Indium Tris(alkylthiolate) Compounds

Seigi Suh and David M. Hoffman*

Department of Chemistry and Materials Research Science and Engineering Center, University of Houston, Houston, Texas 77204

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In[N-*t*-Bu(SiMe$_3$)]$_3$ reacts with RSH to give In(SR)$_3$ (R = *t*-Bu, *i*-Pr). The *tert*-butyl derivative is formulated as the dimer [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ on the basis of NMR data, molecular weight determination, and its solubility. The limited solubility of the isopropylthiolate complex suggests that it is a polymer. [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ and [In(S-*i*-Pr)$_3$]$_n$ react with pyridine and *p*-Me$_2$Npy, respectively, to form In(S-*t*-Bu)$_3$(py) and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$, which were characterized by X-ray crystallography. In(S-*t*-Bu)$_3$(py) is trigonal pyramidal, and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$ is trigonal bipyramidal. In both structures the pyridine ligands occupy the apical positions. Crystal data are as follows: $C_{17}H_{32}InNS_3$ at 223 K: $P2_1/c$ (monoclinic), a = 10.1490(5) Å, b = 24.3811(13) Å, c = 18.8484(10) Å, β = 104.8100(10)°, and Z = 8; $C_{23}H_{41}N_4S_3In\cdot CH_2Cl_2$ at 223 K: $P\bar{1}$ (triclinic), a = 10.620(1) Å, b = 11.568(1) Å, c = 14.892(2) Å, α = 79.54(1)°, β = 75.88(1)°, γ = 66.08(1)°, and Z = 2.

There are relatively few homoleptic indium tris(thiolate) complexes or their neutral ligand adducts reported in the literature. Most of the known examples are aryl thiolate derivatives such as In[S(2,4,6-R$_3$-C$_6$H$_2$)]$_3$ (R = *t*-Bu, *i*-Pr),[1,2] In(SPh)$_3$,[3−5] In(S-*o*-tolyl)$_3$, In(SC$_6$F$_5$)$_3$, and In(SC$_{10}$H$_7$)$_3$.[3] An X-ray crystal structure of one derivative, In[S(2,4,6-*t*-Bu$_3$-C$_6$H$_2$)]$_3$, has been reported.[1] Several neutral adducts of the aryl thiolates have also been structurally characterized including In[S(2,4,6-*i*-Pr$_3$-C$_6$H$_2$)]$_3$(MeCN)$_2$, In(SPh)$_3$(py)$_2$, In[S(2,4,6-*i*-Pr$_3$-C$_6$H$_2$)]$_3$(THF), and In[S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)]$_3$(Et$_2$O).[2,6,7] In contrast it appears that the only known indium tris(alkylthiolate) compounds are In(SEt)$_3$, In(S-*n*-Bu)$_3$, and In(SCMe$_2$Et)$_3$, which Tuck and co-workers synthesized by electrochemical methods.[3] The anions [In(SPh)$_3$Br]$^-$,[5] [In(S-*t*-Bu)$_4$]$^-$, and [In(SCH$_2$CH$_2$S)$_2$]$^-$ have also been prepared and structurally characterized.[8]

We recently reported the syntheses of the homoleptic indium amide complexes In(NRR′)$_3$ (R = Ph or *t*-Bu, R′ = SiMe$_3$; R = *t*-Bu, R′ = SiHMe$_2$).[9] Because main group and transition metal amides react with weak acids to effect ligand substitution,[10] M−NR$_2$ + HX → M−X + HNR$_2$, these new indium amide complexes provide us with a simple chemical route to homoleptic indium tris(alkylthiolate) compounds. In this paper we report the synthesis of In(SR)$_3$ (R = *t*-Bu, *i*-Pr) and the structural characterization of the neutral adducts In(S-*t*-Bu)$_3$(py) and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$.

Expermental Section

General. All manipulations were carried out in a glovebox or by using standard Schlenk techniques. Solvents were purified by using standard techniques after which they were stored in the glovebox over 4-Å molecular sieves. The thiols were purchased from Aldrich and degassed before use. 4-(Dimethylamino)pyridine was purchased from Acros and used as received. In[N-*t*-Bu(SiMe$_3$)]$_3$ was prepared by the literature method.[9] NMR spectra were collected on a 300-MHz instrument. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY).

[In(S-*t*-Bu)$_3$]$_2$. *t*-BuSH (0.25 g, 2.7 mmol) was added dropwise to a suspension of In[N-*t*-Bu(SiMe$_3$)]$_3$ (0.50 g, 0.91 mmol) in cold (−30 °C) hexanes (30 mL). After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature. Stirring was continued for 3 h at room temperature. During this time, a white suspension formed, which was isolated by vacuum filtration. The white solid on the frit was washed with hexanes (15 mL) and then dissolved in hot toluene (≈8 mL). The solution was cooled slowly to room temperature, which caused formation of colorless crystalline blocks (yield 0.29 g, 84%). Anal. Calcd for $C_{24}H_{54}S_6In_2$: C, 37.69; H, 7.12. Found: C, 37.51; H, 7.14. ^{1}H NMR (C_6D_6): δ 1.71 (s, 36, SC*Me*$_3$), 1.62 (br s, 18, μ-SC*Me*$_3$) ^{13}C{^{1}H} NMR (C_7D_8): 54.3 (s, 2, μ-S*C*Me$_3$), 46.4 (s, 4, S*C*Me$_3$), 37.7 (s, 12, SC*Me*$_3$), 35.7 (s, 6, μ-SC*Me*$_3$). IR (Nujol, KBr, cm^{-1}): 1365 s, 1155 s, 1028 w, 810 w, 736 w, 575 m, 559 m.

[In(S-*i*-Pr)$_3$]$_n$. *i*-PrSH (0.22 g, 2.8 mmol) was added dropwise to a suspension of In[N-*t*-Bu(SiMe$_3$)]$_3$ (0.50 g, 0.91 mmol) in cold (−30 °C) ether (15 mL). After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature. The solution slowly became cloudy. After stirring for 7 h at room temperature, the mixture was filtered and the solid collected on the frit was washed with ether (15 mL). The white solid was then dissolved in hot 1,2-dichloroethane, and the solution was cooled slowly to room temperature, which caused formation of fine colorless needles (yield 0.26 g, 84%). Anal. Calcd for $C_{12}H_{27}S_3In$: C, 31.78; H, 6.22. Found: C, 31.86; H, 6.30. IR (Nujol, KBr, cm^{-1}): 1366 s, 1248 s, 1152, s, 1051 s, 926, w, 887 w.

In(S-*t*-Bu)$_3$(py). Excess pyridine (1.4 g, 18 mmol) was added dropwise at room temperature to an ether (10 mL) solution of [In(S-

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Table 1. Crystal Data for In(S-*t*-Bu)$_3$(py) and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$

	In(S-*t*-Bu)$_3$(py)	In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$
empirical formula	$C_{17}H_{32}InNS_3$	$C_{23}H_{41}N_4S_3In\cdot CH_2Cl_2$
fw	461.44	669.52
crystal dimens (mm)	0.45 × 0.40 × 0.25	0.48 × 0.12 × 0.10
radiation (Mo Kα), Å	0.71073	0.71073
space group	$P2_1/c$ (monoclinic)	$P\bar{1}$ (triclinic)
a, Å	10.1490(5)	10.620(1)
b, Å	24.3811(13)	11.568(1)
c, Å	18.8484(10)	14.892(2)
α, deg		79.54(1)
β, deg	104.8100(10)	75.88(1)
γ, deg		66.08(1)
temp, °C	−50(2)	−50(2)
Z	8	2
V, Å^3	4509.0(4)	1614.8(3)
D_{calcd}, g/cm^3	1.359	1.377
μ, cm^{-1}	13.2	11.10
R, R_w[a]	0.0180, 0.0454[b]	0.0270, 0.0701[c]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (0.0113P)^2 + (3.771P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = [\sigma^2(F_o^2) + (0.0200P)^2 + (1.6000P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

t-Bu)$_3$]$_2$ (0.31 g, 1.8 mmol). After stirring for 1 h, the ether and excess pyridine were removed in vacuo. The resulting residue, a white solid, was dissolved in ether (≈3 mL) and the flask was then placed in a freezer (−35 °C). After 15 h, colorless crystalline blocks had formed, which were isolated and dried in vacuo (yield 0.38 g, 79%). Anal. Calcd for $C_{17}H_{32}NS_3In$: C, 44.25; H, 7.00; N 3.04. Found: C, 44.39; H, 7.15; N, 3.37. ^{1}H NMR (C_6D_6): δ 8.91 (m, 2, *o*-py), 6.72 (m, 1, *p*-py), 6.44 (m, 2, *m*-py), 1.70 (s, 27, SC*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): 148.5 (2, *o*-py), 138.9 (1, *p*-py), 124.8 (2, *m*-py), 44.6 (s, 3, S*C*Me$_3$), 37.6 (s, 9, SC*Me*$_3$). IR (Nujol, KBr, cm^{-1}): 1602 s, 1364 s, 1213 w, 1152 s (br), 1064 w, 1037 w, 1012 w, 819 w, 756 w, 698 w.

In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$. 4-(Dimethylamino)pyridine (0.090 g, 0.73 mmol) was added at room temperature to an ether (10 mL) suspension of [In(S-*i*-Pr)$_3$]$_n$ (0.13 g, 0.37 mmol). The reaction mixture became clear immediately. After stirring for 30 min, the ether was removed in vacuo. The resulting residue, a white solid, was dissolved in CH_2Cl_2 (ca. 4 mL), and the flask was placed in the freezer (−35 °C). Fragile colorless needles formed overnight, which were isolated and dried in vacuo (yield 0.32 g, 86%). Anal. Calcd for $C_{23}H_{41}N_4S_3In$: C, 47.25; H, 7.08; N 9.59. Found: C, 47.27; H, 6.85; N, 9.37. ^{1}H NMR (C_6D_6): δ 8.46 (d, 4, *o*-Ph), 5.81 (d, 4, *m*-Ph), 3.72 (septet, 3, $^3J_{HH}$ = 6.6 Hz, SC*H*Me$_2$), 2.02 (s, 12, N*Me*$_2$), 1.63 (d, 18, $^3J_{HH}$ = 6.7 Hz, SCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 154.6 (s, 4, *p*-Ph), 148.9 (s, 4, *o*-Ph), 106.8 (s, 4, *m*-Ph), 38.1 (s, 4, N*Me*$_2$), 33.1 (s, 3, S*C*HMe$_2$), 30.5 (s, 6, SCH*Me*$_2$). IR (Nujol, KBr, cm^{-1}): 1609 s, 1534 s, 1225 s, 1149 w, 1065 w, 1001 s, 949 w, 810 s, 756 w.

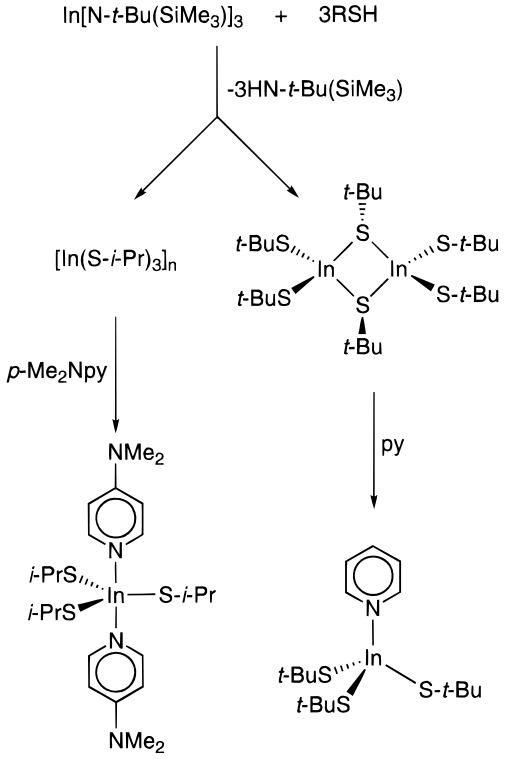
X-ray Crystallography. Crystal data are presented in Table 1. Crystals of In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2\cdot CH_2Cl_2$ are colorless square columns, and In(S-*t*-Bu)$_3$(py) are colorless thick plates. The crystals were handled under mineral oil during the mounting procedure. Data were collected on Siemens SMART CCD (In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2\cdot CH_2Cl_2$) and Siemens P4 (In(S-*t*-Bu)$_3$(py)) instruments. There were no unusual experimental difficulties. Full details can be found in the Supporting Information.

Results and Discussion

Syntheses and Spectroscopic Characterization. A summary of our synthetic results is presented in Scheme 1.

In[N-*t*-Bu(SiMe$_3$)]$_3$ reacts in a few hours at room temperature with RSH to give In(SR)$_3$, where R = *t*-Bu or *i*-Pr. Power and Ruhlandt[1] previously synthesized In[S(2,4,6-*t*-Bu$_3$-C$_6$H$_2$)]$_3$ from In[N(SiMe$_3$)$_2$]$_3$ and the corresponding thiol, but we observed no reaction between In[N(SiMe$_3$)$_2$]$_3$ and *t*-BuSH. This reaction probably does not occur because *t*-BuSH is not as acidic as 2,4,6-*t*-Bu$_3$-C$_6$H$_2$SH (e.g., p$K_a \approx 12$ (RSH) vs 8 (PhSH)) and will not protonate the nitrogen of the amide ligand. Also, it

Scheme 1



can be reasoned that *tert*-butylthiol reacts with In[N-*t*-Bu(SiMe$_3$)]$_3$ and not In[N(SiMe$_3$)$_2$]$_3$ because the amide ligand −N(SiMe$_3$)$_2$ has two electron-withdrawing trimethylsilyl groups while −N(*t*-Bu)(SiMe$_3$) has only one, which makes the nitrogen lone pair of the latter relatively more reactive. Note that on the basis of steric considerations alone In[N(SiMe$_3$)$_2$]$_3$ should be more reactive than In[N-*t*-Bu(SiMe$_3$)]$_3$.

In(S-*t*-Bu)$_3$ is insoluble in hexanes but moderately soluble in benzene, ether, methylene chloride, and THF. Crystals were grown from hot toluene. The isopropylthiolate derivative is virtually insoluble in all noncoordinating solvents, but it was found that fine crystalline needles could be grown from hot 1,2-dichloroethane although the needles were not suitable for X-ray analysis. The insolubility of the complex suggests it is a polymer, with perhaps a structure similar to [In(μ-SePh)$_3$]$_\infty$.[6] Crystals of the *tert*-butylthiolate derivative were well-formed blocks, but repeated attempts to analyze the crystals by X-ray crystallography failed.

The ^{1}H NMR spectrum of In(S-*t*-Bu)$_3$ in toluene-d_8 at −10 °C consists of two closely spaced sharp singlets ($\Delta\delta \approx 0.12$ ppm) with relative intensities 2:1 that can be assigned to the terminal and bridge thiolate ligands, respectively, in a [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ structure (Scheme 1). At room temperature, the chemical shift difference between the singlets is smaller ($\Delta\delta \approx 0.06$ ppm) and the resonance assigned to the bridging thiolate ligands is broadened. At temperatures >30 °C the two singlets overlap or merge completely. We have not been able to find a solvent that gives better peak separation at room temperature (e.g., $CDCl_3$, THF-d_8, and CD_2Cl_2 were tried and all gave spectra with a single resonance at room temperature).

The room temperature ^{13}C{^{1}H} NMR spectrum (toluene-d_8; 75 MHz) is also consistent with the [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ structure in that it has four well-resolved resonances [54.3, 35.7 ppm (μ-SCMe$_3$) and 46.4, 37.7 ppm (terminal SCMe$_3$)]. Both bridging thiolate resonances are broadened slightly. At 45 °C the μ-SC*Me*$_3$ resonance is broadened further and its associated

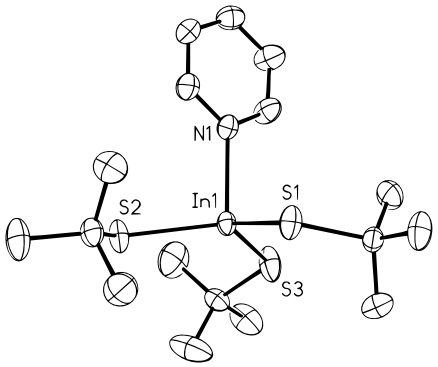


Figure 1. View of one of the independent molecules of In(S-*t*-Bu)$_3$(py) in the unit cell showing the atom-numbering scheme (40% probability ellipsoids).

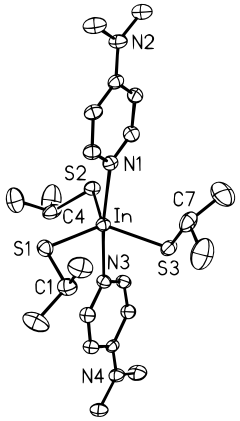


Figure 2. View of In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$ showing the atom-numbering scheme (40% probability ellipsoids).

μ-S*C*Me$_3$ resonance has completely disappeared into the baseline while the resonances arising from the terminal thiolates are also broad. At 65 °C, the highest temperature examined, the bridge and terminal SC*Me*$_3$ resonances have merged into a single broad resonance centered at 37.3 ppm and there is an extremely broad hump around 48 ppm that is presumably the merged bridge and terminal S*C*Me$_3$ resonances. The data are consistent with a dynamic process involving bridge-terminal thiolate exchange.

A molecular weight determination (isothermal distillation; CH_2Cl_2 solvent; Ta[N(SiMe$_3$)$_2$]$_2$Cl$_3$ standard) for the *tert*-butylthiolate derivative gave a molecular weight of 742 ± 45 g/mol, consistent with the dimer formulation.

The difficulty with obtaining an X-ray structure of [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ and the insolubility of [In(S-*i*-Pr)$_3$]$_n$ prompted us to prepare the adducts In(S-*t*-Bu)$_3$(py) and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$, which were synthesized simply by adding the Lewis bases to the parent compounds at room temperature. Both compounds formed crystals suitable for X-ray analysis.

X-ray Crystallographic Studies. Thermal ellipsoid plots of one of the independent molecules of In(S-*t*-Bu)$_3$(py) in the unit cell and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$ are shown in Figures 1 and 2, respectively. Selected bond distances and angles are presented in Table 2. Because the structures of the two molecules of In(S-*t*-Bu)$_3$(py) are very similar, distances and angles are presented for only one of them. Full details are provided in the Supporting Information.

Molecules of In(S-*t*-Bu)$_3$(py) resemble In[S(2,4,6-*i*-Pr$_3$−C$_6$H$_2$)]$_3$(THF) and In[S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)]$_3$(Et$_2$O).[2,7] In(S-*t*-Bu)$_3$(py) can be described as a trigonal pyramid with the pyridine occupying the apical position. The indium and three sulfur atoms are nearly planar ($\sum$(S−In−S) = 351°) with the In atom lying 0.43 Å out of the plane defined by the sulfur atoms. For comparison, in In[S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)]$_3$(Et$_2$O) the three S−In−S angles sum to 354°.[7]

Table 2. Selected Bond Distances (Å) and Angles (deg) for In(S-*t*-Bu)$_3$(py) and In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$

	In(S-*t*-Bu)$_3$(py)	In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$
	Distances	
In−S1	2.4172(6)	2.4519(11)
In−S2	2.4165(6)	2.4580(11)
In−S3	2.4243(7)	2.4428(11)
In−N1	2.311(2)	2.373(3)
In−N3		2.437(3)
av (range) C−S	1.846 (1.830(3)−1.859(2))	1.841 (1.825(4)−1.856(4))
	Angles	
S1−In−S2	115.94(2)	119.01(4)
S2−In−S3	118.45(2)	122.55(4)
S1−In−S3	116.43(2)	117.99(4)
N1−In−S1	103.51(5)	95.61(8)
N1−In−S2	99.15(5)	87.80(8)
N1−In−S3	97.96(5)	93.45(8)
N3−In−S1		92.80(8)
N3−In−S2		87.96(8)
N3−In−S3		82.74(8)
N1−In−N3		171.59(10)
av (range) In−S−C	108.90 (107.85(8)−109.58(8))	105.12 (102.44(14)−109.82(15))

The structure of In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$ is closely related to the structures of In[S(2,4,6-*i*-Pr$_3$−C$_6$H$_2$)]$_3$(MeCN)$_2$ and In(SPh)$_3$(py)$_2$.[2,6] Molecules of In(S-*i*-Pr)$_3$(Me$_2$Npy)$_2$ are trigonal bipyramidal with the *p*-Me$_2$Npy ligands in the apical positions. The indium atom is slightly shifted (0.10 Å) out of the plane of the three sulfur atoms in the direction of one of the *p*-Me$_2$Npy ligands (N1), and the N1−In−N3 angle (172°) is close to linear (cf. N−In−N = 164° in In(SPh)$_3$(py)$_2$).

The In−S distances in In(S-*t*-Bu)$_3$(py) are slightly shorter ($\Delta \approx 0.03$ Å) than those in In(S-*i*-Pr)$_3$(Me$_2$Npy)$_2$, but all the distances fall within the range of In−S distances (2.389(3)−2.472(3) Å) reported for the aryl thiolate compounds In[S(2,4,6-*t*-Bu$_3$-C$_6$H$_2$)]$_3$,[1] In(SPh)$_3$(py)$_2$,[6] and In[S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)]$_3$(Et$_2$O).[7] The In−N distances in In(S-*i*-Pr)$_3$(*p*-Me$_2$Npy)$_2$ (2.37, 2.44 Å) are longer than the one in In(S-*t*-Bu)$_3$(py) (2.31 Å) even though *p*-Me$_2$Npy is a more powerful donor than unsubstituted pyridine. A trans influence is probably the reason for the longer distances in the tbp compound. A similar discrepancy was also noted, however, in the four-coordinate compounds In(NPh$_2$)$_3$(py) and In[N-*t*-Bu(SiHMe$_2$)]$_3$(*p*-Me$_2$Npy) where In−N = 2.264(4) and 2.327(3) Å, respectively, but in this case the difference can be ascribed to the different steric bulk of the amide ligands.[9] The In−N distances in the new compounds may also be compared to those in In(SPh)$_3$(py)$_2$ (2.374(8)−2.408(7) Å),[6] InX$_3$(py)$_3$ where X = Cl or Br (2.28(3)−2.38(2) Å),[11,12] and InCl$_2$(1,3-diphenyltriazide)(3,5-dimethylpyridine)$_2$ (av 2.307(7) Å).[13]

Conclusion

The alkylthiolate complexes In(SR)$_3$ (R = *t*-Bu or *i*-Pr) have been prepared by reacting In[N-*t*-Bu(SiMe$_3$)]$_3$ with the thiols. The *tert*-butyl derivative is proposed to be the dimer [In(S-*t*-Bu)$_2$(μ-S-*t*-Bu)]$_2$ on the basis of NMR data and a molecular weight determination. The degree of oligomerization for [In-

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$(S\text{-}i\text{-}Pr)_3]_n$ was not determined but, on the basis of its insolubility and the structural precedence[6] of $[In(\mu\text{-}SePh)_3]_\infty$, we suggest it is a polymer with six-coordinate indium atoms (i.e., $[In(\mu\text{-}S\text{-}i\text{-}Pr)_3]_\infty$). Both thiolate derivatives form Lewis base adducts. $[In(S\text{-}t\text{-}Bu)_2(\mu\text{-}S\text{-}t\text{-}Bu)]_2$ reacts with pyridine to give four-coordinate $In(S\text{-}t\text{-}Bu)_3(py)$, while the less sterically encumbered $[In(S\text{-}i\text{-}Pr)_3]_n$ reacts with the stronger donor *p*-(dimethylamino)pyridine to form five-coordinate $In(S\text{-}i\text{-}Pr)_3(p\text{-}Me_2Npy)_2$. $In(S\text{-}t\text{-}Bu)_3(py)$ can be described as trigonal pyramidal with the three sulfur atoms lying nearly in a plane, while $In(S\text{-}i\text{-}Pr)_3(p\text{-}Me_2Npy)_2$ is trigonal bipyramidal.

A study related to this one involving the synthesis of indium alkoxides, fluoroalkoxides and aryloxides from indium tris(amide) complexes will be reported shortly.[14]

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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