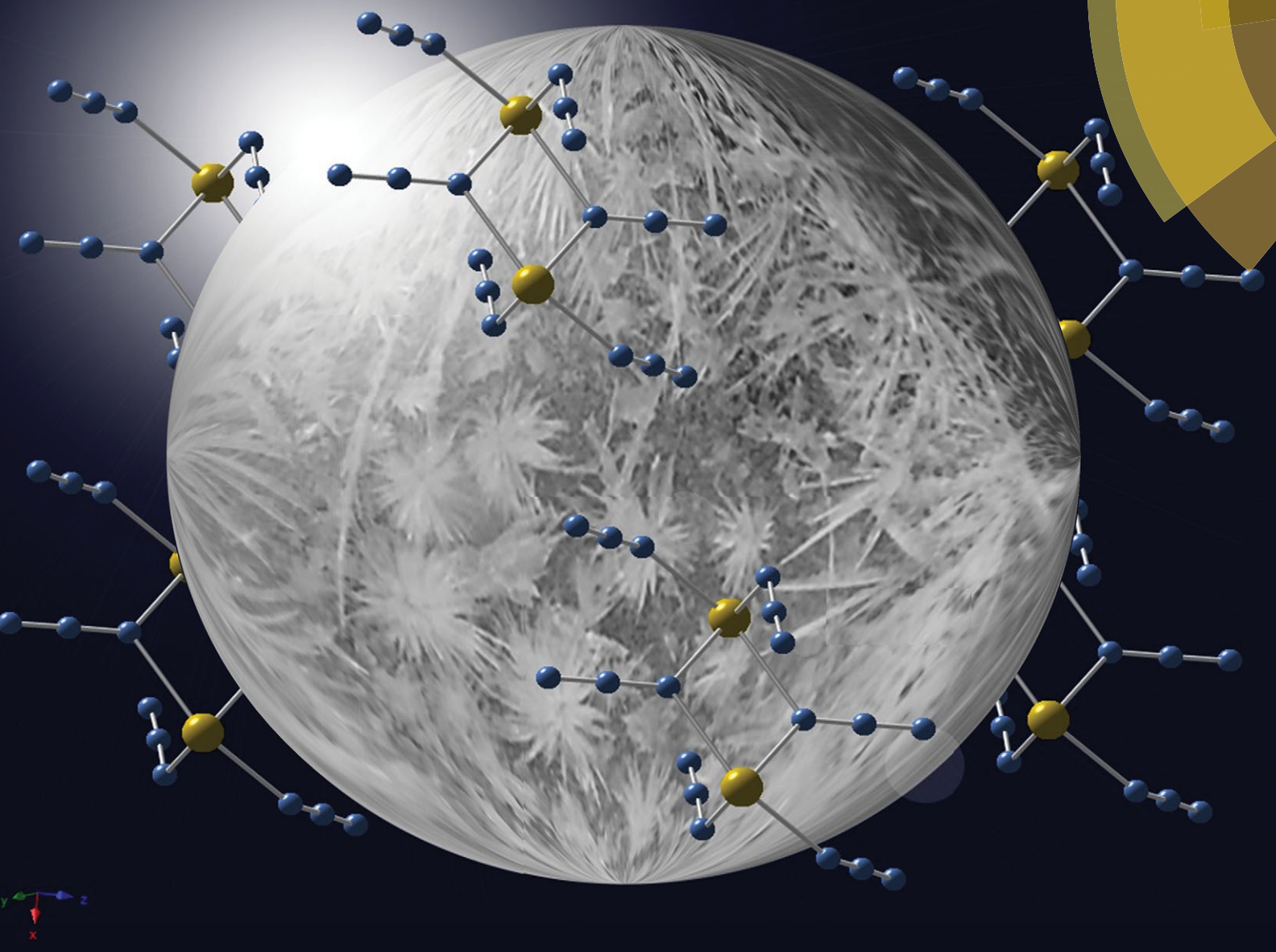


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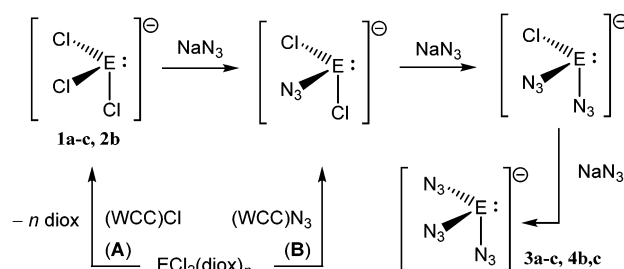
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Homoleptic low-valent polyazides of group 14 elements†

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 ($E = C, Si$),² as hyper-coordinate $E(N_3)_6^{2-}$ complexes ($Si-Pb$)¹ and as $E(N_3)_2$ compounds (Sn, Pb).^{5c} 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.⁵ In contrast, stability-inducing effects of hyper-coordination and of bulky, weakly coordinating counter ions (WCC)⁶ allow many salt-like homoleptic polyazides to be synthesised in bulk and characterised fully, including *via* X-ray crystallography and IR spectroscopy,^{5a} 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 $E(L')(N_3)_2$, $E = Ge, Sn$.^{3,4} On the other hand, the stability of low valent molecules, *e.g.* carbenes, silylenes, germylenes, stannylenes,⁷ 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.^{7a,d} 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.^{4a,8} 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 $GeCl_2(diox)$ adduct¹⁸ and WCC chlorides¹⁹ (Scheme 1, route A).[‡] 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 cm^{-1} , Fig. 1), below those of Ge(IV) azides ($Ge(N_3)_4$, $PPN_2Ge(N_3)_6$, **5c**)^{1b} 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_α and N_γ nuclei of coordinated N_3 groups while the signal for N_β is obscured by solvent.^{5a}

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



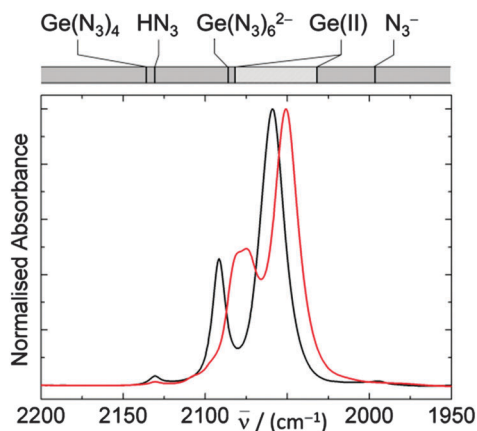


Fig. 1 IR spectra of $\text{Ge}(\text{N}_3)_3^-$ (black), $\text{Sn}(\text{N}_3)_3^-$ (red) in THF; $\nu_{\text{as}}(\text{N}_3)$ frequency ranges of related azides, $\text{Ge}(\text{N}_3)_4$,¹² HN_3 ,¹⁰ $\text{Ge}(\text{N}_3)_6^{2-}$,^{1b} $\text{L}_n\text{Ge}(\text{II})$ azides $\text{L}_1 = (\text{Me}_2^t\text{BuO})\text{Si}_2\text{N}_4$,^{4c} $\text{L}_2 = {}^n\text{Pr}_2\text{ATI}$, Me_5DAP ,^{4f,g} $(\text{NHC})_2$,³ $\text{L}_3 = \text{HB}(\text{R}_2\text{pZ})_3$, $(\text{C}_5\text{R}_5)\text{Co}(\text{P}(\text{O})(\text{OEt})_2)_3$,^{4a,e,10} $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{C}_2\text{H}_2\text{N}_2\text{CGe}(\text{N}_3)_2$ (ref. 8d) and N_3^- ,^{4e} are indicated in the top bar; see Table S1 (ESI[†]) 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 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 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 GeCl_2 (diox) using $\text{WCC}(\text{N}_3)$ and NaN_3 ; however, complete Cl/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 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[†]), and ^{14}N resonances at -218.5 ppm (FWHM $\approx 32\text{ Hz}$) and -260.0 ppm (166 Hz). The ^{14}N NMR signals of **3b** and **4b**, in particular those assigned to N_{oz} , are deshielded in comparison to those of $\text{E}(\text{N}_3)_6^{2-}$ dianions.^{1b,5a,17} **3b** and **4b** are soluble in MeCN, THF and CH_2Cl_2 .

The synthetic strategy was extended to AsPh_4^+ and 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}Sn NMR signal of **4b** ($\delta = -220\text{ ppm}$, see ESI[†]) 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 Cl/N_3 exchange.

Further insight into the nature of intermediates and products of the exchange reactions was obtained from quantum chemical calculations²⁰ on the $\text{ECl}_{(3-n)}(\text{N}_3)_n^-$ species, which were performed at the B3LYP/cc-pVTZ level²¹ with effective core potentials²² for Ge and Sn. Solvent (THF) was described using PCM.²³ 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 N_3 groups are

small (*cf.* GeH_3N_3 , $\sim 1\text{ kJ mol}^{-1}$),¹³ 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,²⁴ 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[†]), 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 method²⁵ verify the assignment of ^{14}N NMR data (see ESI[†]).

Crystals of azido germanates were grown from THF– Et_2O (1:10) solutions at $-18\text{ }^\circ\text{C}$ (**3b**, needles) or by diffusion of Et_2O into concentrated THF solutions (**3c**).^{§¶} According to single crystal X-ray diffraction studies, **3b** consists of 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 \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 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° and 121° . All inter-ligand angles are close to 90° which indicates stereochemical inactivity of the lone electron pair at germanium.¹⁴

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.^{11g} 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[†]) and rather within the range of previously investigated, tricoordinate $\text{Ge}(\text{II})$ azides

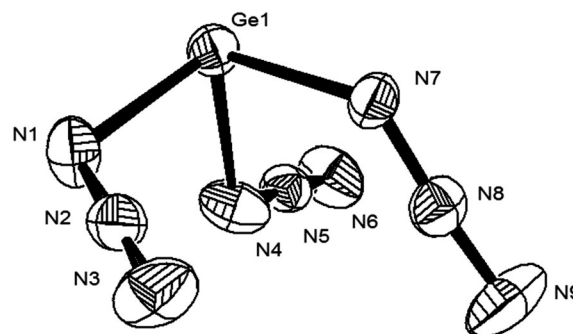


Fig. 2 Thermal ellipsoid plot (50%) of $\text{Ge}(\text{N}_3)_3^-$ in the crystal of $\text{PPh}_4\text{Ge}(\text{N}_3)_3$ (**3b**). Bond lengths [\AA] $\text{Ge1}-\text{N7}$ $1.984(2)$, $\text{Ge1}-\text{N1}$ $1.988(3)$, $\text{Ge1}-\text{N4}$ $2.011(3)$, $\text{N1}-\text{N2}$ $1.213(3)$, $\text{N2}-\text{N3}$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



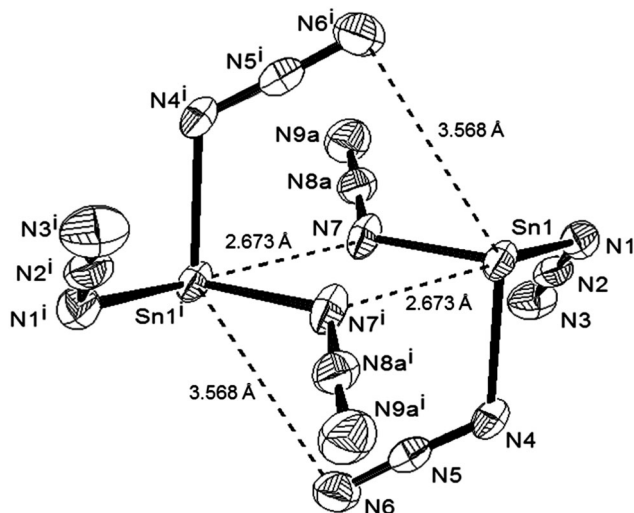


Fig. 3 Thermal ellipsoid plot (50%) of $\{\text{Sn}_2(\text{N}_3)_6\}^{2-}$ in crystals of $\text{PPh}_4\text{Sn}(\text{N}_3)_3$ (**4b**). Bond lengths [Å] Sn–N1 2.262(3), Sn–N4 2.193(3), Sn–N7 2.207(3), 2.674(3), N1–N2 1.203(4), N2–N3 1.148(5), N4–N5 1.200(5), N5–N6 1.143(5), N7–N8 1.185(5), 1.193(5), N8–N9 1.157(6), 1.168(6) Snⁱ–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).

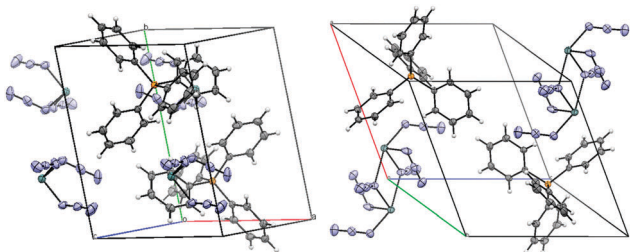


Fig. 4 Packing diagrams of $\text{PPh}_4\text{Ge}(\text{N}_3)_3$ (**3b**, left) and $\text{PPh}_4\text{Sn}(\text{N}_3)_3$ (**4b**, right); H (bright grey), C (dark grey), N (light blue), P (orange), Ge and Sn (turquoise).

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) ^b ^c
Ge, 2	1.969(2)–1.980(3)	1.210(4)–1.214(3)	1.143(3)–1.151(3)	6.5(4) ^c
Sn, 1	2.193(3)–2.262(3)	1.189(6)–1.203(4)	1.143(5)–1.163(6)	4.6(17) ^c
Sn, 2	2.117(3)–2.134(2)	1.182(3)–1.213(3)	1.111(4)–1.148(3)	5.7(10) ^e

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

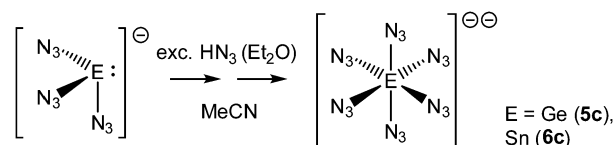
(1.969–2.047(2) Å, Table 1). All other bond lengths and angles are close to those of **5c** (Table 1). The crystallographic structure of $\text{Ge}(\text{N}_3)_3^-$ is consistent with one of the geometries predicted by DFT (*vide supra*).

Single crystalline needles of **4b** were obtained and investigated with the methods used for **3b**.[†] 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).¹⁶ Weak intermolecular interactions have been observed previously between neutral $\text{Sn}(\text{Pr}_2\text{ATI})\text{N}_3$ complexes (*vide supra*),^{4b} 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 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).¹⁵ 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 calculations²⁶ 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⁻¹ 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[†]), compound **3b** decomposes in two exothermic processes with ($\Delta H = -270$ and -467 J g⁻¹). 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),^{1b} 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).^{**} Furthermore, the molar enthalpies of step 2 (-251 vs. -482 kJ mol⁻¹) scale approximately with the complex charge; however, step 1 releases much less energy than expected (145 kJ mol⁻¹, **3b** vs. 705 kJ mol⁻¹, **5c**). This phenomenon is still under investigation. Further experiments show that heating of **3b** at 150 °C produces PPh_4N_3 , which suggests that the release of 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**.¹⁵ 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

‡ GeCl_3^- (ref. 9 and 11) and 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⁻¹, $P\bar{1}$, $a = 7.7712(2)$ Å, $b = 11.4711(4)$ Å, $c = 14.2003(4)$ Å, $\alpha = 93.278(2)^\circ$, $\beta = 99.357(2)^\circ$, $\gamma = 100.865(2)^\circ$, $Z = 2$, $V = 1221.59(6)$ Å³, $D_c = 1.463$ g cm⁻³, $T = 120(2)$ 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⁻³, $T = 180(2)$ 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⁻¹, $P\bar{1}$, $a = 10.7560(6)$ Å, $b = 11.0605(6)$ Å, $c = 12.3540(7)$ Å, $\alpha = 91.668(4)^\circ$, $\beta = 108.414(4)^\circ$, $\gamma = 116.545(3)^\circ$, $Z = 2$, $V = 1222.11(12)$ Å³, $D_c = 1.587$ g cm⁻³, $T = 100(2)$ 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: PPH_4N_3 , mp = 250 °C, $T_{\text{on}}^{\text{ex}} = 291$ °C, ref. 15.

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