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A diarsagermylene and a diarsastannylene stabilised by arene···Ge/Sn interactions†

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The synthesis and structures of two new diarsatetrylenes {(Dipp)$_2$As}$_2$E are presented [E = Ge, Sn; Dipp = 2,6-diisopropylphenyl]. The high barrier to planarisation of As prevents stabilisation by As–E π-interactions; however, arene···Ge/Sn interactions stabilise these compounds by up to 181.4 kJ mol^{-1}. This represents a new stabilisation mode for this class of compounds.

Currently, there is intense interest in low oxidation state main group compounds, particularly with regard to their ability to activate small molecules such as H_2, CO_2 and NH_3.[1,2] This reactivity has been compared to that of transition metal complexes and, consequently, low oxidation state main group compounds have been posited as inexpensive and earth abundant alternatives to precious metal catalysts.[3]

One of the simplest, and most versatile, classes of low oxidation state main group compounds is the tetrylenes R_2E (E = Si, Ge, Sn, Pb). These electron-deficient compounds possess both a lone pair at the tetrel centre and a vacant p-orbital which lies perpendicular to the plane of the molecule and which act as the donor and acceptor orbitals, respectively, in small molecule activations. The energy difference between these donor and acceptor orbitals plays a key role in the reactivity of tetrylenes and, as a consequence, new methods to modulate this frontier orbital energy gap are of great interest. This energy gap is significantly increased by adjacent heteroatoms (*e.g.* N, O, S), which stabilise the tetrel lone pair through σ-withdrawing effects and destabilise the acceptor orbital

through π-interactions between the vacant p-orbital at the tetrel centre and the heteroatom lone pairs, resulting in lower reactivity.

The chemistry of diaminotetrylenes, $(R_2N)_2E$ (E = Si, Ge, Sn, Pb), the heavier group 14 element analogues of N-heterocyclic carbenes and their acyclic analogues, is well established.[4] In contrast, far less is known about their phosphorus- and arsenic-substituted homologues, *i.e.* diphosphatetrylenes, $(R_2P)_2E$, and diarsatetrylenes $(R_2As)_2E$.[5–8] Indeed, only three arsatetrylenes have been crystallographically authenticated (**1–3**), and, of these, compound **3** is the only example of a monomeric diarsatetrylene possessing a two-coordinate tetrel centre.[6a]

(1)

(2)

(3)

Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$

(4)

E = Ge, Sn

Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$
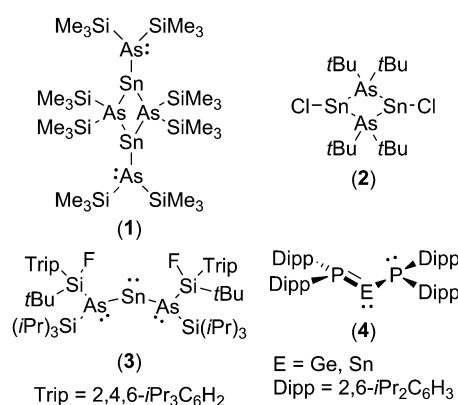
The low number of reported diphospha- and diarsatetrylenes may, at least in part, be attributed to the high barriers to planarisation of the heavier pnictogens, which prevents stabilisation of the electron-deficient tetrel centre through P–E/As–E π-interactions. Given the foregoing it is perhaps unsurprising that the arsenic centres in **3** adopt a pyramidal configuration with no evidence for As–Sn π-interactions.[6a] Nonetheless, it has been calculated that the heavier group 15 elements are as good π-donors as nitrogen if this barrier can be overcome.[9]

The barrier to planarisation of the heavier pnictogens may be lowered by several strategies, including (i) the use of sterically demanding substituents, (ii) the presence of electropositive

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substituents directly adjacent to the tetrel centre, and (iii) incorporation of the pnictogen centre into a ring.[10,11] In this regard, we recently reported the synthesis, solid state structures and dynamic behaviour of the unusual diphosphatetrylenes **4**, in which the phosphorus centres both possess sterically demanding substituents and lie directly adjacent to an electropositive germanium or tin centre[12,13] Compounds **4** adopt a configuration with one planar and one pyramidal phosphorus centre, with a single, stabilising P–E π-interaction.

Based on our successful synthesis of P–E π-stabilised diphosphatetrylenes, we conjectured that the steric and electronic properties of our ligands might be sufficient to enable the synthesis of a similarly stabilised diarsatetrylene. However, we anticipated that the higher barrier to planarisation of the arsenic centres in the target compounds compared to the corresponding phosphorus centres in **4** might have a significant impact on any propensity for As–E π-interactions.[14] We also anticipated that this, combined with the lower electronegativity of arsenic in comparison to phosphorus, would lead to a smaller frontier orbital gap in the resulting diarsatetrylenes and a consequently enhanced reactivity.

The reaction between amine-protected (iPr$_2$N)AsCl$_2$ and two equivalents of DippLi(OEt$_2$), followed by two equivalents of ethereal HCl gives the secondary chloroarsane (Dipp)$_2$AsCl (**5**) (Scheme 1) [Dipp = 2,6-iPr$_2$C$_6$H$_3$]. Treatment of **5** with LiAlH$_4$ gives the secondary arsane (Dipp)$_2$AsH (**6**) in excellent yield. Compound **6** is readily metalated by nBuLi in THF to give the sterically hindered arsanide [(Dipp)$_2$As]Li(THF)$_{2.75}$(Et$_2$O)$_{0.25}$ (**7**), after recrystallisation from diethyl ether, as a yellow crystalline solid; the constitution of **7** was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and X-ray crystallography (see ESI†).

The reaction between two equivalents of in situ generated **7** and GeCl$_2$(1,4-dioxane) in cold THF gives the diarsagermylene {(Dipp)$_2$As}$_2$Ge·PhMe (**8Ge**) as dark red prisms after crystallisation from toluene (Scheme 1). A similar reaction between **7** and SnCl$_2$ gives the diarsastannylene {(Dipp)$_2$As}$_2$Sn·PhMe (**8Sn**) as red-purple blocks. Compounds **8Ge** and **8Sn** are sensitive to air and moisture and solutions of these compounds decompose slowly at room temperature, or more rapidly on exposure to ambient light; in the solid state both **8Ge** and **8Sn** are reasonably stable at room temperature and can be manipulated without significant decomposition when exposure to light is kept to a minimum.
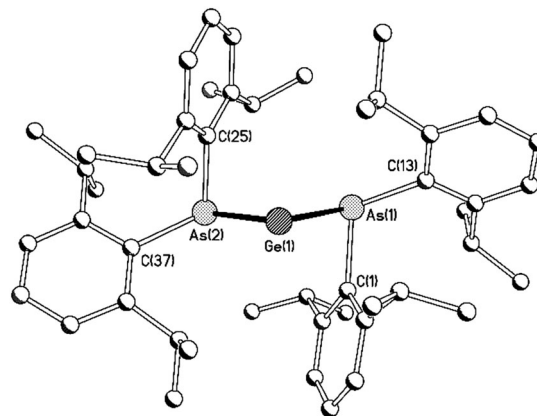

Fig. 1 Molecular structure of **8Ge** with H atoms and solvent of crystallisation omitted for clarity [compound **8Sn** is isostructural]. Selected bond lengths (Å) and angles (°): **8Ge** As(1)–Ge(1) 2.4851(4), As(2)–Ge(1) 2.4771(4), As(1)–C(1) 2.020(3), As(1)–C(13) 2.000(3), As(2)–C(37) 2.023(3), AS(2)–C(37) 2.001(3), Ge(1)···C(1) 2.666(3), Ge(1)···C(25) 2.710(2), As(1)–Ge–As(2) 90.808(13), Ge(1)–As(1)–C(1) 71.75(7), Ge(1)–As(1)–C(13) 108.70(8), Ge(1)–As(2)–C(25) 73.28(7), Ge(1)–As(2)–C(37) 109.94(8); **8Sn** As(1)–Sn(1) 2.6579(4), As(2)–Sn(1) 2.6644(4), As(1)–C(1) 1.994(3), As(1)–C(13) 2.020(3), As(2)–C(37) 1.995(3), AS(2)–C(37) 2.014(3), Sn(1)···C(1) 2.858(2), Sn(1)···C(37) 2.762(3), As(1)–Sn(1)–As(2) 91.004(11), Sn(1)–As(1)–C(1) 110.57(8), Sn(1)–As(1)–C(13) 73.91(7), Sn(1)–As(2)–C(25) 108.49(8), Sn(1)–As(2)–C(37) 70.79(8).

Compounds **8Ge** and **8Sn** are isostructural and isomorphous; each compound crystallises as a discrete molecular species with a molecule of toluene in the asymmetric unit (Fig. 1). Compound **8Ge** represents the first diarsagermylene to be crystallographically characterised, while **8Sn** is only the second monomeric diarsastannylene to be structurally authenticated.

As expected, the As–Ge distances in **8Ge** [2.4851(4) and 2.4771(4) Å] are significantly shorter than the corresponding distances in the tertiary arsane complexes {C$_6$H$_4$-1,2-(AsMe$_2$)$_2$}-GeI$_2$ [2.6210(11) and 2.6313(11) Å] and [{C$_6$H$_4$-1,2-(AsMe$_2$)$_2$}-GeCl][GeCl$_3$] [2.5847(5) Å],[15] the only other reported examples of As–Ge(II) bond lengths. Examples of As–Sn(II) bonds are more numerous and the As–Sn distances in **8Sn** [2.6579(4) and 2.6644(4) Å] are similar to the As–Sn distances in **3** [average 2.652(1) Å for the two crystallographically independent molecules in the asymmetric unit].[6a] The As–E–As angles [90.808(13) and 91.0004(11)° for **8Ge** and **8Sn**, respectively] suggest negligible hybridisation of the tetrel centres in these compounds and this is supported by DFT calculations (see below); the As–Sn–As angle in **8Sn** is slightly smaller than the corresponding angle in **3** [94.64(4)°].

In marked contrast to the phosphorus centres in **4**, both arsenic centres in **8Ge** and **8Sn** adopt a pyramidal geometry [sum of angles at As for **8Ge** = 285.86 and 287.76°; **8Sn** = 285.96 and 289.58°], consistent with the high barrier to planarisation of arsenic compared to phosphorus.[14] The pyramidal geometries of the arsenic centres necessarily preclude any stabilisation of the tetrel centres by As–Ge/Sn π-interactions. However, in both **8Ge** and **8Sn**, the ipso-carbon of one phenyl ring from each arsanide ligand lies in close proximity to the tetrel centre [Ge···C$_{ipso}$ 2.710(2) and 2.666(3) Å; Sn···C$_{ipso}$ 2.762(3) and 2.858(2) Å]. These distances are

Scheme 1 Synthesis of compounds **5–8**.

well within the sums of the van der Waals radii of Ge and C (3.81 Å) and of Sn and C (3.87 Å),[16] suggesting a significant interaction between the electron density at these *ipso*-carbon atoms and the vacant p-orbital at the tetrel centre. Consistent with this, the short Ge/Sn···C$_{ipso}$ distances are associated with rather acute C$_{ipso}$–As–Ge/Sn angles [**8Ge** 71.75(7) and 73.28(7)°; **8Sn** 70.79(8) and 73.91(7)°].

Group 14 element···arene interactions have been observed in a small number of Si(IV)-containing cations,[17] and in a limited number of compounds in which the tetrel centre is in the +2 oxidation state (*e.g.* **9–12**).[18–21] The Ge···C and Sn···C distances in **8Ge** and **8Sn** are similar to the corresponding distances in **11** [Ge···C 2.642(2) and 2.661(2) Å] and **12** [Sn···C 2.821(2) and 2.827(2) Å];[21] for comparison, the closest Sn···C distances in **9** are 3.27 and 3.35 Å,[19] suggesting a much weaker interaction in this case.
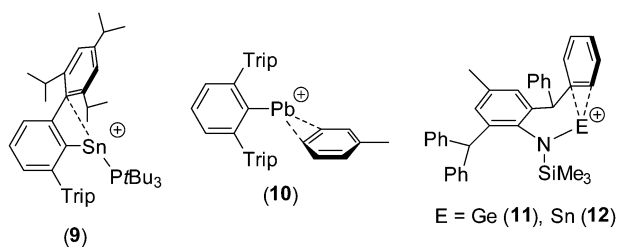
The room temperature ^{1}H NMR spectra of **8Ge** and **8Sn** consist of a single set of extremely broad signals due to the iPr and aromatic protons of the ligands, indicating dynamic exchange between the aromatic rings engaged in the E···C$_{ipso}$ interactions and those that are not. At −60 °C the iPr peaks decoalesce into eight methyl signals (spanning the range 0.48–1.42 ppm for **8Ge** and 0.51–1.52 ppm for **8Sn**) and four methine signals (spanning the range 2.51–4.86 ppm for **8Ge** and 2.80–4.93 ppm for **8Sn**), consistent with the C_2 symmetry of the solid-state structures. The large spread of methyl and methine signals in these spectra is due to the proximity (or not) of these protons to the aromatic rings or the arsenic lone pairs of the ligands.

We noted previously that, due to their inherently broad nature, the ^{119}Sn signals for **4Sn** and its more substituted analogue {(2,4,6-iPr$_3$C$_6$H$_2$)$_2$P}$_2$Sn (**13**) could not be located at room temperature and only a very broad signal (FWHM ca 2000 Hz) could be observed for **13** even at −95 °C.[12,13] This line-broadening is likely to be exacerbated by the presence of two adjacent quadrupolar ^{75}As nuclei in **8Sn** [^{75}As natural abundance 100%, I = 3/2], however, while we could not observe a signal at room temperature, in part due to the thermal instability of this compound in solution, at −60 °C we were able to locate a broad ^{119}Sn signal for **8Sn** at 547 ppm (FWHM 500 Hz). Although no ^{119}Sn NMR data are available for **2** and **3**,[6a,8b] the ^{119}Sn chemical shift of **8Sn** is similar to that observed for **1** (475 and 671 ppm for the *cis* and *trans* isomers, respectively)[8a] and **13** (440 ppm).[15]

The presence of significant Ge/Sn···C$_{ipso}$ interactions in **8Ge** and **8Sn** is supported by DFT calculations. Geometry optimisations at the B97D/6-311G(2d,p) [LANL2DZ for Sn] level of theory
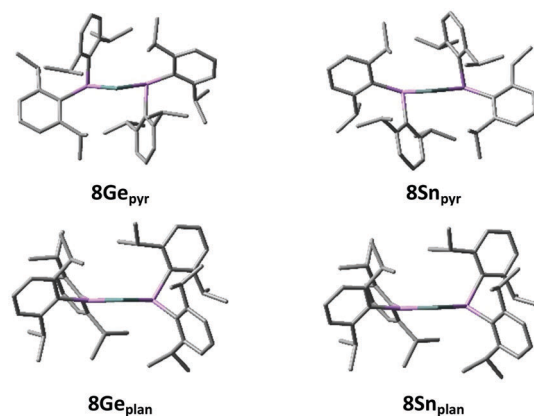

Fig. 2 Optimised geometries for the pyramidal (**8Ge$_{pyr}$** and **8Sn$_{pyr}$**) and planar (**8Ge$_{plan}$** and **8Sn$_{plan}$**) forms of {(Dipp)$_2$As}$_2$E (E = Ge, Sn) [B97D/6311G(2d,p) [LANL2DZ for Sn]].

give structures (**8Ge$_{pyr}$** and **8Sn$_{pyr}$**) which correlate well with those obtained by X-ray crystallography (see Fig. 2 and ESI†). In particular, the calculated structures replicate the short E···C$_{ipso}$ distances rather nicely [Ge···C$_{ipso}$ 2.757/2.644 Å, Sn···C$_{ipso}$ 2.849/2.848 Å].

The HOMO and LUMO for both **8Ge$_{pyr}$** and **8Sn$_{pyr}$** are largely based on the tetrel lone pair and the vacant p-orbital at the tetrel centre, respectively, although the LUMO has a significant component on the two nearby aromatic rings in each case (see ESI†). Natural Bond Orbital (NBO) analysis reveals that the tetrel lone pair in each case has >90% s-character, while the "vacant" orbital has essentially pure p-character. NBO analysis also reveals that this "vacant" orbital has an occupancy of 0.21 electrons in **8Ge$_{pyr}$** and 0.18 electrons in **8Sn$_{pyr}$**. This is associated with significant delocalisation of the As–C$_{ipso}$ σ-bonding electron density into this vacant orbital. Second order perturbation theory analysis shows that the approximate stabilisations afforded by these interactions (the $E(2)$ energies) are 77.2 and 65.8 kJ mol^{-1} for **8Ge$_{pyr}$** and 40.2 and 40.3 kJ mol^{-1} for **8Sn$_{pyr}$**. Consistent with this, the Wiberg Bond Indices (WBIs) for the Ge···C interactions are 0.114 and 0.099, while the WBIs for the Sn···C interactions are both 0.094. Although small, these WBIs indicate a significant bonding interaction in each case (*cf.* WBIs of 0.763 and 0.771 for the As–Ge bonds in **8Ge$_{pyr}$** and 0.726 for the two As–Sn bonds in **8Sn$_{pyr}$**). The foregoing clearly indicates that these C$_{ipso}$···E interactions stabilise the arsatetrylenes to a significant extent. In support of this, NBO deletions (in which the energy of the system is recalculated in the absence of the specified interactions) indicate that these interactions stabilise **8Ge$_{pyr}$** and **8Sn$_{pyr}$** by 181.4 and 106.2 kJ mol^{-1}, respectively.

For comparison, we have located minimum energy geometries for both **8Ge** and **8Sn** in which one of the arsenic centres is planar (*i.e.* the direct analogues of **4**, possessing Ge/Sn–As π-interactions), **8Ge$_{plan}$** and **8Sn$_{plan}$**. These lie 18.0 and 32.1 kJ mol^{-1}, respectively, higher in free energy than the ground state forms **8Ge$_{pyr}$** and **8Sn$_{pyr}$**.

It has been suggested that the energy gap between the singlet and triplet states (Δ_{S-T}) of tetrylenes correlates well with

their reactivities, with smaller gaps indicating higher reactivities.[22] For **8Ge_pyr** and **8Sn_pyr** Δ_{S-T} is calculated to be 79.8 and 90.0 kJ mol^{-1}, respectively, suggesting that these compounds should exhibit interesting reactivities [for comparison, Δ_{S-T} for the prototypical N-heterocyclic germylene $\{CHNH\}_2Ge$ has been calculated to be 195.0 kJ mol^{-1},[22c] consistent with the low reactivity of N-heterocyclic germylenes].

In summary, we have shown that the high barrier to planarisation of arsenic prevents the stabilisation of the diarsatetrylenes $\{(Dipp)_2As\}_2E$ through As–E π-interactions. However, canting of the aromatic rings in these compounds leads to a significant interaction between the *ipso* carbon atoms of the rings and the tetrel centres which stabilises the tetrylenes by up to 181.4 kJ mol^{-1}.

Conflicts of interest

There are no conflicts to declare.

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