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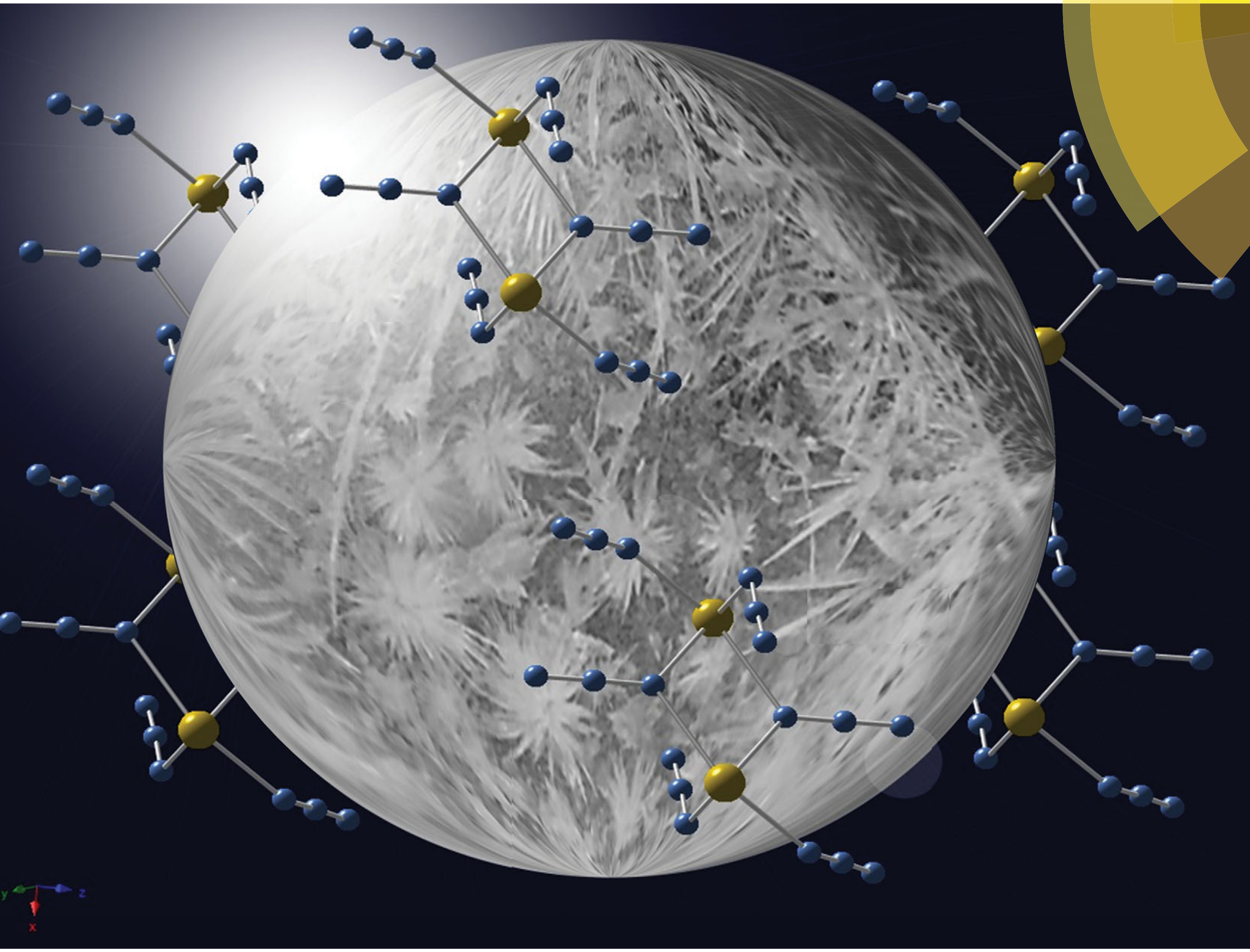

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Homoleptic low-valent polyazides of group 14 elements†

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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 $HC\{(CMe)(2,6\text{-}^iPr_2C_6H_3N)\}_2$ ligands.[7a,d] This insight has led to tri- and tetracoordinate complexes bearing uni-, bi- and terdentate ligands, *e.g.* $E(NHC)X_2$, $Ge(NHC)_2Cl^+$ and $Ge\{HB(Me_2pz)_3\}Cl$, E = Si, Ge; X = Cl-I, N_3; NHC = N-heterocyclic carbene.[4a,8] Exploitation of these concepts has permitted the

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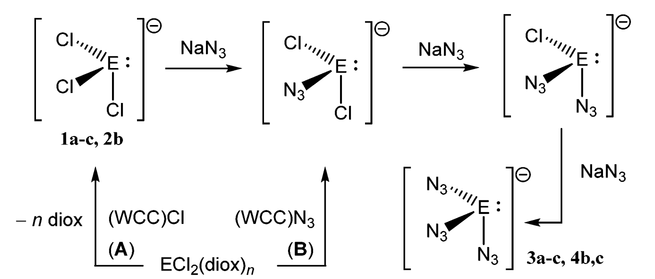
† Electronic supplementary information (ESI) available: Spectra, thermograms, full crystallographic data and computational details. CCDC 1030031 and 1030032. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00259a



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,[9] $PPNGeCl_3$ (ref. 10) (**1a–c**), were prepared in high yield from the $GeCl_2$(diox) adduct[18] and WCC chlorides[19] (Scheme 1, route A).‡[11] 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 $(PPN)N_3$

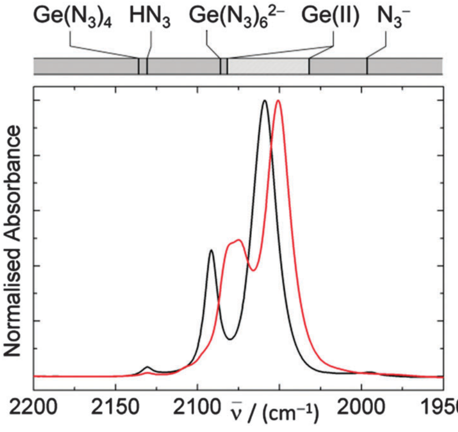


Fig. 1 IR spectra of $Ge(N_3)_3^-$ (black), $Sn(N_3)_3^-$ (red) in THF; $\nu_{as}(N_3)$ frequency ranges of related azides, $Ge(N_3)_4$,[12] HN_3,[10] $Ge(N_3)_6^{2-}$,[1b] L_nGe(II) azides L_1 = {$Me_2(^tBuO)Si$}$_2$N;[4c] L_2 = ^{n}Pr$_2$ATI, Mes$_2$DAP,[4f,g] (NHC)$_2$;[3] L_3 = HB(R$_2$pz)$_3$, (C$_5$R$_5$)Co{P(O)(OEt)$_2$}$_3$,[4a,e,10] (2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_2$H$_2$N$_2$CGe(N$_3$)$_2$ (ref. 8*d*) 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 $\nu_{as}(N_3)$ band (2078 cm^{-1}); increasing the stoichiometric ratio (1 : 2) results in two additional bands (2088, 2066 cm^{-1}), while at ratios of 1 : 9 and above only bands at 2095, 2064 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 WCC(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 $\nu_{as}(N_3)$ band (2064 cm^{-1}) and the ultimate rise of bands of the final product **4b** (2081, 2050 cm^{-1}) in the expected region between $Sn(N_3)_6^{2-}$ and charge-neutral Sn(II) monoazides (Table S1, ESI†), and ^{14}N resonances at −218.5 ppm (FWHM ≈ 32 Hz) and −260.0 ppm (166 Hz). The ^{14}N NMR signals of **3b** and **4b**, in particular those assigned to N$_\alpha$, are deshielded in comparison to those of $E(N_3)_6^{2-}$ dianions.[1b,5a,17] **3b** and **4b** are soluble in MeCN, THF and CH$_2$Cl$_2$.

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** (δ = −220 ppm, see ESI†) point to the formation of anionic complexes in compounds of the type (WCC)E(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 calculations[20] on the $ECl_{(3-n)}(N_3)_n^-$ species, which were performed at the B3LYP/cc-pVTZ level[21] with effective core potentials[22] 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$_3$N$_3$, ~1 kJ mol^{-1}),[13] fast interconversion involves all significantly thermally populated rotamers above the minimum energy conformation (E_{rel} < 5.8 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 $\nu_{as}(N_3)$ stretches and the qualitative intensity ratios could be determined (Table S1, ESI†), which match those observed (*e.g.* $Ge(N_3)_3^-$, 2059, 2091 *vs.* 2060, 2093; $Sn(N_3)_3^-$, 2051, 2080 *vs.* 2050, 2078 cm^{-1}). This approach leads to the assignment of the observed bands of intermediates to $GeCl_2(N_3)^-$, $GeCl(N_3)_2^-$, $SnCl_2(N_3)^-$ and $SnCl(N_3)_2^-$. Calculations using the Gauge-Independent Atomic Orbital method[25] verify the assignment of ^{14}N NMR data (see ESI†).

Crystals of azido germanates were grown from THF–Et$_2$O (1 : 10) solutions at −18 °C (**3b**, needles) or by diffusion of Et$_2$O into concentrated THF solutions (**3c**).§¶ According to single crystal X-ray diffraction studies, **3b** consists of PPh$_4^+$ and $Ge(N_3)_3^-$ ions (Fig. 2). The shortest interionic Ge···N and N···N distances were found to be 4.13 and 5.07 Å, respectively (Fig. 4, left), hence, covalent {[Ge(N$_3$)$_3$]$^-$}···{[Ge(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 Ge[N]$_3$ framework. The ligands are bound in the fashion typical of covalent azides and adopt Ge–N$_\alpha$–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 Ge$_2$(μ-pz*)$_3^+$ GeCl$_3^-$ (ref. 11*f*) and pilocarpine-trichlorogermanate hemihydrate.[11g] The Ge–N$_\alpha$ bonds of **3b** are shorter than those of tetracoordinate Ge(II) azides 2.088(6)–2.094(7) Å (Fig. 1), longer than those of the homoleptic Ge(IV) azide PPN$_2$Ge(N$_3$)$_6$ (**5c**, Table S1, ESI†) and rather within the range of previously investigated, tricoordinate Ge(II) azides

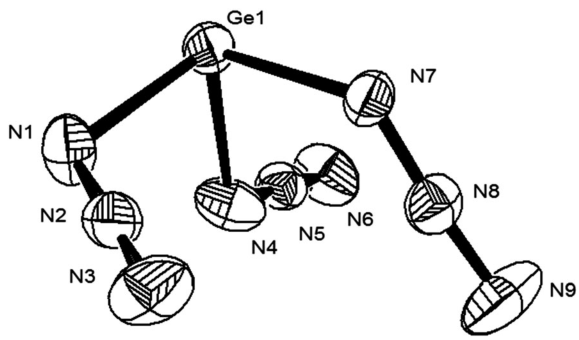


Fig. 2 Thermal ellipsoid plot (50%) of $Ge(N_3)_3^-$ in the crystal of PPh$_4$Ge(N$_3$)$_3$ (**3b**). Bond lengths [Å] Ge1–N7 1.984(2), Ge1–N1 1.988(3), Ge1–N4 2.011(3), N1–N2 1.213(3), N2–N3 1.148(3), N4–N5 1.209(3), N5–N6 1.142(3), N7–N8 1.206(3), N8–N9 1.140(3), angles [°] N7–Ge1–N1 93.59(10), N7–Ge1–N4 94.29(10), N1–Ge1–N4 91.05(11), N2–N1–Ge1 116.4(2), N5–N4–Ge1 118.7(2), N8–N7–Ge1 121.3(2).

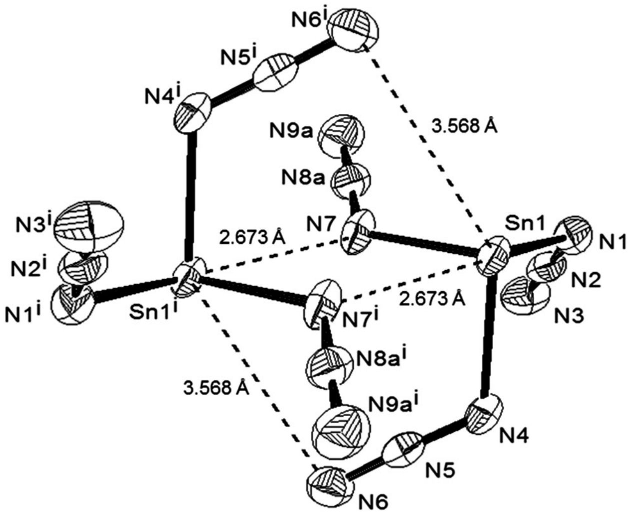


Fig. 3 Thermal ellipsoid plot (50%) of $\{Sn_2(N_3)_6\}^{2-}$ in crystals of $PPh_4Sn(N_3)_3$ (**4b**). Bond lengths [Å] Sn–N1 2.262(3), Sn–N4 2.193(3), Sn–N7 2.207(3), 2.674(3), N1–N2 1.203(4), N2–N3 1.148(5), N4–N5 1.200(5), N5–N6 1.143(5), N7–N8 1.185 (5), 1.193(5), N8–N9 1.157(6), 1.168(6) Sn^i–N6 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).

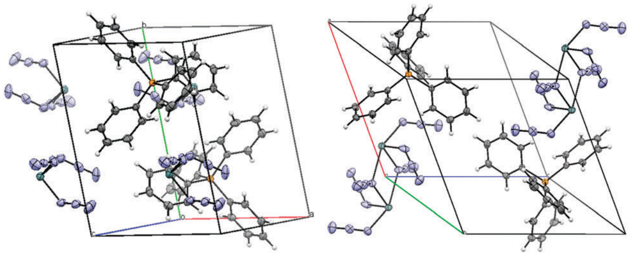


Fig. 4 Packing diagrams of $PPh_4Ge(N_3)_3$ (**3b**, left) and $PPh_4Sn(N_3)_3$ (**4b**, right); H (bright grey), C (dark grey), N (light blue), P (orange), Ge and Sn (turquoise).

Table 1 Bond lengths D/Å in the salt-like homoleptic azides of the type $(WCC)^+{}_n[E(N_3)_{3n}]^{n-}$, E = Ge, Sn; n = 1, WCC = PPh_4^+; n = 2, WCC = $N(PPh_3)_2^+$

E, n	E–N_α	N_α–N_β	N_β–N_γ	ΔNN_{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)	[d]
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]

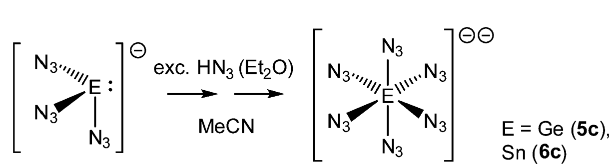
[a] $\Delta NN = \frac{1}{n}\sum_{i=1}^{n}\left[d(N_\alpha - N_\beta)_i - d(N_\beta - N_\gamma)_i\right]$, $s = \left[\frac{1}{n-1}\sum_{i=1}^{n}\left(\Delta NN_i - \Delta NN_{av}\right)^2\right]^{0.5}$ in parentheses. [b] $s \ll \sigma$, error estimated by $\sigma = \left[\sum_{i=1}^{n}\left(\frac{\sigma_i}{N}\right)^2\right]^{0.5}$. [c] This work. [d] Ref. 1*b*. [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 $Ge(N_3)_3^-$ 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 $E(N_3)_3^-$ moiety; however, the packing is at variance with **3b**, which allows $Sn(N_3)_3^-$ to interact *via* two long E···N_α bonds and form $\{Sn(N_3)_3\}_2^{2-}$ 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_α 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 $Sn(^nPr_2ATI)N_3$ complexes (*vide supra*),[4b] where a slightly longer Sn···N_α bond (2.87 Å) was found. The sum of bond angles involving the bridging N_α indicates planarity and effective sp^2 hybridisation. As in the crystal of **3b**, the primary E(II)–N_α bonds are significantly longer (2.193(3)–2.262(3) Å) than those found in the homoleptic E(IV) azide **6** (2.125 Å).[15] The potential for dimerisation was studied by DFT using the geometry of $\{E(N_3)_2(\mu_{1,1}\text{-}N_3)\}_2^{2-}$ in crystalline **4b** as a starting point. Optimisation results in separate anions devoid of covalent interionic interactions in the case of $Ge(N_3)_3^-$, whereas a dimeric structure was found for $Sn(N_3)_3^-$ that resembles the molecular structure in the crystal. Estimates of the basis set superposition error for the solution phase were obtained from BSSE calculations[26] in the gas phase. After BSSE correction, $\{Sn(N_3)_2(\mu_{1,1}\text{-}N_3)\}_2^{2-}$ 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 (ΔH = −270 and −467 J g^{-1}).‖ Remarkably, step 1 occurs at temperatures (T_{on}^{ex1} = 99 °C) that are drastically below the decomposition onset of the related, hypercoordinate azide **5c** (T_{on}^{ex1} = 256 °C),[1b] whereas step 2 sets in at T_p^{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 $Ge(N_3)_3^-$. The tin homologue **4b** melts at T_{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, $Ge(N_3)_3^-$ and $Sn(N_3)_3^-$ react with hydrazoic acid leading to a precipitate with the IR $\nu_{as}(N_3)$ absorptions characteristic for $Ge(N_3)_6^{2-}$ and $Sn(N_3)_6^{2-}$ 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, $ECl_x(N_3)_y^-$. Unlike their hypercoordinate $E(N_3)_6^{2-}$ 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, $E(N_3)_3^-$ 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. 11*c* 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, $C_{24}H_{20}GeN_9P$, 538.07 g mol^{-1}, $P\bar{1}$, a = 7.7712(2) Å, b = 11.4711(4) Å, c = 14.2003(4) Å, α = 93.278 (2)°, β = 99.357(2)°, γ = 100.865(2)°, Z = 2, V = 1221.59(6) Å^3, 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°, β = 100.682(12)°, D_c = 1.414 g cm^{-3}, T = 180(2) K, extensive disorder of $Ge(N_3)_3^-$ part (see ESI† and ref. 10). **4b**, CCDC 1030031, $C_{24}H_{20}N_9PSn$, M = 584.15 g mol^{-1}, $P\bar{1}$, a = 10.7560(6) Å, b = 11.0605(6) Å, c = 12.3540(7) Å, α = 91.668(4)°, β = 108.414(4)°, γ = 116.545(3)°, Z = 2, V = 1222.11(12) Å^3, 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. ±10%.

** This step is assigned tentatively to the thermolysis of $PPN(N_3)$ and PPh_4 (N_3) since enthalpies and onset temperatures are comparable with those of genuine samples of these salts: PPh_4N_3, mp = 250 °C, T_{on}^{ex} = 291 °C, ref. 15.

1 (*a*) A. C. Filippou, P. Portius and G. Schnakenburg, *J. Am. Chem. Soc.*, 2002, **124**, 12396; (*b*) A. C. Filippou, P. Portius, D. U. Neumann and K.-D. Wehrstedt, *Angew. Chem., Int. Ed.*, 2000, **39**, 4333; (*c*) D. Fenske, H. D. Dörner and K. Dehnicke, *Z. Naturforsch., B: J. Chem. Sci.*, 1983, **38**, 1301; (*d*) K. Polborn, E. Leidl and W. Beck, *Z. Naturforsch., B: J. Chem. Sci.*, 1988, **43**, 1206.

2 (*a*) K. Banert, Y.-H. Joo, T. Rüffer, B. Walfort and H. Lang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1168; (*b*) P. Portius, A. C. Filippou, G. Schnakenburg, M. Davis and K.-D. Wehrstedt, *Angew. Chem., Int. Ed.*, 2010, **49**, 8013.

3 Y. Xiong, S. Yao and M. Driess, *Chem. Commun.*, 2014, **50**, 418.

4 (*a*) A. C. Filippou, P. Portius and G. Kociok-Köhn, *Chem. Commun.*, 1998, 2327; (*b*) H. V. R. Dias and A. E. Ayers, *Polyhedron*, 2002, **21**, 611; (*c*) M. Veith and A. Rammo, *Z. Anorg. Allg. Chem.*, 2001, **627**, 662; (*d*) V. N. Khrustalev, I. A. Portnyagin, N. N. Zemlyansky, I. V. Borisova, Y. A. Ustynyuk and M. Y. Antipin, *J. Organomet. Chem.*, 2005, **690**, 1056; (*e*) A. C. Filippou, P. Portius, G. Kociok-Köhn and V. Albrecht, *Dalton Trans.*, 2000, 1759; (*f*) A. E. Ayers, D. S. Marynick and H. V. R. Dias, *Inorg. Chem.*, 2000, **39**, 4147; (*g*) A. E. Ayers, T. M. Klapötke and H. V. R. Dias, *Inorg. Chem.*, 2001, **40**, 1000.

5 (*a*) P. Portius and M. Davis, *Coord. Chem. Rev.*, 2013, **257**, 1011; (*b*) W. P. Fehlhammer and W. Beck, *Z. Anorg. Allg. Chem.*, 2013, **639**, 1053, ref. cited; (*c*) T. Müller, F. Karau, W. Schnick and F. Kraus, *Angew. Chem., Int. Ed.*, 2014, **53**, 13695.

6 (*a*) C. J. Price, H.-Y. Chen, L. M. Launer and S. A. Miller, *Angew. Chem., Int. Ed.*, 2009, **48**, 956; (*b*) I. Krossing and A. Reisinger, *Coord. Chem. Rev.*, 2006, **250**, 2721.

7 (*a*) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (*b*) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457; (*c*) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479; (*d*) B. Blom, M. Stoelzel and M. Driess, *Chem. – Eur. J.*, 2013, **19**, 40; (*e*) M. Mück, K. Junold, J. A. Baus, C. Burschka and R. Tacke, *Eur. J. Inorg. Chem.*, 2013, 5821.

8 (*a*) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem., Int. Ed.*, 2009, **48**, 5683; (*b*) A. C. Filippou, O. Chernov and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2009, **48**, 5687; (*c*) Y. Xiong, S. Yao and M. Driess, *Chem. Commun.*, 2014, **50**, 418; (*d*) B. Lyhs, D. Bläser, C. Wölper, S. Schulz, R. Haack and G. Jansen, *Inorg. Chem.*, 2013, **52**, 7236.

9 U. M. Tripathi, G. L. Wegner, A. Schier, A. Jockisch and H. Schmidbaur, *Z. Naturforsch., B: J. Chem. Sci.*, 1998, **53**, 939.

10 P. Portius, PhD thesis, Humboldt-Universität zu Berlin Weißensee Verlag, Berlin, 2002, ISBN 3-934479-63-4.

11 (*a*) X. Tian, T. Pape and N. W. Mitzel, *Z. Naturforsch., B: J. Chem. Sci.*, 2004, **59**, 1524; (*b*) S. Nogai, A. Schriewer and H. Schmidbaur, *Dalton Trans.*, 2003, 3165; (*c*) G. Kociok-Köhn, J. G. Winter and A. C. Filippou, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, 351; (*d*) G. L. Wegner, A. Jockisch and H. Schmidbaur, *Z. Naturforsch., B: J. Chem. Sci.*, 1998, **53**, 430; (*e*) M. Karnop, W. W. du Mont, P. G. Jones and J. Jeske, *Chem. Ber.*, 1997, **130**, 1611; (*f*) A. Steiner and D. Stalke, *Inorg. Chem.*, 1995, **34**, 4846; (*g*) S. Fregerslev and S. E. Rasmussen, *Acta Chem. Scand.*, 1968, **22**, 2541.

12 J. E. Drake and R. T. Hemmings, *Can. J. Chem.*, 1973, **51**, 302.

13 D. T. Durig, M. S. Durig and J. R. Durig, *Spectrochim. Acta, Part A*, 2005, **61**, 1287.

14 (*a*) D.-K. Seo, N. Gupta, M.-H. Whangbo, H. Hillebrecht and G. Thiele, *Inorg. Chem.*, 1998, **37**, 407; (*b*) U. Schwarz, H. Hillebrecht, M. Kaupp, K. Syassen and H.-G. v. Schnering, *J. Solid State Chem.*, 1995, **118**, 20.

15 R. Campbell, B. Peerless and P. Portius, unpublished results.

16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

17 (*a*) W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt and D. B. Sowerby, *Dalton Trans.*, 1972, 245; (*b*) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer and K. Feldl, *Chem. Ber.*, 1967, **100**, 2335.

18 (*a*) J. Kouvetakis, A. Haaland, D. J. Shorokhov, H. V. Volden, G. V. Girichev, V. I. Sokolov and P. Matsunaga, *J. Am. Chem. Soc.*, 1998, **120**, 6738; (*b*) S. P. Kolesnikov, I. S. Rogozhin and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, **23**, 2379.

19 (*a*) V. Y. Kukushkin and A. I. Moiseev, *Inorg. Chim. Acta*, 1990, **176**, 79; (*b*) A. Martinsen and J. Songstad, *Acta Chem. Scand., Ser. A*, 1977, **31**, 645.

20 M. J. Frisch, *et al.*, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2013.

21 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*c*) T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.

22 K. A. Peterson, *J. Chem. Phys.*, 2003, **119**, 11099.

23 (*a*) B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151; (*b*) M. Cossi, V. Barone, B. Mennucci and J. Tomasi, *Chem. Phys. Lett.*, 1998, **286**, 253 and references therein.

24 K. K. Irikura, R. D. Johnson and R. N. Kacker, *J. Phys. Chem. A*, 2005, **109**, 8430.

25 R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789.

26 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.