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A convenient synthesis of methylindium(III) dithiolate complexes—precursors for indium sulfides

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Methylindium(III) dithiolate complexes of the general formulae [$Me_2In(S^{\cap}S)$] (1) and [$MeIn(S^{\cap}S)_2$] (2) [$S^{\cap}S = (EtO)_2PS_2^-$, $(Pr^iO)_2PS_2^-$, $Et_2NCS_2^-$, $Pr^i_2NCS_2^-$, $O(CH_2CH_2)_2NCS_2^-$, $EtOCS_2^-$ and $Pr^iOCS_2^-$] have been isolated conveniently by the reaction of $Me_3In{\cdot}OEt_2$ with $In(S^{\cap}S)_3$ (3) in an appropriate stoichiometry. Both 1 and 2 have been characterized by indium analysis, IR, NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{H\}$) and mass spectral data. NMR data of 3 are also included for comparison. The Me–In and $S^{\cap}S$ resonances are sensitive to the number of methyl groups attached to indium metal. The mass spectral data indicate that these complexes are monomeric in nature. The thermal behavior of a few complexes has been investigated. The xanthate and dithiocarbamate complexes on pyrolysis under dynamic vacuum or flowing nitrogen atmosphere gave either In_2S_3 or a mixture of InS, In_2S_3 and In_6S_7, which were characterized using EDAX and powder XRD. Copyright © 2005 John Wiley & Sons, Ltd.

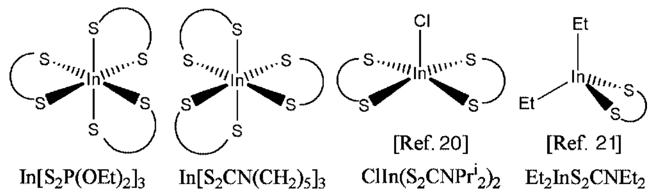
KEYWORDS: methylindium; dithiophosphate; dithiocarbamate; xanthate; NMR; pyrolysis; powder XRD; In_2S_3; InS; In_6S_7

INTRODUCTION

Gallium and indium thiolate complexes have attracted considerable attention owing to their relevance as molecular precursors for metal sulfides and $CuInS_2$.[1,2] Organoindium thiolates, $[R_2InSR']_2$ and $[RIn(SR')_2]_2$, often isolated as dimers, have been employed to deposit indium sulfide films by Nomura *et al.*[3–6] and Barron and co-workers.[7–9] These films showed significant dependence on deposition temperature and the nature of the substituents (both on indium and sulfur), and often contained a mixture of sulfides, viz. InS-In, β-In_2S_3 and In_6S_7.[3–9]

1,1-Dithiolates are yet another versatile family of ligands which have been successfully used for the preparation of metal sulfides. Dithiolates of indium have been known for about four decades[10,11] with a predominance of classical tris derivatives. However, there are only a few reports on diorganoindium derivatives[11–14] and even fewer on monoorganoindium complexes.[12] These complexes are in general monomeric, as shown by molecular weight measurements[11,12] and by X- ray crystallography with structure motifs varying from octahedral/trigonal prismatic,[10,15–19] square pyramidal[20] to tetrahedral[21] (Scheme 1).

Recently [$In(S_2CNR'R'')_3$],[21–23] [$In(S_2COPr^i)_3$][24] and $R_2In(S_2CNR'R'')$[21,22,25,26] have shown promising potential for the preparation of β-In_2S_3. The dialkylindium precursors may have an advantage over the tris derivatives owing to their higher volatility and lower indium-to-sulfur ratio (1 : 2), thus avoiding unwanted wastage of the dithio ligand. The dialkylindium complexes are prepared by (i) alkane elimination reaction between R_3In and a dithio ligand,[11,13,14] (ii) salt elimination reaction of dialkylindium acetate[12]/chloride[21] with sodium salt of dialkyldithiocarbamate, and (iii) redistribution reaction



Scheme 1.

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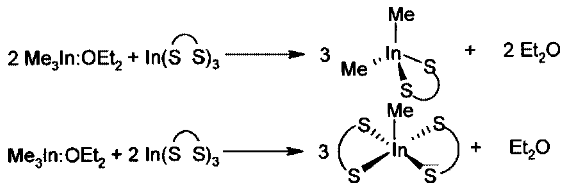
between trialkylindium and tris(dialkydithiocarbamato)indium(III).[21] Reaction (i) is limited to the availability of stable free dithio acids, while reaction route (ii), a two-step synthesis, sometimes yield products contaminated with monoalkylindium(III) derivatives. To evaluate the generality of the reaction (iii) and to extend this route to monoalkylindium derivatives, which are less explored,[12] we have synthesized a series of mono- and dimethyl–indium complexes with dithiophosphates, dithiocarbamates and xanthates. The results of this work are reported herein.

RESULTS AND DISCUSSION

Methylindium(III) dithiolate complexes of the types $[Me_2In(S^{\frown}S)]$ (**1**) and $[MeIn(S^{\frown}S)_2]$ (**2**) $[S^{\frown}S = (EtO)_2PS_2^-$, $(Pr^iO)_2PS_2^-$, $Et_2NCS_2^-$, $Pr^i_2NCS_2^-$, $O(CH_2CH_2)_2NCS_2^-$, $EtOCS_2^-$, $Pr^iOCS_2^-]$ have been prepared by the reaction between $Me_3In{\cdot}OEt_2$ and $In(S^{\frown}S)_3$ (**3**) [eqs (1) and (2)]. These complexes were isolated as colorless solids, liquids or pastes which solidified on standing for a few days.



(1)

(2)

The IR spectra of these complexes displayed absorptions in the region 500–535 cm^{-1} and 380–420 cm^{-1} attributable to ν In-C[11,12,27] and ν In-S[11,12,20,28] stretching, respectively. NMR spectra on freshly prepared complexes were recorded in $CDCl_3$ and the resulting data are summarized in Table 1. The spectra exhibited expected resonances and peak multiplicities. The following characteristic patterns are quite evident from Table 1.

(1) The $^{31}P\{^1H\}$ NMR resonances for dialkyldithiophosphate complexes are deshielded with increasing number of dithiophosphate ligand on indium. Thus they appear

Table 1. NMR data in $CDCl_3$ for methylindium(III) dithiolate complexes

Complex	Yield (%)	Melting point (°C)	In (%)	$^{31}P\{^1H\}$ δ (ppm)	$^{13}C\{^1H\}$ δ (ppm)	^1H NMR δ (ppm)
$[In\{S_2P(OEt)_2\}_3]^a$				100.3	15.8 (d, 8.2 Hz, OCH_2*Me*); 64.7 (d, 5.5 Hz, OCH_2–)	1.43 (t, 7 Hz, OCH_2*Me*); 4.40 (dq, ^3J (H-H) 7 Hz; ^3J (P–H) 10.2 Hz, OCH_2–)
$[MeIn\{S_2P(OEt)_2\}_2]$	97	Liquid	22.4 (22.9)	97.7	2.7 (s, MeIn–); 15.7 (d, 7.7 Hz, OCH_2*Me*); 64.2 (d, 4.6 Hz, OCH_2–)	0.66 (s, MeIn–); 1.38 (t, 7.0 Hz, OCH_2*Me*), 4.24 (m, OCH_2)
$[Me_2In\{S_2P(OEt)_2\}]$	90	Liquid	34.4 (34.8)	96.4	−0.6 (s, Me_2In-); 15.7 (d, 8.3 Hz, OCH_2*Me*); 63.8 (d, 6.3 Hz, OCH_2–)	0.24 (s, Me_2In-); 1.36 (t, 7Hz, OCH_2*Me*); 4.18 (dq, 7.10 Hz; OCH_2–)
$[In\{S_2P(OPr^i)_2\}_3]^a$				96.6	23.4 (d, 4.7 Hz, $OCHMe_2$); 73.7 (d, 5.4 Hz, OCH–)	1.43 (d, 6.2 Hz, $OCHMe_2$); 5.18 (sep, 6.2 Hz, OCH–)
$[MeIn\{S_2P(OPr^i)_2\}_2]$	94	Liquid	19.2 (20.6)	93.9	2.6 (s, MeIn–); 23.5 (s,$OCHMe_2$), 73.8 (d, 5.4 Hz, OCH–)	0.67 (s, MeIn–); 1.41 (d, 6.2Hz, $OCHMe_2$); 4.90 (sep, 6.2 Hz OCH–)
$[Me_2In\{S_2P(OPr^i)_2\}]$	92	>300	31.8 (32.0)	91.8	−1.2 (s, Me_2In-), 23.6 (s, OCH*Me*) 73.4 (s, OCH–)	0.24 (s, Me_2In-), 1.47 (d, 6.2 Hz, $OCHMe_2$); 4.82 (m, OCH–)
$[In(S_2CNEt_2)_3]$				—	12.1 (NCH_2*Me*); 50.7 (NCH_2–) 201.7 (CS_2)	1.33 (t, 7.2 Hz NCH_2*Me*); 3.83 (q, 7.2 Hz, NCH_2)
$[MeIn(S_2CNEt_2)_2]$	95	120 Turns black	27.5 (26.9)	—	−1.8 (s, MeIn); 12.0 (s, NCH_2*Me*); 49.7 (s, NCH_2); 200.7 (s, CS_2)	0.45 (s, MeIn); 1.28 (t, 7.2 Hz, NCH_2*Me*), 3.49 (q, 7.2Hz, NCH_2–)
$[Me_2In(S_2CNEt_2)]$	95	140	38.5 (39.1)	—	−3.3 (s, Me_2In), 11.9 (s, NCH_2*Me*–), 49.3 (s, CH_2–); 201.1 (s, -CS_2)	0.17 (s, Me_2In); 1.29 (t, 7.1 Hz NCH_2*Me*); 3.84 (q NCH_2)

Table 1. (*Continued*)

Complex	Yield (%)	Melting point (°C)	In (%)	$^{31}P\{^1H\}$ δ (ppm)	$^{13}C\{^1H\}$ δ (ppm)	^1H NMR δ (ppm)
$[In(S_2CNPr^i{}_2)_3]$[b]				—	19.9 (s, NCH*Me*$_2$); 57.0 (br, CH); 201.3 (s, CS_2)	1.43 (br, NCH*Me*$_2$); 4.01, 5.12 (br, N*CH*)
$[MeIn(S_2CNPr^i{}_2)_2]$	96	210	22.8 (23.8)	—	−1.7 (s, MeIn); 19.8 (s, NCH*Me*$_2$); 54.7 (br, NCH); 200.2 (s, CS_2)	0.55 (s, MeIn), 1.43 (br, NCH*Me*$_2$); 5.12 (br, NCH)
$[Me_2In(S_2CNPr^i{}_2)]$	96	248–255 Turns black	34.8 (35.7)	—	−3.7 (s, MeIn); 19.9 (s, NCH*Me*$_2$); 53.5 (br, NCH); 200.5 (s, CS_2)	0.14 (s, Me_2In); 1.42 (br, NCH*Me*$_2$); 5.23 (br, NCH−)
$[In\{S_2CN(CH_2CH_2)_2O\}_3]$[c]				—	52.5 (s, NCH_2−); 66.0 (OCH_2−), 203.3 (s, CS_2)	3.76 (t, 4.8 Hz, NCH_2); 4.03 (t, 4.9 Hz, OCH_2−)
$[MeIn\{S_2CN(CH_2CH_2)_2O\}_2]$	97	222	26.7 (25.3)	—	−1.6 (br, MeIn); 51.6 (s, NCH_2) 66.0 (s, OCH_2−); 202.3 (s, CS_2)	0.54 (s, MeIn); 3.76 (t, 4 Hz, NCH_2−); 4.06 (t, 4 Hz, OCH_2)
$[Me_2In\{S_2CN(CH_2CH_2)_2O\}]$	92	255 Turns black	38.1 (37.4)	—	−2.7 (br, Me_2In); 51.5 (NCH_2) 66.0 (s, OCH_2−); 202.4 (s, CS_2)	0.18 (s, Me_2In), 3.76 (t, NCH_2), 4.06 (t, OCH_2)
$[In(S_2COEt)_3]$[d,e]				—	14.1 (s, OCH_2*Me*), 76.2 (s, OCH_2−), 229.9 (s, CS_2)	1.50 (t, 7 Hz, OCH_2*Me*); 4.51(q, 7 Hz OCH_2)
$[MeIn(S_2COEt)_2]$	97	Semisolid	31.2 (30.8)	—	−2.1 (s, MeIn); 13.8 (s, OCH_2*Me*); 74.1 (OCH_2−); 228.4 (s, CS_2)	0.61 (s, MeIn); 1.45 (t, 7 Hz); 4.49 (q, 7 Hz, OCH_2−)
$[Me_2In(S_2COEt)]$	97	263	43.7 (43.1)	—	−3.1 (Me_2In); 13.9 (s, CH_2*Me*), 72.2 (s, OCH_2−); 228.4 (s, CS_2)	0.29 (s, Me_2In); 1.48 (t, 7Hz, OCH_2*Me*), 4.55 (q, 7 Hz, OCH_2−)
$[In(S_2COPr^i)_3]$				—	21.4 (s, NCH*Me*$_2$); 85.7 (s, CH); 228.8 (s, CS_2)	1.45 (d, 6 Hz, CH*Me*$_2$); 5.09 (sep, 6 Hz, OCH−)
$[MeIn(S_2COPr^i)_2]$	97	Semisolid	28.6 (28.7)	—	−2.5 (br, MeIn); 21.4 (s, NCH*Me*$_2$); 85.5 (s, N*CH*); 227.5 (s, CS_2)	0.64 (s, MeIn), 1.46 (d, 6 Hz NCH*Me*$_2$); 5.23 (m, NCH−)
$[Me_2In(S_2COPr^i)]$	94	282 Turns black	40.5 (41.0)	—	−3.1(s, *Me*$_2$In-); 21.2, 21.5 (OPr^i) 81.1 (s, −OCH); 226.8 (CS_2)	−0.28 (s, Me_2In-); 1.44 (d, 6.5Hz, Me_2CHO); 5.39 (m, −OCH)

[a] From Dutta *et al.*[29]
[b] Chemical shift values slightly differ from those reported in Bhattacharya *et al.*[18] and Lindmark and fay.[28]
[c] From Dutta *et al.*[33]
[d] From Abram and Abram.[34]
[e] From Hoskins *et al.*[17]

in the following order: $Me_2In(S^\cap S) < MeIn(S^\cap S)_2 < In(S^\cap S)_3$. The deshielding of the $^{31}P\{^1H\}$ resonance may be attributed either to the +I effect of the methyl group on the indium or the change in coordination number of central metal atom from 4 to 6. The shift in methyl indium complexes can be compared with the corresponding chloro derivatives.[29] A similar trend in the ^{13}C NMR resonance of CS_2 group of isopropylxanthate complexes is observed. However, in other cases, the chemical shift difference in the CS_2 resonance in their ^{13}C NMR spectra is rather small.

(2) The methylindium resonance in ^1H and $^{13}C\{^1H\}$ NMR spectra also showed deshielding on replacing a methyl group on indium by a dithio ligand and followed the trend:

$$Me_3In{\cdot}OEt_2 > Me_2In(S^\cap S) > MeIn(S^\cap S)_2$$

Deshielding of the methyl group resonance in these complexes suggests an increase in electron density at the indium atom, which results from coordination of dithiolate ligands to the metal atom.

The mass spectra (Table 2) of few representative complexes were recorded. None of the spectra showed molecular ion peak (M) nor any peak greater than the molecular ion. The spectra of these complexes generally gave a peak due to M−Me.

THERMAL STUDIES

To assess the suitability of these complexes for preparation of indium sulfides, the thermal behavior of a few representative complexes has been investigated. Pyrolysis of xanthate and dithiocarbamate complexes was carried out at 450 °C, unless otherwise stated, under both flowing nitrogen and vacuum (0.1 mm/Hg). The resulting residues were characterized by powder X-ray diffraction (XRD) patterns and EDAX analysis (Table 3). Pyrolysis under flowing nitrogen in general gave different phases of β-In_2S_3, whereas similar experiments under vacuum gave a mixture of indium sulfides.

The complex [$Me_2In(S_2CNEt_2)$] on heating to 450 °C under flowing nitrogen yielded a mixture of tetragonal and cubic β-In_2S_3. The complex [$Me_2In(S_2CNPr^i_2)$], on the other hand, under similar conditions afforded amorphous InS. However, heating under vacuum led to the formation of a mixture of InS and cubic β-In_2S_3 with the predominance of the former. Clearly, the nature of the R group on the dithiolate ligand has a pronounced effect on the kind of indium sulfide formed. Monomethyl indium complex [$MeIn(S_2CNPr^i_2)_2$] on pyrolysis gave β-In_2S_3, with a cubic phase formed under flowing nitrogen while the tetragonal phase was isolable on vacuum heating.

Both mono- and di-methylindium isopropyl xanthate complexes, [$MeIn(S_2COPr^i)_2$] [Fig. 1(a)] and [$Me_2In(S_2COPr^i)$], on heating under flowing nitrogen at 450 °C afforded a mixture of tetragonal and cubic β-In_2S_3. Similar experiments with both the precursors when carried out under vacuum, however, gave a mixture of indium sulfides (InS, In_2S_3, In_6S_7) [Fig. 1(b)]. It can be inferred that the complex [$MeIn(S_2CNPr^i_2)_2$] appears to be a good candidate as precursor material for the deposition of single-phase β-In_2S_3. In all other cases, a mixture of InS and In_2S_3 or cubic and tetragonal forms of β-In_2S_3 was obtained.

Table 2. Mass spectral data for the methylindium dithiolate complexes

Complex	M/e (species)
[$Me_2In\{S_2CN(CH_2CH_2)_2O\}$] FW = 307	292 [$MeIn(S_2CN(CH_2CH_2)_2O\}]^+$ 175 130 [$MeIn]^+$ 88
[$Me_2In(S_2COPr^i)$] FW = 280	214 175 [$InSCO]^+$ 159 [$InSC]^+$ 145 [$Me_2In]^+$
[$MeIn(S_2CNEt_2)_2$] FW = 426	411 [$In(S_2CNEt_2)_2]^+$ 352 [$In(S_2CNEt_2)_2(S_2CN)]^+$ (353) 278 [$MeIn(S_2CNEt_2)]^+$
[$Me_2In\{S_2P(OPr^i)_2\}$] FW = 358	323 277 259 [$MeIn(S_2P(OH)_2]^+$ 225 [$MeIn(S_2P)]^+$ (225)/[$In(S_2PO)]^+$ 163 [$MeInS]^+$ 149 132 115 [$In]^+$

Table 3. Indium sulfides formed by pyrolysis of methylindium dithiolate complexes[a]

Compound	Heating at 450 °C for 5h under flowing N_2	Heating at 450 °C under vacuum (0.1 mm/Hg)
[$MeIn(S_2CNPr^i_2)_2$]	Cubic β-In_2S_3 (In = 72.8; S = 27.2%)	Tetragonal β-In_2S_3 (In = 74.4; S = 25.6%)
[$Me_2In(S_2CNPr^i_2)$]	Amorphous InS (In = 80.5; S = 19.5%)	Mixture of InS and β-In_2S_3 (In = 72.9; S = 27.1%)
[$Me_2In(S_2CNEt_2)$]	Mixture of tetragonal/cubic β-In_2S_3 (In = 72.9; S = 27.1%)	—
[$Me_2In(S_2COPr^i)$]	Mixture of tetragonal/cubic β-In_2S_3 (In = 73.5; S = 26.5%)	Upto 400 °C amorphous product 450 °C, In_2S_3, InS and In_6S_7 (In = 80.2, S = 19.7%)
[$MeIn(S_2COPr^i)_2$]	Mixture of tetragonal/cubic β-In_2S_3 (In = 73.5; S = 26.5%)	Mixture of InS/β-In_2S_3/In_6S_7 (In = 79.9; S = 20.1%)

[a] Values in parentheses are weight percentages by EDAX. Calcd for In_2S_3: In = 70.5; S = 29.5%. InS: In = 78.2; S = 21.8%. In_6S_7: In = 75.5; S = 24.5%. Tetragonal β-In_2S_3, JCPDS file no. 25−0390; cubic β-In_2S_3, JCPDS file no. 32−0456; orthorhombic InS, JCPDS file no. 19−0588; monoclinic In_6S_7, JCPDS file no. 19−0587.

EXPERIMENTAL

All experiments involving organoindium compounds were performed under anhydrous conditions in a nitrogen atmosphere using Schlenk techniques. Solvents were dried

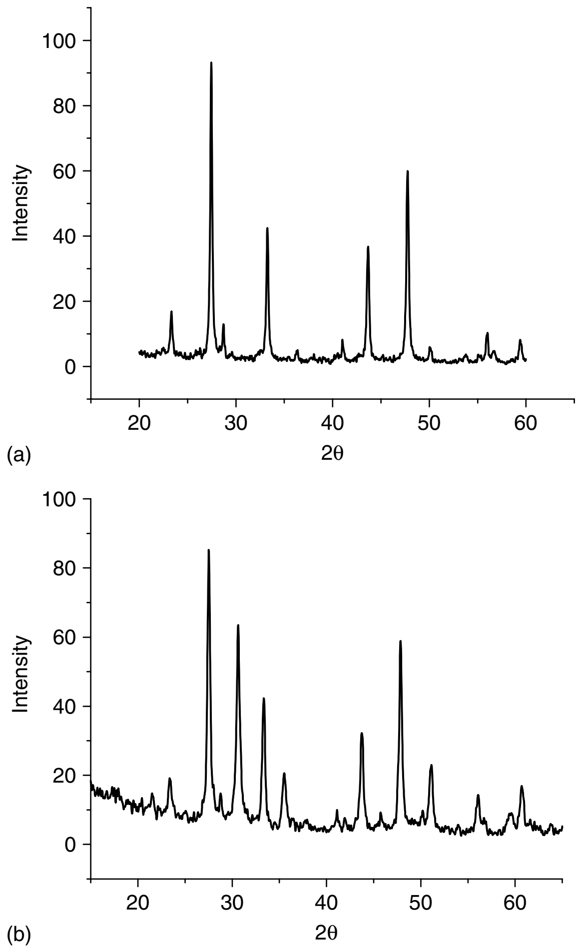


Figure 1. XRD pattern of indium sulfide formed by pyrolysis of $[MeIn(S_2COPr^i)_2]$ at 450 °C: (a) under flowing N_2; (b) under vacuum.

by standard procedures. Anhydrous indium trichloride was used as such. The ether adduct of Me_3In was prepared from MeMgI and indium trichloride.[30] (Trimethylindium usually co-distilled with 3–5 equivalents of ether. The ether contents in each sample were ascertained by ^1H NMR integration.) Me_2InCl and $MeInCl_2$,[27,31] ammonium salts of dialkyldithiophosphoric acids, $(RO)_2PSSH$,[32] sodium or potassium salt of dialkyldithiocarbamate and xanthate[28] and $In(S^\cap S)_3$[17,18,29,33,34] were prepared using reported procedures. Infrared spectra were recorded as neat liquids or as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. The NMR spectra (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) were recorded on a Bruker DPX-300 NMR spectrometer in a 5 mm tube in $CDCl_3$ solution. Chemical shifts were referenced to the internal chloroform peak (δ7.26 and δ77.0 ppm) for ^1H and $^{13}C\{^1H\}$, respectively and external 85% H_3PO_4 for $^{31}P\{^1H\}$. The mass spectra were recorded on a Q-TOF Micromass YA-105 mass spectrometer. Complexes were pyrolysed under vacuum in a furnace at different temperatures; the residues thus obtained were characterized by XRD data. Powder XRD data were collected on a Philips PW 1729 and EDAX experiments were carried out on a Kevex Instrument.

Preparation of $[Me_2In\{S_2P(OPr^i)_2\}]$

(i) To a benzene solution (20 cm^3) of trimethylindium etherate (480 mg, containing 249 mg Me_3In, 1.55 mmol), a solution of $[In\{S_2P(OPr^i)_2\}_3]$ (587 mg, 0.77 mmol) in the same solvent was added and stirred under nitrogen atmosphere for 30 min. The solvent was stripped off under reduced pressure, leaving behind a white solid (yield 770 mg, 92% yield). Similarly, all other dimethylindium complexes were prepared.

(ii) To a benzene solution (20 ml) of Me_2InCl (337 mg, 1.87 mmol; sublimed before use; ^1H NMR in $CDCl_3$ δ0.40 ppm Me_2In) under nitrogen, $NH_4[S_2P(OPr^i)_2]$ (432 mg, 1.87 mmol) was added gradually in parts. The mixture was stirred overnight and filtered through a G-3 filtration unit. Benzene was removed from the filtrate *in vacuo* to give an oily liquid which solidified after few days (640 mg, 95% yield). The spectroscopic data were consistent with those prepared by the above route.

Preparation of $[MeIn\{S_2CNPr^i{}_2\}_2]$

To a benzene solution (20 cm^3) of trimethylindium etherate (176 mg, containing 67 mg Me_3In, 0.42 mmol), a solution of $In(S_2CNPr^i{}_2)_3$ (539 mg, 0.84 mmol) in the same solvent was added and stirred under nitrogen atmosphere for 30 min. The solvent was stripped off under reduced pressure, leaving behind a white solid (590 mg, 96% yield). Similarly, all other monomethylindium complexes were prepared.

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