94–1.99 (m, 33H, PCy <sub>3</sub> )   | 22.2                |  |
|          | 827s, 877m, 1083s,                            | 246w, 295s, 307w, 363m,                       | $6.65 (m, 6H, 4-FH_4C_6S)$  |                     |  |
|          | 1155w, 1223s, 1585m                           | 379w, 388w, 629m                              | $7.59 (m, 6H, 4-FH_4C_6S)$  |                     |  |
| 7c       | 505s, 627s, 694vs,                            | 100w, 157w, 193m, 218m,                       | $6.51 \text{ (m, 6H, 4-F}H_4C_6S)$  | -3.4                |  |
|          | 742vs, 823vs, 876w,                           | 249m, 276w, 290m, 324w,                       | $6.71 \text{ (m, 6H, 4-F}H_4C_6S)$  |                     |  |
|          | 1012w, 1084m,                                 | 359s, 381w, 368w, 420w,                       | 6.85-7.01 (m, 6H, PPh <sub>3</sub> )  |                     |  |
|          | 1157m, 1228s, 1587s                           | 521w, 618w, 626m, 687w                        | 7.34–7.44 (m, 9H, PPh <sub>3</sub> )  |                     |  |
|          |   |   |   |                     |  |

<sup>*a*</sup> Vibrational bands below 1600 cm<sup>-1</sup>. <sup>*b*</sup> Methanol- $d_4$  (5–7), benzene- $d_6$  (5a–c, 6a–c, 7a–c).

employed to prevent contamination with excess phosphine. The complex  $(PhS)_3In \cdot PCy_3$  (**5b**) has been reported previously but was prepared via reaction  $Ph_2S_2$  with the indium hydride adduct  $H_3In \cdot (PCy_3)_2$ .<sup>12</sup> The adducts show no sign of decomposition on standing in air for a period of days.

**Solution NMR studies.** Solution <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>19</sup>F (**7a**-**c**) resonances of all indium thiolate-phosphine complexes (see Table 2 and Supporting Information) show slight changes in frequency compared to the phosphine reactants (**a**-**c**) in the same solvents. Particularly diagnostic, however, are the <sup>31</sup>P{<sup>1</sup>H} resonances, which show a downfield shift for the indium-phosphine adducts versus the uncoordinated phosphine in the same solvent (PEt<sub>3</sub>, -18.7; PCy<sub>3</sub>, 10.9; PPh<sub>3</sub>, -4.8 ppm). Interestingly, these shifts are largest for the PEt<sub>3</sub> adducts **5**-**7a** (13.4-18.2 ppm), smaller for the PCy<sub>3</sub> adducts **5**-**7b** (8.8-11.3 ppm), and only very slight for the PPh<sub>3</sub> adducts **5**-**7c** (0.6-1.4 ppm). These data suggest that the indium-phosphorus bonding interaction is resilient on dissolution of the adducts in weakly coordinating benzene-*d*<sub>6</sub> and is influenced by the phosphine substituents.

Further, these shifts are inversely proportional to the observed In–P bond distances (vide infra). Finally, <sup>31</sup>P{<sup>1</sup>H} spectra of reaction mixtures show no indication of the formation of 1:2 indium thiolate–phosphine adducts in solution.

**Crystallographic Analyses.** Crystals suitable for X-ray crystallographic analysis were isolated for 5a-c, 6a, 6c, and 7a from the slow evaporation of reaction mixtures at 23 °C. Crystallographic data are given in Table 3. Selected bond distances and angles are given in Table 4. Due to a disorder in the phenylthiolate groups in 5a, a satisfactory refinement of the structure could not be obtained. However, useful preliminary data regarding the indium–phosphorus bonding interaction are discernible. The structure of 5b has been reported previously.<sup>12</sup>

Representative structures of  $(4-RC_6H_4S)_3$ In·PR'<sub>3</sub> adducts, indicating atom numbering schemes, are shown in Figures 1 (**6c**) and 2 (**7a**). Compounds **5a** and **6c** crystallize in a hexagonal space group, resulting in a 3-fold symmetry in the complex in each case. All structures show 1:1 tris-(arylthiolato)indium-triorganylphosphine complexes, facili-

| Table 3. | Crystallographic | Data for 5c, | 6a, 6c·MeOH | H <sub>2</sub> O, and 7a |
|----------|------------------|--------------|-------------|--------------------------|
|----------|------------------|--------------|-------------|--------------------------|

|   | 5c  | 6a  | 6c•MeOH•H <sub>2</sub> O | 7a   |
|---|---|---|--------------------------|--|
| formula                                 | C <sub>36</sub> H <sub>30</sub> InPS <sub>3</sub> | C <sub>27</sub> H <sub>36</sub> InPS <sub>3</sub> | C45H62InO7PS3            | C <sub>24</sub> H <sub>27</sub> F <sub>3</sub> InPS <sub>3</sub> |
| fw                                      | 704.57  | 602.53  | 956.92                   | 614.43   |
| crystal system                          | triclinic   | orthorhombic                                      | trigonal                 | monoclinic   |
| space group                             | $P\overline{1}$                                   | Pna2(1)   | P31c                     | P2(1)/n  |
| a (Å)                                   | 9.8480(9)   | 25.3684(14)                                       | 14.8616(10)              | 7.8904(3)  |
| b (Å)                                   | 10.4722(10)                                       | 7.8320(5)   | 14.8616(10)              | 24.3493(10)  |
| c (Å)                                   | 16.0178(14)                                       | 14.3950(8)  | 12.2118(10)              | 13.7357(5)   |
| α (deg)                                 | 94.764(2)   | 90  | 90                       | 90   |
| $\beta$ (deg)                           | 92.905(2)   | 90  | 90                       | 94.428(1)  |
| $\gamma$ (deg)                          | 105.299(2)  | 90  | 120                      | 90   |
| $V(Å^3)$                                | 1583.3(3)   | 2860.1(3)   | 2335.8(3)                | 2631.10(18)  |
| Ζ                                       | 2   | 4   | 2                        | 4  |
| F(000)                                  | 716   | 1240  | 1000                     | 1240   |
| $\rho_{\rm calcd}$ , g cm <sup>-3</sup> | 1.478   | 1.399   | 1.361                    | 1.551  |
| $\mu$ , mm <sup>-1</sup>                | 1.019   | 1.115   | 0.721                    | 1.229  |
| <i>T</i> , K                            | 198(1)  | 198(1)  | 198(1)                   | 198(1)   |
| λ, Å                                    | 0.71073   | 0.71073   | 0.71073                  | 0.71073  |
| $\mathbf{R}1^{a}$                       | 0.0458  | 0.0308  | 0.0292                   | 0.0251   |
| wR2 <sup>b</sup>                        | 0.1176  | 0.0726  | 0.0714                   | 0.0609   |

<sup>*a*</sup> R1 =  $[\sum ||F_o| - |F_c||]/[\sum |F_o|]$  for  $[F_o^2 > 2\sigma(F_o^2)]$ . <sup>*b*</sup> wR2 = { $[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^4)]$ }<sup>1/2</sup>.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5b, 5c, 6a, 6c·MeOH·H<sub>2</sub>O, and 7a

|                        | <b>5b</b> <sup>12</sup> | 5c         | 6a         | 6c·MeOH·H <sub>2</sub> O | 7a          |
|------------------------|-------------------------|------------|------------|--------------------------|-------------|
| In-P                   | 2.6109(8)               | 2.6458(12) | 2.5881(9)  | 2.6493(12)               | 2.5840(5)   |
| In-S(1)                | 2.4456(10)              | 2.4323(12) | 2.4434(12) | 2.4286(8)                | 2.4538(6)   |
| In-S(2)                | 2.4544(9)               | 2.4333(13) | 2.4404(11) |                          | 2.4363(6)   |
| In-S(3)                | 2.4384(9)               | 2.4252(14) | 2.4434(10) |                          | 2.4446(6)   |
| P-C(11)                | 1.843(1)                | 1.811(5)   | 1.806(7)   | 1.810(3)                 | 1.823(2)    |
| P-C(21)                | 1.846(1)                | 1.797(4)   | 1.835(6)   |                          | 1.825(2)    |
| P-C(31)                | 1.840(1)                | 1.805(4)   | 1.818(4)   |                          | 1.819(2)    |
| S(1) - In - S(2)/S(1') | 109.48(3)               | 121.27(5)  | 115.07(4)  | 112.206(18)              | 114.72(2)   |
| S(1) - In - S(3)       | 119.96(4)               | 115.02(5)  | 109.06(4)  |                          | 111.48(2)   |
| S(2)-In-S(3)           | 105.79(4)               | 107.70(5)  | 111.85(4)  |                          | 112.55(2)   |
| C(11)-P-C(21)/C(11')   | 108.12(14)              | 106.6(2)   | 107.3(4)   | 107.28(10)               | 106.14(12)  |
| C(11)-P-C(31)          | 105.97(13)              | 106.8(2)   | 105.5(3)   |                          | 106.74(12)  |
| C(21) - P - C(31)      | 110.90(14)              | 106.5(2)   | 106.5(3)   |                          | 107.79 (12) |

tated via indium—phosphorus bonding interactions. This results in a four-coordinate, distorted tetrahedral bonding environment for both indium and phosphorus. The In–S distances [2.4252(14)-2.4560(6) Å] are similar to those of the known  $(C_6H_5S)_3\text{In}\cdot\text{P}(\text{Cy})_3$  (**5b**)<sup>12</sup> and fall in the range observed for other neutral indium thiolate adducts [2.410-(2)-2.472(3) Å].<sup>4b,5b,6</sup> The In–P bond distances for the PEt<sub>3</sub> (**5–7a**) and PCy<sub>3</sub> (**5b**) adducts are similar to those of previously reported 1:1 InI<sub>3</sub>—phosphine adducts [2.586(6)-2.616(9) Å],<sup>9,10a</sup> while the corresponding distances for the PPh<sub>3</sub> adducts (**5c** and **6c**) are significantly longer. This is presumably an electronic versus a steric effect, as PPh<sub>3</sub> has

the poorest electron donor ability of the three phosphines studied but has an intermediate cone angle (PEt<sub>3</sub> < PPh<sub>3</sub> < PCy<sub>3</sub>).<sup>16</sup> Interestingly, a comparison of the In–P bond distances in **5a**–**c** shows that they are all significantly different and increase in the order **5a** [2.569(5) Å] < **5b** [2.6109(8) Å] < **5c** [2.6458(12) Å]. Comparison of the In–P bond distances for the three PEt<sub>3</sub> derivatives (**5**–**7a**) shows that the values for **5a** and **6a** [2.5881(9) Å] are significantly different. However, distances for the PPh<sub>3</sub> derivatives **5c** and **6c** are within experimental error. These data suggest that the phosphine substituents (**a**–**c**) significantly influence the



**Figure 1.** X-ray structure of **6c** (30% probability ellipsoids). Hydrogen atoms are removed for clarity. Symmetry transformations used to generate equivalent atoms: (') 1 - y, 1 + x - y, z; ('') -x + y, 1 - x, z.



Figure 2. X-ray structure of 7a (30% probability ellipsoids). Hydrogen atoms are removed for clarity.



**Figure 3.** (a) Thermogravimetric analysis and (b) differential scanning calorimetry measurements for  $(C_6H_5S)_3In\cdot PPh_3$  (**5c**).

In-P bond distance, while the 4-substituted phenylthiolate groups on indium (5-7) have a negligible effect. Comparison of the sum of S-In-S bond angles of 5a-c, 6a-c, and 7a-c shows a range of  $333.9(2)-343.99(5)^{\circ}$ , with no correlation to the corresponding In-P bond distances.

Thermal Decomposition Analyses. Compounds 5a-c, 6a-c, and 7a-c were found to have sharp melting points in the range of 88-130 °C. The low melting points are interesting given that the tris(arylthiolato)indium reactants (5-7) thermally decompose above 300 °C without melting. This is a result of the monomeric nature of the indium-phosphine adduct, as compared to the presumably polymeric structure of uncomplexed homoleptic indium tris(arylthiolates).<sup>4,6</sup>

To examine the properties of the indium thiolatephosphine adducts on heating, TGA and DSC data were collected under dinitrogen atmosphere in the temperature range 30-600 °C using a heating rate of 10 °C/min. The respective plots for (PhS)<sub>3</sub>In·PPh<sub>3</sub> (5c) are shown in Figure 3. The DSC trace shows an endothermic process up to 78 °C (temperature range A), which is near the melting point of the compound. Minimal mass loss (2-3%) is observed in the TGA profile in this temperature range but is followed by significant mass loss in two distinct stages (temperature range B). The first stage ends at  $\sim 285$  °C (55% mass remaining), and the second at 395 °C (20% mass remaining). These mass losses are accompanied by two endothermic features in the DSC plot. There is minimal mass loss above  $\sim$ 390 °C (temperature range C), with 17% mass remaining at 600 °C. This corresponds to the mass percent of indium in the compound (16%). The DSC plot shows a second endothermic process in this temperature range.

To aid in the interpretation of these results, electron impact mass spectrometric (EI-MS) analyses were performed on all adducts. The ion flux trace for 5c over the temperature range



**Figure 4.** (a) Temperature programmed EI-MS ion flux trace for  $(C_6H_5S)_{3-}$ In·PPh<sub>3</sub> (**5c**); (b) mass spectrum at 12.5 min (230 °C) showing PPh<sub>3</sub> fragments; and (c) mass spectrum at 18.7 min (300 °C) showing phenylthiolate ligand fragments.

40–300 °C is shown in Figure 4a. Here, the number of ions in the gas phase is negligible below the melting point, then begins to increase exponentially on further temperature elevation. Analysis of the mass spectrum at maximum ion flux (230 °C; Figure 4b) shows ions characteristic of PPh<sub>3</sub> (m/z 183, [PPh<sub>2</sub>]<sup>•+</sup>; m/z 262, [PPh<sub>3</sub>]<sup>•+</sup>; m/z 445, [PPh<sub>3</sub>• PPh<sub>2</sub>]<sup>•+</sup>). The ion flux then decreases rapidly until ~16 min (300 °C). On being held at 300 °C, there is a second rapid increase in ion formation. Analysis of the mass spectrum at 18.6 min (Figure 4c) shows ions resulting from the phenyl thiolate ligand (m/z 110, [PhSH]<sup>•+</sup>; m/z 218, [(PhS)<sub>2</sub>]<sup>•+</sup>). The molecular ion [(4-RC<sub>6</sub>H<sub>4</sub>S)In•PR'<sub>3</sub>]<sup>•+</sup> was not observed in the spectra of any of the adducts.

Taken together, the DSC/TGA and EI-MS data suggest that **5c** thermally decomposes through an initial loss of the phosphine moiety (PPh<sub>3</sub>) in the 78–285 °C temperature range. As the PPh<sub>3</sub> moiety constitutes only 37% mass of the compound, the loss of 45% mass in the TGA data suggests some thiolate ligand is also expunged in this step. This is followed by loss of the majority of thiolate ligand (SPh) in the 285–390 °C temperature range. Loss of the residual thiolate ligand occurs above 390 °C, presumably yielding elemental indium as the final product of decomposition at 600 °C.

The DSC/TGA data and EI-MS ion trace for the remaining adducts (see Supporting Information) suggest similar thermal decomposition pathways. However, a complete loss of phosphine and thiolate ligand is observed for **6b** only (15% mass In; 13% residual mass). Although a loss of some phosphine and thiolate ligand is observed in all cases, TGA

<sup>(16)</sup> Tolman, C. A. Chem. Rev. 1977, 77, 313-348.

data show residual masses of 13-51%, while indium constitutes only 15-20% of the total mass of all adducts. This suggests that the loss of ligand is not complete at 600 °C, and the remaining residue likely contains a significant amount of ligand material.

## Conclusions

The series of indium-phosphine adducts (4-RC<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>In·  $PR'_{3}$  [R = H, R' = Et (5a), Cy (5b), Ph (5c); R = Me, R' = Et (6a), Cy (6b), Ph (6c); R = F, R' = Et (7a), Cy (7b), Ph (7c)] were prepared from the reaction of the appropriate tris(arylthiolate)indium(III) and triorganylphosphine reactants to determine the effect of the thiolate and phosphine substituents on their spectroscopic, structural, and thermal decomposition properties. The X-ray structures of 5c, 6a, 6c, and 7a show monomeric 1:1 adduct complexes in all cases. The In-P bond distances were found to be influenced by the phosphine substituents ( $PEt_3 < PCy_3 < PPh_3$ ) but not by the 4-substituted phenylthiolate ligand. Solution <sup>31</sup>P- $\{^{1}H\}$  spectra show retention of the In-P bond in benzene $d_6$  solution. The phosphine signals are shifted downfield versus the free ligand, the degree of which is inversely proportional to the In-P bond distance. Relatively low melting points were observed for all adducts due to the monomeric nature of the adducts, versus the high-temperature thermal decomposition observed for the polymeric parent indium thiolates (4-RC<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>In (5-7). EI-MS and DSC/TGA data show a two-step thermal decomposition process, involving an initial loss of the phosphine moiety followed by loss of thiolate ligand. These losses are complete in some cases, yielding elemental indium as the final product of decomposition. These results suggest that, although the phosphine substituents significantly affect the strength of the indium phosphorus Lewis acid—base interaction, the bond is too labile to allow for the thermal vaporization of these adducts. Therefore, these compounds are not suitable precursors for the production of InP via thermal decomposition methods. We are currently investigating the thermal decomposition properties of other molecular species incorporating indium phosphorus bonding interactions.

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Supporting Information Available: X-ray crystallographic data for 5c, 6a, 6c·MeOH·H<sub>2</sub>O, and 7a; <sup>13</sup>C{<sup>1</sup>H} and <sup>19</sup>F NMR, DSC/ TGA and EI-MS data for 5a-c, 6a-c, and 7a-c. This material is available free of charge via the Internet at http://pubs.acs.org. IC051138R