

Phosphinidene complexes of p block metals; new routes to cyclic ligands and Zintl phases[☆]

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Abstract

In contrast to the reactions of $E(\text{NMe}_2)_3$ ($E = \text{As}, \text{Sb}, \text{Bi}$) with $[\text{RNHM}]$ ($M = \text{Li} - \text{Cs}$) which generate stable Group 15 imido anions (such as the dianions $[\text{E}_2(\text{NR})_4]^{2-}$ and trianions $[\text{E}(\text{NR})_3]^{3-}$), the phosphide analogues formed in the analogous reactions using $[\text{RPHM}]$ decompose readily to give Zintl compounds. This process is accompanied by the formation of $[\text{RP}]_n$ rings, indicating that the alloy-forming reaction is driven thermodynamically by the bond energy of P–P bonds. The apparent intermediates in this reaction are heterocyclic anions of the type $[(\text{RP})_n\text{E}]^-$ ($n = 3$ or 4). The latter are interesting new ligands for a range of metals, with the potential ability to behave as sources of metal atoms (E). The anions exhibit unusual reactivity with transition metal metallocenes, adding to the cyclopentadienyl rings in preference to the attack of metal–halogen bonds. In addition, the reactions

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of the cyclic anions with electrophiles ($R'X$) furnish a simple selective route to neutral oligophosphine ligands of the type $[(RP)_nR'_2]$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphinidine complexes; p Block metals; Zintl compounds

1. Introduction

Traditionally the design and synthesis of ligand systems has been dominated by arrangements based on organic frameworks. The past few decades have seen a huge growth in highly elaborate ligand sets focused in particular on the selective coordination of specific metal ions and on the construction of complex molecular and supramolecular assemblies [1]. In contrast, apart from a few notable exceptions (such as boranes and carboranes) progress in the development of ligand systems based on classical inorganic frameworks has been sporadic. This is perhaps unsurprising bearing in mind the vastly different chemical reactivities, bonding demands and structural patterns adopted by elements other than carbon, and the resulting inherent difficulty in developing coherent strategies to these species.

A major area of interest to us in the past decade has been the development of new synthetic approaches to anionic ligand systems containing Group 15 element (As, Sb, Bi)/imido frameworks (containing RN^{2-} functionality), and the application of these ligands in the targeted synthesis of heteroatomic cage complexes.[2,3] After a brief survey of the key synthetic approaches involved in the preparation of stable Group 15 imido ligand systems, this review moves on to detail the surprising discovery that analogous phosphinidine cage complexes (containing RP^{2-} functionality) are precursors to Zintl phases and novel heterocyclic anions. The new reactions involved furnish a potentially general strategy to a number of technologically important phases (such as photoactive materials and semiconductors [4]), and give very simple access to a family of terminally substituted tri- and tetraphosphines.

2. Synthetic methodology

2.1. A survey of Group 15 imido anion arrangements

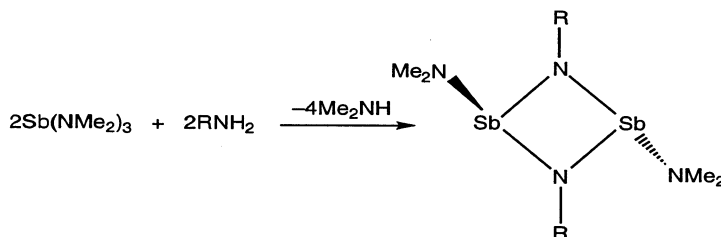
There are a number of important synthetic difficulties associated with the synthesis of Group 15 imido compounds. In particular, complete deprotonation of aliphatic amines (RNH_2) is generally difficult to achieve even using strong bases such as organoalkali metal reagents ($R'M$). Thus there are very few available precursors of the type RNM_2 which can be used in transmetallation reactions with the Group 15 element halides (EX_3) to generate the corresponding imido compounds. Direct reactions of $RNHLi$ with EX_3 at high temperatures can be

employed, but the nature of the products and the degree of substitution is somewhat unpredictable [5,6].

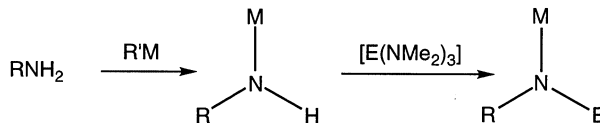
The primary objective at the beginning of our studies in this area was to develop a synthetic approach based on a simple deprotonation procedure. By necessity this required a search for new, readily accessible reagents which were basic enough. One underlying problem is the inherently low basicity of most organo Group 15 compounds. For example, commercially available triphenyl antimony or arsenic are almost unreactive with anything other than stronger organic acids. The breakthrough in this initial stage came with the realisation (based on earlier literature [7]) that the dimethyl amido Group 15 reagents had all the required characteristics. Importantly, it is found that $\text{Sb}(\text{NMe}_2)_3$ (one of the primary reagents used in these studies) will easily doubly-deprotonate even the least acidic aliphatic primary amines [such as $t\text{BuNH}_2$ and CyNH_2 (Cy = cyclohexyl)] at temperatures as low as -78°C , giving dimers of the type $[\text{Me}_2\text{NSb}(\mu\text{-NR})]_2$ (Scheme 1) [8].

An interesting comparison can be made between the reactivity of $\text{Sb}(\text{NMe}_2)_3$ and standard organoalkali metal reagents (such as $t\text{BuLi}$ or $i\text{BuLi}$). Even when in excess the latter will generally only singly deprotonate primary amines (except where conjugation within aromatic groups can occur), giving primary amido alkali metal species containing RNH^- anions. This comparison provides the key to a general approach to a range of anionic Group 15 imido element frameworks, since stepwise deprotonation of one of the amine protons by organoalkali metal reagents can be followed by deprotonation of the second by $\text{E}(\text{NMe}_2)_3$ [giving heterometallic arrangements in which the Group 15 elements (E) and the alkali metals (M) are held together by the imido N centre (as depicted in Scheme 2)] [2,3].

We have already reviewed heterometallic systems derived from this strategy in detail elsewhere [2,3] and it will therefore not be appropriate to give a full account



Scheme 1.



Scheme 2.

of the intricacies of the structural studies in this area. However, an appreciation of the major structural types of imido anion ligand arrangements and of their coordination characteristics will be of value to the following discussion of the chemistry of related phosphinidine systems. Fig. 1, shows the three major anion arrangements which can be prepared using the stepwise metallation procedure described in Scheme 2. Spiro monoanions of the type I are prepared by a number of routes, the simplest being the metallation of $[\text{Sb}(\text{NR})_4]^- \text{Li}^+$ with $\text{Sb}(\text{NMe}_2)_3$ (1:2 equiv., respectively) producing the $[\{\text{Me}_2\text{NSb}(\mu\text{-NR})_2\}_2\text{Sb}]^-$ framework [9,10]. The dianion arrangement of the type II is obtained by the reaction of the dimers $[\text{Me}_2\text{NE}(\mu\text{-NR})_2]$ with RNHM (1:2 equiv.), a process which retains the Sb_2N_2 core of the neutral precursor [10,11]. The simplest type of reaction (adhering most closely to the process outlined in Scheme 1) is that involved in the formation of

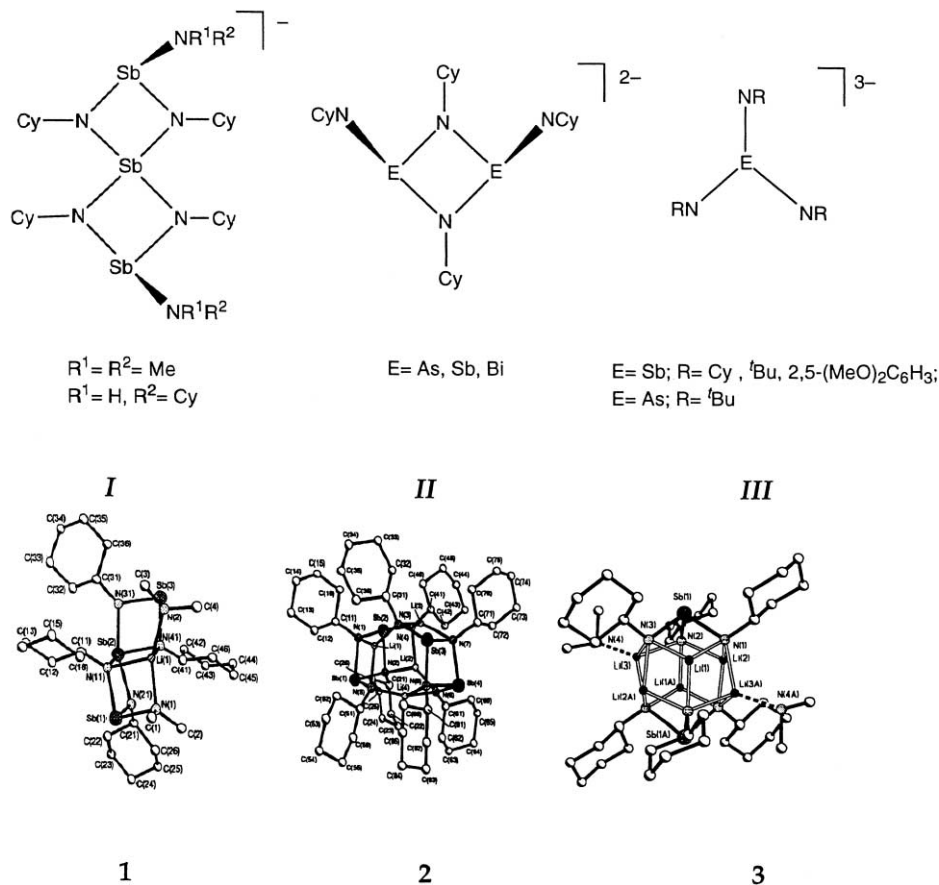


Fig. 1. The three principal Group 15 imido anion ligand frameworks accessible by stepwise metallation (top), and the cage structures adopted by $[\{\text{Me}_2\text{NSb}(\mu\text{-NCy})\}_2\text{Sb}]\text{Li}$ (1), $[\{\text{Sb}_2(\text{NCy})_4\}_2\text{Li}_4]$ (2) and $[\{\text{Sb}(\text{NCy})_3\}_2\text{Li}_6\cdot 2\text{HNMe}_2]$ (3) (bottom).

trianions of type **III**, prepared from RNHM and $E(NMe_2)_3$ (3:1 equiv., respectively) [9,12].

One of the significant points involved in the formation of the imido anions shown in Fig. 1 is that a range of organic substituents (R) can be introduced into these arrangements, including those containing additional donor functionality. The coordination characteristics of each ligand set can be tailored to a given metal by varying the donor set present and geometric demands of the ligand framework. The latter is readily accomplished by varying the Group 15 element (E), and therefore the E–N bond lengths and associated angles involved [13]. A further key issue is that each of the individual ligand types (**I**–**III**) can be obtained containing the same organic substituent (R), e.g. as in the case of the Sb/Li cages **1**, **2** and **3** shown at the bottom of Fig. 1, for R = Cy. In this sense the reactions involved can be described as kinetically controlled, a given ligand arrangement being accessed by a given reaction sequence (rather than the organic substituent dictating the favoured arrangement adopted).

The most important facet of the behaviour of these anion arrangements is that they are readily transferred intact to other main group and transition metals [2]. Thus, the easily accessed heterometallic alkali metal cages (such as **1**, **2** and **3** illustrated in Fig. 1) are sources of the corresponding anions, transmetallation with salts of other metals resulting in clean replacement of the alkali metal cations. The formation of the heterometallic complexes $[\{ Sb_2(NCy)_4 \}_2 Cu_4]$ (**4**) [14] (Fig. 2a) and $[\{ Sb(NCy)_3 \}_2 Pb_3]$ (**5**) [15] (Fig. 2b) from the reactions of the precursors $[\{ Sb_2(NCy)_4 \}_2 Li_4]$ (**2**) and $[\{ Sb(NCy)_3 \}_2 Li_6 \cdot 2 Me_2 NH]$ (**3**) with CuCl and $[Cp_2 Pb \cdot TMEDA]$ [TMEDA = $(Me_2 NCH_2)_2$], respectively, illustrate this general approach.

The ability of this strategy to provide systematic access to heterometallic cage compounds, containing an extensive range of predictable and well-defined metal stoichiometries, has obvious implications for their use as single-source materials to various binary phases. However, for the imido systems there is no obvious (or necessarily realisable) chemical pathway by which a particular cage complex could be converted (thermally or otherwise) to the corresponding Group 15/metal alloy (with the loss of the supporting imido ligand framework). Nonetheless, it is interesting to note that for the heterometallic Sb/Pb cage $[\{ Sb(NCy)_3 \}_2 Pb_3]$ (**5**) stripping of the imido ligand framework away would result in an Sb_2Pb_3 cage, whose trigonal bipyramidal core would conform to a Wade's Rule $(n + 1)$ closo polyhedron.

2.2. 'Cage-to-alloy' reactions — extension of the methodology to phosphides

It was with the above background in mind that we first started to investigate the analogous chemistry involving primary phosphines (RPH_2). Our initial aims were simply to furnish softer anion ligand arrangements of the types shown in Fig. 1, more appropriate to the stabilisation of transition metal organometallics (such as carbonyl fragments). However, concurrent with this we had also developed an interest in the potential use of the Sb/alkali metal cages as low-temperature sources

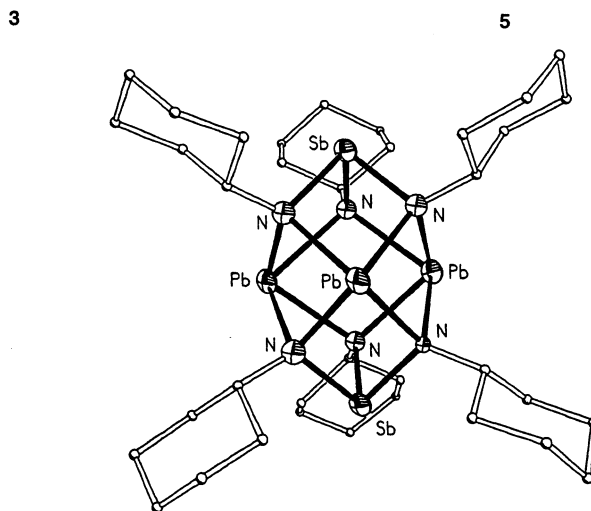
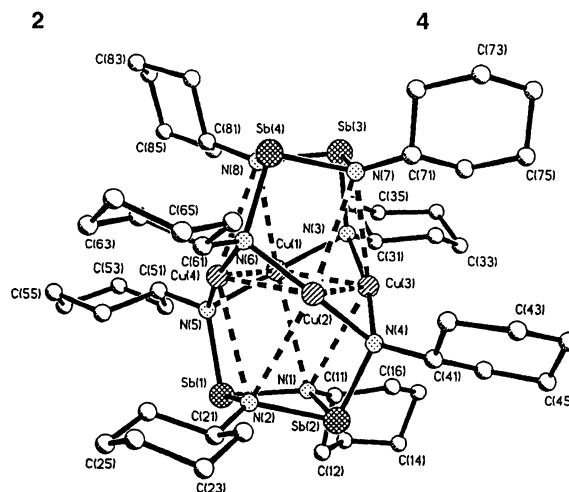
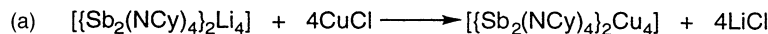
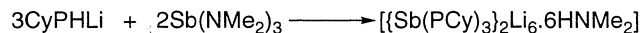


Fig. 2. (a) Transmetallation reaction of **2** with CuCl, giving the Sb/Cu heterometallic cage **4**, and (b) Transmetallation reaction of **3** with [Cp₂Pb·TMEDA], giving the Sb/Pb heterometallic cage **5**.

of alkali metal antimonates for photodiodes. The reaction of Sb(NMe₂)₃ with CyPHLi (1:3 equiv., respectively) at or below 0°C gives [{Sb(PCy)₃}]₂Li₆Me₂NH] (**6**) (Fig. 3) [16]. Although the core arrangement of this complex is similar to that of the imido analogue **3** above, it is interesting to note that solvation of all six Li⁺ cations by Me₂NH occurs in this case (as opposed to only two in **3**). The more extensive solvation of the core of **6** compared to the imido analogue arises for steric



6

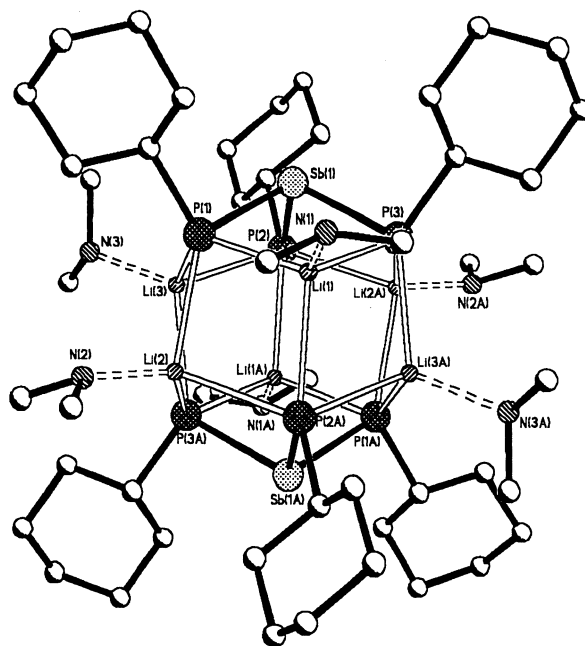


Fig. 3. Synthesis and structure of the thermolabile cage **6**.

reasons (i.e. as a result of Sb–P and P–Li bonds being longer than Sb–N and N–Li bonds, hence more space for solvation in the phosphinidine complex). More significantly, however, the presence of such a labile ligand (a gas above 7°C) attached to the Li⁺ cations of **6** turns out to be particularly advantageous in the decomposition of the complex at ca. 30–40°C. Crystals of the decomposition product [Sb₇Li₃6HNMe₂] (**7**) (Fig. 4) were first isolated as a minor product of the low-temperature reaction. However, this complex is apparently obtained in quantitative yield at higher temperatures [17]. The isolation of complex **7**, a Zintl compound containing a nortricyclic Sb₇³⁻ anion coordinated by three Li⁺ cations at the equatorial Sb centres (Fig. 4), represented the realisation of our notion that heterometallic complexes of this kind could function as sources of heterometallic alloy phases.

Several previous studies on Zintl compounds are worthy of mention here. In research pioneered by Corbett it has been shown that in order to control the stoichiometry of Zintl compounds their formation from stoichiometric Sb/alkali metal alloys is required [18]. These alloys are formed at temperatures as high as 1200°C using specialised apparatus, the alloys then being dissolved in ammonia in the presence of stabilising ligands. In particular, cryptands (such as the ubiquitous

2,2,2-crypt¹) are necessary to produce crystalline Zintl compounds which are resistant to degradation. In the absence of such ligands, which encapsulate the alkali metal cations and prevent electron transfer from the polyatomic Zintl anions to the alkali metal cations, reversion to the intermetallic alloys occurs [18]. In the case of **6**, the presence of labile Me₂NH ligands attached to the three Li⁺ cations means that the complex is, in effect, a metastable source of an alkali metal antimonate alloy. Placing the complex under vacuum or even isolation under inert atmosphere results in the loss of the coordinated Me₂NH and the formation of a lustrous metallic phase (probably a mixture of 3SbLi and 4Sb) [17]. Phosphinidine complexes like **6** therefore provide a unique, solution-phase ‘alloy-paint’ approach for the deposition of alkali metal antimonates at very low temperatures and under mild conditions (Scheme 3). This technique contrasts with the normal mode of manufacture of alkali metal antimonates which involves vapour-phase deposition of the pure metals at low pressure (ca. 10^{−6} atmos). In a related approach, Driess has shown that a high yield of [{(TMEDA)Li}₃As₇] (**8**) (containing a norticyclic As₇^{3−} anion similar to the anion of **7**) is obtained by the addition of TMEDA to the

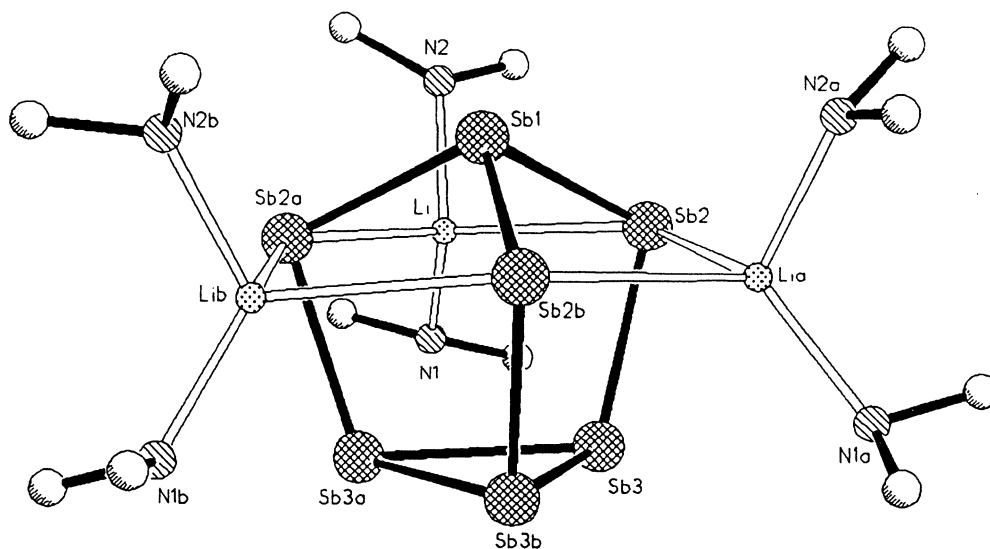


Fig. 4. Structure of the Zintl compound **7**, generated by thermal decomposition of the phosphinidine cage **6**.



Scheme 3.

¹ IUPAC name 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8,8,8)hexarosone.

lithium tetraarsanylalanates $[\text{LiAl}(\text{AsHR})_4]$ ($\text{R} = \text{H}, \text{Si}^i\text{Pr}_3$).[20] However, these thermolabile materials apparently cannot be isolated as solids and are only stable in solution.

Two observations give a clue to the mechanism and driving force of the ‘cage-to-alloy’ reaction involved in the conversion of **6** to **7**. The first is the isolation of the cyclic compound $[\text{CyP}]_4$ from this reaction.[17] This suggests that the thermodynamic driving force is the formation of P–P bonds. These have the greatest bond energy for any single bonds between Group 15 elements, and comparison of this bond energy (ca. 209 kJ mol^{-1}) with that for the N–N bond (ca. 160 kJ mol^{-1}) provides an explanation for the thermal stability of the related imido systems discussed in the previous section. In an attempt to assess the importance of the stoichiometry of the phosphinidine precursor on the stoichiometry of the product, an attempt was made to prepare the precursor complex $[\{\text{Sb}_2(\text{PCy})_4\}_2\text{Na}_4]$ (**9**) from the in situ reaction of $[\text{Me}_2\text{NSb}(\mu\text{-PCy})]_2$ with CyPHNa (1:2 equiv., respectively); the previously characterised imido analogue $[\{\text{Sb}_2(\text{NCy})_4\}_2\text{Na}_4]$ (**10**) having a structure similar to **2** (Fig. 1) but with a square-planar (rather than psuedo-tetrahedral) Na_4 core [13]. At ca. 60°C the Zintl compound $[\text{Sb}_7\text{Na}_3 \cdot 3\text{TMEDA} \cdot 3\text{thf}]$ (**11**) (Fig. 5) is isolated in almost quantitative yield [addition of the Lewis base donor TMEDA being necessary to obtain crystalline product] [21]. Clearly there is no relationship between the stoichiometry of the Zintl compound formed and that of the precursor. However, at ca. 0°C a unique complex $[\{\text{CyP}\}_4\text{SbNa} \cdot \text{TMEDA} \cdot \text{Me}_2\text{NH}]_2$ (**12**) is isolated, in which two

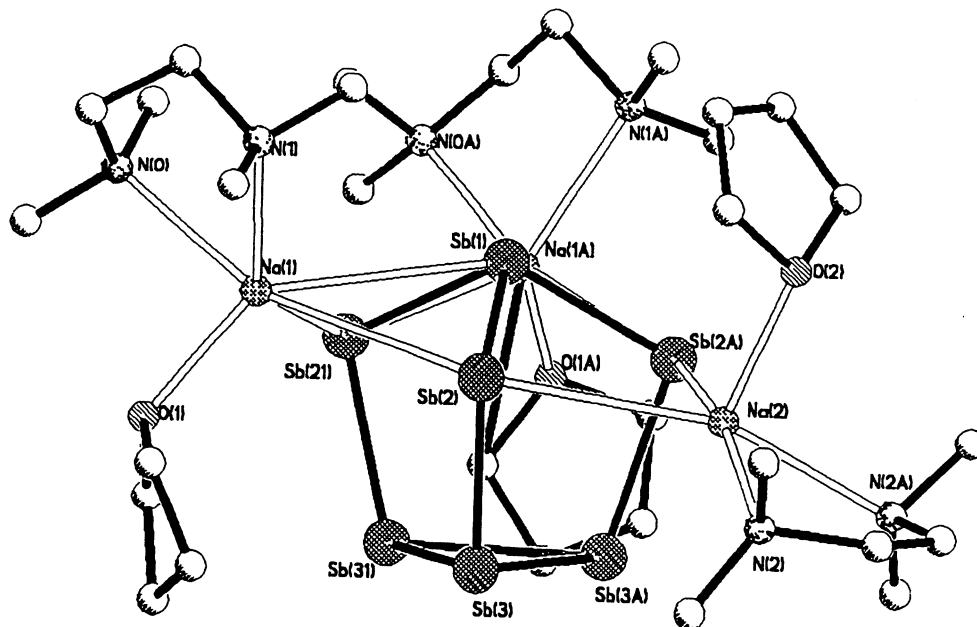


Fig. 5. Structure of the Zintl compound **11**, showing the unusual asymmetrical coordination of the Sb_7^{3-} by the three Na^+ cations.

heterocyclic $[\{\text{CyP}\}_4\text{Sb}]^-$ anions are bridged by Na^+ cations into a dimeric structure (Fig. 6) [21]. This species is a likely intermediate in the formation of the Zintl compound **11**, the $[\{\text{CyP}\}_4\text{Sb}]^-$ anion being set up for elimination of $[\text{CyP}]_4$ (which is again isolated from the reaction producing **11**).

Although cyclic intermediates like **12** appear to be important in the formation of Zintl compounds by this route, it is unlikely that the mechanism of the cage-to-alloy reaction simply involves elimination of $[\text{CyP}_4]$, with the direct formation of the Zintl anion. The presence of Me_2NH (coordinated to the Li^+ cations of the precursor $[\{\text{Sb}(\text{PCy})_3\}_2\text{Li}_6 \cdot 6\text{Me}_2\text{NH}]$ (**6**) and the Na^+ cations of the intermediate **12**) also appears to be vital. For example, if the Me_2NH ligand of **6** are removed by placing the complex under vacuum then the unsolvated complex is in fact relatively thermally stable [22]. A potential scenario involved in the formation of Sb–Sb bonds is protonation of the anionic Sb centre of the heterocycle, followed by elimination of H_2 (Scheme 4). Indeed, during the investigation of the analogous

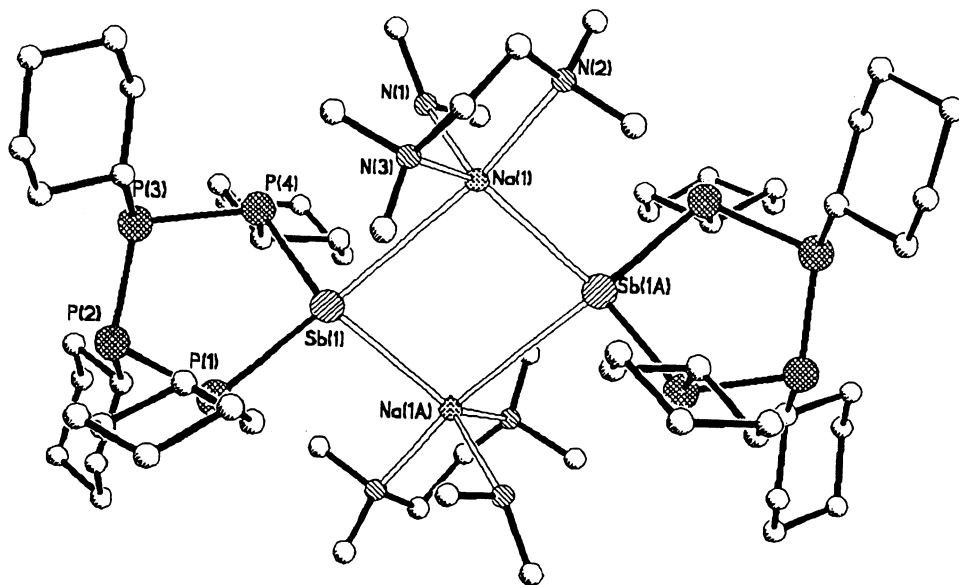
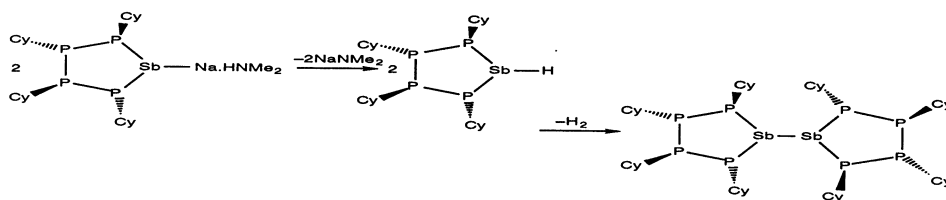


Fig. 6. Dimer structure of **12**.



Scheme 4.

chemistry of primary arsenides the reaction of $t\text{BuAsHLi}$ with $\text{As}(\text{NMe}_2)_3$ (3:1 equiv.) was found to give $[\{t\text{BuAs}\}_3\text{As}]_2$ (**13**) at low temperature (rather than the anticipated $[\{t\text{BuAs}\}_3\text{As}]^-$ anion) [22]. It is also worthy of note that LiNMe_2 has recently been identified as a byproduct of reactions of RPHLi with $\text{As}(\text{NMe}_2)_3$ [22].

The reaction characteristics found in Sb phosphinidine systems are echoed in reactions involving $\text{Bi}(\text{NMe}_2)_3$. The primary interest in this area is the fact that no Zintl compounds containing polyatomic $\text{Bi}(\text{III})$ anions have so far been structurally characterised. It was reasoned that the low temperatures required for these reactions may prevent oxidation of Bi_m^{x-} anions formed (the major problem with existing routes from which only cationic species have been obtained [24]). However, only the highly air-sensitive, thermally unstable complex $[\text{Li}(\text{thf})_4]^+[\text{Bi}\{t\text{BuP}\}_3]_2^-$ (**14**) can be isolated from the 1:3 reaction of $\text{Bi}(\text{NMe}_2)_3$ with $t\text{BuPHLi}$ [25]. The complex, the anion of which is shown in Fig. 7, is the first example of a species containing a bond between an anionic P centre and $\text{Bi}(\text{III})$. Various studies illustrate that the tendency for the precursor Group 15/alkali metal phosphinidine complexes to form Zintl ions increases going down the group. For P at the top of Group 15, the analogous complexes are apparently stable to decomposition, e.g., as in the case of the recently characterised complex $[\{t\text{BuNP}(\mu\text{-N}^t\text{Bu})\text{PPCy}\}\text{Li}_2\cdot\text{thf}]_2$ (containing the asymmetrical imido/phosphinidine dianion $[t\text{BuNP}(\mu\text{-N}^t\text{Bu})\text{-PPCy}]^{2-}$ [26].

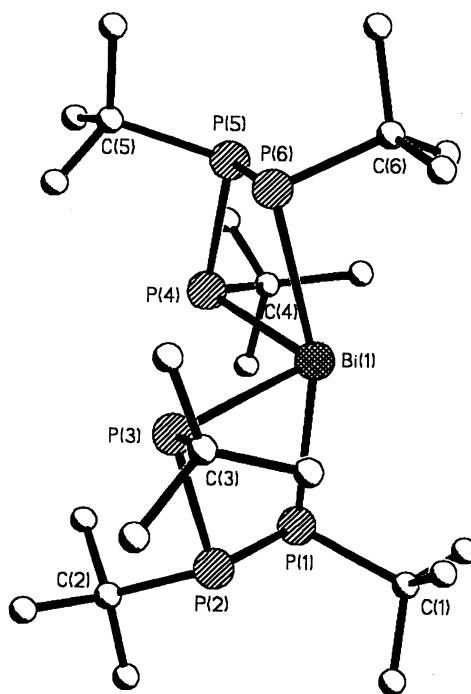


Fig. 7. Structure of the pseudo trigonal bipyramidal $[\text{Bi}\{t\text{BuP}\}_3]_2^-$ anion of **14**.

3. Related arsenic heterocycles

There is a great deal of potential for heterocyclic anions of the type $[\{RP\}_nE]^-$ to function as sources of Group 15 atoms (E). Transmetallation with main group and transition metal salts, followed by thermal degradation of the coordination compounds (with accompanying elimination of $[RP]_n$), may provide an extremely powerful general route to a broad range of transition metal clusters and materials. The thermal instability of the $[\{CyP\}_4Sb]^-$ anion of **11**, which is not stable above room temperature, severely limits the investigation of its coordination chemistry with other main group and transition metals. However, the greater bond energy of P–As bonds compared to P–Sb bonds makes analogous heterocyclic anions of the type $[\{RP\}_nAs]^-$ considerably more thermally stable than their Sb relatives [21,23]. Typically the reactions of RPHM with $As(NMe_2)_3$ (3:1 equiv., respectively) at room temperature give stable, readily isolated complexes containing $[\{RP\}_nAs]^-$ anions in 20–30% yields. For example, the reaction of $tBuPHLi$ with $As(NMe_2)_3$ in the presence of TMEDA/thf gives the monomer $[\{tBuP\}_3AsLi \cdot TMEDA \cdot thf]$ (**15**) (see Fig. 8, which also shows the characteristic A_2M pattern for this type of anion found in the ^{31}P -NMR spectrum). The Zintl compound $[As_7Li_3 \cdot 3TMEDA]$ is only obtained from this reaction after prolonged reflux of this reaction mixture [21,23].

The ring sizes of the $[\{RP\}_nAs]^-$ anions vary between four ($n=3$) and five ($n=4$). In the majority of cases characterised so far four membered anions are found, e.g. for $R = tBu$ or 1-Adamantyl and with a variety of Lewis base ligands coordinated to the alkali metals [21,23]. The stoichiometry of the reaction involved does not influence the ring size, as is illustrated by the formation of complexes containing $[\{tBuP\}_3As]^-$ anions from 3:1 reactions of $tBuPHLi$ with $As(NMe_2)_3$ or from in situ reactions of $[Me_2NAs(\mu-P^tBu)]_2$ with $tBuPHLi$ (1:2 equiv.) [23]. However, very recently we found that the 3:1 reactions of CyPHM ($M = Li$ or Na) with $As(NMe_2)_3$ complexes containing the five-membered ring $[\{CyP\}_4As]^-$ are obtained. An interesting example of this type is the monomer $[\{CyP\}_4AsLi \cdot 3NHMe_2]$ (**16**), in which the Li^+ cation is coordinated by three Me_2NH ligands [22]. The X-ray structure is shown in Fig. 9, which also illustrates the characteristic AA'XX' system found in the ^{31}P -NMR spectrum of five-membered rings of this type, a pattern observed for the Sb relative $[\{CyP\}_4SbNa \cdot TMEDA \cdot Me_2NH]_2$ (**12**). This NMR pattern indicates that the major isomer present for the $[\{CyP\}_4E]^-$ anions in **12** and **16** in solution has the same disposition of the Cy groups relative to the P_4E ring cores as is found in the solid-state structures of the complexes. This is also the favoured conformation found for the chain structure of $[(tBuP)_4H_2]$ in solution [27]. Contrary to our initial belief that the size of the ring formed in these reactions is largely dependent on the Group 15 element (As or Sb) present [23], the formation of the $[\{CyP\}_4As]^-$ heterocyclic ring in the reactions of CyNHM with $As(NMe_2)_3$ shows that the organic substituent (R) has the greatest influence on ring size.

Having determined the major structural patterns found for the more stable $[\{RP\}_nAs]^-$ rings, the next stage of the studies was the investigation of the reactivity of these species with other metals. However, an unforeseen technical

difficulty in transmetallation of these anions with various metal salts is the favourable crystallisation of alkali metal salt complexes of the Lewis base donor present in the precursor and the high solubility of the products. In order to circumvent these problems judicious choice of the precursor complexes is required, such that they contain Lewis base ligands which form insoluble alkali metal halide complexes (which can be readily separated from the product) or a labile Lewis base which can be removed under vacuum. Thus, we found (after considerable effort) that the complexes $[\{\text{CyP}\}_4\text{AsLi}\cdot 3\text{NHMe}_2]$ (**16**) and $[\{\text{'BuP}\}_3\text{AsLi}\cdot 2\text{DABCO}\cdot \text{thf}]$ [$\text{DABCO} = \text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$] (**17**) (for example) are good reagents for transfer of the four- and three-membered heterocyclic anions to other metals [22,23].

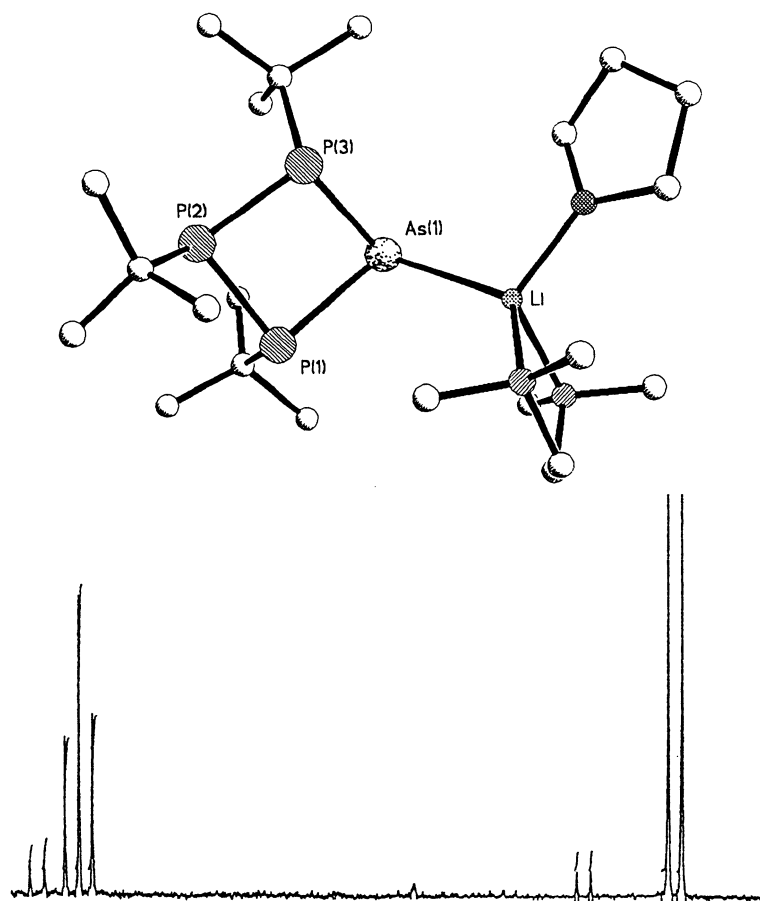


Fig. 8. (a) Monomer structure of **15**, and (b) the A_2M pattern characteristic of $[\{\text{RP}\}_3\text{As}]^-$ anions in the ^{31}P -NMR spectrum.

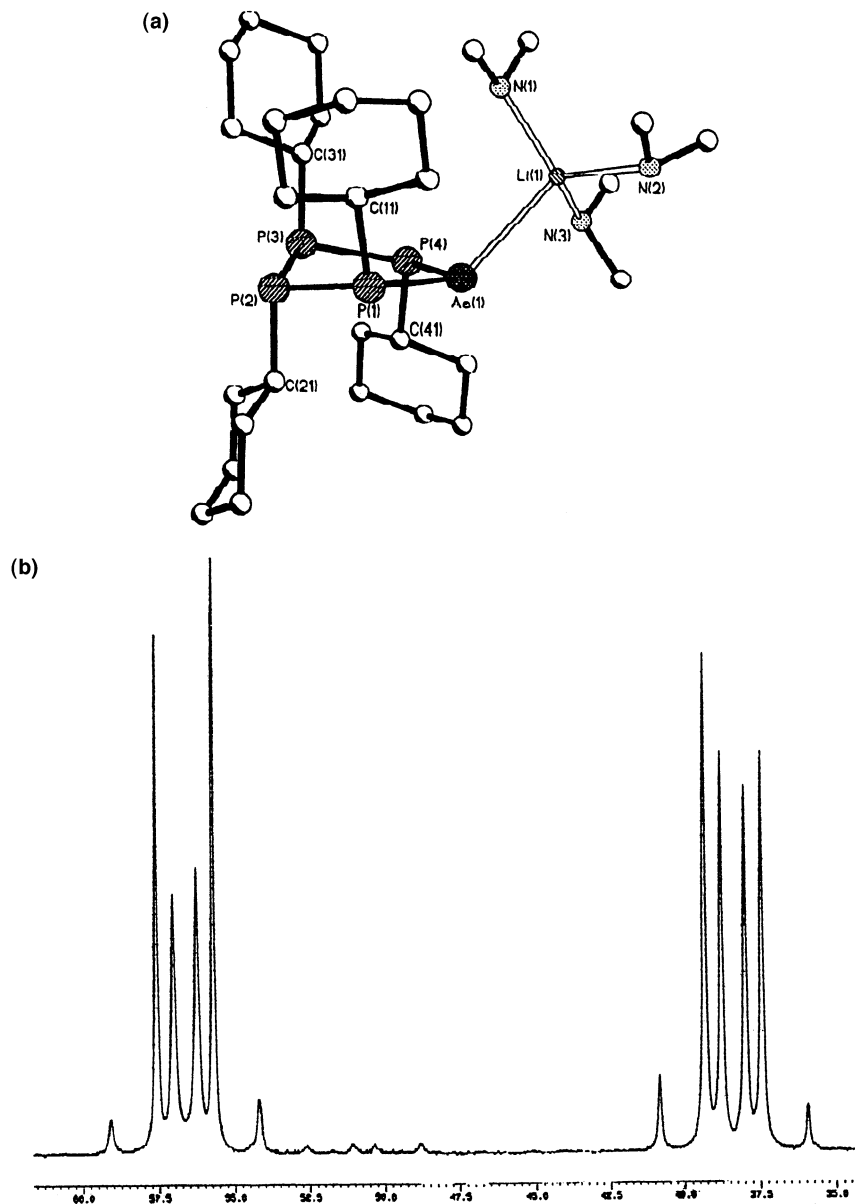


Fig. 9. (a) Monomer structure of **16** and, (b) the AA'XX' pattern characteristic of $[\{\text{CyP}\}_4\text{E}]^-$ anions ($\text{E} = \text{Sb}, \text{As}$) in the ^{31}P -NMR spectrum.

3.1. Unusual reactivity and synthetic utility

Studies of the reactivity of $[(RP)_nE]^-$ anions are still at an early stage. However, two recent investigations will serve to demonstrate the synthetic utility of these species and the extensive future prospects in this area. The first is a study of the reactions of $[\{^t\text{BuP}\}_3\text{AsLi}\cdot 2\text{DABCO}\cdot \text{thf}]$ (**17**) with $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}, \text{W}$) [28]. Although the original intention was the substitution of the labile metal-bonded Cl ligand, unexpectedly the only ring substituted products obtained are $[\{^t\text{BuP}\}_3\text{AsC}_5\text{H}_4\text{M}(\text{CO})_3\text{Cl}]$ [$\text{M} = \text{Mo}$ (**18**), W (**19**)] (Fig. 10). Previous studies of the reactions of the sandwich compounds $[(\text{C}_5\text{H}_5)_2\text{MCl}_2]$ (Mo, W) with various anions have shown that ring substitution can occur [29], however, this type of reaction has never been observed for sterically less crowded half sandwich compounds. The substitution of the C_5H_5 ring of $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{Cl}]$ (involving formal elimination of LiH) probably involves a similar mechanism of the $[\{^t\text{BuP}\}_3\text{As}]^-$ anion adding to the metal followed by transfer to the cyclopentadienyl ring [29]. The adoption of this pathway (as opposed to simple substitution of the Cl ligand) can be attributed to the large steric bulk of the $[\{^t\text{BuP}\}_3\text{As}]^-$ anion, which is witnessed in the restricted rotation of the $[\{^t\text{BuP}\}_3\text{As}]$ units of **18** and **19** (all three P atoms of the ring being inequivalent in the ^{31}P -NMR spectrum at room temperature) [28].

The second study involves the fortuitous discovery that hydrolysis of the $[\{^t\text{BuP}\}_3\text{As}]^-$ anion of $[\{^t\text{BuP}\}_3\text{AsLi}\cdot 2\text{DABCO}\cdot \text{thf}]$ (**17**) generates the terminally substituted tri-phosphine $[\{^t\text{BuP}\}_3\text{H}_2]$ (**20**). Further studies show that addition of a

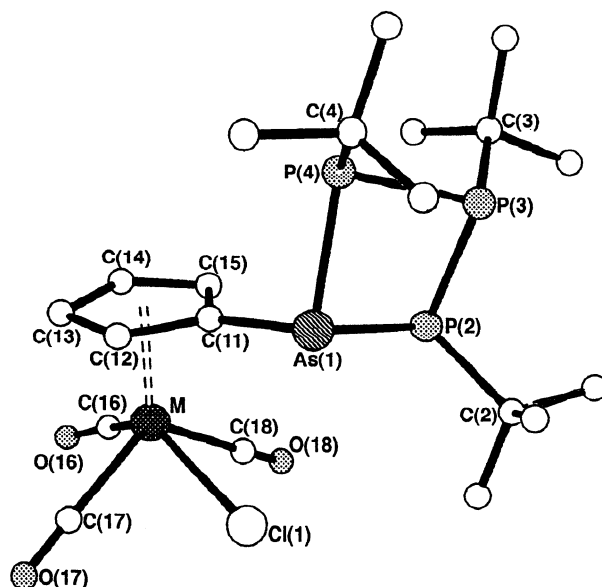
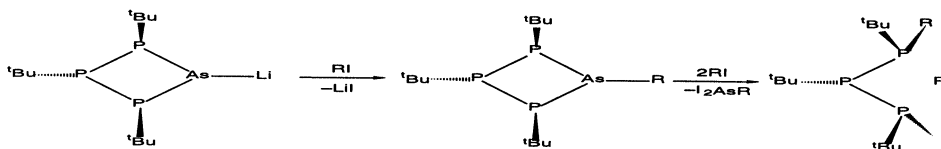
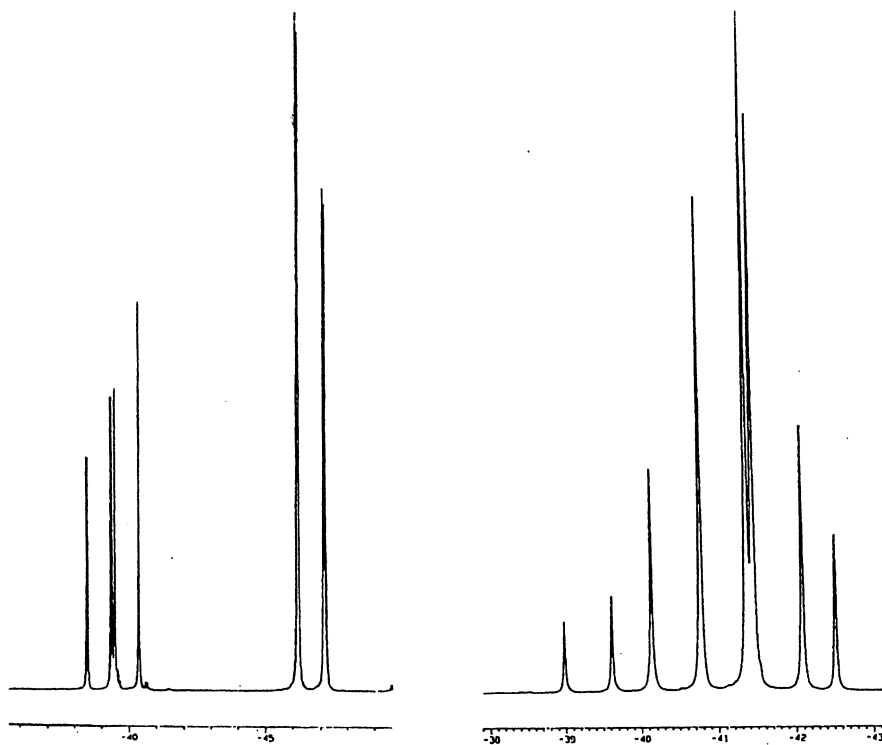


Fig. 10. Structure of **18** and **19** ($\text{M} = \text{Mo}, \text{W}$).

range of electrophiles to **17** generates an extensive range of related triphosphines in ca. 70–100% yield (illustrated in Scheme 5 for the $[\{^t\text{BuP}\}_3\text{As}]^-$ anion [30]. Model ab initio MO calculations show that these reactions are highly favourable, with the reaction of $[\{^t\text{MeP}\}_3\text{As}]\text{Li}$ with 3MeI being exothermic by $66.9 \text{ kcal mol}^{-1}$ (at the 6-311** level). The high purity of the phosphines isolated directly from the reactions (without any purification) is illustrated by ^{31}P -NMR spectra of $[(^t\text{BuP})_3(\text{CH}_2\text{Ph})_2]$ (**21**) and $[(^t\text{BuP})_3(\text{Me})_2]$ (**22**) (Fig. 11) which show almost no impurities. In theory, this new route provides a simple approach by which any primary phosphine (RPH_2) can be converted into a large range of tri-phosphines in two steps. This synthetic approach contrasts with the far more involved specialist



Scheme 5.

Fig. 11. ^{31}P -NMR spectra of the triphosphines **21** (left) and **22** (right).

techniques generally required to access this type of framework [31], and should allow the systematic investigation of the coordination chemistry of this important class of ligands [which are related to the commonly used DPPM ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$)]. Owing presumably to the difficulty in preparing and functionalising this type of ligand, very few studies of their coordination to metals have been reported. The complex $[\{(\text{tBuP})_3\text{H}_2\}\text{W}(\text{CO})_4]$ (**23**) (Fig. 12), prepared from the reaction of $[\text{W}(\text{CO})_5\cdot\text{thf}]$ and $[(\text{tBuP})_3\text{H}_2]$ (**20**) [30] is a rare example of a structurally characterised complex of this type.

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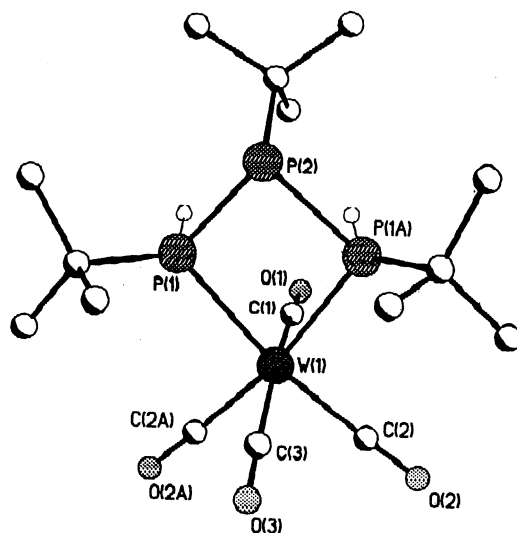


Fig. 12. Structure of the triphosphine complex **23**.

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