# The synthesis and structural characterisation of 2-arsa- and 2-stiba-1,3-dionato complexes of s- and p-block elements

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The syntheses and structural characterisations of a number of 2-arsa- and 2-stiba-1,3-dionato complexes of main group elements are reported. The synthetic methods that were employed in this study include the reaction of lithium heterodionate complexes, [Li{$\eta^2$-*O*,*O*–OC(R)EC(R)O}], E = As or Sb, R = alkyl or aryl, with main group metal halides or the reactions of arsa- and stiba-enols, O=C(R)E=C(R)OH, with either main group alkyl or amide complexes. The hetero-ligands in the prepared complexes have been shown by X-ray crystallographic studies to coordinate the main group metal centre in several modes, that is, in a delocalised form ($\eta^2$-*O*,*O* coordination) as in [{M[$\eta^2$-*O*,*O*–OC(R)EC(R)O](L)}$_2$], M = Li or Na, E = As or Sb, R = Ad (adamantyl) or Ph, L = $Et_2O$ or DME; [Na{$\eta^2$-*O*,*O*–OC(Mes*)EC(Mes*)O}$(DME)_2$], E = As or Sb, Mes* = $C_6H_2Bu^t_3$-2,4,6, and [Mg{$\eta^2$-*O*,*O*–OC(Ph)AsC(Ph)O}$_2$(DME)]; in a localised diacylpnictido form ($\eta^1$-*E* coordination) as in P[As{C(O)R}$_2$]$_3$, R = But or Ph; or as a combination of the two modes ($\eta^1$-*E*–: $\eta^2$-*O*,*O*–) as in [LiCl$(Et_2O)$(DME){$\eta^2$-*O*,*O*–$Cl_3$InAs[C(O)R]$_2$}].

## Introduction

One of our main research interests lies with developing the chemistry of ligand systems in which one or more CR fragments (R = H or alkyl) of classical hydrocarbon-based ligand systems are substituted with the valence isoelectronic heavier group 15 elements, As or Sb.[1] In this context we have recently been examining the transition metal coordination chemistry of the 2-arsa and 2-stiba-1,3-dionates, $[OC(R)EC(R)O]^-$ (**1**, E = As or Sb, R = alkyl or aryl). Although these anions are closely related to the ubiquitous β-diketonato class of ligands they have proved to be much more versatile in their coordination behaviour. For example, whereas β-diketonates generally bind transition metals in variations of the chelating $\eta^2$-*O*,*O* mode, the presence of a low coordinate pnictide centre in **1** allows them to coordinate metals in a variety of ways, which include $\eta^2$-*O*,*O*-; $\eta^1$-*E*; $\eta^1$-*E*:$\eta^1$-*O*:$\eta^2$-CO; $\eta^1$-*E*:$\eta^2$-*O*,*O*- and μ-$\eta^1$:$\eta^1$-*E*.[2,3] In addition, the weakness of the Sb–C bond of 2-stiba-1,3-dionates has led to their use as precursors to previously inaccessible complex types such as the first example of a functionalised distibene, which is stabilised within the coordination sphere of a transition metal fragment: *cis*-[Pt$(PEt_3)_2${$\eta^2$-Sb,Sb–C$(Bu^t)$(O)Sb=SbC(O)$(Bu^t)$}].[4]

Despite the coordinative versatility that heterodionates have shown towards transition metals, little work has looked at their interaction with main group elements. Indeed, this can be confined to the preparation of the lithium salts of these ligands, [Li{$\eta^2$-*O*,*O*–OC(R)EC(R)O}],[5,6] which are invariably used as starting materials in the transition metal based studies. In addition, we have made a preliminary report[7] on the synthesis and structural characterisation of the first tris(diacylarsenido)phosphines, P[As{C(O)R}$_2$]$_3$, R = $Bu^t$ or Ph. We have sought to extend these results to the formation of a variety of heterodionate complexes of both s- and p-block elements and to compare their chemistry with that of their β-diketonate analogues. The results of this study are reported herein.

## Results and discussion

### Group 1

In a prior study, the synthesis and structural characterisation of the *tert*-butyl substituted lithium heterodionates, [{[Li{$\eta^2$-*O*,*O*–OC$(Bu^t)$EC$(Bu^t)$O}$(DME)_{0.5}]_2$}$_\infty$], E = As **2**, Sb **3**, and [{Li[$\eta^2$-*O*,*O*–OC$(Bu^t)$AsC$(Bu^t)$O]$(OEt_2)$}$_2$] **4**, have been reported.[6] It was found that in these syntheses the optimum yield was achieved when the ratio of acid chloride and lithium pnictide reactants was 2:3. In addition, it was revealed that both E$(SiMe_3)_3$ and LiCl were generated as by-products and so the mechanism of formation of **2**–**4** was proposed to be as outlined in Scheme 1.

As **2**–**4** represent the only three structurally characterised lithium arsa- or stibadionates known to date, it was decided to prepare a number more to shed light on the degree of generality of the synthetic technique mentioned above and to allow structural comparisons to be carried out. To this end adamantyl acid chloride, AdC(O)Cl, was reacted with [Li{Sb$(SiMe_3)_2$}] in a 2:3 ratio, which afforded the stibadionato lithium complex, **5**, in high yield after recrystallisation from diethyl ether (Scheme 1). Altering the reaction stoichiometry lowered the yield of **5** but under all conditions Sb$(SiMe_3)_3$ was shown to be a reaction by-product. This strongly suggests the mechanism of formation shown in Scheme 1 is in operation. All the spectroscopic data for **5** are as expected and are similar to those for the closely related complex, **3**. The former is, however, significantly more thermally stable than the latter (**5** dec. 98 °C, **3** dec. 65 °C), presumably due to the enhanced kinetic stability afforded by the bulkier adamantyl substituents.

Interestingly, when an attempt was made to prepare the phenyl substituted analogues of **2** and **4**,that is **6** and **7**, by the 2:3 reaction of PhC(O)Cl with [Li{As$(SiMe_3)_2$}], only low yields were obtained and much of the arsenic starting material

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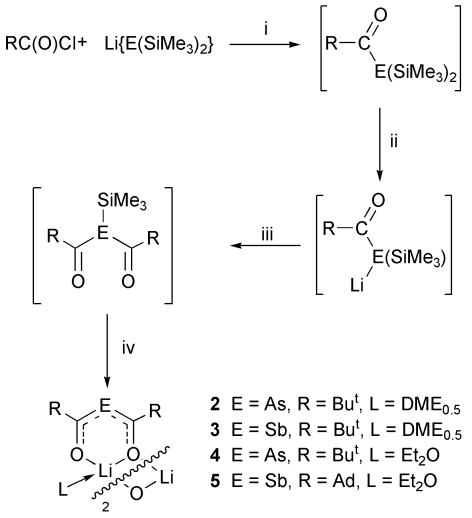
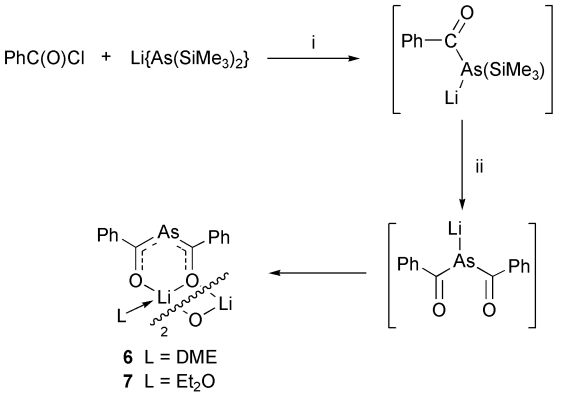



**Scheme 1** *Reagents and conditions*: (*i*) DME, −LiCl; (*ii*) Li{E(SiMe$_3$)$_2$}, −E(SiMe$_3$)$_3$; (*iii*) RC(O)Cl, −LiCl; (*iv*) Li{E(SiMe$_3$)$_2$}, −E(SiMe$_3$)$_3$.

remained unreacted. It was eventually found that the optimum reaction stoichiometry was 2:1 and that no As(SiMe$_3$)$_3$ was generated. Therefore, a different reaction mechanism to that which yielded **2**–**5** must be in operation. This is proposed to be as outlined in Scheme 2. Instead of salt elimination occurring there are two sequential SiMe$_3$Cl eliminations and an intramolecular rearrangement that gives a high yield of the products, **6** or **7**, depending on which solvent is employed to recrystallise the crude product. Evidence for this mechanism came from a GC/MS analysis of the reaction volatiles, which shows both SiMe$_3$Cl and (Me$_3$Si)$_2$O as major reaction by-products. The latter is a known hydrolysis product of SiMe$_3$Cl. It is not known why two very different mechanisms are in operation to form such products but the reason probably lies with the smaller steric bulk of the Ph group relative to the Bu′ substituent, the electronic differences between these groups, or a combination of both. It was attempted to form the stibadionate analogues of **6** and **7** using similar reaction conditions but the products proved to be unstable at ambient temperature and decomposed, affording elemental antimony and many other products.

Again, the spectroscopic data for **6** and **7** are similar to those for the analogous *tert*-butyl substituted complexes, **2** and **4**.[6] As for these complexes the NMR data suggest a more symmetrical structure in solution than was observed in the solid state (*vide infra*) because the acyl carbon centres are chemically equivalent. This is probably due to a fluxional process in




**Scheme 2** *Reagents and conditions*: (*i*) DME, −SiMe$_3$Cl; (*ii*) PhC(O)Cl, −SiMe$_3$Cl.

solution, which involves a rapid breaking and reforming of bridging Li–O bonds as has been suggested for **2** and **4**. Attempts to investigate this process with variable temperature NMR spectroscopic experiments were thwarted by the low solubility of the complexes in non-coordinating solvents at temperatures below 0 °C.

The X-ray crystal structures of **5**–**7** were obtained and are depicted in Figs. 1–3 (see Table 1). All are dimeric and contain essentially planar central Li$_2$O$_2$ four-membered rings. The lithium centres in each compound are chelated by the heterodionate ligand and have an additional intermolecular coordination from the bridging oxygen centre of the other heterodionate ligand in the dimer. Compounds **5** and **7** have further lithium coordination from diethyl ether molecules whilst DME molecules chelate the 5-coordinate lithium centres in **6**. This arrangement is identical to that in the phosphorus analogue of **6**[8] but differs from the situation in **2** where the DME molecules bridge dimeric units into an infinite polymeric chain. The differences here most probably arise from the greater steric crowding about the lithium centres in **2**, which disfavour DME chelation.

In each of **5**–**7** the 6-membered LiOCECO chelate ring is non-planar with the E and Li centres sitting slightly out of the least squares plane defined by both C and O centres. Despite this, there appears to be a significant degree of delocalisation over the heterodionate ligands as the E–C and C–O bond lengths lie between those normally seen for double and single bonded interactions.[9] It must be said, however, that the E–C bond lengths are closer to single than double bonds, which probably reflects a relative accumulation of negative charge at the hetero-centres.

There are no known examples of 2-bisma-1,3-dionato complexes, which is not surprising given the expected decrease in their thermal stability relative to their already thermally frail antimony counterparts. Despite this, an attempt was made to prepare a sterically hindered lithium bismadionato complex,

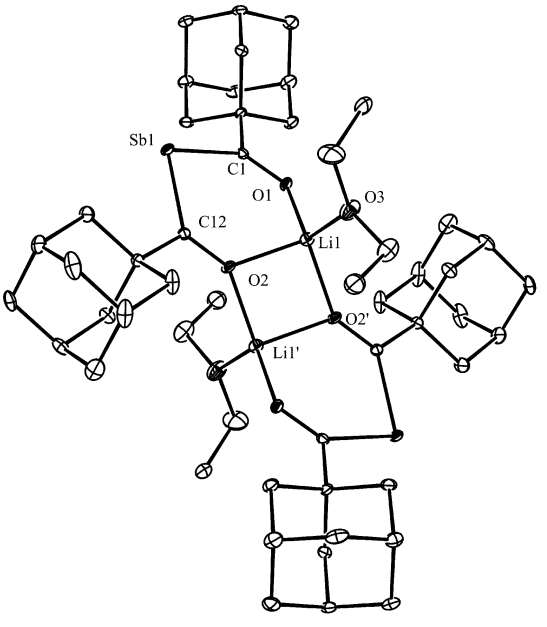



**Fig. 1** Molecular structure of compound **5**. Selected bond lengths (Å) and angles (°): Sb(1)–C(12) 2.119(4), Sb(1)–C(1) 2.187(3), O(1)–C(1) 1.236(4), O(1)–Li(1) 1.916(7), O(2)–C(12) 1.266(4), O(2)–Li(1)′ 1.914(7), O(2)–Li(1) 1.926(7), O(3)–Li(1) 1.950(7), C(12)–Sb(1)–C(1) 95.36(13), C(1)–O(1)–Li(1) 130.8(3), C(12)–O(2)–Li(1)′ 146.6(3), C(12)–O(2)–Li(1) 125.2(3), Li(1)′–O(2)–Li(1) 88.1(3), O(1)–C(1)–Sb(1) 124.4(3), O(2)–C(12)–Sb(1) 124.9(3), O(2)′–Li(1)–O(1) 125.8(4), O(2)′–Li(1)–O(2) 91.9(3), O(1)–Li(1)–O(2) 98.9(3), O(2)′–Li(1)–O(3) 106.6(3), O(1)–Li(1)–O(3) 118.5(3), O(2)–Li(1)–O(3) 110.3(3). Symmetry operation ′: $-x+2$, $-y$, $-z+1$.

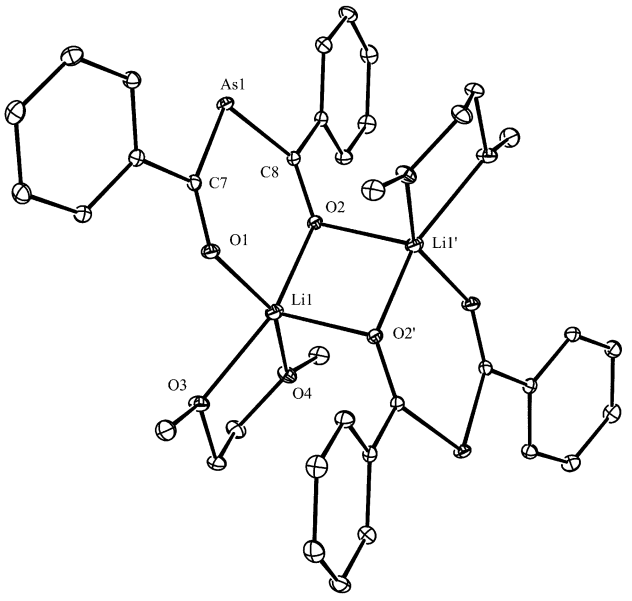



**Fig. 2** Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): As(1)–C(8) 1.915(2), As(1)–C(7) 1.942(2), O(1)–C(7) 1.240(2), O(1)–Li(1) 1.942(3), O(2)–C(8) 1.259(2), O(2)–Li(1) 2.012(3), O(2)–Li(1)′ 2.038(4), O(3)–Li(1) 2.153(4), O(4)–Li(1) 2.092(4), C(8)–As(1)–C(7) 99.19(7), C(7)–O(1)–Li(1) 137.3(2), C(8)–O(2)–Li(1) 133.7(2), C(8)–O(2)–Li(1)′ 120.3(2), Li(1)–O(2)–Li(1)′ 88.0(2), O(1)–C(7)–As(1) 127.50(13), O(2)–C(8)–As(1) 127.64(13), O(1)–Li(1)–O(2) 91.49(14), O(1)–Li(1)–O(2)′ 111.3(2), O(2)–Li(1)–O(2)′ 92.0(3). Symmetry operation ′: $-x+1$, $-y$, $-z$.

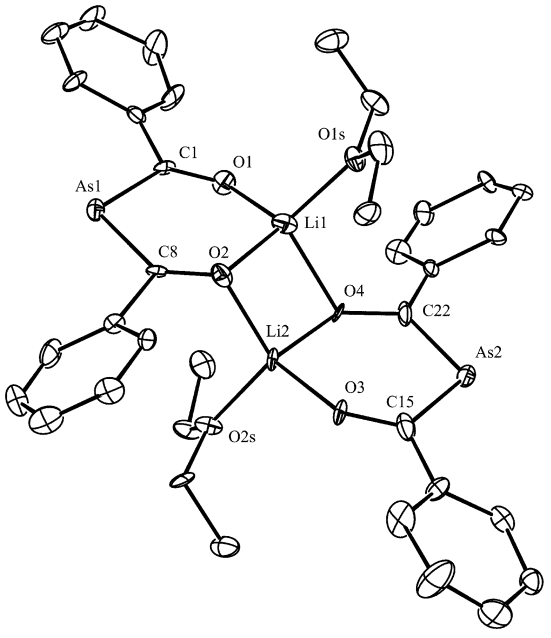



**Fig. 3** Molecular structure of compound **7**. Selected bond lengths (Å) and angles (°): As(1)–C(8) 1.934(8), As(1)–C(1) 1.946(10), As(2)–C(22) 1.869(10), As(2)–C(15) 1.955(11), O(1)–C(1) 1.222(13), O(1)–Li(1) 1.83(2), O(2)–C(8) 1.230(12), O(2)–Li(1) 1.92(2), O(2)–Li(2) 1.903(18), O(3)–C(15) 1.276(13), O(3)–Li(2) 1.919(18), O(4)–C(22) 1.306(12), O(4)–Li(2) 1.918(19), O(4)–Li(1) 2.054(19), Li(1)–O(1S) 1.96(2), Li(2)–O(2S) 1.948(19), C(8)–As(1)–C(1) 98.1(4), C(22)–As(2)–C(15) 102.4(4), C(1)–O(1)–Li(1) 130.2(9), C(8)–O(2)–Li(1) 128.2(8), C(8)–O(2)–Li(2) 124.6(8), Li(1)–O(2)–Li(2) 92.3(8), C(15)–O(3)–Li(2) 133.7(10), C(22)–O(4)–Li(2) 133.2(8), C(22)–O(4)–Li(1) 122.2(8), Li(2)–O(4)–Li(1) 87.9(7), O(1)–C(1)–As(1) 128.3(7), O(3)–C(15)–As(2) 124.7(8), O(4)–C(22)–As(2) 126.8(8).

[Li{$\eta^2$-*O*,*O*–OC(Mes*)BiC(Mes*)O}], Mes* = $C_6H_2Bu^t_3$-2,4,6, by the reaction of 2 equiv. of Mes*C(O)Cl with 3 equiv. of [Li{$Bi(SiMe_3)_2$}] in an analogous fashion to the preparation of **5**. This reaction, however, unexpectedly led to moderate yields of the known dibismuthane, $(Me_3Si)_2BiBi(SiMe_3)_2$,[10] and the α-diketone, $\{Mes^*C(O)\}_2$. Presumably, these arose from the initial formation of $Mes^*C(O)Bi(SiMe_3)_2$, which underwent a thermally or photolytically induced homolytic Bi–C bond cleavage, whilst a subsequent coupling of the generated fragments gave the observed products. As a result of this outcome no further attempts were made to prepare a bismadionate complex.

It was deemed of sufficient interest to attempt the preparation of heterodionate complexes of the heavier alkali metal, sodium. The rationale for this was that sodium heterodionates were considered as having potential as transfer reagents in the synthesis of lanthanide-heterodionate complexes from lanthanide halides where sodium halide elimination would be the reaction driving force. The analogous lithium complexes are not suitable in this respect. They are, however, useful in the formation of arsa- and stiba-enol compounds, **8**, when treated with protonating agents. These hetero-enols have previously been shown to exist predominantly in the enol, and not the keto tautomeric form, in both solution and the solid state.[5,6] Therefore, the treatment of several of these with the sodium amide, [Na{$N(SiMe_3)_2$}], was investigated and in all cases the expected sodium heterodionate complexes, **9**–**11**, were formed in moderate to high yields (Scheme 3).

In the case of **9** the $^1$H NMR spectrum was very similar to that of its lithium analogue, **6**, and was indicative of one molecule of DME per sodium centre. As a result it was proposed that this compound had a related dimeric structure. When the very bulky supermesityl ligand, Mes*, was employed the $^1$H NMR spectra of both the arsa- and stibadionate complexes were very similar and pointed towards two chelating DME molecules per sodium centre. The most likely structural arrangement that would allow this was thought to be monomeric with octahedrally coordinated sodium centres. This was confirmed in the solid state by X-ray crystallography.

The molecular structures of **9**–**11** are depicted in Figs. 4–6 (see Table 1). Compound **9** is isostructural and isomorphous to **6** and as in that compound the As–C and C–O bond lengths lie between those expected for double and single interactions. The only significant difference between the two structures are the metal-oxygen distances, which are, not surprisingly, markedly longer in the sodium complex. The other sodium heterodionate complexes, **10** and **11**, are isostructural but not isomorphous due to the inclusion of half a molecule of crystallisation of DME for each molecule of **10** in its crystal structure. In addition, in **11** there are two crystallographically independent half molecules in the asymmetric unit, which sit on 2-fold rotation axes. The full molecules that are generated by these symmetry elements have very similar geometries and so only one is shown in Fig. 6. As in the previously mentioned dimeric heterodionato lithium and sodium complexes the bond lengths within the heterodionate fragments are consistent with significant delocalisation. One difference that was observed between the monomeric and dimeric complexes is that in the dimeric complexes the 6-membered LiOCECO rings are significantly distorted from planarity, whereas in **10** and **11** the NaOCECO rings are essentially planar. In addition, 6-coordinate metal centres are not observed in the dimers whilst in **10** and **11** the sodium centres possess distorted octahedral geometries arising from two chelating DME molecules and one heterodionate ligand.

## Group 2

Prior to this work there were no reported examples of group 2 heterodionate complexes. This contrasts with the chemistry of

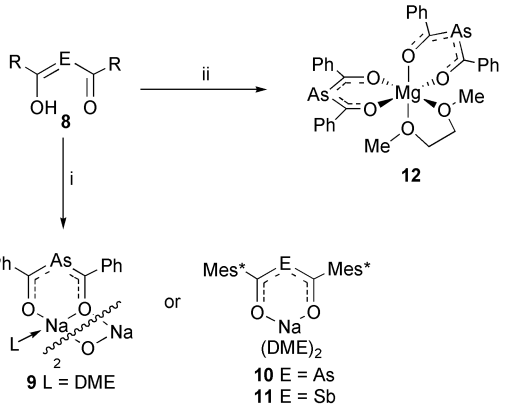
**Table 1** Crystal data for compounds **5**, **6**, **7**, **9**, **10**·$DME_{0.5}$, **11**, **12**, **13**, and **15**·$Et_2O$

| | **5** | **6** | **7** | **9** | **10**·$DME_{0.5}$ | **11** | **12** | **13** | **15**·$Et_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Chemical formula | $C_{26}H_{40}O_3SbLi$ | $C_{18}H_{20}AsLiO_4$ | $C_{18}H_{20}AsLiO_3$ | $C_{18}H_{20}AsNaO_4$ | $C_{48}H_{83}AsNaO_7$ | $C_{46}H_{78}NaO_6Sb$ | $C_{32}H_{30}As_2MgO_6$ | $C_{18}H_{38}AsCl_3InLiO_5$ | $C_{46}H_{40}As_3O_7P$ |
| FW | 529.29 | 382.20 | 366.20 | 398.25 | 870.05 | 871.82 | 684.71 | 637.51 | 960.51 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Triclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P1$ | $P2_1/n$ | $P2_1/c$ | $C2$ | $Cc$ | $Pbca$ | $P\bar{1}$ |
| $a$/Å | 11.7360(5) | 12.5633(3) | 8.5317(3) | 12.5803(10) | 14.440(3) | 27.506(3) | 8.4986(6) | 17.155(3) | 13.075(3) |
| $b$/Å | 17.3904(8) | 7.5209(6) | 9.7835(5) | 7.6097(7) | 19.134(4) | 10.440(2) | 22.694(2) | 18.028(4) | 14.159(3) |
| $c$/Å | 12.5818(6) | 18.9855(8) | 11.7665(6) | 19.678(2) | 19.562(4) | 19.595(3) | 16.2467(11) | 18.480(4) | 15.026(3) |
| $\alpha$/° | 90 | 90 | 112.465(3) | 90 | 90 | 90 | 90 | 90 | 97.50(3) |
| $\beta$/° | 98.619(3) | 105.605(2) | 102.759(3) | 103.446(10) | 109.36(3) | 121.486(12) | 105.137(4) | 90 | 111.62(3) |
| $\gamma$/° | 90 | 90 | 96.788(3) | 90 | 90 | 90 | 90 | 90 | 117.04(3) |
| $U$/Å$^3$ | 2538.9(2) | 1727.8(2) | 862.55(7) | 1832.2(3) | 5099.1(18) | 4798.5(13) | 3024(7) | 5715(2) | 2149.0(7) |
| $Z$ | 4 | 4 | 2 | 4 | 4 | 4 | 4 | 8 | 2 |
| $T$/K | 100(2) | 100(2) | 100(2) | 150(2) | 100(2) | 150(2) | 100(2) | 150(2) | 150(2) |
| μ(Mo–$K_\alpha$)/mm$^{-1}$ | 0.55 | 1.98 | 1.98 | 1.89 | 0.72 | 0.63 | 1.50 | 2.279 | 2.406 |
| Reflections collected | 20 437 | 34 967 | 10 780 | 4196 | 58 037 | 4690 | 34 110 | 91 098 | 35 408 |
| Unique reflections | 5803 | 4451 | 6662 | 3715 | 11 668 | 4585 | 4962 | 6540 | 9793 |
| $R_{int}$ | 0.0573 | 0.0730 | 0.0390 | 0.0300 | 0.0657 | 0.0734 | 0.0600 | 0.1246 | 0.0441 |
| $R1$ [$I > 2\sigma(I)$] | 0.0504 | 0.0340 | 0.0365 | 0.0436 | 0.0471 | 0.0765 | 0.0681 | 0.0665 | 0.0311 |
| w$R2$ (all data) | 0.0977 | 0.1102 | 0.0932 | 0.1199 | 0.1045 | 0.1943 | 0.1630 | 0.1521 | 0.0699 |



group 2 β-diketonate complexes, which has been well developed, primarily due to the wide utilisation these complexes have found as precursors to thin films in MOCVD technology.[11] In this study many attempts were made to prepare both arsa- and stibadionato complexes of group 2 metals *via* the reaction of hetero-enols, **8**, with metal alkyls and amides. In all cases involving the stiba-enols, reactions occurred but decomposition of the products rapidly took place above 0 °C to give elemental antimony and a mixture of other products. The reactions involving arsa-enols were cleaner but in most cases inseparable mixtures of products resulted. The one exception to this was the moderately yielding formation of the bis(arsadionato)magnesium complex, **12**, from the reaction depicted in Scheme 3. The compound is moderately thermally stable (dec. 137 °C) and its NMR spectroscopic data are compatible with a monomeric octahedral complex incorporating one chelating DME molecule. The infrared spectrum of **12** displays strong absorptions ($\nu$ 1524, 1548 cm$^{-1}$) in the expected region for a dionato ligand chelating a metal centre.

An X-ray crystal structure analysis of **12** confirmed this and showed the magnesium centre to have a distorted octahedral geometry (Fig. 7, Table 1). The distances from the metal centre to the arsadionate oxygen centres are all similar (2.016 Å ave.) and close to those normally seen for magnesium β-diketonate complexes, that is 2.006 Å ave. in [Mg{OC(Bu$^t$)C(H)-C(Bu$^t$)O}$_2$(TMEDA)],[12] but longer than the interactions of the DME ligand with the magnesium centre (Mg–O 2.130 Å ave). As in the previously mentioned sodium and lithium arsadionate complexes the ligands are delocalised, as evidenced by the As–C (1.922 Å ave.) and C–O (1.253 Å ave.) bond lengths, which are intermediate between double and single bonded interactions.[9] In addition, both arsadionate ligands are essentially planar and co-planar with the phenyl substituents. Presumably the latter observation arises from the conjugative stability that this arrangement affords the complex.




**Scheme 3** *Reagents and conditions*: (*i*) DME, Na{N(SiMe$_3$)$_2$}, −HN(SiMe$_3$)$_2$; (*ii*) DME, MgBu$_2$, −BuH.

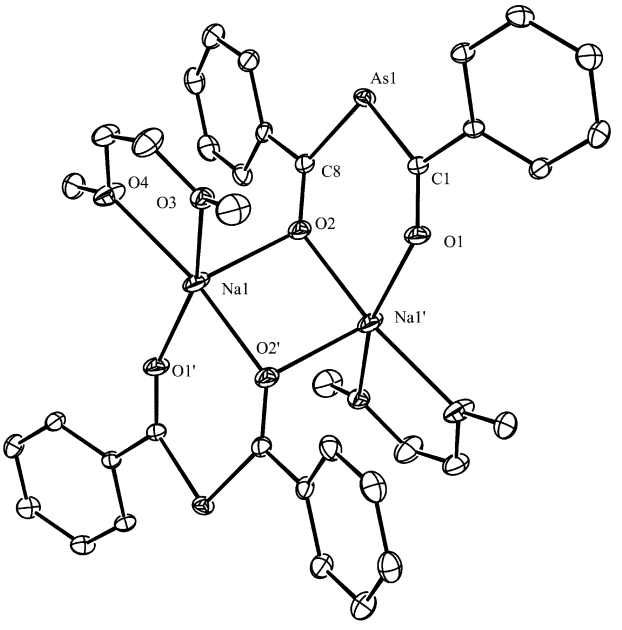



**Fig. 4** Molecular structure of compound **9**. Selected bond lengths (Å) and angles (°): As(1)–C(8) 1.916(3), As(1)–C(1) 1.939(3), O(1)–C(1) 1.242(4), O(2)–C(8) 1.248(4), O(1)–Na(1)′ 2.201(3), O(2)–Na(1)′ 2.261(3), Na(1)–O(4) 2.295(3), Na(1)–O(2) 2.342(4), Na(1)–O(3) 2.554(17), C(8)–As(1)–C(1) 101.24(14), O(1)–C(1)–As(1) 127.6(3), O(2)–C(8)–As(1) 127.1(3), C(8)–O(2)–Na(1) 120.4(3), C(8)–O(2)–Na(1)′ 120.4(3), C(1)–O(1)–Na(1)′ 140.3(3), O(1)′–Na(1)–O(2) 110.08(14), O(2)′–Na(1)–O(2) 89.17(12). Symmetry operation ′: $-x$, $-y+1$, $-z$.

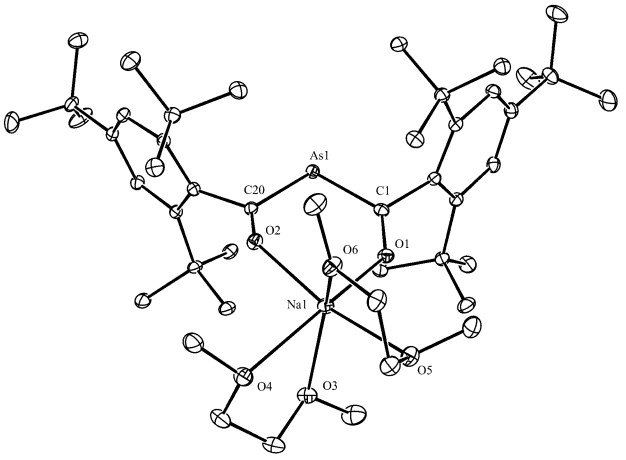



**Fig. 5** Molecular structure of compound **10**. Selected bond lengths (Å) and angles (°): As(1)–C(1) 1.911(2), As(1)–C(20) 1.943(2), Na(1)–O(2) 2.2351(17), Na(1)–O(1) 2.3036(17), Na(1)–O(5) 2.3777(19), Na(1)–O(3) 2.3967(18), Na(1)–O(6) 2.4177(18), Na(1)–O(4) 2.4830(19), O(1)–C(1) 1.243(3), O(2)–C(20) 1.236(3), C(1)–As(1)–C(20) 101.60(9), O(2)–Na(1)–O(1) 83.45(6), O(3)–Na(1)–O(4) 66.25(6), O(5)–Na(1)–O(6) 68.28(6), C(1)–O(1)–Na(1) 135.61(14), C(20)–O(2)–Na(1) 136.27(13), O(1)–C(1)–As(1) 128.20(16), O(2)–C(20)–As(1) 129.06(15).

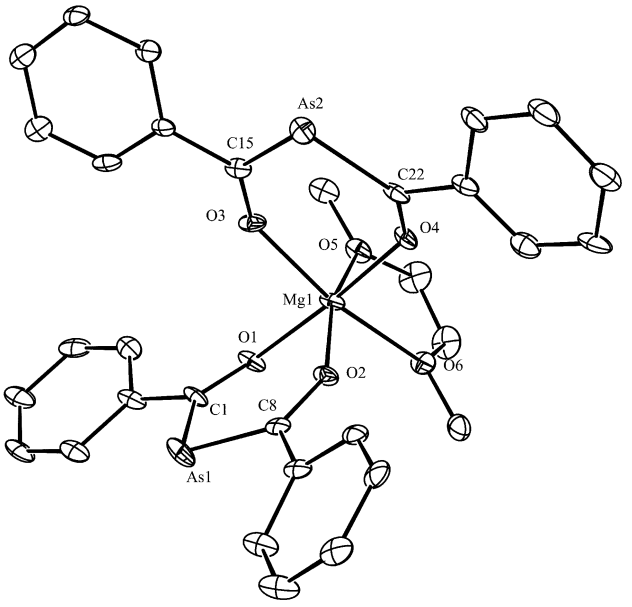



**Fig. 7** Molecular structure of compound **12**. Selected bond lengths (Å) and angles (°): As(1)–C(8) 1.916(10), As(1)–C(1) 1.938(9), As(2)–C(15) 1.908(10), As(2)–C(22) 1.928(9), Mg(1)–O(3) 2.000(6), Mg(1)–O(2) 2.007(6), Mg(1)–O(4) 2.028(7), Mg(1)–O(1) 2.029(7), Mg(1)–O(6) 2.129(6), Mg(1)–O(5) 2.131(6), O(1)–C(1) 1.253(9), O(2)–C(8) 1.251(10), O(4)–C(22) 1.261(9), O(3)–C(15) 1.250(9), C(8)–As(1)–C(1) 99.1(4), O(3)–Mg(1)–O(4) 88.5(3), O(2)–Mg(1)–O(1) 88.4(3), O(6)–Mg(1)–O(5) 74.5(3), C(1)–O(1)–Mg(1) 132.3(6), O(1)–C(1)–As(1) 127.6(8), C(15)–As(2)–C(22) 99.2(4), C(8)–O(2)–Mg(1)–137.7(7), C(15)–O(3)–Mg(1) 137.5(7), C(22)–O(4)–Mg(1) 132.0(6), O(2)–C(8)–As(1) 126.8(7), O(3)–C(15)–As(2) 127.2(8), O(4)–C(22)–As(2) 127.6(8).

## Group 13

There have been no reported examples of arsa- or stibadionato group 13 complexes. In order to initiate this field the reactions of **2** and **3** with "GaI"[13] were examined. The intention here was to utilise the bulky *tert*-butyl substituents on the dionato ligands to stabilise gallium carbene analogues, [:Ga{$\eta^2$-*O*,*O*–OC(Bu$^t$)EC(Bu$^t$)O}], E = As, Sb, related examples of which, derived from diazabutadiene[14] and β-diketiminato[15] ligands, have recently been reported. Unfortunately, these reactions were not clean and led to intractable mixtures of products. It is noteworthy that a similar result occurred when **2** was reacted with $GaCl_3$ in 1:1 or 3:1 stoichiometries.

More success was had when **2** was treated with 1 equiv. of InCl, though the outcome was not expected. When the reaction was carried out in a $Et_2O$–DME mixture, the unusual complex, **13**, was formed in good yield (Scheme 4). This is best considered as containing an anionic arsenic centre that forms a donor-acceptor As–In bond but also possesses an uncoordinated lone pair. The arsadionate ligand in the complex is acting as a localised diacylarsenide, which additionally chelates a cationic Li(OEt$_2$)(DME) fragment through dative interactions with its oxygen centres. This unusual complex can be thought of as an intermediate in a salt elimination reaction that would give [InCl$_2${$\eta^2$-*O*,*O*–OC(Bu$^t$)AsC(Bu$^t$)O}]. However, heating solutions of **13** to 50 °C did not lead to this complex but an inseparable mixture of many products. In addition, attempts to prepare **13** by the direct treatment of $InCl_3$ with **2** in a DME–$Et_2O$ solvent mixture led to no reaction, presumably because of the low solubility of $InCl_3$ in this solvent system.

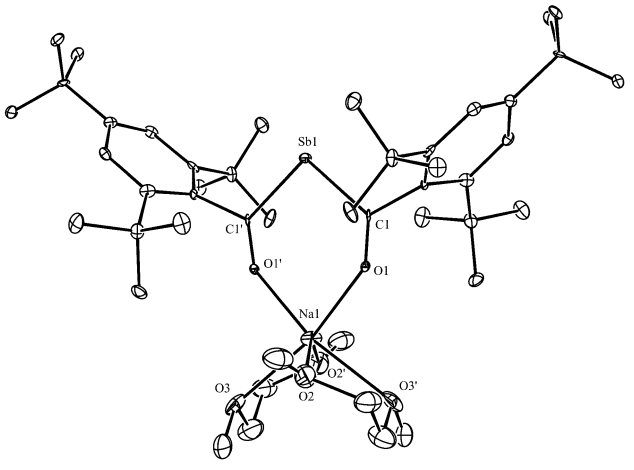
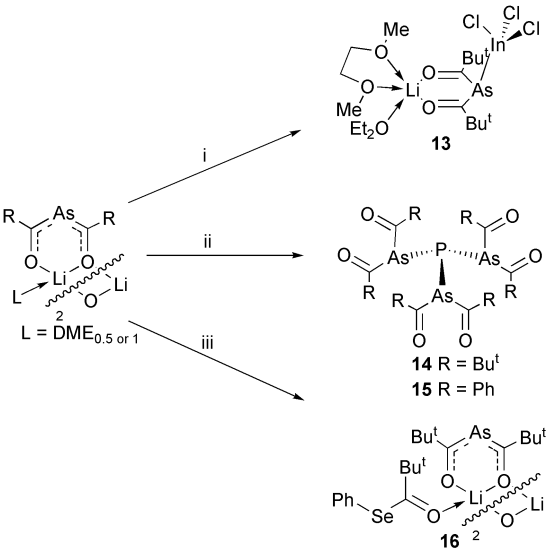



**Fig. 6** Molecular structure of compound **11**. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.156(11), Na(1)–O(1) 2.282(12), Na(1)–O(2) 2.381(12), Na(1)–O(3) 2.474(16), O(1)–C(1) 1.222(16), C(1)–Sb(1)–C(1)′ 96.0(6), O(1)–Na(1)–O(1)′ 83.0(5), O(2)–Na(1)–O(3)′ 75.2(5), O(1)–C(1)–Sb(1) 127.5(8). Symmetry operation ′: $-x+1$, $y$, $-z+1$.




**Scheme 4** *Reagents and conditions*: (*i*) InCl, DME–$Et_2O$, −LiCl, $-In_{(s)}$; (*ii*) $PCl_3$, DME, −LiCl; (*iii*) PhSeCl, DME, −LiCl.

With regards to a mechanism of formation for **13** it seems likely that in the presence of the arsenic lone pairs of **2**, InCl disproportionates into $InCl_3$ and indium metal with a concomitant formation of the observed complex. Indeed, it is well known that when treated with group 15 donors InCl can disproportionate[16] and in the current reaction significant amounts of indium metal deposition were observed.

The spectroscopic data for **13** are fully consistent with its proposed formulation. In particular its infrared spectrum shows acyl C–O stretching bands in the region normally observed for localised diacylarsenide ligands but at higher frequencies than in delocalised arsadionates. The molecular structure of **13** is depicted in Fig. 8 (Table 1). It is monomeric and its lithium centre possesses a distorted trigonal bipyramidal coordination environment with O(2) and O(4) in apical positions and all Li–O interactions in the normal range. An examination of the As–C (2.026 Å ave.) and acyl C–O (1.204 Å) bond lengths shows them to be normal for single and double interactions, and to be respectively longer and shorter than the related bonds in delocalised arsadionato complexes, such as **6**. The geometry about the arsenic centre is heavily distorted pyramidal with both the In–As–C (92.66° ave.) and C–As–C [98.9(3)°] angles being acute. The acuteness of these angles implies that a high degree of p-character exists in the bonds to As(1) and therefore that its lone pair has predominantly s-character. The indium centre in **13** has a slightly distorted tetrahedral environment with the In–Cl bond lengths in the normal range and an As–In bond length [2.6094(9) Å] somewhat shorter than the mean for all crystallographically determined In–As bonds (2.725 Å).[9] The reason for this lies with the fact that compound **13** contains the only example of an In–As bond in which the arsenic centre is 3-coordinate and not bridging two indium centres.

## Group 14

There are no known examples of arsa- or stibadionato-group 14 complexes. In this study a variety of reactions were carried out to address this paucity but all met with failure. These included the treatment of 2 equiv. of the lithium heterodionates, **2** or **3**, with either $SnCl_2$ or $PbCl_2$ which in all cases led to no reaction occurring, presumably as a result of the low solubility of the metal salts. To overcome this problem 2 equiv. of the arsa-enol, **8** R = Ph, E = As, were reacted with $[M\{N(SiMe_3)_2\}_2]$, M = Sn or Pb (*cf.* the formation of **9** and **10**), but only intractable mixtures of products were formed. Similarly, the reactions of **2** or **3** with $Me_2SnCl_2$, $Me_2SiCl_2$ and $Ph_3SnCl$ all afforded oily mixtures of many products that could not be separated by normal techniques.

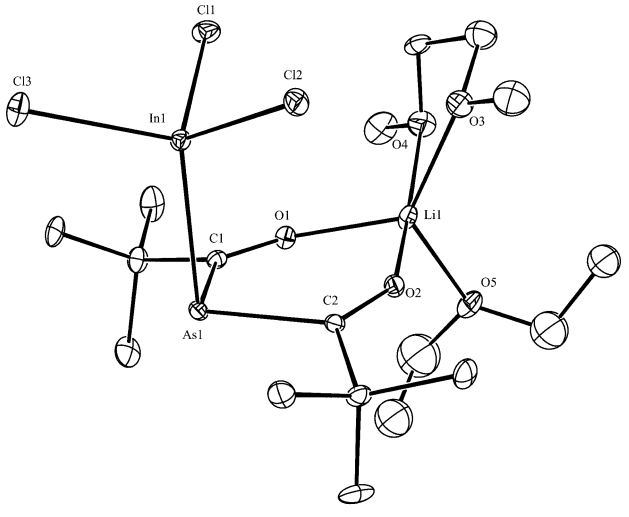



**Fig. 8** Molecular structure of compound **13**. Selected bond lengths (Å) and angles (°): In(1)–Cl(3) 2.3680(18), In(1)–Cl(1) 2.3744(19), In(1)–Cl(2) 2.3748(18), In(1)–As(1) 2.6094(9), As(1)–C(2) 2.024(6), As(1)–C(1) 2.028(6), O(1)–C(1) 1.209(8), O(1)–Li(1) 1.976(13), O(2)–C(2) 1.200(7), O(2)–Li(1) 2.015(12), O(3)–Li(1) 2.135(15), O(4)–Li(1) 2.097(14), O(5)–Li(1) 1.990(14), C(2)–As(1)–C(1) 98.9(3), C(2)–As(1)–In(1) 93.60(17), C(1)–As(1)–In(1) 91.72(18), Cl(3)–In(1)–Cl(1) 106.60(7), Cl(3)–In(1)–Cl(2) 106.84(7), Cl(1)–In(1)–Cl(2) 106.83(8), Cl(3)–In(1)–As(1) 111.51(6), Cl(1)–In(1)–As(1) 112.55(5), Cl(2)–In(1)–As(1) 112.14(5), C(1)–O(1)–Li(1) 141.2(5), C(2)–O(2)–Li(1) 140.7(2), O(1)–C(1)–As(1) 123.5(5), O(2)–C(2)–As(1) 123.5(5).

## Group 15

In a preliminary communication[7] we have recently reported the synthesis of the first diacylarsenido group 15 compounds, $P[As\{C(O)R\}_2]_3$, R = $Bu^t$ **14**, Ph **15**, which were formed in the 3:1 reactions of the lithium arsadionates, **2** and **6**, with $PCl_3$ (Scheme 4). Interestingly, when the analogous reactions with either $AsCl_3$ or $SbCl_3$ were carried out, elemental arsenic or antimony deposited and the known tetraacyldiarsanes, $[As\{C(O)R\}_2]_2$,[2] were formed in high yields *via* oxidative coupling reactions. Reactions of the less stable stibadionate, **3**, with $ECl_3$, E = P, As or Sb, led to intractable mixtures of products. We have subsequently also found that the reactions of 1 or 2 equiv. of **2** or **6** with $PCl_3$ do not lead to the formation of the mono- or bis(arsino)phosphines, $Cl_nP[As\{C(O)R\}_2]_{3-n}$, $n$ = 1 or 2, but instead the tris(arsino)phosphines, **14** or **15**, are formed leaving unreacted $PCl_3$.

The spectroscopic data for both compounds have previously been discussed and will not be further analysed here, though full synthetic details for the two compounds are included in the experimental section. In addition, details of the X-ray crystal structure of **15** are reported here for the first time, Fig. 9

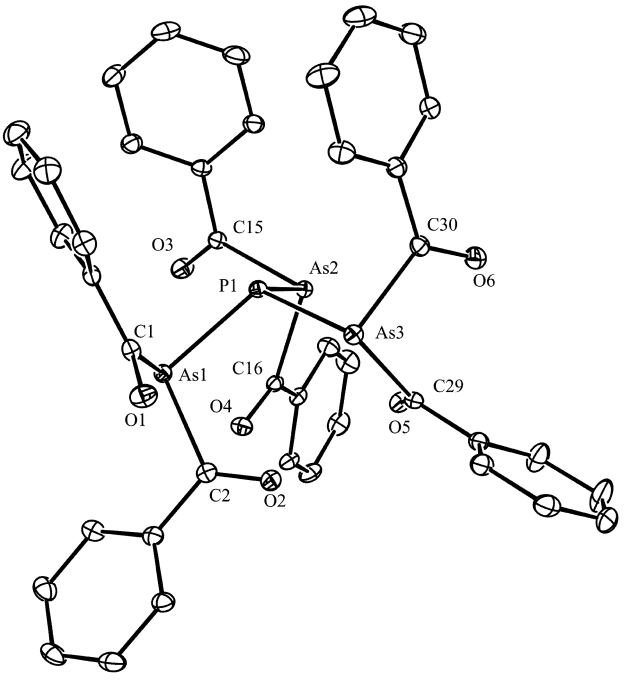



**Fig. 9** Molecular structure of compound **15**. Selected bond lengths (Å) and angles (°): As(1)–C(2) 2.023(2), As(1)–C(1) 2.027(3), As(1)–P(1) 2.3010(9), As(2)–C(15) 2.027(2), As(2)–C(16) 2.037(2), As(2)–P(1) 2.3057(15), As(3)–C(29) 2.031(2), As(3)–C(30) 2.037(2), As(3)–P(1) 2.3063(9), O(1)–C(1) 1.211(3), O(2)–C(2) 1.210(3), O(3)–C(15) 1.209(3), O(4)–C(16) 1.207(3), O(5)–C(29) 1.210(3), O(6)–C(30) 1.209(3), C(2)–As(1)–C(1) 90.94(9), C(15)–As(2)–C(16) 93.39(9), C(29)–As(3)–C(30) 89.18(9), As(1)–P(1)–As(2) 105.79(5), As(1)–P(1)–As(3) 108.63(3), As(2)–P(1)–As(3) 105.72(4), O(1)–C(1)–As(1) 121.22(18), O(2)–C(2)–As(1) 123.12(17), O(3)–C(15)–As(2) 120.33(17), O(4)–C(16)–As(2) 121.03(17), O(5)–C(29)–As(3) 122.00(16), O(6)–C(30)–As(3) 119.39(17).

(see Table 1). The compound is isostructural and isomorphous with its tris(diacylphosphino)phosphine analogue, P[P{C(O)Ph}$_2$]$_3$,[7] and as such contains a molecule of diethyl ether of crystallisation in its asymmetric unit. The structure is also closely related to that of **14** in that it has a central pyramidal phosphorus atom [ave. As–P–As 106.7°, *cf.* 108.39(11)° in **14**] with As–P bonds (2.304 Å ave.) almost equivalent to those in **14** [2.3054(19) Å] but slightly shorter than the mean for all crystallographically determined As–P interactions (2.33 Å).[9] The three diacylarsenido ligands are not planar and contain localised As–C single and C–O double bonds as was the case in **13**. Another similarity with that compound is the acuteness of the angles about each arsenic centre [As(1) 96.0° ave., As(2) 96.3° ave., As(3) 95.1° ave.], which again are compatible with a significant degree of p-character in the bonds involving arsenic centres.

### Group 16

There have been no reported complexes of arsa- or stibadionates with group 16 elements. In this study a number of reactions of **2** and **3** with group 16 halides, such as $Se_2Cl_2$, $SOCl_2$, PhSeCl and PhTeCl, were carried out but all led to the formation of largely inseparable mixtures of decomposition products. It is worth mentioning that in the 1:1 reaction of **2** with PhSeCl one such product, [({PhSeC(Bu$^t$)=O}Li{$\eta^2$-*O*,*O*–OC(Bu$^t$)AsC(Bu$^t$)O})$_2$] **16**, was isolated in very low yield (< 10%) and its preparation could not be reproduced (Scheme 4). The compound was identified by a poor quality X-ray crystal structure that is not included here but unambiguously confirmed the molecular connectivity of the compound. The mechanism of formation of **16** is unknown but presumably involves the selenodiacylarsenide, [PhSeAs{C(O)Bu$^t$}$_2$], as an unstable intermediate that undergoes As–C bond cleavage and rearrangement to generate the selenaester, PhSeC(O)Bu$^t$, which displaces DME of solvation from the lithium arsadionate starting material, **2**, to form the observed complex. Arsenic–carbon bond cleavages in diacylarsenido complexes have been observed before[4] and most likely lead to the decomposition observed in the other group 16 based reactions mentioned above.

## Conclusions

In summary, the preparation and structural characterisation of a variety of group 1, 2, 13 and 15 complexes incorporating 2-arsa-or 2-stiba-1,3-dionato ligands in either their delocalised form ($\eta^2$-*O*,*O* coordination), their localised diacylpnictido form ($\eta^1$-*E* coordination), or a combination of the two modes ($\eta^1$-*E*–:$\eta^2$-*O*,*O*–) has been reported. The study has highlighted the coordinative versatility of heterodionate ligands and has shown that they can behave similarly to β-diketonates in their coordination chemistry but also that significant differences are possible. The utility of the prepared sodium heterodionates as transfer reagents in lanthanide complex formation is currently being explored and will be discussed in a forthcoming publication.

## Experimental details

### General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether, DME and hexane were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. $^1$H, $^{31}$P and $^7$Li NMR spectra were recorded on either Bruker DPX400 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual $^1$H or $^{13}$C resonances of the solvent used ($^1$H and $^{13}$C NMR), external 85% $H_3PO_4$, 0.0 ppm ($^{31}$P NMR), or 1 M $LiNO_3$, 0.0 ppm ($^7$Li NMR). A $^{13}$C NMR spectrum of **5** could not be obtained due to its very low solubility in normal deuterated solvents at ambient temperature. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were obtained from the Warwick Microanalytical Service. Where reproducible microanalyses were not obtained the sample was either extremely air sensitive and/or variable amounts of solvent of crystallisation were present. However, the NMR spectra of these samples suggested their purity was greater than 95%. The starting materials **2**,[6] **8**,[5,6] Li{As(SiMe$_3$)$_2$}[17] and Li{Sb(SiMe$_3$)$_2$}[18] were prepared by literature procedures. All other reagents were used as received.

### Syntheses

**[{Li[$\eta^2$-*O*,*O*–OC(Ad)SbC(Ad)O](OEt$_2$)}$_2$], 5.** A solution of adamantoyl chloride (0.66 g, 3.3 mmol) in DME (20 ml) was added over 20 min to a solution of [Li{Sb(SiMe$_3$)$_2$}(DME)] (1.22 g, 3.3 mmol) in DME (20 ml) at −50 °C. The resulting brown solution was warmed to ambient temperature and stirred overnight in the absence of light. Volatiles were removed *in vacuo* and the residue washed with hexane (40 ml) to leave an orange powder, which was recrystallised from diethyl ether (10 ml) at −30 °C to yield **5** as orange blocks (0.56 g, 73%). M.p. 94–96 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.12 (t, 12H, OCH$_2$C*H*$_3$, $^3J_{HH}$ 8 Hz), 1.66–2.16 (m, 60H, Ad), 3.26 (q, 8H, OC*H*$_2$, $^3J_{HH}$ 8 Hz); IR (Nujol, $\upsilon$/cm$^{-1}$) 1578 s, 1545 s; MS APCI: *m*/*z* 135 (Ad$^+$, 100), 147 (AdC$^+$, 5), 164 (AdCO$^+$, 32%).

**[{Li[$\eta^2$-*O*,*O*–OC(Ph)AsC(Ph)O](DME)}$_2$], 6.** A solution of benzoyl chloride (0.88 ml, 7.5 mmol) in DME (10 ml) was added over 20 min to a solution of [Li{As(SiMe$_3$)$_2$}(DME)] (1.19 g, 3.8 mmol) in DME (20 ml) at −50 °C. The resulting orange solution was warmed to ambient temperature and stirred overnight in the absence of light. Volatiles were removed *in vacuo* and the residue washed with hexane (40 ml) to leave a red powder, which was recrystallised from DME (10 ml) at −30 °C to yield **6** as red rods (1.17 g, 82%). M.p. 106–108 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 2.91 (s, 8H, OCH$_2$), 2.93 (s, 12H, OCH$_3$), 7.42–8.17 (m, 20H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 58.7 (OCH$_3$), 70.6 (OCH$_2$), 125.8, 128.5, 131.7 (Ar–CH), 146.6 (*ipso*-C), 241.1 (AsC); $^7$Li (97.2 MHz, $C_6D_6$) $\delta$ −0.42; IR (Nujol, $\upsilon$/cm$^{-1}$) 1581 s, 1547 s; MS APCI: *m*/*z* 105 (PhCO$^+$, 100%).

**[{Li[$\eta^2$-*O*,*O*–OC(Ph)AsC(Ph)O](OEt$_2$)}$_2$], 7.** A solution of benzoyl chloride (0.88 ml, 7.5 mmol) in DME (10 ml) was added over 20 min to a solution of [Li{As(SiMe$_3$)$_2$}(DME)] (1.19 g, 3.8 mmol) in DME (20 ml) at −50 °C. The resulting orange solution was warmed to ambient temperature and stirred overnight in the absence of light. Volatiles were removed *in vacuo* and the residue washed with hexane (40 ml) to leave a red powder, which was recrystallised from diethyl ether (15 ml) at −30 °C to yield **7** as red rods (0.95 g, 70%). M.p. 124–126 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.13 (t, 12H, OCH$_2$C*H*$_3$, $^3J_{HH}$ 8 Hz), 3.27 (q, 8H, OCH$_2$, $^3J_{HH}$ 8 Hz), 7.02–8.22 (m, 20H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 14.2 (OCH$_2$*C*H$_3$), 64.5 (OCH$_2$), 125.0, 128.4, 131.2 (Ar–CH), 146.2 (*ipso*-C), 241.3 (AsC); $^7$Li (97.2 MHz, $C_6D_6$) $\delta$ −0.22; IR (Nujol, $\upsilon$/cm$^{-1}$) 1595 s, 1579 s; MS APCI: *m*/*z* 105 (PhCO$^+$, 100), 77 (Ph$^+$, 53%).

**[{Na[$\eta^2$-*O*,*O*–OC(Ph)AsC(Ph)O](DME)}$_2$], 9.** A solution of Na{N(SiMe$_3$)$_2$} (0.35 g, 1.9 mmol) in DME (20 ml) was added over 20 min to a solution of the diacylarsane **8**, R = Ph,

E = As, (0.59 g, 2.0 mmol) in DME (20 ml) at −50 °C. The resulting orange solution was warmed to ambient temperature and stirred overnight in the absence of light. Volatiles were removed *in vacuo* and the residue washed with hexane (40 ml) to leave a red powder, which was recrystallised from DME (5 ml) at −30 °C to yield **9** as red rods (0.51 g, 67%). M.p. 118–120 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 2.73 (s, 12H, $OCH_3$), 2.99 (s, 8H, $OCH_2$), 7.55–8.33 (m, 20H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 59.2 ($OCH_3$), 71.2 ($OCH_2$), 126.2, 127.4, 131.8 (Ar–CH), 148.0 (*ipso*-C), 238.1 (AsC); IR (Nujol, $\upsilon$/cm$^{-1}$) 1642 s, 1598 s; MS APCI: $m/z$ 286.8 [PhC(O)As$^+$, 100], 105 (PhCO$^+$, 65%).

**[Na{η$^2$-*O*,*O*–OC(Mes*)AsC(Mes*)O}(DME)$_2$], 10.** A solution of Na{N(SiMe$_3$)$_2$} (0.055 g, 0.3 mmol) in DME (20 ml) was added over 20 min to a solution of the diacylarsane **8**, R = Mes*, E = As, (0.20 g, 0.3 mmol) in DME (20 ml) at 25 °C. The resulting solution was heated at reflux for 3 h after which time the yellow solution was concentrated *in vacuo* to 5 ml and placed at −30 °C overnight to yield **10** as yellow cubic crystals (0.18 g, 71%). M.p. 240–250 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.42 (s, 18H, *p*-Bu$^t$), 1.93 (s, 36H, *o*-Bu$^t$), 3.18 (s, 8H, $OCH_2$), 3.21 (s, 12H, $OCH_2CH_3$), 7.63 (s, 4H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 30.2, 33.4 ($CCH_3$), 33.4, 37.2 ($CCH_3$), 57.4 ($OCH_2CH_3$), 70.0 ($OCH_2$), 121.6 (Ar–CH), 143.7, 146.4, 147.3, (quat. Ar–C), 202.1 (AsC); IR (Nujol, $\upsilon$/cm$^{-1}$) 1599 s, 1568 s; MS APCI: $m/z$ 286.8 [Mes*C(O)$^+$, 100%].

**[Na{η$^2$-*O*,*O*–OC(Mes*)SbC(Mes*)O}(DME)$_2$], 11.** A solution of Na{N(SiMe$_3$)$_2$} (0.10 g, 0.56 mmol) in DME (20 ml) was added over 20 min to a solution of the diacylstibane **8**, R = Mes*, E = Sb, (0.37 g, 0.56 mmol) in DME (20 ml) at 25 °C. The resulting solution was warmed to room temperature over 4 h over which time it became a bright pink colour. The volatiles were remove *in vacuo* and the resulting pink powder was extracted with DME (10 ml). This solution was concentrated *in vacuo* to 5 ml and placed at −30 °C overnight to yield **11** as purple cubic crystals (0.33 g, 68%). M.p. 86–88 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.20 (s, 18H, *p*-Bu$^t$), 1.72 (s, 36H, *o*-Bu$^t$), 3.04 (s, 8H, $OCH_2$), 3.09 (s, 12H, $OCH_2CH_3$), 7.41 (s, 4H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 30.2, 31.6 ($CCH_3$), 34.0, 37.2 ($CCH_3$), 57.5 ($OCH_2CH_3$), 70.0 ($OCH_2$), 121.9 (Ar-CH), 141.5, 146.2, 147.4, (quat. Ar–C), 210.3 (AsC); IR (Nujol, $\upsilon$/cm$^{-1}$) 1598 s, 1572 s; MS APCI: $m/z$ 286.8 [Mes*C(O)$^+$, 100%]; anal. found C 62.87, H 8.88%, calcd for $C_{46}H_{78}NaO_6Sb$: C 63.37, H 9.02%.

**[Mg{η$^2$-*O*,*O*–OC(Ph)AsC(Ph)O}$_2$(DME)], 12.** A solution of $MgBu_2$ (0.25 mmol) in DME (20 ml) was added over 20 min to a solution of the diacylarsane **8**, R = Ph, E = As, (0.15 g, 0.5 mmol) in DME (20 ml) at −50 °C. The resulting orange solution was warmed to ambient temperature and stirred overnight in the absence of light. Volatiles were removed *in vacuo* and the residue washed with hexane (40 ml) to leave a red powder, which was recrystallised from DME (5 ml) at −30 °C to yield **12** as red rods (0.11 g, 67%). M.p. 133–137 °C (dec.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 2.90 (s, 6H, $OCH_3CH_3$), 3.04 (s, 4H, $OCH_2$), 7.21–8.33 (m, 20H, ArH); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 58.0 ($OCH_3$), 69.5 ($OCH_2$), 124.5, 130.9, 132.6 (Ar–CH), 141.0 (*ipso*-C), 201.1 (AsC); IR (Nujol, $\upsilon$/cm$^{-1}$) 1548 s, 1524 s; MS APCI: $m/z$ 77 (Ph$^+$, 100), 105 (PhCO$^+$, 50%).

**[LiCl(Et$_2$O)(DME){η$^2$-*O*,*O*–Cl$_3$InAs[C(O)R]$_2$}], 13.** A solution of **2** (0.452 g, 1.52 mmol) in DME (30 ml) was added dropwise to a suspension of InCl (0.229 g, 1.52 mmol) in DME–$Et_2O$ (50:50, 25 ml) at −78 °C. The resulting pale yellow solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed *in vacuo* leaving indium deposits and a white powder, which was washed with hexane (30 ml), extracted with diethyl ether (50 ml) and filtered; the filtrate was placed at −30 °C overnight, yielding **13** as colourless crystals (yield 0.18 g, 56% based on proposed InCl disproportionation). M.p. 80 °C (decomp.); NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.10 (s, 18H. Bu$^t$), 1.13 [br, 6H, $CH_3$ ($Et_2O$)] 2.95 [s, 6H, $CH_3$ (DME)], 3.18 [s, 4H, $CH_2$ (DME)], 3.28 [br, 4H, $CH_2$ ($Et_2O$)]); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 15.0 [$CH_3$ ($Et_2O$)], 25.7 [C($CH_3$)$_3$], 52.3 ($CMe_3$), 59.1 [$CH_3$ (DME)], 65.8 [$CH_2$ ($Et_2O$)], 69.8 [$CH_2$ (DME)], 244.9 (AsC); IR (Nujol, $\upsilon$/cm$^{-1}$) AsCO 1693 s, 1675 s; MS APCI: $m/z$ 563 (M$^+$ − $Et_2O$, 10%).

**P[As{C(O)Bu$^t$}$_2$]$_3$, 14.** To a solution of **2** (0.840 g, 2.82 mmol) in DME (50 ml) was added $PCl_3$ (0.082 ml, 0.94 mmol) at −78 °C whilst stirring. The resulting yellow solution was stirred at room temperature for 24 h after which time it had turned orange. Volatiles were removed *in vacuo* leaving a yellow-orange residue, which was extracted with hexane (3 × 30 ml). The extract was filtered and place at −30 °C overnight, yielding yellow crystals of **14** (0.150 g, 21%). M.p. 184–186 °C (decomp). NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.29 (s, 54H, Bu$^t$); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 25.4 [C($CH_3$], 49.4 [$C$($CH_3$)], 225.2 (CO); $^{31}$P{$^1$H} (121.7 MHz, $C_6D_6$) $\delta$ −78.9 (s); IR (Nujol, $\upsilon$/cm$^{-1}$) 1708 s, 1660 s, 1475 m, 1363 m; MS APCI: $m/z$ 767.0 (M$^+$, 100); anal. found: C 46.67%, H 7.11%, calcd. for $C_{30}H_{54}O_6PAs_3$: C 47.0%, H 7.05%.

**P[As{C(O)Ph}$_2$]$_3$, 15.** To a solution of **6** (0.226 g, 0.59 mmol) in DME (50 ml) was added $PCl_3$ (0.017 ml, 0.197 mmol) at −78 °C whilst stirring. The resulting yellow solution was stirred at room temperature for 24 h after which it had turned orange. Volatiles were removed *in vacuo* leaving a yellow-orange residue, which was washed with hexane and extracted with diethyl ether (3 × 20 ml). The extract was filtered and placed at −30 °C overnight to yield **15** as yellow crystals (0.03 g, 18%). M.p. 130–132 °C (dec.). NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 6.65–6.75 (m, 12H, *m*-ArH), 6.85 (t, 6H, *p*-ArH, $^3J_{HH}$ = 8 Hz), 7.85 (d, 12H, *o*-ArH, $^3J_{HH}$ = 8 Hz); $^{13}$C (101.6 MHz, $C_6D_6$) $\delta$ 128.9 (*m*-Ar), 129.3 (*o*-Ar), 133.7 (*p*-Ar), 140.8 (*ipso*-Ar), 209.9 (AsC); $^{31}$P{$^1$H} (121.7 MHz, $C_6D_6$) $\delta$ −73.4; IR (Nujol, $\upsilon$/cm$^{-1}$) 1654.6 s, 1629.0 s, 1460 m, 1444 m; MS APCI: $m/z$ 317.1 [PAs(C(O)Ph)$_2^+$, 100], 285.9 [As(C(O)Ph)$_2$, 45%]; Anal. found: C 55.45%, H 3.41%, calcd. for $C_{42}H_{30}O_6PAs_3$: C 56.88%, H 3.39%.

**[({PhSeC(Bu$^t$)=O}Li{η$^2$-*O*,*O*–OC(Bu$^t$)AsC(Bu$^t$)O})$_2$], 16.** A solution of **2** (0.516 g, 1.35 mmol) in DME (30 ml) was added to a solution of PhSeCl (0.259 g, 1.35 mmol) in DME (20 ml) at −78 °C. The resulting yellow solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed *in vacuo* leaving an orange oil, which was extracted with hexane (30 ml), filtered and the filtrate placed at −30 °C overnight yielding **16** as yellow-orange crystals (0.05 g, 8%). M.p. 83–85 °C (dec.). NMR: $^1$H (400 MHz, $C_6D_6$) $\delta$ 1.04 (s, 18H, Bu$^t$), 1.30 (s, 36H, Bu$^t$), 7.04–7.49 (m, 8H, ArH); $^{13}$C (100.6 MHz, $C_6D_6$) $\delta$ 26.7, 28.3 [C($CH_3$)$_3$], 48.9, 49.6 ($CMe_3$), 126.5 (*m*-Ar), 128.7 (*o*-Ar), 129.2 (*p*-Ar), 136.4 (*ipso*-Ar), 208.1 (CO), 264.9 (AsCO); IR (Nujol, $\upsilon$/cm$^{-1}$) 1701 s, 1635 s, 1568 s, 1460 m, 1378 m; MS APCI: $m/z$ 227 [PhSeC(H)Bu$^{t+}$, 20%].

### Structure determinations

Crystals of **5**, **6**, **7**, **9**, **10**, **11**, **12**, **13** and **15** suitable for X-ray structure determination were mounted in silicone oil. Crystallographic measurements were made using either Nonius Kappa CCD or Enraf-Nonius CAD4 diffractometers. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods (SHELXL97[19] or SHELXL93[20]) using all unique data. Crystal data, details of data collections and refinements are given in Table 1. The

relatively high *R* factor for the structural determination of **11** results from the poor quality of the crystal used in the experiment. The assignment of the chiral space group *C*2 to the crystal structure of this compound is unambiguous based on systematic absences, in addition to the facts that the molecule is chiral, crystallises as its pure enantiomers [Flack parameter 0.01(6)] and sits on a 2-fold axis. The molecular structures of the complexes are depicted in Figs. 1–9, showing ellipsoids at the 30% probability level. CCDC reference numbers 195258–66. See http://www.rsc.org/suppdata/nj/b2/b210043f/ for crystallographic files in CIF or electronic format.

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