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Syntheses and structures of the heterometallic complexes $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li \cdot Et_2O)_4$, $[Me_2In(PhMes)_2]^-[Li(TMEDA)_2]^+$ and $[Me_2(PHMes)_2In]^-[K(PMDETA)_2]^+$ [Cy = cyclohexyl, Mes = 2,4,6-$Me_3C_6H_2$, TMEDA = $(Me_2NCH_2)_2$, PMDETA = $(Me_2NCH_2CH_2)_2NMe$]

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Dedicated to Prof. M. F. Lappert.

Abstract

The reaction of CyPHLi (Cy = cyclohexyl) with $InMe_3$ in Et_2O gives the heterometallic cage $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li \cdot Et_2O)_4$ (**1**), containing the heterometallic tetraanion $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2^{4-}$. In contrast, similar reactions of $InMe_3$ with MesPHM (M = Li, K) in the presence of the Lewis bases TMEDA and PMDETA give $[Me_2In(PhMes)_2In]^-[Li(TMEDA)_2]^+$ (**2**) and $[Me_2(PHMes)_2In]^-[K(PMDETA)_2]^+$ (**3**), respectively. The formation of $[Me_2(PHMes)_2In]^-$ anions in these complexes provides key evidence of the mechanism of formation of the metallocyclic tetraanion of **1**.

Keywords: Indium; Phosphorus; X-ray

1. Introduction

A major focus of our current work has been the development of new ligand systems containing p-block metals [1]. We have recently employed the step-wise metallation of primary phosphines with alkali metal organometallics followed by reactions with Group 15 metal dimethylamido compounds in the preparation of a variety of heterometallic phosphinidene compounds. For example, the reaction of $CyPH_2$ with $^{n}BuLi$ followed by further deprotonation with $Sb(NMe_2)_3$ gives the heterometallic cage $[\{Sb(PCy)_3\}_2Li_6] \cdot 6Me_2NH$, containing the $[Sb(PCy)_3]^{3-}$ trianion, which decomposes at 30–40 °C into Zintl compounds containing the Sb_7^{3-} anion along with the cyclo-phosphane $[CyP]_4$ [2,3]. This 'cage-to-alloy' reaction proceeds via cyclic anions of the type $[(RP)_nE]^-$ [4,5], and is driven thermodynamically by the formation of P–P bonds (the strongest homonuclear Group 15 bond) [2,3]. The importance of this new type of reaction is that it provides the potential means by which a host of materials can be deposited from solution at low temperature. An important aim in more recent studies, has therefore been the extension of this synthetic methodology to Group 13 and Group 14 analogues, particularly with a view to developing structural and electronic relationships within p-block element imido and phosphinidene compounds. We recently reported the synthesis of $[\{MeAl(PPh)_3Li_4\}_4(\mu_4\text{–}Cl)]^- \cdot Li^+$, containing the $[MeAl(PPh)_3]^{4-}$ tetraanion [6]

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(Fig. 1(c)), which is valence-isoelectronic with Group 14 and 15 trianions of the type $[E(E'R)_3]^{3-}$ (E = As, Sb; E′ = N, P) [7] (Fig. 1(a)) and $[R'Si(NR)_3]^{3-}$ (Fig. 1(b)) [8–14]. In addition, we have prepared the heterometallic complex $[\{MeAl(\mu\text{-}PMes)(PMes)\}_2Li_4]_2 \cdot 7thf$, containing a $[MeAl(\mu\text{-}PMes)(PMes)_2]_2{}^{4-}$ tetraanion (Mes = $2,4,6\text{–}Me_3\text{–}C_6H_2$) (Fig. 1(f)) [15], which is valence-isoelectronic with Group 14 and 15 anions of the type $[R'Si(\mu\text{-}NR)(NR)]_2{}^{2-}$ (Fig. 1(e)) and $[E(\mu\text{-}NR)(NR)]_2{}^{2-}$ (E = P, As, Sb, Bi) (Fig. 1(d)) [16–22].

Here we report the synthesis of $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li \cdot Et_2O)_4$ (**1**), containing a $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2{}^{4-}$ tetraanion which is valence-isoelectronic with the metallocyclic Group 14 and 15 species $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_2$ (R = ^{t}Bu and ^{i}Pr) (Fig. 2(a)) [23,24] and $[\{Sn(\mu\text{-}PR)\}_2(\mu\text{-}PR)]_2{}^{4-}$ (R = ^{t}Bu and Cy) (Fig. 2(b)) [25]. Complex **1** contains the first heavy Group 13 counterpart of the previously reported Al(III) tetraanion $[\{MeAl(\mu\text{-}PR)\}_2(\mu\text{-}PR)]_2{}^{4-}$ (R = Cy) (Fig. 2(c)) [26]. In addition, we report the syntheses of $[Me_2(PHMes)_2In]^-[Li(TMEDA)_2]^+$ (**2**) and $[Me_2(PHMes)_2In]^-[K(PMDETA)_2]^+$ (**3**), which provide key evidence on the likely mechanism of formation of **1**.

2. Experimental

2.1. General experimental

Compounds **1**–**3** are air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques [27] and under dry/oxygen-free argon. Toluene and thf were dried by distillation over sodium/benzophenone prior to the reactions. Cyclohexylphosphine was was acquired from Strem, and mesityl phosphine ($MesPH_2$) was prepared using the literature procedure [28]. TMEDA and PMDETA was dried by distillation over Na metal and was stored under argon over molecular sieve (4 Å). $InMe_3$ was prepared by the reaction of $InCl_3$ with MeLi in ether, and purified by distillation [29]. This reagent was used as a standardised solution in ether. The products were isolated and characterized with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and

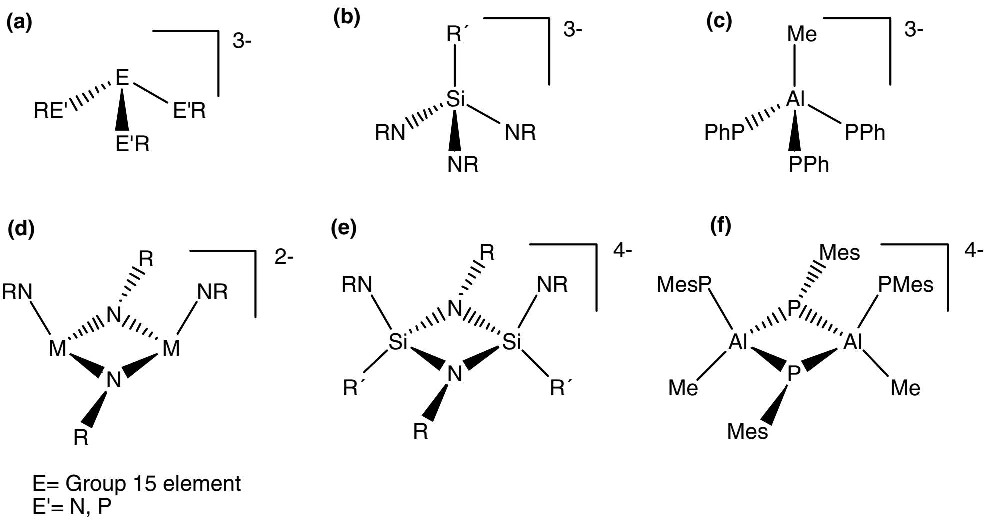


Fig. 1. Series of structurally and electronically related Group 13, Group 14 and Group 15 anions.

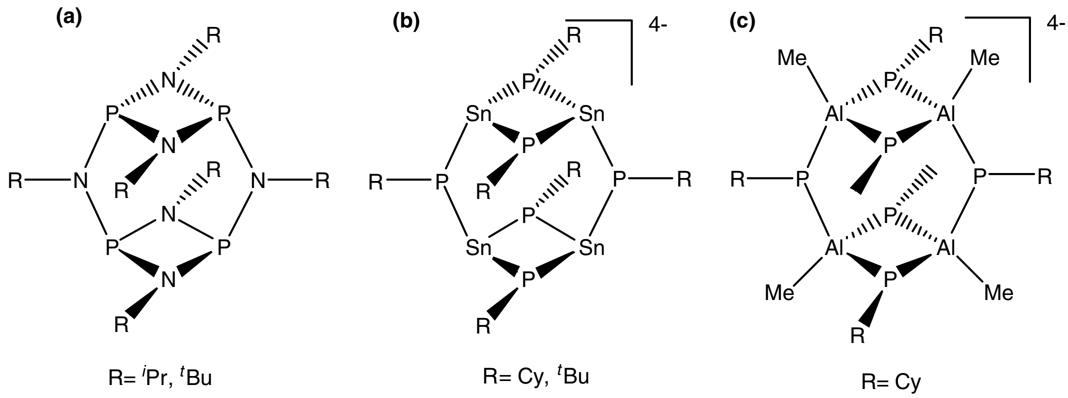


Fig. 2. Groups 13–15 valence-isoelectronic and isostructural macrocyles related to the anion in **1**.

H_2O internal recirculation system. Elemental analyses were performed by first sealing the samples under argon in airtight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440 elemental analyser. P analysis was carried out by spectrophotometric means. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX 500 MHz spectrometer in dry d_6-benzene or d_6-toluene (for variable-temperature studies). The solvent resonances were used as the internal reference standards for ^1H NMR spectroscopic studies, and 85% H_3PO_4/D_2O was employed as the external reference standard for ^{31}P NMR spectroscopic work.

Synthesis of **1**; to a stirred solution of $CyPH_2$ (3.0 mmol, 0.43 mL) in toluene (20 mL) at −78 °C, was added ^nBuLi (3.3 mmol, 2.06 mL, 1.6 mol L^{-1} in hexanes). The reaction mixture was stirred at −78 °C for 20 min and then warmed to room temperature and stirred for a further 45 min, affording a yellow suspension. This mixture was again cooled to −78 °C, and $InMe_3$ (1.0 mL, 1.0 mol L^{-1} in ether, 1.0 mmol) in toluene (35.0 mL) was added. The reaction mixture was stirred at −78 °C for 20 min and then warmed to room temperature and stirred overnight. The reaction mixture was filtered and the filtrate was reduced in volume (to *ca.* 30 mL). Storage at −15 °C for 48 h gave yellow crystals of **1**. Yield, 0.20 g (52%, based on In). ^1H NMR (500.2 MHz, δ/ppm, d_6-benzene, +25 °C), 2.1–0.5 (overlapping multiplet, total 106 H, total Et_2O and Cy), 0.40 (s., In–CH_3, 12H). ^{31}P NMR (161.9 MHz, δ/ppm, d_6-benzene, +25 °C), −117.8 (bs.) −152.0 (br.s.). *Anal.* Calc. for **1**: C, 44.0; H, 7.8. Found: C, 43.9; H, 7.5%.

Synthesis of **2**; to a stirred solution of solution of $MesPH_2$ (3 mmol, 0.7 mL) in toluene (20 mL) at −78 °C, was added ^nBuLi (3.3 mmol, 2.06 mL, 1.6 mol L^{-1} in hexanes). The reaction mixture was stirred at −78 °C for 20 min and then warmed to room temperature and stirred for a further 45 min, affording a yellow suspension. This mixture was cooled again to −78 °C and $InMe_3$ (1.5 mmol, 1.5 mL, 1 mol L^{-1} in ether) in toluene (35.0 mL) was added. The reaction mixture was stirred for 20 min and then warmed to room temperature and stirred overnight. The mixture was filtered and the filtrate was reduced in volume (to ca. 30 mL). Storage at −15 °C for 48 h gave yellow crystals of the toluene solvate **2** toluene. Placing crystals under vacuum (15 min, 10–2 atm.) leads to complete desolvation, giving an amorphous powder of **2** (with no toluene present). The following data refer to this unsolvated material. Yield, 0.60 g (57%, based on In). IR (Nujol, NaCl, ν/cm^{-1}), major bands at 2996s, 2844s, 1470s, 1368, 1242. ^1H NMR (500.2 MHz, δ/ppm, d_6-benzene, +25 °C), 7.26 (s., aryl C–H, 4H), 3.92 (br.s., PH, 2H), 2.72 (s., *o*-CH_3, 12H), 2.64 (s., *p*-CH_3, 6H), 2.25 (s., 4H, CH_2CH_2, TMEDA), 2.09 (s., 12H, Me_2N, TMEDA). ^{31}P NMR (161.9 MHz, δ/ppm, d_6-benzene, +25 °C), −165.89 (br.s.), −167.75 (br.s.). *Anal.* Calc. for **2**: C, 55.8; H, 9.2; N, 10.1. Found: C, 54.1; H, 8.8; N, 10.0%.

Synthesis of **3**; to a stirred solution of $PhCH_2K$ (3.5 mmol, 0.455 g) in toluene (20 mL) at −78 °C was added $MesPH_2$ (0.424 g, 0.7 mL, 3.0 mmol). The reaction mixture was stirred at −78 °C for 20 min and then warmed to room temperature and stirred for a further 45 min, producing a red suspension. This mixture was cooled again to −78 °C and $InMe_3$ (1.5 mmol, 1.5 mL, 1 mol L^{-1} in ether) in toluene (35 mL) was added. The subsequent reaction at −78 °C for 20 min and then at room temperature for a further 16 h, produced a light-yellow suspension. Thf (10 mL) and PMDETA (3.0 mmol, 0.62 mL) were added, the reaction mixture was filtered and the filtrate was reduced in volume (to ca. 30 mL). Storage at −15 °C for 48 h gave colourless crystalline blocks of **3**. Yield, 0.60 g (48%, based on In). IR (Nujol, NaCl, ν/cm^{-1}), major bands at 2995s, 2854s, 2323, 1461s, 1376, 1261. ^1H NMR (500.2 MHz, δ/ppm, d_6-benzene, +25 °C), 7.26 (s., Mes C–H, 4H), 3.92 (br.s., PH, 2H), 2.72 (s., *o*-CH_3, 12H), 2.64 (s., *m*-CH_3, 6H), 2.32–2.19 (overlapping multiplets, PMDETA). ^{31}P NMR (161.9 MHz, δ/ppm, d_6-benzene, +25 °C), −167.3 (br.s.), −168.5 (br.s.). *Anal.* Calc. for **3**: C, 55.8; H, 9.2; N, 10.1. Found: C, 54.1; H, 8.8; N, 10.0%.

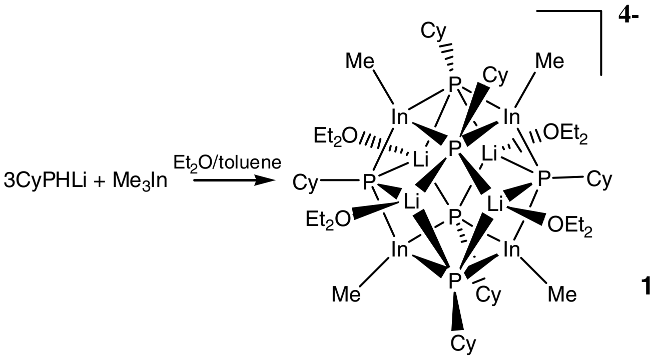
X-ray crystallography on **1**, **2** toluene and **3**; crystals of **1**, **2** toluene and **3** were mounted directly from solution under argon using an inert perfluorohydrocarbon oil which protects them from atmospheric oxygen and moisture [30]. X-ray intensity data were collected using a Nonius Kappa CCD diffractometer and were solved by direct methods and refined by full-matrix least-squares on F^2 [31]. In **1**, the carbon and oxygen atoms of the Et_2O ligand associated with O(1W) are disordered over two sites. There is also some conformational disorder of one of the cyclohexyl groups [at three of the carbon atoms, C(64), C(65), C(66)]. In **2**, the phosphorus atom P(**1**) is disordered over two 50:50 occupancy sites [P(1) and P(1′)], which were allowed to refine freely. No disorder is observed in the structure of **3**. The H-atoms attached to the P centres in **2** and **3** were located directly. These atoms were all refined freely, apart from those attached to the two disordered phosphorus atoms P(1) and P(1′) which were constrained geometrically.

3. Results and discussion

In earlier studies we had observed that the reactions of the Sn(II) and Al(III) cubanes $[SnN^tBu]_4$ and $[MeAlNMes]_4$ with CyPHLi (1:6 equivalents) in thf give the heterometallic complexes $[\{Sn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2[Li(thf)]_4$ and $[\{MeAl(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2[Li(thf)]_4$, containing the $[\{Sn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2^{4-}$ [25a] and $[\{MeAl(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2^{4-}$ [26] tetraanions (shown in Fig. 2(b) and (c)). We also found that Sn(II) complexes containing this type of tetraanion could be obtained directly from reactions of $Sn(NMe_2)_2$ with RPHLi (R = Cy, ^tBu) in thf, (most effectively) using a 1:3 stoichiometric ratio of the reagent [25b]. A primary goal in the current study was to develop a simple synthetic approach to similar metallocyclic frameworks for heavier Group 13 metals [specifically In(III)]. We find that the 1:3 stoichiometric reaction of $InMe_3$ with CyPHLi in Et_2O/toluene gives the heterometallic complex

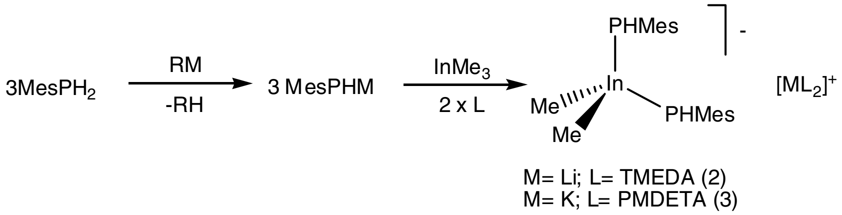
$[\{MeIn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2[Li(Et_2O)]_4$ in 52% yield (Scheme 1).

In an attempt to extend this route to similar metallocyclic arrangements containing other alkali metal cations and organic substituents (R), various alkali metal primary phosphides [RPHM; M = alkali metal] were reacted with $InMe_3$ in the same 3:1 stoichiometric ratio as employed in the synthesis of **1**. In the cases of the reactions of MesPHM [M = Li and K] with $InMe_3$ (3:1 equivalents) the ion-separated, crystalline complexes $[Me_2(PHMes)_2In]^-[Li(TMEDA)_2]^+$ (**2**) and $[Me_2(PHMes)_2In]^-[K(PMDETA)_2]^+$ (**3**) were obtained in good yields, using the Lewis base donors TMEDA and PMDETA to facilitate crystallisation (Scheme 2). The mechanism involved in the formation of the $[Me_2(PHMes)_2In]^-$ anions of these complexes is not understood at this stage.



Scheme 1.

Prior to the X-ray characterizations of **1**, **2** and **3** they were characterized by elemental and spectroscopic analyses. Complex **1** shows a series of complicated overlapping multiples in the region δ 0.5–2.1 in its ^1H NMR spectrum at room temperature, corresponding the cyclohexyl groups and ether ligands. The ^{31}P NMR shows two very broad singlets at δ −117.8 and −152.0, which could not be resolved at low temperature (down to −80 °C). These are assigned to the PCy groups within the $[In(\mu\text{-}PCy)]_2$ dimer units and those linking the dimeric rings into the metallocyclic arrangement of the $[\{MeIn(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2^{4-}$ tetraanion. It can be noted that for the Sn(II) systems $[\{Sn(\mu\text{-}PR)\}_2(\mu\text{-}PR)]^{4-}$ the appearance of the ^{31}P NMR spectrum is highly dependent on the organic group (R) [25]. For R = Cy, distinct doublet and triplet multiplets are observed for the two P-environments, whereas for R = ^{t}Bu (like **1**) two broad resonances only could be



Scheme 2.

Table 1
Crystal data and refinements for $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li \cdot Et_2O)_4$ (**1**), $[Me_2(PHMes)_2In]^-[Li(TMEDA)_2]^+$ (**2** toluene) and $[Me_2(PHMes)_2In]^-[K(2PMDETA)]^+$ (**3**)[a]

Compound	$C_{56}H_{118}P_6In_4Li_4O_4$ (**1**)	$C_{39}H_{70}InLiN_4P_2$ (**2**) toluene	$C_{38}H_{76}InKN_6P_2$(**3**)
Fw	1528.36	778.69	832.91
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	19.972(4)	18.729(4)	11.094(2)
b (Å)	20.013(4)	15.545(3)	11.713(2)
c (Å)	18.609(4)	15.437(3)	18.184(4)
α (°)			85.18(3)
β (°)	92.09(3)	98.20(3)	88.46(3)
γ (°)			85.88(3)
U (Å^3)	7433(3)	4448.4(15)	2348.0(8)
μ (Mo Kα) (mm^{-1})	1.390	0.631	0.690
Z	4	4	2
ρ_{calc} (Mg m^{-3})	1.366	1.163	1.178
Crystal size (mm)	0.18 × 0.12 × 0.12	0.37 × 0.28 × 0.07	0.37 × 0.30 × 0.12
Reflections collected	49171	23686	23051
Independent reflections (R_{int})	10 226 (0.053)	5432 (0.074)	10617 (0.041)
R_1, wR_2 ($I > 2\sigma(I)$)	0.066, 0.154	0.047, 0.108	0.050, 0.078
R_1, wR_2 (all data)	0.078, 0.158	0.086, 0.128	0.086, 0.090

[a] Data in common; $\lambda = 0.71073$ Å, $T = 180(2)$K for 1–3.

Table 2
Selected bond lengths and angles for complex on $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li\cdot Et_2O)_4$ (**1**)

Molecule A		Molecule B	
Bond lengths (Å)			
In(1)–P(1)	2.611(3)	In(3)–P(5)	2.606(**2**)
In(1)–P(2)	2.588(3)	In(3)–P(4)	2.587(3)
In(1)–P(3A)	2.559(3)	In(3)–P(6)	2.546(3)
In(2)–P(1)	2.598(3)	In(4)–P(4)	2.595(3)
In(2)–P(2)	2.601(3)	In(4)–P(5)	2.598(3)
In(2)–P(3)	2.560(3)	In(4)–P(6)	2.557(3)
Molecule 1		Molecule 2	
Bond angles (°)			
P(1)–In(1)–P(2)	95.92(9)	P(4)–In(4)–P(5)	97.57(8)
P(1)–In(1)–P(3A)	108.36(9)	P(6)–In(3)–P(4)	112.29(9)
P(2)–In(1)–P(3A)	97.4(10)	P(6)–In(3)–P(5)	98.92(9)
P(2)–In(2)–P(1)	95.91(9)	P(5)–In(3)–P(4)	97.55(8)
P(2)–In(2)–P(3)	109.44(9)	P(6)–In(4)–P(5)	112.64(9)
P(1)–In(2)–P(3)	99.63(8)	P(6)–In(4)–P(4)	98.33(9)
In(1)–P(1)–In(2)	83.1(1)	In(4)–P(4)–In(3)	81.69(8)
In(1)–P(2)–In(2)	83.46(8)	In(3)–P(5)–In(4)	81.99(8)
In(2)–P(**3**)–In(1A)	112.5(1)	In(3)–P(6)–In(4)	116.9(1)

observed irrespective of the temperature. The ^1H NMR spectra of **2** and **3** are largely as expected, showing resonances for the Mes groups and the presence of the Lewis bases TMEDA (in **2**) and PMDETA (in **3**). Unexpectedly, the P–H protons in **2** and **3** appear as broad singlets, which could not be resolved into the anticipated doublets even at low temperature. ^{31}P NMR spectra of **2** and **3** at room temperature show broad singlets at ca. δ −165 and −167 in both. The spectra are essentially unchanged at low temperature. This behaviour may suggest that the two P-environments in both complexes are rendered inequivalent by restricted rotation of the sterically demanding Mes groups.

Having established the basic identities of the complexes, they were subjected to X-ray structural analysis. Details of the crystal data and refinements are collected in Table 1. Table 2 lists selected bond lengths and angles for complex **1**, while data for **2** and **3** is given in Table 3.

The low-temperature crystal structure of complex **1** shows that it is the mixed-metal cage $[\{MeIn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2(Li\cdot Et_2O)_4$, consisting of a centrosymmetric, fourteen-membered $In_4P_6Li_4$ core (Fig. 3). This structure is closely related to that of the Sn(II) complexes $[\{Sn(\mu\text{-}PR)_2\}_2(\mu\text{-}PR)]_2(Li\cdot thf)_4\cdot(R = Cy, {}^tBu)$ [25] and the Al(III) complex $[\{MeAl(\mu\text{-}PCy)_2\}_2(\mu\text{-}PCy)]_2(Li\cdot thf)_4$ [26]. Crystals of **1** contain two crystallographically-independent molecules which are chemically identical (*molecules A and B*, Table 2). The discussion of its structure will therefore involve the

Table 3
Selected bond length and angles for $[Me_2(PHMes)_2In]^-[Li(TMEDA)_2]^+$ (**2**· toluene) and $[Me_2(PHMes)_2In]^-[K(PMDETA)_2]^+$ (**3**)

	2	3		2	3
Bond lengths (Å)					
In(1)–P(1)	mean 2.608(3)[a]	2.602(1)	In(1)–C	2.179(6)–2.198(6)	2.190(4)–2.195(4)
In(1)–P(2)	2.606(**2**)	2.597(1)	M–N range	2.11(1)–2.14(1)	2.838(3)–3.011(3)
Bond angles (°)					
C–In(1)–C	118.4(2)	109.51(16)	P–In(1)–C range	101.2(2)–114.6(2)[a]	107.66(11)–114.02(11)
P(1)–In(1)–P(2)	mean 106.7[a]	105.66(4)	N–In(1)–N range	86.2(4)–126.2(5)	62.08(1)–151.54(9)

[a] Mean values are quoted for the bond lengths and angles associated with the two disordered sites of the phosphorus atom P(1) and P(1′).

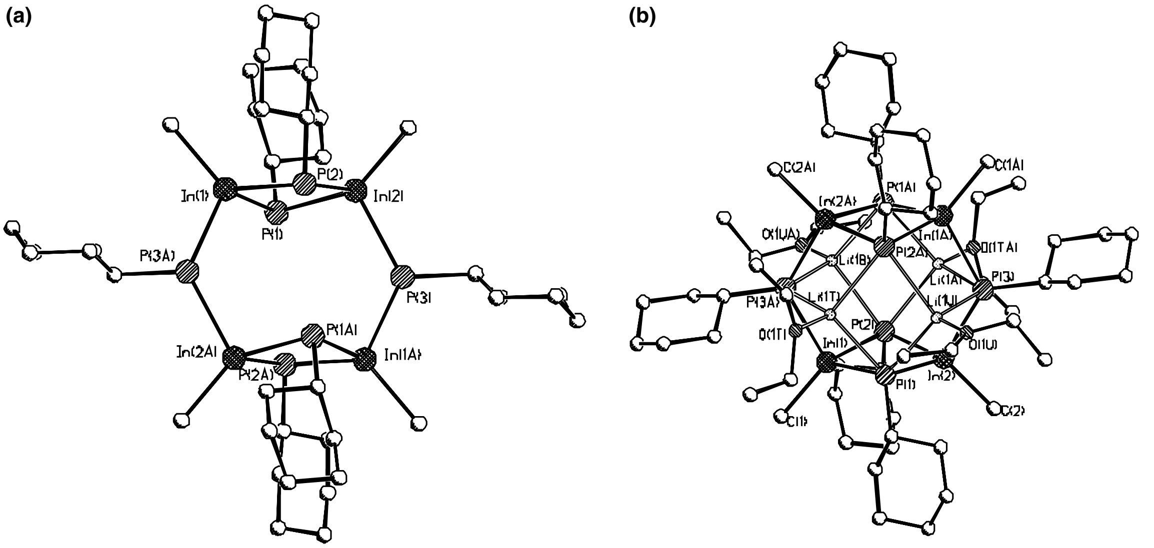


Fig. 3. (a) Metallocyclic structure of the $[\{In(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2^{4-}$tetraanion and (b) Solid-state structure of **1** (*molecule A* is shown). H-atoms and disorder have been omitted for clarity.

range or average of the bond lengths and angles found in both of these molecules of **1** in the crystal lattice. Molecules of **1** are formed by the association of the indium phosphinidene tetraanion $[\{In(\mu\text{-PCy})\}_2(\mu\text{-PCy})]_2^{-4}$ (Fig. 3(a)) (consisting of two $[\{In(\mu\text{-PCy})]_2$ ring units linked by two μ-PCy groups) with four ether-solvated Li^+ cations (Fig. 3(b)).

The In–P bonds within **1** vary in the range 2.546(3)–2.611(3) Å (av. 2.58 Å), and are in the range of In–P distances found for previously reported In–P bonded compounds (av. 2.60 Å) [35]. The In(III) centres adopt tetrahedral geometries (angle at In av. 109.0°). The four Li^+ cations are coordinated by phosphorus atoms within the dimer units of the metallocyclic tetraanion and by the two phosphorus atoms that bridge the dimers together [P–Li range 2.59(1)–2.90(2) Å]. The P–Li distances involved are similar to those observed in a number of previously reported lithium phosphide complexes (range 2.38–2.78 Å) and are typical of bonds between anionic P centres and Li^+ [32]. The Li^+ cations are each solvated by a molecule of ether, producing a pseudo-tetrahedral geometry for the Li^+ ions (Li–O av. 1.95 Å, angle at Li av. 108.7°).

The low-temperature X-ray studies of **2**$\cdot$ toluene (Fig. 4) and **3** (Fig. 5) show that both are ion-separated species in the solid state. Significantly, both of the complexes contain the same $[Me_2In(PHMes)_2]^-$ anion. The $[Me_2In(PHMes)_2]^-$ anions of **2** and **3** have distorted tetrahedral In(III) centres (angles at In av. 109.5° and 108.6° in **2** and **3**, respectively). The In–P bond distances (av. 2.61 Å in **2**, av. 2.60 Å in **3**) are in the range found previously for this type of compound [32]. However, **2** and **3** are relatively rare examples of

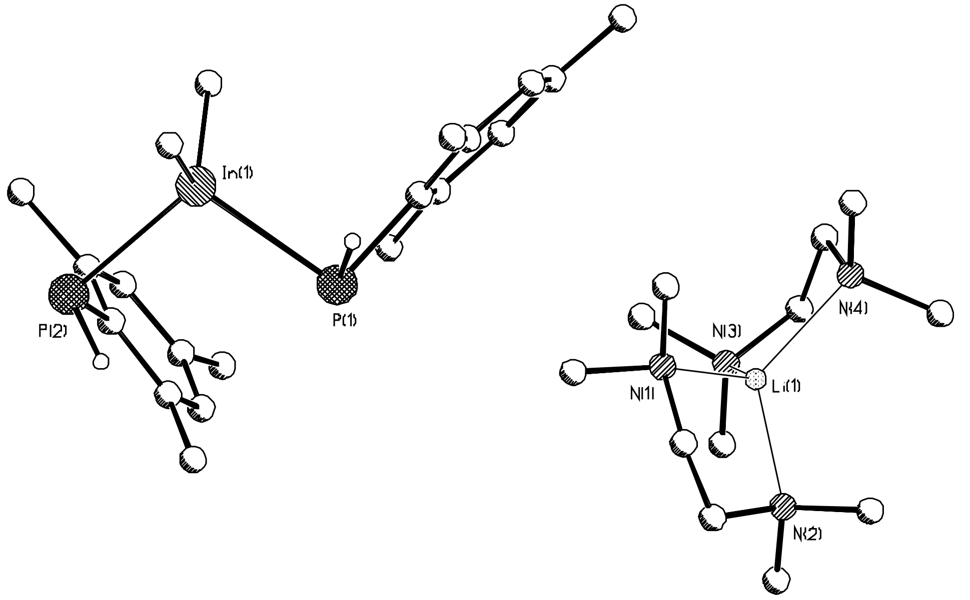


Fig. 4. Structure of **2**. H-atoms and disorder of the cyclohexyl groups and at P(1) have been omitted for clarity (as has toluene salvation in the lattice).

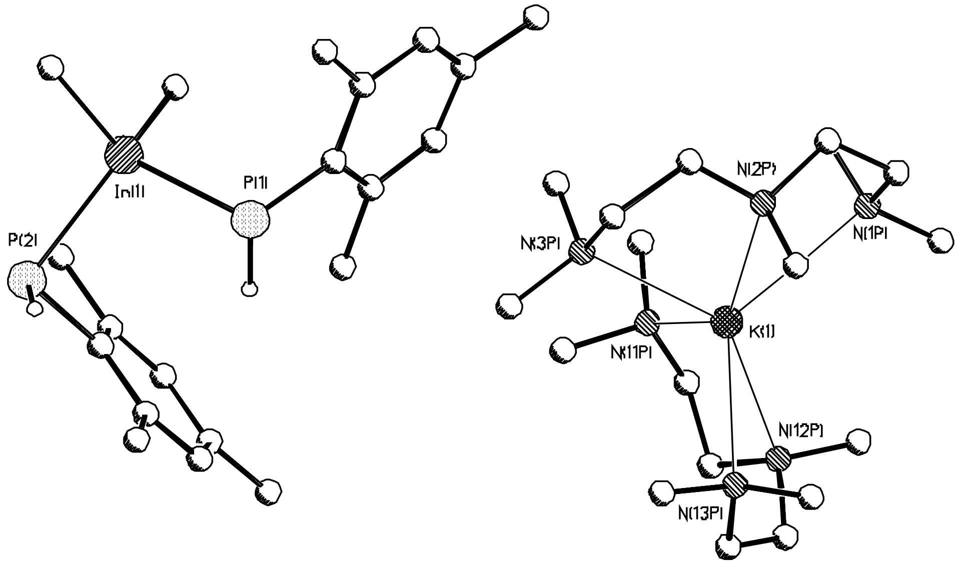
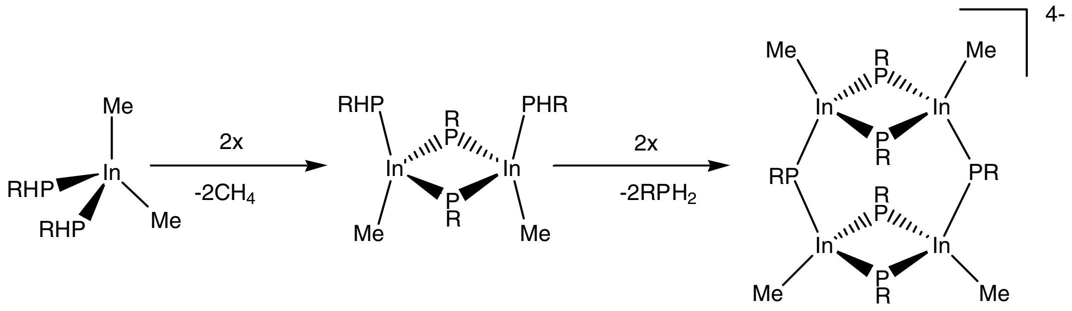


Fig. 5. Structure of **3**. H-atoms have been omitted for clarity.



Scheme 3. Proposed mechanism of formation of the anion of **1** via a $[Me_2InPHR]^-$ anion intermediate.

complexes containing In(III) phosphide anions, other examples of this type being the ion-separated complexes $[(Ph_2P)_4In]^-$ $[Li(thf)]_4{}^+$ [33] and [(2,3,4,5-tetramethylphospholyl-P)$_2$InCl$_2$]$^-$K$^+$(18-crown-6) [34] and the ion-paired complex $\{[(^iPr_3SiPH)_4In]^-K^+\}_\infty$ [35]. The Li^+ and K^+ cations in **2** and **3** are bis-coordinated by the TMEDA and PMDETA ligands, resulting in distorted four- and six-coordinate geometries for these ions, respectively. The $[Li(TMEDA)_2]^+$ and $[K(PMDETA)_2]^+$ cations in these complexes are unremarkable.

4. Closing remarks

Compounds **2** and **3** potentially provide information about the mechanism of formation of **1**. Scheme 3 shows a proposed mechanism in which condensation of two of the $[Me_2In(PHR)_2]^-$ anions (accompanied by the elimination of two molecules of methane) results in the formation of the intermediate dimer $[MeIn(PHR)(\mu\text{-}PR)]_2$ (**A**). The condensation of two molecules of **A** (with the elimination of two molecules of RPH_2) would result in the macrocyclic structure of **1**. A similar mechanism was proposed by us previously for the synthesis of the Sn(II) anions $[\{Sn(\mu\text{-}PR)\}_2(\mu\text{-}PR)]_2{}^{4-}$ [36], in which the macrocyclic arrangements appear to stem from the association of two molecules of the dimeric intermediate $[Sn(PHR)(\mu\text{-}PR)]_2$ (related to **A**). Thus, the current study of In(III) compounds provides some further indication that the reaction pathways found for Groups 14 and 15 phosphides already are related to the mechanisms found for Group 13 counterparts. Further studies will be aimed at establishing closer structural and mechanistic links between the chemistry of p block metal phosphides, particularly at the use of Group 13 phosphinidene complexes in the formation of P–P and metal–metal bonded compounds.

5. Supplementary material

Crystallographic data for the structural analyses of **1**, **2**· toluene and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 289009–289011. Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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