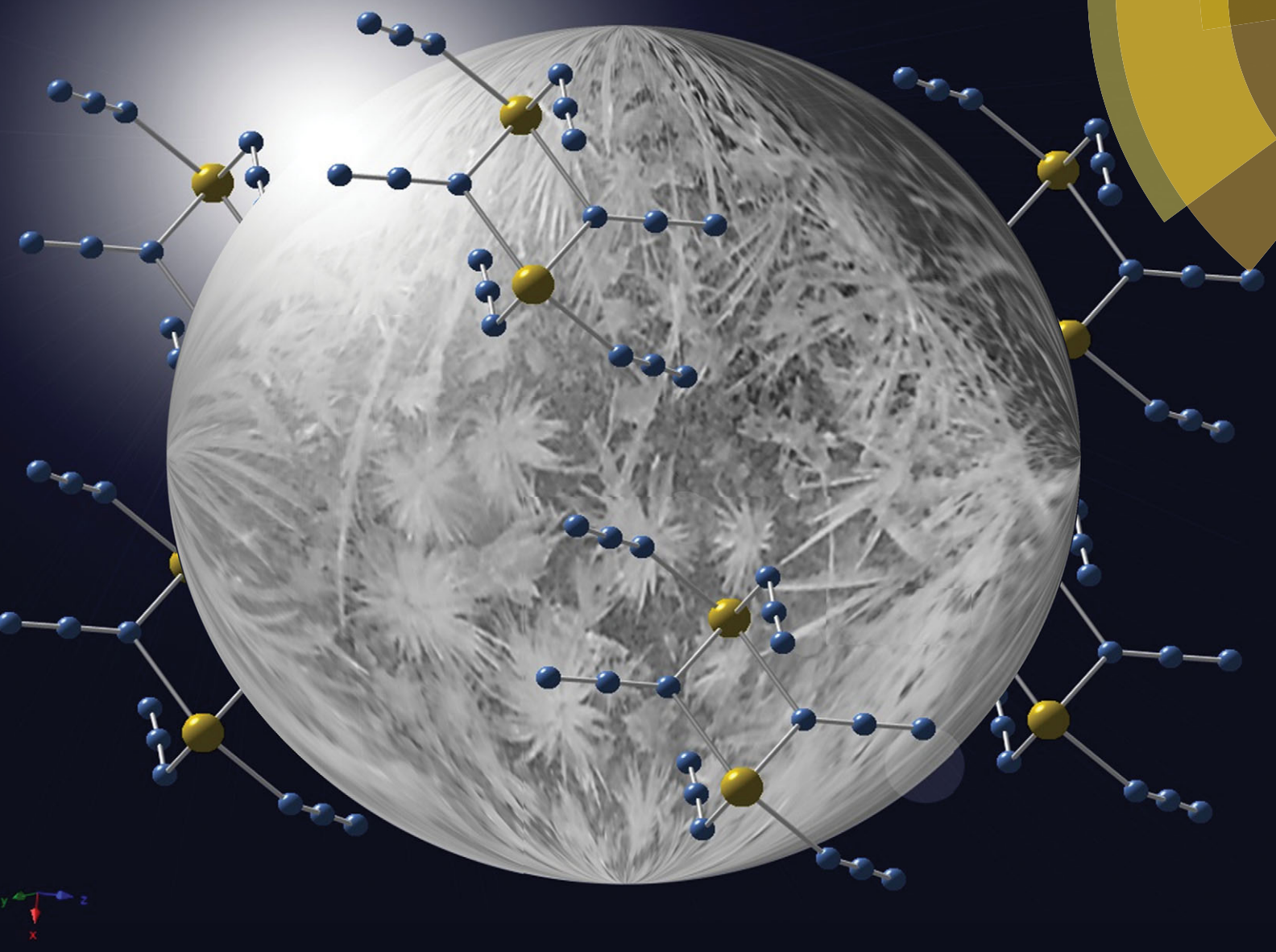


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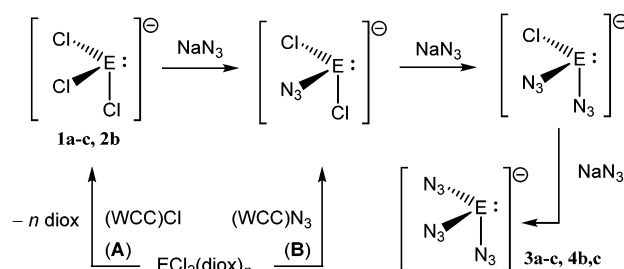
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## Homoleptic low-valent polyazides of group 14 elements†

Benjamin Peerless, Theo Keane, Anthony J. H. M. Meijer and Peter Portius\*

First examples of coordinatively unsaturated, homoleptic azido complexes of low-valent group 14 elements are reported. A simple strategy uses low-valent precursors, ionic azide transfer reagents and bulky cations to obtain salt-like compounds containing  $E(N_3)_3^-$  of Ge(II)/Sn(II) which are fully characterised, including XRD. Remarkably, these compounds are kinetically stable at r.t. and isolable in sub-gram quantities.

Binary azides are known for all elements in group 14 and exist as covalent  $E(N_3)_4$  compounds ( $E = C, Si$ ),<sup>2</sup> as hyper-coordinate  $E(N_3)_6^{2-}$  complexes ( $Si-Pb$ )<sup>1</sup> and as  $E(N_3)_2$  compounds ( $Sn, Pb$ ).<sup>5c</sup> However, no low-valent, homoleptic group 14 complex has yet been reported. All known binary p-block azides are highly endothermic primary explosives most of which possess exceedingly high electrostatic and friction sensitivities and a propensity to release  $N_2$ . As covalent, N-rich compounds, their isolation is generally challenging and experimental characterisation is limited.<sup>5</sup> In contrast, stability-inducing effects of hyper-coordination and of bulky, weakly coordinating counter ions (WCC)<sup>6</sup> allow many salt-like homoleptic polyazides to be synthesised in bulk and characterised fully, including *via* X-ray crystallography and IR spectroscopy,<sup>5a</sup> owing to azide groups ( $N_3$ ) giving rise to intense bands in the mid-IR region. It has been shown that azide anions ( $N_3^-$ ) are able to coordinate to low-valent centres in compounds such as  $E(L)(N_3)$  and  $E(L')(N_3)_2$ ,  $E = Ge, Sn$ .<sup>3,4</sup> On the other hand, the stability of low valent molecules, *e.g.* carbenes, silylenes, germylenes, stannylenes,<sup>7</sup> increases by saturating the electron deficient centre with sterically demanding, electron donating groups, such as N-based  $C(N^iPr)_2(N^iPr_2)$  and  $HC\{(CMe)(2,6-iPr_2C_6H_3N)\}_2$  ligands.<sup>7a,d</sup> This insight has led to tri- and tetracoordinate complexes bearing uni-, bi- and terdentate ligands, *e.g.*  $E(NHC)_2Cl$  and  $Ge\{HB(Me_2pz)_3\}Cl$ ,  $E = Si, Ge$ ;  $X = Cl, N_3$ ;  $NHC = N$ -heterocyclic carbene.<sup>4a,8</sup> Exploitation of these concepts has permitted the



Scheme 1 Synthesis of azido(chloro) germanates (1–) and stannates (1–),  $E = Ge, n = 1$  (**1**, **3**);  $E = Sn, n = 0$  (**2**, **4**); WCC =  $AsPh_4$  (**a**),  $PPh_4$  (**b**),  $N(PPh_3)_2$  (PPN, **c**).

synthesis and characterisation of the first low-valent and homoleptic Ge and Sn azides described in this paper.

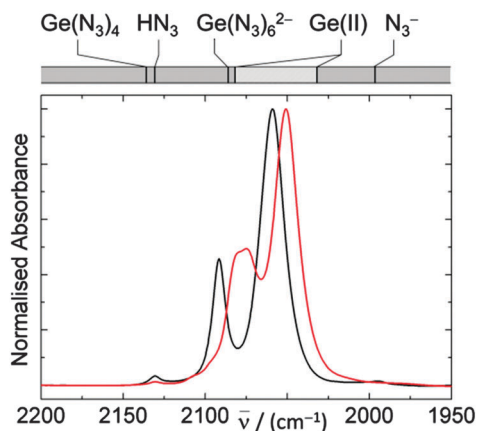
Compounds already containing WCC ions and low-valent germanium,  $AsPh_4GeCl_3$ ,  $PPh_4GeCl_3$ ,  $PPNGeCl_3$  (ref. 10) (**1a–c**), were prepared in high yield from the  $GeCl_2(diox)$  adduct<sup>18</sup> and WCC chlorides<sup>19</sup> (Scheme 1, route A).<sup>‡</sup> These colourless, moderately air sensitive crystalline trichlorogermanates react readily with THF suspensions of  $NaN_3$ . *In situ* IR spectra of the reaction (**2b**) show bands due to asymmetric NNN stretches,  $\nu_{as}(N_3)$ , typical for coordinated  $N_3$  groups at  $\bar{\nu}_{max}/(cm^{-1}) = 2092$  and  $2058$ , which have grown fully after a reaction time of 1 h. Exposure of the reaction solution to fresh  $NaN_3$  results in no further spectral change. From the solution, a highly air sensitive, colourless solid (**3b**) was precipitated, the IR spectrum of which exhibits the finger print of  $PPh_4^+$  and the  $\nu_{as}(N_3)$  bands. The  $\nu_{as}(N_3)$  frequencies lie within the range of those reported previously for semi-covalent germanium(II) azides ( $2027$ – $2077\text{ cm}^{-1}$ , Fig. 1), below those of Ge(IV) azides ( $Ge(N_3)_4$ ,  $PPN_2Ge(N_3)_6$ , **5c**)<sup>1b</sup> and above that of the  $N_3^-$  ion. While solution  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectra of **3b** show signals of the WCC cations only, two peaks are observed in the  $^{14}N$  NMR spectra at  $-263$  and  $-207$  ppm next to the solvent ( $-136$  ppm) with FWHM line widths of 552, 147 and 24 Hz, respectively. These characteristics are typical for the  $N_\alpha$  and  $N_\gamma$  nuclei of coordinated  $N_3$  groups while the signal for  $N_\beta$  is obscured by solvent.<sup>5a</sup>

Alternative routes to **3** and **4** use WCC azides as azide transfer reagents.  $GeCl_2(diox)$  reacts directly also with  $(PPN)N_3$ ,

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† Electronic supplementary information (ESI) available: Spectra, thermograms, full crystallographic data and computational details. CCDC 1030031 and 1030032. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00259a





**Fig. 1** IR spectra of  $\text{Ge}(\text{N}_3)_3^-$  (black),  $\text{Sn}(\text{N}_3)_3^-$  (red) in THF;  $\nu_{\text{as}}(\text{N}_3)$  frequency ranges of related azides,  $\text{Ge}(\text{N}_3)_4$ ,<sup>12</sup>  $\text{HN}_3$ ,<sup>10</sup>  $\text{Ge}(\text{N}_3)_6^{2-}$ ,<sup>1b</sup>  $\text{L}_n\text{Ge}(\text{II})$  azides  $\text{L}_1 = (\text{Me}_2^t\text{BuO})\text{Si}_2\text{N}_4$ ,<sup>4c</sup>  $\text{L}_2 = {}^n\text{Pr}_2\text{ATI}$ ,  $\text{Me}_5\text{DAP}$ ,<sup>4f,g</sup>  $(\text{NHC})_2$ ,<sup>3</sup>  $\text{L}_3 = \text{HB}(\text{R}_2\text{pZ})_3$ ,  $(\text{C}_5\text{R}_5)\text{Co}(\text{P}(\text{O})(\text{OEt})_2)_3$ ,<sup>4a,e,10</sup>  $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}_2\text{H}_2\text{N}_2\text{CGe}(\text{N}_3)_2$  (ref. 8d) and  $\text{N}_3^-$ ,<sup>4e</sup> are indicated in the top bar; see Table S1 (ESI<sup>†</sup>) for exact values.

in MeCN solution (Scheme 1, route B). Intriguingly, equimolar reactant mixtures produce only one  $\nu_{\text{as}}(\text{N}_3)$  band ( $2078\text{ cm}^{-1}$ ); increasing the stoichiometric ratio (1:2) results in two additional bands ( $2088, 2066\text{ cm}^{-1}$ ), while at ratios of 1:9 and above only bands at  $2095, 2064\text{ cm}^{-1}$  and that of  $\text{N}_3^-$  were detected. These observations are interpreted tentatively in terms of the formation of mono, di- and triazido complexes.

Tin dichloride was subjected to a similar treatment as  $\text{GeCl}_2$  (diox) using  $\text{WCC}(\text{N}_3)$  and  $\text{NaN}_3$ ; however, complete  $\text{Cl}/\text{N}_3$  exchange requires a larger excess of azide transfer reagent. Similar observations as with **3b** were made, including the intermediate rise and decay of a  $\nu_{\text{as}}(\text{N}_3)$  band ( $2064\text{ cm}^{-1}$ ) and the ultimate rise of bands of the final product **4b** ( $2081, 2050\text{ cm}^{-1}$ ) in the expected region between  $\text{Sn}(\text{N}_3)_6^{2-}$  and charge-neutral  $\text{Sn}(\text{II})$  monoazides (Table S1, ESI<sup>†</sup>), and  $^{14}\text{N}$  resonances at  $-218.5\text{ ppm}$  (FWHM  $\approx 32\text{ Hz}$ ) and  $-260.0\text{ ppm}$  ( $166\text{ Hz}$ ). The  $^{14}\text{N}$  NMR signals of **3b** and **4b**, in particular those assigned to  $\text{N}_{\text{oz}}$ , are deshielded in comparison to those of  $\text{E}(\text{N}_3)_6^{2-}$  dianions.<sup>1b,5a,17</sup> **3b** and **4b** are soluble in MeCN, THF and  $\text{CH}_2\text{Cl}_2$ .

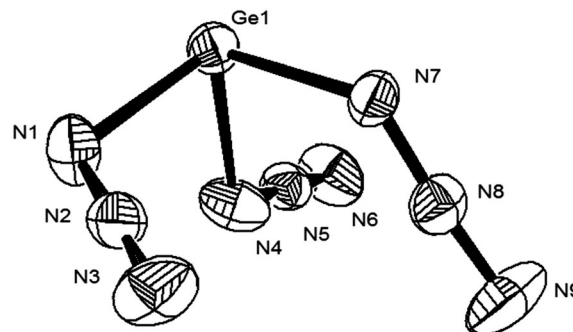
The synthetic strategy was extended to  $\text{AsPh}_4^+$  and  $\text{PPN}^+$  counter ions affording compounds **3a,c** and **4c** (Scheme 1A) which all have spectroscopic properties analogous to those of **3b** and **4b** described already. The combined analytical evidence, including the absence of chlorine in **3b** and the  $^{119}\text{Sn}$  NMR signal of **4b** ( $\delta = -220\text{ ppm}$ , see ESI<sup>†</sup>) point to the formation of anionic complexes in compounds of the type  $(\text{WCC})\text{E}(\text{N}_3)_3$  as the final products of  $\text{Cl}/\text{N}_3$  exchange.

Further insight into the nature of intermediates and products of the exchange reactions was obtained from quantum chemical calculations<sup>20</sup> on the  $\text{ECl}_{(3-n)}(\text{N}_3)_n^-$  species, which were performed at the B3LYP/cc-pVTZ level<sup>21</sup> with effective core potentials<sup>22</sup> for Ge and Sn. Solvent (THF) was described using PCM.<sup>23</sup> The calculations found conformational isomerism resulting in several minima for  $n = 1, 2, 3$ , that were close in energy. These conformers are related by rotation of ligands. Since rotational barriers of sterically unhindered  $\text{N}_3$  groups are

small (*cf.*  $\text{GeH}_3\text{N}_3$ ,  $\sim 1\text{ kJ mol}^{-1}$ ),<sup>13</sup> fast interconversion involves all significantly thermally populated rotamers above the minimum energy conformation ( $E_{\text{rel}} < 5.8\text{ kJ mol}^{-1}$ ). This process is likely to result in averaged absorption bands weighted by the rotamer population (rotamers may have more than one degenerate, absolute spatial configuration, and inter-rotamer vibrational energy transfer is unaccounted for). Taking account of the theoretical equilibrium mole fractions, absorption intensities and scaled vibrational frequencies,<sup>24</sup> approximate average frequencies of the in-phase and out-of-phase  $\nu_{\text{as}}(\text{N}_3)$  stretches and the qualitative intensity ratios could be determined (Table S1, ESI<sup>†</sup>), which match those observed (*e.g.*  $\text{Ge}(\text{N}_3)_3^-$ ,  $2059, 2091\text{ vs. }2060, 2093$ ;  $\text{Sn}(\text{N}_3)_3^-$ ,  $2051, 2080\text{ vs. }2050, 2078\text{ cm}^{-1}$ ). This approach leads to the assignment of the observed bands of intermediates to  $\text{GeCl}_2(\text{N}_3)^-$ ,  $\text{GeCl}(\text{N}_3)_2^-$ ,  $\text{SnCl}_2(\text{N}_3)^-$  and  $\text{SnCl}(\text{N}_3)_2^-$ . Calculations using the Gauge-Independent Atomic Orbital method<sup>25</sup> verify the assignment of  $^{14}\text{N}$  NMR data (see ESI<sup>†</sup>).

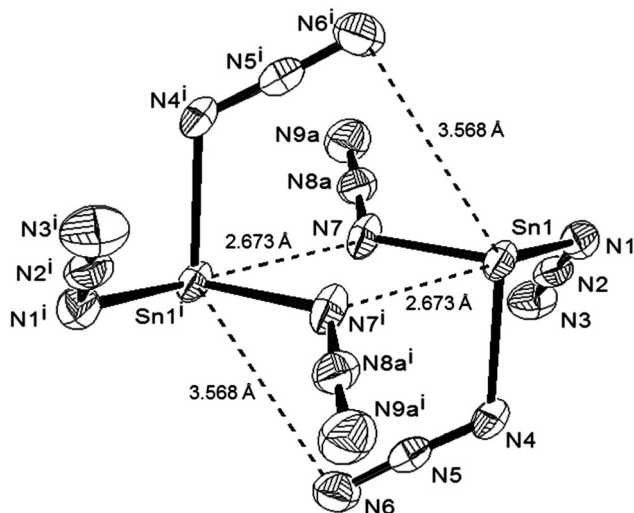
Crystals of azido germanates were grown from THF– $\text{Et}_2\text{O}$  (1:10) solutions at  $-18\text{ }^\circ\text{C}$  (**3b**, needles) or by diffusion of  $\text{Et}_2\text{O}$  into concentrated THF solutions (**3c**).<sup>§¶</sup> According to single crystal X-ray diffraction studies, **3b** consists of  $\text{PPh}_4^+$  and  $\text{Ge}(\text{N}_3)_3^-$  ions (Fig. 2). The shortest interionic  $\text{Ge}\cdots\text{N}$  and  $\text{N}\cdots\text{N}$  distances were found to be  $4.13$  and  $5.07\text{ \AA}$ , respectively (Fig. 4, left), hence, covalent  $\{[\text{Ge}(\text{N}_3)_3]^- \cdots [\text{Ge}(\text{N}_3)_3]^- \}$  interactions are absent (Fig. 3). Germanium is coordinated by three, essentially linear  $\text{N}_3$  ligands and occupies the apical position in a trigonal-pyramidal  $\text{Ge}[\text{N}]_3$  framework. The ligands are bound in the fashion typical of covalent azides and adopt  $\text{Ge}-\text{N}_\alpha-\text{N}_\beta$  angles between  $116^\circ$  and  $121^\circ$ . All inter-ligand angles are close to  $90^\circ$  which indicates stereochemical inactivity of the lone electron pair at germanium.<sup>14</sup>

This structural feature has been found in the valence isoelectronic complexes of  $\text{Ge}_2(\mu\text{-pz}^*)_3^+ \text{GeCl}_3^-$  (ref. 11f) and pilocarpine-trichlorogermanate hemihydrate.<sup>11g</sup> The  $\text{Ge}-\text{N}_\alpha$  bonds of **3b** are shorter than those of tetracoordinate  $\text{Ge}(\text{II})$  azides  $2.088(6)$ – $2.094(7)\text{ \AA}$  (Fig. 1), longer than those of the homoleptic  $\text{Ge}(\text{IV})$  azide  $\text{PPN}_2\text{Ge}(\text{N}_3)_6$  (**5c**, Table S1, ESI<sup>†</sup>) and rather within the range of previously investigated, tricoordinate  $\text{Ge}(\text{II})$  azides

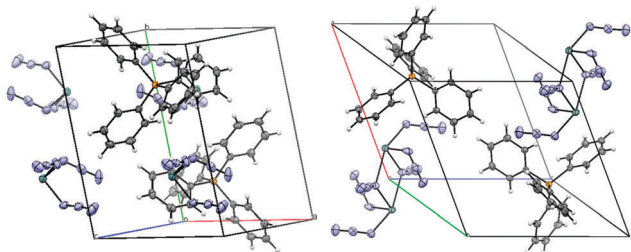


**Fig. 2** Thermal ellipsoid plot (50%) of  $\text{Ge}(\text{N}_3)_3^-$  in the crystal of  $\text{PPh}_4\text{Ge}(\text{N}_3)_3$  (**3b**). Bond lengths [ $\text{\AA}$ ]  $\text{Ge1}-\text{N7}$   $1.984(2)$ ,  $\text{Ge1}-\text{N1}$   $1.988(3)$ ,  $\text{Ge1}-\text{N4}$   $2.011(3)$ ,  $\text{N1}-\text{N2}$   $1.213(3)$ ,  $\text{N2}-\text{N3}$   $1.148(3)$ ,  $\text{N4}-\text{N5}$   $1.209(3)$ ,  $\text{N5}-\text{N6}$   $1.142(3)$ ,  $\text{N7}-\text{N8}$   $1.206(3)$ ,  $\text{N8}-\text{N9}$   $1.140(3)$ , angles [ $^\circ$ ]  $\text{N7}-\text{Ge1}-\text{N1}$   $93.59(10)$ ,  $\text{N7}-\text{Ge1}-\text{N4}$   $94.29(10)$ ,  $\text{N1}-\text{Ge1}-\text{N4}$   $91.05(11)$ ,  $\text{N2}-\text{N1}-\text{Ge1}$   $116.4(2)$ ,  $\text{N5}-\text{N4}-\text{Ge1}$   $118.7(2)$ ,  $\text{N8}-\text{N7}-\text{Ge1}$   $121.3(2)$ .





**Fig. 3** Thermal ellipsoid plot (50%) of  $\{\text{Sn}_2(\text{N}_3)_6\}^{2-}$  in crystals of  $\text{PPh}_4\text{Sn}(\text{N}_3)_3$  (**4b**). Bond lengths [Å] Sn–N1 2.262(3), Sn–N4 2.193(3), Sn–N7 2.207(3), 2.674(3), N1–N2 1.203(4), N2–N3 1.148(5), N4–N5 1.200(5), N5–N6 1.143(5), N7–N8 1.185(5), 1.193(5), N8–N9 1.157(6), 1.168(6) Sn<sup>i</sup>–N6 3.567(4), angles [°] N1–Sn–N4 88.35(12), N4–Sn–N7 89.14(13), N1–Sn–N7 88.59(12), N2–N1–Sn 123.6(3), N5–N4–Sn 119.4(2), N8–N7–Sn 128.2(9), 120.2(8), N7–Sn–N7 68.32(16), Sn–N7–Sn 111.68(18).



**Fig. 4** Packing diagrams of  $\text{PPh}_4\text{Ge}(\text{N}_3)_3$  (**3b**, left) and  $\text{PPh}_4\text{Sn}(\text{N}_3)_3$  (**4b**, right); H (bright grey), C (dark grey), N (light blue), P (orange), Ge and Sn (turquoise).

**Table 1** Bond lengths  $D/\text{Å}$  in the salt-like homoleptic azides of the type  $(\text{WCC})^+_n[\text{E}(\text{N}_3)_3]^{n-}$ , E = Ge, Sn;  $n = 1$ ,  $\text{WCC} = \text{PPh}_4^+$ ;  $n = 2$ ,  $\text{WCC} = \text{N}(\text{PPh}_3)_2^+$

E, $n$	E–N $_{\alpha}$	N $_{\alpha}$ –N $_{\beta}$	N $_{\beta}$ –N $_{\gamma}$	$\Delta\text{NN}_{\text{av}}^a$
Ge, 1	1.984(3)–2.011(2)	1.206(4)–1.213(4)	1.140(4)–1.148(4)	6.6(5) <sup>b</sup> <sup>c</sup>
Ge, 2	1.969(2)–1.980(3)	1.210(4)–1.214(3)	1.143(3)–1.151(3)	6.5(4) <sup>c</sup>
Sn, 1	2.193(3)–2.262(3)	1.189(6)–1.203(4)	1.143(5)–1.163(6)	4.6(17) <sup>c</sup>
Sn, 2	2.117(3)–2.134(2)	1.182(3)–1.213(3)	1.111(4)–1.148(3)	5.7(10) <sup>e</sup>

<sup>a</sup>  $\Delta\text{NN} = \frac{1}{n} \sum_{i=1}^n [d(\text{N}_{\alpha} - \text{N}_{\beta})_i - d(\text{N}_{\beta} - \text{N}_{\gamma})_i]$ ,  $s = \left[ \frac{1}{n-1} \sum_{i=1}^n (\Delta\text{NN}_i - \Delta\text{NN}_{\text{av}})^2 \right]^{0.5}$  in parentheses. <sup>b</sup>  $s \ll \sigma$ , error estimated by  $\sigma = \left[ \sum_{i=1}^n \left( \frac{\sigma_i}{N} \right)^2 \right]^{0.5}$ . <sup>c</sup> This work. <sup>d</sup> Ref. 1b. <sup>e</sup> Ref. 15.

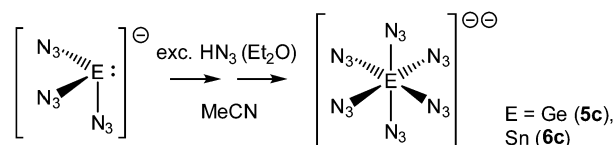
(1.969–2.047(2) Å, Table 1). All other bond lengths and angles are close to those of **5c** (Table 1). The crystallographic structure of  $\text{Ge}(\text{N}_3)_3^-$  is consistent with one of the geometries predicted by DFT (*vide supra*).

Single crystalline needles of **4b** were obtained and investigated with the methods used for **3b**.<sup>†</sup> The asymmetric unit of

**4b** also contains a  $\text{E}(\text{N}_3)_3^-$  moiety; however, the packing is at variance with **3b**, which allows  $\text{Sn}(\text{N}_3)_3^-$  to interact *via* two long  $\text{E} \cdots \text{N}_{\alpha}$  bonds and form  $\{\text{Sn}(\text{N}_3)_3\}_2^{2-}$  dimers (Fig. 3). The interaction involves asymmetric  $\mu_{1,1}$ -N $_3$  bridges with short (2.207(3) Å) and long (2.674(3) Å) Sn–N $_{\alpha}$  bonds, the latter being considerably shorter than the sum of the van der Waals radii (3.72 Å).<sup>16</sup> Weak intermolecular interactions have been observed previously between neutral  $\text{Sn}(\text{Pr}_2\text{ATI})\text{N}_3$  complexes (*vide supra*),<sup>4b</sup> where a slightly longer Sn  $\cdots$  N $_{\alpha}$  bond (2.87 Å) was found. The sum of bond angles involving the bridging N $_{\alpha}$  indicates planarity and effective  $\text{sp}^2$  hybridisation. As in the crystal of **3b**, the primary  $\text{E}(\text{II})$ –N $_{\alpha}$  bonds are significantly longer (2.193(3)–2.262(3) Å) than those found in the homoleptic  $\text{E}(\text{IV})$  azide **6** (2.125 Å).<sup>15</sup> The potential for dimerisation was studied by DFT using the geometry of  $\{\text{E}(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)\}_2^{2-}$  in crystalline **4b** as a starting point. Optimisation results in separate anions devoid of covalent interionic interactions in the case of  $\text{Ge}(\text{N}_3)_3^-$ , whereas a dimeric structure was found for  $\text{Sn}(\text{N}_3)_3^-$  that resembles the molecular structure in the crystal. Estimates of the basis set superposition error for the solution phase were obtained from BSSE calculations<sup>26</sup> in the gas phase. After BSSE correction,  $\{\text{Sn}(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)\}_2^{2-}$  was found to be at least 4 kcal mol<sup>−1</sup> less stable than two monomers, rendering the existence of a dimer in solution highly unlikely.

According to differential scanning calorimetry measurements (Fig. S11 and S12, ESI<sup>†</sup>), compound **3b** decomposes in two exothermic processes with ( $\Delta H = -270$  and  $-467$  J g<sup>−1</sup>). Remarkably, step 1 occurs at temperatures ( $T_{\text{on}}^{\text{ex1}} = 99$  °C) that are drastically below the decomposition onset of the related, hypercoordinate azide **5c** ( $T_{\text{on}}^{\text{ex1}} = 256$  °C),<sup>1b</sup> whereas step 2 sets in at  $T_{\text{p}}^{\text{ex2}} = 310$  °C, which is nearly identical with the temperature found in **5c** (312 °C).<sup>\*\*</sup> Furthermore, the molar enthalpies of step 2 ( $-251$  vs.  $-482$  kJ mol<sup>−1</sup>) scale approximately with the complex charge; however, step 1 releases much less energy than expected (145 kJ mol<sup>−1</sup>, **3b** vs. 705 kJ mol<sup>−1</sup>, **5c**). This phenomenon is still under investigation. Further experiments show that heating of **3b** at 150 °C produces  $\text{PPh}_4\text{N}_3$ , which suggests that the release of  $\text{N}_3^-$  initiates the decomposition of  $\text{Ge}(\text{N}_3)_3^-$ . The tin homologue **4b** melts at  $T_{\text{on}} = 115$  °C and decays at 215 °C and 308 °C and thus behaves as expected relative to **6c**.<sup>15</sup> No sensitivity was noted during preparation and analysis of compounds **3b** and **4b** on the stated reaction scale. The material remains unchanged when struck by a hammer. Upon lighting up, it burns rapidly with an orange flame leaving black residues.

In solution,  $\text{Ge}(\text{N}_3)_3^-$  and  $\text{Sn}(\text{N}_3)_3^-$  react with hydrazoic acid leading to a precipitate with the IR  $\nu_{\text{as}}(\text{N}_3)$  absorptions characteristic for  $\text{Ge}(\text{N}_3)_6^{2-}$  and  $\text{Sn}(\text{N}_3)_6^{2-}$  complexes, respectively,



**Scheme 2** Oxidation of the tri(azido) complexes **3b** and **5b**.



which can be verified by comparison with spectra of the fully characterized salts **5c**, **6c** (Scheme 2, Fig. S13 and S14, ESI†).

The first low-valent homoleptic azido complexes of group 14 have been synthesized and fully characterised. The preparative approach to salt-like compounds containing these complexes has been demonstrated on a 0.2–0.7 g scale for a range of weakly coordinating cations and involves chloro(azido) species,  $\text{ECl}_x(\text{N}_3)_y^-$ . Unlike their hypercoordinate  $\text{E}(\text{N}_3)_6^{2-}$  analogues and despite the presence of innocent cations, the new class of compounds is highly reactive, exhibiting low thermal stability and a propensity to oxidation. Crystallographic analysis revealed that in the solid state,  $\text{E}(\text{N}_3)_3^-$  complexes of group 14 may dimerise *via* azido ligand bridges. Neither of the low-valent coordination centres exhibits a stereochemically active lone electron pair. DFT calculations correctly predict the dimerisation and suggest furthermore that the dimers are unstable in polar solvents.

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## Notes and references

‡  $\text{GeCl}_3^-$  (ref. 9 and 11) and  $\text{SnCl}_3^-$  salts (ref. 11c and *e-g*) with various organic counter ions have been reported previously.

§ All attempts to crystallize compound **3a** have been futile.

¶ Crystallographic data: **3b**, CCDC 1030032,  $\text{C}_{24}\text{H}_{20}\text{GeN}_9\text{P}$ , 538.07 g mol<sup>-1</sup>,  $P\bar{1}$ ,  $a = 7.7712(2)$  Å,  $b = 11.4711(4)$  Å,  $c = 14.2003(4)$  Å,  $\alpha = 93.278(2)^\circ$ ,  $\beta = 99.357(2)^\circ$ ,  $\gamma = 100.865(2)^\circ$ ,  $Z = 2$ ,  $V = 1221.59(6)$  Å<sup>3</sup>,  $D_c = 1.463$  g cm<sup>-3</sup>,  $T = 120(2)$  K,  $F(000) = 548$ ,  $R_1 = 0.0376$  (316 param.),  $wR_2 = 0.0807$ , GOOF = 1.090. **3c**,  $P2_1$ ,  $a = 10.7640(11)$  Å,  $b = 12.732(2)$  Å,  $c = 25.713(3)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 100.682(12)^\circ$ ,  $D_c = 1.414$  g cm<sup>-3</sup>,  $T = 180(2)$  K, extensive disorder of  $\text{Ge}(\text{N}_3)_3^-$  part (see ESI† and ref. 10). **4b**, CCDC 1030031,  $\text{C}_{24}\text{H}_{20}\text{N}_9\text{PSn}$ ,  $M = 584.15$  g mol<sup>-1</sup>,  $P\bar{1}$ ,  $a = 10.7560(6)$  Å,  $b = 11.0605(6)$  Å,  $c = 12.3540(7)$  Å,  $\alpha = 91.668(4)^\circ$ ,  $\beta = 108.414(4)^\circ$ ,  $\gamma = 116.545(3)^\circ$ ,  $Z = 2$ ,  $V = 1222.11(12)$  Å<sup>3</sup>,  $D_c = 1.587$  g cm<sup>-3</sup>,  $T = 100(2)$  K,  $F(000) = 584$ ,  $R_1 = 0.0521$  (334 param.),  $wR_2 = 0.1020$ , GOOF = 1.053.

|| Estimated error approx.  $\pm 10\%$ .

\*\* This step is assigned tentatively to the thermolysis of  $\text{PPN}(\text{N}_3)$  and  $\text{PPH}_4(\text{N}_3)$  since enthalpies and onset temperatures are comparable with those of genuine samples of these salts:  $\text{PPH}_4\text{N}_3$ , mp = 250 °C,  $T_{\text{on}}^{\text{ex}}$  = 291 °C, ref. 15.

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