ELSEVIER

Coordination Chemistry Reviews 227 (2002) 153–173

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Complexes of P-stabilised carbanions with s- and p-elements

Keith Izod

Department of Chemistry, University of Newcastle, Bedson Building, Newcastle upon Tyne NE1 7RU, UK

Received 8 August 2001; accepted 16 October 2001

Contents

Abstract

The chemistry of complexes of the main group metals (Groups 1, 2, 13, 14, and 15, including Si and As) with P-stabilised carbanions is described. Such ligands, in which a carbanion centre is immediately adjacent to a P(III) or P(V) centre are remarkably versatile and adopt a wide range of coordination modes, depending on the nature of the metal centre, the presence of co-ligands and the ligand substituents; certain main group derivatives have also found applications in organic synthesis, especially for the olefination of carbonyl compounds (Horner, or Horner–Wadsworth–Emmons reagents). The focus of the review is on complexes which have been structurally characterised, either by crystallographic means or by unambiguous spectroscopic evidence. © 2002 Elsevier Science B.V. All rights reserved.

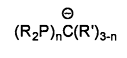
Keywords: P-stabilised; Carbanions; S- and p-elements

1. Introduction

It has been known for many years that phosphorus-containing groups are highly effective at stabilising adjacent carbanion centres (**I**–**IV**, E = O, S, NR). This has been widely exploited in organic synthesis, to the extent that P-stabilised carbanions now rank amongst some of the most useful reagents for a wide range of important organic transformations, especially in variants of the Wittig olefination reaction, such as the Horner or Horner–Wadsworth–Emmons reactions, which employ lithiated phosphine oxides and lithiated (thio)phosphonates/phosphonamides, respectively, for the olefination of carbonyl compounds [1–8]. In general, it is found that P(V)-stabilised carbanions have increased reactivity in comparison to the analogous (Wittig-type) neutral ylide species in these reactions.

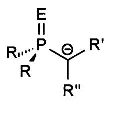
E-mail address: k.j.izod@ncl.ac.uk (K. Izod).

PII: S0010-8545(02)00011-5

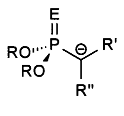


$(R_2P)_nC^{\ominus}(R')_{3-n}$

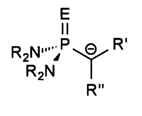
I



II



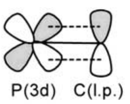
III



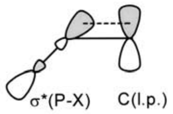
IV

This review is intended to cover complexes of P(III)- and P(V)-stabilised carbanions with the metallic elements from Groups 1, 2, 13, 14 and 15, including those of the elements Si and As, although compounds containing these latter elements and their heavier homologues will only be considered where the P-stabilised carbanion acts as a ligand to the element in the centre of an identifiable *complex* (compounds in which a main group element is α to a carbanion centre, but in which the heteroatom is best regarded as a substituent [e.g. Me_3Si-substituted tertiary phosphines, $R_2PCR_2(SiMe_3)$] are explicitly excluded from this work). Whilst phosphonium ylides ($R_3P{=}CR_2$) may be considered to contain a (partial) carbanion centre, complexes of these neutral molecules will not be described in this review; only ligands which carry a formal negative charge will be considered. The major focus will be on complexes whose structures have been determined unambiguously either by X-ray crystallography or by combinations of spectroscopic techniques, however, certain other aspects, such as the application of P-substituted carbanions in organic synthesis, will also be addressed [complexes which have been structurally characterised by X-ray crystallography are identified in the text by **bold** numerals].

The ability of third row heteroatoms to stabilise negative charge at an adjacent carbanion has been variously attributed to (i) electrostatic interactions due to their increased electropositive character in comparison to second row elements, (ii) dπ–pπ interactions (**V**), (iii) negative hyperconjugation (i.e. delocalisation of negative charge into low-lying P-X σ*-orbitals, **VI**) and (iv) the high polarisability of these elements. It is now widely accepted that dπ–pπ interactions play little part in carbanion stabilisation since the 3d-orbitals are too high in energy for efficient overlap with the lone pair orbital at the carbanion centre [9].



V

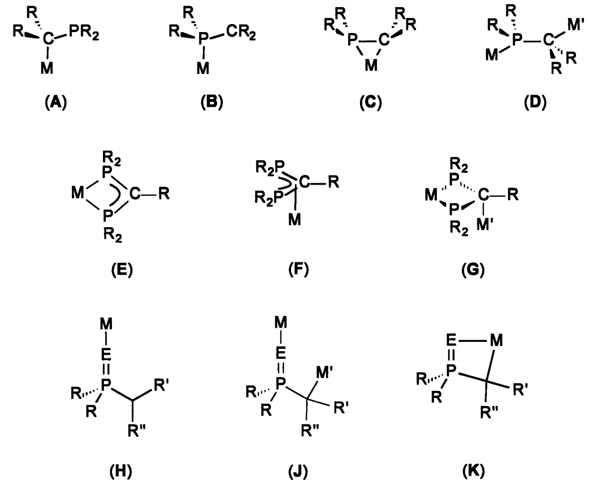


VI

The general consensus now appears to be that carbanion stabilisation by third row elements is due to a combination of negative hyperconjugation and polarisation effects [9–12]. However, theoretical studies have also suggested that any stabilisation seen in the free (gas phase) anions is largely lost on formation of contact ion pairs with lithium or sodium ions which tend to localise charge at the carbanion centre.

It has been calculated, for the reaction $CH_3^- + CH_3X \rightarrow CH_4 + CH_2X^-$, that second row elements stabilise carbanions by 10–20 kcal mol^{-1} more than first row elements. Calculations at the MP2(full)/6–31+G^*// MP2(full)/6–31+G^*+ZPE-(6–31+G^*)-correction level indicate that a PH_2 group stabilises a methyl carbanion by 23.1 kcal mol^{-1}, whilst $P(OH)_2$ and $P(O)(OH)_2$ groups stabilise methyl carbanions by 41.9 and 46.4 kcal mol^{-1}, respectively [10]. A similar calculation at the QCISD(T)/6–31+G^*//MP2/6–31+G^*+ZPE level of theory yields a stabilisation energy of 21.3 kcal mol^{-1} for the PH_2 group [11]. Calculations indicate that negative hyperconjugation should manifest itself in short P–C(carbanion) distances and long P–X distances and in a significant barrier to rotation about the P–C(carbanion) bond, indicating a degree of P–C multiple bond character; these effects are borne out by experiment (see below). Electron photodetachment spectroscopy in an ion cyclotron resonance spectrometer has allowed a quantitative measure of α-phosphinyl carbanion stabilisation as about 20 kcal mol^{-1}, in agreement with theoretical predictions [13].

Phosphorus(III)- and phosphorus(V)-stabilised carbanions exhibit markedly different coordination modes due to the lack of a lone pair of electrons and the presence of a P=E functionality in the latter (E = O, S, NR). In P(III)-stabilised carbanions the presence of a lone pair of electrons at both the P(III) and C centres, combined with the similar electronegativities of C and P (these two elements have Pauling electronegativities of 2.59 and 2.19, respectively [14]) and the valence isoelectronic nature of the two donor groups, enables the P and C atoms to compete as nucleophiles for metal centres. This leads to a variety of coordination modes for such ligands; monophosphinomethanides, $[(R_2P)CR'_2]^-$, commonly act as η^1-C-, η^1-P-, or η^2-P,C-donors (**A**, **B**, **C** in Scheme 1, respectively) or bridging ligands (**D**), whilst diphosphinomethanides, $[(R_2P)_2CR']^-$, and tri-



Scheme 1.

phosphinomethanides, $[(R_2P)_3C]^-$, typically act as η^2-P,P-donors (**E**), heteroallyl ligands (**F**), or combined η^2-P,P/bridging ligands (**G**). The coordination mode adopted is dependent on several factors, including (i) the nature of the metal centre(s), (ii) the presence of additional donor ligands such as THF or tmeda (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and (iii) the nature of the substituents at the P and C centres. In general, the greater the number of charge delocalising and/or sterically demanding substituents (e.g. $SiMe_3$, PR_2) at the carbanion centre, the lower the nucleophilicity of C and the greater the tendency for the ligand to bind through phosphorus.

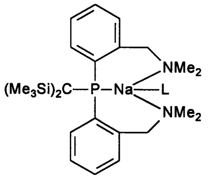
In contrast, P(V)-stabilised carbanions typically bind to metal centres via the electronegative substituents E at phosphorus (**H**, E = e.g. O, S, NR), although examples of such ligands binding through both the E and carbanion centres either as bridging or chelating ligands have been reported (**J**, **K**).

2. Group 1 (Li–Cs)

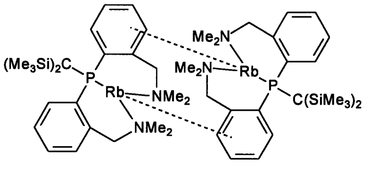
2.1. Complexes with P(III)-stabilised carbanions

The chemistry of Group 1 complexes of phosphorus(III)-stabilised carbanions has recently been reviewed and so will not be discussed further here [15]. However, since publication of that review, several interesting results have been reported, especially in the synthesis of heavier alkali metal derivatives, and these are described below.

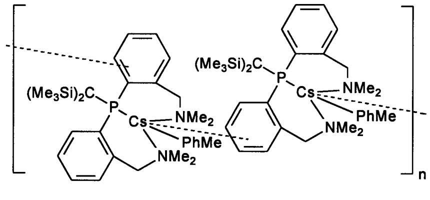
It has been reported that metathesis between $Li\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}$ [16] and $KOBu^t$ yields the first heavier alkali metal phosphinomethanide to be isolated and structurally characterised $[K\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_n$ [17]. This synthetic procedure has recently been extended to the other elements of Group 1; metathesis reactions between $Li\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}$ and MOR [M = Na, R = Bu^t; M = Rb, Cs, R = $CH(Et)(CH_2)_4CH_3$] yield the monomeric complex $[(Et_2O)_{0.5}(DME)_{0.5}Na\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]$ (**1**) [DME = 1,2-dimethoxyethane] and the polymeric species $[M\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}(PhMe)_n]_x$ [M = Rb, $n = 0$ (**2**); M = Cs, $n = 1$ (**3**)], respectively [18,19]. In **1**–**3** the tridentate phosphinomethanide ligand binds the metal centre via its P and N atoms to give two six-membered chelate rings; there is no contact between the metals and the planar carbanion centres. In **1** the coordination sphere of the sodium atom is completed by contacts with the oxygen atoms of either DME or ether, each of which has 50% occupancy in the unit cell. In **2** the RRb units form dimers via η^3-arene–Rb interactions and these dimeric units are further linked into a sheet arrangement by intermolecular Rb...Me–Si interactions. In **3** the RCs units adopt a one-dimensional polymeric arrangement in which individual RCs units are joined by η^4-interactions between the Cs atom and an aryl group from an adjacent ligand; each Cs atom is further coordinated by an η^2-toluene molecule and an intramolecular Cs...Me–Si contact. Compounds **2** and **3** represent the first crystallographically characterised complexes in which a Rb or Cs cation is bound by a formal tertiary phosphine centre.



1: L = $(Et_2O)_{0.5}(DME)_{0.5}$



2



3

All of the derivatives [M = Li–Cs] are highly fluxional in THF and toluene solutions. Variable temperature NMR studies suggest that the process accounting for this fluxionality in THF consists in either reversible M–N or M–P cleavage [18,19]. The entropy and enthalpy of activation for this process increase with decreasing charge: radius ratio of the Group 1 ions [$\Delta S^\ddagger = -101$ (Li), -70 (Na), -67 (K), -49 (Rb), -29 (Cs) J K^{-1} mol^{-1}; $\Delta H^\ddagger = 29$ (Li), 35 (Na), 37 (K), 41 (Rb), 44 (Cs) kJ mol^{-1}].

Müller and co-workers recently reported that metalation of $HC(PMe_2)(SiMe_3)(C_6H_3\text{-}3,5\text{-}Me_2)$ with BuLi/tmeda in hexane yields the solvent-separated ion pair $[Li(tmeda)_2][C(PMe_2)(SiMe_3)(C_6H_3\text{-}3,5\text{-}Me_2)]$, the first example of an isolated P-stabilised carbanion to be crystallographically characterised [20]. The carbanion centre in this complex is strictly planar (sum of angles at C(1) = 359.9°) and exhibits no contacts with the metal.

An example of a phosphavinylidene carbenoid, *Z*-$(mes^*)P{=}C(Cl)\{Li(DME)_2\}$, has recently been described [$mes^* = 2,4,6\text{-}Bu^t_3\text{-}C_6H_2$], obtained by the low temperature metalation of $(mes^*)P{=}CCl_2$ with BuLi in DME [21]. X-ray crystallography shows that the lithium is coordinated by the four oxygen atoms of the DME ligands and the (axial) carbanion centre of the phosphavinylidene moiety in a distorted square pyramidal geometry. Calculations (at both the HF/6–31 + G^* and B3LYP/6–31 + G^* level) and natural population analysis on the model compound *Z*-$MeP{=}C(Cl)\{Li(DME)_2\}$ give molecular parameters which agree well with those determined crystallographically and suggest that the Li–C interaction is essentially ionic; the lithium cation does not significantly perturb the bonding in the phosphavinylidene moiety.

The synthesis and structures of the complexes $[(Et_2O)_nM\{CH(PPh_2)(C_6H_4\text{-}2\text{-}OMe\}]_2$ have also been reported [M = Li, Na], although very briefly [22]. These compounds have been used for the synthesis of a calcium ate complex and an unusual calcium heterocubane (see Section 3 below).

2.2. Complexes with P(V)-stabilised carbanions

Carbanions stabilised by P(V) substituents, i.e. α-metalated (usually lithiated) phosphine oxides (**II**), phosphonates (**III**) and phosphonamides (**IV**) and their sulphur analogues have been the subject of intense investigation since the first reports that these species were able to effect the olefination of carbonyl compounds via a Wittig-type reaction [4–7]. The use of such (Horner (**II**) or Horner–Wadsworth–Emmons (**III/IV**) [HWE]) reagents in olefination reactions is complementary to the use of conventional Wittig-type phosphonium ylide reagents ($R_3P{=}CR_2$); Horner and HWE reagents are frequently found to be more reactive than the corresponding Wittig compounds and conditions can often be found where there is strong *E* or *Z* stereoselectivity for a particular olefination reaction.

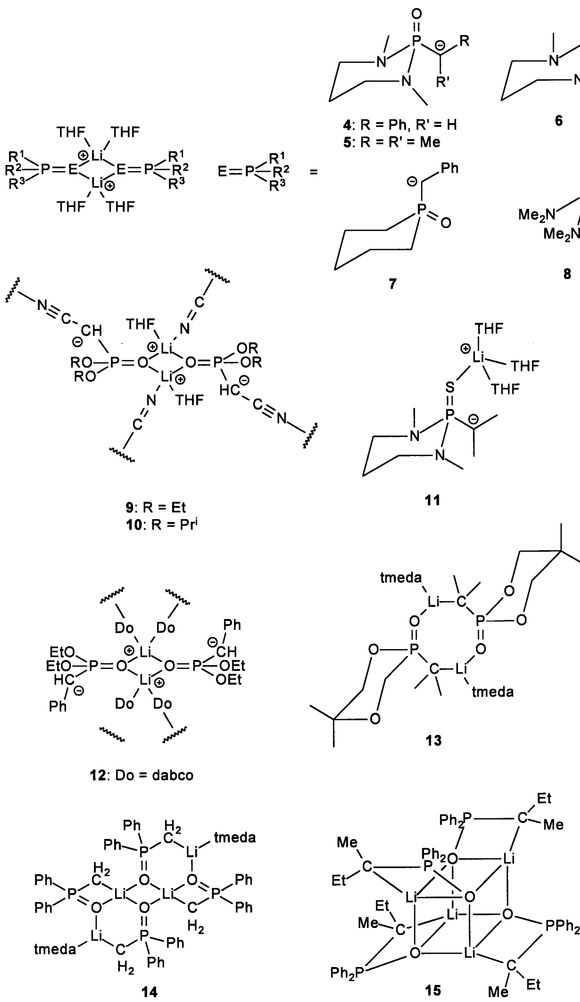
However, in spite of their synthetic utility, it is only relatively recently that detailed structural and theoretical studies of alkali metal derivatives of phosphine oxide-, phosphonate- and phosphonamide-stabilised carbanions have been published, although solution NMR studies of metalated bis- and mono-sulphurised methylene diphosphines were published as early as 1982 [23]. These solution state studies suggested that in the mono-sulphurised species $[Li\{CH(PPh_2)(PSPh_2)\}]$ a Li–P(III) contact was maintained in diethyl ether at 200 K. Solid state structural studies (**4**–**15**, Scheme 2) have revealed several interesting features for lithium derivatives of phosphine oxide-, phosphonate- and phosphonamide-stabilised carbanions [24–33]. There is a strong tendency for coordination of the metal centre via the O- or S-substituent, this atom frequently bridging the metal centres as part of a planar M_2E_2 ring, with little tendency for coordination by the carbanion centre itself. The lithium atoms adopt a distorted tetrahedral geometry in each case, the additional coordination sites being occupied by the carbanion centres of the ligands (in **13**–**15**) and/or additional donor ligands such as THF, tmeda or dabco (**4**–**12**) [dabco = [2.2.2]diazabicyclooctane].

In the set of closely related complexes **4**–**12** there is no contact between lithium and the essentially planar carbanion centres. In the solid state, it has been found that the carbanionic moiety lies parallel to the axially-orientated P=E bond in **4**, **5**, **6**, **8** and **11**. The preference for this conformation has been attributed to increased hyperconjugation between the carbanion lone pair and the acceptor orbitals on P: The P–N and P–O σ*-orbitals are expected to be better acceptor orbitals than the P=E σ*-orbital [34]; thus, the carbanion substituent will align such that its lone pair orbital will have maximum overlap with the σ* P–N/P–O orbitals, i.e. the lone pair will lie perpendicular to the P=E bond, leaving the carbanion substituents in the same plane as the P=E bond (**VII**, Scheme 3). In contrast, the lithiated phosphonate **12** adopts a configuration in which the carbanion is perpendicular to the P=O bond, suggesting that any difference in energy between the two carbanion conformations is small [28].

Theoretical studies suggest that the energy difference between the parallel and perpendicular conformations of the carbanion substituents for a given molecule is ca. 1.0 kcal mol^{-1} [28,33–35] and NMR evidence indicates that the barrier to rotation about the P–C(carbanion) bond (and hence the relative ease of conversion of the two conformations) is low [e.g. $\Delta G^{\ddagger}$ (Me_2O) = 6.7 (± 0.6) kcal mol^{-1} for **5** and $\Delta G^{\ddagger}$ (THF) = 9.8 (±0.3) kcal mol^{-1} for **11**] [29,32,33,36]. The increased barrier to rotation for the P=S versus P=O species is attributed to the greater carbanion stabilisation by the former in the (parallel carbanion) rotational ground state (**VII**) of **11** and favourable carbanion stabilisation in the (perpendicular carbanion) rotational transition state (**VIII**) of **5** (Scheme 3) [34,35]. NMR evidence also suggests that the dimeric structure of **5** is maintained in THF solution, but that **11** exists as monomeric solvent-separated ion pairs under the same conditions [31,32].

In the solid state compound **11** differs from **4** to **10** in that the lithium atom is solvated by an extra molecule of THF, giving a monomeric complex, whilst in **9**, **10** and **12** a polymeric array is produced by bridging between dimeric units either by the incorporation of additional CN donor groups into the phosphonate anion (**9**, **10**) or the use of the bridging diamine dabco (**12**).

An X-ray crystal structure of the lithiated phosphine oxide **7** reveals a dimeric structure similar to those described above. However, in contrast to the structures of **4**–**8** and **11** the carbanion moiety in **7** adopts a *gauche* conformation with respect to the *equatorial* P=O bond [29]. This conformational preference has been attributed to the dominance, in the absence of low energy P–N/O σ*-orbitals, of the $n \rightarrow \sigma^*(P{=}O)$ hyperconjugative interaction (**VIII**) in stabilising the carbanion centre. In ideal circumstances this would lead to a perpendicular carbanion conformation, however, it appears that avoidance of steric interactions between the *ortho* hydrogen atoms of the benzyl group and the equatorial hydrogens of the CH_2P groups of the phosphine oxide ring adjusts the torsional angle.



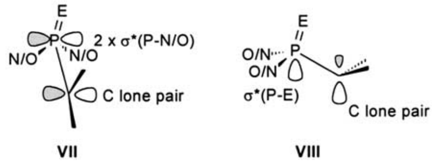
dabco = $N(CH_2CH_2)_3N$, tmeda = $Me_2NCH_2CH_2NMe_2$

Scheme 2.

Complex **13** adopts an alternative dimeric structure in which the two lithium atoms are bridged by η^2-C,O-coordinated phosphonate ligands generating a centrosymmetric, eight-membered $(OPCLi)_2$ ring [24]. The tetrahedral coordination of the lithium atoms is completed by a bidentate molecule of tmeda.

Complexes **14** and **15** form different types of tetrameric aggregate in the solid state, both of which are based on the planar Li_2O_2 ring motif. In **14** a Li_2O_2 ring lies at the centre of a centrosymmetric tetramer, the coordination sphere of these two lithium atoms being completed by a C,O-chelating phosphonate ligand [25]. This ligand further bridges via its oxygen to a third lithium atom which forms part of a puckered six-membered P–O–Li–O–Li–C ring; a bidentate tmeda ligand completes the coordination sphere of the third Li. In contrast, **15** adopts a heterocubane structure in which η^2-O,C bound phosphine oxide anions bridge alternate edges of the cube [27].

The synthetic utility of lithiated phosphine oxides, phosphonates and phosphonamides has been amply demonstrated, both as Horner or HWE carbonyl olefination reagents and as C–C bond forming reagents [for examples see refs. [1–4,37–39] and references therein], and a number of theoretical studies have recently been undertaken in order to rationalise the selectivities of these reactions [40–42]. It has also been reported that, whilst solutions of lithiated alkylphosphonates are somewhat unstable in THF solution,

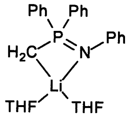


Scheme 3. Hyperconjugation via overlap of the carbanion lone pair with either (**VII**) two P–N/P–N σ*-orbitals or (**VIII**) a P=E σ*-orbital.

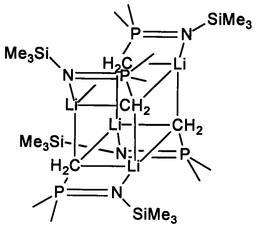
treatment of the parent phosphonates $(RO)_2P(O)CH_2R'$ [R = Me, Et; R′ = H, alkyl, etc.] with two equivalents of Pr^i_2NLi in THF yields a 1:1 amide–carbanion complex which is thermally stable due to the steric hindrance provided by the amide group [43].

Although they would appear to be versatile ligands in transition metal chemistry which mimic acetylacetonate ligands [44–49], few complexes of di- or tri-phosphinoylmethanide ligands ($[\{PR_2(O)\}_nCR'_{3-n}]^-$, $n = 2,3$) or their sulphur analogues have been isolated with the alkali metals. Karsch has reported that metalation of $HC\{P(S)Me_2\}_3$ with Bu^tLi yields the spectroscopically characterised complex $Li[C\{P(S)Me_2\}_3]$ [50], whilst Grim and Savignac and co-workers have independently reported that the reaction of metalated methylenebis(phosphine sulphides), $M[CH\{P(O)R_2\}_2]$, and methylenediphosphonates, $M[CH\{P(O)(OR)_2\}_2]$, with aldehydes spontaneously yields vinyl and/or vinylidene phosphonates/phosphine sulphides [51,52]. There has been no crystallographic study of a di- or tri-(thio)phosphinoylmethanide complex of the alkali metals; the first structurally authenticated alkali metal complex of this type, the bis(iminophosphorano)methanide $Li[CH\{PPh_2{=}N(SiMe_3)\}_2]$, was reported only in 2000 (see below) [53].

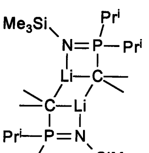
Over the last 6 years there have been several reports of α-metalated phosphinimines derived from the deprotonation of mono- or bis-phosphinimines, $HCR_{(2-n)}\{PR'_2{=}NR''\}_n$ [$n = 1,2$], by e.g. BuLi or $Na\{N(SiMe_3)_2\}$. Although the preparation and reactions of such species had been described previously [54–58], it was only in 1995 that an α-lithiated phosphinimine was isolated in the solid state and structurally characterised [59]. Metalation of $MePh_2P{=}NPh$ with BuLi in THF followed by recrystallisation from THF yields the complex $[Li\{CH_2PPh_2{=}NPh\}(THF)_2]$ (**16**) as colourless crystals. X-ray crystallography shows that the ligand acts as a C,N-chelate, forming a four-membered CPNLi ring; there is no P–Li contact. The chelate ring is close to planar, the lithium atom deviates by only 8.0(1)° from the C–P–N plane. The distorted tetrahedral lithium coordination sphere is completed by two molecules of THF. Multi-element NMR spectroscopy reveals that this complex remains largely intact in solution, although a second species (7%) is also detected; MNDO calculations predict a minimum energy structure which is close to that observed in the solid state.



16



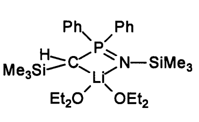
17

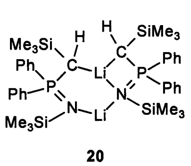


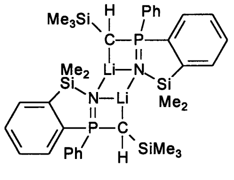
18

Treatment of the silyl-substituted phosphinimines $R_3P{=}N(SiMe_3)$ [R = Me, Pr^i] with BuLi in *n*-hexane yields the homoleptic complexes $[Li\{CH_2PMe_2{=}N(SiMe_3)\}]_4$ (**17**) and $[Li\{CMe_2PPr^i_2{=}N(SiMe_3)\}]_2$ (**18**) [60]. In the absence of additional donor solvents such as THF, the lithium atoms of **17** and **18** achieve four-coordination through oligomerisation. Complex **17** is best described as a heterocubane in which Li and μ_3-CH_2 groups occupy alternate corners of the cuboid. The ligands bind through their C and N atoms, bridging four of the cuboid edges, and thus each ligand acts as a chelate to one lithium atom. In contrast, **18** adopts a dimeric, ladder-type structure which may be viewed as being derived from half of a cuboidal structure similar to **17**. The lithium and carbanion centres form a four-membered Li_2C_2 ring, with the N atoms of each ligand binding to one lithium atom, forming four-membered CPNLi rings. Additional coordination of the lithium atoms in **18** is achieved via short Li...Me–CP agostic-type interactions [C...Li = 2.557(5) Å] between a methyl group of the bridging CMe_2 moiety and the metal centre.

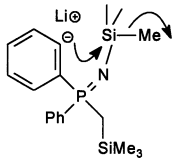
The silyl-substituted phosphinimine $(Me_3Si)CH_2PPh_2{=}N(SiMe_3)$ reacts with BuLi in ether to yield the monomeric complex $Li\{CH(SiMe_3)PPh_2{=}N(SiMe_3)\}(OEt_2)_2$ (**19**) which is structurally analogous to **16** [61]. The ligand binds as a 1-aza-2-phospha(V)allyl group through its N and C centres forming a four-membered CPNLi chelate ring; the coordination sphere of the lithium atom is completed by the oxygen atoms of two molecules of diethyl ether. In contrast to **16**, however, the ether molecules in **19** are only weakly bound and may be removed under vacuum (3 h at 40 °C), yielding the dimeric homoleptic complex $[Li\{CH(SiMe_3)PPh_2{=}N(SiMe_3)\}]_2$ (**20**) [61]. Complex **20** consists of an asymmetric head-to-head dimer in which one lithium is coordinated solely by the nitrogen atoms of the two ligands and the other lithium is coordinated by the two carbanion centres and a bridging N atom. Thus, one phosphinimine ligand acts as a simple C,N-bridge, whilst the other ligand acts as a C,N-chelate ligand and as a μ_2-N-bridging ligand between the two lithium atoms. The bonding in **20** has been described as being similar to a dialkyllithate anion, i.e. a $[\equiv C{-}Li{-}C\equiv]^-$ anion counterbalanced by a bis(imino)lithium cation $[\equiv N{-}Li{-}N\equiv]^+$; the C–Li distances of 2.122(9) and 2.190(9) Å are similar to the C–Li distance in the dialkyllithate complex $[Li(tmeda)_2][Li\{C(SiMe_3)_2SiMe_2CH_2\}_2]$ (2.156(4) Å) [62]. Variable temperature multi-element NMR studies show a single ligand environment for **20** in d_8-toluene even at low temperatures, implying either a monomeric or symmetrical structure in this solvent or rapid, reversible bond cleavage which is too fast to observe on the NMR timescale.


19


20


21

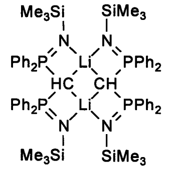
In the presence of 0.2 equivalents of BuLi complex **20** undergoes a rearrangement in hexane to give the *ortho*-silylated derivative [Li{CH($SiMe_3$)[Ph(1,2-C_6H_4)P=$NSiMe_2$]}] (**21**) in 70% yield [63]. Compound **21** may also be accessed in similar yield by the reaction of (Me_3Si)CH_2PPh_2=N($SiMe_3$) with 1.2 equivalents of BuLi in hexane. It has been proposed that the formation of **21** proceeds via an *ortho*-metalated derivative (**IX**) which subsequently undergoes an intramolecular displacement of Me^- by the aromatic anion. Compound **21** is dimeric in the solid state with a ladder-type structure similar to **18**. However, in contrast to **17** and **18**, which have bridging carbanion centres, in **21** the imino nitrogen atoms bridge the lithium centres, generating a central, planar Li_2N_2 ring.

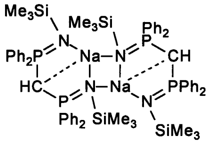

IX

Compound **20** undergoes a metathesis reaction with $KOBu^t$ to yield K{CH($SiMe_3$)PPh_2=N($SiMe_3$)}, although this compound has not been crystallographically characterised. New phosphinimines {Me_2(Et_2N)Si}CH_2PPh_2=N($SiMe_3$) and (Me_3Si)$_2$CHPPh_2=N($SiMe_3$) may be prepared by the reaction of **17** with Me_2(Et_2N)SiCl or **20** with $Me_3SiO_3SCF_3$, respectively, and initial studies suggest that these compounds are readily metalated by BuLi to give the corresponding α-lithiated phosphinimines [61]. Compound **20** also reacts with PhCN to yield a trimethylsilyliminophosphoranylenamidolithium complex Li{N($SiMe_3$)C(Ph)CHPPh_2=N($SiMe_3$)} [64].

The α-lithiated phosphinimine Li{CH(Me)PEt_2=N($SiMe_3$)} reacts with CuI to give the mixed lithium–copper(I) complex CuLi{CH(Me)PEt_2=N($SiMe_3$)} in which the ligands bridge the two metal centres, binding to the Cu centre via C and the Li centre via N [65]. The same lithium derivative reacts with $ZnCl_2$ to give a dodecameric complex [ClZn{CH(Me)PEt_2=N($SiMe_3$)}]$_{12}$ [65]. In contrast, a highly unusual, low yield product has been reported for the reaction between **17** and either $ZnCl_2$ or $CoCl_2$ in toluene in the presence of silicone grease. These two reactions lead to the formation of the Li_{14} cluster [Li_7{CHPMe_2=N($SiMe_3$)}$_3$(OSiMe_2Bu)]$_2$, which contains both C,N-bridging carbdianions {CHPMe_2=N($SiMe_3$)}$^{2-}$ and μ_3-siloxides $OSiMe_2Bu^-$ [66]. The latter ligand is believed to be derived from the reaction between BuLi and silicone grease [the reactivity of silicone grease has been established previously, see refs. [67,68]].

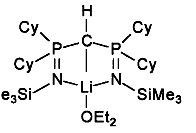
Very recently attention has turned to alkali metal complexes of bis(iminophosphorano)methanide ligands [RC(PR_2'=NR″)$_2$]$^-$. Although bis(iminophosphorano)methanide complexes have been known for some time [69,70], it was only in 2000 that such an alkali metal complex was isolated and structurally characterised [53]. Treatment of CH_2{PPh_2=N($SiMe_3$)}$_2$ with MN($SiMe_3$)$_2$ in toluene yields the dimeric complexes [M{CH_2(PPh_2=N[$SiMe_3$])$_2$}]$_2$ [M = Li (**22**), Na (**23**)].


22

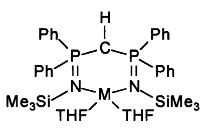

23

Although both complexes are dimeric and homoleptic, they adopt markedly different structures in the solid state. In **22** each methanide carbon bridges two lithium atoms, forming a twisted four-membered Li_2C_2 ring. Each of the four edges of this ring are extended to form nearly planar, four-membered LiCPN rings; the methine hydrogen atoms lie close to the lithium atoms [Li...HC = 2.02–3.02 Å] and the Li–C distances range from 2.370(9) to 2.784(10) Å. Compound **23** adopts a remarkably different structure in which there is a central twisted, four-membered Na_2N_2 ring. Two of the opposite edges of the ring are extended to form six-membered NaNPCPN rings which adopt a twisted boat conformation. The Na...C distances [2.996(4) and 3.017(4) Å] are longer than is usually found for Na–C bonds [71], but the folding of the carbanion centres towards the sodium atoms suggests the presence of weak Na...C interactions.

The dimeric structures of **22** and **23** are in stark contrast to those of the complexes obtained upon metalation of CH_2{PR_2=N($SiMe_3$)}$_2$ [R = Ph, cyclohexyl (Cy)] in donor solvents [72]. Treatment of CH_2{PCy_2=N($SiMe_3$)}$_2$ with MeLi in ether yields the monomeric etherate [Li{CH(PCy_2=N[$SiMe_3$])$_2$}(OEt_2)] (**24**) in which the ligand binds in an unusual N,C,N-tridentate fashion [Li–C = 2.633(7) Å]. The sodium and potassium complexes [M{CH(PPh_2=N[$SiMe_3$])$_2$}-(THF)$_2$] [M = Na (**25**), K (**26**)] are obtained by the reaction of the corresponding bis(iminophosphorano)methane with NaH or KH, respectively, in THF. These two complexes adopt similar structures in the solid state, the metals are bound by the nitrogen atoms of the ligand to give a six-membered chelate ring and a coordination number of four is achieved by the metals through the coordination of two molecules of THF. In both **25** and **26** there is no evidence for a contact between the carbanion centre and the metals. Complex **25** has a two-fold axis of symmetry along the C...Na vector, however, **26** is unsymmetrical, and exhibits short contacts between K and the *ortho* and *ipso* carbons of one of the phenyl rings. Additionally, there is a short agostic-type interaction between the potassium centre and one of the trimethylsilyl groups in **26**. These extra contacts for **26** compared with **25** are a reflection of the greater ionic radius of K compared with Na.



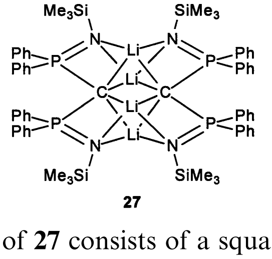
24



25: M = Na
26: M = K

Heteroatom-substituted geminally dimetalated organic compounds, R_2C^{2-} (carbdianions), have been shown in recent years to be extremely useful as reagents in (stereoselective) organic synthesis [73–75]. The majority of such compounds reported to date have carbdianion centres which are stabilised by adjacent sulphone or sulphoxamine substituents and it is largely these compounds that have been exploited as reagents in organic synthesis. However, there very recently have been a number of reports on carbdianions stabilised by P(V) substituents.

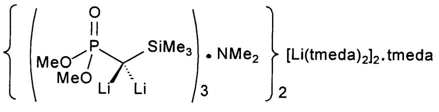
There have been two independent reports of the double deprotonation of $CH_2\{PPh_2{=}N(SiMe_3)\}_2$ to give a dilithiomethane derivative [76,77]. Treatment of $CH_2\{PPh_2{=}N(SiMe_3)\}_2$ with excess MeLi or PhLi in benzene or toluene leads smoothly to the formation of $[Li_2\{C(PPh_2{=}N[SiMe_3])_2\}]_2$ (**27**) as colourless, moisture sensitive crystals in good yield. The formation of **27** contrasts with that of **24**: treatment of $CH_2\{PCy_2{=}N(SiMe_3)\}_2$ with an excess of MeLi does not lead to double deprotonation of the substrate, even under forcing conditions (this has been ascribed to the lower acidity of the methylenic protons in $CH_2\{PCy_2{=}N(SiMe_3)\}_2$ due to the electron-releasing nature of the cyclohexyl groups) [72].



27

The structure of **27** consists of a square plane of four Li atoms capped on each face by a μ_4-C atom of the doubly deprotonated ligand, generating an almost perfect Li_4C_2 octahedron. The N–P–C–P–N units of the ligands are almost perfectly planar and the Si atoms lie only slightly (0.16–0.30 Å) out of this plane; the N–P–C–P–N planes of the two ligands are almost orthogonal [the dihedral angle between the two planes is 88.12(11)°]. Each lithium atom is further coordinated by a bridging imino nitrogen, thus each nitrogen atom of the ligands bridges an edge of the Li_4 square. The Li–C distances range from 2.312(9) to 2.45(1) Å and the carbdianion centres lie 1.67 Å above and below the Li_4 plane; the endocyclic P–C distances average 1.694(5) Å, significantly shorter than typical P–C distances in neutral phosphinimines.

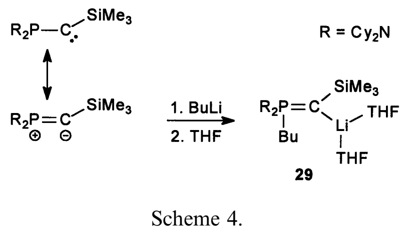
An unusual dilithiated carbdianion stabilised by both a phosphonate and a silyl group has also recently been reported. Treatment of $(MeO)_2P(O)CH_2SiMe_3$ with 2.5 equivalents of BuLi using tmeda as solvent yields the cluster complex $[\{[Li_2\{C(SiMe_3)P(O)(OMe)_2\}]_3(NMe_2)\}_2]^{2-}[Li(tmeda)_2]_2^{+}\cdot$tmeda (**28**) [78]. The hexameric anion contains six lithium atoms, three carbdianions and two dimethylamide anions, giving this component an overall dinegative charge which is counterbalanced by two $[Li(tmeda)_2]^+$ cations.



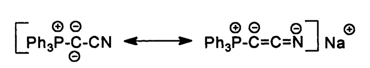
28

The dimethylamide ligands which are incorporated into the cluster di-anion are believed to arise from cleavage of the tmeda solvent by the 0.5 molar excess of BuLi in the reaction.

The coordination chemistry of ylides has been well reviewed [79]. Metalated (usually lithiated) phosphonium ylides, $R_3P{=}CR(M)$ (yldiides), have significant advantages over their neutral analogues in Wittig-type carbonyl olefination reactions [80,81]. These compounds exhibit enhanced reactivity towards sterically hindered and other less reactive carbonyl compounds compared with conventional phosphonium ylides. However, few metalated mono-ylides have been isolated in the solid state. Bestmann et al. described the isolation and spectroscopic characterisation of the sodium derivative of a cyanomethylenephosphorane $Na\{C(CN){=}PPh_3\}$ in 1987, although they suggested that the IR and NMR spectra of this species indicate that the resonance structure **XI** contributes strongly to the electronic distribution in the anion, and hence that the compound is perhaps not best considered as a metalated phosphonium ylide [82].



Scheme 4.



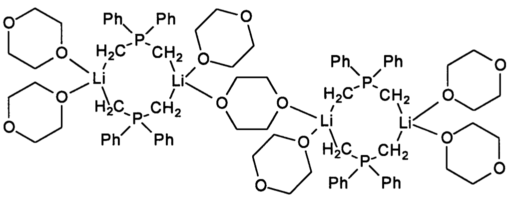
X **XI**

$[Ph_3P^+–C^-(^-)–CN \longleftrightarrow Ph_3P^+–C^-=C=N^-]\,Na^+$

It was not until 1999 that an α-metalated phosphonium ylide was structurally characterised [83]. Reaction of the stable phosphorus-substituted carbene $\{(Cy_2N)_2P\}C(SiMe_3)$ with BuLi yields the lithium phosphonium yldiide **29** (Scheme 4).

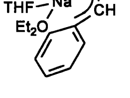
Both the lithium centre and the ylidic carbon are trigonal planar [sum of angles = 359.9° (Li), 359.8° (C)]; the P–C distance [1.636(11) Å] is one of the shortest reported for a P–C(ylide) bond and the C(ylide)–Si distance [1.775(10) Å] is significantly shorter than a typical C–Si single bond. The C–Li bond in **29** almost eclipses the P–C(Bu) bond [Li–C–P–C dihedral angle = 17.4(1)°]. This is in agreement with theoretical studies (at the HF/3–21*G** level) which predict that deprotonation of $H_3P=CH_2$ to give $H_3P=CH(Li)$ would result in a rotation of the P–C bond, leading to an eclipsed configuration for the C–Li and one of the P–H bonds [84].

Although the first α-metalated phosphonium diylide, $[R'_2P(CR_2)_2]^-$, was reported by Wittig and Rieber in 1949 [85] and several groups have employed these compounds for organometallic synthesis [86–88], structural studies of alkali metal derivatives were only reported in the 1980s. Crystals of the phosphonium diylide $[[Li\{(CH_2)PPh_2(CH_2)\}]_2(dioxane)_3]_2\cdot(\mu_2\text{-dioxane})$ (**30**) were fortuitously obtained from a reaction between $ThCl_4$ and $[Li\{(CH_2)PPh_2(CH_2)\}]_n$ in THF–dioxane [89]. The structure of **30** consists in two eight-membered rings, each composed of two Li atoms and two CPC-bridging diylide ligands, the two rings being joined by a bridging dioxane ligand. The coordination spheres of the lithium atoms differ in the number of additional monodentate dioxane molecules to which they are coordinated; Li(1) is coordinated by one additional molecule of dioxane, whereas Li(2) is coordinated by two, giving each lithium a coordination number of four. The P–CH_2 distance of 1.706(6) Å is longer than that typically found in free phosphonium ylides (1.64–1.67 Å) but is typical for a diylide coordinated to a metal centre.

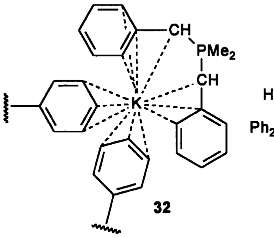


30

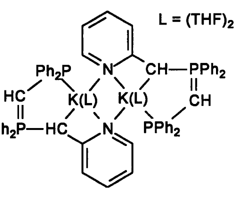
Schmidbaur and co-workers have reported the crystallographic characterisation of a number of Group 1 derivatives of variously substituted phosphonium ylides and diylides. Treatment of $CH_2(PPh_2)_2$ with benzyl bromide, followed by deprotonation of the resulting phosphonium salt with two equivalents of $NaNH_2$ yields $(THF)(Et_2O)Na[PhCHP(Ph)_2CHPPh_2]$ (**31**), whilst reaction of $CH_2(PPh_2)_2$ with two equivalents of benzyl bromide, followed by treatment of the resulting bis(phosphonium) salt with $Me_3P=CH_2$ and $NaNH_2$ yields $(THF)Na[PhCHP(Ph)_2CHP(Ph)_2CHPh]$ [90].



31



32

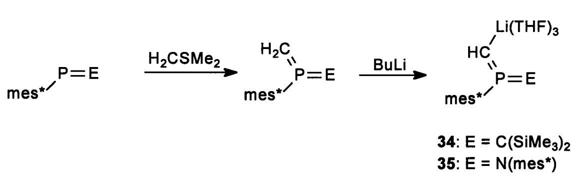


33

The compound $(THF)Na[PhCHP(Ph)_2CHP(Ph)_2CHPh]$ was characterised spectroscopically whereas compound **31** was additionally characterised by X-ray crystallography. The sodium atom in **31** is coordinated by the phosphorus(III) atom of the ligand and the benzylic carbon and associated *ipso* and *ortho* carbons of the phenyl ring of the benzyl group, in addition to the oxygen atoms of a molecule each of THF and ether.

Treatment of $R_2P(CH_2Ph)_2^+Br^-$ with two equivalents of a deprotonating agent such as an alkyllithium, $NaNH_2$ or KH yields the metalated diylides $M\{R_2P(CHPh)_2\}$. Several such compounds have been spectroscopically characterised and the solvent-free complex $[K\{Me_2P(CHPh)_2\}]_n$ (**32**) has been characterised by X-ray crystallography [91]. Compound **32** crystallises as a polymer in which each potassium atom is coordinated by the benzyl, *ipso* and *ortho* carbons of a chelating diylide ligand; these units are linked into a chain via intermolecular Ph...K interactions.

The reaction between $CH_2(PPh_2)_2$ and α-chloropicoline yields the isomeric phosphonium ylides $Ph_2PCH=PPh_2CH_2C_5H_4N$ and $Ph_2PCH_2PPh_2=CHC_5H_4N$, after treatment with base. Reaction of either of these ylides with $NaNH_2$ or KH yields the complexes $LM\{Ph_2PCHPPh_2CHC_5H_4N\}$ [LM = Na(THF), $K(THF)_2$ (**33**)]. The structure of **33** has been determined crystallographically and consists of a centrosymmetric dimer containing a planar K_2N_2 ring in which the pyridyl nitrogen atoms adopt an unusual μ_2-bridging mode [92]. Each potassium is further coordinated by the P(III) centre



Scheme 5.

and the picolyl CH and *ipso* carbons of the pyridyl ring. The coordination sphere of each potassium is completed by two molecules of THF.

Treatment of the phosphaalkene (mes*)P=C($SiMe_3$)$_2$ or the iminophosphine (mes*)P=N(mes*) [mes* = 2,4,6-Bu^t_3-C_6H_2] with dimethylsulphonium methylide yields the corresponding methylene-(ylene)-phosphoranes, which may subsequently be metalated by BuLi to give the diylides [(mes*)P{=C($SiMe_3$)$_2$}=CH]Li(THF)$_3$ (**34**) and [(mes*)P{=N(mes*)}=CH]Li(THF)$_3$ (**35**, Scheme 5), both of which have been crystallographically characterised [93]. Both compounds contain a lithium atom coordinated by the ylidic carbon atom and three molecules of THF in a distorted tetrahedral arrangement. The P and C(ylide) atoms are trigonal planar as expected, however, the central C–P–C [132.7(3)°] and N–P–C [141.4(3)°] angles are somewhat larger than the same angles in neutral ylides with similar substitution patterns. Compound **35** reacts with $HgCl_2$ to give the mercury(II) derivative [(mes*)P{=N(mes*)}=CH]$_2$Hg.

The carbenoids *Z*-[(mes*)P{=C($SiMe_3$)$_2$}=CX]Li(THF)$_3$ [X = F, Cl, Br] and *Z*-[(mes*)P{=N(mes*)}=CCl]Li(THF)$_3$ have also been isolated and crystallographically characterised [94,95]. These compounds were prepared by the low temperature reaction between either (mes*)P{=C($SiMe_3$)$_2$}=CX_2 or (mes*)P{=N(mes*)}=CX_2 and BuLi via a Li/X exchange reaction. The structures of these carbenoids are the same in all major details to the structures of **34** and **35**.

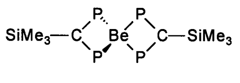
3. Group 2 (Be–Ba)

In comparison to the large number of Group 1 complexes of P-stabilised carbanions very few Group 2 analogues have been isolated, the majority having been reported only in the last 5 years.

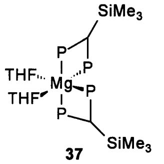
3.1. Complexes with P(III)-stabilised carbanions

Karsch and Reisky have recently used the silicon-substituted diphosphinomethanide ligand [(Me_3Si)C(PMe_2)$_2$]$^-$ to synthesise the first Group 2 complexes with P(III)-stabilised carbanions [96]. Treatment of the dihalides MCl_2 with Li[(Me_3Si)C(PMe_2)$_2$] in THF yielded the complexes [M{(Me_3Si)C(PMe_2)$_2$}$_2$(THF)$_n$] [M = Be, $n = 0$ (**36**); M = Mg, $n = 2$ (**37**); M = Ca, $n = 3$ (**38**)]. Reaction of **37** with a further equivalent of Li[(Me_3Si)C(PMe_2)$_2$] in the presence of 12-crown-4 yields the homoleptic ate complex [Li(12-crown-4)$_2$][Mg{(Me_3Si)C(PMe_2)$_2$}$_3$] (**39**). In each case the diphosphinomethanide ligands act as bidentate P,P-donors, forming four-membered chelate rings, with no contact between the metals and the planar carbanion centres. The homoleptic complex **36** has the Be atom in a distorted tetrahedral geometry whilst the Mg atom in **37** adopts a *cis*-octahedral geometry and the Ca atom in **38** lies at the centre of a distorted pentagonal bipyramid, in which two of the THF oxygen atoms lie in the apical positions; complex **39** has a Mg atom in a distorted octahedral coordination geometry. At low temperature the $^{31}P\{^1H\}$-NMR spectrum of **37** consists of a multiline pattern at $\delta = -16.7$ assigned to an incompletely resolved AA′BB′ spin system, consistent with a *cis*-octahedral coordination geometry similar to that observed in the solid state; at room temperature only a singlet is observed ($\delta = -16.2$) due to rapid axial–equatorial exchange.

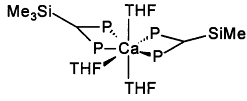
P = PMe_2



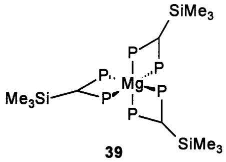
36



37

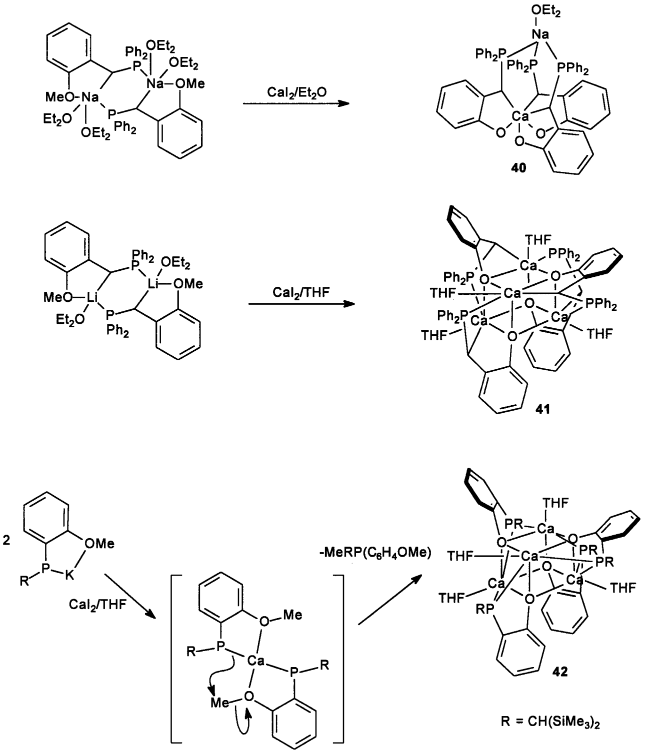


38



39

Very recently Knapp and Müller have described the reactions between CaI_2 and the alkali metal phosphinomethanides (Et_2O)$_n$M{CH(PPh_2)(C_6H_4-2-OMe)} [M = Li, $n = 1$; M = Na, $n = 2$] [22]. Reaction of CaI_2 with either two or three equivalents of (Et_2O)$_2$Na{CH(PPh_2)(C_6H_4-2-OMe)} in ether yields the ate complex (Et_2O)Na[Ca{CH(PPh_2)(C_6H_4-2-OMe)}$_3$] (**40**), in which the Ca atom is coordinated by three bidentate phosphinomethanide ligands, binding through their C and O atoms, whilst the Na atom is bound by the three phosphinomethanide P atoms and the O atom of a molecule of ether. In contrast, reaction of CaI_2 with two equivalents of (Et_2O)Li{CH(PPh_2)(C_6H_4-2-OMe)} in THF yields the organocalcium heterocubane [(THF)Ca{CH(PPh_2)(C_6H_4-2-O)}]$_4$ (**41**) via a ligand cleavage reaction which results in the loss of a methyl group from the aromatic methoxy substituent and the formation of a dianionic alkoxo-phosphinomethanide ligand (Scheme 6). This ligand cleavage reaction parallels that recently reported for the reaction between CaI_2 and the potassium phosphide K[P{CH($SiMe_3$)$_2$}(C_6H_4-2-OMe)], which gives a heterocubane containing alkoxophosphide ligands (**42**, Scheme 6) [97]. In the former case, the ligand cleavage is attributed to nucleophilic attack of I$^-$ at the carbon atom of a coordinated methoxy group, whereas in the latter case the ligand cleavage has been attributed to intramolecular nucleophilic attack of a coordinated phosphido group at the same carbon; in the latter reaction the expected side product MeP{CH($SiMe_3$)$_2$}(C_6H_4-2-OMe) was isolated and spectroscopically characterised. The heterocubane

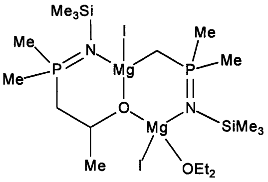


Scheme 6.

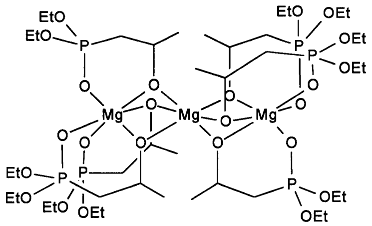
41 has Ca and μ_3-O atoms at alternating corners of the cube, with four of the cube faces bridged by Ca–C–P–Ca linkages.

3.2. Complexes with P(V)-stabilised carbanions

Few complexes have been reported in which a P(V)-stabilised carbanion is bound to a Group 2 centre. The complex $Mg_2I_2\{(Me_3Si)N{=}PMe_2CH_2\}\{(Me_3Si)N{=}PMe_2CH_2CH(Me)O\}\cdot Et_2O$ (**43**) has been isolated as a side-product in the reaction between MeMgI and $Me_3SiN{=}PMe_3$ [98]. The formally anionic $(Me_3Si)N{=}PMe_2CH_2$ ligand bridges the two Mg atoms via its CH_2 and N centres.



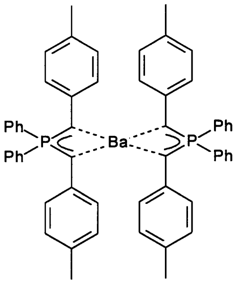
43



44

The magnesium derivative of $[(EtO)_2P(O)CHC(O)Me]^-$, which is analogous to the acetylacetonate ligand (acac), was found to adopt a trimeric structure $Mg_3\{(EtO)_2P(O)CHC(O)Me\}_6$ (**44**) in the solid state, similar to that adopted by $Mg_3(acac)_6$ [99]. The Mg atoms are bridged exclusively by the carbonyl oxygens of the ligands.

The only example of a barium complex with a coordinated P-stabilised carbanion is $[Ph_2P(4\text{-methylbenzylide})_2]_2Ba$ (**45**), prepared by the reaction of $Ba\{N(SiMe_3)_2\}_2$ and the phosphonium ylide $Ph_2P(CH_2Ar)({=}CHAr)$ [Ar = C_6H_4-4-Me] [100]. In toluene solution a dynamic process switches the chirality of one of the dibenzylide ligands in **45** and results in an equilibrium between the crystallographically identified S_4-isomer and an isomer of D_2 symmetry, for which NMR spectroscopy gives a value of $\Delta G^{\ddagger} = 12.4$ kcal mol^{-1} for the activation energy. Ab initio calculations and NPA charge analysis show that the negative charge on the ligand is largely localised on the ylidic carbons.



45

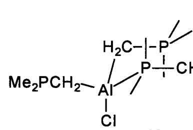
Very recently Hanusa and co-workers have shown that reaction of $K[Me_2P(fluorenyl)_2]$ with MI_2 [M = Ca, Ba] gives the solvent separated ion pair complexes $[MI(THF)_5][Me_2P(fluorenyl)_2]$ in moderate yield [101].

4. Group 13 (Al, Ga, In, Tl)

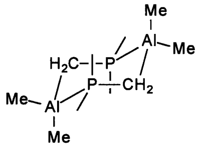
Complexes of aluminium with phosphorus-stabilised carbanions are well represented in the literature; complexes of P(III)-stabilised carbanions have been particularly well studied, due to the efforts of H. H. Karsch and co-workers. Surprisingly, however, there are few reports of complexes of the heavier elements Ga, In and Tl with either P(III)- or P(V)-stabilised carbanions.

4.1. Complexes with P(III)-stabilised carbanions

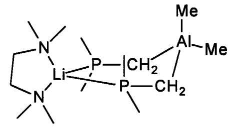
Stepwise reaction of $AlCl_3$ with $LiCH_2PMe_2$ results in the synthesis of $[(Me_2PCH_2)_nAlCl_{(3-n)}]_2$ ($n = 1$–3) as colourless pyrophoric crystals [102]. Spectroscopic evidence and cryoscopic molecular weight determinations suggested that these compounds were dimeric in solution and an X-ray crystallographic analysis of $[(Me_2PCH_2)_2AlCl]_2$ (**46**) confirmed their dimeric nature. Compound **46** consists in a head-to-tail dimer in which one phosphinomethanide ligand is terminal and one bridges the two Al centres via its P and C atoms, forming a six-membered, chair conformation $(AlCP)_2$ heterocycle. NMR spectroscopy shows that the bridging and terminal phosphinomethanide ligands in **46** and in [(Me$_2$PCH$_2$)$_3$Al]$_2$ undergo rapid scrambling on the NMR timescale in toluene solution [$\Delta G^{\ddagger}(-70\ °C) = 8.9$ kcal mol^{-1} for this bridge-terminal exchange process in **46**]. Rapid ligand scrambling is also seen on treatment of [(Me$_2$PCH$_2$)$_3$Al]$_2$ with Me$_3$Al, resulting in the formation of the heteroleptic complex [Me$_2$Al(μ-Me$_2$PCH$_2$)]$_2$ (**47**), which adopts a chair conformation, six-membered heterocyclic ring structure similar to **46** [102].



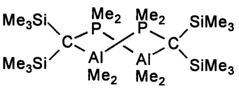
46



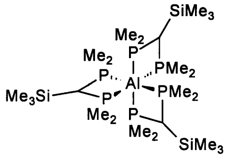
47



48



49

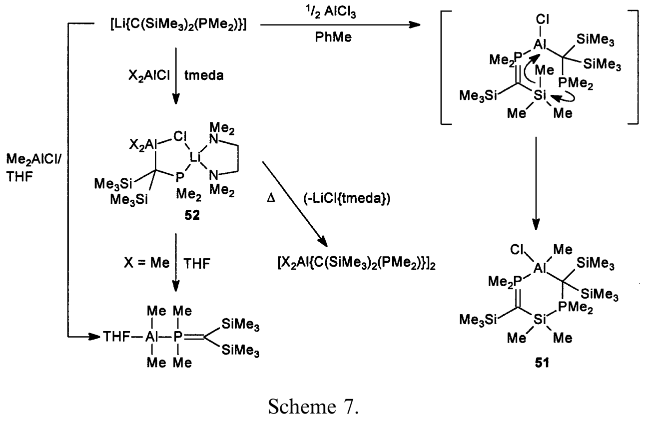


50

Rapid ligand scrambling also occurs when [(Me$_2$P-CH$_2$)$_3$Al]$_2$ is treated with MeLi in the presence of tmeda [103,104]. This reaction leads to the formation of the two ligand redistribution products [(tmeda)Li(μ-Me$_2$P-CH$_2$)$_2$AlMe$_2$] (**48**) and [Li(Me$_2$PCH$_2$)$_4$Al]$_n$; this latter compound is also obtained when [Al(CH$_2$PMe$_2$)$_3$]$_2$ is reacted with one equivalent of LiCH$_2$PMe$_2$. Treatment of **47** with MeLi in ether–THF in the presence of tmeda yields [(THF)(tmeda)Li(Me$_2$PCH$_2$)AlMe$_3$], whilst treatment of **47** with (tmeda)LiCH$_2$PMe$_2$ yields **48**. The compound [(THF)(tmeda)Li(Me$_2$PCH$_2$)AlMe$_3$] is unstable in solution and decomposes over a few days to give **48** and [Li(tmeda)$_2$][AlMe$_4$]. An X-ray crystallographic study of **48** reveals that the phosphinomethanide ligands bridge the Li and Al centres in a head-to-head fashion such that both P atoms are bound to Li and both C atoms are bound to Al. This gives a six-membered LiP$_2$C$_2$Al heterocycle in which only the Al atom deviates significantly from the essentially planar LiP$_2$C$_2$ moiety. The related compounds [(tmeda)$_x$-Li(CH$_2$PMe$_2$)AlMe$_3$] ($x = 1$, 3/2), [(tmeda)$_{3/2}$Li(CH$_2$P-Me$_2$)AlBu^{t}Me$_2$] and [Li(CH$_2$PMe$_2$)$_2$Al(CH$_2$PMe$_2$)$_2$] have also been isolated, but have not been crystallographically characterised [104]. However, the solvent-free complex [Me$_2$Al{C(PMe$_2$)(SiMe$_3$)$_2$}]$_2$ (**49**) has been structurally characterised [105]. As expected the complex crystallises as head-to-tail dimers with terminal Me groups. Unusually, however, the six-membered (AlCP)$_2$ heterocycle at the centre of the dimer adopts a twist conformation, possibly due to the steric requirements of the bulky SiMe$_3$ substituents.

The reaction between Li{CX(PMe$_2$)$_2$} and Me$_2$AlCl yields the complexes [Me$_2$Al{CX(PMe$_2$)$_2$}] [X = H, PMe$_2$, SiMe$_3$] [106]. In solution the complex with X = H exists as an equilibrium mixture of monomeric and dimeric species. The complexes with X = PMe$_2$ or SiMe$_3$ undergo a disproportionation reaction in solution to give the homoleptic compounds Me$_3$Al and [Al{CX(PMe$_2$)$_2$}$_3$]. The crystal structure of [Al{C(Si-Me$_3$)(PMe$_2$)$_2$}$_3$] (**50**) has been determined; the central Al atom is six-coordinate, bound by the P atoms of three bidentate diphosphinomethanide ligands [Al–P = 2.495(2) Å, P–Al–P = 67.4(1)°]. NMR spectroscopy confirms that this structure is maintained in solution for both X = PMe$_2$ and SiMe$_3$; the ^{27}Al-NMR spectra of these two compounds consist of broad unresolved peaks at room temperature which, at +100 °C, resolve into septets (X = PMe$_2$, $J_{\mathrm{AlP}} = 97.7$ Hz; X = SiMe$_3$, $J_{\mathrm{AlP}} = 91.6$ Hz).

The reaction between ClAlX$_2$ and Li{C(Si-Me$_3$)$_2$(PMe$_2$)} in toluene in a 1:2 ratio yields the novel six-membered heterocycle MeXAl$\overline{\mathrm{C(SiMe_3)_2PMe_2SiMe_2C(SiMe_3){=}P}}Me_2$ [X = Me, Cl (**51**)], via a methyl migration from Si to Al (Scheme 7) [107,108]. However, in the presence of tmeda, ClAlX$_2$ reacts with Li{C(SiMe$_3$)$_2$(PMe$_2$)} to give the five-membered heterocycles (tmeda)L$\overline{\mathrm{iPMe_2C(SiMe_3)_2Al(X)_2C}}$l [X = Cl, Me (**52**)], which upon moderate heating eliminate LiCl(tmeda) to give the dimers [X$_2$Al{C(SiMe$_3$)$_2$(PMe$_2$)}]$_2$ [108,109]. In the solid state **52** consists in a five-membered heterocycle containing five different elements in the ring. Dissolution of **52** in THF results in elimination of LiCl(tmeda) and rearrangement to give the aluminium-substituted phosphonium ylide (THF)AlMe$_2$PMe$_2$=C(SiMe$_3$)$_2$, obtained as a yellow oil. The same ylidic species is obtained

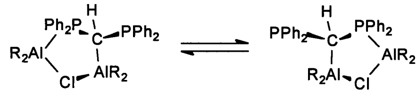


Scheme 7.

from the direct reaction of Me_2AlCl with $[(THF)Li\{C(SiMe_3)_2(PMe_2)\}]_2$.

The reaction between $Li\{CH(PPh_2)_2\}$ and Me_2MCl in a 1:1 ratio is reported to give the insoluble, possibly polymeric species $[Me_2M\{CH(PPh_2)_2\}]_n$ [M = Al, Ga], whereas the reaction of $Li\{CH(PPh_2)_2\}$ with R_2MCl in a 1:2 ratio yields the soluble complexes $[(R_2M)_2Cl\{CH(PPh_2)_2\}]$ [M = Al, Ga; R = Me, Et] [110]. The complex $[(Et_2Al)_2Cl\{CH(PPh_2)_2\}]$ (**53**) has been crystallographically characterised and consists of a five-membered Al_2CPCl heterocycle in which the Cl atom bridges the two Et_2Al units, which are in turn bridged by the C and one of the P atoms of the phosphinomethanide ligand; the remaining PPh_2 moiety does not coordinate to Al. In solution **53** is highly fluxional, the process accounting for this fluxionality has been attributed to a 'windscreen-wiper'-like motion in which the P–Al bond is broken and re-formed to the second phosphorus in a semi-circular movement (Scheme 8).

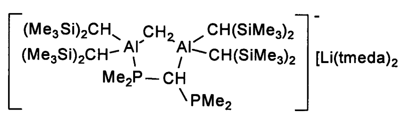
Ate complex formation occurs on treatment of the methylene-bridged dialuminium compound $R_2Al(\mu\text{-}CH_2)AlR_2$ [$R = CH(SiMe_3)_2$] with $LiCH(PMe_2)_2$ giving the five-membered heterocyclic anion $[R_2Al(\mu\text{-}CH_2)\{CH(PMe_2)_2\}AlR_2]^-[Li(tmeda)_2]^+$ (**54**) [111]. The two R_2Al units are bridged by the μ_2-methylene group and by the C and one P atom of the phosphinomethanide ligand, the remaining PMe_2 group does not coordinate to Al.



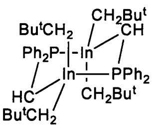
53

Scheme 8.

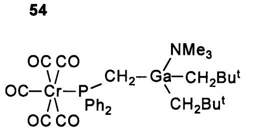
The compounds $R_2M(CH_2PPh_2)$ [$R = Bu^tCH_2$, Me_3SiCH_2; M = Ga, In] have been synthesised by the low temperature reaction of R_2MCl with $LiCH_2PPh_2$ and have been spectroscopically characterised [112]. These represent rare examples of phosphinomethanide complexes of the heavier Group 13 elements. The compound $[(Bu^tCH_2)_2In(CH_2PPh_2)]_2\cdot(C_6D_6)$ (**55**) is dimeric in the solid state with the central six-membered $(InPC)_2$ heterocycle adopting a typical chair conformation.



54



55

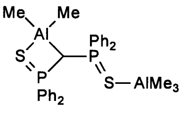


56

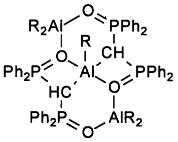
Compounds of the type $R_2M(CH_2PPh_2)$ react with $Cr(CO)_5(NMe_3)$ in benzene to give the spectroscopically characterised complexes $[Cr(CO)_5(\mu\text{-}PPh_2CH_2)MR_2(NMe_3)]$ [M = Ga, In; $R = Bu^tCH_2$, Me_3SiCH_2], in which the phosphinomethanide ligand bridges the Group 13 and Cr centres via its C and P atoms [113]. The X-ray crystal structure of $[Cr(CO)_5(\mu\text{-}Ph_2PCH_2)Ga(CH_2Bu^t)_2(NMe_3)]$ (**56**) has been determined; the phosphinomethanide ligand is bound to the Ga centre via its C atom and bridges to the Cr atom via its P centre, the displaced NMe_3 acts as a ligand for the Ga centre.

4.2. Complexes with P(V)-stabilised carbanions

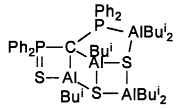
The reaction of triorganoaluminiums with $Ph_2P(E)CH_2P(E)Ph_2$ [E = O, S] leads to either single or double deprotonation of the methylenic carbon, depending upon the reaction stoichiometry. Single deprotonation is observed when Me_3Al is reacted with $Ph_2P(S)CH_2P(S)Ph_2$ in a 2:1 ratio, yielding $[AlMe_2][Ph_2P(S)CHP(S)Ph_2][AlMe_3]$ (**57**) as a crystalline solid [114]. There are two types of aluminium centre in **57**, a Me_3Al moiety acts simply as a Lewis acid, binding the S atom of one phosphine sulphide moiety, whilst a Me_2Al moiety binds to both the carbanion centre and the other phosphine sulphide S atom, generating a four-membered chelate ring. Reactions between Me_3Al and either the diphosphine $Ph_2PCH_2PPh_2$ or the disulphide $Ph_2P(S)CH_2CH_2P(S)Ph_2$ yield only 1:2 adducts, with no methylene carbon deprotonation, clearly demonstrating the increased stability of carbanions adjacent to two P(V) centres [114,115].



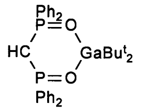
57



58: R = Me
59: R = Et



60



61

Treatment of $Ph_2P(O)CH_2P(O)Ph_2$ with an excess of Me_3Al in chlorobenzene at 100 °C gives the doubly deprotonated product $(MeAl)[Ph_2P(O)CP(O)Ph_2]_2(AlMe_2)_2$ (**58**) in quantitative yield [116]. X-ray crystallography shows that the central (Me)Al atom is coordinated by the central carbon and one of the O atoms of each carbdianion ligand to give two four-membered chelate rings. The second $(Me_2)Al$ atom is coordinated by the O atom of the same ligand, such that it forms a μ_2-bridge between the two Al atoms, and by the second O atom of the other carbdianion ligand. The reaction between $Ph_2P(O)CH_2P(O)Ph_2$ and Et_3Al in hot toluene–heptane yields an isostructural product $(EtAl)[Ph_2P(O)CP(O)Ph_2]_2(AlEt_2)_2$ (**59**) [117], however, treatment of $Ph_2P(S)CH_2P(S)Ph_2$ with Bu^i_2AlH in toluene–heptane at 160 °C results in ligand degradation and isolation of the unusual sulphide complex $(Bu^iAl)_2[Ph_2P(S)CPPh_2](S)_2(AlBu^i_2)_2$ (**60**) [118]. It has been proposed that this product results from an initial desulphurisation reaction, yielding H_2S, and that the desulphurisation products undergo further reaction with Bu^i_2AlH to give **60** according to 1.

(i)

$$\begin{aligned}&Ph_2P(S)CH_2P(S)Ph_2 + Bu^i_2AlH\\&\quad \rightarrow Ph_2P(S)CH_2PPh_2 + H_2S\end{aligned}$$

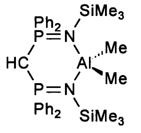
(ii)

$$\begin{aligned}&Ph_2P(S)CH_2PPh_2 + H_2S + 4Bu^i_2AlH\\&\quad \rightarrow 60 + 4H_2 + 2Bu^iH\end{aligned} \qquad (1)$$

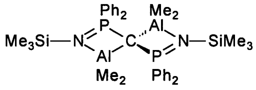
The complex solid state structure of **60** contains three edge-sharing four-membered rings, two of which further form the edges of a five-membered ring. The central carbon of the ligand has been doubly deprotonated and forms a bridge between two Bu^iAl fragments; the desulphurised P atom of the ligand acts as a donor towards a Bu^i_2Al fragment.

Thermolysis of the Lewis acid–base complex $Bu^t_3Ga\{Ph_2P(O)CH_2P(O)Ph_2\}$ in hexane solution heated under reflux yields the complex $Bu^t_2Ga\{Ph_2P(O)CHP(O)Ph_2\}$ (**61**) [119]. X-ray crystallography shows that the ligand binds the Ga centre through its two oxygen atoms, forming a planar six-membered chelate ring. Compound **61** may also be accessed through the oxidation of $Ph_2PCH_2PPh_2$ with $[Bu^t_2Ga(\mu\text{-}OOBu^t)]_2$ at room temperature.

Several complexes of Group 13 elements with singly and doubly deprotonated bisphosphinimines have been reported by Cavell and co-workers and Stephan and co-workers over the last 2 years. Reaction of $CH_2\{PPh_2{=}N(SiMe_3)\}_2$ with either one or two equivalents of Me_3Al in toluene gives the deprotonation products $(Me_2Al)[CH\{PPh_2{=}N(SiMe_3)\}_2]$ (**62**) and $(Me_2Al)_2[C\{PPh_2{=}N(SiMe_3)\}_2]$ (**63**), respectively [120,121]. In **62** the uninegative bis(iminophosphorano)methanide ligand binds the Me_2Al centre through its two N atoms, forming a six-membered chelate ring. Compound **63**, however, adopts a spirocyclic structure in which two nearly planar four-membered rings are fused at the carbdianion centre; the dihedral angle between the two planes is 75.28(5)°. The coordination sphere of each of the two Me_2Al centres in **63** is completed by one of the N atoms of the iminophosphorano units. Compound **62** converts to **63** upon heating in toluene under reflux.

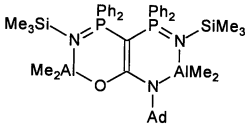


62

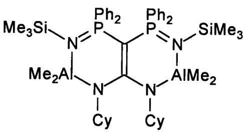


63

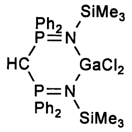
The reaction of **63** with certain unsaturated organic species leads to the formation of new C=C double bonds. For example, **63** reacts with adamantylisocyanate and with dicyclohexylcarbodiimide to give compounds **64** and **65**, respectively [122]. Using an excess of the heteroallene did not lead to further homologation or additional insertion reactions (e.g. into the Me–Al bonds).



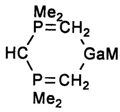
64



65



66



67

The compounds $[MR_2\{CH(PPh_2{=}N[SiMe_3])_2\}]$ [M = Al, Ga, In; R = Cl, Me, Ch_2Ph] have been prepared by the reaction of $LiCH\{PPh_2{=}N(SiMe_3)_2\}$ with the relevant metal chloride, followed by metathesis with RLi, and have been characterised by elemental analysis and NMR spectroscopy [121]. In addition, $[GaCl_2\{CH(PPh_2{=}N[SiMe_3])_2\}]$ (**66**) has been structurally characterised by X-ray crystallography. Compound **66** is mononuclear in the solid state, with the bis(iminophosphorano)methanide ligand binding the metal centre through its two N centres, generating a six-membered chelate ring with a pseudo-chair conformation. Attempts to form stable cationic species of the form $[RM\{CH(PPh_2{=}N[SiMe_3])_2\}]^+[B(C_6F_5)_3R]^-$ or $[RM\{CH(PPh_2 = N[SiMe_3])_2\}]^+[B(C_6F_5)_4]^-$ by the reaction of the neutral complexes with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ were unsuccessful [121].

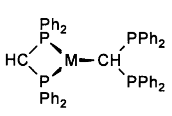
Reports of complexes of the Group 13 elements with diylides are sparse. The dimeric complexes $[Me_2M\{CH_2PMe_2CH_2\}]_2$ [M = Ga, In, Tl] have been isolated from the reaction of Me_2MCl and the phosphonium ylide $Me_3P{=}CH_2$ and have been characterised by molecular weight measurements and NMR spectroscopy [123]. From this it was inferred that the complexes consisted of head-to-tail dimers. The spectroscopically characterised monomeric complex $Me_2Al\{CH_2PMe_2CHPMe_2CH_2\}$ has been isolated from the reaction of $Li[AlMe_4]$ with $Me_3P{=}CH{-}P(F)Me_3$, whilst the crystallographically characterised gallium analogue $Me_2Ga\{CH_2PMe_2CHPMe_2CH_2\}$ (**67**) has been prepared by the reaction of $Me_3Ga(OEt_2)$ with the bisylide $Me_3P{=}C{=}PMe_3$ [124]. In the solid state **67** consists of monomers in which the ligand binds the Ga centre through its ylidic C atoms, forming a pseudo-chair conformation six-membered chelate ring similar to that observed in **66**.

5. Group 14 (Si, Ge, Sn, Pb)

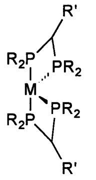
In contrast to the dearth of information regarding the coordination of heavier Group 13 elements by P-stabilised carbanions, there are many reported examples of complexes of the heavier Group 14 elements Ge, Sn and Pb with these ligands. Once again, this is largely due to the efforts of H.H. Karsch and co-workers, who have reported the majority of such complexes with P(III)-stabilised carbanions [125].

5.1. Complexes with P(III)-stabilised carbanions

The homoleptic bis(diphosphinomethanides) $M\{CH(PPh_2)_2\}_2$ [M = Ge, Sn, Pb] are isolated from metathesis reactions between MCl_2 and two equivalents of $LiCH(PPh_2)_2$ in THF [126–129]. The complexes with M = Sn (**68**) and M = Pb (**69**) have been crystallographically characterised and found to be essentially isostructural. In the solid state the metals are three coordinate, bound by the central carbanion of one phosphinomethanide ligand [Sn–C = 2.286(16) Å; Pb–C = 2.371(12) Å] and by the two P atoms of the second phosphinomethanide ligand, forming one four-membered chelate ring [Sn–P = 2.676(5) and 2.659(5) Å; Pb–P = 2.782(4) and 2.758(4) Å]. The tin (or lead) atoms adopt a pyramidal (ψ-tetrahedral) geometry due to the presence of a stereochemically active lone pair. The observation of two phosphinomethanide binding modes in one complex amply demonstrates the delicate balance between steric and electronic effects on the binding mode of these ambidentate ligands. In solution **68** and **69** exhibit fluxional behaviour. The low temperature ^{31}P-NMR spectra of **68** and **69** in toluene solution consist of two signals of equal intensity, exhibiting ^{117}Sn/^{119}Sn and ^{207}Pb satellites, respectively. The low field signal in each case is assigned to the chelating ligand due to the large J_{SnP} and J_{PbP} coupling constants ($J = 1106/1158$ and 1970 Hz, respectively; c.f. $J = 276/336$ and 165 Hz, respectively, for the C-bound ligand). At −90 °C the ^{31}P-NMR spectrum of **69** clearly shows the presence of four inequivalent P centres. At 70 °C the ^{31}P-NMR spectra of **68** and **69** consist of single broad resonances. This behaviour has been attributed to rapid interconversion of the two ligands between the PP- and C-donor modes.



68: M = Sn
69: M = Pb

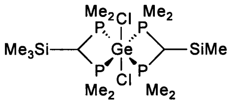


70: M = Pb, R = Ph, R' = $SiMe_3$
71: M = Si, R = Me, R' = $SiMe_3$
72: M = Ge, R = Me, R' = $SiMe_3$
73: M = Ge, R = Me, R' = PMe_2
74: M = Sn, R = Me, R' = PMe_2

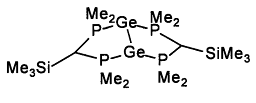
Interestingly, in the related complex $Pb\{C(SiMe_3)(PPh_2)_2\}_2$ (**70**) both ligands bind in a P,P-chelating manner [Pb–P = 2.715(5)–2.971(5) Å], forming two four-membered chelate rings [128]. The Pb centre once again has a stereochemically active lone pair and adopts a pyramidal (ψ-tbp) geometry.

The less sterically demanding, although structurally comparable, ligand $C(SiMe_3)(PMe_2)_2$ has been employed for the synthesis of the homoleptic complexes $M\{C(SiMe_3)(PMe_2)_2\}_2$ [M = Si (**71**), Ge (**72**), Sn]. The complexes with M = Ge, Sn are synthesised straightforwardly by metathesis reactions between $Li\{C(SiMe_3)(PMe_2)_2\}$ and either $GeCl_2$(dioxane) or $SnCl_2$, respectively [129–131], whereas **71** is synthesised by the in situ reduction of a mixture of Si_2Cl_6 and $Li\{C(SiMe_3)(PMe_2)_2\}$ by either Mg or $Li(C_{10}H_8)$ in THF [132]. Both **71** and **72** adopt pyramidal (ψ-tbp) geometries due to the presence of a stereochemically active lone pair on Si/Ge. The related complexes $M\{C(PMe_2)_3\}_2$ [M = Ge (**73**), Sn (**74**)] have also been isolated and structurally characterised [129,133]. Once again these complexes adopt a pyramidal (ψ-tbp) geometry with the triphosphinomethanide ligands acting as bidentate PP-donors; the remaining PMe_2 units do not coordinate to the Ge or Sn centres. Multi-element variable temperature NMR spectroscopy reveals that in solution both **73** and **74** are subject to two distinct fluxional processes [129,130,133]. At −100 °C the ^{31}P-NMR spectrum of **73** consists of three signals, assigned to the uncoordinated, axial and equatorial P atoms. As the temperature is raised these signals broaden and at −50 °C two broad signals are observed. These are assigned to the non-coordinated P atom and an averaged signal for the axial and equatorial P atoms due to rapid pseudorotation. At +30 °C a single singlet is observed due to rapid exchange between the coordinated and non-coordinated P atoms. The variable temperature ^{31}P-NMR spectra of **74** are similar, although the different axial and equatorial P environments were not observed over the measured temperature range. Variable temperature ^{119}Sn-NMR spectra of **74** confirm this fluxionality: at −70 °C a quintet of triplets is observed due to one-bond coupling to four equivalent ^{31}P nuclei and three-bond coupling to two equivalent ^{31}P nuclei; at +70 °C a binomial septet is observed due to coupling to six equivalent P centres (due to rapid exchange between the bound and unbound P atoms).

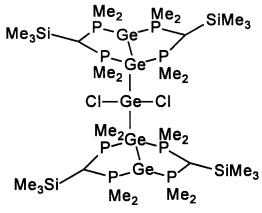
The products of the reaction of Li{$C(SiMe_3)(PMe_2)_2$} and $GeCl_2$(dioxane) are strongly dependent upon the ratio of the two reagents. Somewhat surprisingly, the reaction of four equivalents of Li{$C(SiMe_3)(PMe_2)_2$} with three equivalents of $GeCl_2$(dioxane) results in a disproportionation reaction, yielding the Ge(IV) species {$C(Me_3Si)(Me_2P)_2$}$_2GeCl_2$ (**75**) and the Ge(I) dimer [{$C(Me_3Si)(Me_2P)_2$}Ge]$_2$ (**76**) [134]. Complex **75** may be more simply prepared by the reaction of $GeCl_4$ with two equivalents of Li{$C(SiMe_3)(PMe_2)_2$}, whilst **76** may be synthesised by the in situ reduction of a 1:1 mixture of $GeCl_2$(dioxane) and Li{$C(SiMe_3)(PMe_2)_2$} in THF by Mg. Complex **75** consists of a *trans*-octahedral complex with bidentate P,P-coordinated phosphinomethanide ligands; complex **76** contains a Ge–Ge single bond bridged by two phosphinomethanide ligands, the geometry around the Ge atoms is best described as ψ-tetrahedral due to the presence of a lone pair on each Ge. The Ge–Ge distance in **76** of 2.540(1) Å is ca. 0.1 Å longer than that typically observed in polygermane compounds.



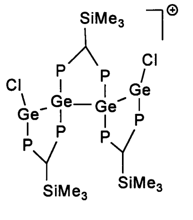
75



76



77

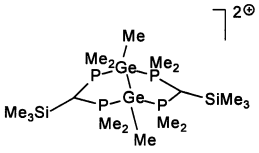


78

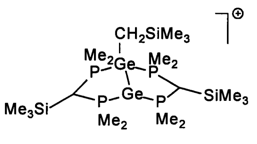
When $GeCl_2$(dioxane) and Li{$C(SiMe_3)(PMe_2)_2$} are combined in a 3:8 ratio both **75** and [{μ-($Me_3Si)(Me_2P)_2C$}$_2Ge_2$]$_2GeCl_2$ (**77**), a 2:1 adduct of **76** with $GeCl_2$, are isolated [135]. Compound **77** is also isolated when two equivalents of **76** are reacted with $GeCl_2$(dioxane). In contrast, when Li{$C(SiMe_3)(PMe_2)_2$} and $GeCl_2$(dioxane) are combined in a 3:5 ratio in the presence of Mg, the cationic complex [{μ-$C(Me_3Si)(PMe_2)_2$}$_3Ge_4Cl_2$]$^+$[$GeCl_3$]$^-$ (**78**) results [136]. The cation consists of a chain of four Ge atoms, each with a formal (average) oxidation state of +1.5, bridged by the three phosphinomethanide ligands through their P atoms, with terminal Cl atoms at each end of the chain; the [$GeCl_3$]$^-$ units form discrete anions in the lattice.

The reactivity of the Ge(I) dimer **76** has been extensively studied by Karsch and co-workers. Compound **76** is an excellent nucleophile, forming strong complexes with electrophilic main group and transition metal centres such as BBr_3, $AlCl_3$, and $Cr(CO)_5$ [125]. The Ge atoms in **76** are readily methylated by either [Me_3O][BF_4] or RI to give the cationic complexes [{$C(Me_3Si)(Me_2P)_2$}$_2Ge_2Me_2$][BF_4]$_2$ (**79**) and [{$C(Me_3Si)(Me_2P)_2$}$_2Ge_2R$]I [R = Me, CH_2SiMe_3 (**80**)], respectively. The reaction of **76** with I_2 could proceed by Ge–Ge bond cleavage or electrophilic attack at the lone pairs on Ge to give a variety of products. The white solid obtained from the reaction of I_2 with **76** has been recrystallised from toluene and found by X-ray crystallography to be {$C(Me_3Si)(Me_2P)_2$}$_2Ge_2I_2$ (**81**) [137]. Both of the iodine atoms are coordinated to one Ge(II) centre, whilst one of the previously bridging phosphinomethanide ligands chelates the second Ge(II) centre. The Ge–Ge distance in **81** of 2.458 Å is significantly shorter than that observed in **76**, consistent with oxidation of the Ge centres to Ge(II). The reaction of **76** with Bu^{t}Li results in the elimination of Li{$C(SiMe_3)(PMe_2)_2$} and the formation of the Ge_4 ring species Ge_4{$C(SiMe_3)(PMe_2)_2$}$_2Bu^t_2$ (**82**) [138]. The core of the centrosymmetric complex **82** consists in a planar Ge_4 ring, bridged on two sides by P,P-donor phosphinomethanide ligands, one above and one below the Ge_4 plane. In addition, two of the Ge(I) atoms are bonded to terminal Bu^t groups. The Ge–Ge distances in **82** of 2.489(1) Å (P,P-bridged) and 2.529(1) Å (unbridged) are comparable to the Ge–Ge distance in **76**.

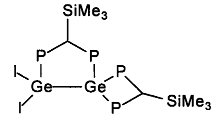
P = PMe_2



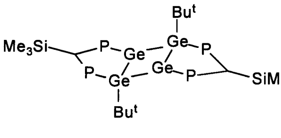
79



80



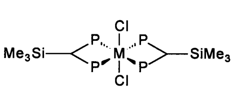
81



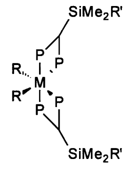
82

A number of hexacoordinated Group 14 complexes with P(III)-stabilised carbanions have recently been reported. The reaction of two equivalents of Li{$C(SiMe_3)(PMe_2)_2$} with R_2MX_2 yields the complexes R_2M{$C(SiMe_3)(PMe_2)_2$}$_2$ [M = Si, Ge, Sn; R = Me, Cl; X = Cl, Br]. The complexes Cl_2M{$C(SiMe_3)(PMe_2)_2$}$_2$ [M = Si (**83**), Ge (**75**), Sn (**84**)] adopt a *trans*-octahedral geometry with the phosphinomethanide ligands binding through their P atoms in a symmetrical bidentate fashion; NMR spectroscopy demonstrates that this geometry is essentially maintained in solution [139]. However, the complexes with R = Me [M = Si (**85**), Ge (**86**), Sn (**87**)] adopt a distorted *cis*-octahedral geometry about the central Group 14 atom [140]. The phosphinomethanide ligands again bind in a bidentate P,P-fashion, although in each case the M–P_{axial} distances are significantly shorter than the M–$P_{equatorial}$ distances, suggesting that this second interaction is only very weak [e.g. Si–P_{axial} = 2.306(1)/2.300(1) Å, Si–$P_{equatorial}$ = 2.868(2)/2.962(3) Å for **85**]. Attempts to prepare monosubstitution products were unsuccessful, even reactions starting from $MeSiCl_3$ gave the disubstituted product **85** and $SiCl_4$.

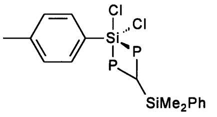
P = PMe_2



83: M = Si
84: M = Sn

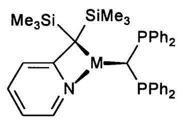


85: M = Si, R = R' = Me
86: M = Ge, R = R' = Me
87: M = Sn, R = R' = Me
88: M = Si, R = ½(CH₂)₃, R' = Ph



89

Hypervalent silicon compounds are also isolated when Li{C($SiMe_2Ph$)(PMe_2)$_2$}(tmeda) is reacted with either (*cyclo*-$CH_2CH_2CH_2$)$SiCl_2$ or (*p*-tolyl)$SiCl_3$ [141]. The complex (*cyclo*-$CH_2CH_2CH_2$)Si{C($SiMe_2Ph$)(PMe_2)$_2$}$_2$ (**88**) has a hexacoordinated Si atom in a distorted *cis* geometry with all four of the Si–P distances roughly comparable (cf. **85**). The compound (*p*-tolyl)$SiCl_2${C($SiMe_2Ph$)(PMe_2)$_2$} (**89**) has a pentacoordinate Si centre with a geometry that is mid-way between trigonal bipyramidal and tetragonal pyramidal.

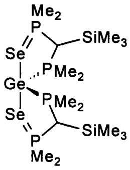


90: M = Ge
91: M = Sn

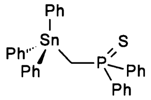
Two heteroleptic Sn(II) and Ge(II) phosphinomethanide complexes have recently been reported. The reaction of {(Me_3Si)$_2$C(C_5H_4N)}MCl with Li{CH(PPh_2)$_2$} yields the complexes {(Me_3Si)$_2$C(C_5H_4N)}M{CH(PPh_2)$_2$} [M = Ge (**90**), Sn (**91**)] [142,143]. In both cases the Ge/Sn atom is trigonal pyramidal with a stereochemically active lone pair, the pyridylmethyl ligand is bidentate, forming a four-membered chelate ring, and the phosphinomethanide is monodentate, binding through its central C atom.

5.2. Complexes with P(V)-stabilised carbanions

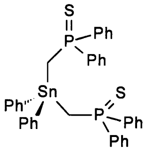
In comparison to the wealth of reports of Group 14 complexes with P(III)-stabilised carbanions, relatively few structurally characterised complexes have been reported with P(V)-stabilised carbanions. Karsch and co-workers have reported that the Ge(II) complex Ge{C($SiMe_3$)(PMe_2)$_2$}$_2$ (**72**) undergoes stepwise oxidation by elemental S at phosphorus rather than at the low oxidation state germanium centre [144]. The symmetrical complexes Ge[C($SiMe_3$)(PMe_2){P(S)Me_2}]$_2$ and Ge[C($SiMe_3$){P(S)Me_2}$_2$]$_2$ have been isolated in pure form whilst the oxidation products containing odd numbers of sulphur atoms have been characterised only in solution, where they are in equilibrium with the oxidation products containing even numbers of S atoms. Oxidation of **72** by grey selenium in toluene yields the complex Ge[C($SiMe_3$)(PMe_2){P(Se)Me_2}]$_2$ (**92**), which has been crystallographically characterised [144]. The Ge(II) centre is bound by the phosphorus and selenium atoms of the ligands to form two five-membered chelate rings; the Se–Ge–Se angle is almost linear [174.8(1)°], consistent with the presence of a stereochemically active lone pair and a ψ-tbp geometry at Ge.



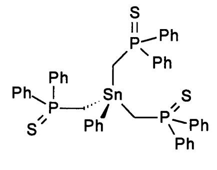
92



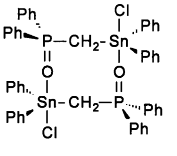
93



94



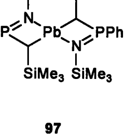
95



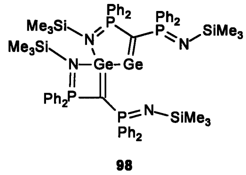
96

The compounds [$Ph_{(4-n)}$Sn{$CH_2P(S)Ph_2$}$_n$] [n = 1 (**93**), 2 (**94**), 3 (**95**) or 4] and [Ph_2SnCl{$CH_2P(O)Ph_2$}]$_2$ (**96**) have recently been isolated and, for **93**–**96**, structurally characterised [145]. Compounds **93**–**95** are mononuclear with the phosphine sulphide ligands binding to tin via their carbanion centres. In contrast, compound **96** is dimeric with the phosphine oxide ligands bridging the two five-coordinate Sn centres via their carbanionic C and O centres to form an eight-membered $(SnCPO)_2$ heterocycle with a twisted chair conformation. The dimeric nature of **96** has been attributed to the known affinity of Sn for O-donor ligands.

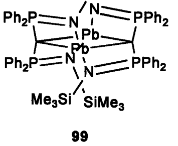
The reaction of the iminophosphoranomethyllithium complex [Li{CH($SiMe_3$)PPh_2=N($SiMe_3$)}]$_2$ (**20**) with $PbCl_2$ in diethyl ether yields the lead(II) complex [Pb{CH($SiMe_3$)PPh_2=N($SiMe_3$)}$_2$] (**97**) [63]. The P(V) ligand binds through its N and C centres to form two four-membered chelate rings, giving the Pb centre a distorted tetragonal pyramidal geometry due to the presence of a stereochemically active lone pair on Pb.



97



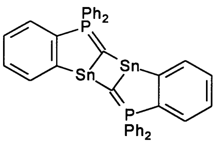
98



99

The bis(iminophosphorano)methyllithium complex (THF)Li[$CH_2\{PPh_2{=}N(SiMe_3)\}_2$] reacts with $GeCl_2$(dioxane) to give the unusual Ge(II) complex [$\{CH_2(PPh_2{=}N[SiMe_3])_2\}Ge\{\mu\text{-}CH_2(PPh_2{=}N[SiMe_3])_2\}Ge$] (**98**) [146]. There are two distinct Ge environments in the complex, one Ge atom is bonded to both the carbdianion and N centres of one P(V) ligand, whilst the other is bound by the carbdianion centre of the P(V) ligand alone, the two Ge atoms are linked by a Ge–Ge interaction [Ge–Ge = 2.483(1) Å] and by a Ge–C–P–N–Ge bridge. Thus, **98** may be viewed as a donor–acceptor complex, with the four-coordinate Ge acting as the donor and the two-coordinate Ge acting as the acceptor. Interestingly, on formation of **98**, the central carbon of the imonophosphoranomethanide ligand undergoes a second deprotonation to give a dianion. The reaction of (THF)Li[$CH_2\{PPh_2{=}N(SiMe_3)\}_2$] with MX_2 [M = Sn, X = Cl, $N(SiMe_3)_2$; M = Pb, X = $N(SiMe_3)_2$] yields the complexes [$M\{CH_2(PPh_2{=}N[SiMe_3])\}]_2$ [M = Sn, Pb (**99**)] via a similar second deprotonation of the mono-anionic ligand [146]. Compound **99** consists of two Pb atoms bridged by two carbdianion carbon atoms in a Pb_2C_2 ring; the two imino nitrogen atoms of each ligand coordinate to the tetrahedral metal centres forming four-membered PbCPN rings.

There has been one report of a crystallographically characterised α-stannylated phosphonium ylide. Heating $Me_2(NBu^t)_2Sn$ with Ph_3PCH_2 in toluene at 120 °C results in decomposition to the tricyclic compound [$Sn\{CH(C_6H_4)PPh_2\}]_2$ (**100**) [147]. The deprotonated ylidic C atoms bridge the two Sn atoms in a planar Sn_2C_2 ring; the Sn atoms are further coordinated by the *ortho*-metalated carbon atoms of one of the phenyl rings.

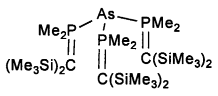


100

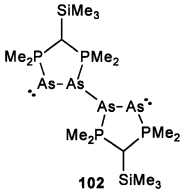
6. Group 15 (As, Sb, Bi)

Relatively few compounds have been isolated that can genuinely be described as *complexes* of the Group 15 elements with P-stabilised carbanions. In part this is due to the facile oxidative coupling of phosphinomethanide ligands, which is readily mediated by compounds of the heavier Group 15 elements. For example, whilst $LiCH_2(PMe_2)_2$ reacts with $BiCl_3$ to give an isolable, but thermally unstable, compound of composition $Bi\{CH_2(PMe_2)_2\}_3$, which has not been well characterised, reactions between $Li\{CX(SiMe_3)(PMe_2)\}$ [X = $SiMe_3$, PMe_2] and $BiCl_3$ yield P–P coupling products $(Me_3Si)XC{=}PMe_2{-}PMe_2{=}CX(SiMe_3)$ and Bi metal [148–150].

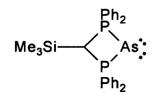
In contrast, the compound $Li\{C(SiMe_3)_2(PMe_2)\}$ reacts with $AsCl_3$ or $SbCl_3$ to give the isolable tris(ylides) $E\{PMe_2{=}C(SiMe_3)_2\}_3$ [E = As (**101**), Sb] [150,151], whereas the reaction between $Li\{C(SiMe_3)(PMe_2)_2\}$ and $AsCl_3$ yields the partial reduction product [$\mu\text{-}\{C(SiMe_3)(PMe_2)_2\}As_2]_2$ (**102**) [150]. This latter compound contains a chain of four As atoms with an average oxidation state of 0.5, bridged at either end by the phosphinomethanide ligands to give two linked five-membered As_2PCP heterocycles. The reaction of (tmeda)$Li\{C(SiMe_3)_2(PPh_2)\}$ with $AsCl_3$ yields the four-membered heterocycle $(Me_3Si)C(PMe_2)_2As$ (**103**) and the chloro-ylide $Ph_2P(Cl){=}C(PPh_2)(SiMe_3)$ [150,152].



101



102



103

7. Conclusion

This review has sought to describe the versatility of P-stabilised carbanions as ligands for the main group metals and to highlight the structural diversity of such complexes. Although there is already a considerable body of work in this area, it is clear that there are many areas still to be developed and that the future will hold many surprises. For example, the isolation of carbdianions stabilised by two adjacent P(V) functionalities opens the way for rich and potentially highly rewarding chemistry with the main group elements—this is, as yet, a relatively unexplored area with many possibilities for the isolation of highly novel species. Similarly, the dearth of information regarding the structures and reactions of complexes between the heavier s- and p-elements and P-stabilised carbanions remains to be addressed, as does the chemistry of more highly functionalised carbanions stabilised by two, or even three, (thio)phosphoryl substituents.

References

[1] J.G. Cadogan, Organophosphorus Reagents in Organic Synthesis (Chapter 3), Academic Press, New York, 1979.

[2] S.E. Kelly, in: S.L. Schreiber (Ed.), Comprehensive Organic Synthesis, Additions to C–X π-bonds, vol. 1 (Chapter 3.1), Pergamon Press, Oxford, 1991.
[3] G.L. Edwards, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), Comprehensive Organic Functional Group Transformations, Elsevier, Oxford, 1995, p. 579.
[4] B.E. Maryanoff, A.B. Reitz, Chem. Rev. 89 (1989) 863.
[5] L. Horner, H. Hoffmann, H.G. Wippel, G. Klahre, Chem. Ber. 91 (1958) 61.
[6] L. Horner, H. Hoffmann, H.G. Wippel, G. Klahre, Chem. Ber. 92 (1959) 2499.
[7] W.S. Wadsworth, W.D. Emmons, J. Am. Chem. Soc. 83 (1961) 1783.
[8] M.J. Peterson, Top. Stereochem. 21 (1994) 1.
[9] P. von R. Schleyer, T. Clark, A.J. Kos, G.W. Spitznagel, C. Rohde, D. Arad, K.N. Houk, N.G. Rondan, J. Am. Chem. Soc. 106 (1984) 6467.
[10] R. Koch, E. Anders, J. Org. Chem. 60 (1995) 5861.
[11] A.M. El-Nahas, P. von R. Schleyer, J. Comput. Chem. 15 (1994) 596.
[12] K.B. Wiberg, H. Castejon, J. Am. Chem. Soc. 116 (1994) 10489.
[13] D.M. Wetzel, J.I. Brauman, J. Am. Chem. Soc. 110 (1988) 8333.
[14] A.L. Allred, J. Inorg. Nucl. Chem. 17 (1961) 215.
[15] K. Izod, Adv. Inorg. Chem. 50 (2000) 33.
[16] W. Clegg, S. Doherty, K. Izod, P. O'Shaughnessy, J. Chem. Soc. Chem. Commun. (1998) 1129.
[17] W. Clegg, K. Izod, P. O'Shaughnessy, Organometallics 18 (1999) 2939.
[18] K. Izod, W. Clegg, S.T. Liddle, Organometallics 20 (2001) 367.
[19] M.N.S. Hill, K. Izod, P. O'Shaughnessy, W. Clegg, Organometallics 19 (2000) 4531.
[20] V. Knapp, M. Winkler, G. Müller, Z. Naturforsch. 55b (2000) 1114.
[21] E. Niecke, M. Nieger, O. Schmidt, D. Gudat, W.W. Schoeller, J. Am. Chem. Soc. 121 (1999) 519.
[22] V. Knapp, G. Müller, Angew. Chem. Int. Ed. Engl. 40 (2001) 183.
[23] I.J. Colquhoun, H.C.E. McFarlane, W. McFarlane, J. Chem. Soc. Chem. Commun. (1982) 220.
[24] S.E. Denmark, K.A. Swiss, P.C. Miller, S.R. Wilson, Heteroatom Chem. 9 (1998) 209.
[25] W. Clegg, R.P. Davies, L. Dunbar, N. Feeder, S.T. Liddle, R.E. Mulvey, R. Snaith, A.E.H. Wheatley, J. Chem. Soc. Chem. Commun. (1999) 1401.
[26] K.W. Henderson, A.R. Kennedy, A.E. McKeown, D. Strachan, J. Chem. Soc. Dalton Trans. (2000) 4348.
[27] J.E. Davies, R.P. Davies, L. Dunbar, P.R. Raithby, M.G. Russel, R. Snaith, S. Warren, A.E.H. Wheatley, Angew. Chem. Int. Ed. Engl. 36 (1997) 2334.
[28] W. Zarges, M. Marsch, K. Harms, F. Haller, G. Frenking, G. Boche, Chem. Ber. 124 (1991) 861.
[29] S.E. Denmark, K.A. Swiss, S.R. Wilson, Angew. Chem. Int. Ed. Engl. 35 (1996) 2515.
[30] S.E. Denmark, R.L. Dorow, J. Am. Chem. Soc. 112 (1990) 864.
[31] S.E. Denmark, P.C. Miller, S.R. Wilson, J. Am. Chem. Soc. 113 (1991) 1468.
[32] S.E. Denmark, K.A. Swiss, S.R. Wilson, J. Am. Chem. Soc. 115 (1993) 3826.
[33] C.J. Cramer, S.E. Denmark, P.C. Miller, R.L. Dorow, K.A. Swiss, S.R. Wilson, J. Am. Chem. Soc. 116 (1994) 2437.
[34] M. Kranz, S.E. Denmark, J. Org. Chem. 60 (1995) 5867.
[35] M. Kranz, S.E. Denmark, K.A. Swiss, S.R. Wilson, J. Org. Chem. 61 (1996) 8551.
[36] S.E. Denmark, K.A. Swiss, J. Am. Chem. Soc. 115 (1993) 12195.
[37] S.E. Denmark, C.-T. Chen, J. Am. Chem. Soc. 117 (1995) 11897.
[38] A.M. Modro, T.A. Modro, M.J. Mphahlele, W. Perlikowska, A. Pienaar, M. Sales, P.H. van Rooyen, Can. J. Chem. 76 (1998) 1344.
[39] S.E. Denmark, J.-H. Kim, Can. J. Chem. 78 (2000) 673.
[40] D.R. Armstrong, D. Barr, M.G. Davidson, G. Hutton, P. O'Brien, R. Snaith, S. Warren, J. Organomet. Chem. 529 (1997) 29.
[41] K. Ando, J. Org. Chem. 64 (1999) 6815.
[42] P. Brandt, P.-O. Norrby, I. Martin, T. Rein, J. Org. Chem. 63 (1998) 1280.
[43] M.-P. Teulade, P. Savignac, E. About-Jaudet, N. Collignon, Phosphorus Sulfur 40 (1988) 105.
[44] J. Browning, K.R. Dixon, R.W. Hilts, Organometallics 8 (1989) 552.
[45] S.O. Grim, P.B. Kettler, J.S. Merola, Inorg. Chim. Acta 185 (1991) 57.
[46] M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, Chem. Ber. 129 (1996) 585.
[47] D.M.C. Smit, S.S. Basson, A. Roodt, E.C. Steynberg, Acta Crystallogr. Sect. C 51 (1995) 1278.
[48] J. Browning, G.W. Bushnell, K.R. Dixon, A. Pidcock, Inorg. Chem. 22 (1983) 2226.
[49] D.E. Berry, J. Browning, K.R. Dixon, R.W. Hilts, A. Pidcock, Inorg. Chem. 31 (1992) 1479.
[50] H.H. Karsch, Chem. Ber. 115 (1982) 818.
[51] M.B. Goli, S.O. Grim, Tetrahedron Lett. 32 (1991) 3631.
[52] M.-P. Teulade, P. Savignac, E.E. Aboujaoude, S. Liétge, N. Collignon, J. Organomet. Chem. 304 (1986) 283.
[53] R.P. Kamalesh Babu, K. Aparna, R. McDonald, R.G. Cavell, Inorg. Chem. 39 (2000) 4981.
[54] C.G. Stuckwisch, J. Org. Chem. 41 (1976) 1173.
[55] J. Barlengua, F. López, F. Palacios, J. Chem. Res. (S) (1985) 211.
[56] U.G. Wettermark, P. Wisian-Neilson, G.M. Scheide, R.H. Neilson, Organometallics 6 (1987) 959.
[57] R.H. Neilson, P. Wisian-Neilson, Chem. Rev. 88 (1988) 541.
[58] J. Barlengua, F. López, F. Palacios, J. Organomet. Chem. 382 (1990) 61.
[59] F. López-Ortiz, E. Peláez-Arango, B. Tejerina, E. Pérez-Carreño, S. García-Granda, J. Am. Chem. Soc. 117 (1995) 9972.
[60] A. Müller, B. Neumüller, K. Dehnicke, Chem. Ber. 129 (1996) 253.
[61] P.B. Hitchcock, M.F. Lappert, P.G.H. Uiterweerd, Z.-X. Wang, J. Chem. Soc. Dalton Trans. (1999) 3413.
[62] C. Eaborn, Z.-R. Lu, P.B. Hitchcock, J.D. Smith, Organometallics 15 (1996) 1651.
[63] P.B. Hitchcock, M.F. Lappert, Z.-X. Wang, J. Chem. Soc. Chem. Commun. (1997) 1113.
[64] P.B. Hitchcock, M.F. Lappert, Z.-X. Wang, J. Chem. Soc. Dalton Trans. (1997) 1953.
[65] A. Müller, B. Neumüller, K. Dehnicke, Angew. Chem. Int. Ed. Engl. 36 (1997) 2350.
[66] A. Müller, B. Neumüller, K. Dehnicke, J. Magull, D. Fenske, Z. Anorg. Allg. Chem. 623 (1997) 1306.
[67] M.R. Churchill, C.H. Lake, S.-H.L. Chao, O.T. Beachley, J. Chem. Soc. Chem. Commun. (1993) 1577.
[68] C. Eaborn, P.B. Hitchcock, K. Izod, J.D. Smith, Angew. Chem. Int. Ed. Engl. 34 (1995) 2679.
[69] M.W. Avis, K. Vrieze, J.M. Ernsting, C.J. Elsevier, N. Veldman, A.L. Spek, K.V. Katti, C.L. Barnes, Organometallics 15 (1996) 2376.
[70] P. Imhoff, R. van Asselt, C.J. Elsevier, K. Goubitz, K.F. van Malssen, C.H. Stam, Phosphours, Sulfur, Silicon Relat. Elem. 147 (1990) 401.
[71] J.D. Smith, Adv. Organomet. Chem. 43 (1999) 267.
[72] R.P. Kamalesh Babu, K. Aparna, R. McDonald, R.G. Cavell, Organometallics 20 (2001) 1451.
[73] J.F.K. Müller, Eur. J. Inorg. Chem. (2000) 789.

[74] I. Marek, J.-F. Normant, Chem. Rev. 96 (1996) 3241.
[75] B. Iorga, F. Eymery, P. Savignac, Tetrahedron Lett. 39 (1998) 3693.
[76] C.M. Ong, D.W. Stephan, J. Am. Chem. Soc. 121 (1999) 2939.
[77] A. Kasani, R.P. Kamalesh Babu, R. McDonald, R.G. Cavell, Angew. Chem. Int. Ed. Engl. 38 (1999) 1483.
[78] J.F.K. Müller, M. Neuburger, B. Spingler, Angew. Chem. Int. Ed. Engl. 38 (1999) 92.
[79] W.A. Johnson, W.C. Kaska, K.A.O. Starzewski, D. Dixon, Ylides and Imines of Phosphorus, Wiley, New York, 1993.
[80] H.-J. Cristau, Chem. Rev. 94 (1994) 1299 (and references therein).
[81] E.J. Corey, J. Kang, J. Am. Chem. Soc. 104 (1982) 4724.
[82] H.J. Bestmann, M. Schmidt, Angew. Chem. Int. Ed. Engl. 26 (1987) 79.
[83] S. Goumri-Magnet, H. Gornitzka, A. Baceiredo, G. Bertrand, Angew. Chem. Int. Ed. Engl. 38 (1999) 678.
[84] R.S. McDowell, A. Streitwieser, Jr., J. Am. Chem. Soc. 106 (1984) 4046.
[85] G. Wittig, M. Rieber, Justus Liebigs Ann. Chem. 562 (1949) 177.
[86] H. Schmidbaur, W. Tronich, Chem. Ber. 101 (1968) 3556.
[87] L.E. Manzer, Inorg. Chem. 15 (1976) 2567.
[88] R.E. Cramer, R.B. Maynard, J.W. Gilje, Inorg. Chem. 20 (1981) 2466.
[89] R.E. Cramer, M.A. Bruck, J.W. Gilje, Organometallics 5 (1986) 1496.
[90] H. Schmidbaur, U. Deschler, B. Zimmer-Gasse, D. Neugebauer, U. Schubert, Chem. Ber. 113 (1980) 902.
[91] H. Schmidbaur, U. Deschler, B. Milewski-Mahrla, B. Zimmer-Gasse, Chem. Ber. 114 (1981) 608.
[92] H. Schmidbaur, U. Deschler, B. Milewski-Mahrla, Chem. Ber. 115 (1982) 3290.
[93] T. Baumgartner, B. Schinkels, D. Gudat, M. Neiger, E. Niecke, J. Am. Chem. Soc. 119 (1997) 12410.
[94] E. Niecke, P. Becker, M. Nieger, D. Stalke, W.W. Schoeller, Angew. Chem. Int. Ed. Engl. 34 (1995) 1849.
[95] T. Baumgartner, D. Gudat, M. Nieger, E. Niecke, T.J. Schiffer, J. Am. Chem. Soc. 121 (1999) 5953.
[96] H.H. Karsch, M. Reisky, Eur. J. Inorg. Chem. (1998) 905.
[97] K. Izod, W. Clegg, S.T. Liddle, Organometallics 19 (2000) 3640.
[98] A. Müller, M. Krieger, B. Neumüller, K. Dehnicke, J. Magull, Z. Anorg. Allg. Chem. 623 (1997) 1081.
[99] B. Römer, G.G. Gatev, M. Zhong, J.I. Brauman, J. Am. Chem. Soc. 120 (1998) 2919.
[100] S. Harder, M. Lutz, Organometallics 16 (1997) 225.
[101] E.D. Brady, T.P. Hanusa, M. Pink, V.G. Young, Jr., Inorg. Chem. 39 (2000) 6028.
[102] H.H. Karsch, A. Appelt, F.H. Köhler, G. Müller, Organometallics 4 (1985) 231.
[103] H.H. Karsch, A. Appelt, G. Müller, J. Chem. Soc. Chem. Commun. (1984) 1415.
[104] H.H. Karsch, A. Appelt, G. Müller, Organometallics 4 (1985) 1624.
[105] H.H. Karsch, K. Zellner, J. Lachmann, G. Müller, J. Organomet. Chem. 409 (1991) 109.
[106] H.H. Karsch, A. Appelt, J. Riede, G. Müller, Organometallics 6 (1987) 316.
[107] H.H. Karsch, K. Zellner, G. Müller, J. Chem. Soc. Chem. Commun. (1990) 1621.
[108] H.H. Karsch, K. Zellner, G. Müller, Organometallics 10 (1991) 2884.
[109] H.H. Karsch, K. Zellner, G. Müller, J. Chem. Soc. Chem. Commun. (1991) 466.
[110] H. Schmidbaur, S. Lauteschläger, G. Müller, J. Organomet. Chem. 281 (1985) 33.
[111] W. Uhl, M. Koch, M. Heckel, W. Hiller, H.H. Karsch, Z. Anorg. Allg. Chem. 620 (1994) 1427.
[112] O.T. Beachley, Jr., M.A. Banks, M.R. Churchill, W.G. Feighery, J.C. Fettinger, Organometallics 10 (1991) 3036.
[113] O.T. Beachley, Jr., M.A. Banks, J.P. Kopasz, R.D. Rogers, Organometallics 15 (1996) 5170.
[114] M.F. Self, B. Lee, S.A. Sangokoya, W.T. Pennington, G.H. Robinson, Polyhedron 9 (1990) 313.
[115] G.H. Robinson, M.F. Self, S.A. Sangokoya, W.T. Pennington, J. Cryst. Spectrosc. Res. 18 (1988) 285.
[116] G.H. Robinson, B. Lee, W.T. Pennington, S.A. Sangokoya, J. Am. Chem. Soc. 110 (1988) 6260.
[117] B. Lee, S.A. Sangokoya, W.T. Pennington, G.H. Robinson, J. Coord. Chem. 21 (1990) 99.
[118] G.H. Robinson, M.F. Self, W.T. Pennington, S.A. Sangokoya, Organometallics 7 (1988) 2424.
[119] M.B. Power, J.W. Ziller, A.R. Barron, Organometallics 12 (1993) 4908.
[120] K. Aparna, R. McDonald, M. Ferguson, R.G. Cavell, Organometallics 18 (1999) 4241.
[121] C.M. Ong, P. McKarns, D.W. Stephan, Organometallics 18 (1999) 4197.
[122] K. Aparna, R. McDonald, R.G. Cavell, J. Am. Chem. Soc. 122 (2000) 9314.
[123] H. Schmidbaur, H.-J. Füller, Chem. Ber. 107 (1974) 3674.
[124] H. Schmidbaur, O. Gasser, C. Kruger, J.C. Sekutowski, Chem. Ber. 110 (1977) 3517.
[125] H.H. Karsch, Russ. Chem. Bull. 42 (1993) 1937.
[126] H.H. Karsch, A. Appelt, G. Hanika, J. Organomet. Chem. 312 (1986) C1.
[127] A.L. Balch, D.E. Oram, Organometallics 5 (1986) 2159.
[128] A.L. Balch, D.E. Oram, Inorg. Chem. 26 (1987) 1906.
[129] H.H. Karsch, A. Appelt, G. Müller, Organometallics 5 (1986) 1664.
[130] H.H. Karsch, B. Deubelly, G. Hanika, J. Riede, G. Müller, J. Organomet. Chem. 344 (1988) 153.
[131] H.H. Karsch, B. Deubelly, J. Riede, G. Müller, J. Organomet. Chem. 342 (1988) C29.
[132] H.H. Karsch, U. Keller, S. Gamper, G. Müller, Angew. Chem. Int. Ed. Engl. 29 (1990) 295.
[133] H.H. Karsch, A. Appelt, G. Müller, Angew. Chem. Int. Ed. Engl. 24 (1985) 402.
[134] H.H. Karsch, B. Deubelly, J. Riede, G. Müller, Angew. Chem. Int. Ed. Engl. 26 (1987) 673.
[135] H.H. Karsch, B. Deubelly, J. Riede, G. Müller, Angew. Chem. Int. Ed. Engl. 26 (1987) 674.
[136] H.H. Karsch, B. Deubelly, J. Riede, G. Müller, J. Organomet. Chem. 336 (1987) C37.
[137] H.H. Karsch, J. Hoffmann, G. Müller, J. Chem. Soc. Chem. Commun. (1988) 516.
[138] H.H. Karsch, G. Baumgartner, S. Gamper, J. Organomet. Chem. 462 (1993) C3.
[139] H.H. Karsch, B. Deubelly, U. Keller, O. Steigelmann, J. Lachmann, G. Müller, Chem. Ber. 129 (1996) 671.
[140] H.H. Karsch, B. Deubelly, U. Keller, F. Bienlein, R. Richter, P. Bissinger, M. Heckel, G. Müller, Chem. Ber. 129 (1996) 759.
[141] H.H. Karsch, R. Richter, E. Witt, J. Organomet. Chem. 521 (1996) 185.
[142] S. Benet, C.J. Cardin, D.J. Cardin, S.P. Constantine, P. Heath, H. Rashid, S. Teixeira, J.H. Thorpe, A.K. Todd, Organometallics 18 (1999) 389.
[143] C.J. Cardin, D.J. Cardin, S.P. Constantine, M.G.B. Drew, H. Rashid, M.A. Convery, D. Fenske, J. Chem. Soc. Dalton Trans. (1998) 2749.
[144] H.H. Karsch, G. Baumgartner, S. Gamper, J. Lachmann, G. Müller, Chem. Ber. 125 (1992) 1333.

[145] J.P. Fackler, Jr., G. Garzon, R.A. Kresinski, H.H. Murray, III, R.G. Raptis, Polyhedron 13 (1994) 1705.

[146] W.-P. Leung, Z.-X. Wang, H.-W. Li, T.C.W. Mak, Angew. Chem. Int. Ed. Engl. 40 (2001) 2501.

[147] M. Veith, V. Huch, J. Organomet. Chem. 308 (1986) 263.

[148] H.H. Karsch, B. Deubelly, G. Müller, J. Chem. Soc. Chem. Commun. (1988) 517.

[149] H.H. Karsch, B. Deubelly, G. Grauvogl, G. Müller, J. Organomet. Chem. 459 (1993) 95.

[150] H.H. Karsch, E. Witt, J. Organomet. Chem. 529 (1997) 151.

[151] H.H. Karsch, E. Witt, A. Schneider, E. Herdtweck, M. Heckel, Angew. Chem. Int. Ed. Engl. 34 (1995) 557.

[152] H.H. Karsch, E. Witt, F.E. Hahn, Angew. Chem. Int. Ed. Engl. 35 (1996) 2242.