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Phosphine and phosphido indium hydride complexes and their use in inorganic synthesis

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Reaction of PR_3, R = cyclohexyl (Cy), cyclopentyl (Cy^p) or phenyl, with $[InH_3(NMe_3)]$ affords the 1 : 1 indium trihydride complexes, $[InH_3(PR_3)]$. The stabilities and spectroscopic properties of these complexes are described in terms of the phosphine ligands' steric bulk and nucleophilicity. Reaction of two equivalents of PCy_3 with $[InH_3(NMe_3)]$ yields the complex $[InH_3(PCy_3)_2]$ which has been characterised by X-ray crystallography. The first phosphido–indium hydride complex, $[\{InH_2(PCy_2)\}_3]$, has been prepared by a novel synthetic route which involves treatment of $[InH_3(NMe_3)]$ with $LiPCy_2$. Its crystal structure shows it to exist as a cyclic trimer in the solid state. The complex, $[InH_3(PCy_3)]$ has been used to prepare a range of monomeric indium chalcogenolato complexes, $[In(EPh)_3(PCy_3)]$, E = S, Se or Te, all of which have been structurally characterised.

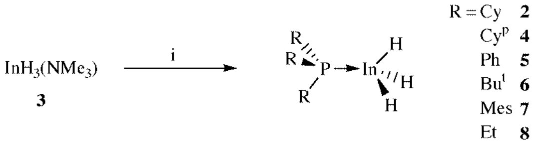
Introduction

The chemistry of both aluminium and gallium hydride complexes is now well established.[1] Over the years such compounds have found a remarkable variety of applications in areas including organic synthesis,[2] inorganic synthesis[3] and materials chemistry.[4] It would perhaps be thought that the chemistry of indium hydride complexes would now be equally developed, especially considering the potential applications of these compounds. This is, however, not the case and indeed after Wiberg's original synthesis of $LiInH_4$ in 1957,[5] and before 1998, only five structurally characterised compounds containing In–H bonds had been described, *viz.* $[Li(thf)_2][\{(Me_3Si)_3C\}_2In_2H_5]$,[6] $K[H\{In(CH_2CMe_3)_3\}_2]$,[7] $K_3[K(Me_2SiO)_7][InH(CH_2CMe_3)_3]_4$,[8] $[InH\{2\text{-}Me_2NCH_2(C_6H_4)\}_2]$[9] and $[Me_2InB_3H_8]$.[10] We have since reported the first indium trihydride complexes, $[InH_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}]$ **1**[11] and $[InH_3(PCy_3)]$ **2**,[12] which are stabilised by either a highly nucleophilic "Arduengo" carbene or a bulky tertiary phosphine ligand. In addition, the ionic indium hydride complex, $[(Me_3In)_2H][Li(tmen)_2]$, has been reported by us.[13]

Compound **2** possesses remarkable stability in that it does not decompose in the solid state at temperatures below 50 °C and is stable in air for days. This unexpected stability has prompted us to begin a systematic study aimed at the preparation of a range of thermally stable indium hydride complexes and comparing their chemistry to those of their aluminium and gallium counterparts. Moreover, the ease of handling of **2** should lend it to an array of applications similar to those that have already been found for aluminium and gallium trihydride complexes. The work described herein addresses this potential with the preparation of several monomeric indium chalcogenolato complexes. In addition, the synthesis and characterisation of several phosphine–InH_3 adducts related to **2**, and the first phosphido–indium hydride complex are discussed.

Results and discussion

In a preliminary communication[12] we have described the synthesis and characterisation of the indium trihydride complex, **2**; full synthetic details of which are included herein. In order to examine the generality of formation of phosphine–InH_3 adducts a series of other tertiary phosphines were reacted with $[InH_3(NMe_3)]$ **3** as outlined in Scheme 1. When PCy^p_3, Cy^p = cyclopentyl, was employed the product, **4**, precipitated from the reaction solution and was readily recrystallised from DME in moderate yield (39%). The reaction involving PPh_3 also lead to a precipitate forming which could be isolated at −20 °C but all attempts to recrystallise this crude product led to its decomposition to indium metal and PPh_3 with the generation of a gas. It is assumed that this precipitate is $[InH_3(PPh_3)]$ **5** on the basis of infrared data (see below). After treating $[InH_3(NMe_3)]$ with either PBu^t_3, $PMes_3$ or PEt_3 at −30 °C no precipitate formed and so volatiles were removed from the reaction mixture *in vacuo* which resulted in decomposition, even at −30 °C. The reaction precursor, **3**, cannot be isolated in the solid state and shows a similar instability in solution, and thus it is difficult to be sure if the three adducts **6**–**8** have been formed or if no reaction has occurred with these phosphines. Alternate routes to $[InH_3(PR_3)]$ were examined whereby $LiInH_4$ was treated with either PR_3 or $PR_3{\cdot}HCl$ at −20 °C in the expectation that LiH or LiCl elimination would yield the target phosphine–indane adducts. Similar routes have been successful in the formation of related alane or gallane adducts, $[MH_3(PCy_3)]$ M = Al,[14] Ga,[15] though in the present cases no reactions occurred. The most likely reason for this lies with the inability to carry out these reactions above −10 °C due to the thermal instability of $LiInH_4$.



Scheme 1 i, PR_3, Et_2O.

At the outset of this study it was thought that the thermal stability of any formed complexes would largely depend upon two phosphine characteristics, their basicity and their steric bulk. The more basic the phosphine, the stronger the bond between it and the InH_3 unit should be. In the case of Lewis base adducts of AlH_3 and GaH_3 their primary decomposition process is Lewis base loss[1] and it would seem that this should also be the case for InH_3 adducts. Therefore, the stronger the phosphine donor, the more stable should be the formed indane complex. In terms of steric protection Downs and Pulham[16] have suggested that the thermal instability of the binary heavier Group 13 hydrides may not be solely thermodynamic in nature but may have a kinetic aspect whereby decomposition may occur through intermediates containing M–H–M bridges. This could also be the case for complexes of the type $[InH_3(PR_3)]$, especially considering indium's tendency to form five- or six-coordinate complexes.[17] Therefore it was hypothesised that the greater the steric bulk of the phosphine ligand, the greater the thermal stability of the resulting complex should be, as the formation of intermolecular hydride bridges would be circumvented.

This seemed to be borne out by the stability of **2** which has been attributed to the 170° cone angle of the phosphine ligand. However, its stability is also likely to result from the relatively strong σ-donor characteristics of the ligand. There are some surprises in the stabilities of the other complexes, **4**–**8**, if these are correlated to ligand cone angles [$PMes_3$ (212°) > PBu^t_3 (182°) > PCy_3 (170°) > PPh_3 (145°) > PEt_3 (132°)][18] and ligand basicities [$PBu^t_3 > PCy_3 \approx PEt_3 > PMes_3 > PPh_3$].[19] Although no cone angle or basicity data could be obtained for PCy^p_3 it would seem likely that these are slightly less than for PCy_3 which is in line with the lower thermal stability of **4** (decomp. 20 °C) relative to **2** and the fact that it is slightly air sensitive. Interestingly, PBu^t_3 is both bulkier and more nucleophilic than PCy_3 but no stable indane complex incorporating it could be formed. It is unlikely that the ligand is too bulky to form a complex as the corresponding gallane complex, $[GaH_3(PBu^t_3)]$, is known,[20] though it is less stable than $[GaH_3(PCy_3)]$. The $PMes_3$ ligand is a weaker σ-donor but is very bulky and in this case is perhaps too much so to displace NMe_3 from **3** to form **7**. No stable complex could be formed with PEt_3 which is a good σ-donor, but has a relatively small cone angle. Finally, PPh_3 has only a moderate cone angle and is a weak σ-donor, yet forms a complex, **5**, which can be isolated in the solid state and is moderately thermally stable for an indane complex (decomp. *ca.* 0 °C). It is probable that PPh_3 forms an isolable indane complex when ligands such as PBu^t_3 do not because the complex, **5**, precipitates from the reaction mixture and is considerably more stable in the solid state than in solution. Indeed, when dissolution of **5** in thf is attempted at −70 °C decomposition rapidly occurs.

The infrared spectra of solid samples of the three isolated phosphine–indane complexes show characteristic strong, broad In–H stretching absorptions at 1661 cm^{-1} **2**, 1649 cm^{-1} **4** and 1681 cm^{-1} **5**. Those for **2** and **4** are close to each other and to that of the carbene–InH_3 adduct **1** (1640 cm^{-1}).[11] All are at considerably lower wavenumbers than either their alane or gallane analogues, a fact which reflects the relative weakness of the In–H bond. It is noteworthy that the In–H stretch for **5** is at a significantly higher frequency than in the other indane adducts which is probably a result of the weak σ-donating properties of PPh_3.

Although **2** is stable in the solid state for weeks at room temperature, in benzene solutions it will decompose giving indium metal, PCy_3 and a gas at 25 °C over 1 hour. Compound **4** is less stable in solution and completely decomposes over 15 minutes at room temperature. Because of the thermal instability of **5** in solution NMR data on only **2** and **4** could be obtained. Those for **2** have been reported[12] but most importantly its ^1H NMR spectrum shows a broad hydride resonance at δ 5.61 which is downfield of the related resonances in the spectra of its alane, $[AlH_3(PCy_3)]$, and gallane, $[GaH_3(PCy_3)]$, counterparts, *viz.* δ 4.32[14] and 4.25[15] respectively. A similar pattern was observed for the carbene–metal trihydride complexes, $[MH_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}]$ M = Al (δ 4.63), Ga (δ 4.48), In (δ 5.58).[11] Not surprisingly the hydride resonance of **4** (δ 5.14) occurs in a similar position to **2**. The signal integrates for 3 hydrogens and is very broad as a result of the influence of the quadrupolar indium centre. Presumably this is also the reason why no hydride–phosphorus coupling is observed in its ^1H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **4** is unremarkable and exhibits a singlet (δ 3.45) close to that of the free ligand (δ 1.38).

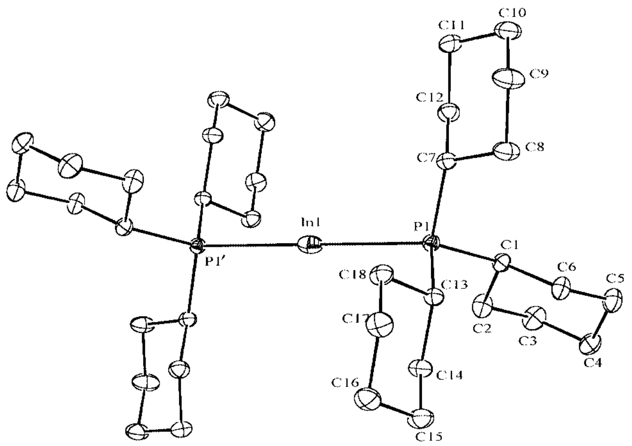
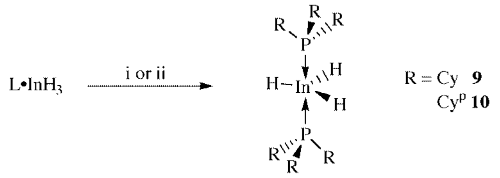


Fig. 1 Molecular structure of compound **9**. Selected bond lengths (Å) and angles (°): In–P(1) 2.9869(5), P(1)–C(13) 1.8548(14), P(1)–C(7) 1.8567(14), P(1)–C(1) 1.8674(14); P(1)–In(1)–P(1′) 180.000(17).

Five-coordinate bis(phosphine) adducts of alane and gallane are unknown though alane does form polymeric five-coordinate complexes of the type $[\{AlH_3(R_2PCH_2CH_2PR_2)\}_\infty]$, R = alkyl, with diphosphine ligands.[14] As indium has a larger covalent radius (1.55 Å) than aluminium or gallium (1.25 Å) it was thought that it might be possible to form bis(phosphine) adducts of indane. This was attempted by reacting either two equivalents of PCy_3 with *in-situ* generated $[InH_3(NMe_3)]$ or an equimolar amount of PCy_3 or PCy^p_3 with **2** or **4** respectively (Scheme 2). In each case the anticipated product, **9** or **10**, formed in moderate yield and could be recrystallised from DME. An attempt was also made to prepare $[InH_3(PPh_3)_2]$ by reaction of two equivalents of PPh_3 with **3** at −30 °C, however this led to the precipitation of **5** from solution in the early stages of reaction and the second equivalent of PPh_3 remained unreacted.



Scheme 2 i, PCy_3, Et_2O, L = NMe_3; ii, PR_3, DME, L = PR_3.

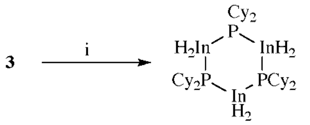
Complex **9** is moderately stable at room temperature in the solid state and does not decompose until 37 °C to indium metal and the free phosphine. It is surprising that its decomposition temperature is lower than that of **2** as it would be expected that the primary decomposition process would be phosphine loss to form **2** which is stable to 50 °C. Indeed, compound **9**, unlike **2**, does fully decompose over several days at room temperature. Not surprisingly, the thermal stability of **10** is slightly lower than **9** and it decomposes at 15 °C.

The infrared spectra (Nujol mulls) of **9** and **10** display strong, broad In–H stretches at 1666 and 1644 cm^{-1} respectively which are close to those of their 1 : 1 analogues. Both complexes are not stable in solution and will decompose at 25 °C in a matter of minutes. However, at low temperature their ^1H NMR spectra exhibit broad resonances (δ 5.81 **9** and 5.23 **10**) which correspond to the hydride ligands in each complex. These are shifted slightly downfield with respect to **2** and **4**. Their $^{31}P\{^1H\}$ NMR spectra display singlet resonances close to those of the free phosphine ligands.

The crystal structure of **9** is depicted in Fig. 1. The indium atom sits on a centre of inversion and consequently the hydride ligands attached to it are necessarily disordered and thus could not be located from difference maps. It is clear, however, that the indium centre has a trigonal bipyramidal coordination environment with the two phosphine ligands in axial positions and the hydride ligands in equatorial positions. The phosphine ligands are staggered and, interestingly, the In–P bond lengths [2.9869(5) Å] are almost 0.34 Å longer than in **2** [2.6474(6) Å]. Indeed, the lengths of these bonds are second only to the In–P bonds (3.054 Å) in $[\{InI_3(PPh_3)\}\{InI_3(PPh_3)_2\}]$.[21] It may be thought that the very long In–P bond lengths in **9** are partly due to steric buttressing of the two bulky phosphine ligands but this is probably not the major reason. We have recently carried out high level *ab initio* calculations (DFT/B3-LYP) on $[InH_3(PMe_3)]$ and $[InH_3(PMe_3)_2]$ which show similar differences between their In–P bond lengths (2.755 Å and 3.038 Å respectively)[22] as compared to those of **2** and **9**. However, in the model compounds the ligands are not bulky and so there is most likely more of an electronic rather than a steric basis to the lengths of the In–P bonds in **9**.

Considering the stability of **2** and **4** we thought it might be possible to prepare phosphido–indium hydride complexes of the type $[\{InH_2(PR_2)\}_n]$, R = alkyl, which could also be stable at room temperature if bulky alkyl groups were employed. Compounds of this type are worthy synthetic targets as related Group 15–Group 13 hydride complexes have been used as fixed stoichiometry single source precursors to III/V semiconducting materials.[23] It was hoped that if such compounds could be prepared they would cleanly thermally decompose to InP *via* the loss of alkane.

The dicyclohexylphosphide ligand was chosen for this study because of its steric bulk which has previously been used to stabilise the gallium hydride complex, $[\{GaH_2(PCy_2)\}_3]$,[24] to temperatures in excess of 150 °C. Initial attempts to form an analogous indium hydride complex by reaction of $LiInH_4$ with a 1 : 1 mixture of PCy_2H and anhydrous HCl, or PCy_2H with **3** both led to decomposition. An alternative strategy was devised whereby $LiPCy_2$ was reacted with one equivalent of **3**. This proved successful and resulted in the formation of $[\{InH_2(PCy_2)\}_3]$ **11** in moderate yield (43%) *via* LiH elimination (Scheme 3). Compound **11** is readily recrystallised from diethyl ether to give colourless crystals which are stable in air for hours and decompose at 64 °C. Although this is a higher decomposition temperature than for **2** crystals of **11** will slowly decompose at room temperature over a period of days. Solutions of **11** are stable at room temperature for only 15 minutes. Unfortunately, in both solution and the solid state this compound does not decompose to InP but to indium metal and PCy_2H with the evolution of a gas, presumably H_2.



11

Scheme 3 i, $LiPCy_2$, Et_2O, −LiH.

As with the phosphine–InH_3 adducts, complex **11** exhibits a strong broad In–H absorption in its infrared spectrum, but at significantly higher frequency, 1686 cm^{-1}. The reason for this shift is probably an inductive effect of the anionic phosphido ligand which strengthens its In–H bonds relative to those of **2** and **4**. In solution the ^{31}P NMR spectrum of **11** displays a singlet at δ −47 (*cf.* δ −33 in $[\{GaH_2(PCy_2)\}_3]$[24]). Its ^1H NMR spectrum shows only a single broad hydride resonance at δ 5.88 over a range of temperatures which is in contrast to the hydride resonance of $[\{GaH_2(PCy_2)\}_3]$[24] which exists as a broad triplet at δ 4.68 due to coupling to the two equivalent P-centres adjacent to each In centre. This difference is not surprising as P–H coupling through the more quadrupolar indium centre would be difficult to observe. Although **11** is trimeric in the solid state it would be interesting to carry out a solution state molecular weight determination to shed light on the nuclearity of this complex in solution. Unfortunately such an experiment proved unfeasible due to the instability of the compound in solution.

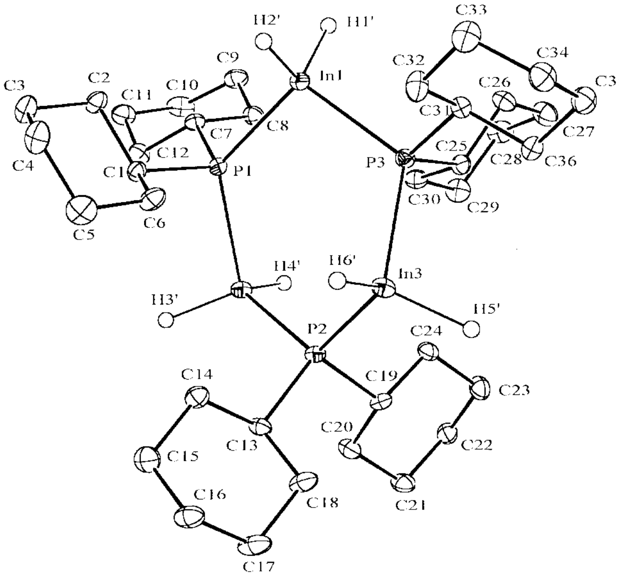


Fig. 2 Molecular structure of compound **11**. Selected bond lengths (Å) and angles (°): P(1)–In(1) 2.5818(8), P(1)–In(2) 2.5985(8), P(2)–In(2) 2.5778(8), P(2)–In(3) 2.5862(9), P(3)–In(1) 2.5666(8), P(3)–In(3) 2.6044(8), In(1)–H(1) 1.77(5), In(1)–H(2) 1.70(4), In(2)–H(3) 1.63(4), In(2)–H(4) 1.74(5), In(3)–H(5) 1.79(5), In(3)–H(6) 1.64(5); P(3)–In(1)–P(1) 103.95(2), P(3)–In(1)–H(1) 108.2(15), P(1)–In(1)–H(1) 107.0(15), P(3)–In(1)–H(2) 108.4(14), P(1)–In(1)–H(2) 112.8(15), H(1)–In(1)–H(2) 115.7(21), P(2)–In(2)–P(1) 108.83(3), P(2)–In(2)–H(3) 112.7(13), P(1)–In(2)–H(3) 101.9(14), P(2)–In(2)–H(4) 110.0(15), P(1)–In(2)–H(4) 107.2(15), H(3)–In(2)–H(4) 115.6(20), P(2)–In(3)–P(3) 107.97(2), P(2)–In(3)–H(5) 106.0(17), P(3)–In(3)–H(5) 105.4(17), P(2)–In(3)–H(6) 113.1(18), P(3)–In(3)–H(6) 107.2(17), H(5)–In(3)–H(6) 116.6(24), In(1)–P(1)–In(2) 128.40(3), In(2)–P(2)–In(3) 121.08(3), In(1)–P(3)–In(3) 119.53(3).

The molecular structure of **11** (Fig. 2) confirmed that it exists as a cyclic trimer in the solid state as does its gallium analogue. The geometry of the In_3P_3 core is best described as a flattened or twisted boat conformation which, although unusual, has been seen in related complexes, *e.g.* $[\{GaH_2(PCy_2)\}_3]$[24] and $[\{Me_2Ga(PPr^i_2)\}_3]$.[25] The In–P bond lengths are all similar (2.596 Å ave.) and lie in the normal region for such interactions. The quality of the X-ray data was sufficient for the hydride ligands to be located from difference maps and refined isotropically. Although not accurate, the In–H distances (1.71 Å ave.) are in the expected region for terminal In–H bonds (*cf.* 1.68 Å ave. in **2**[12]).

Lewis base adducts of AlH_3 and GaH_3 have proved to be valuable in a range of inorganic syntheses.[1] It seemed logical that this would also be the case for thermally stable InH_3 adducts. In the final part of this study we wished to demonstrate this with the preparation of a series of monomeric tris(chalcogenolato)indium complexes. There were a number of reasons for choosing these systems which include their potential use as precursors to III/VI materials, *e.g.* In_xSe_y, that have useful opto-electronic properties.[26] In addition, monomeric tris-thiolato- and -selenolato-indium complexes are rare, whilst structurally characterised tris(tellurolato)indium complexes are unknown.

A synthetic route that has been shown to be facile for alane and gallane complexes[27] was utilised whereby complex **2** was reacted with 3/2 equivalents of the diphenyldichalcogenides, E_2Ph_2, E = S, Se or Te, which afforded **12**–**14** in moderate yields (Scheme 4) *via* elimination of dihydrogen. All prepared complexes are thermally robust and appear to be stable to the atmosphere indefinitely.

In solution **12**–**14** display similar NMR spectra and in the case of their $^{31}P\{^1H\}$ NMR spectra singlets were observed at

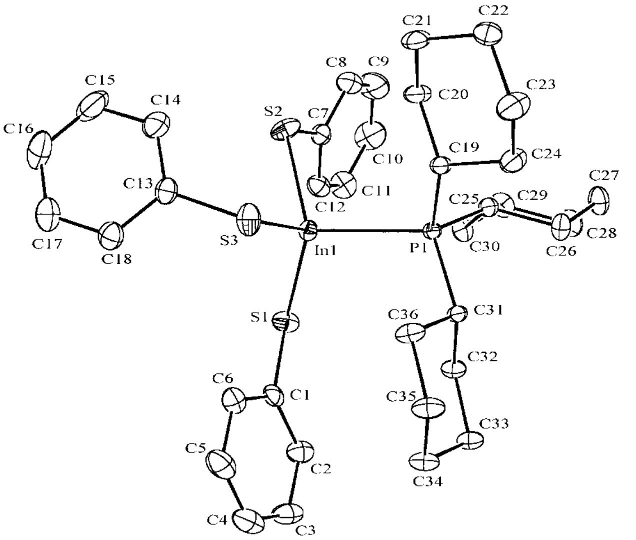


Fig. 3 Molecular structure of compound **12**. Selected bond lengths (Å) and angles (°): P(1)–In(1) 2.6109(8), S(1)–In(1) 2.4456(10), S(2)–In(1) 2.4544(9), S(3)–In(1) 2.4384(9); S(3)–In(1)–S(1) 119.96(4), S(3)–In(1)–S(2) 105.79(4), S(1)–In(1)–S(2) 109.48(3), S(3)–In(1)–P(1) 97.85(3), S(1)–In(1)–P(1) 112.56(3), S(2)–In(1)–P(1) 110.48(3), C(1)–S(1)–In(1) 108.92(12), C(7)–S(2)–In(1) 110.45(12), C(13)–S(3)–In(1) 101.50(12).

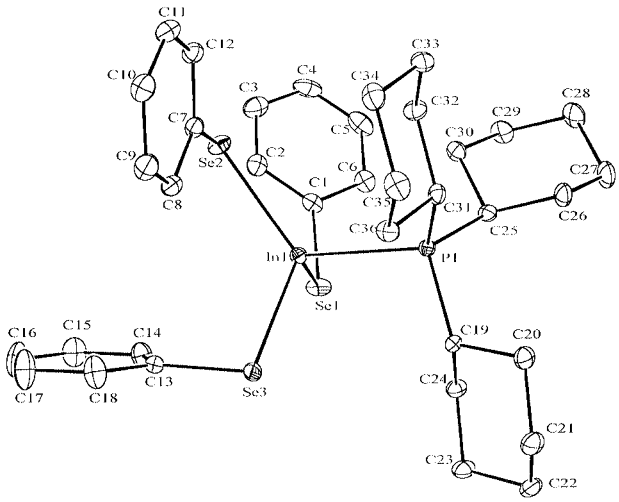
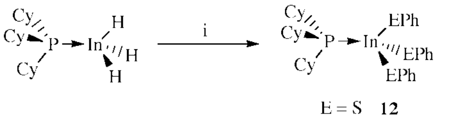


Fig. 4 Molecular structure of compound **13**. Selected bond lengths (Å) and angles (°): In(1)–P(1) 2.6145(11), In(1)–Se(1) 2.5760(7), In(1)–Se(2) 2.5537(8), In(1)–Se(3) 2.5604(5); Se(2)–In(1)–Se(3) 116.76(3), Se(2)–In(1)–Se(1) 110.736(19), Se(3)–In(1)–Se(1) 106.60(3), Se(2)–In(1)–P(1) 117.28(4), Se(3)–In(1)–P(1) 98.66(4), Se(1)–In(1)–P(1) 105.47(3), C(1)–Se(1)–In(1) 101.50(11), C(7)–Se(2)–In(1) 105.21(10), C(13)–Se(3)–In(1) 97.49(11).



E = S **12**
E = Se **13**
E = Te **14**

Scheme 4 i, 3/2 E_2Ph_2, DME, $-H_2$.

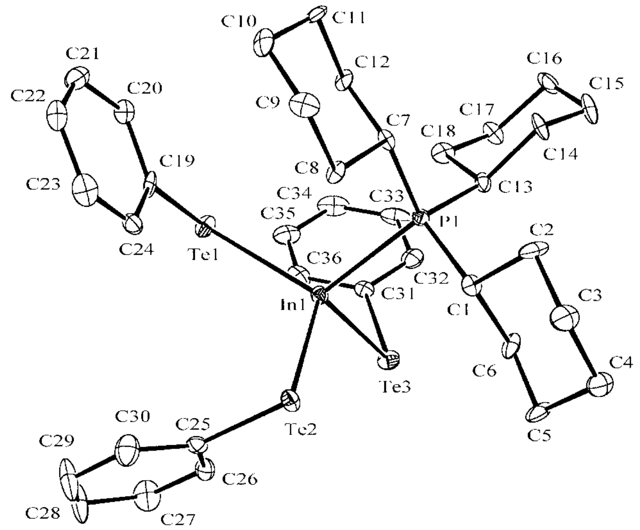


Fig. 5 Molecular structure of compound **14**. Selected bond lengths (Å) and angles (°): In(1)–P(1) 2.642(3), In(1)–Te(1) 2.7301(13), In(1)–Te(2) 2.7435(13), In(1)–Te(3) 2.7681(13); P(1)–In(1)–Te(1) 118.06(8), P(1)–In(1)–Te(2) 98.05(8), Te(1)–In(1)–Te(2) 115.66(4), P(1)–In(1)–Te(3) 105.72(8), Te(1)–In(1)–Te(3) 109.96(4), Te(2)–In(1)–Te(3) 108.31(4), C(19)–Te(1)–In(1) 101.6(3), C(25)–Te(2)–In(1) 96.4(3), C(31)–Te(3)–In(1) 98.6(3).

δ 18.61, 10.01 and −7.10 respectively (*cf.* δ 7.43 for **2**[12]). It is noteworthy that the related signal for the gallium analogue of **14**, *viz.* $[Ga(TePh)_3(PCy_3)]$,[27] has been reported to occur at significantly lower field (δ 68.6) though no explanation for this difference can be offered here.

The molecular structures of **12**–**14** (Figs. 3–5) show all these compounds to be monomeric. Compounds **13** and **14** are isomorphous with each other but not with the thiolato complex, **12**. Interestingly, this complex is isomorphous to the related complex, $[Ga(TePh)_3(PCy_3)]$.[27] Despite this, the geometries of all three compounds are similar and the indium centre in each sits in a heavily distorted tetrahedral environment which presumably results from the steric congestion within the molecule. The In–E distances in each are in the normal regions and average 2.446 Å (**12**), 2.563 Å (**13**) and 2.747 Å (**14**). Finally the In–P distances in all compounds are similar and close to that in **2** [2.6474(6) Å].[12]

Conclusions

A series of phosphine–indium trihydride complexes has been prepared and found to have varying thermal stabilities depending on the choice of phosphine ligand. The first examples of 2:1 phosphine–InH_3 and phosphido–indium hydride complexes have been prepared and structurally characterised. The utility of phosphine–InH_3 complexes in inorganic synthesis has been partly addressed with the preparation of a series of indium chalcogenolato complexes. Overall, the study shows that relatively stable and easily handled indium hydride complexes are accessible and suggests they will find further uses in synthesis and as materials precursors. These applications will be the subject of a series of forthcoming papers.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether, hexane, toluene and DME were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL FX90, Bruker AMX360 or Bruker DPX400 spectrometer in C_6D_6 or C_7D_8 and were referenced to the residual ^1H or ^{13}C resonances of the solvent used, or to external 85% H_3PO_4, δ 0.0 (^{31}P NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under EI or APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Elemental analyses were carried out at either the Chemistry Department at Cardiff or the Warwick Analytical Service. Analyses for **4**, **5**, **9**, **10** and **11** could not be obtained due to the thermal instability of these compounds. The starting material $[InH_3(NMe_3)]$

was prepared by a literature procedure.[11] All other reagents were used as received.

Syntheses

[$InH_3(PCy_3)$] 2.[12] PCy_3 (0.72 g, 2.6 mmol) in diethyl ether (20 cm^3) was added to a solution of [$InH_3(NMe_3)$] (2.6 mmol) in diethyl ether (40 cm^3) at −50 °C forming a white precipitate. The reaction mixture was allowed to warm to −20 °C and stirred for a further 2 h. After this time the solution was filtered to leave a white solid, which was washed with cold hexane (20 cm^3). Extraction with toluene (30 cm^3) at −20 °C and cooling to −35 °C overnight afforded colourless cubic crystals. Yield 0.71 g, 71%; mp 50 °C (decomp.). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.92–1.75 [mult, 33H, C_6H_{11}], 5.61 [br s, 3H, In-*H*]. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 26.6 [s, *C*H_2], 27.7 [d, *C*H_2, $^2J_{PC}$ 10.2 Hz], 30.5 [s, *C*H_2], 31.8 [d, *C*H, $^1J_{PC}$ 13.0 Hz]. ^{31}P NMR (36.3 MHz, C_6D_6, 85% H_3PO_4, 298 K): δ 7.43. MS EI: *m*/*z* (%) 280 [PCy_3^+, 63], 197 [PCy_2^+, 100], 114 [PCy^+, 78]. IR (Nujol) *v*/cm^{-1}: 1661 (s, br, In–H str).

[$InH_3(PCy^p{}_3)$] 4. $PCy^p{}_3$ (0.65 g, 2.54 mmol) was added to a solution of [$InH_3(NMe)_3$] (≈2.54 mmol) in diethyl ether (*ca.* 70 cm^3) at −70 °C. The resulting solution was warmed to −30 °C and stirred for 2 h whereupon it was cooled to −70 °C to yield a colourless precipitate. This was washed with cold diethyl ether (*ca.* 10 cm^3) and dried *in vacuo*. Subsequent extraction with cold (−25 °C) DME (*ca.* 40 cm^3), filtration and placement at −30 °C yielded **4** as colourless needles (0.36 g, 39%), decomp. +20 °C. ^1H NMR (400 MHz, $C_6D_5CD_3$, 300 K): δ 1.12–1.56 (m, 27H, C_5H_9), 5.14 (br s, 3H, In–H). ^{13}C NMR (100.6 MHz, $C_6D_5CD_3$, 300 K): δ 26.7 (d, CH, $^1J_{PC}$ 20.8 Hz), 30.6 (s, CH_2), 31.8 (d, CH_2, $^2J_{PC}$ 14.3 Hz). ^{31}P NMR (36.3 MHz, $C_6D_5CD_3$, 85% H_3PO_4, 233 K): δ 3.45 (s). MS EI: *m*/*z* (%) 169 [$P(C_5H_9)_2^+$, 4], 100 [$P(C_5H_9)^+$, 100], 69 [$C_5H_9^+$, 79]. IR (Nujol) *v*/cm^{-1}: 1649 (s, br, In–H str.).

[$InH_3(PPh_3)$] 5. A solution of PPh_3 (0.67 g, 2.55 mmol) in diethyl ether (30 cm^3) was slowly added to a solution of [$InH_3(NMe_3)$] (≈2.54 mmol) in diethyl ether (70 cm^3) at −70 °C. The solution was warmed to −30 °C and stirred for 2 h whereupon a precipitate of **5** deposited. This was washed with cold diethyl ether (*ca.* 10 cm^3) and dried *in vacuo* (0.67 g, 69%), decomp. *ca.* 0 °C. IR (Nujol) *v*/cm^{-1}: 1681 (s, br, In–H str.).

[$InH_3(PCy_3)_2$] 9. *Method (i).* A solution of PCy_3 (1.43 g, 5.10 mmol) in diethyl ether (*ca.* 30 cm^3) was slowly added to a solution of [$InH_3(NMe_3)$] (≈2.54 mmol) in diethyl ether (*ca.* 70 cm^3) at −70 °C. The resulting solution was warmed to −30 °C and stirred for 2 h whereupon volatiles were removed *in vacuo* to yield a white solid. This was washed with cold diethyl ether (*ca.* 10 cm^3) and extracted with cold (−20 °C) DME (*ca.* 50 cm^3), filtered and the filtrate placed at −30 °C to yield **9** as colourless needles (1.09 g, 63%).

Method (ii). A solution of PCy_3 (0.32 g, 1.14 mmol) in DME (*ca.* 20 cm^3) was added slowly to a stirred solution of [$InH_3\{PCy_3\}$] (0.44 g, 1.10 mmol) in DME (*ca.* 30 cm^3) at −70 °C. The resulting solution was warmed to −30 °C and stirred for 2 h whereupon the volatiles were removed *in vacuo* to yield a white solid. This was washed with cold diethyl ether (*ca.* 5 cm^3) and extracted with cold (−20 °C) DME (*ca.* 30 cm^3), concentrated *in vacuo*, filtered and the filtrate placed at −30 °C to yield **9** as colourless needles (0.57 g, 76%), decomp. +37 °C. ^1H NMR (400 MHz, C_6D_6, 300 K): δ 1.23–1.97 (m, 66H, C_6H_{11}), 5.81 (br s, 3H, In–H). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 27.3 (s, CH_2), 28.4 (d, CH_2, $^3J_{PC}$ 9.1 Hz), 32.0 (d, CH_2, $^2J_{PC}$ 12.6 Hz), 32.6 (d, CH, $^1J_{PC}$ 18.6 Hz). ^{31}P NMR (36.3 MHz, C_6D_6, 85% H_3PO_4, 298 K): δ 7.32 (s). MS EI: *m*/*z* (%) 280 [$P(C_6H_{11})_3^+$, 23], 198 [$P(C_6H_{11})_2 + H^+$, 74], 116 [InH^+, 100], 83 [$C_6H_{11}^+$, 65]. IR (Nujol) *v*/cm^{-1}: 1666 (s, br, In–H str.).

[$InH_3(PCy^p{}_3)_2$] 10. $PCy^p{}_3$ (0.23 cm^3, 0.96 mmol) was added to a stirred solution of [$InH_3\{PCy^p{}_3\}$] (0.35 g, 0.98 mmol) in DME (*ca.* 40 cm^3) at −50 °C. The resulting solution was warmed to −30 °C and stirred for 2 h whereupon the volatiles were removed *in vacuo* to yield a white solid. This was washed with cold diethyl ether (*ca.* 5 cm^3) and extracted with cold (−20 °C) DME (*ca.* 30 cm^3), concentrated *in vacuo*, filtered and the filtrate placed at −30 °C to yield **10** as colourless plates (0.12 g, 21%), decomp. +15 °C. ^1H NMR (400 MHz, $C_6D_5CD_3$, 300 K): δ 1.17–1.74 (m, 54H, C_5H_9), 5.23 (br s, 3H, In–H). ^{13}C NMR (100.6 MHz, $C_6D_5CD_3$, 300 K): δ 26.7 (d, CH, $^1J_{PC}$ 19.8 Hz), 30.6 (s, CH_2), 31.9 (d, CH_2, $^2J_{PC}$ 15.0 Hz). ^{31}P NMR (36.3 MHz, $C_6D_5CD_3$, 85% H_3PO_4, 233 K): δ 3.45 (s). MS EI: *m*/*z* (%) 238 [$P(C_5H_9)_3^+$, 15], 169 [$P(C_5H_9)_2^+$, 63], 117 [InH_2^+, 7], 116 [InH^+, 6], 100 [$P(C_5H_9)^+$, 100], 69 [$C_5H_9^+$, 63]. IR (Nujol) *v*/cm^{-1}: 1644 (s, br, In–H str.).

[$\{InH_2(PCy_2)\}_3$] 11. A solution of [$Li\{PCy_2\}(thf)_n$] (2.50 mmol), prepared *in situ* from $HPCy_2$ and Bu^nLi, in thf (*ca.* 20 cm^3) was added to a solution of [$InH_3(NMe_3)$] (≈2.54 mmol) in diethyl ether (*ca.* 70 cm^3) at −70 °C. The solution was warmed to −30 °C and stirred for 2 h whereupon volatiles were removed *in vacuo* to yield an oily off-white solid. This was extracted with cold (−40 °C) toluene (*ca.* 50 cm^3), filtered and the filtrate dried *in vacuo* prior to further extraction with cold (−15 °C) diethyl ether (*ca.* 30 cm^3). Concentration, filtration and placement at −30 °C yielded **11** as colourless blocks (0.33 g, 43%), decomp. +64 °C. ^1H NMR (400 MHz, $C_6D_5CD_3$, 300 K): δ 1.00–1.94 (m, 66H, C_6H_{11}), 5.88 (br s, 6H, In–H). ^{13}C NMR (100.6 MHz, $C_6D_5CD_3$, 300 K): δ 27.0 (s, CH_2), 27.8 (s, CH_2), 33.3 (d, CH, $^1J_{PC}$ 21.4 Hz), 33.9 (d, CH_2, $^2J_{PC}$ 10.3 Hz). ^{31}P NMR (145.8 MHz, $C_6D_5CD_3$, 85% H_3PO_4, 298 K): δ −47.12 (s). MS EI: *m*/*z* (%) 198 [$P(C_6H_{11})_2^+$, 14], 117 [InH_2^+, 57], 83 [$C_6H_{11}^+$, 96]; IR (Nujol) *v*/cm^{-1}: 1686 (s, br, In–H str.).

[$In(SPh)_3(PCy_3)$] 12. S_2Ph_2 (0.20 g, 0.93 mmol) in DME (10 cm^3) was added to a solution of [$InH_3(PCy_3)$] (0.25 g, 0.62 mmol) at −50 °C. The resulting solution was allowed to slowly warm to room temperature and stirred for 4 h. Filtration afforded a colourless solution, which was reduced in volume and placed at −35 °C overnight yielding cubic colourless crystals. Yield 0.23 g, 51%; mp 140 °C. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 1.0–2.0 [mult, 33H, C_6H_{11}], 6.9–7.4 [aromatics, mult, 15H]. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 25.9 [s, *C*H_2], 27.4 [d, *C*H_2, $^2J_{PC}$ 10.2 Hz], 29.9 [s, *C*H_2], 31.85 [d, *C*H, $^1J_{PC}$ 13.0 Hz], 125.4, 128.8, 134.8, 136.3 [aromatics]. ^{31}P (36.3 MHz, C_6D_6, 298 K): δ 18.61. MS EI: *m*/*z* (%) 280 [PCy_3^+, 100]. IR (Nujol) *v*/cm^{-1}: 1573w, 1296m, 1080m, 1022m, 850m (Found: C, 59.22; H, 6.81. Calc. for $C_{36}H_{48}InPS_3$: C, 59.82; H, 6.69%).

[$In(SePh)_3(PCy_3)$] 13. Se_2Ph_2 (0.15 g, 0.9 mmol) in DME (10 cm^3) was added to a solution of [$InH_3(PCy_3)$] (0.25 g, 0.62 mmol) at −50 °C. The resulting solution was allowed to slowly warm to room temperature and stirred for 4 h. Filtration produced a yellow solution, which was reduced in volume and placed at −35 °C overnight yielding cubic yellow crystals. Yield 0.27 g, 49%; mp 143–145 °C. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.9–2.0 [mult, 33H, C_6H_{11}], 6.9–8.0 [aromatics, mult, 15*H*]. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 25.99 [s, *C*H_2], 27.49 [d, *C*H_2, $^2J_{PC}$ 11.0 Hz], 29.86 [s, *C*H_2], 31.94 [d, *C*H, $^1J_{PC}$ 13.0 Hz], 126.17, 128.50, 128.90, 136.83 [aromatics]. ^{31}P (36.3 MHz, C_6D_6, 298 K): δ 10.01. MS APCI: *m*/*z* (%) 280 [PCy_3^+, 100], 198 [PCy_2^+, 48]. IR (Nujol) *v*/cm^{-1}: 1572w, 1296m, 1261m, 1114m, 1020m, 850m (Found: C, 48.96; H, 5.50. Calc. for $C_{36}H_{48}InPSe_3$: C, 50.08; H, 5.60%).

[$In(TePh)_3(PCy_3)$] 14. Te_2Ph_2 (0.39 g, 0.93 mmol) in DME (10 cm^3) was added to a solution of [$InH_3(PCy_3)$] (0.25 g, 0.6 mmol) at −50 °C. The resulting solution was allowed to slowly warm to room temperature and stirred for 4 h. Filtration afforded an

Table 1 Crystal data for compounds **9** and **11**–**14**

	9	**11**	**12**	**13**	**14**
Chemical formula	$C_{36}H_{69}InP_2$	$C_{36}H_{72}In_3P_3$	$C_{36}H_{48}InPS_3$	$C_{36}H_{48}InPSe_3$	$C_{36}H_{48}InPTe_3$
M	678.67	942.31	722.71	863.41	1009.33
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	8.036(2)	10.2825(9)	11.6650(10)	10.4085(7)	10.3689(10)
b/Å	9.8530(10)	30.403(2)	33.359(2)	11.6417(9)	12.0296(19)
c/Å	12.361(2)	13.5672(10)	19.122(2)	15.5724(11)	15.862(2)
α/°	80.611(9)			85.84(3)	85.164(9)
β/°	93.060(12)	94.14(2)	107.258(10)	82.96(3)	82.62(2)
γ/°	68.470(7)			70.98(3)	72.022(10)
V/Å^3	896.9(3)	4230.3(6)	7106.0(11)	1769.4(2)	1864.2(4)
Z	1	4	4	2	2
T/K	150(2)	150(2)	293(2)	150(2)	150(2)
μ(Mo-Kα)/cm^{-1}	7.70	17.57	9.10	38.22	30.00
Reflections collected	5411	8567	15141	7434	7958
No. unique reflections	5411	8567	14420	7159	7524
R (all data)	0.0373	0.0440	0.0816	0.0623	0.1498
R ($I > 2\sigma(I)$)	0.0275	0.0281	0.0352	0.0300	0.0653
wR' (all data)	0.0754	0.0698	0.0954	0.0755	0.1700
wR' ($I > 2\sigma(I)$)	0.0731	0.0665	0.0822	0.0676	0.1487

orange solution, which was reduced in volume and placed at −35 °C overnight yielding cubic orange crystals. Yield 0.26 g, 41%; mp 127–128 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.1–2.1 [mult, 33H, C_6H_{11}], 6.9–8.3 [aromatics, mult, 15H]. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ 24.58 [s, CH_2], 26.05 [d, CH_2, $^2J_{PC}$ 10.1 Hz], 28.54 [s, CH_2], 31.83 [d, CH, $^1J_{PC}$ 12.9 Hz], 125.59, 127.66, 128.26, 139.53 [aromatics]. ^{31}P (36.3 MHz, C_6D_6, 298 K): δ −7.1. MS EI: m/z (%) 280 [PCy_3^+, 100], 198 [PCy_2, 52]. IR (Nujol) ν/cm^{-1}: 1569w, 1261m, 1101m, 804m (Found: C, 41.65; H, 4.75. Calc. for $C_{36}H_{48}InPTe_3$: C, 42.84; H, 4.79%).

Structure determinations

Crystals of **9**, **11**, **13** and **14** suitable for X-ray structure determination were mounted in silicone oil and a crystal of **12** was mounted in contact cement. All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[28] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model) except the hydride ligands of **11** for which the positions and isotropic displacement parameters were refined. Empirical absorption corrections were carried out by the DIFABS method[29] on **9** and **11**, and using ψ scans for **13** and **14**. Crystal data, details of data collections and refinement are given in Table 1. Compound **12** crystallised with 2 crystallographically independent molecules in the asymmetric unit. There are no significant geometric differences between the 2 molecules so the molecular structure of only one is shown in Fig. 3. The molecular structures of the other complexes are depicted in Figs. 1, 2, 4 and 5.

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See http://www.rsc.org/suppdata/dt/a9/a908418e/ for crystallographic files in .cif format.

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