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Low-co-ordination arsenic and antimony compounds: synthesis and characterisation of 2-arsa- and 2-stiba-1,3-dionatolithium(I) complexes, $[\mathrm{Li\{\overline{OC(R)EC(R)O}\}L}]$ (E = As or Sb; R = $\mathrm{Bu^t}$, $\mathrm{C_6H_2Pr^i{}_3}$-2,4,6 or $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6; L = $\mathrm{Et_2O}$ or $\mathrm{MeOCH_2CH_2OMe}$)

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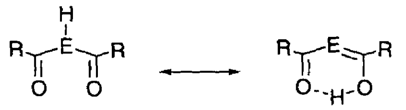
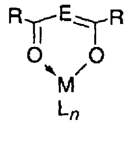
Reactions of $[\mathrm{Li\{E(SiMe_3)_2\}(dme)}]$ (E = As or Sb, dme = $\mathrm{MeOCH_2CH_2OMe}$), with a range of acid chlorides, RCOCl, afforded the novel 2-arsa-1,3-dionatolithium(I) complexes $[\mathrm{Li\{\overline{OC(R)AsC(R)O}\}L}]$ (R = $\mathrm{Bu^t}$, L = $\frac{1}{2}$ dme or $\mathrm{Et_2O}$; R = $\mathrm{C_6H_2Pr^i{}_3}$-2,4,6, L = $\mathrm{Et_2O}$; R = $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6, L = dme), and the first example of a 2-stiba-1,3-dionatolithium(I) complex $[\{[\mathrm{Li\{\overline{OC(Bu^t)SbC(Bu^t)O}\}(dme)_{0.5}}]_2\}_\infty]$. X-Ray crystal structural analyses for the complexes with R = $\mathrm{Bu^t}$, L = $\frac{1}{2}$ dme or $\mathrm{Et_2O}$ and the antimony compound show them to be dimeric in the solid state with respect to the metal and anionic ligands, the dimeric units being linked in an infinite polymeric chain by bridging dme molecules or solvated with $\mathrm{Et_2O}$. A dimeric structure can also be inferred when R = $\mathrm{C_6H_2Pr^i{}_3}$-2,4,6, L = $\mathrm{Et_2O}$. In solution these four compounds display fluxional behaviour. Treatment with HCl of the monomeric compound having R = $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6, L = dme yields the known diacylarsane $[\mathrm{As\{C(C_6H_2Bu^t{}_3\text{-}2,4,6)O\}\{C(C_6H_2Bu^t{}_3\text{-}2,4,6)OH\}}]$ the crystal structure of which reveals the enol form with the alcoholic proton intramolecularly hydrogen bonded to the opposing oxygen centre of the ligand.

The chemistry of low-co-ordination phosphorus compounds is a rapidly expanding field that has highlighted a remarkable ability for phosphorus to mimic the chemistry of carbon.[1] This is, perhaps, best exemplified by phosphaalkynes, P≡CR, which behave much more like alkynes than nitriles.[2] The analogy between carbon and phosphorus has been observed in a range of other systems, not least of which are the diacylphosphanes **Ia**–**Ii**[3] which display a solvent- and temperature-dependent keto–enol tautomerism in solution similar to that commonly observed for 1,3-diketones. X-Ray crystallographic studies have shown that diacylphosphanes **Id** and **Ih**[3c,d] normally occur in the enol form in the solid state. These similarities extend to metal complexes derived from analogous 2-phospha-1,3-dionato ligands, **1a**–**1o**,[3c,d,4] all structural studies of which, **1a**–**1c**, **1k**,[4a–c] show metal chelation through the oxygen atoms of the ligand in preference to phosphorus lone-pair co-ordination.

To the best of our knowledge the arsenic counterparts of these systems, *viz.* diacylarsanes and 2-arsa-1,3-dionates, can be confined to several examples, **Ij** and **Ik**[3d,e] and **1p**,[3d] only one of which, **Ij**,[3d] has been crystallographically characterised. Prior to this study there were no examples of related diacylstibanes or 2-stiba-1,3-dionates. This is not surprising considering the known decrease in stability of low-co-ordination Group 15 compounds with increasing molecular weight of the Group 15 element, a situation exemplified by the fact that compounds containing λ^3, σ^2-antimony centres are rare indeed.[5] As part of a continuing study aimed at stabilising low-co-ordination arsenic and antimony compounds[5,6] we have successfully synthesised and structurally characterised a series of novel 2-arsa- and 2-stiba-1,3-dionatolithium(I) complexes **2**–**6**, in addition to structurally characterising the known diacylarsane **Ik**. The results of these investigations are reported herein.



I E = P, R = Me **a**, $\mathrm{Bu^t}$ **b**, $\mathrm{C_6H_{11}}$ **c**, adamantyl **d**, $\mathrm{Pr^i}$ **e**, $\mathrm{CH_2Ph}$ **f**,
Ph **g**, $\mathrm{C_6H_2Me_3}$-2,4,6 **h** or $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6 **i**
E = As, R = $\mathrm{C_6H_2Me_3}$-2,4,6 **j** or $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6 **k**

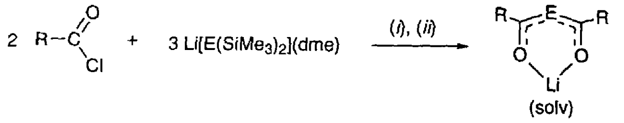


1 E = P, M = Ni, L_n = $[\mathrm{OC(Bu^t)PC(Bu^t)O}]$(dme), R = $\mathrm{Bu^t}$ **a**
M = Al, L_n = $[\mathrm{OC(Ph)PC(Ph)O}]_2$, R = Ph **b**
M = B, L_n = 1,5-$\mathrm{C_8H_{14}}$, R = Me **c** or Ph **d**,
M = Li, L_n = dme, R = Me **e**, Et **f**, $\mathrm{Pr^i}$ **g**, $\mathrm{Bu^t}$ **h**, $\mathrm{CH_2Ph}$ **i**,
$\mathrm{C_6H_{11}}$ **j**, Ph **k**, or *p*-$\mathrm{ClC_6H_4}$ **l**
M = Li, L_n = $(\mathrm{thf})_2$, R = adamantyl **m**, $\mathrm{C_6H_2Me_3}$-2,4,6 **n**
or $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6 **o**,
E = As, M = Li, L_n = $(\mathrm{thf})_{2\text{ or }3}$, R = $\mathrm{C_6H_2Me_3}$-2,4,6 **p**

dme = 1,2-dimethoxyethane, thf = tetrahydrofuran

Results and Discussion

Compounds **2**–**6** were prepared in moderate to high yields by the reactions outlined in Scheme 1. All reactions were carried out at −50 °C using 1,2-dimethoxyethane as solvent and slow warming to room temperature. In the cases of **3** and **4** the crude product was recrystallised from diethyl ether, which readily



	E	R	solv
2	As	Bu^t	$^1/_2$ dme
3	As	Bu^t	Et$_2$O
4	As	C$_6$H$_2$Pr$^i_3$-2,4,6	Et$_2$O
5	As	C$_6$H$_2$Bu$^t_3$-2,4,6	dme
6	Sb	Bu^t	$^1/_2$ dme

Scheme 1 (*i*) dme, −50 °C, −2 LiCl, −2 E(SiMe$_3$)$_3$; (*ii*) recrystallisation from solvent

effected exchange of lithium-co-ordinated dme for Et$_2$O. A similar exchange was observed for compound **6** but the resulting ether adduct was not fully characterised. Recrystallisation of **5** from Et$_2$O did not result in dme displacement. All compounds were characterised by their ^{1}H, ^{13}C and ^{7}Li NMR spectra, and elemental analyses where possible. Reproducible elemental analyses could not be obtained for **2**, **3** and **6** due to extreme thermal, photo- and oxygen sensitivity in the case of **6** and slow decomposition of **2** and **3** at room temperature. X-Ray crystallography, however, unequivocally identifies the molecular structures of these compounds. It is noteworthy that the only thermally stable arsaalkyne, As≡C(C$_6$H$_2$Bu$^t_3$-2,4,6),[7] is obtained as a by-product in the preparation of **5**.

The molecular structures of compounds **2** and **6** are depicted in Figs. 1 and 2 respectively with selective bond lengths and angles given in Tables 1 and 2. Their structures consist of dimeric units, [Li{OC(Bu^t)EC(Bu^t)O}]$_2$, E = As **2** or Sb **6**, linked in infinite polymeric chains by bridging dme molecules. Each dimeric moiety is generated by an inversion centre which gives rise to planar Li$_2$O$_2$ four-membered rings within the dimers. In a similar fashion the structure of **3** (Fig. 3, Table 3) consists of centrosymmetric dimers, [Li{OC(Bu^t)AsC(Bu^t)O}]$_2$, but in this case the availability of only one oxygen donor centre on the solvating Et$_2$O molecule prevents further oligomerisation. The lithium atoms in all structures have a similar distorted-tetrahedral geometry and are co-ordinated to four oxygen centres; two oxygens from one chelate ligand, one donor ether oxygen and one bridging oxygen from the symmetry-generated ligand. Interestingly in all known 2-phospha or 2-arsa-1,3-dionatolithium(I) complexes **1e**–**1p**,[3c,d,4c,d] each lithium centre is co-ordinated to at least two solvent oxygen centres, which in the only structurally characterised example, **1k**,[4c] at least, gives rise to a five-co-ordinate lithium. Why lower lithium co-ordination numbers were observed in this study is not known. In **2**, **3** and **6** the four-membered Li$_2$O$_2$ rings are necessarily planar and each six-membered chelate ring is non-planar with both the Group 15 element and lithium lying above the least-squares plane defined by both ring carbons and oxygens as follows: **2**, As (0.496, mean), Li (0.646, mean); **3**, As (0.106), Li (0.547); **6**, Sb (0.132, mean), Li (0.432 Å, mean).

The bond lengths within the six-membered chelate rings are suggestive of considerable double-bond delocalisation over the OCECO (E = As or Sb) frameworks of compounds **2**, **3** and **6**. All the As–C distances in **2** and **3** lie between normal single (1.96 Å)[8] and double bond lengths [*e.g.* 1.821(3) Å in (C$_5$H$_5$)Fe(CO)$_2$As=CBu^t(OSiMe$_3$),[9] 1.77 Å (theoretical) in HAs=CH$_2$[10]] but are considerably longer than other delocalised As–C double bonds (*e.g.* 1.85 Å in arsabenzene[11]). Similarly the Sb–C distances in **6** are shorter than normal single bond lengths (*e.g.* 2.21 Å mean in [Fe{η^2-[(Me$_3$Si)$_2$CH]$_2$Sb$_2$}(CO)$_4$][12]). The only localised Sb–C double bond which is available for comparison is 2.056(4) Å in the 2,3-distibabutadiene, [{Sb=C(C$_6$H$_2$Bu$^t_3$-2,4,6)(OSiMe$_3$)}$_2$],[5] which lies close to the theoretical value for the parent stibaalkene, HSb=CH$_2$ (2.01 Å),[10] and delocalised

Table 1 Selected bond lengths (Å) and angles (°) for [{[Li{OC(Bu^t)AsC(Bu^t)O}(dme)$_{0.5}$]$_2$}$_\infty$] **2**

As(1)–C(1)	1.886(7)	As(1)–C(2)	1.945(6)
As(2)–C(15)	1.926(5)	As(2)–C(16)	1.887(7)
O(1)–C(1)	1.254(6)	O(2)–C(2)	1.233(7)
O(3)–C(16)	1.235(7)	O(4)–C(15)	1.235(7)
O(5)–C(11)	1.427(11)	O(5)–C(12)	1.435(7)
O(6)–C(13)	1.420(10)	O(6)–C(14)	1.418(9)
Li(1)–O(1)	1.924(13)	Li(1)–O(1′)	1.945(10)
Li(1)–O(2)	1.849(13)	Li(1)–O(5)	2.001(11)
Li(2)–O(3)	1.919(10)	Li(2)–O(3″)	1.929(13)
Li(2)–O(4)	1.865(13)	Li(2)–O(6)	2.004(13)
C(1)–As(1)–C(2)	98.4(3)	C(15)–As(2)–C(16)	98.9(3)
As(1)–C(1)–O(1)	128.1(5)	As(1)–C(2)–O(2)	125.4(5)
As(2)–C(15)–O(4)	127.1(5)	As(2)–C(16)–O(3)	128.8(4)
Li(1)–O(1)–C(1)	125.5(6)	Li(1)–O(2)–C(2)	133.4(6)
Li(2)–O(3)–C(16)	127.2(6)	Li(2)–O(4)–C(15)	132.3(5)
Li(1)–O(5)–C(11)	115.9(5)	Li(1)–O(5)–C(12)	131.3(5)
Li(2)–O(6)–C(13)	126.7(5)	Li(2)–O(6)–C(14)	110.9(6)
O(1)–Li(1)–O(1′)	93.0(6)	O(1)–Li(1)–O(2)	96.5(5)
O(1)–Li(1)–O(5)	112.1(5)	O(1′)–Li(1)–O(2)	119.0(5)
O(1′)–Li(1)–O(5)	114.0(6)	O(2)–Li(1)–O(5)	117.3(6)
O(3)–Li(2)–O(3″)	91.1(6)	O(3)–Li(2)–O(4)	96.4(5)
O(3)–Li(2)–O(6)	106.8(5)	O(3″)–Li(2)–O(4)	126.9(7)
O(3″)–Li(2)–O(6)	106.2(6)	O(4)–Li(2)–O(6)	121.3(7)
Li(1)–O(1)–Li(1′)	87.0(5)	Li(2)–O(3)–Li(2″)	88.9(5)

Table 2 Selected bond lengths (Å) and angles (°) for [{[Li{OC(Bu^t)SbC(Bu^t)O}(dme)$_{0.5}$]$_2$}$_\infty$] **6**

Sb(1)–C(1)	2.184(7)	Sb(1)–C(2)	2.122(5)
Sb(2)–C(15)	2.173(5)	Sb(2)–C(16)	2.128(7)
O(1)–C(1)	1.219(7)	O(2)–C(2)	1.255(7)
O(3)–C(16)	1.247(7)	O(4)–C(15)	1.210(7)
O(5)–C(11)	1.415(9)	O(5)–C(12)	1.422(7)
O(6)–C(13)	1.409(11)	O(6)–C(14)	1.405(10)
Li(1)–O(1)	1.861(11)	Li(2)–O(6)	1.916(13)
Li(1)–O(2)	1.908(13)	Li(1)–O(5)	1.926(10)
Li(2)–O(3)	1.915(10)	Li(2)–O(3″)	1.896(11)
Li(2)–O(4)	1.874(12)		
C(1)–Sb(1)–C(2)	94.5(2)	C(15)–Sb(2)–C(16)	95.7(2)
Sb(1)–C(1)–O(1)	124.4(4)	Sb(1)–C(2)–O(2)	125.2(4)
Sb(2)–C(15)–O(4)	124.3(5)	Sb(2)–C(16)–O(3)	124.2(4)
Li(1)–O(1)–C(1)	135.9(6)	Li(1)–O(2)–C(2)	130.1(6)
Li(2)–O(3)–C(16)	128.0(5)	Li(2)–O(4)–C(15)	134.0(5)
Li(1)–O(5)–C(11)	113.7(5)	Li(1)–O(5)–C(12)	120.2(5)
Li(2)–O(6)–C(13)	121.4(6)	Li(2)–O(6)–C(14)	119.8(6)
O(2)–Li(1)–O(2′)	95.5(6)	O(1)–Li(1)–O(2)	99.4(5)
O(1)–Li(1)–O(5)	116.9(7)	O(1)–Li(1)–O(2′)	120.6(6)
O(2′)–Li(1)–O(5)	112.0(5)	O(2)–Li(1)–O(5)	107.8(6)
O(3)–Li(2)–O(3″)	93.9(5)	O(3)–Li(2)–O(4)	100.5(5)
O(3)–Li(2)–O(6)	107.6(5)	O(3″)–Li(2)–O(4)	123.6(6)
O(3″)–Li(2)–O(6)	111.2(5)	O(4)–Li(2)–O(6)	115.4(6)
Li(1)–O(2)–Li(1′)	84.5(5)	Li(2)–O(3)–Li(2″)	86.1(4)

Table 3 Selected bond lengths (Å) and angles (°) for [{Li[OC(Bu^t)AsC(Bu^t)O](Et$_2$O)}$_2$] **3**

As(1)–C(1)	1.947(5)	As(1)–C(6)	1.901(5)
Li(1)–O(1)	1.847(9)	Li(1)–O(2′)	1.899(9)
Li(1)–O(3)	1.914(10)	Li(1)–O(2)	1.934(9)
Li(1) · · · Li(1′)	2.61(2)	O(1)–C(1)	1.225(6)
O(2)–C(6)	1.256(6)	O(2)–Li(1′)	1.899(9)
O(3)–C(11)	1.413(9)	O(3)–C(13)	1.448(9)
C(6)–As(1)–C(1)	100.2(2)	O(1)–C(1)–As(1)	126.4(4)
O(2)–As(1)–C(6)	125.8(4)	C(2)–C(1)–As(1)	116.6(4)
C(7)–C(6)–As(1)	117.2(4)	C(1)–O(1)–Li(1)	131.8(4)
C(6)–O(2)–Li(1)	125.8(4)	Li(1′)–O(2)–Li(1)	85.8(4)
O(1)–Li(1)–O(2′)	121.8(5)	O(1)–Li(1)–O(3)	115.0(5)
O(2′)–Li(1)–O(3)	112.6(5)	O(1)–Li(1)–O(2)	96.8(4)
O(2′)–Li(1)–O(2)	94.2(4)	O(3)–Li(1)–O(2)	112.4(5)
C(6)–O(2)–Li(1′)	145.5(4)		

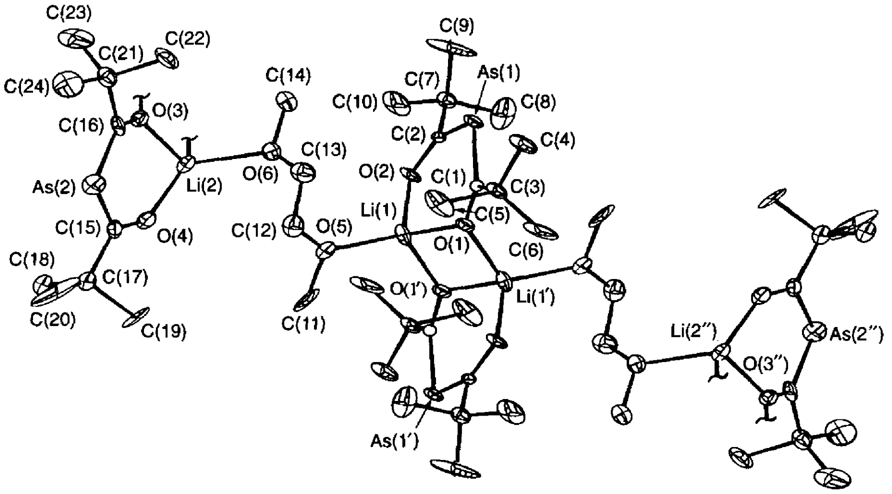


Fig. 1 Molecular structure of $[\{[\overline{\mathrm{Li}\{\mathrm{OC(Bu^t)AsC(Bu^t)O}}\}(\mathrm{dme})_{0.5}]_2\}_\infty]$ **2** showing 20% probability ellipsoids

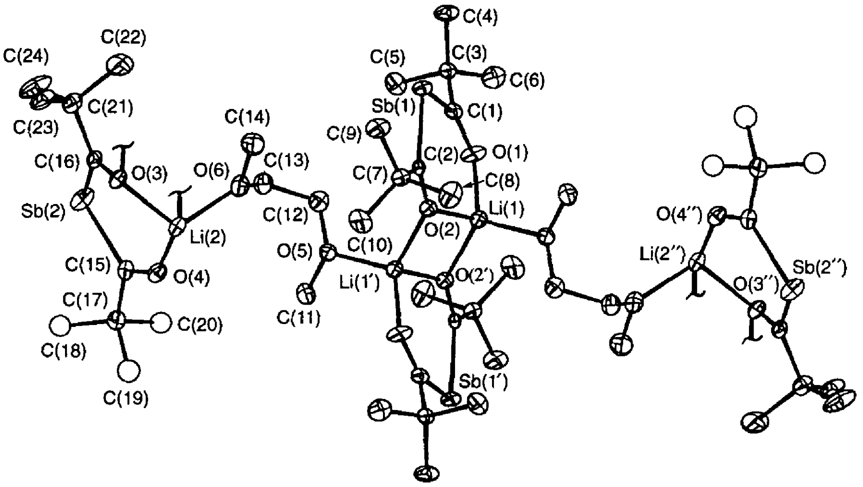


Fig. 2 Molecular structure of $[\{[\overline{\mathrm{Li}\{\mathrm{OC(Bu^t)SbC(Bu^t)O}}\}(\mathrm{dme})_{0.5}]_2\}_\infty]$ **6** showing 50% probability ellipsoids

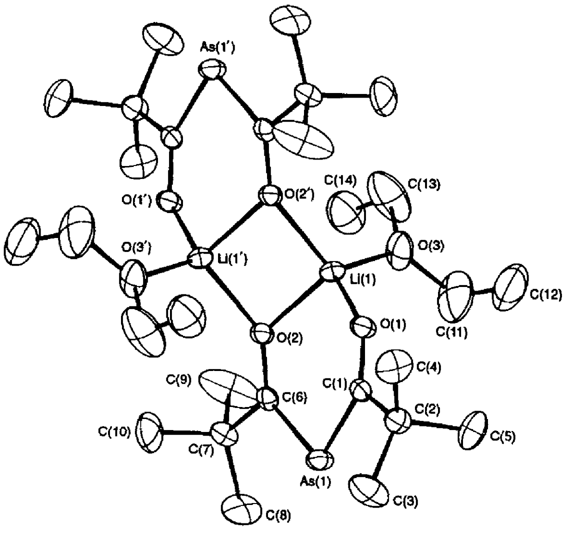


Fig. 3 Molecular structure of $[\{\overline{\mathrm{Li[OC(Bu^t)AsC(Bu^t)O}}](\mathrm{Et_2O})\}_2]$ **3** showing 50% probability ellipsoids

Sb–C double bonds (*e.g.* 2.05 Å in stibabenzene [13]). The fact that the E–C (E = As or Sb) bond lengths in **2**, **3** and **6** are closer to single than double bonds probably reflects the presence of a partial negative charge on the heterocentre. Further evidence for double-bond delocalisation comes from the intraring C–O distances which all lie between normal sp^2 (enol) single (1.33 Å) [8] and sp^2 (ketone) double bonds (1.19 Å).[8] Finally, the Li–O bonds in all structures lie in the normal range,[8] the oxygen-centres involved in bridging two lithium centres or belonging to the co-ordinated ether being further from Li than the two-co-ordinate chelate oxygens.

The solution ^{1}H and ^{13}C NMR spectra of compounds **2**–**6** are more symmetrical than would be expected if these compounds retained their solid-state structures in solution. This is most probably due to a rapid breaking and reforming of bridging Li–O bonds giving rise to a monomer–dimer equilibrium for these species in solution. Unfortunately, their low solubility in non-co-ordinating solvents precluded molecular-weight determinations. In addition, the low solubility in co-ordinating solvents at low temperature hindered attempts to observe a 'freezing out' of the proposed equilibrium by variable-temperature NMR studies.

As already mentioned, compound **5** does not exchange co-ordinated dme with Et$_2$O in solutions of the latter. The opposite is true for **2** and **6**, presumably because the dme molecule is not chelating in these cases but co-ordinates to the lithium centre *via* one oxygen, as found in the solid state. This suggests that the dme molecule chelates the Li atom in **5** and is therefore more difficult to exchange than in **2**. Considering that the steric bulk of the aryl substituent is considerably greater in this compound than in **2** and **6**, we propose that **5** exists as a monomer in solution and the solid state with a dme chelated, and thus a four-co-ordinate lithium centre. Unfortunately X-ray-quality crystals of **5** could not be grown and solution-state molecular-weight determinations could not be carried out (see above).

Solution-state NMR data for compound **4** highlight an inequivalence of the methyl groups within the isopropyl groups at the *ortho* positions of the aryl substituents. This is most likely a result of these groups being unable to rotate freely due to a steric preference for the methyne protons to be directed toward the six-membered dionato chelate ring, Fig. 4. As a result, in the ^{1}H NMR spectrum the inequivalent B and C methyl groups appear as broad doublets, each being coupled to the methyne proton A. The broadness of these doublets arises from poorly resolved ^4J(HH) coupling between the B and C groups. The methyne proton A has an equivalent 6 Hz coupling to the B and C methyl groups which gives rise to a quartet of quartets appearing as a virtual septet. The *p*-isopropyl substituent is freely rotating and is therefore manifested as a methyne proton septet coupled to six equivalent methyl protons. The ^{13}C NMR spectrum of **4** supports this assignment.

Our observation that As≡C(C$_6$H$_2$Bu$^t_3$-2,4,6) is obtained in the synthesis of compound **5** (Scheme 1) is at odds with a previous report by Märkl and Sejpka[3e] which describes the same reaction as affording the arsaalkyne and the related diacylarsane **Ik**. However, in that study the total reaction products were purified by column chromatography (silica gel) which probably caused the hydrolysis of **5** to **Ik**. Since structural studies on diacylarsanes are limited to only one example, **Ij**,[3d] we were keen to synthesise **Ik** under controlled conditions and investigate its structure in the solid state.

Compound **Ik** was prepared in good yield by the addition of a stoichiometric amount of anhydrous HCl to an ether solution of **5** (Scheme 2). The spectral data for **Ik** are consistent with the original report[3e] and point to it existing predominantly in the enol form in solution. The ^{1}H NMR spectrum displays a low-field resonance at δ 16.24 in the region normally associated with strongly hydrogen-bonded protons. Moreover, the symmetry of this spectrum is in accord with a fully delocalised structure undergoing rapid exchange of the alcoholic proton between the two oxygen centres of the molecule.

In the solid state, however, the molecular structure of compound **Ik** (Fig. 5, Table 4) shows it to exist in the enol form, but with localised As–C and C–O double bonds [As(1)–C(38) 1.855(4), C(37)–O(1) 1.264(4) Å] which compare well with the norms for these interactions mentioned earlier, and are significantly shorter than the As–C and C–O single bond interactions [As(1)–C(37) 1.952(4), C(38)–O(2) 1.331(4) Å]. The alcoholic proton, H(2), was located in Fourier-difference maps, refined isotropically, and found to be within bonding distance of O(2) [1.10(5) Å] with a more distant interaction with O(1) [1.44(5) Å], the angle O(1)–H(2)–O(2) being close to linear at 167.4°. The results of this crystal structure determination contrast with those for the only other structurally characterised diacylarsane **Ij**[3d] which displays fully delocalised As–C and C–O double bonds and an alcoholic proton that is predicted to have an equal interaction with both oxygen centres of the ligand.

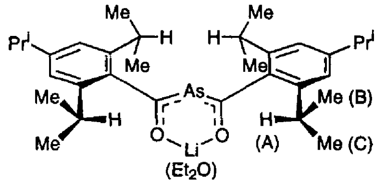
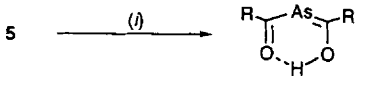


Fig. 4 Schematic representation of the static isopropyl groups in the solution structure of compound **4**



Ik R = C$_6$H$_2$Bu$^t_3$-2,4,6

Scheme 2 (*i*) HCl, Et$_2$O–dme, −50 °C, −LiCl

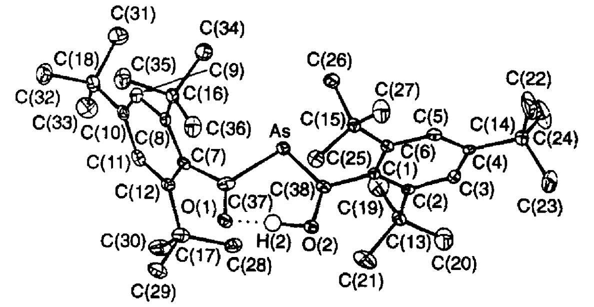


Fig. 5 Molecular structure of [As{C(C$_6$H$_2$Bu$^t_3$-2,4,6)O}{C(C$_6$H$_2$Bu$^t_3$-2,4,6)OH}] **Ik** showing 50% probability ellipsoids

Table 4 Selected bond lengths (Å) and angles (°) for [As{C(C$_6$H$_2$Bu$^t_3$-2,4,6)O}{C(C$_6$H$_2$Bu$^t_3$-2,4,6)OH}] **Ik**

As–C(38)	1.855(4)	As–C(37)	1.952(4)
O(1)–C(37)	1.264(4)	O(2)–C(38)	1.331(4)
O(2)–H(2)	1.10(5)	C(7)–C(37)	1.505(5)
C(1)–C(38)	1.500(5)	O(1)–H(2)	1.44(5)
C(38)–As–C(37)	97.1(2)	O(1)–C(37)–As	123.3(3)
O(2)–C(38)–As	124.8(3)	C(38)–O(2)–H(2)	98(2)
O(2)–H(2)–O(1)	167.4(5)	C(7)–C(37)–O(1)	123.2(4)
C(7)–C(37)–As	113.5(3)	O(2)–C(38)–C(1)	120.3(3)
O(2)–C(38)–C(1)	114.9(3)		

Experimental

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or dinitrogen. Solvents were distilled over Na/K alloy then freeze–thaw degassed prior to use. Pivaloyl chloride, 2,4,6-triisopropylbenzoyl chloride and 1 mol dm^{-3} anhydrous HCl solution in Et$_2$O were obtained from Aldrich and used without further purification. 2,4,6-Tri-*tert*-butylbenzoyl chloride,[14] [Li{As(SiMe$_3$)$_2$}(dme)][15] and [Li{Sb(SiMe$_3$)$_2$}(dme)][16] were prepared according to the literature procedures. Proton and ^{7}Li NMR spectra were recorded on a Bruker WM-250 spectrometer in deuteriated benzene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15) and 1 mol dm^{-3} LiNO$_3$ (δ 0.0) respectively, ^{13}C NMR spectra in deuteriated benzene (or mixtures with dme when greater solubility was required) on a Bruker AM 400 spectrometer using broad-band proton decoupling and referenced to the ^{13}C resonances of the deuteriated solvent (δ 128.00). Elemental analyses were performed by the Department of Chemistry Microanalytical Service, University of Wales, Cardiff. Melting points were determined in sealed glass capillaries under argon, and are uncorrected.

Syntheses

[{[Li{OC(Bu^t)AsC(Bu^t)O}(dme)$_{0.5}$]$_2$}$_\infty$] 2. A solution of pivaloyl chloride (0.46 g, 3.8 mmol) in dme (5 cm^3) was added over 30 min to a solution of [Li{As(SiMe$_3$)$_2$}(dme)] (1.80 g, 5.6 mmol) in dme (30 cm^3) at −50 °C. The resulting yellow-orange solution was warmed to room temperature and stirred overnight in the absence of light. Volatiles were removed under vacuum and the dark oily residue washed with hexane (2 × 30 cm^3) to leave a brown powder which was recrystallised from dme at −30 °C to yield compound **2** as pale yellow needles (0.26 g, 46% yield), m.p. 136 °C (decomp.) (298 K) NMR: ^{1}H (250 MHz, C$_6$D$_6$), δ 1.12 (18 H, s, Bu^t), 3.01 (3 H, s, OMe) and 3.10 (2 H, s, OCH$_2$); ^{13}C (100.6 MHz, C$_6$D$_6$–dme), δ 25.5 [C(*C*H$_3$)$_3$], 28.6 [*C*(CH$_3$)$_3$], 50.9 (OMe), 64.5 (OCH$_2$) and 223.5 (AsC); ^{7}Li (97.2 MHz, C$_6$D$_6$), δ 1.66.

Table 5 Crystal data for compounds [As{C(C$_6$H$_2$Bu$^t_3$-2,4,6)O}{C(C$_6$H$_2$Bu$^t_3$-2,4,6)OH}] **1k**, [{{Li[OC(Bu^t)AsC(Bu^t)O](dme)$_{0.5}$}$_2$}$_\infty$] **3**, [{Li[OC(Bu^t)AsC(Bu^t)O](Et$_2$O)}$_2$] **4** and [{{Li[OC(Bu^t)SbC(Bu^t)O](dme)$_{0.5}$}$_2$}$_\infty$] **7**

Compound	**1k**	**3**	**4**	**7**
Chemical formula	$C_{38}H_{59}AsO_2$	$C_{24}H_{46}As_2Li_2O_6$	$C_{28}H_{56}As_2Li_2O_6$	$C_{24}H_{46}Sb_2Li_2O_6$
M_w	622.77	594.4	652.5	688.0
Space group	*Pbca*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	20.607(3)	10.253(3)	9.847(3)	10.615(4)
b/Å	11.551(6)	10.933(15)	11.132(3)	10.696(4)
c/Å	29.973(9)	15.366(20)	16.420(5)	15.183(6)
α/°	90.0	110.05(10)	90.0	107.64(3)
β/°	90.0	100.52(7)	95.57(2)	102.16(3)
γ/°	90.0	96.62(7)	90.0	92.51(3)
U/Å^3	7135(5)	1561.2(8)	1791.4(9)	1595(1)
Z	8	2	2	2
T/K	150(2)	173(2)	173(2)	173(2)
λ/Å	0.710 69	0.710 73	0.710 73	0.710 73
D_c/g cm^{-3}	1.160	1.26	1.210	1.43
μ(Mo-Kα)/cm^{-1}	9.82	21.6	19.89	17.3
F(000)	2688	620	688	692
No. unique reflections	5651	5476	3150	7667
No. reflections with $I > 2\sigma(I)$	3110	3656	2024	5103
Crystal size/mm	0.24 × 0.26 × 0.22	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.2 × 0.2 × 0.15
Index range	$-22 \leqslant h \leqslant 23$, $-9 \leqslant k \leqslant 12$, $-32 \leqslant l \leqslant 33$	$0 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 18$	$0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 19$	$0 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-20 \leqslant l \leqslant 20$
θ range/°	2–25	2–25	2–25	2–28
Absorption correction factors T_{max}, T_{min}	1.15, 0.89	1.35, 0.72	1.00, 0.91	1.00, 0.96
R^a [for $I > 2\sigma(I)$]	0.0455	0.063	0.0546	0.054
wR^b (for all data)	0.1010	—	0.1078	—
[for $I > 2\sigma(I)$]	—	0.061	—	0.057

$^a R = \Sigma(\Delta F)/\Sigma(F_o)$; $\Delta F = |F_o| - |F_c|$. $^b wR = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o{}^2)^2\}]^{\frac{1}{2}}$ for **1k** and **4**; $[\Sigma\{w(\Delta F)^2\}/\Sigma\{w(F_o)^2\}]^{\frac{1}{2}}$ for **3** and **7**.

[{Li[OC(Bu^t)AsC(Bu^t)O](Et$_2$O)}$_2$] 3. Compound **2** (0.35 g, 1.18 mmol) was recrystallised twice from diethyl ether (10 cm^3) at −30 °C to afford pale yellow blocks of **3** (0.31 g, 82% yield), m.p. 123 °C (decomp.) NMR (298 K): ^{1}H (250 MHz, C$_6$D$_6$), δ 1.09 [6 H, t, CH$_2$C*H*$_3$, ^3J(HH) = 7], 1.15 (18 H, s, Bu^t) and 3.15 [4 H, q, OCH$_2$, ^3J(HH) = 7 Hz]; ^{13}C (100.6 MHz, C$_6$D$_6$–dme), δ 15.4 (CH$_2$*C*H$_3$), 25.5 [C(*C*H$_3$)$_3$], 28.5 [(*C*(CH$_3$)$_3$], 65.8 (OCH$_2$) and 223.4 (AsC); ^{7}Li (97.2 MHz, C$_6$D$_6$), δ 1.38.

[Li{OC(C$_6$H$_2$Pr$^i_3$-2,4,6)AsC(C$_6$H$_2$Pr$^i_3$-2,4,6)O}(Et$_2$O)] 4. A solution of 2,4,6-triisopropylbenzoyl chloride (1.34 g, 5.03 mmol) in dme (5 cm^3) was added over 30 min to a solution of [Li{As(SiMe$_3$)$_2$}(dme)] (2.40 g, 7.55 mmol) in dme (50 cm^3) at −50 °C. The resulting deep red solution was warmed to room temperature and stirred overnight in the absence of light. Volatiles were removed under vacuum and the dark oily residue washed with hexane (2 × 30 cm^3) to leave a red-orange powder which was recrystallised from diethyl ether (15 cm^3) at −30 °C to yield compound **4** as bright yellow needles (1.45 g, 86% yield), m.p. 143 °C (decomp.) NMR (298 K): ^{1}H (250 MHz, C$_6$D$_6$), δ 1.06 [6 H, t, CH$_2$C*H*$_3$, ^3J(HH) = 7], 1.12 [12 H, d, *p*-CH(C*H*$_3$)$_2$, ^3J(HH) = 6], 1.22 [12 H, br d, *o*-CH(C*H*$_3$)$_2$, ^3J(HH) = 6], 1.36 [12 H, br d, *o*-CH(C*H*$_3$)$_2$, ^3J(HH) = 6], 2.70 [2 H, spt, *p*-C*H*(CH$_3$)$_2$, ^3J(HH) = 6], 3.20 [4 H, q, OCH$_2$, ^3J(HH) = 7], 3.52 [4 H, spt, *o*-C*H*(CH$_3$)$_2$, ^3J(HH) = 6 Hz], and 7.02 (4 H, aryl H); ^{13}C (100.6 MHz, C$_6$D$_6$–dme), δ 13.7 (CH$_2$*C*H$_3$), 22.8 [*p*-*C*H(CH$_3$)$_2$], 23.7, 24.0 [*o*-*C*H(CH$_3$)$_2$], 64.3 (OCH$_2$), 119.9 (aryl CH), 141.3, 142.8, 147.6 (quaternary aryl) and 194.3 (AsC); ^{7}Li (97.2 MHz, C$_6$D$_6$), δ −0.50 (Found: C, 69.9; H, 10.05. C$_{36}$H$_{56}$AsLiO$_3$ requires C, 69.9; H, 9.10%).

[Li{OC(C$_6$H$_2$Bu$^t_3$-2,4,6)AsC(C$_6$H$_2$Bu$^t_3$-2,4,6)O}(dme)] 5. A solution of 2,4,6-tri-*tert*-butylbenzoyl chloride (1.42 g, 4.61 mmol) in dme (10 cm^3) was added over 30 min to a solution of [Li{As(SiMe$_3$)$_2$}(dme)] (2.20 g, 6.92 mmol) in dme (50 cm^3) at −50 °C. The resulting deep red solution was warmed to room temperature and stirred overnight in the absence of light. Volatiles were removed under vacuum and the dark oily residue washed with hexane (2 × 30 cm^3) to leave a yellow powder which was recrystallised from dme (5 cm^3) at −30 °C to yield compound **5** as bright yellow blocks (1.08 g, 65% yield), m.p. 153 °C (decomp.) NMR (298 K): ^{1}H (250 MHz, C$_6$D$_6$) δ, 1.28 (18 H, s, Bu^t), 1.78 (36 H, s, Bu^t), 2.96 (4 H, s, OCH$_2$), 3.18 (6 H, s, OMe) and 7.58 (4 H, s, aryl H); ^{13}C (100.6 MHz, C$_6$D$_6$–dme), δ 31.5, 34.7 (C*C*H$_3$), 34.9, 38.6 (*C*CH$_3$), 59.2 (OMe), 70.4 (OCH$_2$), 123.0 (aryl CH), 143.2, 145.1, 148.2 (quaternary aryl) and 195.3 (AsC); ^{7}Li (97.2 MHz, C$_6$D$_6$), δ −0.64 (Found: C, 70.0; H, 10.1. C$_{42}$H$_{68}$AsLiO$_4$ requires C, 70.15; H, 9.55%).

[{[Li{OC(Bu^t)SbC(Bu^t)O}(dme)$_{0.5}$]$_2$}$_\infty$] 6. A solution of pivaloyl chloride (0.57 g, 4.76 mmol) in dme (5 cm^3) was added over 30 min to a solution of [Li{Sb(SiMe$_3$)$_2$}(dme)] (2.60 g, 7.14 mmol) in dme (40 cm^3) at −50 °C. The resulting deep red solution was warmed to room temperature and stirred overnight in the absence of light. Volatiles were removed under vacuum and the deep red oily residue washed with hexane (2 × 30 cm^3) to leave a dark powder which was recrystallised from dme at −30 °C to yield compound **6** as bright orange blocks (0.28 g, 34% yield), m.p. 65 °C (decomp.) NMR (298 K): ^{1}H (250 MHz, C$_6$D$_6$), δ 1.24 (18 H, s, Bu^t), 2.95 (3 H, s, OMe) and 3.06 (2 H, s, OCH$_2$); ^{13}C (100.6 MHz, C$_6$D$_6$–dme), δ 27.3 [C(*C*H$_3$)$_3$], 30.6 [*C*(CH$_3$)$_3$], 51.2 (OMe), 62.1 (OCH$_2$) and 228.6 (SbC); ^{7}Li (97.2 MHz, C$_6$D$_6$), δ 1.54.

[As{C(C$_6$H$_2$Bu$^t_3$-2,4,6)O}{C(C$_6$H$_2$Bu$^t_3$-2,4,6)OH}] 1k. A 1 mol dm^{-3} solution of anhydrous HCl (0.8 mmol) in diethyl ether (0.8 cm^3) was added over 10 min to a solution of compound **5** (0.56 g, 0.8 mmol) in dme (15 cm^3) at −50 °C. The resulting yellow solution was warmed to room temperature, volatiles removed under vacuum and the yellow residue recrystallised from diethyl ether (7 cm^3) at −30 °C to yield **1k** as bright yellow needles (0.44 g, 88% yield) m.p. 211 °C. NMR (298 K): ^{1}H (250 MHz, C$_6$D$_6$), δ 1.37 (18 H, s, Bu^t), 1.76 (36 H, s, Bu^t), 7.68 (4 H, s, aryl H) and 16.24 (1 H, s, OHO); ^{13}C (100.6 MHz, C$_6$D$_6$), δ

31.3, 34.2 (CCH_3), 34.9, 38.2 (CCH_3), 123.2 (aryl CH), 138.0, 146.1, 150.4 (quaternary aryl) and 195.4 (AsC).

Crystallography

Crystals suitable for X-ray diffraction analysis were grown by crystallisation from diethyl ether, compound **3** and **Ik**, or dme, **2** and **6**, and mounted in oil. Intensity data were measured using either Enraf-Nonius CAD4 (**2**, **3** and **6**) or FAST[17] area detector diffractometers (**Ik**) using Mo-Kα radiation. The structures were solved either by direct (**2**, **3** and **Ik**), or heavy atom (**6**) methods (SHELXS 86[18]) and refined by least squares using the SHELXL 93,[19] (**Ik** and **3**) or MOLEN[20] (**2** and **6**) programs. The structures were refined on F using data with $I > 2\sigma(I)$ (**2** and **6**) or on F^2 using all data (**Ik** and **3**). Neutral-atom complex scattering factors were employed.[21] Empirical absorption corrections were carried out from ψ scans on **2** and **6** or by the DIFABS method[22] (**3** and **Ik**). Crystal data, details of data collections and refinement are given in Table 5. Anisotropic thermal parameters were refined for all non-hydrogen atoms of **Ik** and all but the lower-occupancy site for the disordered carbon C(7) in **3**, and the ordered carbons, C(1) in **2** and C(18)–C(20) in **6**. The hydrogen atoms in all structures were included in calculated positions (riding model) except H(2) in **Ik** which was located from difference maps and refined isotropically.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/135.

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