

# Indium: Inorganic Chemistry

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## 1 INTRODUCTION

Indium is a very soft, silvery–white metal with a brilliant luster, rather like tin in appearance, located behind gallium in the periodic table of the elements. It is considered a nontoxic metal, and is ductile, malleable and diamagnetic. The pure metal gives a high-pitched ‘scream’ when bent. It wets glass, as does gallium, and so it can be used to seal glass to metals. It can form alloys with extremely low-melting points, down to below room temperature (The alloy of 24% indium and 76% gallium is liquid at room temperature). It is used for electric fuses, safety plugs for storage tanks, and mainly for the automatic release of fire alarm and sprinkler systems, and also for cooling and as a heat-exchange medium in nuclear technology. The majority of the world’s supply of indium is produced in Canada, where it would not normally be made in laboratory as it is commercially available. Indium is a by-product of the formation of lead and zinc. Indium metal is isolated by the electrolysis of indium salts in water. Further processes are required to make very pure indium for electronics purposes.

Indium is stable in air or in oxygen at room temperature, and does not react with water even at the boiling point but on heating goes to the oxide.<sup>1</sup> Indium oxide, an n-type semiconductor with a wide band gap of about 3.6 eV, is an ideal material for flat-panel displays owing to its high electrical conductivity and optical transparency, and also is used for gas sensors and conducting glass.<sup>2</sup> When heated, elemental indium easily reacts with the halogens to form the corresponding halide, and with sulfur,

selenium, nitrogen, and phosphorous to give the corresponding indium-containing III-V/VI compounds that are well-known semiconductor materials and have technological importance for blue/violet light-emitting diodes (LEDs), laser diodes, solar cells and other optoelectronic devices. In addition, indium and its compounds are also used to promote some organic synthesis.<sup>3</sup>

The inorganic chemistry of indium during the past decade has received unbroken attention that originates from two aspects. One stems from the resurgence of the chemistry of low-valent indium, which is currently extended to various fields. A special highlight is the use of CpIn (Cp = C<sub>5</sub>H<sub>5</sub>), R<sub>4</sub>In<sub>4</sub> (R = Cp, C(SiMe<sub>3</sub>)<sub>3</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub>), and R<sub>4</sub>In<sub>2</sub> (R = SiBu<sup>t</sup><sub>3</sub>, CH(SiMe<sub>3</sub>)<sub>2</sub>) compounds to further prepare new compounds and clusters, which illustrate the lively development and the current trends in this field.<sup>4,5</sup> The other is from the understanding that indium compounds are potential precursors for applications in the field of new materials. In addition, the development of nanotechnology and the utility of indium reagents in organic synthesis present new and exciting opportunities for indium chemistry.

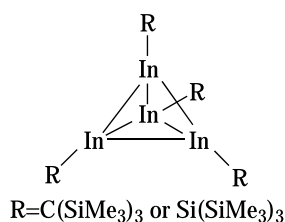
## 2 INDIUM (I) CHEMISTRY

### 2.1 Introduction

The current interest in monovalent indium compounds originates from the understanding of the structures and properties of these novel compounds, with particular focus on InX, CpIn, and In<sub>4</sub>R<sub>4</sub> complexes. Indium (I) halides can be used as starting materials to prepare other indium (I) compounds and play an important role in the study of the oxidation chemistry of indium (I). The cyclopentadienylindium (I) (CpIn), obtained from the reaction of indium halide with LiCp, is another starting point for the synthesis of a number of indium (I) derivatives. The third approach to obtain indium (I) compounds depends on the tetraalkyltetraindium (I) compounds In<sub>4</sub>R<sub>4</sub> (R = C(SiMe<sub>3</sub>)<sub>3</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub>) as a source of In (I) compounds, which exhibits a distinctive chemical reactivity (Scheme 1).<sup>4</sup> The monomer fragment InR has similar frontier orbitals to carbon monoxide, and can form transition metal compounds analogous to metal carbonyls with bridging or terminal InR ligands. Furthermore, In<sub>4</sub>R<sub>4</sub> can be oxidized with oxygen, sulfur, selenium, or halide to form heterocubane-type structures containing four indium atoms. These reactions open a new route to organometallic compounds and lead to novel compounds with unusual structures.

### 2.2 Halogen Derivatives

Indium (I) halides can be prepared by dissolving an excess of indium in hydrohalide acid or reduction of trihalides with metal. The structures of the bromides have been



**Scheme 1** The molecule structure of  $In_4R_4$  with  $R = C(SiMe_3)_3$  and  $Si(SiMe_3)_3$ , Ref. 4

reinvestigated.<sup>6</sup> Some theoretic calculations indicate that the reduced phases ( $InBr$ ,  $In_2Br_3$ , and  $In_3Br_7$ ), among the binary indium bromides, are 'soft' and easy to perturb upon chemical reaction, and the coordination polyhedra around  $In^+$  ions are highly irregular. The total  $In-Br$  bonding interaction is weak, but in none of the cases has there been found a directed electron 'lone-pair' effect for  $In^+$ .<sup>7</sup> The bromide  $In_5Br_7$  exists in two polymorphs, both of which have a layer structure and consist of the structure fragments  $[In^I_6Br_2]^{4+}$  and  $[In^{II}_4Br_{12}]^{4-}$ . The latter is composed of two ethane-like  $[In^{II}_2Br_6]^{2-}$  units, which contain  $In-In$  bonds.<sup>8</sup> The mixed-valence species also are found in the compounds  $In_4Br_7$  and  $In_7Br_9$ , which can be described as  $(In^{3+})_3(In^+)_5(Br^-)_{14}$  and  $(In^+)_6(In^{3+})(Br^-)_9$  respectively.<sup>9</sup>

The mixed transition metal indium bromides  $InMBr_3$  ( $M = Fe, Mn$ ),  $In_2MBr_6$  ( $M = Th, Zr$ ), and  $In_3Ti_2Br_9$  are known.  $In_2ThBr_6$  adopts monoclinic crystal structure, which is built up from three-dimensional (3D) interconnected  $ThBr_8^{4-}$  bisdisphenoids and  $InBr_9^{8-}$  monocapped cubes, the latter polyhedra being significantly distorted. Within  $InMBr_3$ , the transition metal cations are octahedrally coordinated by  $Br^-$  anions; monovalent indium cations are found in strongly distorted trigonal  $Br^-$  prisms, which are tricapped by additional  $Br^-$  anions.<sup>10,11</sup>

Fluoride compound,  $PtIn_7F_{13}$  is prepared by reduction of  $InF_3$  with  $In$  powder, which is built up from the  $[PtIn_6]$  octahedra. These units are stacked in an alternating fashion together with  $[InPt_6]$  octahedra along  $[001]$ . Within the  $[InPt_6]$  cluster, platinum centers are octahedrally coordinated by six  $In$  atoms. The  $Pt-In$  bond lengths are significantly shorter than that in intermetallic phases with sixfold coordinated  $Pt$  atoms, and the  $In-In$  distances are only slightly longer than in elemental  $In$  or molecular  $In$  clusters.<sup>12</sup> The compound  $InBF_4$  is isotypical to  $KBF_4$ .

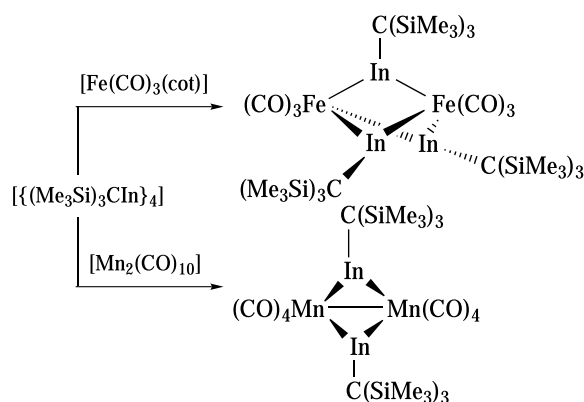
Indium (I) halides insert into nickel halogen bonds of carbonyl group free organonickel complexes to form  $Ni-In$  bond compounds, which can be viewed as derivatives of trimethylindium or indiumtrihalides.<sup>13</sup>

### 2.3 Reaction of $In_4R_4$ ( $R = C(SiMe_3)_3$ )

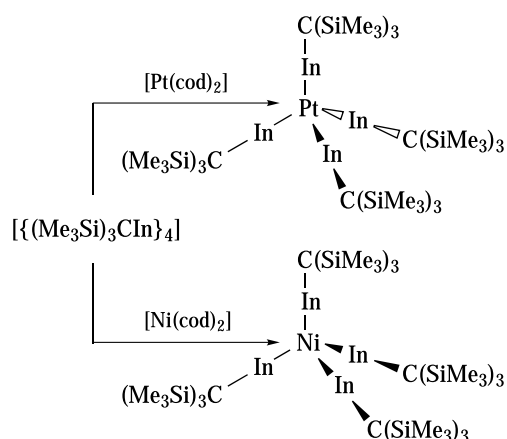
The tetrahedral tetraindium (I) compound  $In_4R_4$  ( $R = C(SiMe_3)_3$ ) is readily available by the reaction of indium

monohalides with  $LiR$  ( $R = C(SiMe_3)_3$ ). The monomeric fragments, possessing two empty p orbitals perpendicular to the  $In-C$  bond axis and an electron lone pair, thus making it isolobal to carbon monoxide. It can be used to form transition metal compounds that are similar to the metal carbonyls. The cubane  $In_4R_4$  reacts with  $(CO)_5Mn-Mn(CO)_5$  to form bis  $\{\mu-[tris(trimethylsilyl)methyl]indanyl\}$ -di-manganese, in which two  $CO$  ligands are replaced by two  $InR$  fragments. Thus, two  $Mn(CO)_4$  groups are bridged by two monoalkylindium units and a planar  $Mn_2In_2$  molecular center.<sup>14</sup> Reaction with tricarbonyl-ironcyclooctatetraene produces  $Fe_2(CO)_6(InR)_3$ , which is one of the very rare examples of a compound with two  $Fe(CO)_3$  fragments symmetrically bridged by three main-group elements. It involves a trigonal-bipyramidal  $Fe_2In_3$  moiety with all indium atoms in equatorial positions (Scheme 2).<sup>15</sup> Similar replacements of  $CO$  ligands by  $InR$  is also demonstrated for  $Ni_2Cp_2(\mu-CO)_2$ ,  $Fe_2(CO)_9$ , and  $Fe_3(CO)_{12}$  by insertion of  $InR$  into the  $M-M$  bond and further replacement of one or both bridging carbonyl complexes.<sup>16,17</sup> The reaction of  $In_4R_4$  with bis(cyclooctadiene) nickel (0) gives  $Ni(InR)_4$ , which is an analogue of the thermally unstable carbonyl complex  $Ni(CO)_4$  with a nickel atom tetrahedrally coordinated by four  $InR$  ligands. The  $Ni-In-C$  units with two-coordinated  $In$  atoms are exactly linear ( $Ni-In-C$ ,  $180.0^\circ$ ).<sup>18</sup> Similar reaction with bis(cyclooctadiene) platinum (0) also gives  $Pt(InR)_4$  complex (Scheme 3).<sup>19</sup> In addition,  $CpIn$  is also isolobal to  $CO$  and displays transition metal carbonyl fragments. The structure of  $Pd_3(InCp)_4(\mu_2-InCp)_4$  exhibits three edge-bridging  $PdIn_4$  tetrahedrons. The three central palladium atoms are arranged with only a small deviation from linearity of  $10^\circ$ . The distortion of the  $PdIn_4$  tetrahedrons is expressed in the  $In-Pd-In$  angles, which are smaller than  $109^\circ$  for the terminal  $In$  atoms and larger than  $109^\circ$  for the bridging  $In$  atoms.<sup>20</sup>

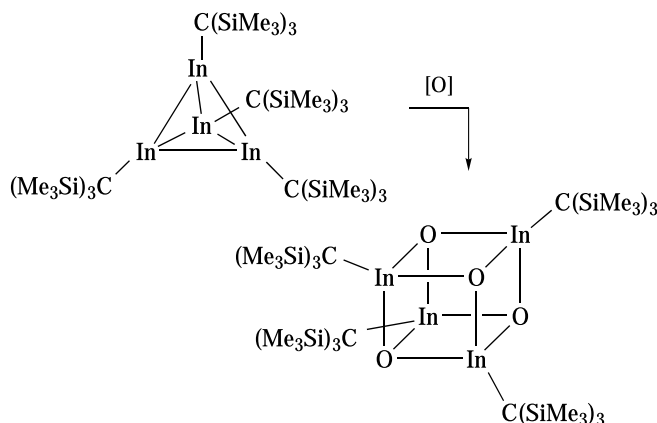
The  $In_4$  cluster can be completely or partial oxidized with halogen or chalcogen to form  $In_4X_4$  heterocubanes or mixed-valence compounds. The complex  $In_4[C(SiMe_3)_3]_4$  abstracts  $O$  from *o*-nitrosotoluene forming the extremely



**Scheme 2** Reaction of  $In_4R_4$  ( $R = C(SiMe_3)_3$ ) with  $Fe(CO)_3(cot)$  and  $Mn_2(CO)_{10}$ . cot = cyclooctatetraene, Refs. 14,15



**Scheme 3** Reaction of  $\text{In}_4\text{R}_4$  ( $\text{R} = \text{C}(\text{SiMe}_3)_3$ ) with  $\text{Pt}(\text{cod})_2$  and  $\text{Ni}(\text{cod})_2$ . cod = cyclooctadiene, Refs. 18,19



**Scheme 4** The oxidation reaction of  $[\text{InC}(\text{SiMe}_3)_3]_4$  to produce  $\text{In}_4\text{O}_4[\text{C}(\text{SiMe}_3)_3]_4$ , Ref. 21

hygroscopic  $\text{In}_4\text{O}_4[\text{C}(\text{SiMe}_3)_3]_4$  (Scheme 4). The structure exhibits a distorted  $\text{In}_4\text{O}_4$  moiety with normal In–O bond lengths, but short intracage In to In and O to O distances.<sup>21</sup> The reaction with chalcogen gives the compounds  $\text{In}_4\text{X}_4\text{R}_4$ , which adopt a slightly distorted  $\text{In}_4\text{X}_4$  heterocubane structure with an alternating arrangement of In and X atoms ( $\text{X} = \text{chalcogen atom}$ ).<sup>22</sup> Partial oxidation of  $\text{In}_4\text{R}_4$  with the sulfur atom donor yields the mixed-valent compound  $[\text{In}_4\text{S}\{\text{C}(\text{SiMe}_3)_3\}_4]$ , in which only one face of the  $\text{In}_4$  tetrahedron of  $\text{In}_4\text{R}_4$  is bridged by a sulfur atom. Partial oxidation of  $\text{In}_4\text{R}_4$  with halogen donors affords novel alkylindium halides  $\text{In}_2\text{X}_2\text{R}_2$  ( $\text{R} = \text{C}(\text{SiMe}_3)_3$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and  $\text{In}_3\text{I}_2\text{R}_3$ , in which the indium atoms still possess low oxidation states. The tetrahedral arrangement of four indium atoms in a cluster is retained in the compound  $\text{In}_4\text{Br}_2\text{R}_4$ , in which one bromine atom occupied a  $\mu_3$ -bridging position above one triangular face of the  $\text{In}_4$  tetrahedron, and one

edge of that triangle is bridged by the second bromine atom.<sup>4</sup>

## 2.4 In Cluster Compounds

Several interesting new forms of indium cluster compounds have been described during the last decade. The compound  $(\text{Bu}'_3\text{Si})_6\text{In}_8$ , prepared by the reaction of  $\text{CpIn}$  with  $\text{Bu}'_3\text{SiNa}$ , has a novel eight-indium cluster framework in which a distorted cube of indium atoms is surrounded by the silyl groups;<sup>23</sup> the compound  $[(\text{Bu}'_3\text{Si})_8\text{In}]_{12}$  possesses an  $\text{In}_{12}$  deltahedral framework with 20 triangular faces and 12 In atoms. The compound is not spherical, but resembles a stretched ellipsoid.<sup>24</sup> The reaction of  $\text{LiC}_6\text{H}_3\text{-2,6-mes}_2$  ( $\text{mes} = \text{C}_6\text{H}_2\text{-2,4,6-Me}_3$ ) with  $\text{InCl}$  produces the complex  $\text{In}_8(\text{C}_6\text{H}_3\text{-2,6-mes}_2)_4$ , possessing a distorted cubane arrangement of eight indium atoms, in which only four atoms of the metal carry a terphenyl substituent.<sup>25</sup>

## 2.5 Indium–Boron/Phosphorous Compounds

The most interesting aspect of the pyrazolylborates (pz) for indium is their ability to stabilize the univalent indium oxidation state. Thus, bulky poly(pyrazolyl)borate ligands such as  $[\text{HB}(3\text{-Bu}'\text{pz})_3]^-$ ,  $[\text{HB}(3\text{-Phpz})_3]^-$ ,  $[\text{HB}(3,5\text{-Bu}'\text{pz})_3]^-$ , and  $[\text{HB}(3,5\text{-(CF}_3)_2\text{pz})_3]^-$  are used to stabilize the indium (I) species.<sup>26,27</sup> The complex  $(3,5\text{-Bu}'\text{pz})\text{In}$  is synthesized by the treatment of  $\text{Na}(3,5\text{-Bu}'\text{pz})$  with  $\text{InCl}$ , in which the 3,5-Bu'pz ligand adopts a highly twisted configuration owing to steric interactions of the *tert*-butyl substituents in the 5 positions of the pyrazolyl groups. The compound  $(3,5\text{-Bu}'\text{pz})\text{In}$  can undergo oxidative-addition reactions with  $\text{I}_2$  and  $\text{S}_8$  to give the complex  $(3,5\text{-Bu}'\text{pz})\text{InI}_2$  and  $(3,5\text{-Bu}'\text{pz})\text{In}(\mu^2\text{-S}_4)$ , respectively. In addition,  $[\text{In}(\eta^5\text{-P}_2\text{C}_3\text{Bu}'_3)]$  and  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}'_2)]$  are also prepared, which have a half-sandwich structure, similar to the  $\eta^5$ -coordination mode  $[\text{In}(\eta\text{-C}_5\text{H}_5)]$  or  $\text{InCp}$ .<sup>28</sup>

## 2.6 Aqueous Solution Chemistry

Solutions of indium (I) can be prepared by treatment of indium amalgam with silver triflate in dry acetonitrile in the absence of oxygen, and then diluted with water to give the low-concentration aqueous solution, which plays a sizable role in the study of the details of intermolecular electron transfer processes in solution.<sup>29</sup> Aqueous  $\text{In(I)}$  solution has been used to examine the behavior of this hypovalent center in inorganic redox transformations. Reactions with complexes of the type  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{Lig})]$  and  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{Lig})]$  ( $\text{Lig} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  or  $\text{HC}_2\text{O}_4^-$ ) show two consecutive one-electron reactions initiated by the formation of the metastable state  $\text{In}^{\text{II}}$ , which is then rapidly oxidized to  $\text{In}^{\text{III}}$ , and the first of which is predominating an inner-sphere mechanism.<sup>30,31</sup>

### 3 INDIUM (II) CHEMISTRY

#### 3.1 Introduction

Most of the divalent indium compounds appear in the dimeric form, which involves an indium–indium bonded species or  $R_4In_2$ . The structure of the indium (II) halides has been identified, in which the divalent  $In^{2+}$  ions is present in the dimeric species  $[In_2X_6]^{2-}$ .<sup>32</sup> A special highlight is the compound  $R_4In_2$  ( $R = CH(SiMe_3)_2$ ,  $SiBu'_3$ ,  $SiBu'_2Ph$ ), which has a remarkable reactivity and is used in the preparation of various indium complexes including indium cluster compounds.<sup>33</sup>

#### 3.2 Halogen Derivatives

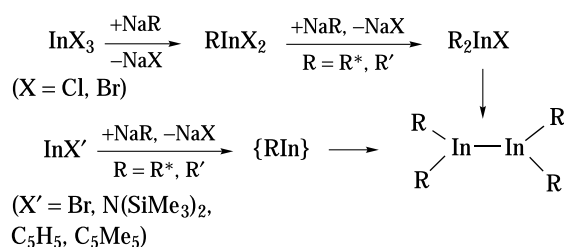
The halides of indium (II) can be prepared by heating together the appropriate mixture of elements, or by reduction of the trihalides with indium metal. In the compounds  $In_2Br_3$  and  $In_5Br_7$ , the divalent  $In^{2+}$  ions are bonded within the dimeric species  $[In_2Br_6]^{2-}$ , in which each  $In^{2+}$  ion is threefold coordinated by  $Br^-$  ions, with a mean distance of 257 pm. The other  $In^{2+}$  ion augments the coordinating geometry via an  $In^{2+}$ – $In^{2+}$  single bond (270 pm) to form a distorted tetrahedron.<sup>7,8</sup>  $KInBr_3$  is the first ternary indium bromide containing divalent indium. The divalent  $In^{2+}$  ions are found in an  $[In_2Br_6]^{2-}$  unit in an eclipsed ethane structure, while potassium ions are located in two different polyhedra.<sup>32</sup> The ethane analogous  $In_2X_6$  ( $X = S, Se$ ) units are also found in the structures of  $MIn_5S_7$  ( $M = Na, K, Tl$ ),  $MIn_5S_6$  ( $M = K, Tl$ ), and  $MIn_7X_9$  ( $M = Rb, Cs; X = S, Se$ ).<sup>34</sup>

#### 3.3 Synthesis of $R_4In_2$ Derivatives

Diindanes  $R_2InInR_2$  ( $R = SiBu'_3$ ) can be prepared by the reactions of  $NaR$  ( $R = SiBu'_3$ ) with  $InX_3$  ( $X = Cl, Br$ ) through  $RInX_2$  and  $R_2InX$  intermediate process.<sup>5</sup> The reactions of  $NaR$  ( $R = SiBu'_3$ ,  $SiBu'_2Ph$ ) with  $InX$  ( $X = N(SiMe_3)_2$ ,  $C_5H_5$ ,  $C_5Me_5$ ) also produces  $R_2InInR_2$ .<sup>22</sup>  $R_2InInR_2$  ( $R = CH(SiMe_3)_2$ ) is also prepared by the reaction of  $[LiN(SiMe_3)_2]$  with  $C_5H_5In$ , whereas the reaction of  $InCl_3$  and  $LiSi(SiMe_3)_3$  gives  $[(Me_3Si)_3Si]_4In_2$  (Scheme 5).<sup>35</sup> The reaction of  $In_2Br \cdot 2TMEDA$  ( $TMEDA =$  tetramethylethylenediamine) with  $[LiCH(SiMe_3)_2]$  can lead to  $[(Me_3Si)_2CH]_4In_2$ . The reaction of indium metal with  $Pr'''_3PI_2$  also yields the 'subvalent' indium (II) complex  $In_2I_4(PPr''')_2$ , which is the first example of an indium tertiary phosphine complex containing an indium–indium bond.<sup>36</sup>

#### 3.4 Reaction of $R_4In_2$ Derivatives

Reaction of  $R_2InInR_2$  ( $R = CH(SiMe_3)_2$ ) with the chalcogen compounds can give the corresponding homoleptic compounds  $R_2InEInR_2$  ( $E = S, Se$  or  $Te$ ) by insertion of



**Scheme 5** Syntheses of ditriindanes  $R_4In_2$  with  $R = R^* = SiBu'_3$  and  $R = R' = SiBu'_2Ph$ , Refs. 5,22,35

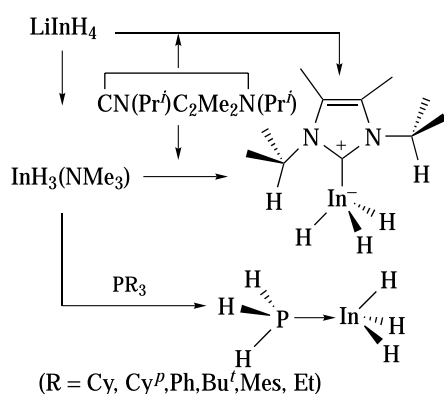
chalcogen atoms into the  $In-In$  bond, while reaction with lithium phenylethyne produces, by the addition of one ethynido ligand to one of the central  $In$  atoms, the anionic adducts with intact  $In-In$  single bonds.<sup>33</sup>  $R_2InInR_2$  reacts with  $LiCH_2SMe$  to afford  $[R_2In(CH_2SMe)_2][Li(TMEDA)]$  probably formed by a metal exchange reaction.<sup>37</sup> Reaction with trimethylamine N-oxide by the insertion of oxygen atoms in their  $In-In$  single bonds produces  $R_2In-O-InR_2$ , which is monomeric in the solid state owing to the high steric shielding by the voluminous bis(trimethylsilyl)methyl groups,<sup>38</sup> while with protic reagents results in the cleavage of the  $In-In$  bond and precipitation of element indium.<sup>39</sup>

$R_4In_2$  ( $R = SiBu'_3$ ) can transform, with excess hydrogen bromide, into  $RInBr_2$  and  $RH$  (molar ratio 1:1). Here  $R_4In_2$  behaves as a Lewis base against  $HBr$ .  $R_4In_2$  can be oxidized (e.g. with halogens or chalcogens) or reduced with metal. Bromination of  $R_4In_2$  into  $RInBr_2$  may proceed either by  $In-In$  or by  $In-Si$  bond cleavage via  $R_2InBr$  or  $R_2In_2Br_2$ . Fluorination of  $R_4In_2$  with  $AgF_2$  also produces  $RInF_2$ . The reaction of  $R_4In_2$  with selenium can produce the heterocubane  $R_4In_4Se_4$ .<sup>5</sup>

### 4 INDIUM (III) CHEMISTRY

#### 4.1 Introduction

The main development of the indium chemistry during the last decade has centered on the indium (III) compounds, particularly  $InH_3$ ,  $InX_3$ , and  $R_3In$ . Indium hydride ( $InH_3$  or  $In_2H_6$ ) is unstable in the gas phase or solid state, but the stable indium trihydride complexes can be obtained in the form of adducts.<sup>40</sup>  $InX_3$  and  $R_3In$  compounds are electron deficient and can accept pairs of electrons and form their neutral adducts or coordination compounds with the electron-pair donor ligands. This is potentially relevant to the fabrication of the III-V/VI semiconductor materials. The behavior of  $In^{3+}$  in solution has been investigated and a large number of stable and soluble  $In^{3+}$  complexes are obtained, which can be used as dyes, diagnostic radiopharmaceuticals, and other applications in materials sciences.



**Scheme 6** Syntheses of Indium hydride compounds, Refs. 43,44

## 4.2 Hydrides and Related Compounds

Indium hydrides are thermodynamically unstable, and  $\text{Me}_2\text{InB}_3\text{H}_8$  is the first reported example of a volatile indium hydride.<sup>41</sup> Reaction of  $\text{InCl}_3$  with  $\text{HSnBu}_3$  generates the compound  $\text{HInCl}_2$ , which is stable up to ambient temperature.<sup>42</sup> The thermally stable indium trihydride complexes are obtained with phosphines or carbenes.  $\text{LiInH}_4$  with  $\text{NMe}_3 \cdot \text{HCl}$  gives the adduct  $\text{InH}_3(\text{NMe}_3)$ , and further reacts with the stable carbene  $[\text{:CN}(\text{Pr}^i)\text{C}_2\text{Me}_2\text{N}(\text{Pr}^i)]$  to afford the carbene-metal trihydride complex  $[\text{InH}_3\{\text{:CN}(\text{Pr}^i)\text{C}_2\text{Me}_2\text{N}(\text{Pr}^i)\}]$  (Scheme 6).<sup>43</sup> The reaction of  $\text{InH}_3(\text{NMe}_3)$  with  $\text{PR}_3$  (R = cyclohexyl (Cy), cyclopentyl (Cp) or phenyl) affords the indium trihydride complexes  $[\text{InH}_3(\text{PR}_3)]$  and  $[\text{InH}_3(\text{PCy}_3)_2]$ . The first phosphido-indium hydride complex  $[\{\text{InH}_2(\text{PCy}_2)\}_3]$  is obtained by the treatment of  $[\text{InH}_3(\text{NMe}_3)]$  with  $\text{LiPCy}_2$ . These complexes possess remarkable stability that may be attributed to the phosphine ligand's steric bulk and nucleophilicity. The complex  $[\text{InH}_3(\text{PCy}_3)]$  is used to prepare a range of monomeric indium chalcogenolato complexes  $[\text{In}(\text{Eph})_3(\text{PCy}_3)]$  (E = S, Se or Te) (Scheme 6).<sup>44,45</sup>

## 4.3 Indium (III) Halides and their Derivatives

Indium trihalides can be easily prepared from the reaction of indium metal with halide acids, which can form various complexes with water molecules and other ligands. *Trans*- $[\text{InCl}_2(\text{H}_2\text{O})_4]^+$  and *trans*- $[\text{InCl}_4(\text{H}_2\text{O})_4]^-$  species are isolated for the first time as parts of supramolecular adducts with cucurbituril are isolated from aqueous solutions and structurally characterized.<sup>46</sup> The behavior of  $\text{Br}_2\text{InCH}_2\text{Br}$  as Lewis acid against  $\text{NEt}_4\text{Br}$ , 1,4-dioxane and  $\text{THF}(\text{OC}_4\text{H}_8)$  is examined, which shows that by complete intramolecular tautomeric transfer of the bromide it is possible to obtain  $[\text{Br}_3\text{InCH}_2]^-$  as an anion.<sup>47</sup> Reduction of  $\text{R}_3\text{PI}_2$  (R = Ph,  $\text{Pr}^i$ ) with indium powder produces the four- and five-coordinate complex  $\text{InI}_3(\text{PPh}_3)_2 \cdot \text{InI}_3(\text{PPh}_4)$  and the monomeric tetrahedral indium (III) complex  $\text{InI}_3(\text{PPr}^i)_3$ , which illustrates the subtle

effect of the organic substituents on the phosphorus atom for the reaction of  $\text{R}_3\text{PI}_2$  with indium metal.<sup>37</sup>

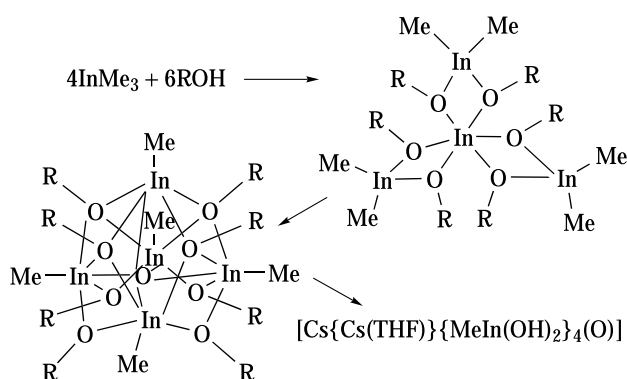
## 4.4 Adducts of $\text{InX}_3$

The adducts of the indium trihalides are readily prepared by simple nonaqueous phase reactions. A series of adducts of  $\text{InBr}_3$  has been obtained from the treatment of  $\text{InBr}_3$  with THF (tetrahydrofuran), DMF (dimethyl formamide), and other ligands, which have a pyramidal coordination sphere.<sup>48</sup> In a similar fashion, the coordination geometry of the adduct  $\text{InCl}_3(\text{THF})_2$  also is a trigonal bipyramid with three Cl atoms in equatorial positions and two axial THF ligands. Reaction of  $\text{InBr}_3$  with  $\text{HN}(\text{SiMe}_3)_2$  gives stable adducts  $\text{Br}_3\text{In} \cdot \text{H}_2\text{NSiMe}_3$  and  $\text{Br}_3\text{In} \cdot \text{HN}(\text{SiMe}_3)_2$ ;<sup>49</sup> with  $\text{LiR} \cdot (\text{THF})_n$  (R =  $\text{C}(\text{SiMe}_3)_3$ ,  $\text{THF} = \text{OC}_4\text{H}_8$ ), it produces  $[\text{Li}(\text{THF})_4][\text{RInBr}_3]$  in good yield.<sup>50</sup>  $\text{InCl}_3$  with amines can give the corresponding adducts, in which In atoms have a trigonal-bipyramidal coordination sphere with the amines in apical position.<sup>51</sup> The complex  $[(\text{Me})_2\text{ATI}]_2\text{InCl}$  (ATI = aminotroponimate) was prepared and characterized, showing fluxional behavior in solution at room temperature and adopting trigonal-bipyramidal geometry around the metal center with the halide occupying an equatorial site.<sup>52</sup> The complex  $(\text{PPh}_3)_4\text{Pt}_2(\mu^3\text{-S})\text{InCl}_3$  represents the first report of a square-based pyramidal structure of a five-coordinated adduct of  $\text{InX}_3$ .<sup>53</sup>

The reactions of indium trihalides with DP or TP ligands (DP = 1, 2-bis-(diphenylphosphanyl) benzene, TP = bis[(2-diphenylphosphanyl)phenyl] phenylphosphane) lead to a variety of molecular and ionic complexes, such as  $[(\text{DP})_2\text{InCl}_2]^+ [\text{InCl}_4]^-$ ,  $(\text{DP})\text{InX}_3$ ,  $[(\text{DP})\text{InX}_2]^+ [\text{InX}_4]^-$  (X = Br, I), and  $[(\text{TP})\text{InX}_2]^+ [\text{InX}_4]^-$  (X = I). The environment of the metal center is octahedral, square pyramidal, and tetrahedral in the cations respectively.<sup>54</sup>

## 4.5 Indium Alkoxides

The reaction of  $\text{Me}_3\text{In}$  with  $\text{ROH}$  (R =  $\text{PhCH}_2$ , Hex and  $\text{Bu}^i$ ) leads to tetranuclear complex  $[\text{In}\{(\text{RO})_2\text{InMe}_2\}_3]$ , described also as  $[\{\text{Me}_2\text{InOR}\}_2\{\text{MeIn}(\text{OR})_2\}_2]$ , then at higher temperature forms an O-centered corner-cut rhombic dodecahedron,  $[(\text{MeIn})_5(\text{OR})_8\text{O}]$ , in which the four  $\mu_2$ -bridging oxygen atoms form a basal plane and the In-O skeleton can be degraded with elemental cesium to a hexa- and heteronuclear complex  $[\text{Cs}\{\text{Cs}(\text{THF})\}\{\text{MeIn}(\text{OR})_2\}_4\text{O}]$  (Scheme 7).<sup>55,56</sup> The compound  $[\text{In}(\text{OBu}^i)_3]_2$  is the first example of a homoleptic and homometallic indium alkoxide, which is obtained by alcoholysis of  $\text{In}(\text{N}(\text{SiMe}_3)_2)_3$  with  $\text{Bu}^i\text{OH}$ .<sup>57</sup> The *N,O*-5 chelates  $[\text{Me}_2\text{In}(\mu\text{-ORNMe}_2)]_2$  (R =  $\text{CH}_2\text{CHR}'$ ; R' = Me,  $\text{Pr}^i$ ,  $\text{Bu}^i$ ) are synthesized from trimethylindium and the dimethylamino alcohols by elimination of methane. The coordinative N  $\rightarrow$  In bonds of the five-coordinate indium complexes show dynamic dissociation/association processes.<sup>58</sup>



**Scheme 7** Syntheses of Indium alkoxides, Refs. 55,56

The reaction of  $\text{InX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with sodium alkyloxistannate gives  $\text{THF} \cdot \text{X}_2\text{In}(\text{OR})_3\text{Sn}$  ( $\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Bu}'$ ), in which the indium atoms are in the centers of distorted octahedral from 4 oxygen and 2 halogen atoms whereas the tin atoms are coordinated by three oxygen atoms in a trigonal pyramidal fashion.<sup>59</sup> Reaction of  $\text{InMe}_3$  or  $\text{InCl}_3$  with the  $\text{Li}^+$  salt of S-BINOLate (S-BINOL = (S)-(-)-2,2'-dihydroxy-1,1'-binaphthyl) gives alkoxides with a tetranuclear  $\text{InO}_6\text{Li}_3$  skeleton, which forms a distorted octahedral coordination sphere around In atoms, built up by three BINOLate ligands, the three  $\text{Li}^+$  counterions acting as bridging units by metal-oxygen coordination.<sup>60</sup>

#### 4.6 $\text{InMe}_3$ Adducts and Derivatives

The  $\text{Me}_3\text{In}$  adducts also have the similar bipyramidal structure to that of  $\text{InX}_3$  adducts. The adduct  $\text{Me}_3\text{In} \cdot 2(\text{mbda})$  ( $\text{mbda} = N,N,N',N'$ -tetramethyl-4,4'-methylene-bis-aniline), with a trigonalbipyramidal In, is said to have the longest known In-N bonds.<sup>61</sup>  $\text{Me}_3\text{In}$  reacting with isocyanides  $\text{CNR}$  ( $\text{R} = p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$ ) gives the corresponding adducts  $\text{Me}_3\text{InCNR}$ , then reacts with pyrrolidine by insertion of the isocyanide into the In-N-Pyr bond to form  $[\text{Me}_2\text{InC}(=\text{NR})(\text{Pyr})]$  ( $\text{Pyr} = \text{conjugate base of pyrrolidine}$ ).<sup>62</sup>

The adducts  $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{R}_3$  ( $\text{R} = \text{Me}, \text{Pr}^i$  or  $\text{Bu}^t$ ) are prepared by simple mixing of the Lewis acid and base in diethylether solution and the adducting bonding of three lone pairs is slightly stronger than a standard one lone-pair adduct bond.<sup>63</sup> Reaction of  $\text{Me}_3\text{In}$  with  $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeE}(\text{NMe}_2)_2]$  ( $\text{E} = \text{P}$  and  $\text{As}$ ) affords the adducts  $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeE}\{\text{InMe}_3\}(\text{NMe}_2)_2]$ , which feature  $\eta^1$ -coordination of the phosphalkene or the arsaalkene ligand towards the Lewis acid via the pnictogen atom.<sup>64</sup>

#### 4.7 Indium-Nitrogen Compounds

Reactions of  $\text{InX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with various amines give the corresponding neutral or ionic complexes in

which indium atoms locate in trigonal-bipyramidal, trigonal planar, or distorted tetrahedral environments. In the structure of  $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ , a chloride and one amide group of  $[\text{MeN}(\text{SiMe}_2\text{NMe}_2)_2]^{2-}$  ligand are bonded to each In atom in terminal positions and the other amide group of the chelating ligand is shared between two In atoms.<sup>65</sup> Reaction of  $[\text{RNC}(\text{R}')\text{NR}]\text{Li}$  with  $\text{InCl}_3$  affords a novel family of monomeric five-coordinate compounds  $\text{In}[\text{RNC}(\text{R}')\text{NR}]_2\text{Cl}$  ( $\text{R} = \text{cyclohexyl}, \text{SiMe}_3; \text{R}' = \text{Me}, \text{Bu}^t$ ), possessing a distorted trigonal-bipyramidal coordination.<sup>66</sup>

The first azaindatrane  $[\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_3)\text{In}]_2$  is prepared by the reaction of  $[\text{In}(\text{NEt}_2)_3]_2$  with  $\text{N}(\text{CH}_2\text{CH}_2\text{NMeH})_3$ , in which both indium atoms are pentacoordinate, with widely differing In-N distances.<sup>67</sup> Within  $[\text{py}_2\text{Na}][\text{py}_2\text{In}(\text{N}_3)]_4$ , the In and Na atoms are each hexacoordinated by four azido group and two additional solvent molecules.<sup>68</sup>

The reaction of  $\text{RSi}(\text{NH}_2)_3$  ( $\text{R} = 2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{NSiMe}_2\text{Pr}^i$ ) with  $\text{InR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) leads to Si-NH-In cage molecules, which may be regarded as a model system for In metal-containing iminosilicates. Further functionalization without cleavage of the cage molecule is achieved by reaction with elemental bromine and iodine.<sup>69</sup>

Indium diphthalocyanine  $\text{In}(\text{Pc})_2$  contains sandwich-type molecules in which the indium atom is eight-coordinate by the isoindole nitrogens of two phthalocyanine rings. The distance between the phthalocyanine planes in this sandwich macromolecule is equal to 274.1 pm, and the two phthalocyaninato moieties are rotated about  $41.2(4)^\circ$  with respect to each other.<sup>70</sup>

The chloro(phthalocyaninato or naphthalocyaninato) indium  $\text{R}^1_4\text{R}^2_4\text{PcInCl}$  or  $\text{R}^1_4\text{R}^2_4\text{NcInCl}$  react with  $\text{R}^3\text{MgBr}$  to produce the axially substituted aryl (phthalocyaninato or naphthalocyaninato) indium compound,  $\text{R}^1_4\text{R}^2_4\text{PcInR}^3$  or  $\text{R}^1_4\text{R}^2_4\text{NcInR}^3$ , which has high solubility owing to steric crowding arising from the new unsymmetrical peripheral substitution pattern and the bulky electron-withdrawing axial ligands.<sup>71,72</sup>

The structure of  $\text{In}_4\text{X}_4(\text{NBu}^t)_4$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) contains heterocubane  $\text{In}_4\text{N}_4$  cores with an alternating arrangement of In and N atoms. The In atoms are coordinated nearly tetrahedrally by three N atoms and a terminal halogen atom.  $\text{In}_3\text{Br}_4(\text{NBu}^t)(\text{HNBu}^t)_3$  contains a tricyclic  $\text{In}_3\text{N}_4$  core, which can be formally derived from an  $\text{In}_4\text{N}_4$  heterocubane by removing one In atom.<sup>73</sup>

$\text{MeCN}$  can be trimerized in the presence of  $\text{InMe}_3$  and a trace of  $\text{CsF}$  to form the  $\text{InN}_2\text{C}_3$  heterocycle  $[\text{Me}_2\text{In}\{\text{HNC}(\text{Me})_2\text{C}(\text{CN})\}]_n$ , which forms an infinite chain-like coordination polymer,  $[\text{Me}_2\text{In}\{\text{HNC}(\text{Me})_2\text{C}(\text{CN})\}]_n$ , along [001] by the cooperative interactions of  $\text{In} \cdots \text{N}$  contacts and  $\text{N-H} \cdots \text{N}$  bridges.<sup>74</sup>

#### 4.8 Indium-Phosphorous Compounds

The organoindium phosphides are dimeric, trimeric, and tetrameric in benzene solution. The compounds

$[\text{Pr}^i_2\text{InPPh}_2]$  and  $[(\text{PhCH}_2)_2\text{InPPh}_2]$  exist as a monomer-dimer equilibrium mixture in solution and a trimer in the solid state. The dimer  $[\{\text{InPR}_2(\text{CH}_2\text{CMe}_3)_2\}_2]$  ( $\text{R} = \text{Et}, \text{Pr}^i$ ) contains a planar  $\text{In}_2\text{P}_2$  core, and the trimer  $[\{\text{InP}(\text{H})(\text{C}_6\text{H}_{11})(\text{CH}_2\text{CMe}_3)_2\}_3]$  has an  $\text{In}_3\text{P}_3$  six-membered ring in a boat conformation. The similar  $\text{In}_3\text{P}_3$  six-membered rings are also observed in the trimers  $[\text{Pr}^i_2\text{InPPh}_2]_3$ ,  $[\text{Me}_2\text{InP}(\text{SnMe}_3)_2]_3$  and  $[(\text{PhCH}_2)_2\text{InPPh}_2]_3 \cdot \text{OEt}_2$ . The compound  $[(\text{mes})\text{InP}(\text{mes})]_4$  is tetrameric in solution, but crystallized as  $[(\text{mes})\text{InP}(\text{mes})]_4 \cdot 4.5\text{THF}$ , a heterocubane with an  $\text{In}_4\text{P}_4$  core shield by the bulky organic groups.<sup>75</sup> The analogous heterocubanes with an  $\text{In}_4\text{P}_4$  core is also observed in compound  $[\text{EtInPSiPr}^i_3]_4$ . The four-membered-ring compounds  $[\text{R}_2\text{InP}(\text{Bu}^t)_2]_2$  ( $\text{R} = \text{vinyl}, \text{allyl}, \text{or benzyl}$ ) could absorb light at relatively long wavelengths with cutoffs ranging from  $\sim 300 \text{ nm}$  to  $330 \text{ nm}$  depending on  $\text{R}$  groups.<sup>76</sup> The central structural motif of  $[\text{Pr}^i_2\text{Si}\{\text{P}(\text{H})\text{InEt}_2\}_2]_2$  is an adamantine-like cage composed of four indium, four phosphorous, and two silicon atoms, which is the first ternary cluster with combinations of these elements.<sup>77</sup> The one-dimensional compound  $[\text{Ph}_4][\text{In}(\text{P}_2\text{Se}_6)]$  contains infinite  $[\text{In}(\text{P}_2\text{Se}_6)]_n^-$  chains with a structure related to that of  $\text{K}_2\text{FeP}_2\text{Se}_6$ .<sup>78</sup>

#### 4.9 Indium Phosphate Compounds

A new series of layered indium phosphate complexes have potential applications in the areas of sorption, ion exchange, and sensors. The first organically templated indium phosphate is prepared as single crystals from a nonaqueous pyridine-butan-2-ol medium and has a unique two-dimensional (2D) structure consisting of  $[\text{Hpy}][\text{In}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]^-$  layers held together by hydrogen bonding to generate cavities containing the pyridium cations. The layers consist of corrugated sheets constructed from ribbons of edge-sharing four-membered rings of alternating  $\text{InO}_6$  and  $\text{PO}_4$  units linked via  $\text{PO}_2(\text{OH})_2$  groups.<sup>79</sup> The layered structure also exists in the complexes,  $\text{In}(\text{O}_3\text{PR})(\text{O}_2\text{P})(\text{OH})\text{R} \cdot \text{H}_2\text{O}$  ( $\text{R} = \text{C}_6\text{H}_5$  or  $\text{CH}_2\text{C}_6\text{H}_5$ ) and  $\text{In}(\text{O}_2\text{P}(\text{H})\text{C}_6\text{H}_5)_3$ , in which the ligand is present as both a mono- and dianion.<sup>80</sup> A pillared layer structure of the indium phosphate,  $[\text{In}_8(\text{HPO}_4)_{14}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_5(\text{H}_3\text{O})(\text{C}_3\text{N}_2\text{H}_5)_3]$ , consists of layers assembled from  $\text{InO}_6$  and  $\text{InO}_5(\text{H}_2\text{O})$  octahedra and  $\text{PO}_3(\text{OH})$  tetrahedra which are pillared through  $\text{InO}_6$  octahedra to produce a 3D framework. The framework contains a 2D array of channels in which sit imidazolium cations, hydroxonium ions, and water molecules.<sup>81</sup> The similar pillared layer structure is observed in complexes  $[\text{In}_4(4,4'\text{-bipy})_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_4] \cdot 4\text{H}_2\text{O}$  and  $[\text{In}_4(4,4'\text{-bipy})_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_4]$ . The structure of  $\text{PbIn}(\text{OH})\text{PO}_4$  consists of spirals of *cis* corner-sharing  $\text{InO}_6$  octahedra with hydroxyl  $\text{O}$  as the bridging atom, and the  $\text{In}-\text{O}-\text{In}$  bonds nearly equidistant.<sup>82</sup> The framework of  $\text{Ca}_2(\text{In}_{1-x}\text{Fe}_x)(\text{PO}_4)(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  is based on linear chains formed by  $(\text{MO}_6)$  octahedral and  $(\text{PO}_4)(\text{HPO}_4)$  tetrahedral sharing corners. The  $(\text{HPO}_4)$  groups and water molecules link

the chains through hydrogen bonding to form layers stacked perpendicular to the  $c$  axis. The calcium cations are located between the layers and are coordinated by nine oxide anions.<sup>83</sup>

#### 4.10 Indium Chalcogenide Compounds

The indium chalcogenide compounds may be prepared by the insertion of chalcogenide into either an  $\text{In}-\text{C}$  or  $\text{In}-\text{S}$  bond. The reaction of  $\text{InR}_3$  ( $\text{R} = \text{Bu}^t, \text{Bu}^n$  or  $\text{CMe}_2\text{Et}$ ) with selenium or tellurium yields the corresponding compounds  $[\{\text{RIn}(\mu_3\text{-E})\}_4]$  ( $\text{E} = \text{Se}$  or  $\text{Te}$ ).<sup>84</sup> Reaction of  $[\text{In}(\text{mes})_3]$  ( $\text{mes} = 2, 4, 6\text{-trimethylphenyl}$ ) with various  $\text{A}(\text{ER})$  ( $\text{A} = \text{H}$  or  $\text{Li}$ ;  $\text{E} = \text{S}$  or  $\text{Se}$ ;  $\text{R} = \text{Bu}^t, \text{tert-amyl}, 2\text{-}t\text{-BuC}_6\text{H}_4, \text{SiPh}_3$ ) gives  $[\{\text{In}(\text{mes})_2(\mu\text{-ER})\}_2]$ . A trimeric indium thiolate,  $[\{\text{InMe}_2(\mu\text{-SSiPh}_3)\}_3]$ , is isolated from the reaction of  $\text{InMe}_3$  with  $\text{HSSiPh}_3$ .<sup>85</sup> Similar selenium compounds are also described as  $[\text{InMe}(\mu\text{-SePh})(\text{SePh})]_\infty$ , a spiral chain composed of alternative four-coordinate indium atoms and three-coordinate selenium atoms.<sup>86</sup>

Homoleptic chalcogenolates  $\text{In}[\text{ESi}(\text{SiMe}_3)_3]_3$  ( $\text{E} = \text{Se}, \text{Te}$ ) are also prepared by chalcogenolysis of  $\text{InCp}_3$ . Addition of  $\text{L}$  ligand ( $\text{L} = \text{THF}, \text{TMEDA}$  ( $N,N,N',N'$ -tetramethyl ethylene diamine), or  $\text{DMPE}$  (1,2-bis(dimethylphosphino)ethane)) to  $\text{In}[\text{SeSi}(\text{SiMe}_3)_3]_3$  gives 1:1 adducts  $(\text{L})\text{In}[\text{SeSi}(\text{SiMe}_3)_3]_3$ .<sup>87</sup> The  $\text{SePy}$  ( $\text{SePy} = 2\text{-Se-NC}_5\text{H}_4$ ) and  $\text{SePy}^*$  ( $\text{SePy}^* = 3\text{-Me}_3\text{Si-Se-NC}_5\text{H}_4$ ) ligands form air-stable homoleptic coordination compounds of indium (III)  $[\text{In}(\text{SePy})_3]$  and  $[\text{In}(\text{SePy}^*)_3]$ , which are distorted fac-octahedra molecules with chelating  $\text{SePy}$  ligands and are useful low-temperature precursors to  $\text{In}_2\text{Se}_3$ .<sup>88</sup>

The tellurides  $\text{K}_6\text{In}_2\text{Te}_6 \cdot 4\text{en}$  ( $\text{en} = \text{C}_2\text{H}_8\text{N}_2$ ) and  $(\text{Ph}_4\text{P})_2\text{In}_2\text{Te}_6$  are known. The former possesses a highly charged dimeric  $[\text{In}_2\text{Te}_6]^{6-}$  anion, which is composed of two edge-sharing  $\text{InTe}_4$  tetrahedra. The  $\text{InTe}_4$  tetrahedra are linked together by sharing two  $\text{Te}$  corners and by joining the two other  $\text{Te}$  corners to form two  $\text{Te}_2^{2-}$  units with neighboring tetrahedra.<sup>89</sup> The complex  $[\text{InCl}(\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{S})\text{Ph}_2\text{-Se,S})]$  exhibits a very distorted trigonal-bipyramidal geometry at indium, where both the selenium and chlorine atoms are in equatorial positions, while the sulfur atoms are in axial positions.<sup>90</sup>

The reaction of  $\text{InCl}_3$  with  $\text{PhC}\{\text{O}\}\text{S}^- \text{A}^+$  ( $\text{A} = \text{Li}, \text{Na}, \text{and K}$ ) in the molar ratio 1:4 gives the corresponding ionic complexes  $[\text{A}(\text{MeCN})_x\{\text{In}(\text{SC}\{\text{O}\}\text{Ph})_4\}]$ , ( $\text{A} = \text{Li}, \text{X} = 0$ ;  $\text{A} = \text{Na}, \text{X} = 1$ ;  $\text{A} = \text{K}, \text{X} = 2$ ), which have a one-dimensional polymeric structure. The structural variations may be attributed to the change in the alkali metal ion from  $\text{Li}$  to  $\text{Na}$  to  $\text{K}$ .<sup>91</sup>

Thioindates of alkali metal compounds can be prepared by starting from stoichiometric mixtures of the elements, and several compounds  $\text{MIn}_3\text{S}_5$  ( $\text{M} = \text{Rb}, \text{Cs}$ ),  $\text{KIn}_5\text{S}_6$ ,  $\text{MIn}_5\text{S}_7$  ( $\text{M}: \text{Na}, \text{K}$ ), and  $\text{MIn}_7\text{X}_9$  ( $\text{M} = \text{Rb}, \text{Cs}; \text{X} = \text{S}, \text{Se}$ ) are known.  $\text{MIn}_3\text{S}_5$  ( $\text{M} = \text{Rb}, \text{Cs}$ ) represents a new type of ternary chalcogenide. On the quasi binary section  $\text{M}_2\text{S}-\text{In}_2\text{S}_5$  with the two binary phases in a molar ratio of 1:3, in which the indium

atoms are coordinated by sulfur atoms with tetrahedral as well as octahedral arrangement, the coordination numbers of the independent M atoms are nine or ten, and the sulfur and alkali metal atoms are in slightly distorted ccp arrangement.<sup>92,93</sup>

## 5 INDIUM PRECURSORS FOR CVD

### 5.1 Introduction

The recent interest in organoindium compounds stems from the finding that organoindium compounds are potential precursors for a wide variety of applications in material science. The deposition of In-containing semiconductor layers is important to diverse areas of research. Generally, the preparation of these thin films involves metal organic chemical vapor deposition (MOCVD). Despite its commercial use, several precursor issues are associated with the conventional MOCVD method, such as safe precursor handling and 'snowing' of the films. Moreover, under the condition of separate precursors, the composition control of such multinary films is affected by a precise adjustment of the mole fractions of the different precursors for the film constituting components in the gas phase. This makes it very difficult to obtain multinary films owing to the differences of precursors in volatility, thermal reactivity, and surface mobility.

An alternative route to make the films is the use of a precursor that contains the required atoms in a single molecule. The process control is shifted to the constitutional and structural optimization of the precursor. Therefore, single-source precursors have considerable advantages over conventional separate sources.

### 5.2 Intermetallic Phase Precursor Compounds

Indium-containing intermetallic phases are especially suitable as epitaxial metallizations, being inert against unwanted interface reactions and useful for Schottky barriers for semiconductor techniques. Thus, MOCVD processes are of interest for these materials and many organoindium precursors have been synthesized for this end. A special highlight is the compound  $[\text{Ni}(\text{InR})_4]$  ( $\text{R} = \text{C}(\text{SiMe}_3)_3$ ), a first example for the existence of compounds that are homoleptic with regard to an earth metal as ligator, which can be used as a single-source precursor for NiIn films.<sup>94</sup> Ni/In films can also be prepared from the compounds  $\{[\text{Cp}(\text{PEt}_3)\text{Ni}]_2\text{InCl}\}_2$ ,  $[\text{Cp}(\text{PEt}_3)\text{Ni}]_3\text{In}$ , and  $\text{Cp}(\text{PEt}_3)\text{NiInI}_2$ . In the Co/In system, only  $\text{CoIn}_2$  and  $\text{CoIn}_3$  are stable.  $(\text{CO})_4\text{CoInR}_2$  ( $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ ) can give CoIn films with Ni/In = 3.0 to 1.0 depending on the substrate temperature, which can be assigned to these phases;  $[\text{Cp}(\text{CO})\text{CoInR}_2]$  at 350 °C can provide single-phase films with the hexagonal  $\epsilon$ -NiIn phase. This is an example of an unexpected Cp transferring to the In atom, leading to stable

$\text{CpIn}$  that desorbs and gets into the exhaust gas.<sup>95</sup> In the case of  $\text{Cp}(\text{CO})_2\text{Fe-InR}_2$ , the deposition of Fe/In films is proceeded by the release of ferrocene.<sup>96</sup>

In addition, Cr/In, W/In, Mn/In, and Au/In films have also been obtained from the corresponding organometal compounds respectively, which indicate lively development in this field.

### 5.3 Indium Chalcogenide Precursor Compounds

Indium chalcogenides are potentially useful as single-source precursors for the synthesis of III-VI semiconductor materials. The complex  $[\text{InMe}_2(\text{S}_2\text{CNET}_2)]$  is the ideal precursor for deposition of indium sulfide ( $\text{InS}$  and  $\text{In}_6\text{S}_7$  phases) films, and  $[\text{InEt}_2(\text{S}_2\text{CNET}_2)]$  can give single phase, cubic  $\beta$ - $\text{In}_2\text{S}_3$  films at a temperature of 325–400 °C.<sup>97</sup>  $\beta$ - $\text{In}_2\text{S}_3$  films can also be prepared from  $[\text{In}(\text{SOCNET}_2)_3]$  and  $[\text{In}(\text{SOCNPr}_2)_3]$  respectively.<sup>98,99</sup> The deposition of  $\alpha$ - $\text{In}_2\text{S}_3$  films can be obtained from the precursor,  $[\text{In}(\text{S}_2\text{COPr})_3]$  or  $[\text{In}(\text{S}_2\text{CNET}_2)_3]$ .<sup>100</sup>  $[\text{mes}_2\text{In}(\mu\text{-SR})]_2$  ( $\text{mes} = 2, 4, 6$ -trimethylphenyl,  $\text{R} = t\text{-Bu}, t\text{-amyl}, \text{SiPh}_3$ ) and  $[\text{Me}_2\text{In}(\mu\text{-SSiPh}_3)]_3$  are also used as a single-source precursor for deposition of indium sulfide films.<sup>101</sup> In addition,  $[\text{HL}][\text{In}(\text{SCOMe})_4]$  is also used to deposit tetragonal  $\beta$ - $\text{In}_2\text{S}_3$  films.

Indium selenide films can be produced from the corresponding compounds containing selenium by MOCVD, and the film quality is dependent on the growth temperature.  $[\text{In}^t\text{Bu}_2(\text{Se}^t\text{Bu})_2]$  gives indium-rich films at a temperature of 230–420 °C, and  $[\text{In}(\text{CEtMe}_2)(\mu_3\text{-Se})_4]$  produces crystalline  $\text{InSe}$  films.<sup>102</sup> Pyrolysis of  $\text{In}(\text{SePh})_3$  can form hexagonal  $\text{In}_2\text{Se}_3$  films at 470–530 °C, and of  $[\text{Me}_2\text{EtC}]\text{InSe}_4$  can provide hexagonal  $\text{InSe}$  films at temperatures between 290–350 °C.<sup>103</sup> The cubic  $\text{In}_2\text{Se}_3$  films can be obtained from  $[\text{In}(\text{Se}_2\text{CNMe}^n\text{Hex})_3]$  and  $[\text{In}\{\text{SeC}(\text{SiMe}_3)_3\}_3]$ , respectively.

Films of chalcopyrite  $\text{CuInE}_2$  are formed by MOCVD from the precursor  $[(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-ER})_2\text{In}(\text{ER})_2]$  ( $\text{E} = \text{S}$  or  $\text{Se}$  and  $\text{R} = \text{Et}$  or  $^t\text{Bu}$ ).<sup>104</sup> The compound  $[\text{Bu}_2\text{In}(\text{SPr})\text{Cu}(\text{S}_2\text{CNPr}_2)]$  is also reported to deposit  $\text{CuInS}_2$  films by MOCVD.  $[(n\text{-Bu}_3\text{P})_2\text{Cu}(\text{SR})_2\text{In}(\text{SR})_2]$  ( $\text{R} = \text{Et}$  and  $n\text{-Pr}$ ) and  $[\text{Bu}_2\text{In}(\text{SPr})\text{Cu}(\text{S}_2\text{CNPr}_2)]$  are also used to deposit  $\text{CuInS}_2$  films.<sup>105</sup> The thiocarboxylates,  $[(\text{Ph}_3\text{P})_2\text{AgIn}(\text{SC}(\text{O})\text{R}_4)]$  ( $\text{R} = \text{Me}, \text{Ph}$ ), were excellent single-source precursors for  $\text{AgInS}_2$  and  $\text{AgIn}_5\text{S}_8$  films by MOCVD.<sup>106</sup>

### 5.4 Indium Nitride Precursor Compounds

The first adduct stabilized, volatile covalent indium bis-azide compound,  $[(\text{InN}_3)_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$ , has been characterized by single crystal X-ray diffraction. It has been used as a precursor for indium nitride thin films.<sup>107</sup> Other azide derivatives of indium, such as  $[\text{Cl}_2\text{InN}_3]$ ,  $[\text{Br}_2\text{InN}_3]$ ,  $[\text{py}_2\text{Na}][\text{py}_2\text{In}(\text{N}_3)_4]$ , pyridine, and tetrahydrofuran adducts, are also being studied as



precursors for InN materials.<sup>108</sup> Amido derivatives of indium compounds are also important in the preparation of InN materials. Synthesis and characterization of  $[\text{H}_2\text{InNH}_2]$ ,  $[\text{N}(\text{CH}_2\text{CH}_2\text{NMe})_3\text{In}]_2$ ,  $[\text{InNH}_2\text{CH}_3]$ , and  $[\text{InNH}(\text{CH}_3)_2]$ , which are potential precursors for InN materials, have been reported.<sup>109,110</sup> The reaction of  $[\text{Li}(\text{Me}_3\text{Si})\text{N}-\text{NHBu}^t]$  with  $[\text{MeInCl}]$  can give different hydrazine derivatives of indanes, which are dependent on the solvent. With hexane as a solvent, the dimeric compound  $[\text{Me}_3\text{In}(\text{Li})(\text{Me}_3\text{Si})\text{N}-\text{NHBu}^t]_2$  is produced. In diethyl ether, the cage compound  $[\text{MeIn}\{\text{N}(\text{SiMe}_3)\text{LiN}(\text{SiMe}_3)\text{NHBu}^t\}]$ , which can be regarded as an  $(\text{Me}_3\text{SiN}=\text{InMe})_2$  adduct with  $[\text{Li}(\text{Me}_3\text{Si})\text{N}-\text{NHBu}^t]_2$ , is isolated. These compounds are good single-source precursors in MOCVD processes for InN thin films.<sup>111</sup>

The thermally stable In(I) compounds  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)]$  and  $[\text{In}(\eta^5\text{-P}_2\text{C}_3\text{Bu}^t_3)]$  have a half-sandwich structure, and are potential single sources for chemical vapor deposition of InP semiconductors.<sup>28</sup> The reaction of  $\text{R}_3\text{PI}_2$  with indium metal produces a variety of novel indium compounds  $[\text{InI}_3(\text{PPh}_3)_2 \cdot \text{InI}_3(\text{PPh}_3)]$ ,  $\text{In}_2\text{I}_4(\text{PPr}^n_3)_2$ , and  $\text{InI}_3(\text{PPh}^i_3)_3$ , which may have applications in the microelectronics industry as precursors for MOCVD.<sup>37</sup> A key feature of  $[\text{R}_2\text{InPBu}^t_2]$  ( $\text{R} = \text{vinyl, allyl, and benzyl}$ ) is the presence of alkyl groups that are capable of facile  $\beta$ -hydride and/or alkyl radical elimination reactions, thus lowering deposition temperature into the range 400–590 °C.<sup>76</sup> In addition,  $\{\text{Et}_2\text{InSb}(\text{SiMe}_3)_2\}_3$  is also used as precursor for the CVD of indium antimonide materials.<sup>112</sup>

## 6 INDIUM NANOMATERIALS

### 6.1 Introduction

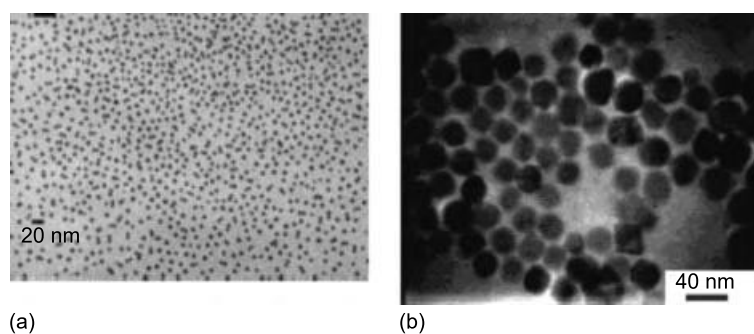
Inorganic nanomaterials have attracted considerable attention owing to their novel physical and chemical properties that arise from size reduction and the potential applications in diverse areas. Moreover, these materials can also be used as

‘building blocks’ to assemble new generations of nanoscale electronic and optical devices. Indium, a low-melting metal, is easily alloyed and converted to InP, InAs, and InS, which are III-V/VI semiconductors that display interesting optoelectronic properties. Indium is easily oxidized to  $\text{In}_2\text{O}_3$ , which can be used as a sensor and light-emitting material. Indium oxides can form with  $\text{SnO}_2$  the mixed indium tin oxide (ITO), a conducting glass.<sup>2</sup> Therefore, various indium-containing nanomaterials have been prepared in the last ten years.

### 6.2 Indium Nanomaterials

Indium nanoparticles can be prepared by metal vapor deposition, by evaporation of metal into a polymerizable monomer, or by reduction of  $\text{InCl}_3$  with the appropriate quantity of alkalides or electrides.<sup>113,114</sup> In the latter, the indium particles often display an oxidized surface. The monodispersed indium nanoparticles can be obtained by thermal decomposition of organometal precursor  $[\text{In}(\eta^5\text{-C}_5\text{H}_5)]$  using polyvinylpyrrolidone (PVP) or trioctylphosphane oxide (TOPO) as a ligand. These particles can be further oxidized into well-crystallized  $\text{In}_2\text{O}_3$  particles with unchanged morphology.<sup>115,116</sup> The bare indium nanoparticles have been prepared by solution dispersion route from bulk indium granules, which may be the simplest and cheapest method for making indium nanoparticles (Figure 1).<sup>117</sup> The cationic indium nanoparticles are also synthesized in a single crystal of zeolite X through an indium-exchanging process.<sup>118</sup>

The organometallic route can be extended to the formation of one-dimensional indium materials. On the use of long-chain amines as templates, In and  $\text{In}_3\text{Sn}$  nanowires have been prepared from the organometallic precursors  $\text{InCp}$  ( $\text{Cp} = \text{C}_5\text{H}_5^-$ ) in the presence of UV irradiation. In this case, irradiation is crucial for the formation of the wires. In nanowires are also produced in the metal organic chemical vapor deposition grown InGaN layers.<sup>119,120</sup>

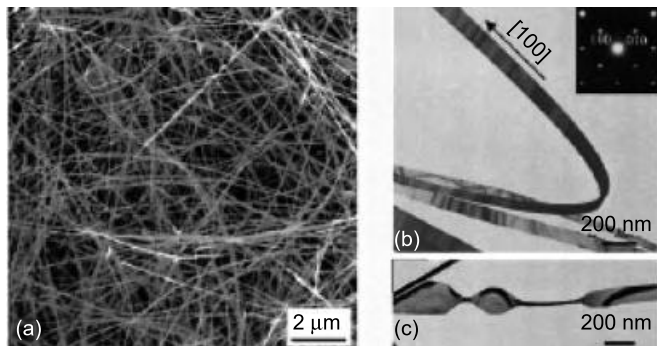


**Figure 1** Transmission electron microscopy (TEM) images of indium nanoparticles. ((a) Reproduced from Ref. 115 by permission of Wiley-VCH; (b) Reprinted with permission from Ref. 117. © 2074 American Chemical Society)

### 6.3 Indium Oxide Nanomaterials

Indium oxide, an *n*-type semiconductor with a wide band gap of about 3.6 eV, has been widely used as microelectronic device materials in solar cells, sensors, and conducting glasses.  $\text{In}_2\text{O}_3$  nanoparticles can be prepared by sol-gel processes, or by thermal decomposition of  $\text{In}(\text{acac})_3$  precursors in the presence of a surfactant.<sup>121</sup> Oxidation of indium nanoparticles also gives  $\text{In}_2\text{O}_3$  nanoparticles.<sup>116</sup> Without the presence of catalyst, the evaporation of  $\text{In}_2\text{O}_3$  powders at 1400 °C can yield  $\text{In}_2\text{O}_3$  nanobelts, which are single crystalline and grow along the 100 plane, with the surfaces being enclosed by {100} (Figure 2).<sup>122</sup> Under an  $\text{H}_2\text{O}$ /oxygen-containing argon atmosphere, thermal evaporation of indium granules also yields  $\text{In}_2\text{O}_3$  nanowires. In this case, the growth of  $\text{In}_2\text{O}_3$  nanowires is more likely to be controlled by the vapor–solid process.<sup>123</sup>  $\text{In}_2\text{O}_3$  nanofibers are also obtained by annealing  $\text{InOOH}$  nanofibers at 490 °C. The  $\text{InOOH}$  nanofibers are prepared by controlling hydrolysis of  $\text{InCl}_3$  at 190–240 °C.<sup>124</sup> Under argon/oxygen atmosphere, rapidly heating an indium-containing target covered with a thin Au layer can also give  $\text{In}_2\text{O}_3$  nanowires. In this case, Au nanoclusters play a crucial role in directing the growth of  $\text{In}_2\text{O}_3$  nanowires.<sup>125</sup>

$\text{In}_2\text{O}_3$  nanotubes have been synthesized by a sol-gel porous alumina templating method. The length and diameters of nanotubes can be varied by selecting the template dimensions and sol immersion time.<sup>126</sup> Evaporation of a mixture of  $\text{In}/\text{In}_2\text{O}_3$  under vacuum also gives  $\text{In}_2\text{O}_3$  nanotubes. Interestingly, the  $\text{In}_2\text{O}_3$  nanotubes are filled with metallic indium, and the length and the position of In fillings can be modified by electron-beam irradiation.<sup>127</sup> Under argon/oxygen atmosphere, heating an indium–tin mixture also produces ITO nanofibers. The tin plays a crucial role in directing the growth of the ITO nanofibers based on the vapor-liquid-solid mechanism.<sup>128</sup>



**Figure 2** TEM images of  $\text{In}_2\text{O}_3$  nanobelts and an electron diffraction pattern (insert). (Reprinted with permission from Z.W. Pan, Z.R. Dai, and Z.L. Wang, *Science*, 2001, **291**, 1947. © 2001 AAAS)

### 6.4 Indium Nitride Nanomaterials

Indium nitride plays an important role in blue/violet light-emitting diodes and laser diodes. Nanocrystalline  $\text{InN}$  can be prepared by the reaction of azido-indium compounds such as  $i\text{Pr}_2\text{InN}_3$  or  $t\text{Bu}_2\text{InN}_3$  with  $\text{H}_2\text{NNMe}_2$  used as a reductant at 203 °C.  $\text{H}_2\text{NNMe}_2$  not only serves as a stoichiometric hydrogen-atom donor to assist alkane elimination, but also can reduce some of the azido precursor to form metallic indium, which should promote both precursor decomposition and crystal-lattice construction.<sup>129</sup> A benzene thermal conversion route has been developed to prepare nanocrystalline indium nitride through the reaction of  $\text{In}_2\text{S}_3$  with  $\text{Na}_2\text{S}$  at 180–200 °C. This may be the lowest temperature at which crystalline  $\text{InN}$  has been obtained.<sup>130</sup> In addition, crystalline  $\text{InN}$  powders with the size of 50–300 nm are also prepared by the nitridation of  $\text{In}_2\text{O}_3$  and  $\text{In}(\text{OH})_3$  with  $\text{NH}_3$  gas.<sup>131</sup>

$\text{InP}$  nanocrystals can be made by dehalosilylation of  $\text{InCl}_3$  and  $(\text{Me}_3\text{Si})_3\text{P}$  with subsequent thermolysis at 200–400 °C.<sup>132</sup> Monodisperse and soluble  $\text{InP}$  nanocrystals are obtained by thermolysis reactions in trioctylphosphine oxide.  $\text{InP}$  nanoparticles can also be obtained by the decomposition of organometallic precursors.<sup>133,134</sup> A novel route has been developed to prepare nanocrystalline  $\text{InP}$  by the reaction of  $\text{InCl}_3$ ,  $\text{P}_4$ , and  $\text{KBH}_4$  at temperatures as low as 80 °C, which is the lowest temperature reported for  $\text{InP}$  nanocrystals.<sup>135</sup> The synthesis of  $\text{InP}$  nanotubes by laser ablation is also reported.<sup>136</sup>

Nanocrystalline  $\text{InAs}$  is obtained by the reaction of  $(\text{Me}_3\text{Si})_3\text{As}$  with  $\text{InCl}_3$  or by reaction of  $\text{InCl}_3$  with  $\text{Na}_3\text{As}$ , respectively. A solvothermal route has been proposed to prepare  $\text{InAs}$  nanocrystals, which involves co-reduction of  $\text{InCl}_3$  and  $\text{AsCl}_3$  by  $\text{Zn}$ .<sup>137</sup> The high quality nanocrystalline  $\text{InAs}$  can be obtained by the thermolysis of a mixture of  $\text{InCl}_3$  and  $\text{As}(\text{NMe}_2)_3$ .<sup>138</sup> In addition,  $\text{InSb}$  nanocrystals can also be obtained by the solvothermal reduction route.<sup>139</sup>

### 6.5 Indium Chalcogenide Nanomaterials

Copper indium chalcogenides  $\text{CuInE}_2$  (where  $\text{E} = \text{S}, \text{Se},$  and  $\text{Te}$ ) are ternary semiconductors, which have emerged as a leading material for high efficiency and radiation-hard solar cell applications.  $\text{CuInS}_2$  nanocrystals are prepared by a simple colloidal route, using  $\text{InCl}_3$ ,  $\text{CuI}$ , and bis(trimethylsilyl) sulfide as starting materials and TTP (triphenyl phosphite) as surfactant. In this case, the particle surface is shielded by a surfactant.<sup>140</sup>  $\text{CuInSe}_2$  nanocrystals are also prepared using a two-step reaction from  $\text{InCl}_3$  and  $\text{CuCl}$  in a suitable solvent, followed by the addition of trioctylphosphine selenide.<sup>141</sup> Solvothermal routes are also used in the synthesis of  $\text{CuInSe}_2$ ,  $\text{AgInS}_2$ , and  $\text{CdIn}_2\text{S}_4$  nanocrystals.<sup>142–144</sup>

## 7 INTERMETALLIC COMPOUNDS

### 7.1 Introduction

The development of new intermetallic compounds demands greater understanding of the relationship among structure, bonding, and properties. The Zintl concept provides an effective way to describe the structures of compounds formed between electropositive metals and main-group elements, in which the electropositive atoms serve to donate their valence electrons to main-group atoms. Elements to the right of the Zintl border (separating group 13 and 14) with electropositive metals usually form valence compounds (Zintl compounds), with narrow ranges of composition and the valence electron concentration per atom (vec) exceeding 4. On the other hand, the compounds with elements to the left of the Zintl border behave like traditional intermetallic compounds (Hume-Rothery phases) with wide ranges of homogeneity for different structures and vec values between 1 and 2. There are no clear classification schemes for the range between 2 and 4. Furthermore, many indium-containing intermetallic compounds have a vec near 3 and the degree of In–In bonding in these compounds depends strongly on the indium content as well as the electron count.<sup>145</sup> Therefore, much attention has been directed to understanding the indium-containing compounds ‘between’ Hume-Rothery and Zintl phases in the past ten years.

### 7.2 Binary Compounds

The binary indium-rich transition metal compounds show a variety of different indium networks. In the structures of  $T_2In_5$  ( $T = Ti, Hf$ ), the indium atoms form infinite two-dimensional (2D) planar networks, which can be described as a tessellation of triangles, squares, and pentagons. The 2D network is also found in the structures of the  $La_3In_5$  compounds, which contain well-defined indium square pyramids and some intercluster indium–indium distances that are only 11–15% greater than the average intracluster bond lengths. The apparent  $In_5^{9-}$  cluster in  $La_3In_5$  can be described as a closed shell nido-deltahedron, and the compound structurally as a Zintl phase. The  $\beta$ - $Y_3In_5$  compounds with a similar structure to  $La_3In_5$  present a slow first-order phase transition to  $\alpha$ - $Y_3In_5$  at high temperature. Clusters in the low-temperature  $\alpha$ - $Y_3In_5$  phase are twisted and joined by short bonds at trans-basal positions into chains that are more weakly interconnected into a three-dimensional structure.<sup>146</sup>

The 3D network of indium atoms is found in the  $TIn_3$  ( $T = Co, Rh, Ir$ ) compounds. The compounds  $TIn_3$  ( $T = Co, Rh, Ir$ ) belong to a large family and are built up from tungsten-like building blocks of indium atoms and  $AlB_2$ -like slabs of compositions  $In\Box Co$ ,  $In\Box Rh$ , and  $In\Box Ir$ , respectively, where  $\Box$  represents the vacancies in the  $AlB_2$  fragments of  $TIn_3$ .  $RhIn_3$  shows evident antibonding Rh–Rh

interactions, and three compounds display similar bonding characteristics to  $RuIn_3$ .<sup>147</sup>

### 7.3 Alkaline Earth-transition Metal–Indium Compounds

The main features of ternary alkaline earth-transition metal–indium compounds are 2D or 3D infinite transition metal–indium polyanions in which the degree of In–In bonding strongly depends on the indium content and the structure type.  $CaAuIn$  compounds adopt the  $KHg_2$ -type structure with an ordered arrangement of gold and indium atoms on the mercury position. Each calcium atom has a distinctly ordered near-neighbor environment of six gold and six indium atoms in the form of two  $Au_3In_3$  hexagons.<sup>148</sup> Within  $SrPtIn$ , the indium atoms have a distorted tetrahedral platinum coordination. These  $InPt_{4/4}$  tetrahedra are edge- and corner-shared, forming a 3D  $[PtIn]$  polyanion in which the strontium atoms are embedded.<sup>149</sup> The  $CaRhIn$  structure also consists of strongly puckered  $Rh_3In_3$  hexagons in which each rhodium atom has a distorted tetrahedral indium environment and the calcium atoms fill the channels within the 3D  $[RhIn]$  polyanion.<sup>150</sup>

The structures of  $CaTIn_2$  ( $T = Pd, Pt, Au$ ) are transition metal (T)-centered trigonal prisms formed by the calcium and indium atoms. The transition metal and indium atoms form a 3D  $[TIn_2]$  polyanion in which the large alkaline earth metal atoms occupy one-dimensional pentagonal tubes, and the strongest bonding interactions are found for the In–In and T–In contacts.<sup>150,151</sup>

The 3D  $[TIn_4]$  polyanions are also found in the structure of  $CaTIn_4$  ( $T = Rh, Pd, Ir$ ), in which the calcium atoms occupy distorted pentagonal tubes formed by indium and transition metal.<sup>152</sup> The main motifs of both  $Ca_2Au_3In_4$  and  $Sr_2Pt_3In_4$  are condensed, platinum (gold)-centered trigonal prisms formed by the alkaline earth and indium atoms. The platinum (gold) and indium atoms form complex 3D  $[Pt_3In_4]$  and  $[Au_3In_4]$  polyanions respectively, and the alkaline earth cations are located in distorted hexagonal tubes.<sup>149</sup>

### 7.4 Rare Earth-transition Metal–Indium Compounds

The ternary rare earth-transition metal–indium compounds display a pronounced tendency for clustering of the transition metal atoms and a 2D and sometimes 3D indium substructure depending on the relative content of indium. The structures of  $(RE)In_{1-x}Sb_2$  ( $RE = La-Nd$ ) is built up of alternating layers of compositions  $[Sb]_m$  and  $[In_{0.8}Sb]_m$  ( $m = 2 \sim \infty$ ), separated by the La atoms. The  $[Sb]_m$  layer is described as a nearly square net of Sb atoms held by weak one-electron bonds, while the  $[In_{0.8}Sb]_m$  layer is derived from an edge-sharing  $[InSb_4]$  tetrahedron distorted in such a way as to produce In–In zigzag chains.<sup>153</sup> The one-dimensional  $[Ni_7]$  clusters are observed in the compound  $LaNi_7In_6$ .<sup>154</sup>

The complexes (RE)TIn<sub>2</sub> (RE = Eu, Yb; T = Pd, Au) also form transition metal (T)-centered trigonal prisms by the rare earth metal and indium atoms. The transition metal and indium atoms form a 3D [TIn<sub>2</sub>] polyanion in which the large rare earth metal atoms occupy one-dimensional pentagonal tubes.<sup>155</sup> The strongest bonding interactions are found for the In–In and Pd–In contacts; the Eu–Pd and Eu–In interactions are much weaker.

The structural motifs of LaPtIn<sub>3</sub> are condensed distorted trigonal [PtIn<sub>6</sub>] prisms, and Pt–In and In–In bonding play an important role in the structure. The La atoms occupy large cavities within the polyhedral network.<sup>156</sup> Within LaPtIn<sub>4</sub> or YbPtIn<sub>4</sub>, together with indium atoms platinum atoms form a complex 3D [PtIn<sub>4</sub>] polyanion in which the lanthanum or ytterbium atoms occupy large hexagonal tubes.<sup>157</sup> In the structure of LaNiIn<sub>4</sub>, the nickel and indium atoms also form a 3D [NiIn<sub>4</sub>] polyanion and the indium substructure consists of distorted bcc-like indium cubes.<sup>154</sup>

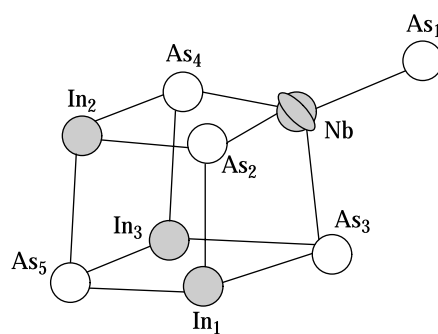
Within YbCoIn<sub>5</sub> and YbRhIn<sub>5</sub>, the transition metal atoms have eight indium neighbors in a square prismatic coordination by indium atoms; these prisms are condensed via common edges, forming layers. The ytterbium and additional indium atoms are located between these layers. The ytterbium atoms are cubooctahedrally coordinated by 12 indium atoms.<sup>157</sup>

The gold and indium atoms in La<sub>3</sub>Au<sub>4</sub>In<sub>7</sub> build a 3D [Au<sub>4</sub>In<sub>7</sub>] polyanion in which the lanthanum atoms fill distorted pentagonal and hexagonal channels. Within the polyanion, short Au–In and In–In distances are indicative of strongly bonding Au–In and In–In interactions.<sup>158</sup> Within EuRh<sub>2</sub>In<sub>8</sub>, the rhodium and indium atoms together build a complex 3D [Rh<sub>2</sub>In<sub>8</sub>] polyanion in which the europium atoms are located within distorted pentagonal channels. In RE<sub>4</sub>Pd<sub>10</sub>In<sub>21</sub> (RE = La, Ce, Pr, Nd, Sm), all palladium atoms have a trigonal prismatic coordination. The strongest bonding interactions occur for the Pd–In and In–In contacts. The structures are composed of covalently bonded three-dimensional [Pd<sub>10</sub>In<sub>21</sub>] networks in which the rare earth metal atoms fill distorted pentagonal channels.<sup>159,160</sup> In addition, the 3D [Pt<sub>12</sub>In<sub>32</sub>] network is also observed in the structures of Gd<sub>3</sub>Pt<sub>4</sub>In<sub>12</sub> and Tb<sub>3</sub>Pt<sub>4</sub>In<sub>12</sub>.<sup>161</sup>

## 7.5 Multinary Compounds

The compound Cs<sub>7</sub>NbIn<sub>3</sub>As<sub>5</sub> contains an unprecedented anion, [(In<sub>3</sub>As<sub>4</sub>Nb)–As]<sup>7–</sup>, a cubane made of three indium, four arsenic, and one niobium atom and a ‘handle’ composed of an arsenic atom that is multiply bonded to the niobium corner (Scheme 8).<sup>162</sup>

The structure of [PtIn<sub>6</sub>][GaO<sub>4</sub>]<sub>2</sub> contains the [PtIn<sub>6</sub>] octahedral, which are linked via [GaO<sub>4</sub>]<sup>5–</sup> tetrahedral to a 3D network. Starting from [PtIn<sub>6</sub>][GaO<sub>4</sub>]<sub>2</sub>, the substitution of Ga<sup>3+</sup> ions by larger In<sup>3+</sup> ions leads to the formation of a solid solution series according to the general formula



**Scheme 8** Structure of the cubane with a ‘handle’ [(As(InAs)<sub>3</sub>)Nb–As]<sup>7–</sup>, Ref. 162

[PtIn<sub>6</sub>][GaO<sub>4</sub>]<sub>2–x</sub>[InO<sub>4</sub>]<sub>x</sub> and becomes apparent in an increase of the lattice parameter.<sup>163</sup>

The first compound representing the next stage of a structural hierarchy, that is supertetrahedra of supertetrahedra, specifically is a T<sub>2</sub> supertetrahedron of T<sub>4</sub>, a discrete anionic cluster of 214 atoms and 80 tetrahedral centers. The structure contains the finite tetrahedral anionic units of [Cd<sub>16</sub>In<sub>64</sub>S<sub>134</sub>]<sup>44–</sup> that have an underlying T<sub>2</sub> type of structure in which the individual tetrahedra have each been replaced by a T<sub>4</sub> supertetrahedron forming a super-supertetrahedron.<sup>164</sup>

In the compound Ba<sub>6</sub>ZnIn<sub>2</sub>Cl<sub>20</sub>, Zn<sup>2+</sup> is surrounded tetrahedrally and In<sup>3+</sup> octahedrally by chloride ions. Half of the [InCl<sub>6</sub>] octahedra are isolated from each other; the other half share common edges to form [In<sub>2</sub>Cl<sub>10</sub>] double octahedra. Ba<sup>2+</sup> has coordination numbers of eight and nine.<sup>165</sup>

Na<sub>3</sub>K<sub>23</sub>Cd<sub>12</sub>In<sub>48</sub> is obtained by stoichiometric fusion of the elements and is composed of indium icosahedra, indium triangular clusters, and the novel Cd<sub>12</sub>In<sub>6</sub> tubular cluster. The latter contains two Na<sup>+</sup> ions and a 96-atom polyhedra (fullerane), and is sheathed by 20 K<sup>+</sup> and 12Na<sup>+</sup>. The clusters are linked together through two-center two-electron bonds with a 3D anionic network.<sup>166</sup>

## 8 INDIUM CATALYZED ORGANIC SYNTHESIS

### 8.1 Introduction

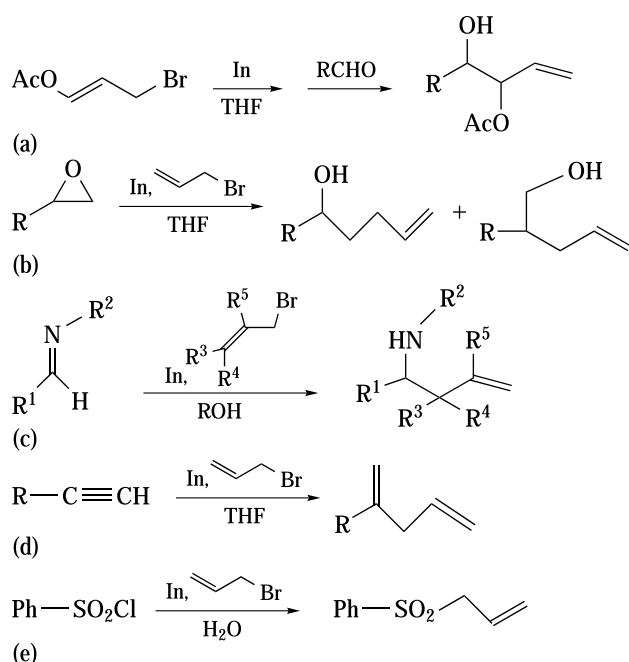
Since the discovery of the indium-mediated Barbier–Grignard reaction in 1991, indium reagents have become more popular in organic synthesis.<sup>167</sup> The attraction of indium catalysis is that it provides the ability to perform organic reactions in water. During the last decade, a large proportion of this work has been focused on the use of indium reagents to promote organic reactions in aqueous media. Moreover, indium-assisted reactions often display a low heterophilicity and low nucleophilicity that imparts high regio- and chemoselectivity in various chemical transformations of groups of similar reactivity, without protecting other groups.

The recent emergence of indium halides as efficient Lewis acid catalysts presents new and exciting opportunities for indium chemistry.<sup>168</sup>

## 8.2 Allylation

The indium-mediated allylation reaction is an aldol-type reaction where the nucleophile is an allylindium species usually generated from allylic halide and indium. By far the greatest number of indium-mediated organic reactions involves the allylation of unsaturated compounds, and the list of indium-mediated allylations is formidable. In principle, there are five types of indium-mediated allylation reactions depending on the unsaturated functional groups (Scheme 9). (a) Treatment of allylindium reagents with carbonyl compounds can produce the corresponding allyl alcohols;<sup>169–171</sup> (b) Reaction with terminal epoxides affords the corresponding bishomoalcohols;<sup>172</sup> (c) Allylation of aldimines gives the corresponding homoallylic amines;<sup>173,174</sup> (d) Reaction with alkenes or terminal alkynes gives the corresponding alkenes and 1,4-dienes respectively;<sup>175,176</sup> (e) Aromatic sulfonyl halides react with allyl indium reagents to give the corresponding sulfones.<sup>177</sup>

In general, solvent effect can play a significant role in the reactions and the regio- and stereo-selectivity of allylations is determined by the location of other functional groups in the molecules and the reaction solvents; several reports on the effect of other functional groups and solvents on the selectivity are published. Araki's group has noted that hydroxy-bearing cyclopropenes can be allylated both in organic and aqueous media, but the regio- and stereo-selectivity can be regulated



**Scheme 9** Indium-mediated allylation reactions

by both the location of the hydroxyl group in the molecules and the reaction solvents.<sup>178</sup>

## 8.3 Acylation

The acylation of alcohols and amines is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting hydroxy and amino groups in a multistep synthetic process. The Lewis acid catalyzed acylation is a mild alternative to conventional acidic or basic catalyst. The extremely efficient acylation of a diverse range of substrates has been noted using indium halides. Using this method, acylation of a primary OH group in the presence of secondary and phenolic OH groups, and of a primary NH<sub>2</sub> in the presence of secondary NH and primary OH, has been achieved with high selectivity. The practical utility of indium halides is reflected in the high-yielding acylation of polyhydroxy compounds.<sup>179,180</sup>

## 8.4 Addition to Imines

$\alpha$ -Aminophosphonates have been the subject of considerable recent interest owing to their structural analogy to  $\alpha$ -amino acids, and several synthetic methods for the compounds have been developed. Of these, the nucleophilic addition of phosphates to imines, catalyzed by Lewis acids such as SnCl<sub>2</sub>, ZnCl<sub>2</sub>, and MgBr<sub>2</sub>, is the most convenient. However, these reactions cannot be carried out in a one-pot operation starting from a carbonyl compound, an amine, and dialkyl phosphite because the amines and water present during imine formation are likely to decompose or deactivate Lewis acids. To circumvent this disadvantage, an elegant procedure has been developed employing indium (III) chloride as catalyst from the reaction of a carbonyl compound, amine, and diethyl phosphite. The method is operationally simple and applicable to aldehydes and ketones. The reaction is tolerant of sensitive functional groups and chelating groups.<sup>181</sup> In this way, a wide range of structurally diverse carbonyl compounds was converted into the corresponding  $\alpha$ -Aminophosphonates in high yields.<sup>3,182</sup> In addition, indium agents are also effective for the conversion of azides to carbamates.<sup>183</sup>

## 8.5 Reduction

Indium is reported to be an efficient catalyst for the debromination processes of vic-dibromides. An illustration of the utility of this method is in the debromination of aryl-substituted vic-dibromides to produce the corresponding (E)-alkenes with indium metal in MeOH. In general, the reaction proceeds via a common, relatively stable radical intermediate, collapse of which leads directly to the (E)-alkenes, and methanol is found to be the best solvent for this reaction.<sup>184</sup>

Indium metal is equally effective for the reductive of  $\alpha$ -halocarbonyl compounds as demonstrated by the

transformation of  $\text{PhCOCH}_2\text{Br}$  to the dehalogenated product  $\text{PhCOCH}_3$ .<sup>185</sup> A wide range of structurally diverse  $\alpha$ -halo ketones and esters has been reduced according to this procedure to provide the corresponding dehalogenated carbonyl compounds.<sup>186</sup>

### 8.6 Other Reaction

A catalytic amount of indium metal effectively promotes the homocoupling of alkyl and aryl halides to provide the corresponding dialkyls and biaryls.<sup>187</sup> Ranu's group has reported that indium (III) chloride is very effective in effecting the rearrangement of epoxides in THF solution to give the corresponding carbonyl compounds very selectively.<sup>188</sup> Indium (III) chloride is effective in catalyst amounts for the Michael reaction between amines and  $\alpha,\beta$ -ethylenic compounds in water,<sup>189</sup> Diels–Alder reaction between various dienes and dienophiles in water,<sup>190</sup> and the synthesis of alkyl and aryl 2,3-unstaturated C-glycosides through the Ferrier rearrangement.<sup>191</sup> The combination of indium catalyst and other catalyst is extremely effective for deoxygenation process. For example, treatment of tetralone with  $\text{Me}_2\text{SiClH}$  in the presence of indium (III) chloride at room temperature produces tetralin in excellent yields.<sup>192</sup> In addition,  $\text{InBr}_3$ , indium (III) triflate, and In (I) compounds used for catalyst also are reported.<sup>193</sup>

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# Indium: Organometallic Chemistry

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## 1 INTRODUCTION

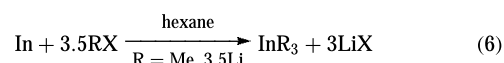
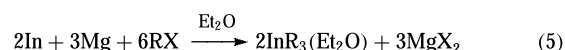
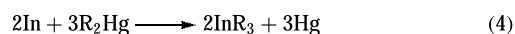
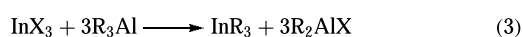
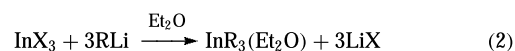
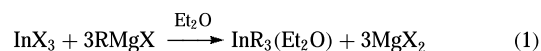
The importance of organoindium derivatives has been perpetuated in the last decade by their application as precursors to materials for advanced technologies, in particular, for fabricating multi-component alloys classified as III-V and I-III-VI semiconductors. Key areas that have helped advance the drive for new indium derivatives are thin-film technologies and, more recently, nanotechnology. A number of reviews and reports have been published that discuss in whole, or in part, organometallic compounds of indium.<sup>1–15</sup> Furthermore, general overviews of the chemistry of organoindium compounds related to thin-film technology were presented in books and annual reviews.<sup>16–32</sup> Another area where the use of indium organometallics has found increased use is for organic synthesis, more precisely the formation of indium organometallics *in situ* from elemental indium.<sup>33–38</sup> An area of interest that has gathered considerable interest is the indium mediated coupling of allyl and propargyl halides with aldehydes to give the corresponding alcohols in high yields.<sup>39</sup> An important aspect of this reaction is the ability to obtain good regioselectivity and diastereoselectivity by steric or chelation control.<sup>37</sup>

## 2 ALKYL AND ARYL DERIVATIVES, InR<sub>3</sub>

### 2.1 Synthesis

The established method of choice for synthesizing indium derivatives follows those classically defined and used for

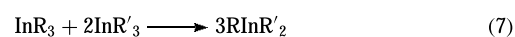
generic organometallic synthesis. These are (a) Metathesis: equations (1), (2), and (3); (b) Transmetallation/Mercuration: equation (4); (c) Mixed metal Synthesis (direct): equation (5); (d) Metal plus organic halide (direct): equation (6).

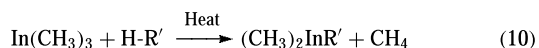


A limiting factor for the use of group I organometallic reagents for the preparation of InR<sub>3</sub> from InX<sub>3</sub> (equation 2) is that many sodium or lithium reagents often act as reducing agents, affording In(I)R derivatives in poor to good yields instead of the desired In(III) organometallics. The use of Grignard reagents (RMgX) or AlR<sub>3</sub> does circumvent reduction of In(III) to In(I). With the exception of the metathesis route using AlR<sub>3</sub>, both group I and Grignard reagents require the synthesis to be conducted in a coordinating solvent that subsequently forms an adduct to the desired product, e.g. [InR<sub>3</sub>·(OEt<sub>2</sub>)]. However, repeated vacuum distillation, or azeotropic distillation with noncoordinating aromatic/aliphatic solvents results in the removal of the diethyl ether. Alternatively, it has recently been shown that thermal decomposition of [InR<sub>3</sub>·(OEt<sub>2</sub>)] in the presence of CsF affords the adduct free InMe<sub>3</sub> in very high yields.<sup>40</sup>

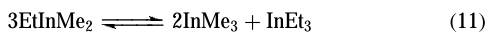
The use of mercurating agents (R<sub>2</sub>Hg) has become obsolete owing to extended reaction times and elevated reaction temperatures, but more importantly due to the associated toxicity of mercury compounds. Mixed metal synthesis (equation 5) has proved to be versatile and is widely used owing to the high product yields and purity.<sup>41</sup> The propensity for ultra-high purity InR<sub>3</sub> via mixed metal synthesis has largely been driven by the semiconductor industry and its need to eliminate extrinsic dopants during synthesis (equation 6). This has warranted numerous patents for the preparation of InR<sub>3</sub>.<sup>41–51</sup> The use of photoexcited indium atoms and their reaction with CH<sub>4</sub> to afford low-valent In(I) and In(II) has also been studied, and is expanded in Section 8.

Limited heteroleptic organoindium examples are known since they have a tendency to rearrange to form the more stable symmetrical derivatives. The preparation of the majority of the heteroleptic compounds has been investigated via (a) ligand redistribution (equation 7–8), (b) metathesis (equation 9), or (c) methane elimination (equation 10);





The synthesis of mixed alkyl indium organometallics has again been driven by the need for more volatile and enhanced properties for use in CVD and related areas. This has been a subject of recent review and discussion with attention being focused on the existence of liquid ethyldimethylindium ( $\text{EtInMe}_2$ ).<sup>27</sup> Although two patents currently exist for the preparation of high purity  $\text{EtInMe}_2$ ,<sup>48,51</sup> an early study by two independent research groups demonstrated that  $\text{EtInMe}_2$  was indeed a mixture of  $\text{InMe}_3$  and  $\text{InEt}_3$  (equation 11).

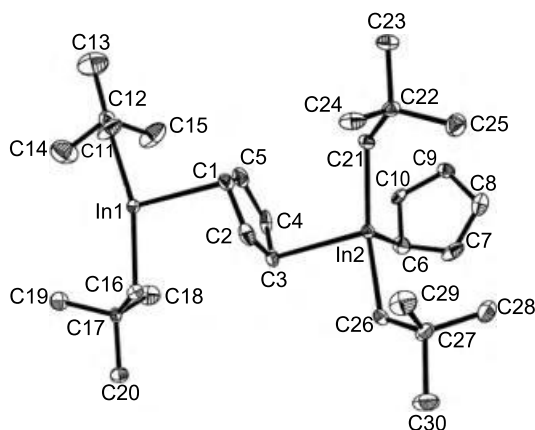


The most definitive examples of heteroleptic organoindium (III) compounds are generally found for mixed alkyl-cyclic systems. Ligand redistribution reactions between  $\text{InCp}_3$

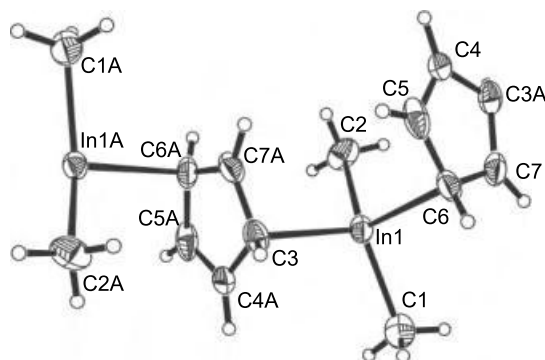
and  $\text{InR}_3$  ( $\text{R} = \text{Me}$  and  $\text{CH}_2\text{CMe}_3$ ) in THF solution provided  $\text{R}_2\text{In}(\text{C}_5\text{H}_5)$  and  $\text{RIn}(\text{C}_5\text{H}_5)_2$ .<sup>52</sup> These heteroleptic organoindium(III) compounds were isolated as analytically pure crystalline solids; however, in THF solution, the compounds underwent a redistribution mechanism to afford equilibrium mixtures of the THF-adducts of  $\text{InR}_3$ ,  $\text{R}_2\text{In}(\text{C}_5\text{H}_5)$ ,  $\text{RIn}(\text{C}_5\text{H}_5)_2$ , and  $\text{In}(\text{C}_5\text{H}_5)_3$ . Single-crystal X-ray structural studies unequivocally showed the existence of the mixed alkyl-cyclic derivative  $[(\text{Me}_3\text{CCH}_2)_2\text{In}(\text{C}_5\text{H}_5)]$ , which revealed the compound to exist as a polymer with cyclopentadienide units bridging  $\text{In}(\text{CH}_2\text{CMe}_3)_2$  moieties (Figure 1).

Heteroleptic derivatives have also been prepared via metathesis and methane elimination reactions as illustrated by the synthesis of  $[\text{Me}_2\text{In}(\text{C}_5\text{H}_5)]$ , which was obtained by the reaction between  $[\text{Me}_2\text{InCl}]$  and  $\text{Li}(\text{C}_5\text{H}_5)$  in THF at  $145-160^\circ\text{C}$ .<sup>53</sup> An X-ray structural study identified an infinite linear polymer with cyclopentadienide units bridging  $\text{InMe}_2$  moieties through the 1 and 3 positions of the ring (Figures 2 and 3).

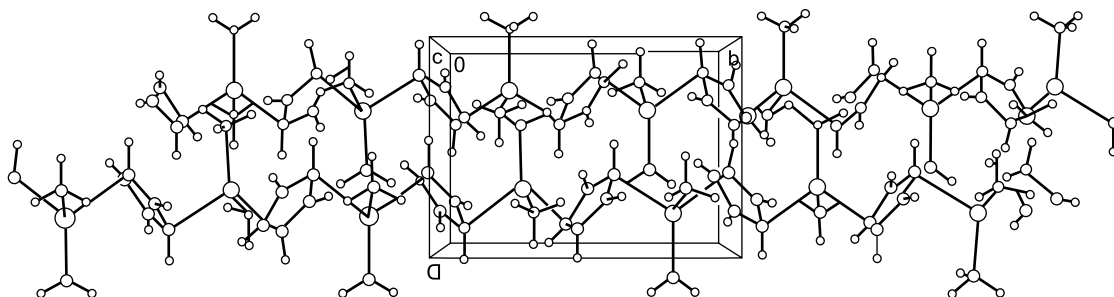
Like most heteroleptic derivatives,  $[\text{Me}_2\text{In}(\text{C}_5\text{H}_5)]$  when dissolved in THF exists as an equilibrium mixture of components  $[\text{Me}_2\text{In}(\text{C}_5\text{H}_5)]\cdot\text{THF}$ ,  $[\text{MeIn}(\text{C}_5\text{H}_5)_2]\cdot\text{THF}$ , and  $[\text{InMe}_3]\cdot\text{THF}$ .



**Figure 1** Single-crystal structure of  $[(\text{Me}_3\text{CCH}_2)_2\text{In}(\text{C}_5\text{H}_5)]_n$



**Figure 2** Polymeric chain of  $[\text{Me}_2\text{In}(\text{C}_5\text{H}_5)]_n$



**Figure 3** Unit cell of  $[\text{Me}_2\text{In}(\text{C}_5\text{H}_5)]_n$

**Table 1** Selective reported physical properties of some organoindium compounds

Compound	Phase	Mp (°C)	Bp (°C) (torr)	Sub. (°C) (torr)	Vapor press
InMe <sub>3</sub>	Solid	89	136 66–67(12)		
InEt <sub>3</sub>	liquid	–32	184 83–84(12)		$\log p = 2790/T + 8.98$
InPr <sub>3</sub>	liquid	–51	178 97(12)		$\log p = -3051/T + 9.20$
In( <i>i</i> -Pr) <sub>3</sub>	liquid	–	88 (12)		
InBu <sub>3</sub>	liquid	–	85–6(1)		$\log p = 3124/T + 8.72$
In( <i>i</i> -Bu) <sub>3</sub>	liquid	–	71–2(0.05)		$\log p = -3009/T + 8.81$
In( <i>s</i> -Bu) <sub>3</sub>	solid	–	70–2(0.1)		
In( <i>t</i> -Bu) <sub>3</sub>	solid	53–57		30(10 <sup>–2</sup> )	
InCp <sub>3</sub>	yellow solid	~160–164 dec.			
InCp	Pale yellow solid	169–170 dec. 170–171 dec.		50(0.01)	
Me <sub>2</sub> InCp	Colorless	190–196 dec.			
	Solid	195–200 dec.			
MeInCp <sub>2</sub>	Yellow Solid	151–160			
In(Ph) <sub>3</sub>	Solid	212	–		
In(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Solid	176–178			
InNp <sub>3</sub>	Solid	54–55	–	27(0.01)	
Np <sub>2</sub> InCp	Solid	188–190 dec.			
NpInCp <sub>2</sub>	Yellow Solid	126–127 dec.			
In(C≡C <i>t</i> -Bu) <sub>3</sub> ·NEt <sub>3</sub>	Solid	220 <sup>57</sup>			

## 2.2 Properties

Indium organometallics are generally pyrophoric and sensitive to air and moisture, with some exceptions.<sup>54</sup> The thermal decomposition pathway has been studied largely in order to understand how to achieve derivatives that will pyrolyze at lower temperatures with minimal impurities such as carbon. InR<sub>3</sub> with  $\beta$ -hydrogen's have been shown to decompose via a  $\beta$ -hydride elimination pathway to give the respective olefins and metal hydride.<sup>54</sup> Generally the possibility of  $\beta$ -elimination lowers the decomposition temperature of the metal alkyls, and in addition some branching at the  $\beta$  position weakens the In–C bond. Furthermore, the onset for the decomposition temperature decreases upon introduction of increased alkyl chain length and steric encumbrance.<sup>27,55</sup> In contrast, thermal solution decomposition studies of indium trialkyls possessing an  $\alpha$ -branch, for example, [In(*s*-Bu)<sub>3</sub>] and [In(*i*-Pr)<sub>3</sub>], have demonstrated decomposition to occur predominately through an  $\alpha$ -fission pathway to selectively give the corresponding alkyl radicals.<sup>54</sup>

A recent study on the stability of various indium alkyl derivatives has been performed using differential scanning calorimetry (DSC), which provides a comprehensive thermal “fingerprint” of the compounds.<sup>55</sup> In addition, when this method of thermal analyses is used in conjunction with thermogravimetric analysis coupled to FTIR and/or GCMS evolved gas analysis, it can provide a complete mechanism for the decomposition pathway of prospective compounds.<sup>56</sup>

Selective physical properties of some organoindium compounds are listed in Table 1.

Studies on the properties of trialkyl indium derivatives and their designated use in MOCVD have also been reported,<sup>58,59</sup> and for the first time a detailed study on the vibrational spectrum for InMe<sub>3</sub> has been reported.<sup>60</sup>

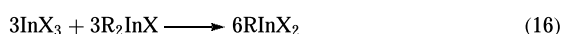
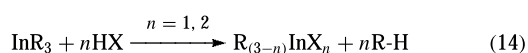
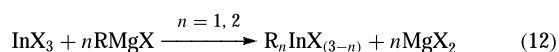
## 2.3 In(III) Adducts

Organoindium derivatives behave as Lewis acids, readily forming adducts with electron-donating species. A large number of organoindium chelating compounds have been identified and studied.<sup>55</sup> One of the most noticeable differences between chelated and nonchelated InR<sub>3</sub> is the associated reduced reactivity due in part to the saturation of the indium-metal coordination sphere. A novel use of alkyl indium chelate chemistry is for the purification of InR<sub>3</sub> by removal of extrinsic impurities for the semiconductor industry. This method is in commercial practice by Epichem. The method involves reacting InR<sub>3</sub> with an ultra-pure Lewis base to afford the trialkyl indium chelate as a stabilized nonvolatile adduct. This can subsequently be purified via recrystallization or distillation. The purified InR<sub>3</sub> is then obtained by controlled thermal dissociation of the adduct.<sup>55</sup> InMe<sub>3</sub> purified via this technique has been shown to have reduced silicon impurities by a factor of 100 and when used to fabricate III–V semiconductors thin films, enhanced carrier concentration and mobility were recorded.<sup>27</sup>

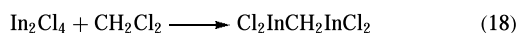
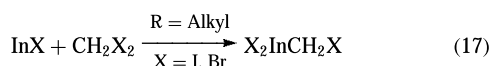
### 3 ORGANOINDIUM HALIDES

#### 3.1 Synthesis

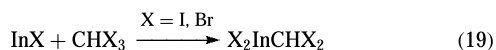
Organoindium halides can readily be prepared by many of the synthetic methods outlined for the preparation of organotin derivatives, but with stoichiometric control to afford the organoindium halide derivative.<sup>61–73</sup> For example, (a) reaction of  $\text{InX}_3$  with less than three equivalents of a lithium or Grignard reagent (equations 12–13), (b) reaction of  $\text{R}_3\text{In}$  with  $\text{HX}$ , which proceeds by elimination of a simple organic moiety (equation 14), (c) a redistribution reaction between  $\text{InX}_3$  and  $\text{R}_3\text{In}$  (equations 15–16).



Specialized methods include (a) reaction of halogens with  $\text{R}_3\text{In}$  to yield  $\text{R}_n\text{InX}_{3-n}$  compounds, and (b) reaction of an indium(I) or indium(II) halide with an organic halide via *Oxidative Addition* (equations 17–18).<sup>74–76</sup>



These indium halomethyl derivatives possess two-electron donor sites, namely the indium atom and the  $\text{CH}_2$  group where coordination may occur. Anionic ligands preferentially coordinate to indium atom (e.g.  $[\text{R}_4\text{N}]^+[\text{X}_3\text{InCH}_2\text{X}]^-$ ), while neutral ligands attack the  $\text{CH}_2$  group via nucleophilic substitution of the methylene halide following concomitant halide transfer to the indium atom to give  $\text{X}_3\text{InCH}_2\text{L}$ .<sup>77</sup> The potential application as indium metal ylids was also investigated for adducts with group 16 ligands.<sup>77</sup> An extension to the novel preparation of indium(III) halomethyl derivatives via oxidative insertion of  $\text{InX}$  into the carbon–halide bond of methylene dihalides ( $\text{X-CH}_2\text{X}$ ) (equation 17) has now been demonstrated to be feasible for haloforms ( $\text{CHX}_3$ ) for the preparation of  $\text{X}_2\text{InCHX}_2$  compounds (equation 19).<sup>78</sup>



The reactivity of  $\text{X}_2\text{InCHX}_2$  with anionic ligands is analogous to  $\text{X}_2\text{InCH}_2\text{X}$ , where the corresponding salts  $[\text{X}_3\text{InCHX}_2]^-$  and  $[\text{X}_3\text{InCH}_2\text{X}]^-$  can be isolated respectively. However, unlike  $\text{X}_2\text{InCH}_2\text{X}$ , when  $\text{X}_2\text{InCHX}_2$  derivatives undergo reaction with neutral ligands (L) the associated adduct

of  $\text{InX}_3$  is formed. This suggests that the decomposition of the dihalomethyl indium compounds ( $\text{X}_2\text{InCHX}_2$ ) proceeds via carbene elimination (equation 20).

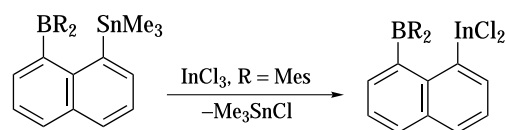


The transmetalation of organotin derivatives to their indium counterparts (Scheme 1) has recently been used to investigate a new route to Group 13 polyfunctional Lewis acids, which are becoming important in catalysis, molecular recognition, and materials synthesis.<sup>79–82</sup>

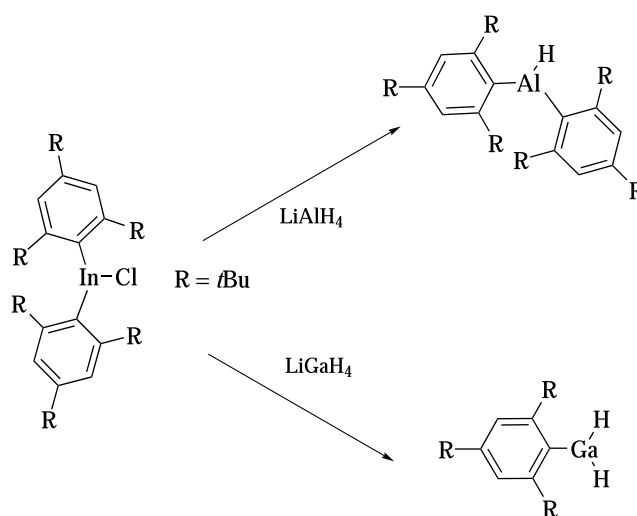
As synthetic reagents, sterically encumbered organoindium halides have been used in transmetalation reactions to prepare the first example of a monomeric base-free group 13 hydride complex (Scheme 2).<sup>83</sup>

The first example of the indium carbene complexes have been reported using the stable imidazolidene carbene derivatives (Scheme 3).<sup>84–86</sup>

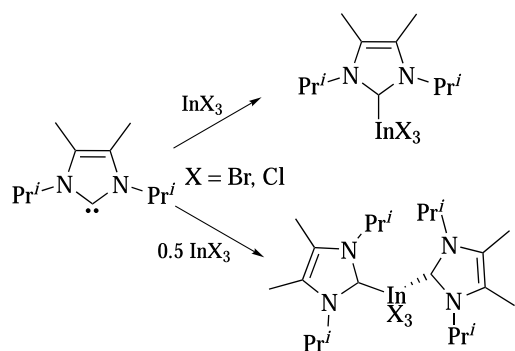
The indium carbene derivatives were prepared from a THF solution at room temperature. The reaction of excess carbene to the  $\text{InX}_3$  (5:1) only afforded the 2:1 adduct and unreacted carbene, which suggested that higher adduct formation was not sterically viable. X-ray crystallography showed the 1:1 indium bromide adduct to be monomeric and tetrahedral



**Scheme 1** Transmetalation of organotin to organoindium derivatives



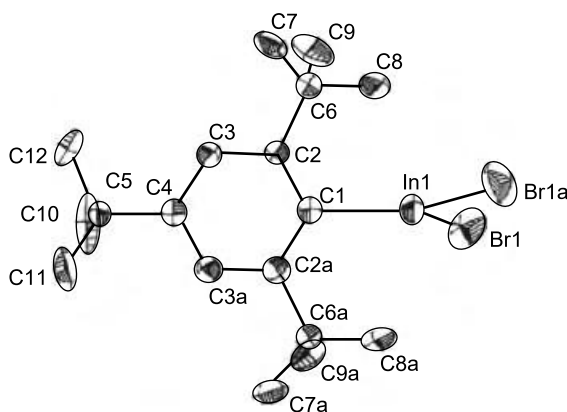
**Scheme 2** Preparation of a monomeric base-free group 13 hydride complexes



**Scheme 3** Formation of organoindium carbene halide derivatives

and both bromo and chloro 2:1 adducts to have a trigonal-bipyramidal geometry, and surprisingly two axial halides and one equatorial. The treatment of the indium halide with one equivalent of the carbene in the presence of water was found adventitiously to afford a novel ionic indium imidazolium species (Scheme 4).<sup>84,87</sup> Additional indium analogues with increasing steric encumbrance provided by the carbene moiety have been investigated to determine the stabilizing effect on the indium coordination sphere.<sup>85,86</sup>

The preparation of “inert” organoindium halides with sterically demanding ligands such as Mes (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), Trip (2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), or Mes\* (2,4,6-*t*-BuC<sub>6</sub>H<sub>2</sub>), and so on has become a recent trend.<sup>88–90</sup> Most of these derivatives are prepared via the normal synthetic routes outlined earlier. A



**Figure 4** Structure of [In(Mes\*)X<sub>2</sub>], X = Br, Cl

key property provided by the added steric protection from the ligands is the lack of dimerization, and association of the reaction solvent such as THF or ether (e.g. [In(Mes\*)X<sub>2</sub>], Figure 4).<sup>89,90</sup>

## 4 ORGANOINDIUM PNICTOGENS

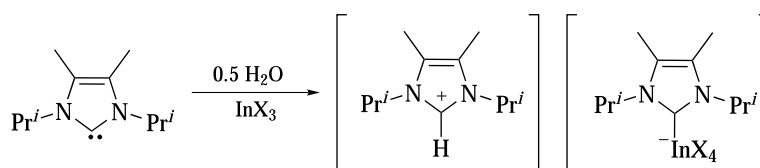
The number of indium and other Group 13 inter and intra pnictogen adducts have been attributed to an investigation of their coordination chemistry, kinetic reactivity, and application as single-source precursors to binary III-V semiconductors and catalysis. Organometallic adducts of Group 13 have been largely dominated by tetrahedral coordination mode. However, there has been a strong impetus to synthesize and characterize organoindium derivatives of higher coordination number, which can be achieved with bulky substituents, the aspiration being to form derivatives with a monomeric nature and inert or reduced kinetic reactivity, and compounds free from reaction solvent incorporation.

There are three main bonding modes which are prevalent for organoindium pnictogens: (a) inter-datively, (b) intra-datively, and (c) direct. In addition, mixed bonding modes (d) are also commonplace (Scheme 5).

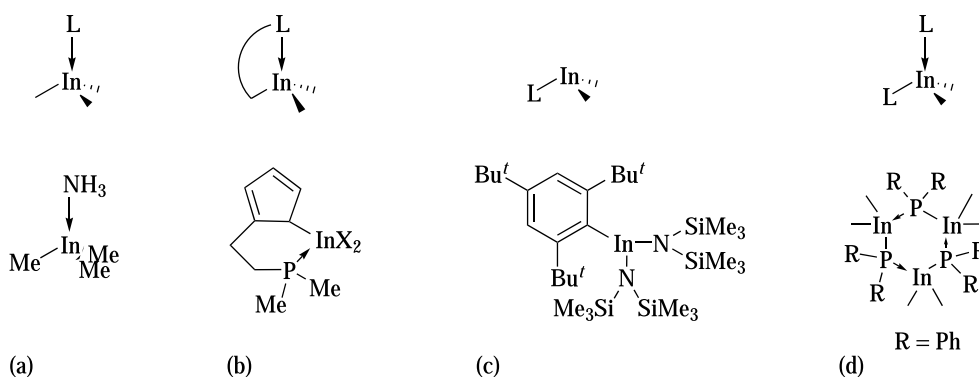
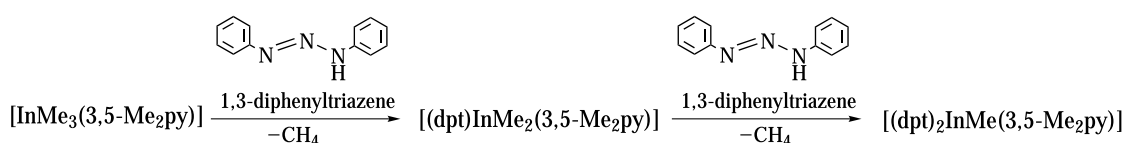
The mixed bonding mode generally occurs for indium pnictogen adducts with reduced steric demand, leading to the formation of the heterocyclic [Me<sub>2</sub>InL(SiR<sub>3</sub>)<sub>2</sub>]<sub>x</sub> compounds. These III-V heterocycles are made up of the amphoteric R<sub>2</sub>M-LR<sub>2</sub> moiety, which simultaneously reacts as a Lewis acid (In) and a Lewis base (pnictogens). The lone pair character of the heavier pnictogen and the presence of an adjacent empty orbital of indium ensure that associated species with “head to tail” ring-coordinate centers are normally observed. Additionally, the affinity of both In and the pnictogen groups toward attaining tetrahedral coordination geometry limits monomeric compound formation (R<sub>2</sub>M-ER<sub>2</sub>), which is realized by the use of highly sterically demanding substituents.

### 4.1 Synthesis

Intermolecular adducts of organoindium can be prepared in a hydrocarbon solvent by reaction with a Lewis base<sup>91,92</sup> (equation 21), or via displacement of more labile adducts

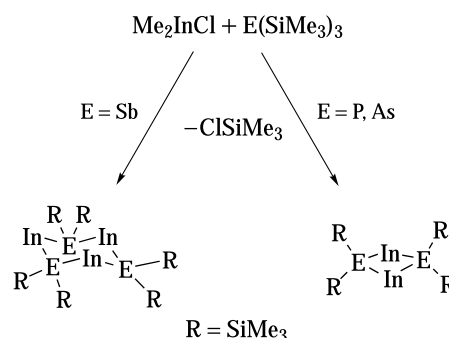
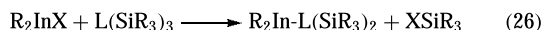
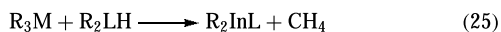
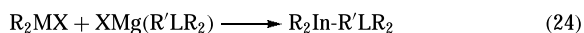
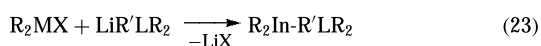
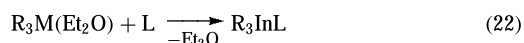


**Scheme 4** Formation of ionic indium imidazolium species

**Scheme 5** Bonding modes for organoindium pnictogens**Scheme 6** Synthesis of organoindium compounds via methane elimination

such as etherates<sup>93</sup> (equation 22). Adduct formation can generally be reversed cleanly by controlled distillation to obtain adduct free derivatives.<sup>27,55,93</sup> Intramolecular adducts can be formed by metathesis type reactions between organoindium halides with lithium<sup>94–115</sup> and Grignard<sup>93,116–119</sup> reagents (equations 23–24) or by elimination of small gaseous molecules<sup>120–151</sup> (equation 25, e.g. Scheme 6).<sup>137,151</sup>

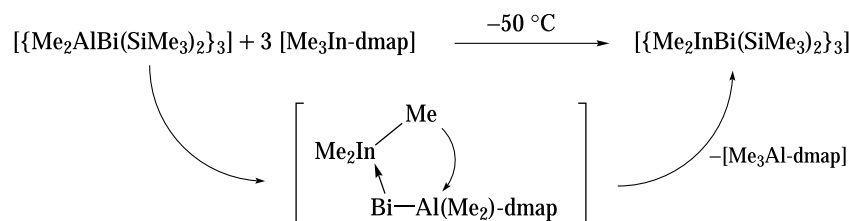
Additionally, the use of metal halides has been shown to accelerate alkane elimination and product formation, for example, the reaction of phenylacetonitrile with  $\text{InMe}_3$ . The introduction of  $\text{CsF}$  has been perceived to act as a catalyst by forming intermediate metalates of the types  $[\text{XMMe}_3]^-$  and  $[\text{Me}_3\text{MXMMe}_3]^-$ .<sup>120</sup>

**Scheme 7** Dehalosilylation synthetic pathway

Dehalosilylation reactions involving  $\text{L}(\text{SiR}_3)_x$  and  $\text{XInR}_2$  also prove to be a versatile synthetic pathway.<sup>152–156</sup> The driving force for the reaction is the high propensity for  $\text{Si-X}$  bond formation ( $381 \text{ kJ mol}^{-1}$ ,  $\text{X} = \text{Cl}$ ), resulting in the elimination of  $\text{R}_3\text{Si-X}$  (equation 26, Scheme 7).

The dehalosilylation route, however, has not been utilized for the preparation of the analogous  $[(\text{Me}_2\text{In})\text{Bi}(\text{SiMe}_3)_2]_3$

owing to the lack of stable  $\text{In-Bi}$  reagents. This has been recently overcome by the low-temperature ( $-50^\circ\text{C}$ ) metathesis reaction involving  $[(\text{Me}_2\text{Al})\text{Bi}(\text{SiMe}_3)_2]_3$  and the Indium Lewis base adduct  $[\text{InMe}_3(\text{dmap})]$ , ( $\text{dmap} = 4\text{-dimethylaminopyridine}$ ).<sup>157</sup> The key factor in the reaction pathway is the presence of the strong Lewis base, which increases the reactivity of  $[(\text{Me}_2\text{Al})\text{Bi}(\text{SiMe}_3)_2]_3$  by  $\text{Al-Bi}$  cleavage of the  $\text{Al-Bi}$  heterocycle. The concerted coordination of  $\text{InMe}_3$  affords the Lewis base stabilized intermediate  $[\text{InMe}_3(\text{Me}_3\text{Si})_2\text{BiAlMe}_2(\text{dmap})]$ , which rearranges to give  $[(\text{Me}_2\text{In})\text{Bi}(\text{SiMe}_3)_2]_3$ .<sup>124,157</sup> In the absence of the Lewis base, no reaction was found to occur. Furthermore, this reaction pathway has also been successfully implemented for the preparation of other Group 13 adducts of group 15 (Scheme 8).<sup>152</sup>



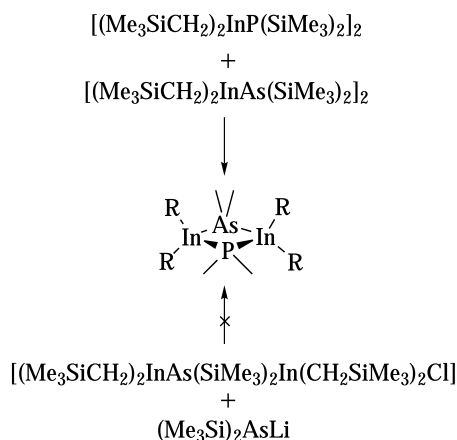
**Scheme 8** Formation of In-Bi hetrocyclic derivatives

## 4.2 Mixed Organoindium Pnictogens

The only example of a mixed organoindium pnictogen was obtained by equilibration of  $[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$  with  $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$  in a 1:1 mol ratio.<sup>158</sup> The formation of the  $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{P}(\text{SiMe}_3)_2]$  was confirmed by X-ray crystallography, which showed the In-As-In-P ring to be planar (Table 2). In addition, a combination of elemental analysis, multinuclear NMR, and EI-MS shows no residual indication that the product is a mixture of the starting reagents. Attempts to prepare the mixed indium pnictogen via the reaction between  $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]$  and  $(\text{Me}_3\text{Si})_2\text{AsLi}$  failed to give the desired compound, but rather  $[(\text{Me}_3\text{SiCH}_2)_3\text{In-As}(\text{SiMe}_3)_3]$ , Scheme 9.

## 4.3 Structures

The structural motifs of organoindium pnictogens bear consequence to the large coordination sphere of the indium center and good overlap between metal and ligand orbitals.<sup>162–166</sup> Variation in the geometric structures can also be influenced by the peripheral groups attached to the pnictogens.<sup>167</sup> For example, in the reaction between  $\text{InEt}_3$  and  $\text{R}_3\text{SiPH}_2$ ,  $[\text{EtInPSi}(\text{Pr}^i)_3]$  is cubane,<sup>168</sup>  $[\text{EtInPSiMe}_2(\text{Pr}^i)]$  is hexagonal prismatic,<sup>168</sup> and  $[\text{EtInPSiMe}_3]$  is a cyclic



**Scheme 9** Preparation of mixed indium pnictogen

structure.<sup>169</sup> As a result, organoindium derivatives can form elaborate geometric structures such as hetrocyclic rings in planar, boat, or chair conformation, in addition to hetrocubane and clusters (Table 2). Additionally, a good understanding of the geometric conformation is sought after for use in MOCVD thin film and nanocrystallite III-V fabrication processes.<sup>27,170–172</sup> Two reported indium hetrocubanes have been prepared by two differing routes. The first by reaction between haloorganoindium derivatives with a lithium phosphide,<sup>115</sup> whilst the second route entailed intramolecular methane elimination of the indiumamino derivative  $[(\text{C}_6\text{F}_5)\text{NHInMe}_2]$ .<sup>150</sup> In both cases, the 'In-P' and 'In-N' angles of P-In-P 88.8(1), In-P-In 91.2(1)°, N-In-N 84.3(4), and In-N-In 95.5(4)° respectively deviate from those of an ideal cube; however, this is more prevalent in the In-N cubane owing to the larger difference in III-V atomic radii (see Table 2 for structures).

## 5 ORGANOINDIUM CHALCOGENIDES

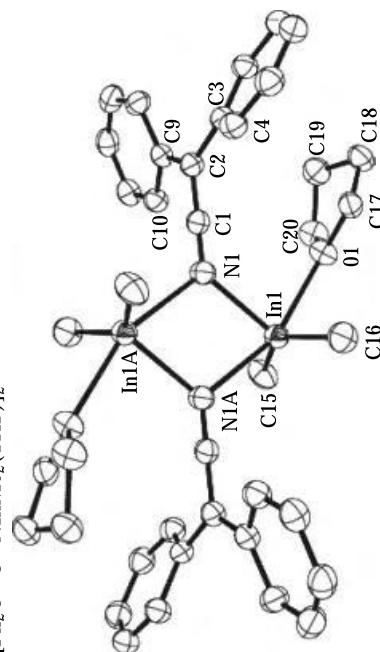
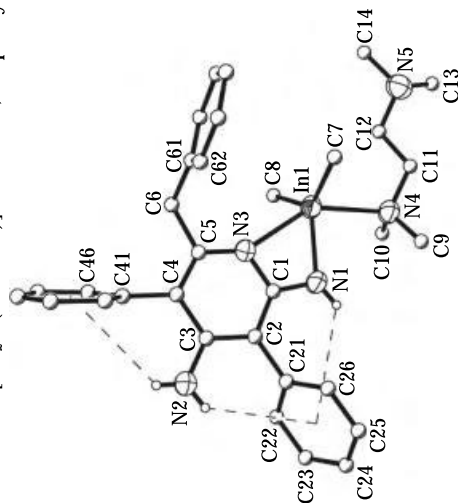
Without question, the predominant organoindium chalcogenides prepared and studied are the oxygen-containing derivatives (O-In-C), which are notable for their use as precursors for the fabrication of thin-film  $\text{In}_2\text{O}_3$ . Many of the O-In-C compounds bear the diketone,<sup>121,123,173–175</sup> Schiff base,<sup>130,134,136,140,176</sup> carboxylate, or alkoxide<sup>177–179</sup> ligands. The heavier organoindium chalcogenides are now receiving greater attention for their use in attaining thin film or nanocrystallite-semiconducting  $\text{In}_2\text{S}_3$  phases, which amongst other things are highly important for third generation solar cell hetrojunction formation.<sup>180–190</sup> Deposition of  $\text{In}_2\text{S}_3$  phases has been realized by using precursors such as the heteroleptic dithiocarbamate complexes  $[\text{R}_2\text{InS}_2\text{CNMe}(\text{CH}_2)_3\text{NMe}_2]$  ( $\text{R} = \text{Me}, \text{Et}, \text{naphthyl}, \text{C}_5\text{H}_{11}$ )<sup>188,189</sup> or thiocarboxylate and thiolate complexes.<sup>190</sup>

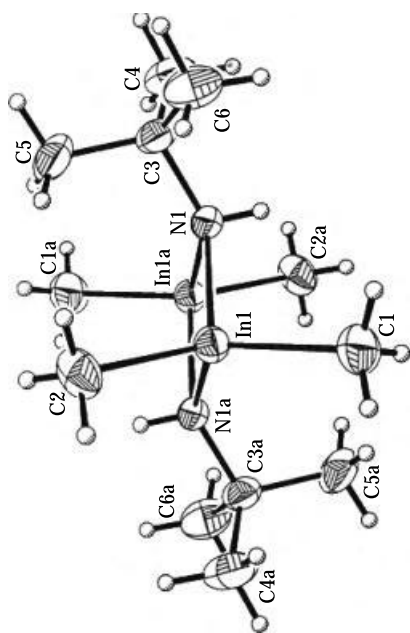
Organoindium oxygen derivatives have also been determined to be valuable catalysts in organic synthesis.<sup>191–194</sup> Chiral organoindium chalcogenides have been utilized as catalysts in asymmetric ring openings of cyclohexene norbornylene, and cyclooctene oxides with  $\text{TMSCN}$  (Scheme 10). The expected  $\beta$ -isocyanohydrins were obtained in yields varying from 45% to 80%, with the enantioselectivity varying from



**Table 2** Selected bond lengths and angles for organoindium pnictogens

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
<b>In-N</b> 2-Amino-1-[Me <sub>2</sub> In(TMEDA)]-4-amino-3,5-diphenyl-6-benzylpyridine	<b>In-N</b> In(1)-N(1) 2.180(3) In(1)-N(3) 2.439(3) In(1)-N(4) 2.523(3)	<b>N-In-C</b> N(1)-In(1)-C(7) 112.6(1) N(1)-In(1)-C(8) 114.5(2) N(3)-In(1)-C(8) 93.1(1)  <b>Other</b> N(1)-In(1)-N(3) 57.72(9) N(1)-In(1)-N(4) 90.01(9)	21
<b>In-N</b> [Ph <sub>2</sub> C=C=NInMe <sub>2</sub> (THF)] <sub>2</sub>	<b>In-N</b> In(1)-N(1) 2.252(3) In(1)-N(1A) 2.458(3)	<b>N-In-C</b> N(1)-In(1)-C(15) 112.2(2) N(1)-In(1)-C(16) 108.2(2)  <b>Other</b> N(1)-In(1)-N(1A) 73.9(1)	21



$[\text{Me}_2\text{InNH}(t\text{-Bu})]_2$ 

121

**N-In-C**

N(1)-In(1)-C(1) 106.6(1)  
N(1)-In(1)-C(2) 116.1(1)

**Other**

N(1)-In(1)-N(1A) 82.9(1)  
N(1)-In(1)···In(1A) 41.3(1)

**In-N**

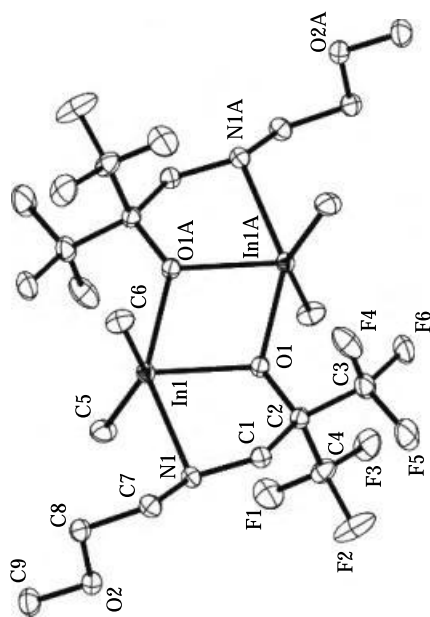
In(1)-N(1) 2.230(3)  
In(1a)-N(1) 2.220(3)  
In(1)-N(1A) 2.220(3)

**In-C**

In(1)-C(2) 2.157(4)  
In(1)-C(1) 2.160(4)  
In(1)···In(1A) 3.335(2)

**Other**

N-H 0.81(3)

 $[\text{InMe}_2(\text{OC}(\text{CF}_3)_2\text{CH}_2\text{NH}(\text{CH}_2\text{CH}_2\text{OMe}))_2]_2$ 

122

**N-In-C**

C(5)-In(1)-N(1) 93.20(5)

**Other**

O(1)-In(1)-N(1) 73.79(3)  
O(1A)-In(1)-N(1) 147.58(3)

**In-N**

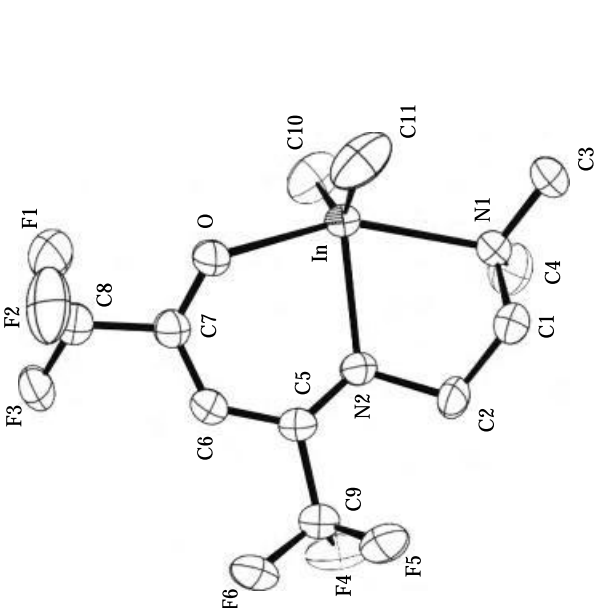
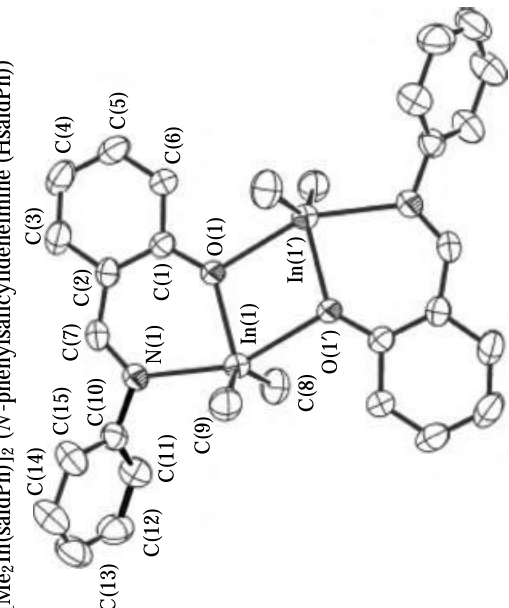
In(1)-N(1) 2.4655(10)

**In-C**

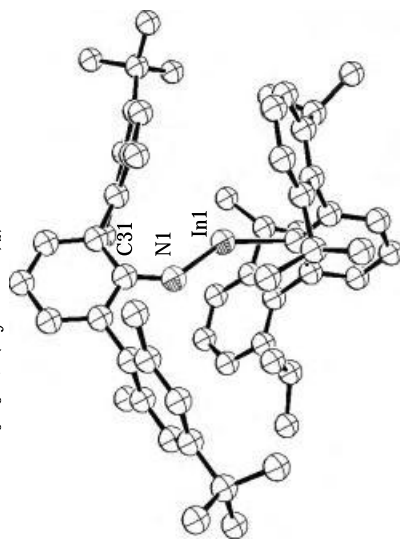
In(1)-C(5) 2.1397(14)

(cont'd overleaf)

Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
 $[\text{InMe}_2(\text{OC}(\text{CF}_3)\text{CH}_2\text{C}(\text{CF}_3)=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$	<b>In-N</b> In-N(1) 2.428(2) In-N(2) 2.321(2)	<b>N-In-C</b> C(10)-In-N(2) 111.2(1) C(11)-In-N(2) 112.9(1) N(1)-In-C(10) 96.1(1)	122
	<b>In-C</b> In-C(11) 2.142(2) In-C(10) 2.141(2) <b>Other</b> In-O 2.251(3)	<b>Other</b> O-In-N(1) 153.3(1) O-In-N(2) 80.4(1) C(10)-In-C(11) 135.9(11)	
 $[\text{Me}_2\text{In}(\text{saldPh})]_2$ (N-phenylsalicylideneimine (HsaldPh))	<b>In-N</b> In(1)-N(1) 2.366(3)	<b>Other</b> O(1)-In(1)-N(1) 82.01(11) O(1)-In(1)-O(1') 74.51(11) N(1)-In(1)-O(1') 156.23(11) In(1)-O(1)-In(1) 105.49(11)	123
	<b>In-C</b> In(1)-C(8) 2.137(5) In(1)-C(9) 2.133(5) <b>Other</b> In(1)-O(1') 2.477(3)		

Ar'InNAr'' (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>, Dipp = C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>,  
Ar'' = C<sub>6</sub>H<sub>3</sub>-2,6(Xyl-4-Bu')<sub>2</sub>)



**N-In-C**  
N-In-C 142.2(1)  
In-N-C 134.9(2)  
C-In-N-C 173.5(3)

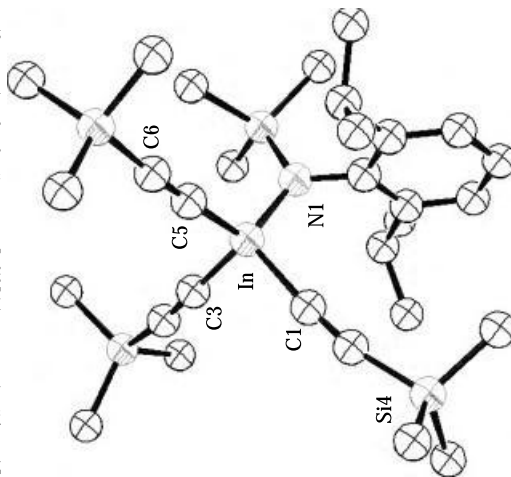
**In-N**  
In-N 1.928(3)

**In-C**  
In-C 2.127(3)

**Other**  
N-C 1.355(4)

127

[(Li<sup>+</sup>)<sub>2</sub> · (dioxane)<sub>7</sub>]<sub>0.5</sub> [2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>)In(C≡CSiMe<sub>3</sub>)<sub>3</sub>]<sup>-</sup> · 1.5 dioxane



**Other**  
In-C(1)-C(2) 170.9(2)  
In-C(3)-C(4) 169.0(2)  
In-C(5)-C(6) 168.1(2)  
C(1)-In-C(3) 112.5(7)  
C(1)-In-C(5) 106.9(7)  
C(3)-In-C(5) 112.5(7)

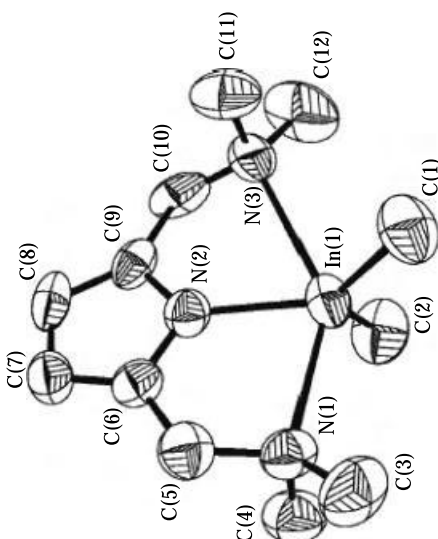
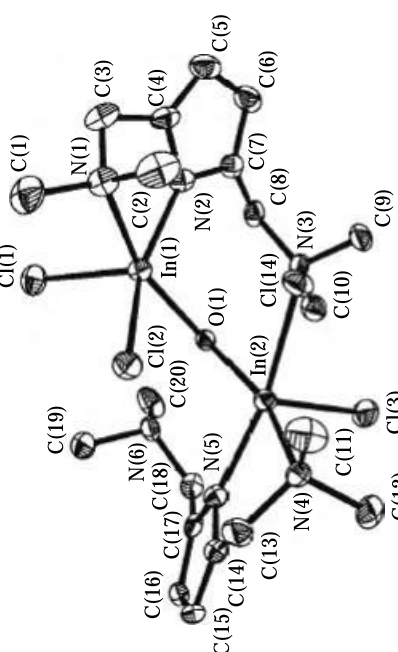
**In-N**  
In-N(1) 2.113(2)

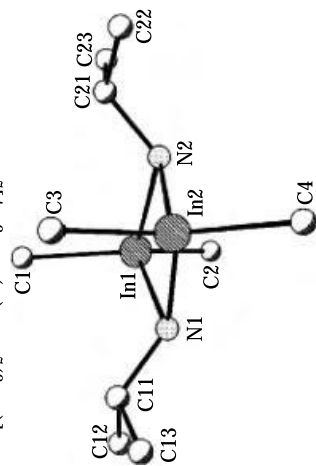
**In-C**  
In-C(1) 2.148(2)  
In-C(3) 2.154(2)  
In-C(5) 2.169(2)

57

(cont'd overleaf)

Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
	<b>In-N</b> In(1)-N(2) 2.108(5) In(1)-N(1) 2.519(5) In(1)-N(3) 2.681(6)  <b>In-C</b> In(1)-C(1) 2.187 (6) In(1)-C(2) 2.173(6)	<b>N-In-C</b> N(2)-In(1)-C(2) 113.1(2) N(2)-In(1)-C(1) 121.2(2) C(2)-In(1)-N(1) 105.4(2) C(1)-In(1)-N(1) 101.3(2) C(2)-In(1)-N(3) 94.5(3) C(1)-In(1)-N(3) 94.0(2)  <b>Other</b> N(2)-In(1)-N(3) 69.5(2) N(1)-In(1)-N(3) 140.96(19) C(2)-In(1)-C(1) 124.6(3) N(2)-In(1)-N(1) 71.9(2)	96
	<b>In-N</b> In(1)-N(2) 2.167(5) In(1)-N(1) 2.334(5) In(2)-N(5) 2.146(5) In(2)-N(4) 2.366(5)  <b>Other</b> In(1)-O(1) 2.136(4) In(1)-Cl(1) 2.434(2) In(1)-Cl(1) 2.519(2) In(2)-O(1) 2.175(4) In(2)-Cl(3) 2.462(2) In(2)-Cl(4) 2.4750(14)	<b>Other</b> N(2)-In(1)-N(1) 78.7(2) N(5)-In(2)-N(4) 77.6(2) O(1)-In(1)-N(2) 97.5(2) O(1)-In(1)-N(1) 156.9(2) N(1)-In(1)-Cl(1) 96.4(1) O(1)-In(1)-Cl(2) 84.7(1)	96

*cis*-[(CH<sub>3</sub>)<sub>2</sub>In-N(H)*i*-C<sub>3</sub>H<sub>7</sub>]<sub>2</sub>**In-N**

In(1)-N(1) 2.218(4)  
In(1)-N(2) 2.211(4)  
In(2)-N(1) 2.214(4)  
In(2)-N(2) 2.200(4)

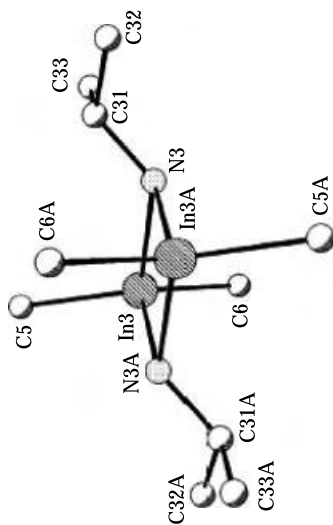
**In-C**

In(1)-C(1) 2.144(5)  
In(1)-C(2) 2.144(5)

**Other**

N(1)-In(1)-N(2) 83.92(14)  
N(2)-In(2)-N(1) 84.16(14)  
In(2)-N(1)-In(1) 95.0(2)  
In(2)-N(2)-In(1) 95.5(2)  
C(1)-In(1)-C(2) 129.2(2)  
C(3)-In(2)-C(4) 129.8(2)

128

*trans*-[(CH<sub>3</sub>)<sub>2</sub>In-N(H)*i*-C<sub>3</sub>H<sub>7</sub>]<sub>2</sub>**In-N**

In(3)-N(3) 2.221(4)  
In(3)-N(3A) 2.229(5)

**In-C**

In(3)-C(5) 2.140(7)  
In(3)-C(6) 2.134(7)

**Other**

In(3)-In(3A)  
3.2828(8)

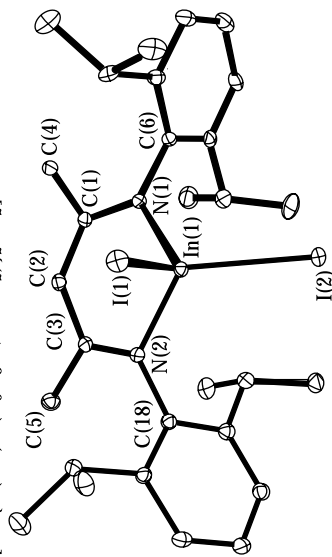
**N-In-C**

In(3)-N(3)-C(31) 119.8(4)  
In(3A)-N(3)-C(31) 122.5(4)

**Other**

N(3)-In(3)-N(3A) 84.9(2)  
In(3)-N(3)-In(3A) 95.1(2)  
C(5)-In(3)-C(6) 131.5(3)

128

[HC{C(Me)N(C<sub>6</sub>H<sub>3</sub>-2,6-*i*-Pr<sub>2</sub>)}<sub>2</sub>ML<sub>2</sub>]**In-N**

In(1)-N(1) 2.121(2)  
In(1)-N(2) 2.147(1)

**Other**

In(1)-I(1) 2.7008(2)  
In(1)-I(2) 2.6050(2)

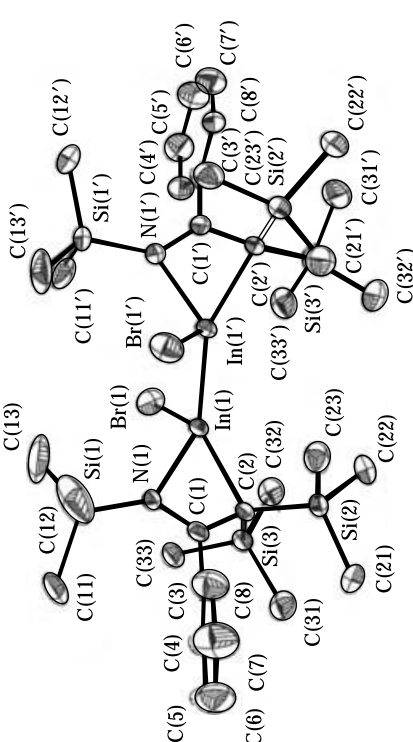
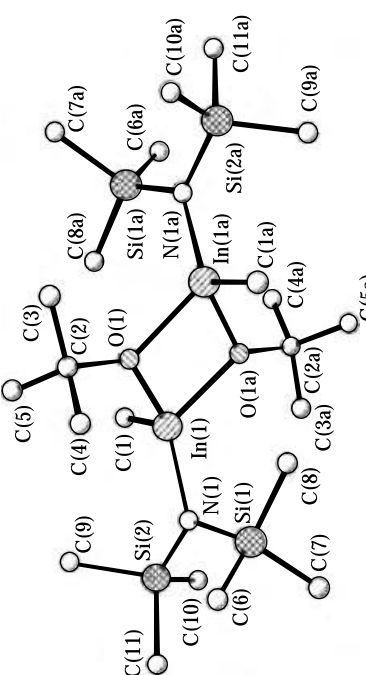
**Other**

In(1)-N(1)-C(1) 118.9(1)  
In(1)-N(2)-C(3) 118.9(1)  
N(1)-In(1)-N(2) 92.42(5)  
I(1)-In(1)-I(2) 111.748(6)  
N(1)-C(1)-C(2) 125.0(2)  
C(1)-C(2)-C(3) 131.3(2)  
C(2)-C(3)-N(2) 125.1(2)

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Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
	<b>In-N</b> In(1)-N(1) 2.254(5) In(1')-N(1') 2.251(5)	<b>N-In-C</b> N(1)-In(1)-C(2) 63.1(2) N(1')-In(1')-C(2') 63.4(2)	98
	<b>In-C</b> In(1')-C(2') 2.279(6) In(1')-C(1') 2.635(6) In(1)-C(2) 2.281(6) In(1)-C(1) 2.633(6) <b>Other</b> In(1')-Br(1') 2.561(2) In(1)-Br(1) 2.567(4) In(1)-In(1') 2.728(4)	<b>Other</b> C(2)-In(1)-Br(1) 121.9(2) N(1)-In(1)-In(1') 113.5(2) Br(1)-In(1)-In(1') 106.8(10) C(2')-In(1')-Br(1') 119.6(2) N(1')-In(1')-In(1) 117.4(2) Br(1')-In(1')-In(1) 107.4(10) N(1)-In(1)-Br(1) 110.2(2)	
	<b>In-N</b> In(1)-N(1) 2.093(4)	<b>N-In-C</b> N(1)-In(1)-C(1) 119.5(2)	101
	<b>In-C</b> In(1)-C(1) 2.160(5) <b>Other</b> In(1)-O(1) 2.138(3) O(1)-C(2) 1.459(5) In(1)-O(1a) 2.153(3) O(1)-In(1a) 2.153(3) In(1)-In(1a) 3.405(9)	<b>Other</b> N(1)-In(1)-O(1) 113.2(1) O(1a)-In(1)-C(1) 109.3(2) N(1)-In(1)-O(1a) 117.7(1) N(1)-In(1)-In(1a) 122.8(1) Si(1)-N(1)-In(1) 125.1(2) O(1)-In(1)-O(1a) 75.0(1) C(1)-In(1)-In(1a) 117(1) O(1)-In(1)-C(1) 114.1(2) In(1)-O(1)-In(1a) 105.0(1)	

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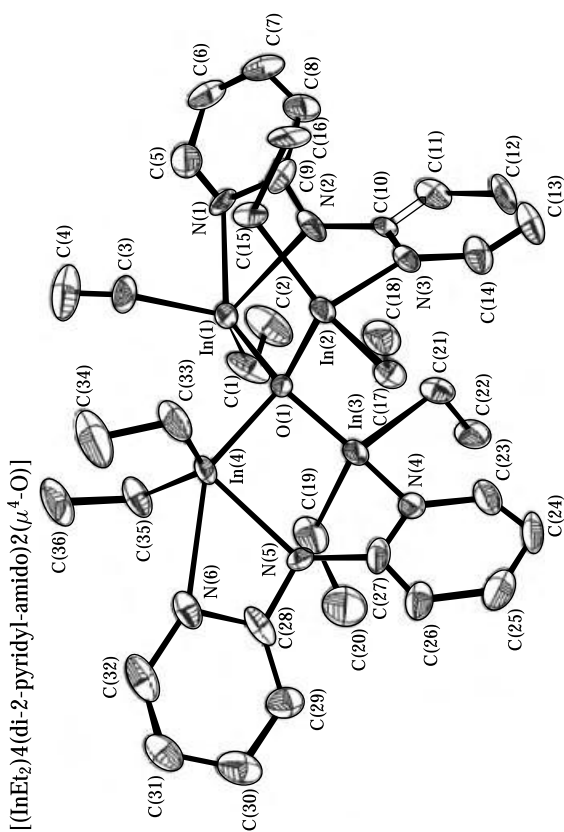
**N-In-C**  
 C(3)–In(1)–N(2) 115.3(2)  
 C(3)–In(1)–N(1) 90.1(2)  
 C(1)–In(1)–N(1) 94.8(2)

**Other**  
 O(1)–In(1)–O(1) 91.6(2)  
 N(2)–In(1)–N(1) 54.1(2)  
 In(2)–O(1)–In(4) 105.94(14)  
 In(2)–O(1)–In(3) 120.0(2)

**In-N**  
 In(1)–N(2) 2.361(4)  
 In(1)–N(1) 2.431(5)  
 In(2)–N(3) 2.240(4)  
 In(4)–N(5) 2.299(6)  
 In(4)–N(6) 2.546(5)

**In-C**  
 In(1)–C(1) 2.145(6)  
 In(2)–C(15) 2.129(5)  
 In(1)–C(3) 2.172(6)  
 In(4)–C(35) 2.182(4)

**Other**  
 In(4)–O(1) 2.273(3)  
 In(3)–O(1) 2.175(4)  
 In(2)–O(1) 2.160(3)



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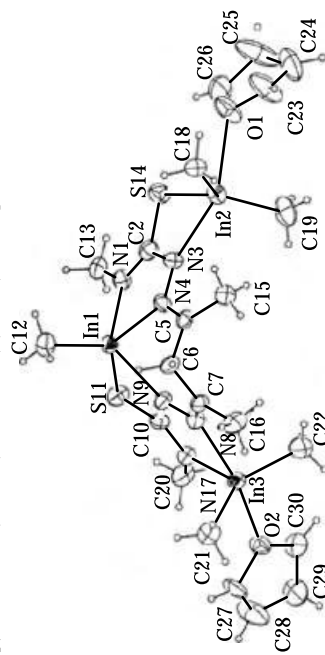
**Other**  
 N(9)–In(1)–N(1) = 124.0(4)  
 S(11)–In(1)–N(4) = 132.4(2)  
 S(14)–In(2)–C(19) = 112.5(5)  
 O(1)–In(2)–N(3) = 145.8(4)  
 O(2)–In(3)–N(8) = 161.4(3)

**In-N**  
 In(1)–N(1) 2.16(1)  
 In(1)–N(4) 2.30(1)  
 In(1)–N(9) 2.271(9)  
 In(2)–N(3) 2.33(1)  
 In(3)–N(17) 2.19(1)

**In-C**  
 In(1)–C(12) 2.17(4)  
 In(3)–C(21) 2.13(1)

**Other**  
 In(2)–O(1) 2.57(1)  
 In(1)–S(11) 2.550(4)  
 In(2)–S(14) 2.561(4)

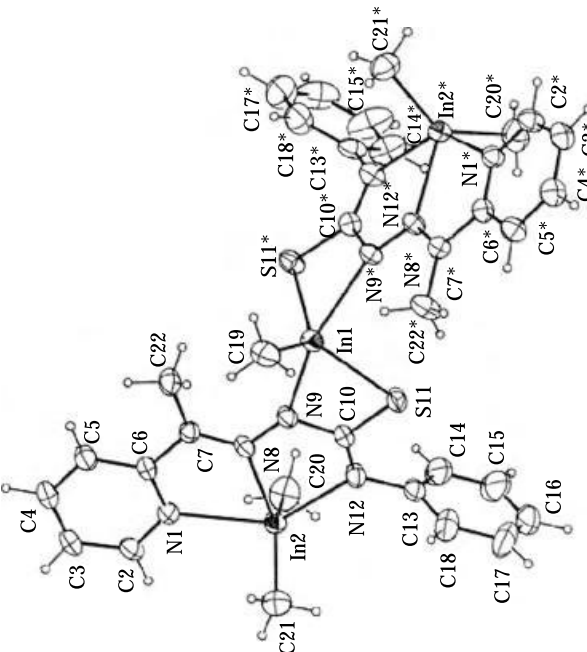
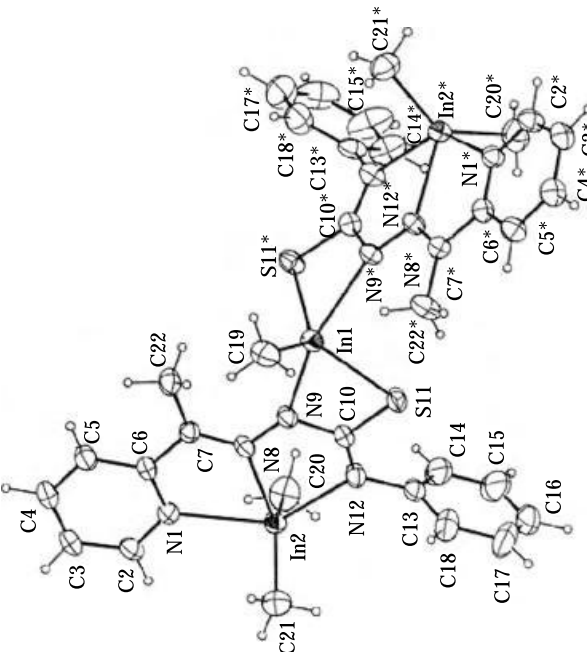
[(THF·Me<sub>2</sub>In)<sub>2</sub>CH<sub>2</sub>(MeCNNC(S)NMe)<sub>2</sub>InMe]

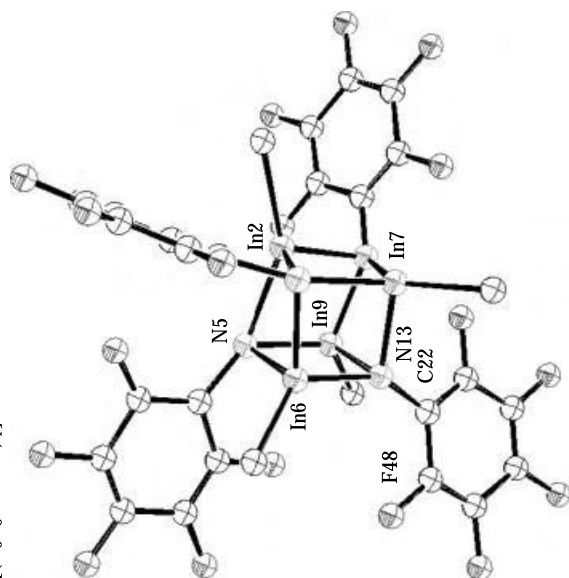


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Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
 <p><math>[(\text{Me}_2\text{In})_2(\text{NC}_5\text{H}_4\text{CMeNNC}(\text{S})\text{NC}_6\text{H}_5)_2\text{InMe}] \cdot \text{THF}</math></p>	<b>In-N</b> In(1)-N(9) 2.394(4) In(2)-N(1) 2.418(4) In(2)-N(8) 2.317(4) In(2)-N(12) 2.298(4)	<b>N-In-C</b> N(8)-In(2)-C(20) = 111.2(2)	145
	<b>In-C</b> In(1)-C(19) 2.10(1) In(2)-C(20) 2.151(7) In(2)-C(21) 2.143(7)	<b>Other</b> N(9)-In(1)-N(9*) 144.1(2) S(11)-In(1)-S(11*) 109.38(8) N(1)-In(2)-N(12) 137.4(1)	
	<b>Other</b> In(1)-S(1) 2.491(2)		
 <p><math>[(t\text{-Bu})_2\text{InN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{SiPh}_3]</math> (A)  <math>[\text{In}(\text{N}(\text{SiMe}_3)_2)_3]</math> (B)</p>	<b>In-N</b> In-N 2.104 (3) (A) In-N 2.049 (1) (B)	-	108

[C<sub>6</sub>F<sub>5</sub>NInMe<sub>4</sub>]**In-N**

In(1)-N(3) 2.202(9)  
In(3)-N(2) 2.167(10)  
In(4)-N(2) 2.227(10)

**In-C**

In(1)-C(1) 2.115(12)  
In(4)-C(4) 2.09.9(14)

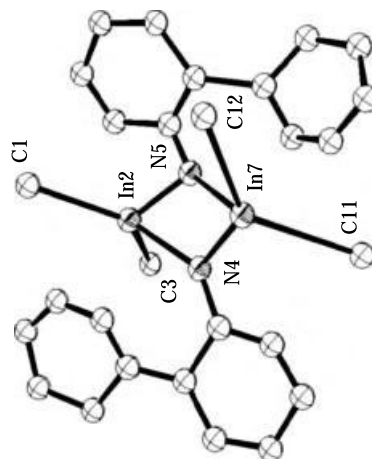
**Other**

In-In 3.26  
N-N 2.96 (average)

**Other**

N(1)-In(1)-N(3) 85.4(3)  
In(1)-N(1)-In(3) 94.9(4)

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[Me<sub>2</sub>InN(H)Ph]<sub>2</sub>**In-N**

In(2)-N(4) 2.242(7)  
In(2)-N(5) 2.236(5)  
In(7)-N(4) 2.238(4)  
In(7)-N(5) 2.255(7)

**In-C**

In(2)-C(1) 2.135(9)  
In(7)-C(12) 2.117(9)  
In(2)-In(7) 3.3275(9)

**N-In-C**

N(4)-In(2)-C(1) 107.6(3)  
N(4)-In(7)-C(11) 111.7(3)  
N(5)-In(2)-C(1) 111.8(3)  
N(5)-In(7)-C(12) 101.5(3)

**Other**

In(2)-N(4)-In(7) 95.9(2)  
In(2)-N(5)-In(7) 95.6(2)  
N(4)-In(2)-N(5) 82.6(2)  
N(4)-In(7)-N(5) 82.3(2)

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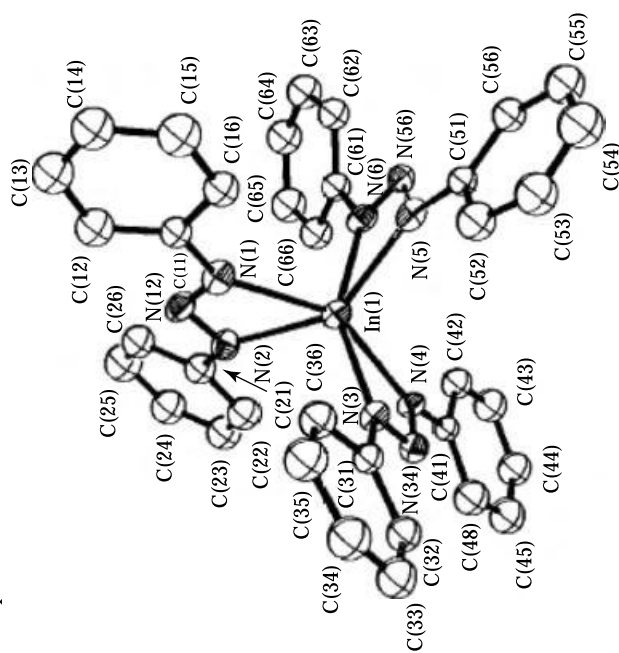
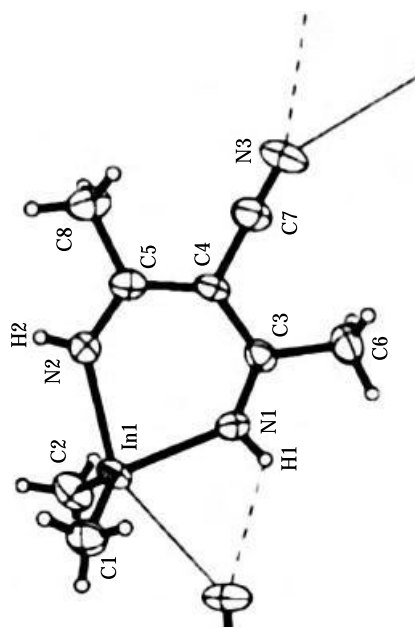
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[In(dpt)<sub>3</sub>]

**In-N**  
 In(1)-N(1) 2.259(9)  
 In(1)-N(2) 2.26(1)  
 In(1)-N(3) 2.22(1)  
 In(1)-N(4) 2.231(9)  
 In(1)-N(5) 2.24(1)  
 In(1)-N(6) 2.21(1)

**Other**  
 N(0)-In(0)-N(2) 55.2(4)  
 N(0)-In(0)-N(3) 105.6(4)  
 N(1)-In(1)-N(4) 148.9(4)  
 N(0)-In(0)-N(5) 102.0(3)  
 N(1)-In(1)-N(6) 99.7(4)  
 N(2)-In(0)-N(3) 107.8(4)  
 N(2)-In(1)-N(4) 102.9(4)  
 N(2)-In(1)-N(5) 144.1(4)  
 N(56)-N(6)-C(61) 117(1)  
 N(0)-N(12)-N(2) 109(1)  
 In(1)-N(1)-C(11) 143.6(9)  
 N(12)-N(1)-C(11) 118(1)


 [Me<sub>2</sub>In{HNC(Me)}<sub>2</sub>C(CN)]


**In-N**  
 In(1)-N(1) 2.179(2)  
 In(1)-N(2) 2.229(2)

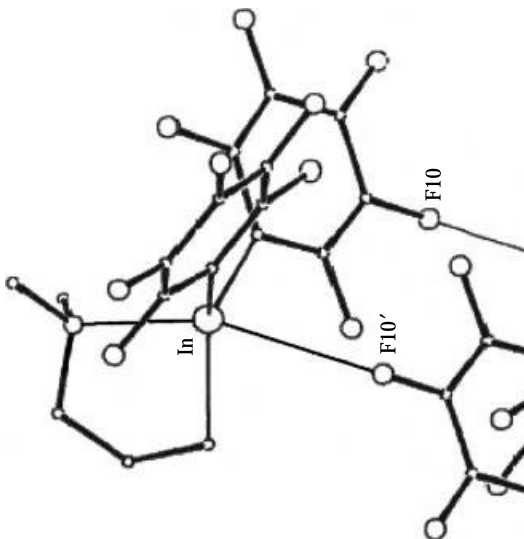
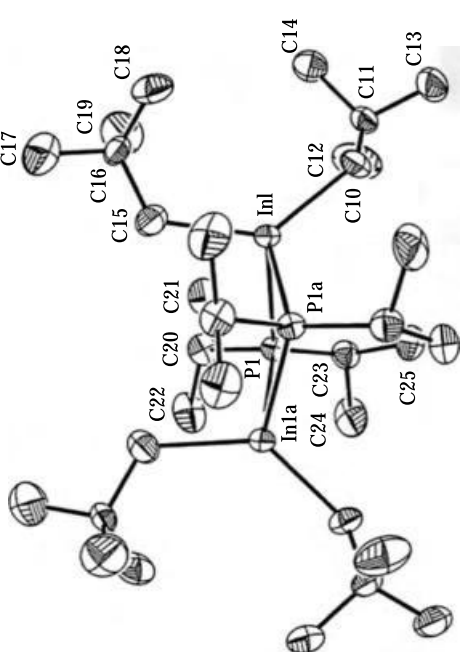
**In-C**  
 In(1)-C(1) 2.149(4)  
 In(1)-C(2) 2.147(4)

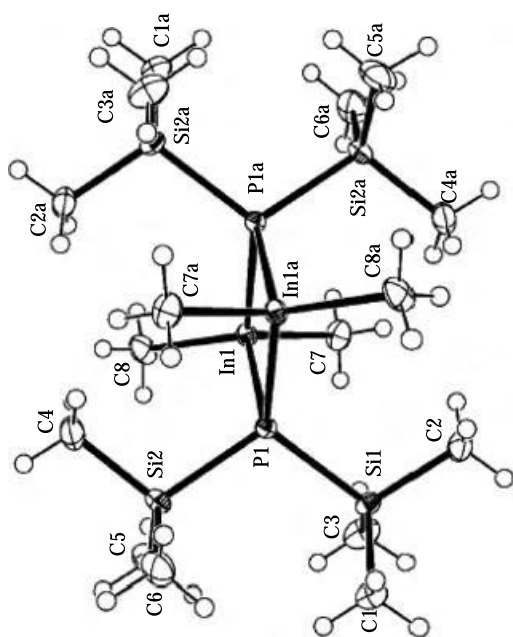
**N-In-C**  
 N(2)-In(1)-C(1) 105.0(1)  
 N(1)-In(1)-N(2) 80.91(9)  
 N(1)-In(1)-C(1) 112.3(1)  
 N(1)-In(1)-C(2) 111.6(1)  
 N(2)-In(1)-C(2) 103.4(1)

**Other**  
 C(1)-In(1)-C(2) 130.6(2)

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Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
$[(C_6F_5)_2In(CH_2)_3NMe_2]$	<b>In-N</b> In-N 2.310(5)  <b>In-C</b> In-C(12) 2.196(8) In-C(13) 2.151(6) In-C(6) 2.194(9)  <b>Other</b> In-F(10) 3.175(5)	<b>N-In-C</b> C(6)-In-N 107.3(2)  <b>Other</b> C(6)-In-C(12) 109.0(3)	109
			
<b>In-P</b> $[(Me_3CCH_2)_2InP(i-Pr)_2]_2$	<b>In-P</b> In(1)-P(1) 2.638(2) In(1)-P(1A) 2.664(2) In(2)-P(2) 2.663(2) In(2)-P(2A) 2.631(3)  <b>In-C</b> In(1)-C(10) 2.201(9) In(1)-C(15) 2.248(9) In(2)-C(30) 2.206(9) In(2)-C(35) 2.222(20)	<b>P-In-C</b> P(1)-In(1)-C(10) 117.3(2) P(1)-In(1)-C(15) 102.9(2) C(10)-In(1)-P(1A) 108.0(2) C(15)-In(1)-P(1A) 98.6(3) P(2)-In(2)-C(30) 99.7(3) P(2)-In(2)-C(35) 104.7(5) C(30)-In(2)-P(2A) 100.9(3) C(35)-In(2)-P(2A) 117.6(6)  <b>P-In-P</b> P(1)-In(1)-P(1A) 83.6(1) P(2)-In(2)-P(2A) 83.3(1)	133
			

[Me<sub>2</sub>InP(SiMe<sub>3</sub>)<sub>2</sub>]

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**P-In-P**

P(1)-In(1)-P(1a) 86.7(1)

**Other**

In(1)-P(1)-In(1a) 93.3(1)  
 C(7)-In(1)-C(8) 116.9(1)  
 Si(1)-P(1)-Si(2) 109.8(1)

**In-P**

In(1)-P(1) 2.632(1)

In(1)-P(1a) 2.628(1)

**In-C**

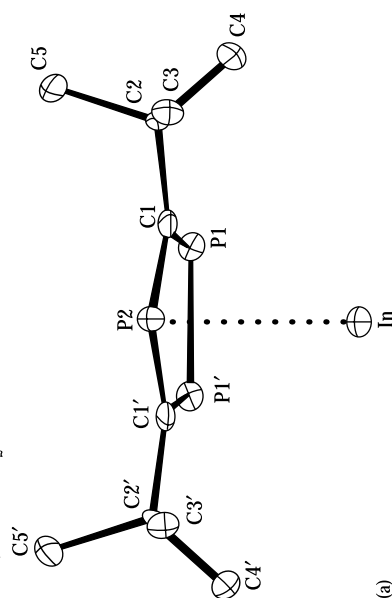
In(1)-C(7) 2.173(2)

In(1)-C(8) 2.174(2)

**Other**

P(1)-Si(1) 2.251(1)

P(1)-Si(2) 2.251(1)

[In( $\eta^5$ -P<sub>3</sub>C<sub>2</sub>Bu<sub>t</sub>)]

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C(1)-P(1)-P(1') 100.2(3)

C(2)-C(1)-P(1) 119.8(6)

P(1)-C(1)-P(2) 119.8(6)

C(1)-P(2)-C(1') 100.0(7)

**In-P**

In-P(1) 3.035(3)

In-P(2) 3.108(4)

**In-C**

In-C(1) 2.981(9)

**Other**

P(1)-C(1) 1.748(10)

P(1)-P(1') 2.111(5)

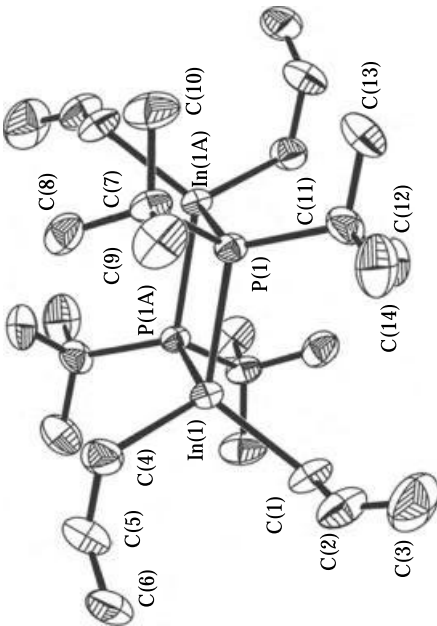
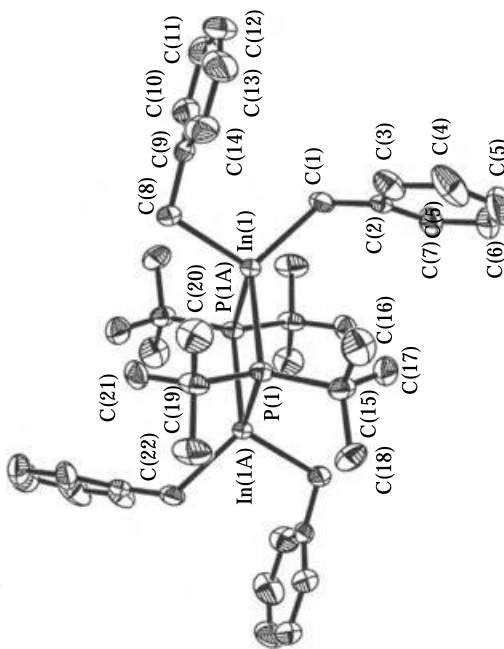
In-centroid 2.598(9)

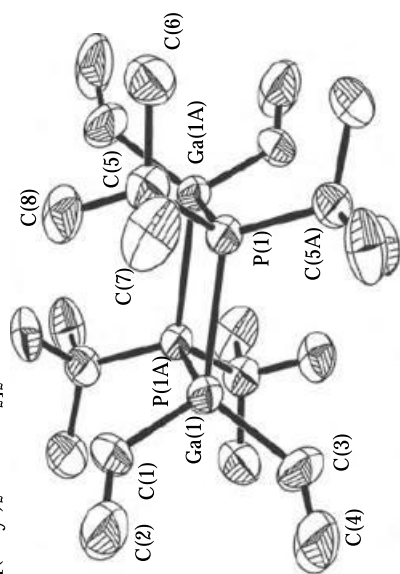
P(2)-C(1) 1.781(10)

(a)

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Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
[(allyl) <sub>2</sub> InP( <i>ν</i> -Bu) <sub>2</sub> ] <sub>2</sub> 	<b>In-P</b> In(1)-P(1) 2.639(1) In(1)-P(1A) 2.645(1)	<b>P-In-P</b> P(1)-In(1)-P(1A) 86.34(3)	102
	<b>In-C</b> In(1)-C(1) 2.204(4) In(1)-C(4) 2.218(4)	<b>Other</b> In(1)-P(1)-In(1A) 93.66(3) C(1)-In(1)-C(4) 107.3(2) C(7)-P(1)-C(11) 112.2(2)	
	<b>Other</b> P(1)-C(7) 1.895(4) P(1)-C(11) 1.898(4)		
[(benzyl) <sub>2</sub> InP- <i>t</i> -Bu <sub>2</sub> ] <sub>2</sub> 	<b>In-P</b> In(1)-P(1) 2.637(2) In(1)-P(1A) 2.649(2)	<b>P-In-P</b> P(1)-In(1)-P(1A) 85.11(6)	102
	<b>In-C</b> In(1)-C(1) 2.212(7) In(1)-C(8) 2.228(7)	<b>Other</b> In(1)-P(1)-In(1A) 94.89(6) C(1)-In(1)-C(8) 105.0(3) C(15)-P(1)-C(19) 112.8(4) C(1)-In(1)-P(1) 125.9(2) C(1)-In(1)-P(1A) 113.6(2) C(8)-In(1)-P(1) 112.7(2) C(8)-In(1)-P(1A) 113.8(2) C(2)-C(1)-In(1) 121.5(5) C(9)-C(8)-In(1) 111.5(5)	
	<b>Other</b> P(1)-C(15) 1.889(8) P(1)-C(19) 1.892(8)		

[(vinyl)<sub>2</sub>InP-*t*-Bu<sub>2</sub>]<sub>2</sub>

102

**P-In-P**

P(1)-In(1)-P(1A) 86.42(3)

**Other**

In(1)-P(1)-In(1A) 93.58(3)  
 C(5)-P(1)-C(5A) 112.5(2)  
 C(2)-C(1)-In(1) 131.1(7)  
 C(4)-C(3)-In(1) 131.2(7)  
 C(1)-In(1)-C(3) 110.3(3)

**In-P**

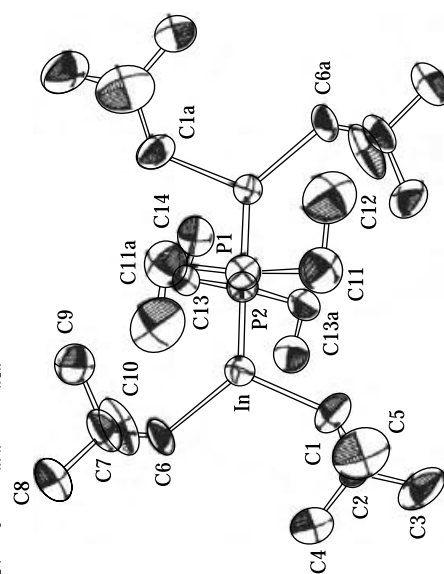
In(1)-P(1) 2.6211(8)

**In-C**

In(1)-C(1) 2.166(6)  
 In(1)-C(3) 2.163(6)

**Other**

P(1)-C(5) 1.894(3)

[(Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>InPEt<sub>2</sub>]<sub>2</sub>

146

**P-In-P**

P(1)-In-P(2) 82.91(6)

**Other**

P(1)-In-C(1) 111.1(2)  
 P(1)-In-C(6) 115.7(4)  
 P(1)-In-C(6') 101.2(7)  
 P(2)-In-C(1) 100.5(2)  
 P(2)-In-C(6) 124.6(4)  
 P(2)-In-C(6') 118.1(6)

**In-P**

In-P(1) 2.623(2)

In-P(2) 2.641(2)

**In-C**

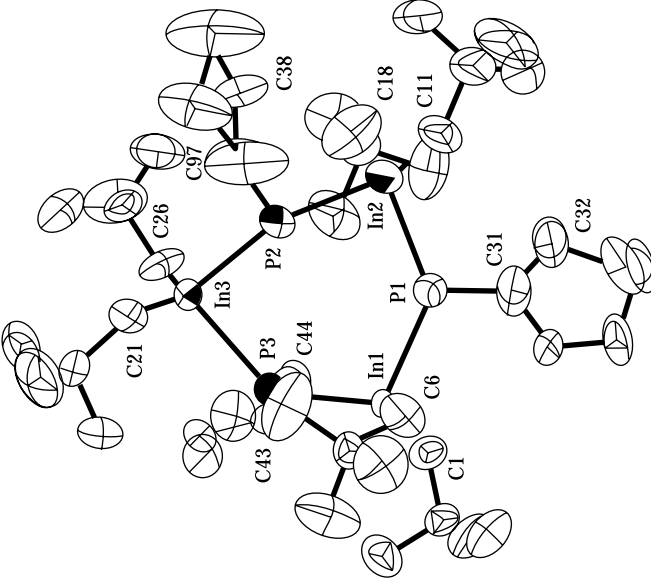
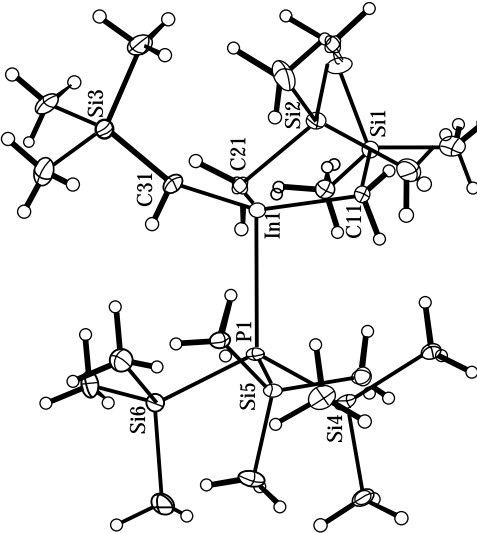
In-C(1) 2.211(8)

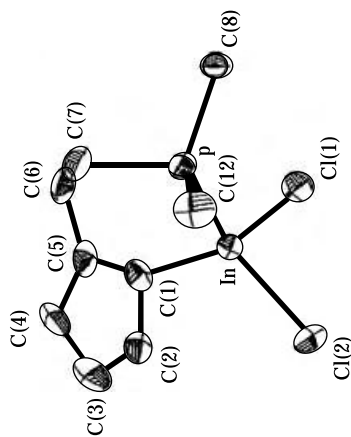
In-C(6) 2.17(2)

(cont'd overleaf)



Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
	<b>In-P</b> In(1)-P(1) 2.644(3) In(1)-P(3) 2.613(3) In(2)-P(2) 2.645(3) In(2)-P(1) 2.637(3) In(3)-P(3) 2.659(2) In(3)-P(2) 2.625(3)  <b>In-C</b> In(1)-C(1) 2.195(8) In(1)-C(6) 2.22(1) In(2)-C(11) 2.20(1) In(2)-C(16) 2.19(2) In(3)-C(21) 2.188(9) In(3)-C(26) 2.16(1)	<b>P-In-P</b> P(1)-In(1)-P(3) 101.18(9) P(1)-In(2)-P(2) 92.85(8) P(2)-In(3)-P(3) 93.69(8)  <b>Other</b> P(1)-In(1)-C(1) 98.1(3) P(3)-In(1)-C(6) 106.5(3) P(1)-In(1)-C(6) 104.4(3) P(3)-In(1)-C(6) 113.3(3) P(1)-In(2)-C(11) 105.5(3) P(2)-In(2)-C(11) 104.5(3) P(1)-In(2)-C(16) 118.3(4) P(2)-In(2)-C(16) 103.5(5) P(2)-In(3)-C(21) 98.4(3) P(3)-In(3)-C(21) 108.0(3) P(2)-In(3)-C(26) 113.9(3)	146
	<b>In-P</b> In(1)-P(1) 2.7713(15)  <b>In-C</b> In(1)-C(31) 2.207(6) In(1)-C(11) 2.206(6) In(1)-C(21) 2.218(6)  <b>Other</b> P(1)-Si(5) 2.2809(23)	<b>P-In-C</b> P(1)-In(1)-C(11) 98.45(16)  <b>Other</b> P(1)-Si(4)-C(42) 109.39(20) C(11)-In(1)-C(31) 117.53(22) In(1)-P(1)-Si(5) 112.73(7) In(1)-C(31)-Si(5) 117.7(3)	160

(i-Bu)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)InCl<sub>2</sub>

**P-In-C**  
P-In-C(1) 104.2(2)

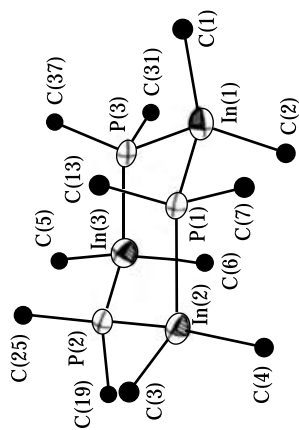
**In-P-C**  
In-P-C(7) 103.7(3)  
In-P-C(8) 112.3(3)  
In-P-C(12) 111.4(3)

**Other**  
Cl(1)-In-C(1) 108.2(3)  
C1(2)-In-C(1) 118.6(2)  
Cl(1)-In-Cl(2) 101.9(1)  
P-In-Cl(1) 113.0(1)  
P-In-Cl(2) 111.2(1)

**In-P**  
In-P 2.595(2)

**In-C**  
In-C(1) 2.202(9)

**Other**  
P-C(7) 1.843(9)  
P-C(8) 1.860(9)  
P-C(12) 1.854(10)  
In-Cl(1) 2.383(3)  
In-Cl(2) 2.364(3)

[Me<sub>2</sub>InPPh<sub>2</sub>]<sub>3</sub>

**P-In-P**  
P(1)-In(1)-P(3) 104.0(1)  
P(1)-In(2)-P(2) 99.8(1)  
P(2)-In(3)-P(3) 102.5(1)

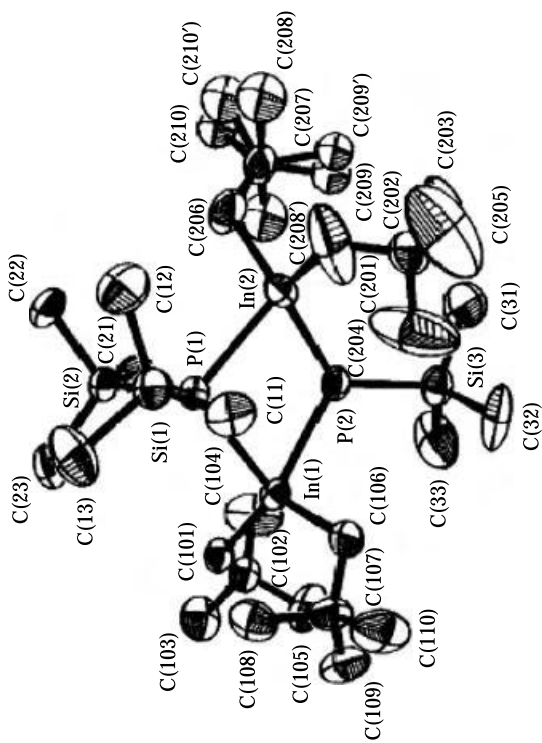
**Other**  
In(1)-P(3)-In(3) 118.2(1)  
P(1)-In(1)-C(1) 106.7(2)  
P(1)-In(2)-C(4) 109.0(2)  
P(2)-In(3)-C(5) 108.0(2)

**In-P**  
In(1)-P(1) 2.593(1)  
In(1)-P(3) 2.625(2)  
In(2)-P(1) 2.622(1)  
In(2)-P(2) 2.612(2)  
In(3)-P(2) 2.633(2)  
In(3)-P(3) 2.628(2)

**In-C**  
In(1)-C(1) 2.172(6)  
In(1)-C(2) 2.151(6)  
In(2)-C(3) 2.178(7)  
In(2)-C(4) 2.172(7)  
In(3)-C(5) 2.168(9)  
In(3)-C(6) 2.156(7)

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$(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PH}(\text{SiMe}_3)$ 

161

**P-In-P**

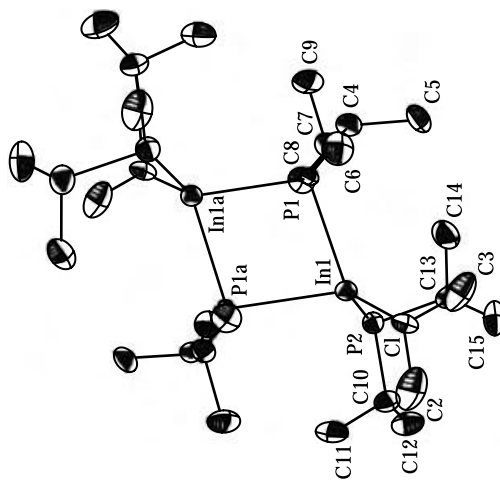
P(1)-In(1)-P(2) 82.43(7)  
P(1)-In(2)-P(2) 83.12(7)

**In-P-In**

In(1)-P(1)-In(2) 94.52(7)  
In(1)-P(2)-In(2) 95.08(7)

**Other**

C(101)-In(1)-C(106) 124.8(4)  
C(201)-In(2)-C(206) 112.8(8)  
In(1)-P(2)-Si(3) 123.0(1)  
In(2)-P(2)-Si(3) 127.9(1)

 $[i\text{-Pr}(\text{-Pr}_2\text{P})\text{In}(\mu\text{-P}(\text{-Pr})_2)_2]$ 

114

**P-In-P**

P(1)-In(1)-P(1') 107.3(8)  
P(1)-In(1)-P(2) 111.83(5)

**In-P-In**

In(1)-P(1)-In(1') 72.6(1)

**Other**

P(1)-In(1)-C(1) 117.7(2)  
P(2)-In(1)-C(1) 118.0(1)  
In(1)-P(1)-C(4) 112.0(2)

**In-P**

In(1)-P(1) 2.642(1)

**Endo**

In(1)-P(2) 2.574(1)

**Exo****In-C**

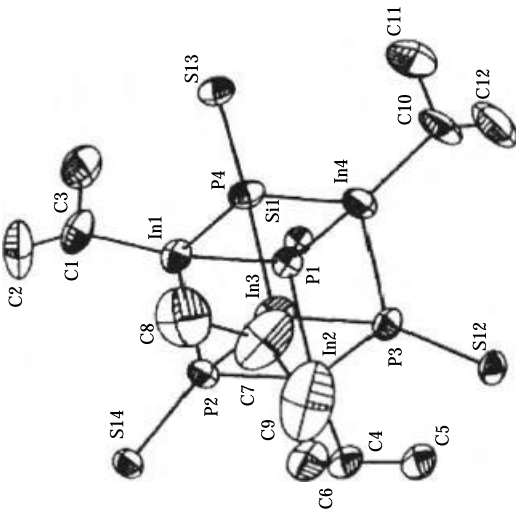
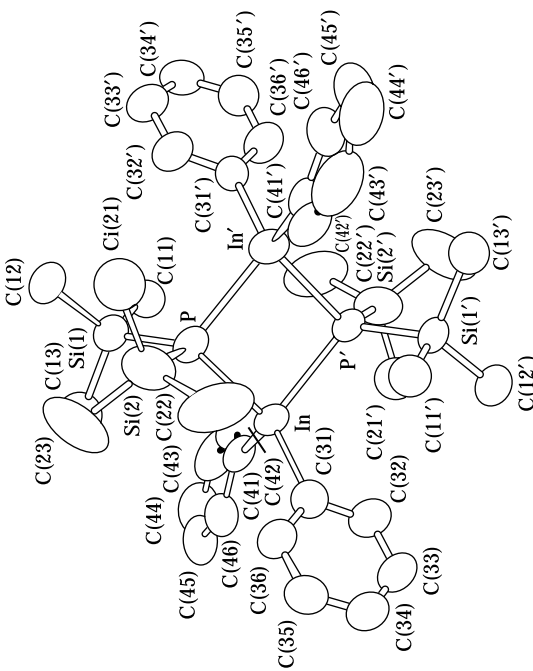
In(1)-C(1) 2.302(5)

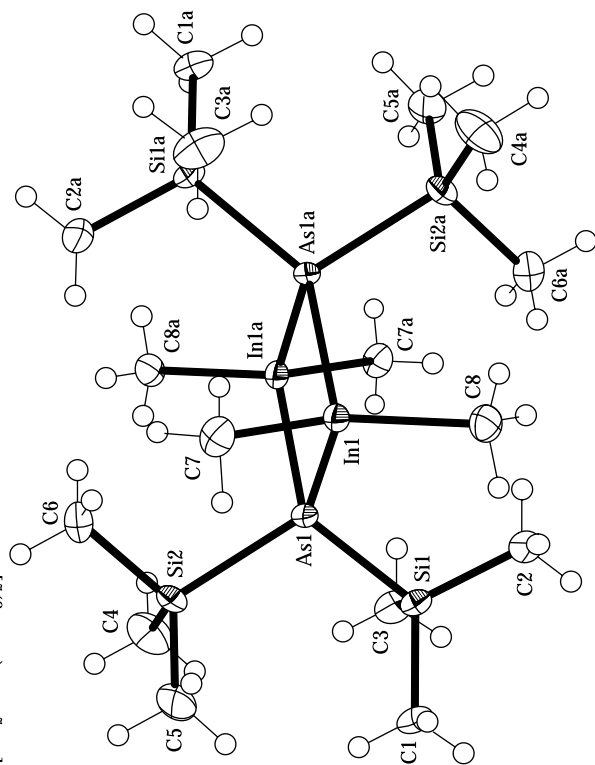
**Other**

P(1)-C(7) 1.856(5)  
P(2)-C(10) 1.873(6)  
P(2)-C(13) 1.883(6)

(cont'd overleaf)

Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
 $[i\text{-PrIn}(\mu^3\text{-PSiPh}_3)]_4$	<b>In-P</b> In(1)-P(2) 2.599(4) In(2)-P(2) 2.595(4) In(3)-P(2) 2.60(4) In(3)-P(4) 2.590(4) In(4)-P(1) 2.582(4) In(4)-P(4) 2.583(4)	<b>P-In-P</b> P(1)-In(1)-P(2) 89.7(1) P(2)-In(3)-P(3) 89.3(1) P(3)-In(3)-P(4) 89.4(1) P(1)-In(4)-P(4) 87.6(1) P(3)-In(3)-P(4) 89.4(1) P(1)-In(4)-P(4) 87.6(1) P(3)-In(3)-P(4) 89.4(1) P(1)-In(4)-P(4) 87.6(1) P(2)-In(1)-P(4) 89.4(1)	115
 $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$	<b>In-P</b> P-In 2.612(1) P'-In 2.612(1)  <b>In-C</b> In-C(31) 2.178(6) In-C(41) 2.185(5)  <b>Other</b> P-Si(1) 2.262(2) P-Si(2) 2.261(3)	<b>P-In-P</b> P-In-P' 87.03(4)  <b>In-P-In</b> In-P-In' 92.97(4)	156

**In-As**  
**[Me<sub>2</sub>InAs(SiMe<sub>3</sub>)<sub>2</sub>]****In-As**

In(1)-As(1) 2.703(1)  
In(1a)-As(1) 2.170(2)

**In-C**

In(1)-C(7) 2.168(2)  
In(1)-C(8) 2.170(2)

**Other**

As(1)-Si(1) 2.343(1)  
As(1)-Si(2) 2.341(1)

**As-In-As**

As(1a)-In(1)-As(1) 85.5(1)

**In-As-In**

In(1a)-As(1)-In(1) 94.5(1)

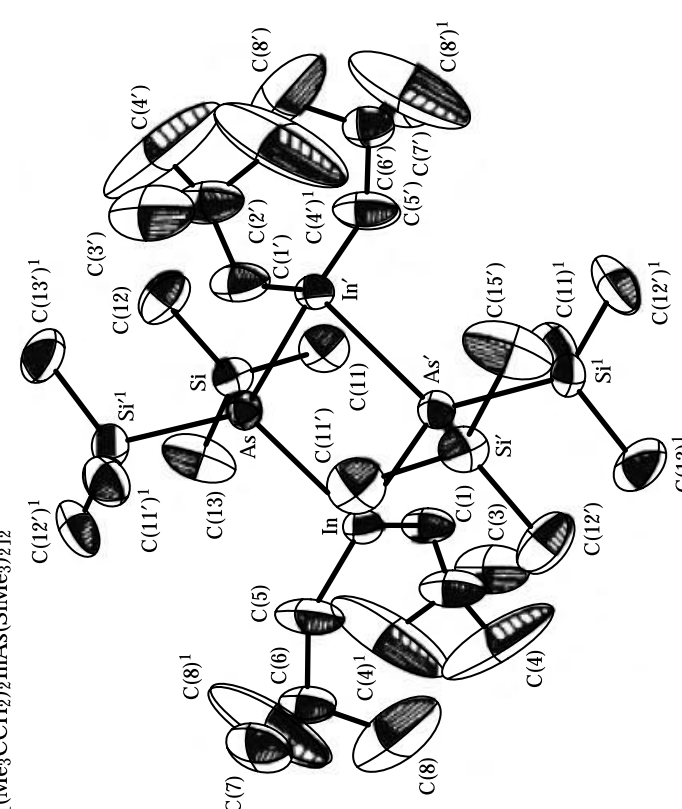
**Other**

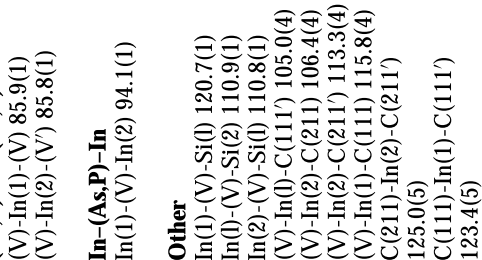
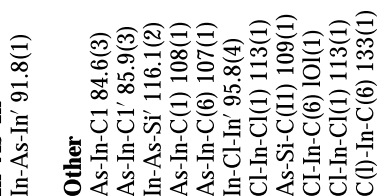
C(7)-In(1)-C(8) 118.8(1)  
Si(1)-As(1)-Si(2) 109.4(1)

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(cont'd overleaf)

Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
	<b>In-As</b> In-As 2.752 (1)	<b>As-In-As</b> As-In-As' 83.46(2)	153
	<b>In-C</b> In-C(l) 2.17(1) In-C(5) 2.17(2)	<b>In-As-In</b> In-As-In' 96.54(3)	
	<b>Other</b> As-Si 2.350(3)	<b>Other</b> As-In-C(1) 106.2 (1) In-As-Si 112.91(5) As-In-C(5) 105.4(2) In-As-Si'' 114.91(2) C(l)-In-C(5) 137.2(4) Si-As-Si'' 105.0 (1) In-C(1)-C(2) 128(1) In-C(5)-C(6) 133(1)	



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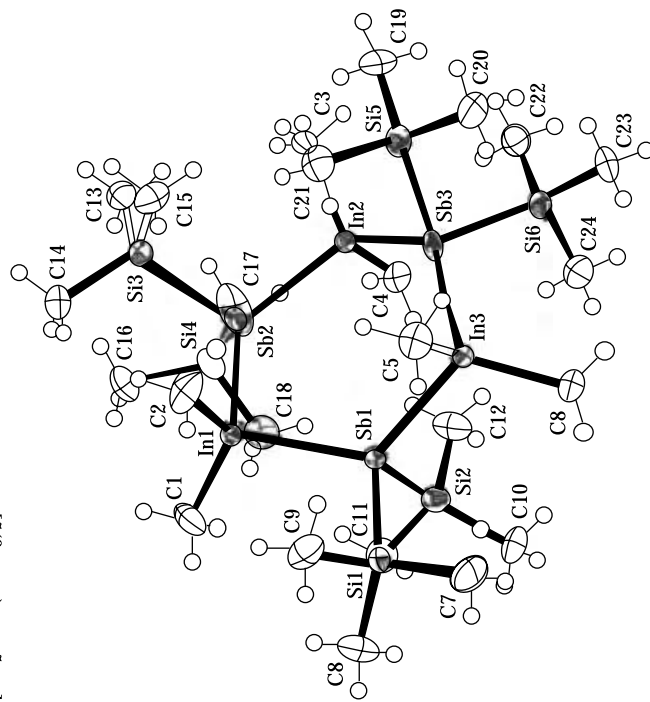
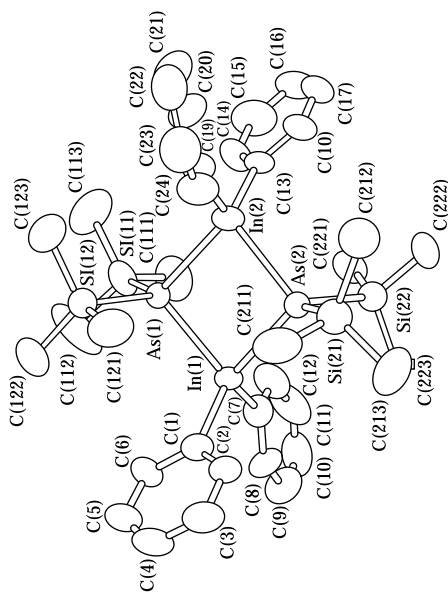
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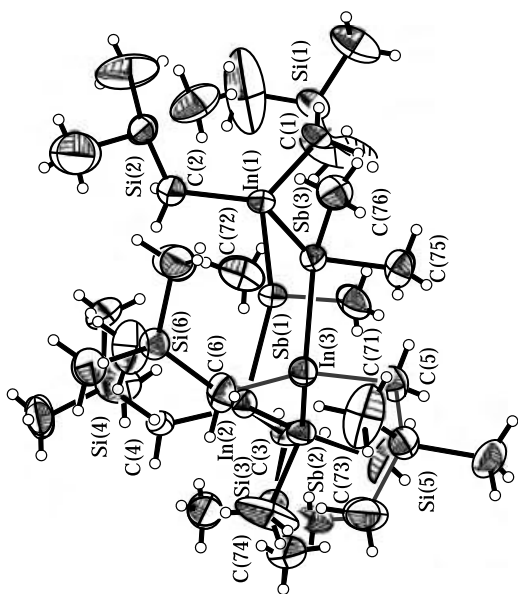
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Table 2 cont'd

Compound	M-V Bond length (Å)	M-V-C Bond angle (° Deg)	Ref.
<b>[Ph<sub>2</sub>InAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub></b>			156
	<b>In-As</b> As(1)-In(1) 2.689(1) As(2)-In(1) 2.689(1) As(1)-In(2) 2.683(0) As(2)-In(2) 2.682(1)	<b>In-As-In</b> In(0)-As(1)-In(2) 93.47(4) In(0)-As(2)-In(2) 93.48(4)	
	<b>In-C</b> In(0)-C(0) 2.19(0) In(2)-C(13) 2.17(0) In(0)-C(7) 2.17(0) In(2)-C(19) 2.17(0)	<b>As-In-As</b> As(0)-In(0)-As(2) 86.22(4) As(0)-In(2)-As(2) 86.49(3)	
	<b>Other</b> As(1)-Si(11) 2.344(4) As(2)-Si(21) 2.370(4) As(0)-Si(02) 2.352(2) As(2)-Si(22) 2.353(2)	<b>Other</b> In(0)-As(2)-Si(21) 121.6(0) In(1)-As(2)-Si(22) 107.8(1) In(2)-As(2)-Si(21) 116.6(0) In(2)-As(2)-Si(22) 111.3(0) In(0)-As(0)-Si(01) 119.8(0) In(0)-As(0)-Si(02) 110.3(0) In(2)-As(1)-Si(11) 118.2(0) In(2)-As(0)-Si(02) 107.5(0)	
<b>In-Sb</b> <b>[Me<sub>2</sub>InSb(SiMe<sub>3</sub>)<sub>2</sub>]</b>			152
	<b>In-Sb</b> In(1)-Sb(1) 2.844(1) In(2)-Sb(2) 2.847(1) In(3)-Sb(1) 2.845(1) In(1)-Sb(2) 2.851(1) In(2)-Sb(3) 2.861(1) In(3)-Sb(3) 2.870(1)	<b>In-Sb-In</b> In(1)-Sb(2)-In(1) 126.0(1) In(2)-Sb(2)-In(1) 126.0(1) In(2)-Sb(3)-In(3) 127.0(1)	
	<b>In-C</b> In(1)-C(1) 2.168(3) In(1)-C(3) 2.180(3) In(3)-C(5) 2.176(3)	<b>Sb-In-Sb</b> Sb(1)-In(1)-Sb(2) 102.8(1) Sb(2)-In(2)-Sb(3) 106.8(1) Sb(2)-In(3)-Sb(3) 102.7(1)	
	<b>Other</b> Sb(1)-Si(1) 2.553(1) Sb(2)-Si(3) 2.563(1) Sb(3)-Si(5) 2.563(1)	<b>Other</b> C(1)-In(1)-C(2) 122.6(2) C(1)-In(2)-C(4) 114.1(2) Si(20)-Sb(1)-Si(1) 103.9(1)	



[Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>InSbMe<sub>2</sub>]<sub>3</sub>**In-Sb**

Sb(1)-In(1) 2.8693(5)  
 Sb(1)-In(2) 2.8604(6)  
 Sb(2)-In(2) 2.8677(6)  
 Sb(2)-In(3) 2.8541(6)  
 Sb(3)-In(1) 2.8653(6)  
 Sb(3)-In(3) 2.8519(6)

**In-Sb-In**

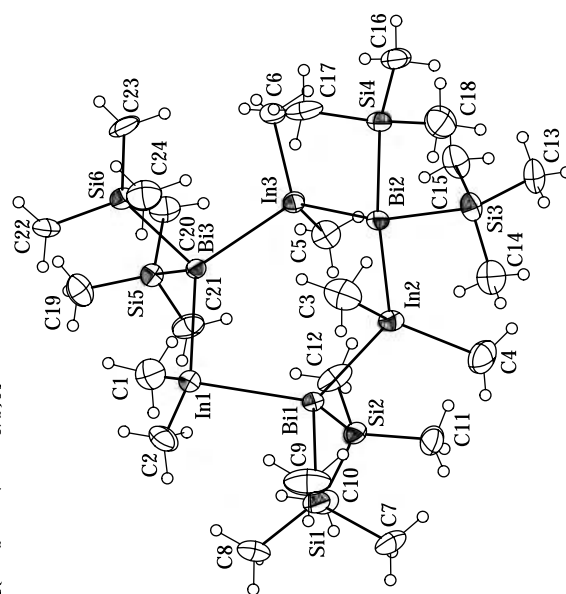
In(2)-Sb(1)-In(1) 131.58(2)  
 In(3)-Sb(2)-In(2) 129.22(2)  
 In(3)-Sb(3)-In(1) 137.68(2)

**Sb-In-Sb**

Sb(3)-In(1)-Sb(1) 92.38(2)  
 Sb(1)-In(2)-Sb(2) 98.56(2)  
 Sb(3)-In(3)-Sb(2) 96.87(2)

**Other**

C(2)-In(1)-C(1) 126.1(2)  
 C(4)-In(2)-C(3) 124.6(2)  
 C(6)-In(3)-C(5) 120.2(2)

**In-Bi**[(Me<sub>2</sub>InBi(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>]**In-Bi**

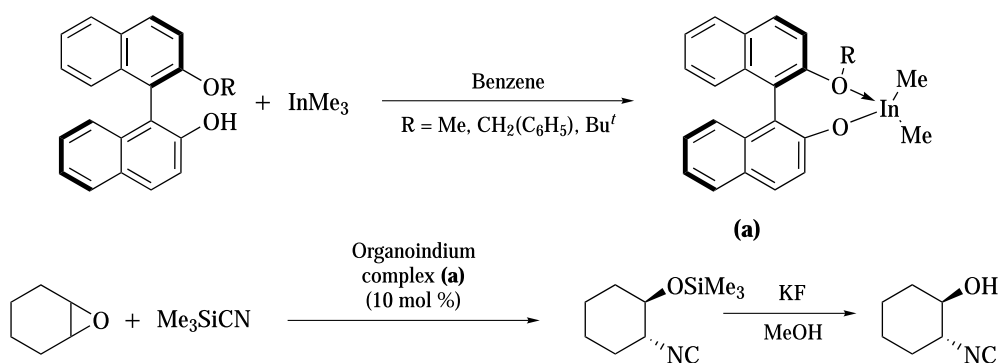
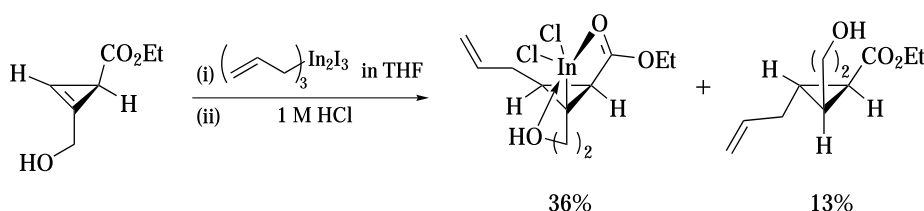
Bi1-In1 2.907(1)  
 Bi1-In2 2.903(1)  
 Bi2-In2 2.914(1)  
 Bi2-In3 2.911(1)  
 Bi3-In1 2.935(1)  
 Bi3-In3 2.920(1)

**In-Bi-In**

In1-Bi1-In2 123.0(1)  
 In2-Bi2-In3 129.1(1)  
 In1-Bi3-In3 129.2(1)

**Bi-In-Bi**

Bi1-In1-Bi3 99.7(1)  
 Bi1-In2-Bi2 99.4(1)

**Scheme 10** Use of asymmetric indium catalysts in organic synthesis**Scheme 11** Allylindination of cyclopropenes using allylindium reagents

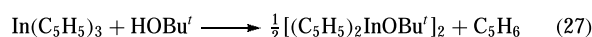
10% to 95% depending on the nature of the epoxide and the catalyst used. Although the gallium complexes were found to give better enantioselectivities, they gave lower yields than indium complexes (Scheme 10).<sup>191</sup>

Hydroxy-bearing cyclopropenes have been shown to react with allylindium reagents to undergo clean allylindination, in which the chelation of the hydroxyl group to indium plays the central role. The regio- and stereoselectivity is regulated both by the location of the hydroxyl group in the cyclopropenes and the reaction solvent. In particular, the allylindination in water shows marked differences from that in organic solvents.<sup>192</sup> Consequently, hydrolysis stable cyclopropylindium derivatives have been isolated from the reaction of 1-( $\omega$ -hydroxyalkyl)cyclopropenes and the structure for 3-Allyl-2-ethoxycarbonyl-1-(2-hydroxyethyl)cyclopropylindium dichloride has been resolved by X-ray crystallography.<sup>192</sup> Allylindination of these cyclopropenes was conducted with allylindium reagents prepared *in situ* (Grignard-type reaction) or, more conveniently, by mixing allyl halides, indium, and the cyclopropenes together (Barbier-type reaction) with both methods giving almost identical results (Scheme 11).

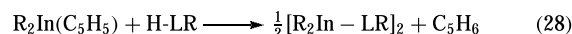
## 5.1 Synthesis

The preparation of the organoindium chalcogenides resembles that outlined for the organoindium pnictogens. In general, by elimination of gaseous molecules<sup>144,174,178,195–198</sup> (e.g. cyclopentadiene,<sup>121,195</sup> equation 27), which can be cross-defined as alcoholysis, or by reacting organoindium halides

with lithium chalcogenides,<sup>57,199,200</sup>



The cyclopentadiene elimination reaction has proven extremely useful for the synthesis of organoindium(III) chalcogenide derivatives. Products of the types  $\text{R}_2\text{InLR}$  ( $\text{R} = \text{Me}, \text{CH}_2\text{CMe}_3$ ;  $\text{L} = \text{O}, \text{S}$ ) have been formed in nearly quantitative yields and in excellent purity.<sup>121,195</sup> Interestingly, although  $\text{R}_2\text{In}(\text{C}_5\text{H}_5)$  incorporates two different organic ligands, only the cyclopentadiene is preferentially eliminated over the more thermodynamically stable compounds,  $\text{CH}_4$  or  $\text{CMe}_4$ , (equation 28). Thus, it is believed that the cyclopentadiene elimination reaction must be controlled by kinetic rather than thermodynamic factors.<sup>195</sup>



Attempts to prepare the heteroleptic cyclopentadienide-indium-diketonate derivatives  $[(\text{C}_5\text{H}_5)_{3-x}\text{In}(\text{acac})_x]$  ( $\text{acac} = \text{CH}_3\text{COCH}_2\text{COCH}_3$ ;  $x = 1, 2$ ) products via cyclopentadiene elimination reactions from  $[\text{In}(\text{C}_5\text{H}_5)_3]$  and  $\text{acac}$  fail to yield the expected products, since both  $[(\text{C}_5\text{H}_5)_2\text{In}(\text{acac})]$  and  $[(\text{C}_5\text{H}_5)\text{In}(\text{acac})_2]$  are unstable and undergo ligand redistribution reactions to form  $[\text{In}(\text{C}_5\text{H}_5)_3]$  and  $[\text{In}(\text{acac})_3]$ , respectively.<sup>121</sup>

The preparation of organoindium Schiff base derivatives also encompasses the mechanistic pathway of hydrocarbon

elimination and has received a renewed interest in part owing to their low costs and ease of ligand synthesis. Furthermore, the ligands can be readily engineered to cause change in both steric and electronic properties by directed functionalization. This area has recently been comprehensively reviewed.<sup>176</sup>

The reaction between lithium tetramethylindate  $\text{Li}[\text{InMe}_4]$  and disilanol  $[(\text{Ph}_2\text{SiOH})_2\text{O}]$  yields the rare Lithium indium siloxane  $[\text{InMe}\{(\text{OPh}_2\text{Si})_2\text{O}\}_2-\mu-\{\text{Li}(\text{THF})_2\}_2]$ , which can also be synthesized from  $\text{Ph}_2\text{Si}(\text{OH})_2$  and  $\text{Li}[\text{InMe}_4]$  in good yields.<sup>201</sup> The solid-state structure determined by single-crystal X-ray crystallography reveals that the central indium atom is surrounded by four oxygen atoms of the two disilanolate ligands and a methyl group in a square-pyramidal geometry. The  $\text{InO}_4\text{C}$  coordination environment observed is rare among organometallic compounds of indium (Scheme 12).

An example of methane elimination preparation is the reaction between  $\text{InMe}_3$  with two equivalents of  $\text{HO}(\text{C}_6\text{H}_{11})$  in toluene.<sup>177</sup> The reaction was predicted to afford the expected stoichiometric driven product  $[\text{MeIn}(\text{O}(\text{C}_6\text{H}_{11}))_2]_n$ , but instead yielded only the sesquialkoxide  $[\text{In}\{\text{Me}_2\text{In}(\text{OCH}_2\text{Ph})_2\}_3]$ , which can be described also as  $[\{\text{Me}_2\text{In}(\text{O}(\text{C}_6\text{H}_{11}))\}_2\{-\text{MeIn}(\text{O}(\text{C}_6\text{H}_{11}))_2\}]$  (Scheme 13).

Only a limited number of S, Se, or Te organoindium derivatives are known, the majority of which have been prepared and isolated with large sterically demanding ligands. The supermesityl ligand ( $\text{Mes}^* = 2,4,6\text{-Bu}_3^t(\text{C}_6\text{H}_2)$ ) and mesityl ligand ( $\text{Mes} = 2,4,6\text{-Me}_3(\text{C}_6\text{H}_3)$ ) have been effectively used to prepare several stabilized organoindium derivatives owing to the kinetic stabilization effect these ligands have on the metal center.  $[\text{Mes}^*\text{In}(\text{SePh})_2]$  has been prepared via Grignard synthesis and isolated as a monomer and base-free ligand.<sup>62</sup> The reaction of  $\text{In}(\text{Mes})_3$  with

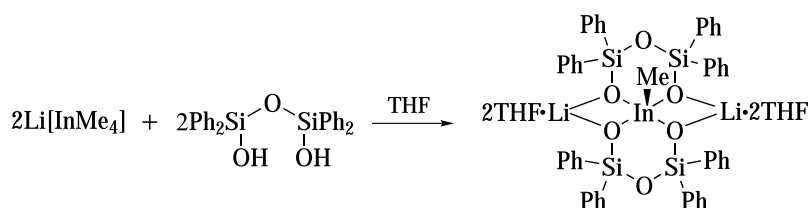
diselenides  $\text{R}_2\text{Se}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) at room temperature yields  $[\text{Mes}_2\text{In}(\mu\text{-SeR})]_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) and  $[\text{Mes}_2\text{In}(\mu\text{-SeMes})]_2$  can be synthesized by the reaction of  $\text{In}(\text{Mes})_3$  with elemental Se in refluxing toluene. However, under similar conditions, the reaction of  $\text{InMe}_3$  with  $\text{Ph}_2\text{Se}_2$  failed to give the target product, but afforded the rearranged product  $[\text{MeIn}(\mu\text{-SePh})(\text{SePh})]_n$ . Single-crystal analysis of the structures revealed that both  $[\text{Mes}_2\text{In}(\mu\text{-SePh})]_2$  and  $[\text{Mes}_2\text{In}(\mu\text{-SeMes})]_2$  were dimeric with planar  $(\text{In-Se})_2$  rings,<sup>62</sup> (see Table 3).

The analogous organotellurolates  $[\text{Mes}_2\text{In}(\mu\text{-TePr})]_2$  and  $[\text{Mes}_2\text{In}(\mu\text{-TePh})]_2$  can also be prepared via a similar reaction using the ditellurides ( $\text{Pr}_2\text{Te}_2$ ) and  $\text{Ph}_2\text{Te}_2$  as starting reagents. Like their Se congeners, the organotellurolates have a dimeric configuration with a planar  $(\text{InTe})_2$  ring. An advantage of this synthetic route is that it avoids the requirement of organochalcogenide protic compounds (REH), which is generally unstable, thus providing a simple synthetic pathway to binary single-source precursors capable of delivering III-VI materials upon pyrolysis.<sup>62</sup>

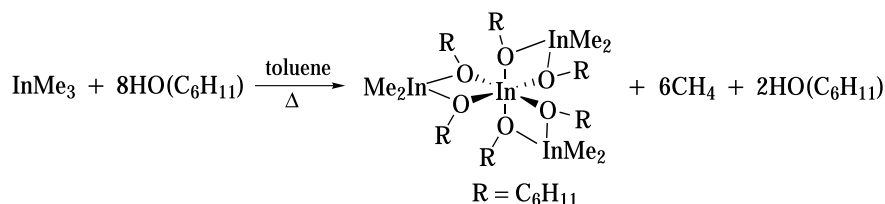
## 5.2 Structures

The organoindium chalcogenides also exhibit extended ring, cage, and cluster-like structures as is commonly found for III-V derivatives. For example, intra-dative coordination is demonstrated by  $[\text{Me}_2\text{InCH}_2\text{SMe}]_2$ , which adopts conformations where the S-bound Me groups are placed in equatorial positions of the chair-like six-membered ring systems.<sup>95</sup>

Cage structures are exemplified by the first reported polyhedral indium siloxanes synthesized when  $\text{RSi}(\text{OH})_3$  ( $\text{R} = 1,3\text{-Pr}_2\text{C}_6\text{H}_3$ ) is reacted with  $\text{InMe}_3$  in a 1:2 ratio via partial elimination of the  $\text{CH}_3$  groups, leading to a drum-shaped indium siloxane.<sup>198</sup> Complete elimination of all



**Scheme 12** Indium siloxane  $[\text{InMe}\{(\text{OPh}_2\text{Si})_2\text{O}\}_2-\mu-\{\text{Li}(\text{THF})_2\}_2]$



**Scheme 13** Sesquialkoxide  $[\text{In}\{\text{Me}_2\text{In}(\text{OCH}_2\text{Ph})_2\}_3]$

**Table 3** Selected bond angles and lengths for organoindium chalcogenides

Organoindium chalcogenides	Bond distances (Å)	Angles (deg)	Ref.
	<b>In–O</b>	<b>O–In–C</b>	
[Me <sub>2</sub> In(acac)]	2.198(1) 2.551(1) 2.256(1)	105.67(7) 90.97(6)	121
[(Me <sub>3</sub> CCH <sub>2</sub> ) <sub>2</sub> In(acac)]	2.195(1) 2.203(1)	106.42(7) 103.53(7) 109.23(7) 103.36(7)	121
[(Me)(Me <sub>3</sub> CCH <sub>2</sub> )In(acac)]	2.206(2) 2.262(2) 2.569(2)	107.38(8) 93.12(8)	121
[InMe <sub>2</sub> (OC(CF <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> OMe)] <sub>2</sub>	2.2034(8) 2.3959(8)	110.94(5) 105.19(5)	122
[InMe <sub>2</sub> (OC(CF <sub>3</sub> )=CHC(CF <sub>3</sub> )=NCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	2.251(3)	100.4(1) 86.9(1)	141
[Me <sub>2</sub> In(saldPh)] <sub>2</sub>	2.158(3) 2.477(3)	110.58(16) 108.29(17)	123
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> InO( <i>t</i> -Bu)] <sub>2</sub>	2.118(2) 2.141(2)	118.26(7) 111.96(7)	195
[InMe{(OPh <sub>2</sub> Si) <sub>2</sub> O} <sub>2</sub> -μ-{Li(THF) <sub>2</sub> } <sub>2</sub> ]	2.186(4)	109.1(2) 110.8(2) 109.4(2)	201
[{Me <sub>2</sub> In(OCy)} <sub>2</sub> {MeIn(OCy) <sub>2</sub> } <sub>2</sub> ]	2.145(4) 2.151(4) 2.149(3) 2.139(3) 2.147(3) 2.155(3)	112.3(2) 107.2(2) 108.9(2) 112.4(2) 115.0(2) 104.7(2)	177
[In{(PhCH <sub>2</sub> O) <sub>2</sub> InMe <sub>2</sub> } <sub>3</sub> ]	2.174(2) 2.147(2) 2.162(4) 2.141(2)	108.2(1) 108.8(1) 107.4(1) 109.5(2)	196
[(3-Allyl-2-ethoxycarbonyl-1-(2-hydroxyethyl)cyclopropylindium dichloride C <sub>11</sub> H <sub>17</sub> Cl <sub>2</sub> InO <sub>3</sub> )]	2.521(8) (OH)  2.532(7)	87.6(2)  84.0(2) 92.0(2)	192
[C <sub>42</sub> H <sub>50</sub> In <sub>2</sub> N <sub>4</sub> O <sub>8</sub> ]	2.199(2) 2.172(2) 2.517(3)	91.0(2) 104.2(1)	132
Br <sub>2</sub> In[OP(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> CH <sub>2</sub> Br	2.281(6)	89.2(3) Mean values	74
[(Me <sub>2</sub> In)(OC <sub>4</sub> H <sub>3</sub> CHNNC <sub>6</sub> H <sub>5</sub> )] <sub>2</sub> O	2.182(7) 2.189(6)	–	137
[(μ-9-BBN-9-O)InMe <sub>2</sub> ] <sub>2</sub> {C <sub>20</sub> H <sub>40</sub> B <sub>2</sub> In <sub>2</sub> O <sub>2</sub> }	2.174(10) 2.177(7)	–	203
[ClMeIn(OBu')]	2.109(3) 2.122(4) 2.109(3)	122.9(2)	61
[BrMeIn(OBu')] <sub>2</sub>	2.114(7) 2.129(8) 2.113(7)	121.8(5) 115.4(4)	61

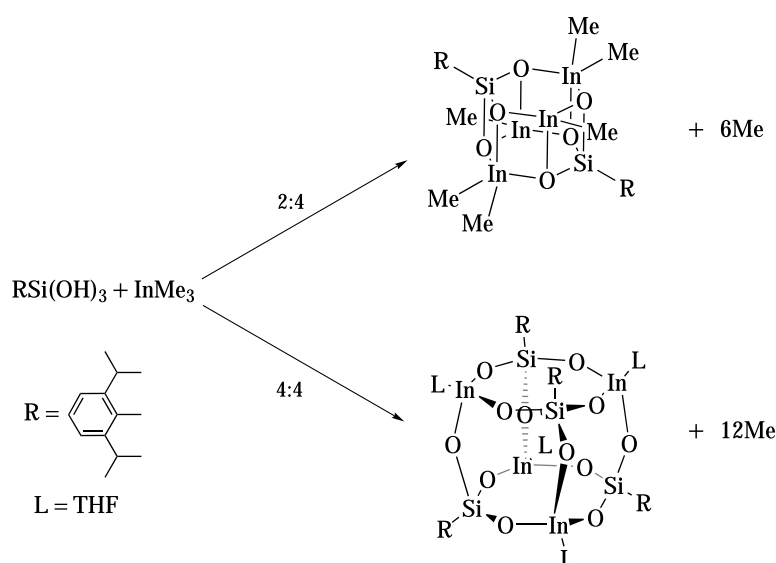
**Table 3** cont'd

Organoindium chalcogenides	Bond distances (Å)	Angles (deg)	Ref.
[ClMeIn(OC <sub>6</sub> H <sub>4</sub> OMe)] <sub>2</sub>	2.136(4) 2.204(4) 2.406(5) 2.204(4)	129.2(3) 110.2(3) 95.7(3)	61
[(N(SiMe <sub>3</sub> ) <sub>2</sub> )MeInOtBu] <sub>2</sub>	2.138(3) 2.153(3)	114.1(2) 109.3(2)	61
[MeIn(OBu') <sub>2</sub> ] <sub>2</sub>	2.006(4) 2.126(4) 2.131(4)	129.0(3) 116.8(3) 117.3(3)	61
[(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>2</sub> In] <sub>2</sub> O]	1.989(2) 1.981(2) (Bridging)	–	204
[{(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>3</sub> C(C <sub>3</sub> H <sub>7</sub> )In(μ-OH)] <sub>3</sub>	2.162(2) 2.167(2) 2.160(2) 2.166(2) 2.155(2) 2.171(2)	–	200
[(InEt <sub>2</sub> ) <sub>4</sub> ( <i>di</i> -2-pyridylamido) <sub>2</sub> (μ <sup>4</sup> -O)]	2.252(3) 2.160(3) 2.175(4) 2.273(3)	110.73(14) 116.4(2) 101.8(2) 129.1(2) 104.69(14)	144
[( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (InBr(THF)) <sub>2</sub> ) <sub>2</sub> ]	2.407(3) 2.492(3)	–	32
[(Ph <sub>2</sub> InOSiMe <sub>3</sub> ) <sub>2</sub> ]	2.159(7) 2.149(8)	–	179
[C <sub>36</sub> H <sub>70</sub> In <sub>4</sub> N <sub>2</sub> O <sub>6</sub> Si <sub>4</sub> ]	2.148(6) 2.150(6) 2.033(6)	–	198
[(Me <sub>2</sub> In) <sub>2</sub> {NC <sub>5</sub> H <sub>4</sub> CMeNNC(S)NC <sub>6</sub> H <sub>5</sub> ] <sub>2</sub> (InMe)]·THF	<b>In–S</b> 2.491(2)	<b>S–In–C</b> 125.31(4)	145
[((THF)Me <sub>2</sub> In) <sub>2</sub> {CH <sub>2</sub> (MeCNC(S)NMe) <sub>2</sub> }(InMe)]	2.550(4) 2.561(4)	119.5(4)	145
[Mes <sub>2</sub> In(μ-SBu')]	2.622(5) 2.615(5)	–	205
[Mes <sub>2</sub> In(μ-Samy1')] <sub>2</sub>	2.595(4) 2.598(4)	–	205
[Mes <sub>2</sub> In(μ-SSiPh <sub>3</sub> )] <sub>2</sub>	2.698(1) 2.172(3)	–	205
Me <sub>2</sub> In(μ-SSiPh <sub>3</sub> ) <sub>3</sub>	2.644(3) 2.617(3) 2.627(3)	–	205
[(2,4,6- <i>i</i> Bu <sub>3</sub> (C <sub>6</sub> H <sub>2</sub> ))In(SePh) <sub>2</sub> ]	<b>In–Se</b> 2.5261(12) 2.5507(11)	<b>Se–In–C</b> 134.9(2) 121.8(2)	164
[(2,4,6- <i>i</i> Bu <sub>3</sub> (C <sub>6</sub> H <sub>2</sub> )) <sub>2</sub> In(μ-SePh)] <sub>2</sub>	2.7272(7) 2.7369(8)	97.64(12) 105.09(14)	206
[(2,4,6- <i>i</i> Bu <sub>3</sub> (C <sub>6</sub> H <sub>2</sub> )) <sub>2</sub> In(μ-Se(Mes))] <sub>2</sub>	2.705(3) 2.728(3)	117.5(5) 109.3(6)	206
[MeIn(μ-SePh)(SePh)] <sub>n</sub>	2.640(3) bridging 2.726(4) bridging 2.633(4) terminal 2.542(3) terminal 2.541(4) terminal	–	206

(cont'd overleaf)

**Table 3** cont'd

Organoindium chalcogenides	Bond distances (Å)	Angles (deg)	Ref.
$[(2,4,6\text{-}t\text{Bu}_3(\text{C}_6\text{H}_2))\text{In}(\text{SePh})_2]$	2.5261(12) 2.5507(11)	134.9(2) 121.8(4)	206
$[\text{Mes}_2\text{In}(\mu\text{-TePr})_2]$	<b>In-Te</b> 2.906(1) 2.911(1)	<b>In-Te-C</b> 93.8(2) 92.8(2)	207
$[\text{Mes}_2\text{In}(\mu\text{-TePh})_2]$	2.919(1) 2.911(1)	103.0(2) 95.2(2)	207

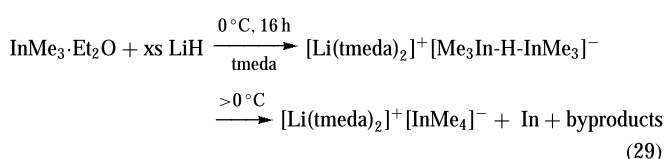
**Scheme 14** Synthesis of indium siloxanes

the  $\text{CH}_3$  groups can also be performed when the reaction is carried out in a 1:1 ratio, affording the cube shaped indium siloxane (Scheme 14). These indium siloxanes are considered to be important catalysts in the reduction of nitrogen oxides.

A detailed computational study using density functional theory has been used to examine the structural properties of a combination of group 13 and group 16 chalcogenide heterocubanes  $[\text{RM}(\mu_3\text{-E})]_4$  ( $\text{R} = \text{H}, \text{CH}_3$ ;  $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ). Geometries and thermodynamic properties were computed at the B3LYP/SRLC level and all structures were found to be true minima with at most a deviation of 0.08 Å and  $2.5^\circ$  in bond lengths and angles respectively from the experimental geometries reported in Table 3. The  $\text{M}_4\text{E}_4$  core for each structure proved to be insensitive to ligand choice for the group 13–16 heterocubanes. Density functional theory also suggested that the difficulty for the preparation and isolation of earlier group 13 derivatives  $[\text{RM}(\mu_3\text{-O})]_4$  can be attributed to the synthesis being favored by enthalpy but disfavored by entropy; thus, the products might be achievable when prepared at low temperatures.<sup>202</sup>

## 6 ORGANOINDIUM HYDRIDES

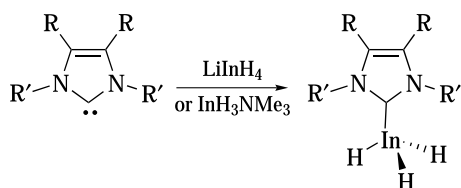
Only an exclusive number of organoindium hydrides are known owing to the inherently weak  $\text{In-H}$  bond, thus making their synthesis and isolation difficult. Two groups of organoindium hydrides have been characterized, bridging ( $\text{C-In-H-In}$ ) and terminal ( $\text{C-In-H}$ ). The reaction of either  $\text{InMe}_3 \cdot \text{Et}_2\text{O}$  or  $\text{InMe}_2\text{Cl}$  with an excess of  $\text{LiH}$  at reduced temperatures followed by treatment with TMEDA affords the bridged hydride derivative  $[\text{Li}(\text{TMEDA})_2][\text{Me}_3\text{In}(\text{H})\text{InMe}_3]$ .<sup>208</sup> The compound is stable in solution or solid state for extended periods when kept below  $0^\circ\text{C}$ , above which it auto catalytically decomposes to  $[\text{Li}(\text{TMEDA})_2][\text{InMe}_4]$ , indium metal, and gaseous by-products, (equation 29).



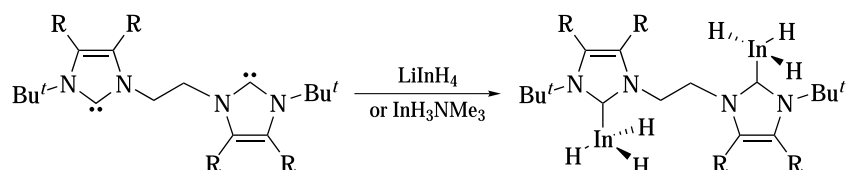
An interesting feature of  $[\text{Li}(\text{TMEDA})_2][\text{Me}_3\text{In}(\text{H})\text{InMe}_3]$  as determined from its crystallographic structure is the presence of a bent hydride bridge formation, this is in contrast to its aluminum analogue, which possesses a linear structure.<sup>208</sup> Examples of organoindium with terminal hydride have been pioneered recently by the use of bulky carbene ligands such as  $\{\text{:CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})\}$  or  $\{\text{:CN}(\text{Pr}^i)\text{C}_2(\text{R})_2\text{CN}(\text{Pr}^i)\}$ , where  $\text{R} = \text{Me}, \text{H}$ , these have been described as ‘‘Arduengo-type’’ carbenes<sup>209–212</sup> (Scheme 15).

The organoindium carbene hydrides are synthesized by reacting either  $\text{LiInH}_4$  or  $[\text{InH}_3(\text{NMe}_3)]$  with the Arduengo-type carbene  $\{\text{:CN}(\text{R}')\text{C}_2(\text{R})_2\text{CN}(\text{R}')\}$  at low temperatures, to afford the indium trihydride complexes  $[\text{InH}_3\{\text{CN}(\text{R}')\text{C}_2(\text{R})_2\text{N}(\text{R}')\}]$ . The thermal stability of these derivatives can be tailored via the substituents on the ring system. In the case of  $[\text{InH}_3\{\text{CN}(\text{Pr}^i)\text{C}_2\text{Me}_2\text{CN}(\text{Pr}^i)\}]$ , the compound decomposes in the solid state at temperatures  $> -5^\circ\text{C}$  and in solution at  $> -20^\circ\text{C}$ .<sup>210</sup> In contrast, in the use of the more sterically demanding groups where  $\text{R}' = \text{Mes} = \text{C}_6\text{H}_2\text{Me}_3-2,4,6$ , the indium hydride has exceptionally solid-state stability (dec.  $> 115^\circ\text{C}$ ).<sup>209</sup> Additionally, its decomposition in solution was found to be solvent dependent. For example, in toluene decomposition results in liberation of the free carbene and precipitation of In metal, whilst in THF, H transfer occurs to give  $\text{H}_2\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})$  and In metal. In dichloromethane, chloride abstraction occurs from the solvent to yield the trihalide,  $[\text{InCl}_3\{\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})\}]$ . In addition, a mixed indium hydride halide complex  $[\text{InH}_2\text{Cl}\{\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})\}]$  can be prepared by the reaction of the carbene organoindium hydride with  $\text{HCl}$ -quinuclidine ( $\text{C}_7\text{H}_{13}\text{N}\cdot\text{HCl}$ ).

The use of bidentate chelating carbene has also been investigated (Scheme 16); however, in thermal stability studies of the organoindium carbene hydride derivative, the



**Scheme 15** Synthesis of organoindium carbene hydrides



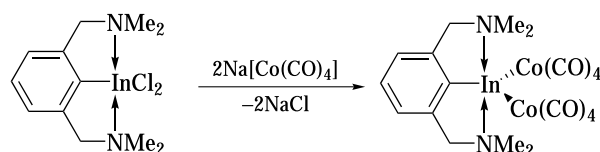
**Scheme 16** Bidentate carbene organoindium hydride derivative

bidentate ligand was found not to enhance stability (dec.  $10-12^\circ\text{C}$ ).<sup>212</sup>

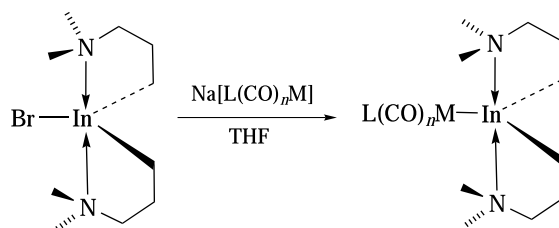
## 7 ORGANOINDIUM METAL COMPLEXES

Most of the reported intermetallic indium complexes are those where the indium is in low oxidation state and are hence discussed in Section 8. Examples where the indium metal center is in higher oxidation states are given below. The intermetallic *bis*(dialkylaminomethyl)-phenylindium derivative is synthesized via metathesis as outlined in Scheme 17.<sup>213</sup> The compound exists as a distorted trigonal bipyramid since the  $\text{N-In-N}$  angle of  $143.1(2)$  falls considerably short of an ideal trigonal bipyramid ( $180^\circ$ ).

In similar investigative studies for bimetallic single-source precursors, an iron indane derivative was synthesized by the reaction  $\text{Na}[(\text{Cp})(\text{CO})_2\text{Fe}]0.5\text{THF}$  with  $\text{BrIn}[(\text{CH}_2)_3\text{NMe}_2]_2$  in THF (Scheme 18)). The analogous Ni, Co, and Mn intermetallic complexes were also successfully prepared with either cyclopentadiene or carbonyl ligands.<sup>214</sup> Photolysis of the indium-iron derivative  $[(\text{Cp}(\text{CO})_2\text{Fe})_2\text{In}(\text{CH}_2)_3\text{NMe}_2)_2]$

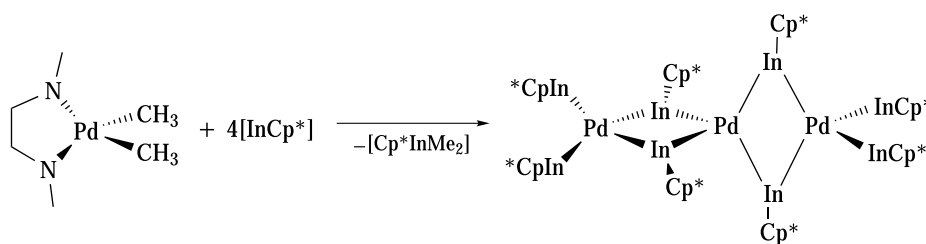


**Scheme 17** Synthetic route to intermetallic *bis*(dialkylaminomethyl)-phenylindium derivative



**Scheme 18** ( $\text{M} = \text{Fe}, \text{L} = \text{Cp}, n = 2$ ;  $\text{M} = \text{Ni}, \text{L} = \text{Cp}, n = 1$ ;  $\text{M} = \text{Mn}, \text{L} = \text{CO}, n = 4$ ;  $\text{M} = \text{Co}, \text{L} = \text{CO}, n = 3$ )





**Scheme 19** Formation of low-valent In–M bonds via ligand displacement

in daylight leads to the rearrangement product  $[(\mu\text{-CO}) (\mu\text{-In}(\text{CH}_2)_3\text{NMe}_2)\{\text{Cp}(\text{CO})\text{Fe}_2\}_2]$ .

Attempts to prepare the analogous indium derivative of  $[(\text{Me}_3)_3\text{SiCH}_2)_2\text{Ga}\{\text{Co}(\text{CO})_4\}]$  failed to yield the desired product from the reaction between  $[(\text{Me}_3)_3\text{SiCH}_2)_2\text{InCl}]$  and  $\text{Na}[(\text{CO})_3\text{Co}]$ , but instead gave the unexpected indane cobaltate product  $[(\text{CO})_4\text{Co}]_2\text{In}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ .<sup>214</sup> In all cases, these bimetallic compounds were studied to see if they could be viable candidates in CVD process to afford bimetallic thin films.

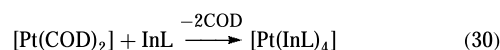
## 8 ORGANOINDIUM LOW VALENCY COMPOUNDS

The paucity of organoindium(I) and (II) derivatives is evidenced by the limited number of articles in this area in comparison to those for organoindium(III). This is largely due to the high propensity for In(I) to disproportionate to In(III) and elemental indium.<sup>215</sup> The bulk of low-valent organoindium compounds have been derived with cyclic groups such as Cp, Cp\*, etc and functionalized derivatives thereof. The main preparative routes for these species are reduction of  $\text{InX}_3$  with alkali salts, controlled reaction of organolithium, or Grignard reagents with  $\text{InX}$ , co-condensation of indium vapor with the respective organic moiety and matrix isolation. The area of lower oxidation state indium derivatives has been extensively reviewed, and their synthesis, reactivity, and properties examined,<sup>215</sup> thus, this section will be an overview with recent additions. Again the two areas which have perpetuated the increase for organoindium(I) derivatives are the semiconductor industry and the search for intermetallic precursors to thin films and nanocrystallites,<sup>216–218</sup> and organic synthesis, which reported an organoindium(I) derivative ( $\text{InCp}$ ) as an effective reagent for the preparation of highly functionalized organic cyclopentadienes in aqueous media, thus paving the way for a new role for organoindium(I) derivatives.<sup>219</sup>

### 8.1 Intermetallic Organoindium Derivatives

The most common synthetic pathway for the formation of low-valent In–M bonds is the replacement of labile ligands

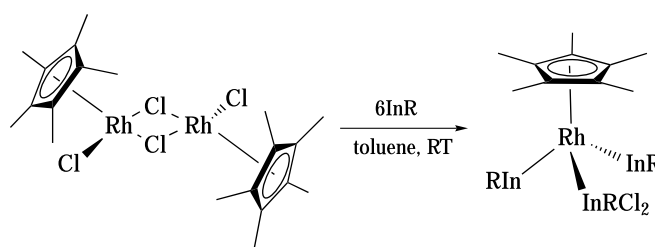
on the incoming metal with  $\text{InR}$ .<sup>112,220–225</sup> For example, the labile COD ligands in  $[\text{Pt}(\text{COD})_2]$  and  $[\text{Ni}(\text{COD})_2]$  are readily replaced by  $\text{InC}(\text{SiMe}_3)_3$ ,  $\text{InCp}^*$  and other group 13 derivatives (i.e.  $\text{GaCp}^*$ ,  $\text{GaC}(\text{SiMe}_3)_3$ ), yielding monomeric complexes of the type  $[\text{M}(\text{InR})_4]$  ( $\text{M} = \text{Pt}, \text{Ni}$ ) (equation 30). Elimination reactions have also been employed to prepare novel In–M derivatives (Scheme 19).<sup>221</sup>



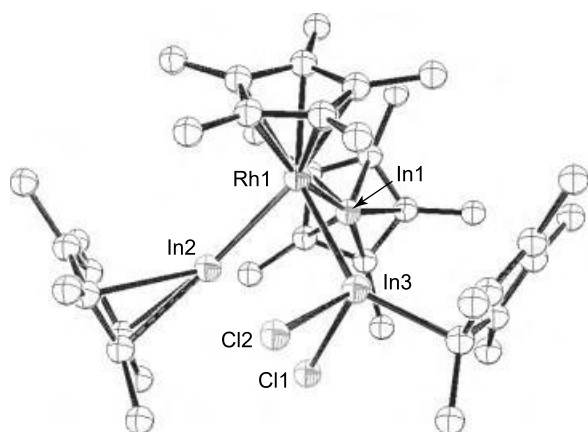
Another successful synthetic route to indium-metal species is via insertion of organoindium(I) compounds into metal-halide or metal-metal bonds.<sup>225–227</sup> The organoindium subhalide  $[\text{R}(\text{Cl})\text{In-In}(\text{Cl})\text{R}]_2$  [ $\text{R} = \text{C}(\text{SiMe}_3)_3$ ] reacts with  $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$  to form an iron-indium coordination compound, which is isolated as the NaCl adduct  $[\text{Na}(\text{THF})_4\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-InR})_2\text{Cl}]$ .<sup>226</sup> The iron atoms are bridged by a CO ligand and two  $\text{InR}$  groups, and the indium atoms are further connected by the  $\mu^2$ -bridging chlorine atom. Similarly, the insertion of  $\text{InR}$  ( $\text{R} = \text{Cp}^*$ ,  $\text{C}(\text{SiMe}_3)_3$ ) into the  $\text{Rh}\text{-Cl}$  bond of  $[(\text{Cp}^*\text{RhCl}_2)_2]$  affords the intermetallic derivatives  $[(\text{Cp}^*\text{Rh}\{\text{InCp}^*\}_3\text{Cl}_2)]$  and  $[(\text{Cp}^*\text{Rh}(\mu^2\text{-Cl}_2)\{\text{In-C}(\text{SiMe}_3)_3\}_3)]$  (Scheme 20).<sup>227</sup>

A very interesting feature determined from the single-crystal structure for  $[(\text{Cp}^*\text{Rh}\{\text{InCp}^*\}_3\text{Cl}_2)]$  is the difference in bonding of the  $\text{Cp}^*$  rings to indium, varying from a sigma bonded mode ( $\text{InCp}^*\text{Cl}_2$ ) to a hapticity of  $\eta^5$ , and one between  $\eta^2$ – $\eta^3$ , Figure 5.

As is the case for most indium-metallic derivatives in solution, rapid fluxional exchanges are prevalent as can be



**Scheme 20** Synthetic route to  $[(\text{Cp}^*\text{Rh}\{\text{InCp}^*\}_3\text{Cl}_2)]$  and  $[(\text{Cp}^*\text{Rh}(\mu^2\text{-Cl}_2)\{\text{In-C}(\text{SiMe}_3)_3\}_3)]$



**Figure 5** Single-crystal structure for  $[(\text{Cp}^*\text{Rh}\{\text{InCp}^*\}_3)\text{Cl}_2]$

observed by NMR spectroscopic studies. In the case of both the In-Rh derivatives,  $^1\text{H}$ -NMR of both complexes shows chemical shifts for only one InR entity and not the three as expected; thus, rapid exchange between the chloride and the In(I) and In(III) centers is occurring.<sup>227</sup>

## 8.2 In(0), In(I) and In(II) Organo Derivatives

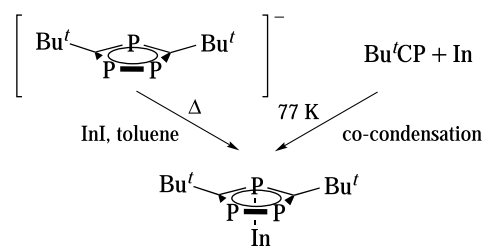
Matrix isolation provides a unique insight into otherwise unattainable compounds by isolating the trapped molecule in a rigid and inert matrix such as argon, which is non-invasive during spectroscopic measurements. This novel technique has been used successfully for the fabrication and spectroscopic study of In(0) derivatives, namely  $\text{In}(\text{CO})$ ,  $\text{In-In}(\text{CO})$ ,  $\text{In}(\text{CO})_2$ , and  $\text{In}(\text{CO})_2\cdot\text{In}$  (Scheme 21).<sup>228</sup> Additionally,  $\text{InMe}$  and  $\text{GaMe}$  have been reported via the reaction of the respective group 13 atoms with methane in solid Ar matrix.<sup>229</sup> The products are formed via UV photolysis ( $\lambda = 200\text{--}400\text{ nm}$ ) to give the alkylmetalhydride followed by photodissociation on broad-band irradiation ( $\lambda = 200\text{--}800\text{ nm}$ ) to yield  $\text{MeM}(\text{I})$  derivative.<sup>229,230</sup>

Co-condensation of indium vapor and *tert*-butylphosphaethyne at 77 K yields the volatile In(I) complexes  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_t)]$  and 1,3-diphosphacyclopentadienyl complex  $[\text{In}(\eta^5\text{-P}_2\text{C}_3\text{Bu}_3)]$ .<sup>159</sup> Single-crystal x-ray diffraction studies for  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_t)]$  reveals a discrete molecular structure, involving half-sandwich coordination of the

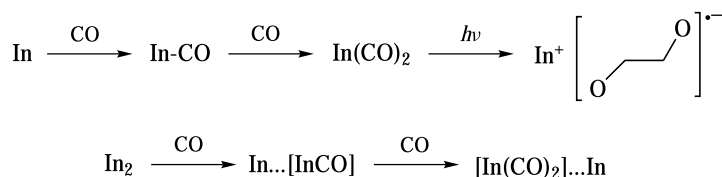
$\text{P}_3\text{C}_2\text{Bu}_t$  ring around the indium center. Cyclization of the  $\text{Bu}_t\text{C}\equiv\text{P}$  ligand to afford the cyclic ring is thought to occur by the “naked” indium atoms. The crystal structure of  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_t)]$  (see Table 2) confirms that the ring is coordinated to the indium metal center with a  $\eta^5$ -hapacity. In contrast to  $[\text{In}(\eta^5\text{-C}_5\text{H}_4\text{R})]$  derivatives, where polymeric zigzag chains are evident, the greater steric bulk of the phosphine substituted ring affords discrete molecular units with no aggregation (intermonomer distance = 3.526 Å).<sup>159</sup> Coincidentally,  $[\text{In}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_t)]$  can also be synthesized in good yields by treating InI with the base-free ligand salt  $\text{K}(\text{P}_3\text{C}_2\text{Bu}_t)$  (Scheme 22). A study of the molecular and electronic structure of these indium(I) phospholyls including computational modeling has been performed.<sup>231</sup>

Low oxidation state derivatives also have the tendency to be isolated in cage like structures; for example, the tetrahedral derivative  $\text{In}_4[\text{C}(\text{SiMe}_3)_3]_4$  is readily prepared from the reaction between InBr and  $\text{Li}[\text{C}(\text{SiMe}_3)_3]$ .<sup>232,233</sup>  $\text{In}_4[\text{C}(\text{SiMe}_3)_3]_4$  is a highly versatile synthon to many other novel organoindium compounds (Scheme 23). For example, reaction with elemental Se affords the unique In-Se hetrocubane,<sup>232</sup> and halogenation studies of  $\text{In}_4[\text{C}(\text{SiMe}_3)_3]_4$  afford novel alkylindium(I) halides,<sup>234,235</sup> while reaction with bimetallic species demonstrates its ability to be inserted into the metal–metal bond.<sup>236</sup> The main by-product from the reaction of InBr with the THF adduct of  $\text{LiC}(\text{SiMe}_3)_3$  is  $[\text{In}_3\text{Br}_3[\text{C}(\text{SiMe}_3)_3]_3]^-[\text{Li}(\text{THF})_3]^+$  whose geometrical configuration is analogous to that of  $\text{In}_3\text{I}_2[\text{C}(\text{SiMe}_3)_3]_3$ , except the inner In atom is attached to a bromide ion which bridges the  $\text{In}_3$  chain and the counterion  $[\text{Li}(\text{THF})_3]^+$ .<sup>237</sup>

A clear example of how ligand steric encumbrance has been implemented to control geometrical conformation for organoindium(I) species from monomeric to aggregated is



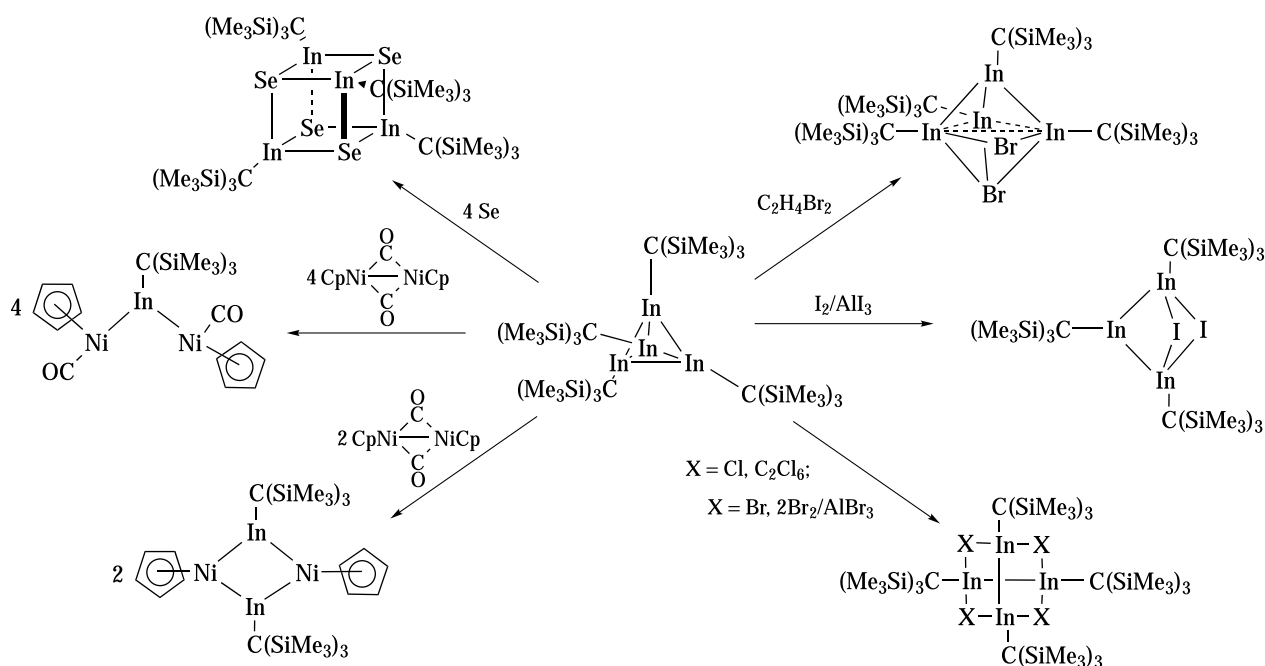
**Scheme 22** Preparative routes to these indium(I) phospholyls



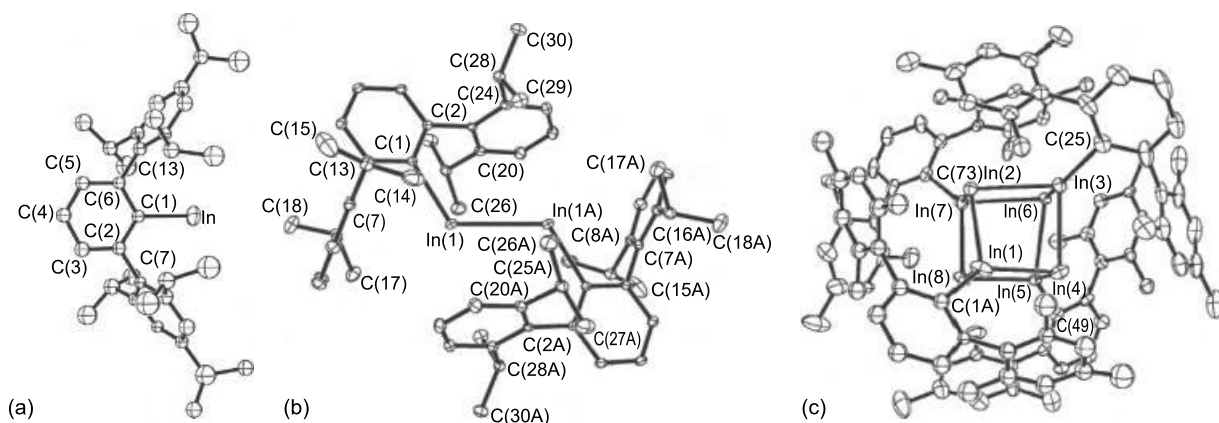
**Scheme 21** Pathways for matrix reactions of Indium with CO

the reaction of  $\text{InX}$  with lithium-terphenyls of various sizes. Molecular  $\text{In(I)}$  derivatives of monodentate ligands of any kind are limited; however, the use of the sterically demanding *o*-terphenyl ligand  $\{-\text{C}_6\text{H}_3\text{-2,6-Trip}_2$  ( $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-Pr}_3^i$ ), the monomeric compound  $\text{InC}_6\text{H}_3\text{-2,6-Trip}_2$ , has been prepared and isolated, (Figure 6a).<sup>112</sup> The modified terphenyl ligand  $-\text{C}_6\text{H}_3\text{-2,6-Dipp}_2$  ( $\text{Dipp} = \text{C}_6\text{H}_3\text{-2,6-Pr}_2^i$ ) enables the isolation of a stable dimeric group 13 “dimetallene” species  $\text{ArInInAr}$  ( $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$ ) (Figure 6b),<sup>238</sup> whereas using the less crowded ligand  $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$  ( $\text{Mes} = \text{C}_6\text{H}_2\text{-2,4,6-Me}_3$ ) affords the aggregated distorted cubane  $\text{In}_8(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_4$  (Figure 6c).<sup>239</sup>

A common trait of organoindium(II) complexes is the presence of  $\text{In-In}$  bonding. The preparation of the first carbene and diazabutadiene  $\text{In(II)}$  compound has been achieved by the reaction of  $\{\text{:CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})\}$  with  $\text{InBr}$  in either a 1:1 or 1:2 ratio, and  $((\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})\text{N}=\text{CH})_2$  with  $\text{InCl}$  in a 3:2 ratio.<sup>240</sup> Structural characterization reveals  $\text{In-In}$  bond lengths of 2.7436(7) and 2.7280(9) respectively. A comparison with reported  $\text{In-In}$  bond distances (Table 4) shows that  $\text{In-In}$  bond distances fall within the reported range since the  $\text{In-In}$  bond length is known to vary owing to the steric demand of substituents on the ligands.<sup>98</sup>



**Scheme 23** Reaction pathways for  $\text{In}_4[\text{C}(\text{SiMe}_3)_3]_4$



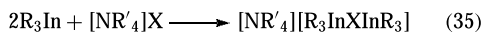
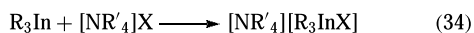
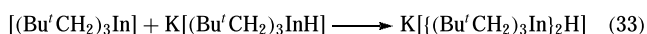
**Figure 6** Organoindium-terphenyl complexes

**Table 4** Metal–metal bond lengths of structurally characterized organoindium derivatives

Compound	In–In bond length (Å)	Ref.
[In <sub>2</sub> Br <sub>4</sub> (IMes) <sub>2</sub> ]	2.7436(7)	240
[In <sub>2</sub> Cl <sub>2</sub> (DAB) <sub>2</sub> ]	2.7280(9)	240
[((Me <sub>3</sub> Si) <sub>2</sub> C(Ph)C(Me <sub>3</sub> Si)N)InBr] <sub>2</sub>	2.728(4)	98
[(2,4,6-Pr <sup>i</sup> <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> In] <sub>2</sub>	2.775(2)	241
[(2,4,6-(CF <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> In] <sub>2</sub>	2.744(2)	242
[(Me <sub>3</sub> Si) <sub>3</sub> CIn] <sub>4</sub>	3.002(1)	232
[(EtMe <sub>2</sub> Si) <sub>3</sub> CIn] <sub>4</sub>	3.004(1)	101
[(Pr <sup>i</sup> Me <sub>2</sub> Si) <sub>3</sub> CIn] <sub>4</sub>	3.145(1)	101
[(Me <sub>3</sub> Si) <sub>2</sub> CHIn] <sub>2</sub>	2.8534(4)	243
[(2,6-Dipp <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> In] <sub>2</sub>	2.9786(5)	238
[In <sub>8</sub> (C <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> ) <sub>4</sub> ]	2.8754(13)–2.9328(13)	239

## 9 ORGANOINDIUM ANIONIC DERIVATIVES

The reaction of organoindium derivatives with alkali metals<sup>54,244,245</sup> results in the isolation of the appropriate tetraorgano anionic complex M[InR<sub>4</sub>] (M = K, Rb, Cs; R = Me and M = Li, Na, K, Rb, Cs; R = Ph) (equation 31), and they prove to be valuable synthons for the preparation of indium compounds.

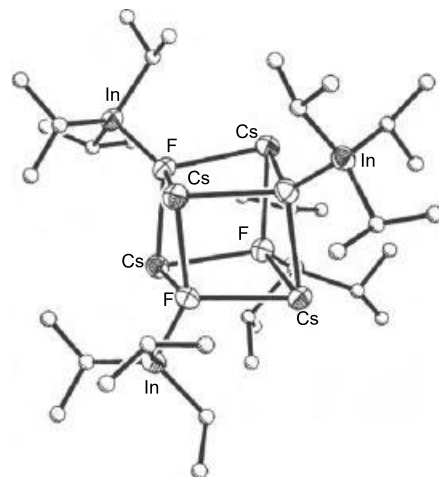
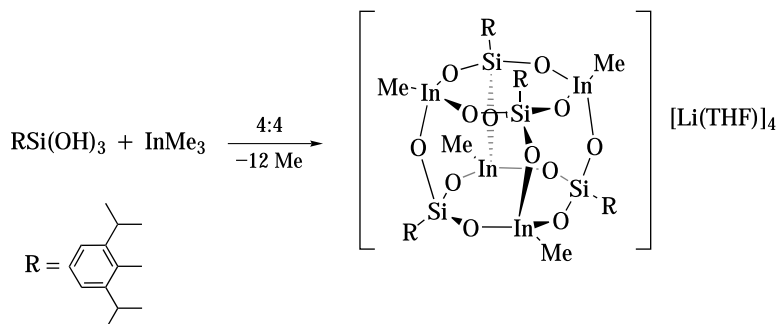


Organoindium anionic compounds in which indium coordinates to both alkyl and hydride ligands have been synthesized via the reaction of R<sub>3</sub>In with KH (equation 32); the product, however, combines with unreacted trialkyl to give K[{(t-BuCH<sub>2</sub>)<sub>3</sub>In}<sub>2</sub>H] (equation 33).<sup>54</sup> Complexes in which indium coordinates to both alkyl and halide ligands can be prepared by the reaction of R<sub>3</sub>In with [NR'<sub>4</sub>]X (X = F, Cl,

Br) (equation 34). If two equivalents of R<sub>3</sub>In are used, the products are dimeric with bridging halides (equation 35).

An example of a novel synthesis to triple stacked InCp cations is via the reaction of [InCp\*]<sub>6</sub> with an equimolar mixture of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene to afford [(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)In(μ-η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)In(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BO(H)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>.<sup>246</sup> Given the very long indium–ring-centroid distances of 3.490(4) and 3.325(4) Å in conjunction with molecular orbital calculations, the authors view the molecule as an inverse sandwich cation.<sup>247</sup> Ionic cage structures are exemplified by an extension to the first reported polyhedral indium siloxanes<sup>198</sup> when RSi(OH)<sub>3</sub> (R = 1,3-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) is reacted with M[InMe<sub>4</sub>] (M = Li, Na) in a 4:4 ratio via elimination of the CH<sub>3</sub> groups, leading to a ionic poly-organoindium siloxane (Scheme 24).<sup>198</sup>

In another example, the reaction of CsF with organoindium compounds in acetonitrile provides a novel route to the respective cesium organoindium heterocubane in high yields (Figure 7).<sup>248,249</sup> In contrast to Cs[InMe<sub>4</sub>], no short intra- and intermolecular Cs···C contacts are noted for [Cs{Pr<sup>i</sup>In}]<sub>4</sub>, thus indicating that there are no significant intermolecular interactions between the heterocubane units.

**Figure 7** Single-crystal structure of the ionic heterocubane [Cs{Pr<sup>i</sup>In}]<sub>4</sub>**Scheme 24** Ionic polyhedron organoindium siloxane

## 10 RELATED ARTICLES

Alloys; Aluminum: Inorganic Chemistry; Coordination & Organometallic Chemistry: Principles; Gallium: Inorganic Chemistry; Gallium: Organometallic Chemistry; Indium: Inorganic Chemistry; Organic Synthesis Using Metal-mediated Coupling Reactions; Organic Synthesis Using Metal-mediated Metathesis Reactions.

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