

Reactions of metallated cyclohexyl phosphine (CyPHM) with $\text{As}(\text{NMe}_2)_3$; synthesis of $[(\text{CyP})_4\text{As}]^-$ anions ($\text{M} = \text{Li}$ or Na , $\text{Cy} = \text{cyclohexyl}$)

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The reactions of CyPHM ($\text{M} = \text{Li}, \text{Na}$) with $\text{As}(\text{NMe}_2)_3$ in the presence of various Lewis-base donor ligands leads to the formation of five-membered, heterocyclic $[(\text{CyP})_4\text{As}]^-$ anions. The syntheses and structures of the new complexes $[(\text{CyP})_4\text{AsLi}\cdot\text{TMEDA}\cdot\text{thf}]$ (**1**), $[(\text{CyP})_4\text{AsNa}\cdot\text{TMEDA}]$ (**2**) ($\text{TMEDA} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) and $[(\text{CyP})_4\text{AsLi}(\text{HNMe}_2)_3]$ (**3**) are reported.

Introduction

In contrast to the Group 15 imido anions shown in Fig. 1,¹ the phosphide analogues are highly thermally labile.² This was first shown for the cage complex $[\text{Sb}(\text{PCy})_3]_2\text{Li}_6\cdot 6\text{Me}_2\text{NH}$ ($\text{Cy} = \text{cyclohexyl}$),³ obtained from the reaction of $\text{Sb}(\text{NMe}_2)_3$ with CyPHLi (1 : 3 equivalents, respectively), which decomposes at temperatures as low as 30 °C to form the Zintl compound $[\text{Sb}_7\text{Li}_3\cdot 6\text{Me}_2\text{NH}]$ and the cyclophosphane $[\text{CyP}]_4$.⁴ The isolation of the intermediate $[(\text{CyP})_4\text{SbNa}\cdot\text{TMEDA}\cdot\text{NHMe}_2]_2$ (containing the five-membered heterocyclic anion $[(\text{CyP})_4\text{Sb}]^-$) from the low-temperature reaction of the dimer $[\text{Me}_2\text{NSb}(\mu\text{-PCy})_2]_2$ with CyPHNa indicates that a key step in the formation of a Zintl compound at higher temperature in this reaction is the elimination of $[\text{CyP}]_4$ from the $[(\text{CyP})_4\text{Sb}]^-$ anion, with the delivery of Sb to the Zintl anion.⁵ The formation of P–P bonds in this process (having the highest homoatomic single bond energy for any of the Group 15 elements) provides one of the principal thermodynamic driving force for the conversion of the phosphide cages into the Zintl phases.

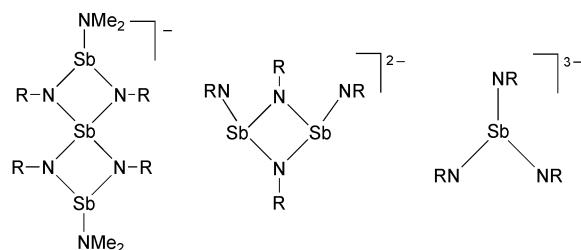


Fig. 1 Common imido anion frameworks of Group 15 elements: [bicyclic monoanion (left), ring dianion (centre), tripodal trianion (right)].

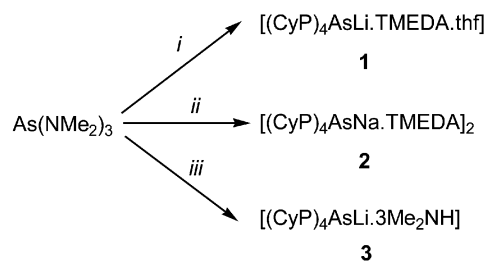
Despite the considerable mechanistic detail uncovered so far on the formation of Zintl compounds in these reactions, some important questions remain to be answered. In particular, it was unclear what factor(s) dictate the ring size of heterocyclic $[(\text{RP})_n\text{E}]^-$ anions ($\text{E} = \text{As}, \text{Sb}$) formed in reactions of Group 15 dimethylamido compounds with RPHM ($\text{M} = \text{alkali metal}$). We had been able to show that the stoichiometry employed in these reactions and the alkali metal and Lewis-base donor present had no influence on the ring size.^{5b} However, the formation of four-membered heterocyclic $[(\text{RP})_3\text{As}]^-$ anions in the reactions of $\text{As}(\text{NMe}_2)_3$ or $[\text{Me}_2\text{NAs}(\mu\text{-PR})_2]_2$ with the lithium phosphides BuPHLi and $(1\text{-adamantyl})\text{PH}_2$ (*cf.* the five-membered $[(\text{CyP})_4\text{Sb}]^-$ anion noted previously) lead us to conclude tentatively that the size of the Group 15 atom may have the greatest

influence.^{5b} We present here a study of the reactions of CyPHM with $\text{As}(\text{NMe}_2)_3$ designed to test this proposition. The isolation of the new complexes $[(\text{CyP})_4\text{AsLi}\cdot\text{TMEDA}\cdot\text{thf}]$ (**1**), $[(\text{CyP})_4\text{AsNa}\cdot\text{TMEDA}]_2$ (**2**) and $[(\text{CyP})_4\text{AsLi}\cdot 3\text{Me}_2\text{NH}]$ (**3**), all containing five-membered $[(\text{CyP})_4\text{As}]^-$ anions, shows that ring size is in fact largely directed by the steric demands of the organic substituents. In addition, this study provides potentially synthetically useful sources of the $[(\text{CyP})_4\text{As}]^-$ anion which are far more stable than the Sb counterparts.^{6–8}

Results and discussion

Synthesis and characterisation of 1–3

The reactions of $\text{As}(\text{NMe}_2)_3$ with CyPHM ($\text{M} = \text{Li}, \text{Na}$) (1 : 3 equivalents) in the presence of the Lewis-base ligand TMEDA ($\text{TMEDA} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) give the new complexes $[(\text{CyP})_4\text{AsLi}\cdot\text{TMEDA}\cdot\text{thf}]$ (**1**) and $[(\text{CyP})_4\text{AsNa}\cdot\text{TMEDA}]_2$ (**2**) only after prolonged storage of the thf/toluene solutions at –20 °C (Scheme 1) (see Experimental section). Interestingly, performing the reaction of CyPHLi with $\text{As}(\text{NMe}_2)_3$ in only toluene as the solvent, in the absence of any added Lewis-base ligand, gives the tris-dimethylamine complex $[(\text{CyP})_4\text{AsLi}\cdot 3\text{Me}_2\text{NH}]$ (**3**) (Scheme 1) (see Experimental section). Solvation of alkali metal cations by Me_2NH (bp 7 °C) is still rare, this has been observed previously only in the cage complex $[\text{Sb}(\text{PCy})_3]_2\text{Li}_6\cdot 6\text{NHMe}_2$,³ the Zintl compound $[\text{Sb}_7\text{Li}_6\cdot 6\text{NHMe}_2]_4$ ⁴ and in $[(\text{CyP})_4\text{SbNa}\cdot\text{TMEDA}\cdot\text{NHMe}_2]_2$.^{5a} The low yields of crystalline 1–3 obtained (11–21%) in part stem from the very high solubilities of the complexes in organic solvents, making isolation at room temperature difficult. In addition, *in situ* ³¹P NMR studies reveal the presence of other products in the reaction mixtures (including the cyclic phosphane $[\text{CyP}]_4$ as well as other unidentified phosphide chain species).



Scheme 1

Table 1 Coupling constants (Hz) and chemical shifts (δ /ppm) for the major isomers of **1–3**, **A** and **B** in D_8 -thf

	1	2	3	A	B
$\delta P(1)$	38.2	40.6	38.4	19.7	-50.3
$\delta P(2)$	63.4	58.0	56.6	59.5	-29.8
$\delta P(3)$	63.4	58.0	56.6	59.5	-29.8
$\delta P(4)$	38.2	40.6	38.4	19.7	-50.3
$J_{1,2}$	-325.7	-334.2	-309.7	-333.6	-218.6
$J_{1,3}$	-6.1	-17.9	-4.4	-12.8	-6.8
$J_{1,4}$	-	45.8	-	3.0	22.1
$J_{2,3}$	-	-376.8	-	-340.9	-342.4
$J_{2,4}$	-6.1	-17.9	-4.4	-12.8	-6.8
$J_{3,4}$	-325.7	-334.2	-309.7	-333.6	-218.6

Although **1** and **3** are stable at room temperature, complex **2** decomposes at or around ambient temperature. Particular care therefore had to be taken in the isolation and characterisation of **2**, which was prepared freshly prior to all analytical and spectroscopic work. The 1H NMR spectra of **1–3** are largely uninformative. In each of the complexes the Cy resonances appear as a collection of overlapping multiplets within the region δ 0.9–2.0. The presence of Li-bonded Me_2NH ligands in **3** is indicated by an apparent 1 : 1 doublet at δ 2.33 ($^3J_{P-H} = 6.3$ Hz). The observation of coupling through the essentially ionically bonded P–Li–N(H) fragment in **2** is rare. A similar set of circumstances has been observed previously in the LiBr salt complex $[(LiBr)_2 \cdot 3O=P(NMe_2)_3]$, where coupling of the P atoms of the three μ_2 -O=P(NMe₂)₃ ligands connecting the two LiBr monomer units results in the splitting of the 7Li resonance into a quartet ($^2J_{P-Li} = 3.8$ Hz).⁹

The $^{31}P\{^1H\}$ NMR spectra of **1–3** provide direct evidence of the presence of five-membered $[(CyP)_4As]^-$ anions in the complexes. Like the previously reported Sb(III) complex $[(CyP)_4SbNa \cdot TMEDA \cdot NHMe_2]_2$, containing a similar $[(CyP)_4Sb]^-$ anion, the $[(CyP)_4As]^-$ anions of **1–3** appear as AA'BB' spin systems.¹⁰ Since the minor *ab* structure lines at the periphery of the AA'BB' resonances in the spectra of **1** and **3** (Fig. 3) overlap, only the values of $J_{1,2}$ ($= J_{3,4}$) and $J_{1,3}$ ($= J_{2,4}$) could be determined in these cases. Only in the case of **2** could full coupling information be determined by algebraic analysis.¹⁰ Table 1 lists the relevant coupling constants (where they could be determined) and chemical shifts for the major conformers of **1–3** found in thf solution. The preferred conformation of the $[(CyP)_4As]^-$ anions of **1–3** is most likely to be the *all-trans* arrangement shown in Fig. 2. Other minor conformers (having different orientations of the Cy groups above and below the P₄As rings to that shown in Fig. 2(a)) are also found in the ^{31}P NMR spectrum of **2** and **3**, and appear as weak multiplets at δ 34 and -15 for **2** and δ 51 and 32 for **3** (e.g., see Fig. 3, marked *). Similar minor isomers are also found for the $[(CyP)_4Sb]^-$ anion in solution.^{5a} The ^{31}P NMR data for **1–3** are compared to those observed previously for $[(CyP)_4SbNa \cdot TMEDA \cdot NHMe_2]_2$ (**A**)^{5a} and for the dominant *all-trans* isomer of $[(^tBuP)_4H_2]^-$ (**B**) reported previously by Baudler *et al.* (Fig. 2(b)).¹¹ The signs of the coupling constants for **1–3** were assigned on the basis of those previously determined for $[(CyP)_4SbNa \cdot TMEDA \cdot NHMe_2]_2$ (**A**)^{5a} and $[(^tBuP)_4H_2]^-$ (**B**).¹¹

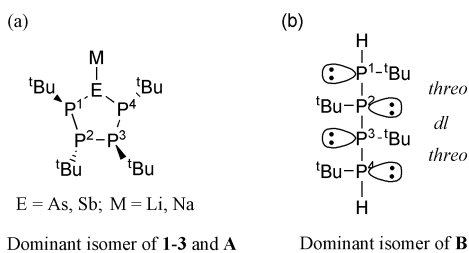


Fig. 2 (a) Conformation of the major isomer of $[(CyP)_4E]^-$ anion and numbering of the P centres; (b) conformation of the dominant *all-trans* isomer of $[(^tBuP)_4H_2]^-$.

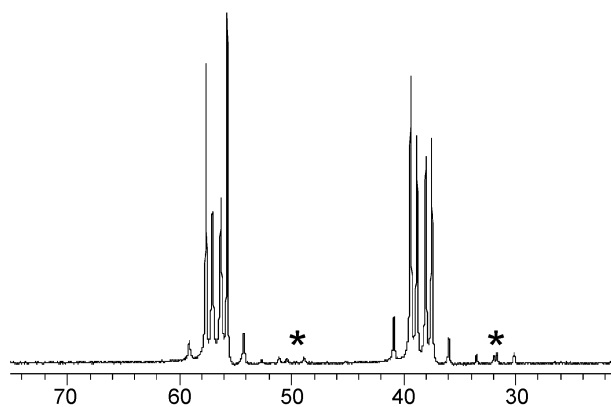


Fig. 3 $^{31}P\{^1H\}$ NMR spectrum of **3** (the resonances due to the minor isomer are marked with asterisks).

Although the chemical shifts for P(2) and P(3) of the $[(CyP)_4As]^-$ anions of **1–3** are very similar to those observed for the $[(CyP)_4Sb]^-$ anion of **A**,^{5a} the chemical shifts for the As-bonded P atoms P(1) and P(4) have considerably more positive values. This is consistent with the lower polarity of the P–As bonds within the $[(CyP)_4As]^-$ anion compared to the P–Sb bonds of the Sb(III) counterpart, as expected on the basis of the electronegativity differences between the elements involved. Thus, there is a lower development of negative charge for the As-bonded P centres of the $[(CyP)_4As]^-$ anion. Overall, the coupling constants observed for the major isomers of **1–3** are similar to those found for the $[(CyP)_4Sb]^-$ anion of **A**. The significantly higher value of $J_{1,4}$ in the $[(CyP)_4As]^-$ anion of **2** (45.6 Hz) than in the $[(CyP)_4Sb]^-$ anion (3.0 Hz) may be a consequence of the lower polarity (greater covalent character) of the P–As bond, compared to the P–Sb bond. A recent report of the synthesis and structure of $[(^tBuP)_4PNa \cdot 4thf]$, containing a five-membered $[(^tBuP)_4P]^-$ anion (a phosphorus-centred counterpart of the $[(CyP)_4As]^-$ anion), is of particular interest in regard to the ^{31}P NMR spectroscopic behaviour of **1–3**.¹² This complex, which is prepared by the reaction of PCl_3 , tBuPCl_2 and Na in thf, is characterised by an ABB'CC' ^{31}P spin system. Comparison of the BB'CC' portion of the latter [*i.e.*, the coupling within the $(^tBuP)_4$ unit] with the spectra of **1–3** reveals close similarities between the absolute values of the coupling constants involved [$J_{1,2} = J_{3,4} = -317.2$, $J_{1,3} = J_{2,4} = -5.4$, $J_{1,4} = -17.2$, $J_{2,3} = -309.4$ Hz¹²]. The difference between the chemical shifts for the two tBuP environments of the $[(^tBuP)_4P]^-$ anion ($\delta_{1,4} = 82.7$, $\delta_{2,3} = 75.0$ [$\Delta\delta = 7.7$ ppm]¹²) is significantly smaller than for the $[(CyP)_4As]^-$ anion ($\Delta\delta = 17.4$ – 25.2 ppm).

X-Ray structure determinations of **1–3**

The low-temperature X-ray structures of **1–3** were determined. Details of the data collections and refinements are given in Table 2. Table 3 lists key bond lengths and angles for complexes **1–3**.

The solid-state structures of **1**, **2** and **3** confirm the overall conclusions drawn from preliminary spectroscopic and analytical studies, all of the complexes containing $[(CyP)_4As]^-$ anions. The structure of **1** is that of a monomer, in which the Li⁺ cation is solvated by a chelating TMEDA ligand and coordinated by a thf molecule (Fig. 4). The As–Li bond in **1** [2.68(2) Å] is similar to that found in $[(^tBuP)_3AsLi \cdot TMEDA \cdot thf]$ [2.62(2) Å^{5a}], in which the same set of Lewis-base ligands coordinates the Li⁺ cation. The fact that a five-membered heterocycle is found in **1** and a four-membered ring is present in $[(^tBuP)_3AsLi \cdot TMEDA \cdot thf]$ (with the same set of Lewis-base donor ligands being present in both complexes) provides the clearest evidence yet that the Lewis-base donor present has no effect on the ring size of the heterocycle generated in these reactions.

Table 2 Details of the data collections and structural refinements of 1–3

Compound	1	2	3
Empirical formula	C ₃₄ H ₆₈ AsN ₂ LiOP ₄	C ₃₀ H ₆₀ AsN ₂ NaP ₄	C ₃₀ H ₆₅ AsLiN ₃ P ₄
<i>M</i>	726.64	670.59	673.59
<i>T</i> /K	293(2)	180(2)	180(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
Cell parameters			
<i>a</i> /Å	19.204(4)	10.8971(3)	10.2635(3)
<i>b</i> /Å	19.464(6)	17.5762(6)	15.4835(5)
<i>c</i> /Å	21.771(4)	19.5359(7)	24.3220(4)
<i>a</i> ^o	–	–	–
<i>β</i> ^o	–	92.037(2)	96.165(2)
<i>γ</i> ^o	–	–	–
<i>Z</i>	8	4	4
<i>U</i> /Å ³	8138(3)	3739.3(2)	3842.8(2)
<i>D_c</i> /Mg m ⁻³	1.186	1.191	1.164
<i>μ</i> (Mo-Kα)/mm ⁻¹	1.019	1.112	1.073
Independent reflections (<i>R</i> _{int})	4317 (0.112)	6530 (0.073)	8768 (0.064)
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.082, <i>wR</i> 2 = 0.113	<i>R</i> 1 = 0.039, <i>wR</i> 2 = 0.071	<i>R</i> 1 = 0.040, <i>wR</i> 2 = 0.074
<i>R</i> indices (all data)	<i>R</i> 1 = 0.264, <i>wR</i> 2 = 0.141	<i>R</i> 1 = 0.065, <i>wR</i> 2 = 0.168	<i>R</i> 1 = 0.079, <i>wR</i> 2 = 0.084

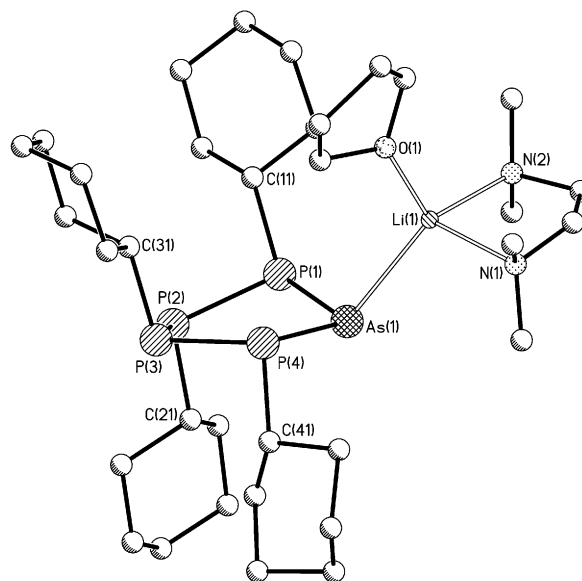
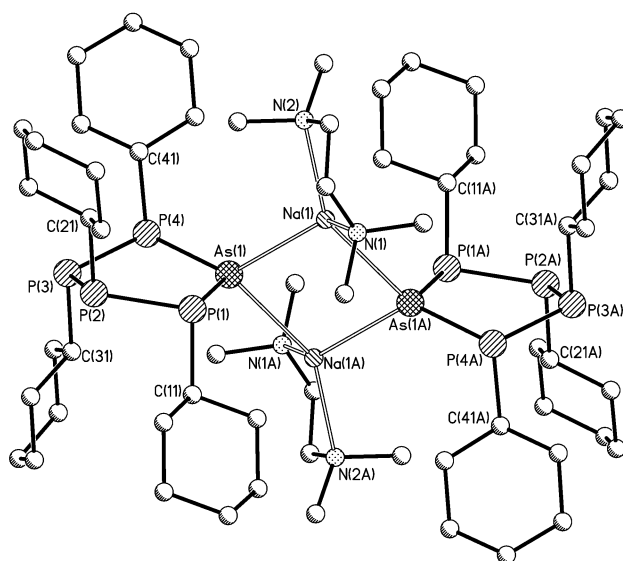
Table 3 Selected bond lengths and angles for 1–3

	1	2	3
Bond lengths (Å)			
P(1)–P(2)	2.196(5)	2.190(1)	2.1825(8)
P(2)–P(3)	2.214(5)	2.205(1)	2.2069(8)
P(3)–P(4)	2.181(5)	2.187(1)	2.1867(8)
P(1)–As(1)	2.258(4)	2.3201(8)	2.3107(7)
P(4)–As(1)	2.321(4)	2.2810(7)	2.3083(6)
C–P(1,2,3,4) mean	1.879	1.876	1.878
As(1)–M(1)	2.68(2)	2.958(1)	2.784(4)
As(1)–M(1A) ^a	–	2.987(1)	–
Bond angles (°)			
P(1)–As(1)–P(4)	103.0(1)	105.12(3)	104.70(2)
As(1)–P(1)–P(2)	105.2(2)	106.49(3)	106.30(3)
As(1)–P(4)–P(3)	107.0(2)	105.25(3)	106.82(3)
P(1)–P(2)–P(3)	106.0(2)	107.45(4)	107.86(3)
P(2)–P(3)–P(4)	107.8(2)	107.48(4)	106.66(3)
P(1)–As(1)–M(1)	109.9(5)	83.40(3)	130.01(9)
P(4)–As(1)–M(1)	102.6(4)	132.01(3)	94.49(8)
P(1)–As(1)–M(1A) ^a	–	116.26(3)	–
P(4)–As(1)–M(1A) ^a	–	120.68(3)	–
M(1)–As(1)–M(1A) ^a	–	94.61(3)	–
As(1)–M(1)–As(1A) ^a	–	85.39(3)	–

^a Data labelled A refer to the structure of complex 2 only.

Complex 2 is a centrosymmetric dimer in the solid state, in which the Na⁺ cations are each solvated by a chelating TMEDA ligand (Fig. 5). The structure is similar to that of the previously characterised complex [(CyP)₄SbNa·TMEDA·NHMe₂]₂,^{5a} except that the Na⁺ cations of 2 are not coordinated by Me₂NH ligands. We assume that this difference arises for steric reasons, the relative shortness of the As–Na bonds in 2 [As(1)–Na(1) 2.958(1), As(1)–Na(1A) 2.987(1) Å] compared to the Sb–Na bonds in [(CyP)₄SbNa·TMEDA·NHMe₂]₂ [3.617(4) and 3.229(4) Å^{5a}] resulting in more space for coordination of the Me₂NH ligand to Na⁺ in the Sb(III) complex. Despite these differences in the Group 15 element–Na bond lengths in these complexes, the bond angles within their central Na₂(μ-As)₂ and Na₂(μ-Sb)₂ cores are very similar: [As(1)–Na(1)–As(1A) 85.39(3), Na(1)–As(1)–Na(1A) 94.61(3)°; cf. 87.0(1) and 93.0(1)° for the corresponding angles in [(CyP)₄SbNa·TMEDA·NHMe₂]₂]. Complex 2 contains only the second example of an As–Na bond, the first example being found in the polymer [Ph₂AsNa·(C₄H₈O₂)]_∞ [mean 2.950(4) Å].¹³

Like 1, the structure of 3 is monomeric in the solid state (Fig. 6(a)). One of the unusual features of the complex is the

**Fig. 4** Structure of monomeric [(CyP)₄AsLi·TMEDA·thf] (1).**Fig. 5** Structure of the centrosymmetric dimer [(CyP)₄AsNa·TMEDA]₂ (2).

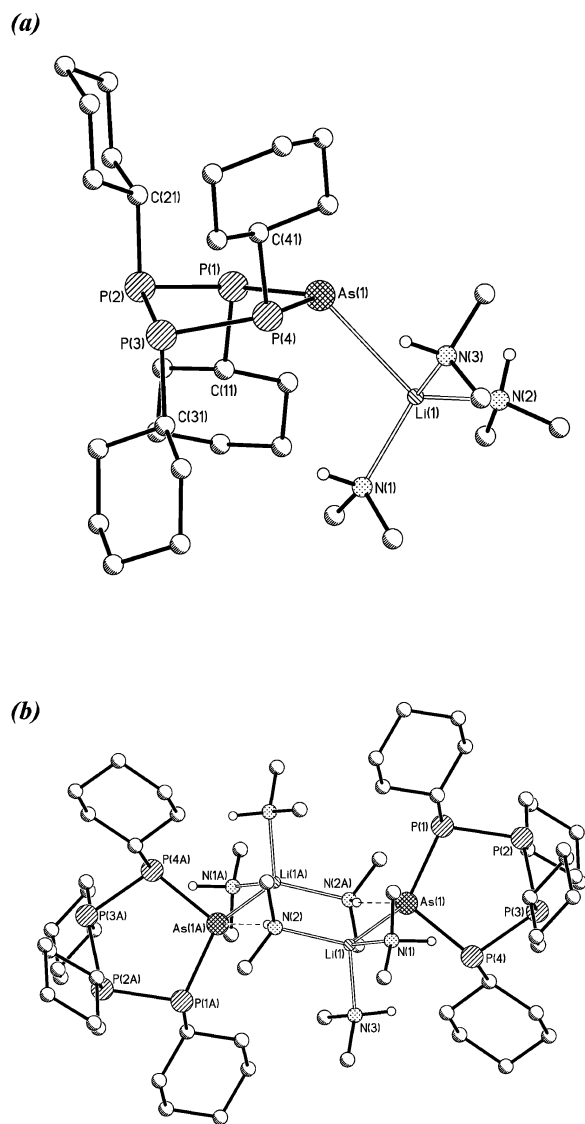


Fig. 6 (a) Structure of the monomer units of $[(\text{CyP})_4\text{AsLi}\cdot 3\text{Me}_2\text{NH}]$ (**3**); (b) the association of molecules of **3** into centrosymmetric dimeric units via $\text{N-H}\cdots\text{As}$ H-bonding.

coordination of three Me_2NH ligands to the Li^+ cation, in addition to bonding to the As centre of the $[(\text{CyP})_4\text{As}]^-$ anion. The As–Li bond in **3** [2.784(4) Å] is noticeably longer than that of 2.68(2) Å in **1** and is in fact the longest As–Li bond we have observed in any complex containing $[(\text{RP})_n\text{As}]^-$ anions bonded to Li^+ (whether with $n = 3$ or 4) [range 2.62(2)–2.702(4) Å].⁵ The coordination of the As(III) centre of the $[(\text{CyP})_4\text{As}]^-$ anion to the Li^+ cation is highly distorted in **3**, as witnessed by the vastly different P(1,4)–As(1)–Li(1) bond angles present [130.1(9) and 94.49(8)°]. This distorted coordination in **3** is similar to that occurring in **2**, required in order to facilitate dimerisation of the monomer units, and is unlike the more symmetrical coordination of the $[(\text{CyP})_4\text{As}]^-$ anion to Li^+ in **1**. The underlying reason for both the presence of a long As–Li bond and for the distortion in the coordination of the anion in **3** is the association of monomer units into centrosymmetric dimers via $\text{As}\cdots\text{H-N}$ H-bonds [N(2)–H \cdots As(1A) 2.81 Å, 163°] (Fig. 6(b)). This association may also explain the presence of a shorter Li–N bond to the H-bonding Me_2NH ligand [N(2)–Li(1) 2.076(4) Å] than to the remaining Me_2NH ligands [2.103(4) and 2.103(5) Å]. Such N–H \cdots As H-bonding has only previously been observed, to our knowledge, in the Zintl compound $[\text{As}_7\text{Li}_3\cdot 3\text{CyNH}_2\cdot 3\text{Me}_2\text{NH}]$ [H \cdots As range 2.78–2.83 Å].¹⁴

Finally, some general comments can be made concerning the structures of the $[(\text{CyP})_4\text{As}]^-$ anions of **1–3**. In all three complexes the $[(\text{CyP})_4\text{As}]^-$ anions adopt flattened, envelope conformations, in which the As atom and three P atoms are approximately coplanar [maximum deviation 0.03 Å (**1** and **2**) and 0.08 Å (**3**)] with the remaining P atom being displaced markedly from this mean plane [deviations/Å P(1) in **1**, 0.73; P(3) in **2**, 0.61; P(2) in **3**, 0.56]. Overall the five atoms within P_4As rings of the $[(\text{CyP})_4\text{As}]^-$ anions in **1–3** deviate by 0.15–0.19 Å from the mean planes of the rings. This distortion of the ring units, and the *threo*, *dl*, *threo* (*all-trans*) conformation of the Cy groups, presumably minimises steric and lone-pair repulsion to a greater extent than would, for example, result from the deformation of the ring at the anionic As centre. The As–P [range 2.258(4)–2.321(4) Å] and P–P bonds [range 2.181(5)–2.214(5) Å] in **1–3** are generally shorter than the As–P and P–P bonds in $[(\text{RP})_3\text{As}]^-$ anions [ranges 2.327(2)–2.356(1) and 2.198(4)–2.242(1) Å, respectively]⁵ This is most probably a consequence of reduced ring strain in the five-membered heterocyclic anions, in which better alignment of the P and As orbitals can occur. This is shown by the P–P–P [106.0(2)–107.86(3)°], P–P–As [105.1(1)–106.9(2)°] and P–As–P [103.0(1)–105.12(3)°] angles in **1–3**, which better match the sp^3 hybridisation of the P and As than in four-membered $[(\text{RP})_3\text{As}]^-$ anions [range of endocyclic P–P–P, P–P–As and P–As–P angles 86.67(4)–91.4(2)°⁵].

Conclusions

The study presented here illustrates that the size of $[(\text{RP})_n\text{E}]^-$ rings generated by reactions of RPHM with $\text{E}(\text{NMe}_2)_3$ depends primarily on the organic group (R) and not on the Group 15 element (E), the Lewis-base present or the alkali metal (M). The new complexes described in this paper provide useable (relatively thermally stable) sources of the $[(\text{CyP})_4\text{As}]^-$ anion, which may be of value in the further study of their coordination chemistry with a range of main group and transition metals.

Experimental

General experimental

Compounds **1–3** are air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry/oxygen-free argon.¹⁵ Toluene and thf were dried by distillation over sodium/benzophenone prior to the reactions. Cyclohexyl phosphine (CyPH_2) was used as supplied (Strem). PhCH_2Na was prepared by the reaction of $^n\text{BuLi}$ with $^t\text{BuONa}$ in toluene–hexane, the product being isolated in almost quantitative yield by this method. TMEDA was dried by distillation over Na metal and was stored under argon over molecular sieve. The products were isolated and characterized with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system. $\text{As}(\text{NMe}_2)_3$ was prepared from the reaction of AsCl_3 with a suspension of LiNMe_2 in Et_2O , and purified by distillation.¹⁶ This reagent was used as standardised solution in toluene. Elemental analyses were performed by first sealing the samples under argon in air-tight 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. Samples (1–2 mg) were again prepared in aluminium boats prior to analysis. ^1H and ^{31}P NMR spectra were recorded on a Bruker AM 400 MHz spectrometer in dry D_8 -thf. The solvent resonances were used as the internal reference standard for ^1H NMR studies, and 85% $\text{H}_3\text{PO}_4\text{-D}_2\text{O}$ was employed as the external reference standard for ^{31}P NMR work.

General method. Solutions of CyPH_2 (1.6 ml, 12.0 mmol) in toluene (30 ml for **1**; 15 ml for **2** and **3**) at -78°C were reacted

with the organometallic bases $^n\text{BuLi}$ (8.0 ml, 1.5 mol dm^{-3} in hexanes, 12.0 mmol) for **1** and **3**; suspension of PhCH_2Na (1.20 g, 12 mmol) in toluene (15 ml) for **2**. After warming to room temperature and stirring for 1 h, yellow suspensions of CyPM ($M = \text{Li}, \text{Na}$) were obtained. The suspensions were cooled to -78°C and $\text{As}(\text{NMe}_2)_3$ (2.0 ml, 2.0 mol dm^{-3} in toluene, 4.0 mmol) was added dropwise. For **1** and **3**, thf (10 ml) and TMEDA (1.51 ml, 4.0 mmol) were then added. For **2**, no donor solvents were used. The reactions were allowed to warm to room temperature and stirred (48 h for **1**, 5 h for **2**, 24 h for **3**), to give bright orange solutions for **1** and **3** and a brown solution for **2**. The volume of solvent was reduced under vacuum (to ca. 15 ml for **1** and **2**, to ca. 10 ml for **3**). For **1** and **3**, this led to the precipitation of orange solids which were warmed gently back into solution. For **2**, no precipitation occurred. The solutions were stored at -20°C for up to two weeks to afford crystals of **1**, **2** or **3**. Crystals of **1** and **3** were isolated by filtration. However, during the isolation of crystals of **2**, the reaction mixture was kept cold while the mother-liquor was removed by syringe. Crystals were washed with hexane (3×2 ml) and the solid dried *in vacuo*.

Data for 1: Yield 0.23 g (11%); ^1H NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 400.129 MHz), δ 2.25 (s, 4H, CH_2CH_2 , TMEDA), 2.09 (s, 12H, Me_2N , TMEDA), 2.0–0.8 (m, 44H, Cy); ^{31}P NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 161.975 MHz), δ 63.4 [m, P(2,3)], 38.2 [m, P(1,4)] (no other conformers); elemental analysis, found: C 56.4, H 9.6, N 4.4; calc. for **1**: C 56.1, H 9.4, N 3.8%.

Data for 2: Yield 0.42 g (21%); ^1H NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 400.129 MHz), δ 2.51 (s, 12H, Me_2N , TMEDA), 2.31 (s, 4H, CH_2 , TMEDA), 1.76–1.25 (m, 55H, Cy); ^{31}P NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 161.975 MHz), δ 50.0 [m, P(2,3)], 40.6 [m, P(1,4)] (minor conformers: δ -15 to 34); Elemental analysis, found: C 52.3, H 8.8, P 4.2; calc. for **2**: C 53.7, H 9.0, P 4.2%.

Data for 3: Yield 0.28 g (14%); ^1H NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 400.129 MHz), δ 2.33 (d, 18H, Me_2NH), 1.70–0.91 (m, 55H, Cy); ^{31}P NMR ($\text{D}_8\text{-thf}$, $+25^\circ\text{C}$, 161.975 MHz), δ 56.6 [m, P(2,3)], 38.4 [m, P(1,4)] (-70.1 (s) [CyP]₄ trace) (minor conformers: δ 32–51); Elemental analysis, found: C 51.8, H 9.1, P 6.3; calc. for **3**: C 53.5, H 9.7, P 6.2%.

X-Ray crystallographic studies of 1–3

Crystals of **1–3** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture.¹⁷ X-Ray intensity data were collected using a Nonius Kappa CCD diffractometer for **2** and **3**, and a Bruker P4 diffractometer for **1**. Details of the data collections and structural refinements are given in Table 1. The structures were solved by direct methods and refined by full-matrix least squares on F^2 .¹⁸ The crystals of **1** diffracted relatively weakly at high angle, which may be attributed to some disorder of all the ligands as indicated by marked anisotropy of the displacement parameters. This disorder was resolved for eleven of the carbon atoms which were each refined as two components of approximately equal occupancy, with chemically equivalent bonds in the two components constrained to be equal within an esd of 0.04 Å. Despite relatively high R indices resulting from the disorder in **1** the molecular structure is well established. The amino

hydrogen atoms in **3** were directly located and refined freely; all other hydrogen atoms in all three structures were included in idealised positions.

CCDC reference numbers 197231–197233.

See <http://www.rsc.org/suppdata/dt/b2/b211037g/> for crystallographic data in CIF or other electronic format.

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