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Substituent Effects on Indium–Phosphorus Bonding in $(4\text{-}RC_6H_4S)_3In{\cdot}PR'_3$ 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 $(4\text{-}RC_6H_4S)_3In$ [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 $(4\text{-}RC_6H_4S)_3In{\cdot}PR'_3$ [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**)]. These compounds were characterized via elemental analysis, FT-IR, FT-Raman, solution ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}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_6 solution, with phosphine $^{31}P\{^1H\}$ 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 is observed for the indium thiolate reactants **5**–**7**. DSC/TGA and EI-MS data show a two-step 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.[1] In particular, 1:1 adducts with tertiary phosphines have been studied as potential single-source precursors to indium phosphide (InP).[2] 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.[3]

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 $(RS)_3In{\cdot}PR'_3$ are ideal candidates for these investigations, as the requisite homoleptic alkyl- and arylindium thiolates $(RS)_3In$ [R = Et; *i*-Pr; *n*-Bu; *t*-Bu; C_5H_{11}; Ph; C_6F_5; 2-MeC_6H_4; 2,4,6-$(CF_3)C_6H_2$; 2,4,6-*t*-$Bu_3C_6H_2$; $C_{10}H_7$] have been prepared in high yield via metathesis,[4,5] redox,[6,7] or electrochemical[8] routes. However, the alkyl- and unsubstituted phenylthiolate derivatives have

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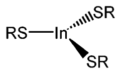
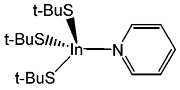
not been structurally characterized due to limited solubility in organic solvents. This is presumably a result of extensive intermolecular In···S interactions and polymeric structures in the solid state.[4,6] The introduction of sterically encumbered arylthiolate ligands has facilitated an increased solubility and the structural characterization of the monomeric species $(2,4,6\text{-}t\text{-}Bu_3C_6H_2S)_3In$ (**1**), which exhibits a distorted trigonal planar geometry at indium.[5a] The Lewis acidic nature of $(RS)_3In$ species has also allowed for the isolation of monomeric 1:1 [$(t\text{-}BuS)_3In(py)$ (**2**)[4b]] and 1:2 [$(PhS)_3In(py)_2$ (**3**),[6] $(i\text{-}PrS)_3In(dmap)_2$ (**4**)[4b]] 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.

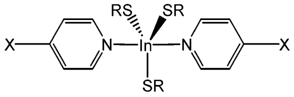
Extensive studies into phosphine adducts of the related indium(III) halides have yielded similar 1:1[9,10] and 1:2,[10,11] complexes, while 1:3 adducts have only been characterized spectroscopically.[10g] With regard to indium thiolate−phosphine adducts, only the 1:1 complex $(PhS)_3In{\cdot}PCy_3$ (**5b**) has been structurally characterized and was prepared in moderate yield from the reaction of the 1:2 hydride intermediate $H_3In{\cdot}(PCy_3)_2$ with Ph_2S_2.[12] 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 $(4\text{-}RC_6H_4S)In{\cdot}PR'_3$ [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.



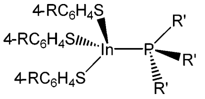
1, R = 2,4,6-t-BuC$_6$H$_2$



2



3, R = Ph, X = H
4, R = Et, X = NMe$_2$



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**)

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 cm^{-1}. FT-Ramam spectra were obtained on a Bruker RFS 100 spectrometer. Solution ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ 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 $(4\text{-}RC_6H_4S)_2$ 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 $(C_6H_5S)_3In$ (**5**) is a modification of a previously reported procedure.[7] All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques.

Preparation of $(4\text{-}RC_6H_4S)_3In$ [R = H (5), Me (6), F (7)]. A solution of $(4\text{-}RC_6H_4S)_2$ 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**.

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

compound	reagents (g, mmol)	isolation conditions	yield (g, mmol, %)	elemental analysis [% calcd (found)][a]	mp (°C)
5	In(0.25, 2.1) $(C_6H_5S)_2$ (0.70, 3.3)	pumped to dryness	0.44, 2.0, 95	C: [48.87 (48.46)] H: [3.42 (2.96)]	208 (dec)
6	In(0.25, 2.1) $(4\text{-}MeC_6H_4)_2S_2$ (0.80, 3.3)	pumped to dryness	0.48, 1.9, 90	C: [52.06 (51.97)] H: [4.38 (4.22)]	210 (dec)
7	In (0.25, 2.1) $(4\text{-}FC_6H_4)_2S_2$ (0.83, 3.3)	pumped to dryness	0.45, 1.8, 82	C: [43.56 (43.25)] H: [2.44 (2.06)]	220 (dec)
5a	PEt_3 (0.11, 0.90) $(C_6H_5S)_3In$ (0.20, 0.45) toluene	1 day at 23 °C	0.16, 0.28, 63	C: [51.52 (51.93)] H: [5.54 (5.93)]	103
5b	$P(C_6H_{11})_3$ (0.11, 0.90) $(C_6H_5S)_3In$ (0.20, 0.45) toluene	2 day at 23 °C	0.21, 0.30, 66	C: [59.82 (59.97)] H: [6.71 (7.07)]	130
5c	PPh_3 (0.24, 0.90) $(C_6H_5S)_3In$ (0.20, 0.45) toluene	12 h at 23 °C	0.089, 0.13, 28	C: [61.44 (61.52)] H: [4.30 (4.21)]	88
6a	PEt_3 (0.10, 0.83) $(4\text{-}MeC_6H_4S)_3In$ (0.20, 0.41) benzene	layered with hexane 1 h at 23 °C	0.092, 0.16, 38	C: [53.80 (53.72)] H: [6.03 (6.11)]	118
6b	$P(C_6H_{11})_3$ (0.18, 0.83) $(4\text{-}MeC_6H_4S)_3In$ (0.20, 0.41) benzene	layered with hexane 2 d at 23 °C	0.19, 0.24, 59	C: [61.20 (61.70)] H: [7.13 (7.31)]	110
6c	PPh_3 (0.22, 0.83) $(4\text{-}MeC_6H_4S)_3In$ (0.20, 0.41) methanol	2 d at 23 °C	0.11, 0.15, 36	C: [62.70 (62.55)] H: [4.87 (4.53)]	122
7a	PEt_3 (0.095, 0.81) $(4\text{-}FC_6H_4S)_3In$ (0.20, 0.40) toluene	layered with hexane 1 h at 23 °C	0.13, 0.20, 51		111
7b	$P(C_6H_{11})_3$ (0.11, 0.40) $(4\text{-}FC_6H_4S)_3In$ (0.20, 0.40) toluene	pumped to dryness	0.27, 0.36, 89		104
7c	PPh_3 (0.11, 0.40) $(4\text{-}FC_6H_4S)_3In$ (0.20, 0.40) toluene	pumped to dryness	0.28, 0.37, 93		123

[a] $N < 0.5\%$ for all compounds.

Preparation of $(4\text{-}RC_6H_4S)In\cdot PR'_3$ [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)]. A solution of PR'_3 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_2O were isolated from the 1:2 reaction of $(4\text{-}MeC_6H_4S)_3In$ and PPh_3 in methanol in air. Single crystals of **5c**, **6a**, **6c**·MeOH·H_2O, 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 ω and θ scans with a scan width of 0.3° and exposure times of 10 (**5c**, **7a**), 30 (**6a**), or 40 s (**6c**·MeOH·H_2O). The detector distance was 5 cm. The data were reduced (SAINT)[13] and corrected for absorption (SADABS).[14] The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL).[15] 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_2O). Due to a disorder in the phenylthiolate groups in **5a**, a satisfactory refinement of the structure could not be obtained. [Crystal data for **5a**: $C_{24}H_{30}InPS_3$, fw = 560.45, trigonal, space group *P*31*c*, $a = 13.9347(18)$ Å, $c = 7.7828(12)$ Å, $V = 1308.8(3)$ Å^3, $Z = 2$].

Results and Discussion

Syntheses. The aryl disulfides $(4\text{-}RC_6H_4S)_2$ (R = H, Me, F) were prepared in high yield by oxidation of the corresponding aryl thiol with 30% H_2O_2 in methanol or water. The 2:3 reaction of indium powder with the corresponding aryl disulfide in methanol under reflux gives $(4\text{-}RC_6H_4S)_3In$ [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**.[7]

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 $(4\text{-}RC_6H_4S)In\cdot PR'_3$ (**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

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[13] *SAINT 6.02*; Bruker AXS, Inc.: Madison, WI, 1997−1999.

[14] Sheldrick, G. *SADABS*; Bruker AXS, Inc.: Madison, WI, 1999.

[15] Sheldrick, G. *SHELXTL 5.1*; Bruker AXS, Inc.: Madison, WI, 1997.

Table 2. Vibrational Bands and NMR Data

compound	FT-IR (cm^{-1})[a]	FT-Raman (cm^{-1})[a]	NMR (ppm)[b]	
			^{1}H	^{31}P{^{1}H}
5	669m, 731m, 825w, 877s, 1099w, 1252m, 1643m, 2359s	119m, 161s, 281w, 325w, 392m, 491w, 628s, 638w	6.99 (m, 9H, H_5C_6S) 7.28 (m, 6H, H_5C_6S)	
6	721s, 798vs, 877w, 1016s, 1084m, 1184w, 1633m	97m, 134w, 177vs, 253m, 314m, 426s, 616m, 694m	2.22 (s, 9H, 4-MeH_4C_6S) 6.82 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S) 7.17 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S)	
7	513s, 625s, 762s, 827vs, 877m, 1159s, 1234vs, 1296w, 1587s	116s, 160s, 208w, 229m, 292s, 319w, 352m, 389s, 420w, 511w, 626s	6.51 (m, 6H, 4-FH_4C_6S) 6.71 (m, 6H, 4-FH_4C_6S)	
5a	692vs, 739vs, 769s, 1022m, 1082m, 1261m, 1574s	110s, 226w, 285m, 335m, 388m, 628m	0.56−1.00 (m, 15H, PEt_3) 6.84−7.00 (m, 9H, H_5C_6S) 7.76−7.79 (m, 6H, H_5C_6S)	−5.3
5b	850m, 1020m, 1114m, 1261m, 1296m, 1572w	105s, 247w, 285w	1.00−1.93 (m, 33H, PCy) 6.89 (t, $^3J_{H,H} = 9$ Hz, 3H, H_5C_6S) 7.01 (m, 6H, H_5C_6S) 7.81 (d, $^3J_{H,H} = 7$ Hz, 6H, H_5C_6S)	19.8
5c	694vs, 742vs, 877w, 1024s, 1080s, 1153m, 1576s	103s, 196w, 214w, 253m	6.85−6.88 (m, 9H, H_5C_6S) 6.96−7.02 (m, 9H, PPh_3) 7.26−7.33 (m, 6H, PPh_3) 7.48−7.51 (m, 6H, H_5C_6S)	−4.2
6a	498s, 627m, 812vs, 876w, 1043m, 1088vs, 1210w, 1267m, 1595w	116s, 160vs, 209w, 230m, 292s, 319w, 352m, 389s, 421w, 510w, 626s	0.58−1.16 (m, 15H, PEt_3) 2.01 (s, 9H, 4-MeH_4C_6S) 6.81 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S) 7.73 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S)	−2.0
6b	721s, 808s, 877m, 1020s, 1086m, 1261m, 1621s, 2727w	145w, 245m, 273m, 341m, 384m, 687w	1.02−1.96 (m, 33H, PCy_3) 2.03 (s, 9H, 4-MeH_4C_6S) 6.85 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S) 7.77 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S)	19.7
6c	694s, 721s, 741m, 800s, 1026s, 1086s, 1261s, 1621m	93m, 111m, 189m, 262m, 322m, 421w	1.96 (s, 9H, 4-MeH_4C_6S) 6.72 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S) 6.97 (d, $^3J_{H,H} = 8$ Hz, 6H, 4-MeH_4C_6S) 7.00−7.06 (m, 9H, PPh_3) 7.32−7.42 (m, 6H, PPh_3)	−4.2
7a	723s, 804m, 876w, 1018m, 1084m, 1153w, 1223w, 1261m, 1601m	113s, 188s, 262s, 324s, 420m, 616m, 695m	0.51−0.67 (m, 9H, PEt_3) 0.88−0.94 (m, 6H, PEt_3) 6.63 (m, 6H, 4-FH_4C_6S) 7.49 (m, 6H, 4-FH_4C_6S)	−0.46
7b	509m, 627s, 721m, 827s, 877m, 1083s, 1155w, 1223s, 1585m	94w, 142m, 180w, 228m, 246w, 295s, 307w, 363m, 379w, 388w, 629m	0.94−1.99 (m, 33H, PCy_3) 6.65 (m, 6H, 4-FH_4C_6S) 7.59 (m, 6H, 4-FH_4C_6S)	22.2
7c	505s, 627s, 694vs, 742vs, 823vs, 876w, 1012w, 1084m, 1157m, 1228s, 1587s	100w, 157w, 193m, 218m, 249m, 276w, 290m, 324w, 359s, 381w, 368w, 420w, 521w, 618w, 626m, 687w	6.51 (m, 6H, 4-FH_4C_6S) 6.71 (m, 6H,4-FH_4C_6S) 6.85−7.01 (m, 6H, PPh_3) 7.34−7.44 (m, 9H, PPh_3)	−3.4

[a] Vibrational bands below 1600 cm^{-1}. [b] 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 $H_3In \cdot (PCy_3)_2$.[12] The adducts show no sign of decomposition on standing in air for a period of days.

Solution NMR studies. Solution ^{1}H, ^{13}C{^{1}H}, and ^{19}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 ^{31}P{^{1}H} resonances, which show a downfield shift for the indium−phosphine adducts versus the uncoordinated phosphine in the same solvent (PEt_3, −18.7; PCy_3, 10.9; PPh_3, −4.8 ppm). Interestingly, these shifts are largest for the PEt_3 adducts **5**−**7a** (13.4−18.2 ppm), smaller for the PCy_3 adducts **5**−**7b** (8.8−11.3 ppm), and only very slight for the PPh_3 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_6 and is influenced by the phosphine substituents. Further, these shifts are inversely proportional to the observed In−P bond distances (vide infra). Finally, ^{31}P{^{1}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.[12]

Representative structures of $(4\text{-}RC_6H_4S)_3In \cdot PR'_3$ 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_2O, and **7a**

	5c	**6a**	**6c**·MeOH·H_2O	**7a**
formula	$C_{36}H_{30}InPS_3$	$C_{27}H_{36}InPS_3$	$C_{45}H_{62}InO_7PS_3$	$C_{24}H_{27}F_3InPS_3$
fw	704.57	602.53	956.92	614.43
crystal system	triclinic	orthorhombic	trigonal	monoclinic
space group	$P\bar{1}$	*Pna*2(1)	*P*31*c*	*P*2(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
β (deg)	92.905(2)	90	90	94.428(1)
γ (deg)	105.299(2)	90	120	90
V ($Å^3$)	1583.3(3)	2860.1(3)	2335.8(3)	2631.10(18)
Z	2	4	2	4
F(000)	716	1240	1000	1240
ρ_{calcd}, g cm^{-3}	1.478	1.399	1.361	1.551
μ, mm^{-1}	1.019	1.115	0.721	1.229
T, K	198(1)	198(1)	198(1)	198(1)
λ, Å	0.71073	0.71073	0.71073	0.71073
R1[a]	0.0458	0.0308	0.0292	0.0251
wR2[b]	0.1176	0.0726	0.0714	0.0609

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

Table 4. Selected Bond Distances (Å) and Angles (deg) for **5b**, **5c**, **6a**, **6c**·MeOH·H_2O, and **7a**

	5b[12]	**5c**	**6a**	**6c**·MeOH·H_2O	**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 $(C_6H_5S)_3In{\cdot}P(Cy)_3$ (**5b**)[12] and fall in the range observed for other neutral indium thiolate adducts [2.410-(2)−2.472(3) Å].[4b,5b,6] The In−P bond distances for the PEt_3 (**5**−**7a**) and PCy_3 (**5b**) adducts are similar to those of previously reported 1:1 InI_3−phosphine adducts [2.586(6)−2.616(9) Å],[9,10a] while the corresponding distances for the PPh_3 adducts (**5c** and **6c**) are significantly longer. This is presumably an electronic versus a steric effect, as PPh_3 has the poorest electron donor ability of the three phosphines studied but has an intermediate cone angle (PEt_3 < PPh_3 < PCy_3).[16] 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_3 derivatives (**5**−**7a**) shows that the values for **5a** and **6a** [2.5881(9) Å] are significantly different. However, distances for the PPh_3 derivatives **5c** and **6c** are within experimental error. These data suggest that the phosphine substituents (**a**−**c**) significantly influence the

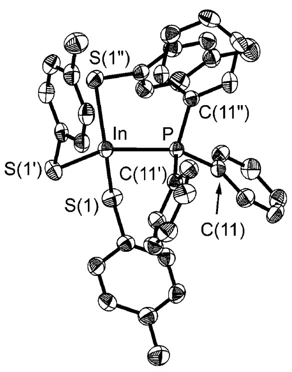

Figure 1. X-ray structure of **6c** (30% probability ellipsoids). Hydrogen atoms are removed for clarity. Symmetry transformations used to generate equivalent atoms: (′) $1 - y, 1 + x - y, z$; (″) $-x + y, 1 - x, z$.

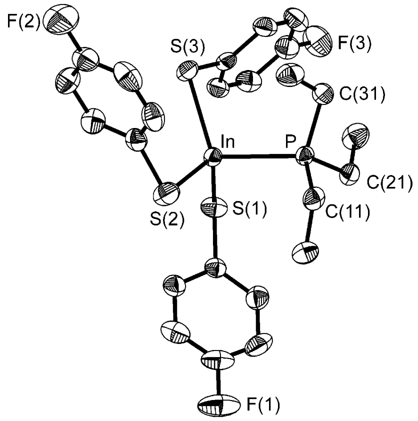

Figure 2. X-ray structure of **7a** (30% probability ellipsoids). Hydrogen atoms are removed for clarity.

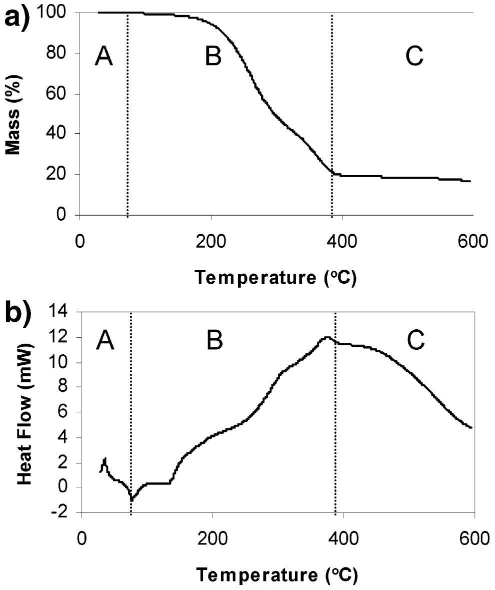

Figure 3. (a) Thermogravimetric analysis and (b) differential scanning calorimetry measurements for $(C_6H_5S)_3In{\cdot}PPh_3$ (**5c**).

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)°, 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).[4,6]

To examine the properties of the indium thiolate−phosphine 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 $(PhS)_3In{\cdot}PPh_3$ (**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 ∼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 ∼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 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_3 (*m*/*z* 183, $[PPh_2]^{\bullet+}$; *m*/*z* 262, $[PPh_3]^{\bullet+}$; *m*/*z* 445, $[PPh_3{\cdot}PPh_2]^{\bullet+}$). 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, $[PhSH]^{\bullet+}$; *m*/*z* 218, $[(PhS)_2]^{\bullet+}$). The molecular ion $[(4\text{-}RC_6H_4S)In{\cdot}PR'_3]^{\bullet+}$ was not observed in the spectra of any of the adducts.

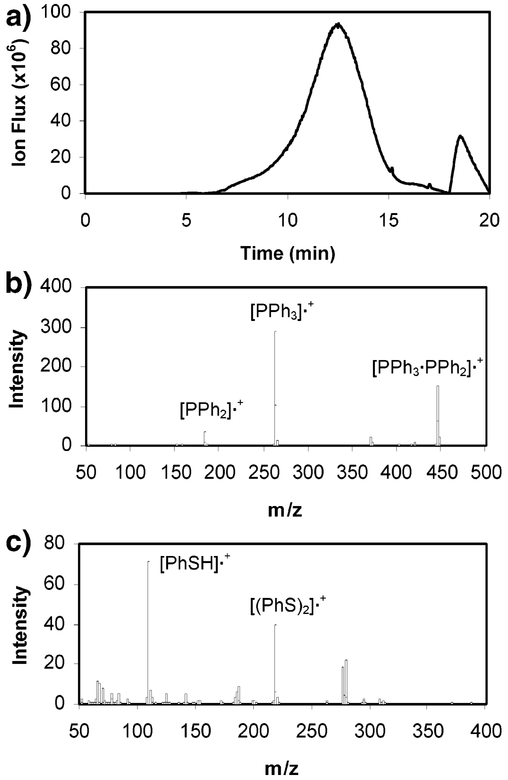

Figure 4. (a) Temperature programmed EI-MS ion flux trace for $(C_6H_5S)_3$-$In{\cdot}PPh_3$ (**5c**); (b) mass spectrum at 12.5 min (230 °C) showing PPh_3 fragments; and (c) mass spectrum at 18.7 min (300 °C) showing phenylthiolate ligand fragments.

Taken together, the DSC/TGA and EI-MS data suggest that **5c** thermally decomposes through an initial loss of the phosphine moiety (PPh_3) in the 78−285 °C temperature range. As the PPh_3 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

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(16) 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 $(4\text{-RC}_6H_4S)_3In\cdot PR'_3$ [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**)] 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 $^{31}P\{^1H\}$ 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 $(4\text{-RC}_6H_4S)_3In$ (**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**$\cdot$MeOH$\cdot H_2O$, and **7a**; $^{13}C\{^1H\}$ and ^{19}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.

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