Supporting Information

Homoleptic Low-Valent Polyazides of Group 14 Elements

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Contents

Preparative details

Polyazides are potentially explosive; *appropriate care should be taken during all preparative procedures*. Compounds should be stored in the cold, away from heat and acids. All residues should be destroyed safely. Details of general experimental conditions, the treatment of starting material and the analytical instrumentation can be found in previous publications, see ref. 3 and 4.

Preparation of $\mathbf{(PPh_4)Ge(N_3)Cl_2}$ (2b). $\mathrm{GeCl_2}$(1,4-dioxane) (0.349 g, 1.50 mmol) and $\mathrm{(PPh_4)}$-$\mathrm{N_3}$ (0.577 g 1.51 mmol) were combined in a Schlenk tube, cooled to −40°C and dissolved in acetonitrile (20 mL). The colourless solution was allowed to warm up to room temperature with stirring and then stirred for a further 0.5 hrs, after which the solvent was removed under a dynamic vacuum precipitating a colourless solid. The solid was dissolved in THF (10 mL) followed with the addition of diethyl ether (1 mL) resulting in a white suspension which was filtered and the residue discarded. The supernatant solution was concentrated to approximately 2 mL and diethyl ether (20 mL) was added resulting in the immediate formation of a white powder, which was filtered, washed (cold diethyl ether) and dried in vacuo; yield 643 mg (82 % from $\mathrm{GeCl_2}$(diox)). IR (MeCN) ν / (cm^{-1}) = 3163w, 2075vs, 2062s).

Preparation of $\mathbf{(PPh_4)Ge(N_3)_3}$ (3b). $\mathrm{NaN_3}$ (1.840 g, 28.3 mmol) and **1a** (0.643 g, 1.05 mmol) were combined in a Schlenk tube and suspended in THF (20 mL). The suspension was stirred for 16 hours after which the suspension was filtered into a Schlenk tube containing $\mathrm{NaN_3}$ (1.945 g, 29.9 mmol) and stirred for a further 24 hours. The second suspension was filtered giving a clear, colourless supernatant solution and the filter residue was discarded. Diethyl ether (10 mL) was added to the supernatant solution resulting in a white precipitate which was filtered and discarded. The supernatant solution was concentrated to approximately 2 mL and diethyl ether (30 mL) was added resulting in a turbid solution. On cooling at −18°C for 48 hours colourless, needle crystals of **(1)** were obtained. The crystals were isolated by filtration, washed with diethyl ether and dried under vacuum; yield 400 mg (71 % from **1a**). Analysis: Elem. anal. calcd. for $\mathrm{C_{24}H_{20}N_9PGe}$ (538.06 g mol^{-1}): C, 53.55; H, 3.75; N, 23.43%; found: C, 53.66; H, 3.83; N, 22.68%. IR ν / (cm^{-1}) = 2092vs, 2058s (THF), 2095, 2063 ($\mathrm{CH_2Cl_2}$), 2098, 2064 (MeCN). ^{14}N NMR ($\mathrm{CD_2Cl_2}$, 29 MHz) δ / ppm = −136 (N$_\beta$, $\Delta\nu_{1/2}$ = 24 Hz), −207 (N$_\gamma$, $\Delta\nu_{1/2}$ = 147 Hz), −263 (N$_\alpha$, $\Delta\nu_{1/2}$ = 552 Hz). DSC (10 K min^{-1}) $T_{\mathrm{on}}^{\mathrm{endo1}}$ = 61°C,* $T_{\mathrm{p}}^{\mathrm{endo1}}$ = 63°C, ΔH^1= 27 J g^{-1}, $T_{\mathrm{on}}^{\mathrm{ex1}}$ = 99°C, $T_{\mathrm{p}}^{\mathrm{ex1}}$ = 109°C, ΔH^2= −319 J g^{-1}, $T_{\mathrm{on}}^{\mathrm{endo2}}$ = 196°C, $T_{\mathrm{p}}^{\mathrm{endo2}}$ = 199°C, ΔH^3= 4 J g^{-1}, $T_{\mathrm{on}}^{\mathrm{endo3}}$ = 248°C, $T_{\mathrm{p}}^{\mathrm{endo3}}$ = 250°C, ΔH^4= 8 J g^{-1}, $T_{\mathrm{on}}^{\mathrm{ex2}}$ = 310°C, $T_{\mathrm{p}}^{\mathrm{ex2}}$ = 317°C, ΔH^5= −468 J g^{-1}.

*) average of measurements.

Preparation of (PPh$_4$)Sn(N$_3$)$_3$ (4b). The same procedure was applied to prepare (PPh$_4$)Sn(N$_3$)$_3$ from SnCl$_2$ affording 714 mg of **2** (72 % yield with respect to SnCl$_2$). IR (THF) ν / (cm^{-1}) = 2081vs, 2073m 2050m. ^{14}N NMR (CD$_3$CN, 29 MHz) δ [ppm] = −136 (N$_\beta$, $\Delta\nu_{1/2}$ = 24 Hz), −218 (N$_\gamma$, $\Delta\nu_{1/2}$ = 29 Hz), −260 (N$_\alpha$, $\Delta\nu_{1/2}$ = 116 Hz). ^{119}Sn NMR (CD$_3$CN, 149 MHz) δ / ppm = −220 ($\Delta\nu_{1/2}$ = 270 Hz).

Preparation of (PPN)GeCl$_3$ (1c).[1] GeCl$_2$(1,4-dioxane) (248 mg, 1.07 mmol) was combined with bis(triphenylphosphine)iminium chloride (580 mg, 1.07 mmol) in a Schlenk tube and cooled to −80°C. Acetonitrile (20 mL) was added via a cannula and the Schlenk tube was removed from the cold bath. The colourless, turbid solution was left to stir for 2 hrs and on warming to room temperature the solution became clear. The solvent was removed *in vacuo* resulting in an off-white solid. This solid was dissolved in THF / Et$_2$O (2 : 1, 2 x 20 mL) and any remaining solid was filtered off and discarded. The filtrate solution was concentrated to approximately 2 mL and treated with Et$_2$O (40 mL) resulting in an immediate white precipitate. The suspension was cooled to −18°C overnight and filtered affording 675 mg of (PPN)GeCl$_3$ (88 % yield with respect to GeCl$_2$(1,4-dioxane). Analysis: Elem. anal. calcd. for C$_{36}$H$_{30}$Cl$_3$GeNP$_2$ (717.56 g mol^{-1}): C, 60.26; H, 4.21; Cl, 14.82 N, 1.95%; found: C, 60.23; H, 4.36; Cl, 14.58; N, 1.91%. Melting point = 170-172°C. ^{1}H-NMR (CD$_3$CN) δ / ppm = 7.54-7.68 (m, 18H), 7.44-7.50 (m, 12H), 2.11 - 2.13 (s, 1H, MeCN/CD$_2$HCN). ^{31}P{^{1}H}-NMR (CD$_3$CN) δ / ppm = 22.3. IR (nujol) ν / (cm^{-1}) = 3057m, 1973w, 1825w, 1588m, 1482m, 1438s, 1315s, 1300s, 1259s, 1182m, 1162w, 1113s, 1074w, 1026m, 998m, 798w, 760m, 743s, 722s, 691s, 550s, 530s.

Preparation of (PPN)Ge(N$_3$)$_3$ (3c).[1] A Schlenk tube was charged with a mixture of (PPN)GeCl$_3$ (**1c**) (343 mg, 0.478 mmol) und NaN$_3$ (1.583 g, 24.35 mmol) and degassed for 0.5 h at 40°C under a high vacuum (HV) after with THF (27 ml) was added by trap-to-trap condensation. The resultant white suspension was stirred vigorously for 24 h at r.t. which left the appearance of the mixture unchanged. For the purpose of precipitating traces of NaN$_3$ and (PPN)N$_3$ by-products from the reaction solution, Et$_2$O (13 ml) was added by trap-to-trap condensation which resulted in some clouding of the supernatant solution. The solution was separated by filtration resulting in a clear and colourless solution which was evaporated under a dynamic vacuum until a clear and colourless oil was obtained which slowly crystallises upon standing at r.t. Crystallisation was completed by addition of Et2O (19 ml) and the mixture was stirred until the product had solidified completely and then cooled to −78°C. The supernatant solution was decanted off and the decantation residue dried for 0.5 h in HV which afforded 308 mg of a microcrystalline, odourless, white powder (raw yield 87.4%, elem. anal. C, 58.87; H, 4.52; Cl, 0.42; N, 16.78%). This chlorine containing substance was treated with fresh NaN_3 (1.135 g, 17.46 mmol) and worked up using the method detailed above (but without warming, reaction time of 8 h) which yielded 241 mg **3c** (68% with respect to **1c**). Upon rapid heating, compound **3c** decomposes between 105°C and 109°C under evolution of a gas. Upon slow heating, the only visible phase change occurs at a temperature above 180°C; elem. anal. for $C_{36}H_{30}GeN_{10}P_2$ (737.26 g mol^{-1}), calcd. C, 58.65; H, 4.10; Cl, 0; N, 19.00; P, 8.40; gef.: C, 60.01; H, 4.15; Cl, ca. 0.1$^{(2}$; N 17.64, P 8.50%$^{(2}$. ^{1}H NMR (CD_3CN, rt): δ / ppm = 7.54 - 7.68 [m, 18H, *o*/*p*-H(Ph)], 7.44 - 7.50 [m, 12H, *m*-H(Ph)]; contains traces of Et_2O (1.0 mol%) and THF (2.4 mol%). $^{31}P\{^1H\}$ NMR (CD_3CN, rt): δ / ppm = 22.3 [s]. IR (Nujol,): ν / (cm^{-1}) = 3358(vw), 3313(vw), 3056(w), 2095(vs), 2061(vs), 1995(w), aromatic fingerprint (vw), 1588 (w), 1482(m), 1439(s), 1316(m), 1252(vs), 1182(w), 1163(vw), 1114(vs), 1027(w), 998(w), 803(m), 747(s), 723(vs), 695(vs), 667(vw), 553(vw), 534(vw), (PPN)N_3 (~3 mol%) present as can be shown by comparison with a spectrum of genuine (PPN)N_3. IR (THF, cm^{-1}): ν / (cm^{-1}) = 2092 (m), 2059 (vs, $\nu_{as}N_3$), 1589, 1484 (wv, Ph); (toluene): ν / (cm^{-1}) = 2091 (m), 2058 (vs, $\nu_{as}(N_3)$); (CH_2Cl_2): ν = 2094 (m), 2063 [vs, $\nu_{as}(N_3)$], 1590 (vw, Ph); (MeCN): ν / (cm^{-1}) = 2095 (m), 2064 (vs, $\nu_{as}(N_3)$)], 1590 (vw, Ph). The following spectral information was obtained from the product of the reaction of (PPN)N_3 with $GeCl_2$-(diox) in the molar ratio of 1 : 1, (PPN)$GeCl_2(N_3)$, 2078 cm^{-1} (in MeCN) and 2077 cm^{-1} (in nujol); (PPN)$GeCl(N_3)_2$, 2088, 2066 cm^{-1} (in MeCN).

Spectral Data

Fig. S1. IR spectrum of compound 1b (paraffin mull)

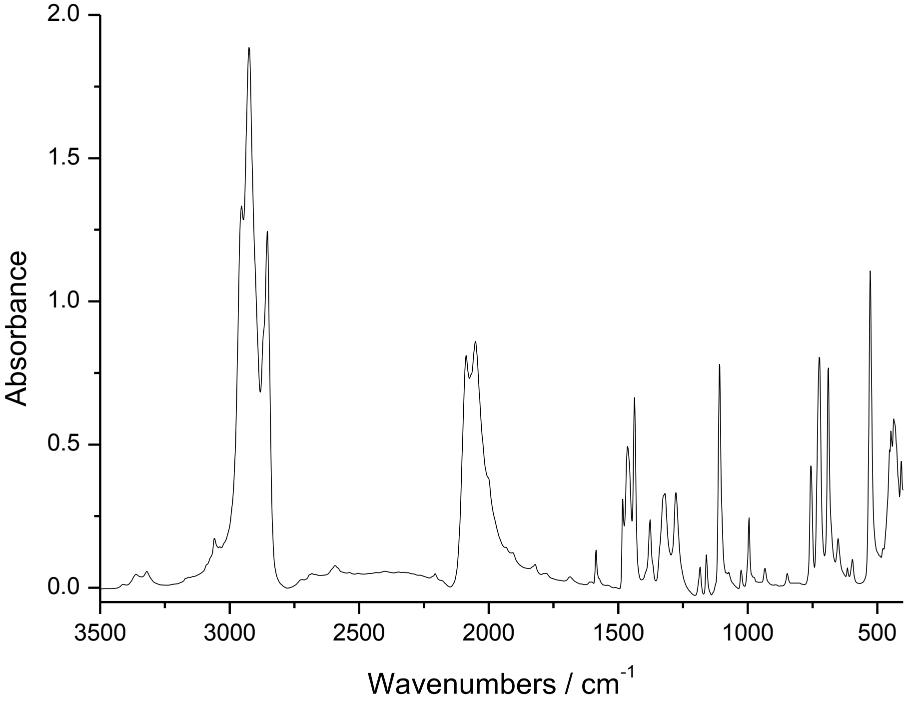


Fig. S2. IR spectrum of compound 3b (paraffin mull)

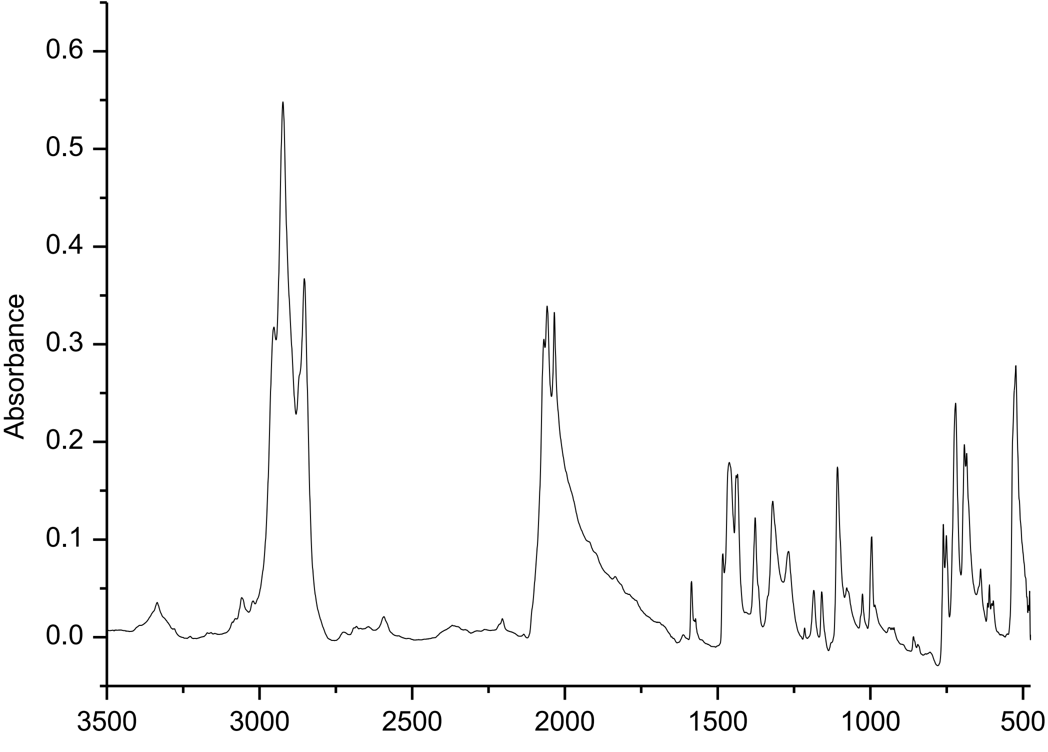


Fig. S3. IR spectrum of 1c (PPN)$GeCl_3$, paraffin mull)

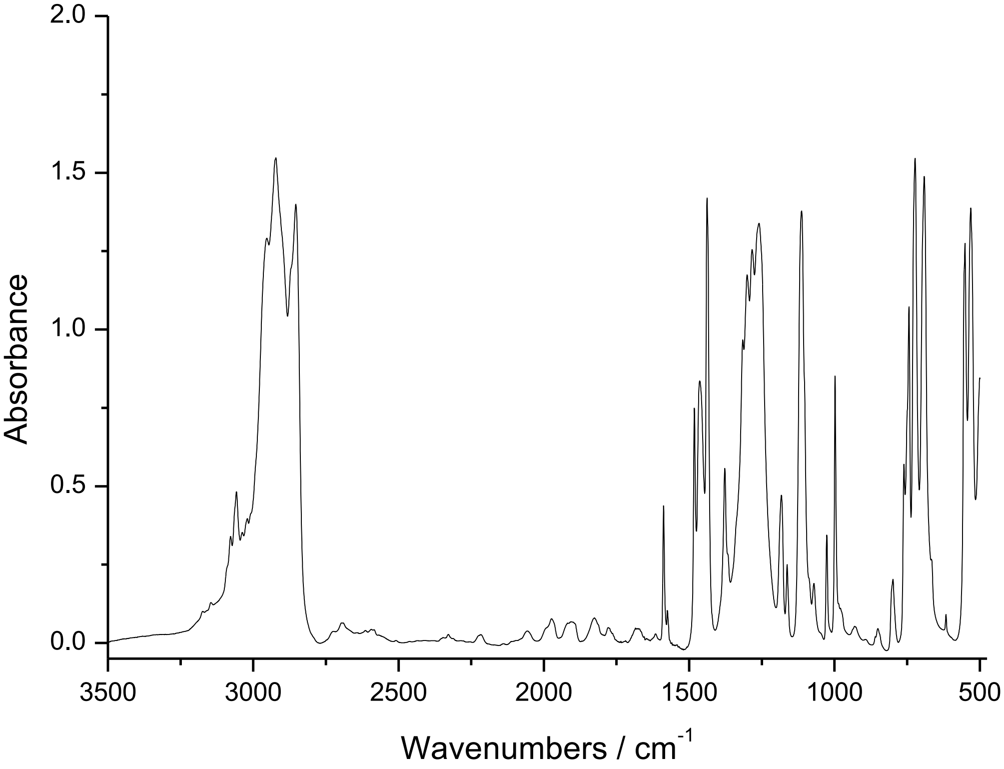


Fig. S4. FTIR Spectra of $(PPh_4)Ge(N_3)_3$ (3b) and $(PPh_4)Sn(N_3)_3$ (4b) in THF solution (normalised, baseline corrected, HN_3, $Sn(N_3)_6^{2-}$ and N_3^- impurities indicated)

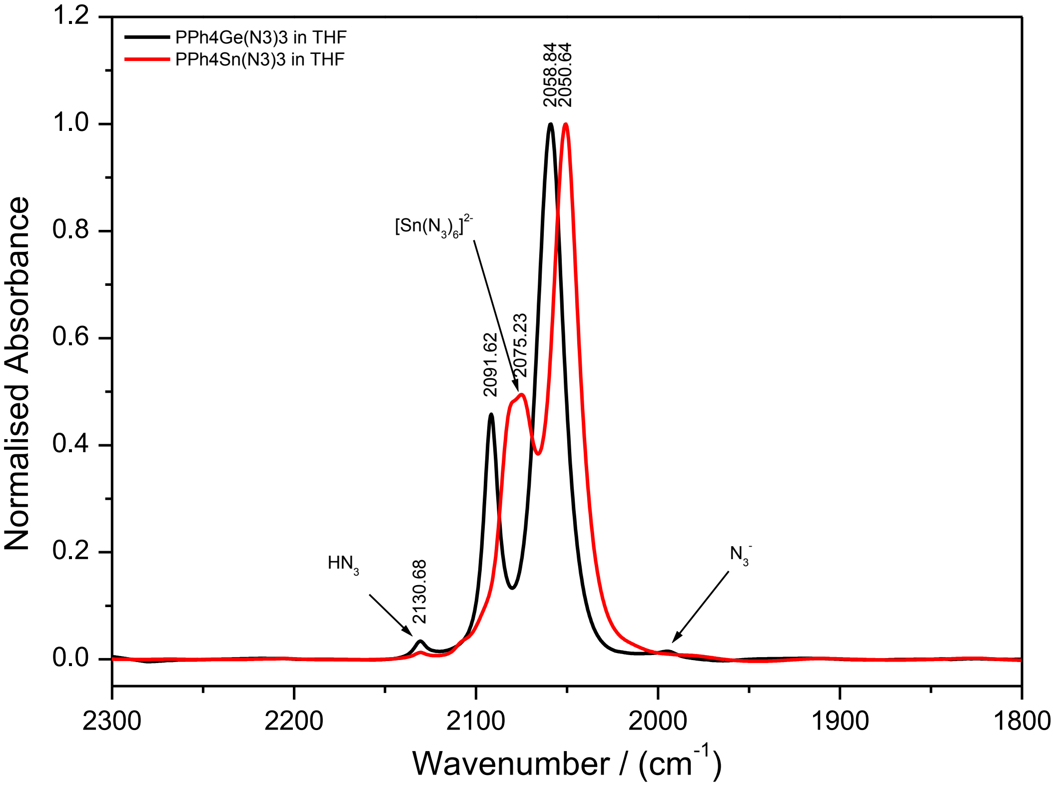


Table S1. Frequencies of the $\nu_{as}(N_3)$ stretching vibrations [a] in homoleptic and low-valent germanium and tin azides.

	E = Ge [b]	E = Ge [c]	E = Sn [b]	E = Sn [c]
$[E(N_3)_3]^-$	2098, 2064 [e] 2091, 2059 [d]	2092, 2060	2085,2055 [e] 2080,2051 [d]	2078, 2050
$[ECl(N_3)_2]^-$	2088, 2066 [e]	2084, 2067	2071, 2051	2069, 2051
$[ECl_2(N_3)]^-$	2078 [e]	2080	2064 [d]	2064, 2054[n]
$[L_nE{-}N_3]$	2027,[f] 2043-2063,[d g] 2048-2062,[h,i] 2075,[j ,k] 2077 [h,l]	-	2039, 2060 [h,i]	-
$E(N_3)_4$	2053 [m]	-	-	-
$[E(N_3)_6]^{2-}$	2083 [d]	-	2112,2079 [d]	-

[a] $\nu_{as}(N_3)$ / (cm^{-1}); [b] observed, [c] calculated, scaling factor 0.957; [d] in THF; [e] in MeCN; [f] L_1 = $\{Me_2(^tBuO)Si\}_2N$ [4c]; [g] L_3 = $HB(R_2pz)_3$, $(C_5R_5)Co\{P(O)(OEt)_2\}_3$ [4a,e,10]; [h] in KBr; [i] L_2 = $^nPr_2ATI$ and Mes_2DAP [4f,g]; [j] attenuated total reflection; [k] $(2,6\text{-}^iPr_2C_6H_3)_2C_2H_2N_2CGe(N_3)_2$ [8d]; [l] L_2 = $(NHC)_2^+$ [3]; [m] C_6H_5 [12]; [n] bands of both rotamers are likely to coalesce in solution; all references refer to the main paper.

Fig. S5. ^1H NMR spectrum of compound 3b

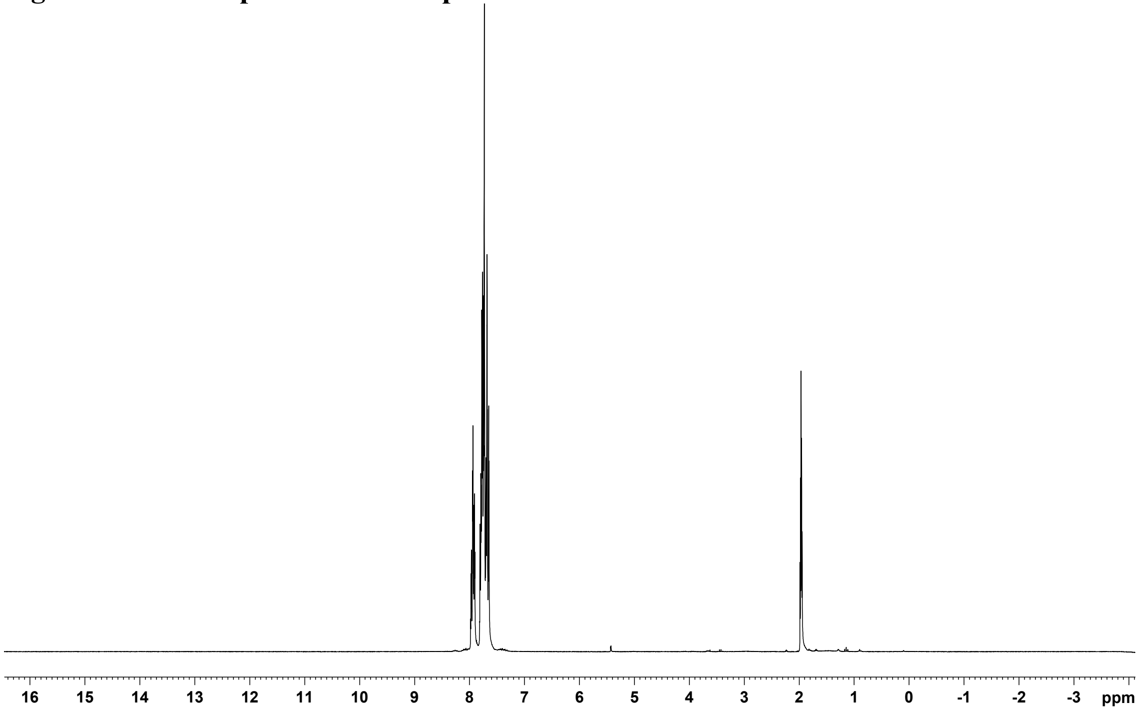


Fig. S6. DEPTQ ^{13}C NMR spectrum of compound 3b

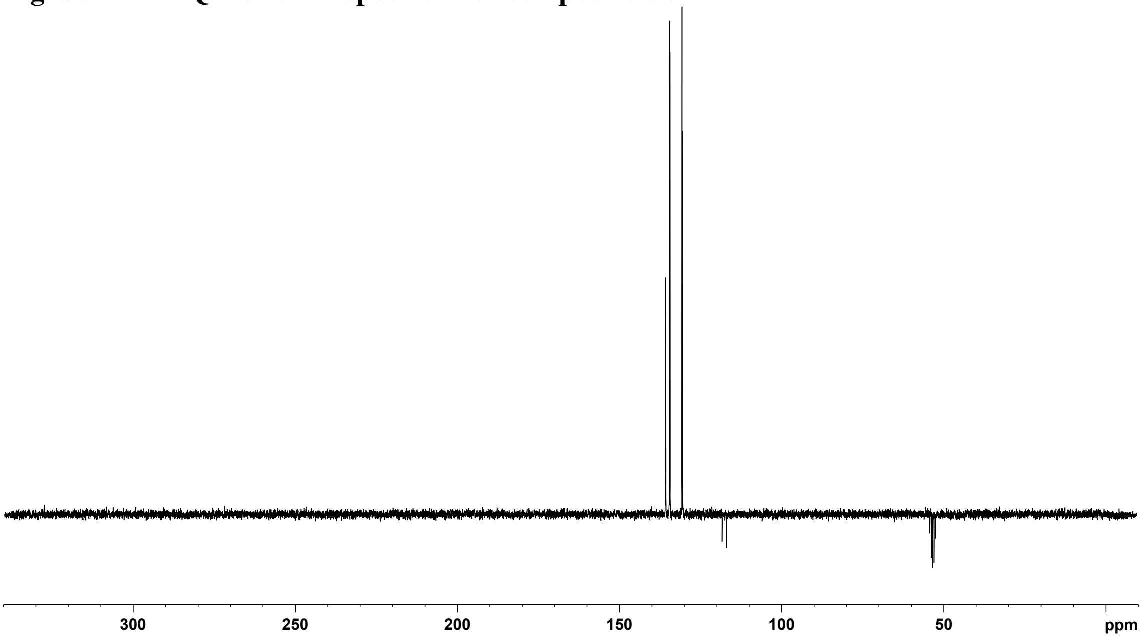


Fig. S7. ^{31}P NMR spectrum o f compound 3b

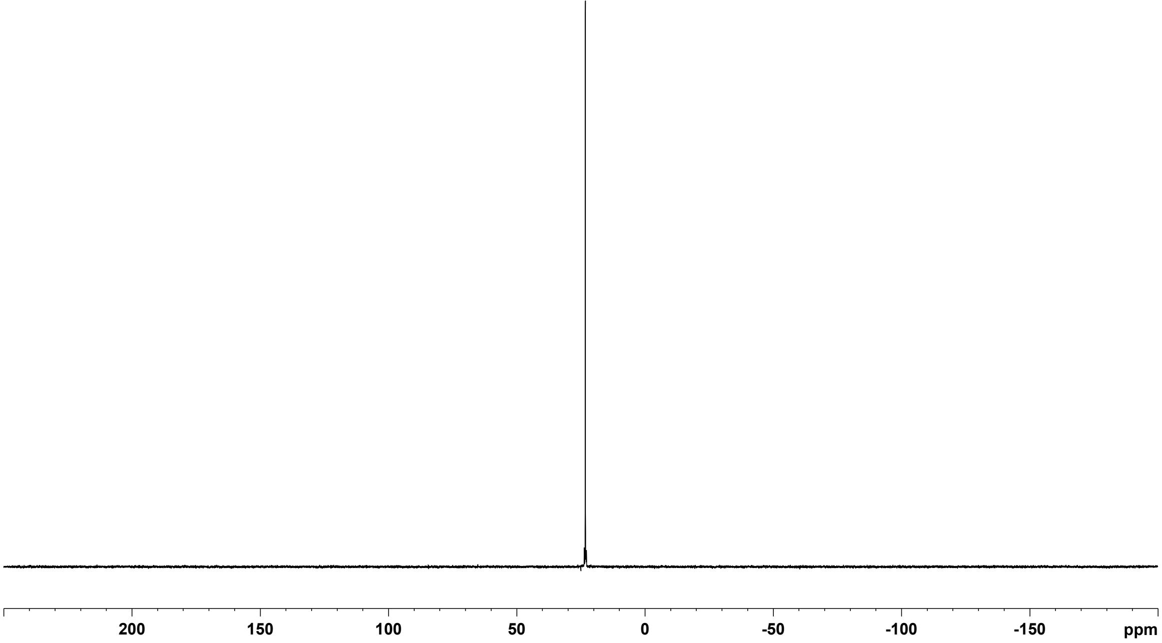


Fig. S8. ^{14}N NMR spectrum of compound 3b

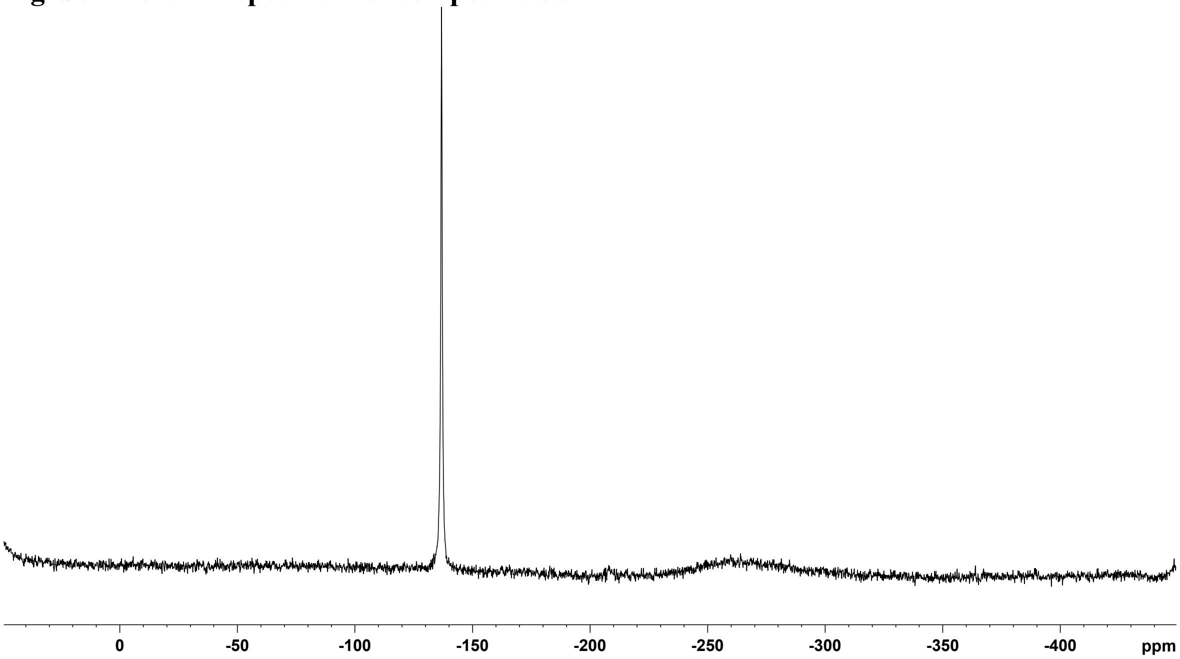
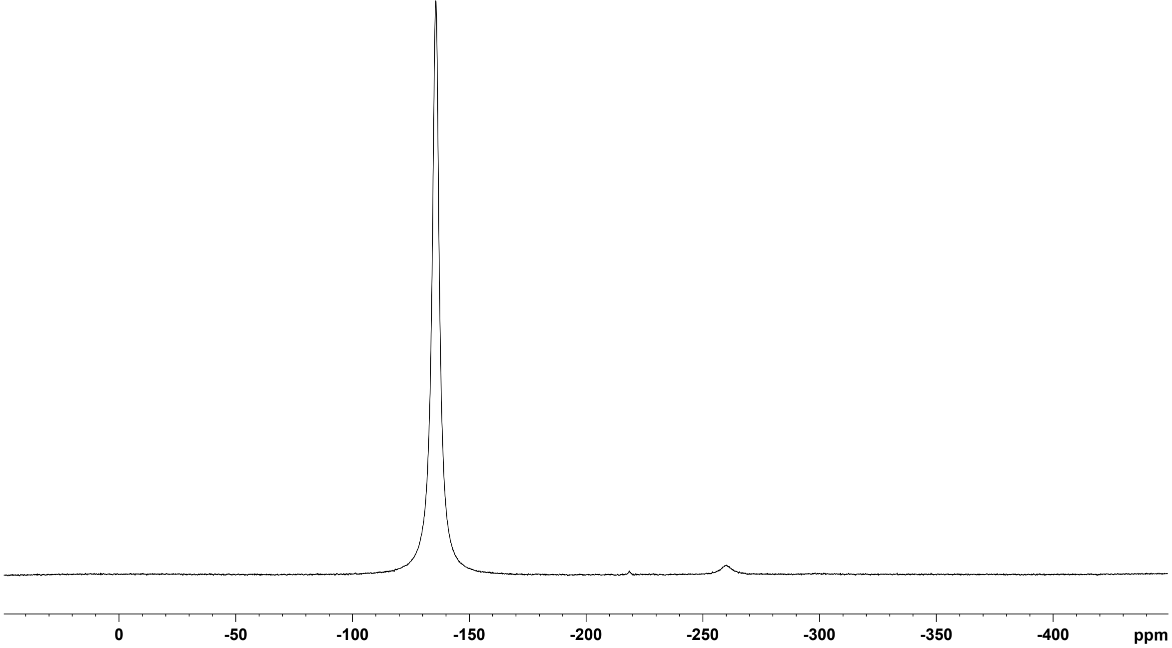


Fig. S9. ^{14}N NMR spectrum of compound 4b



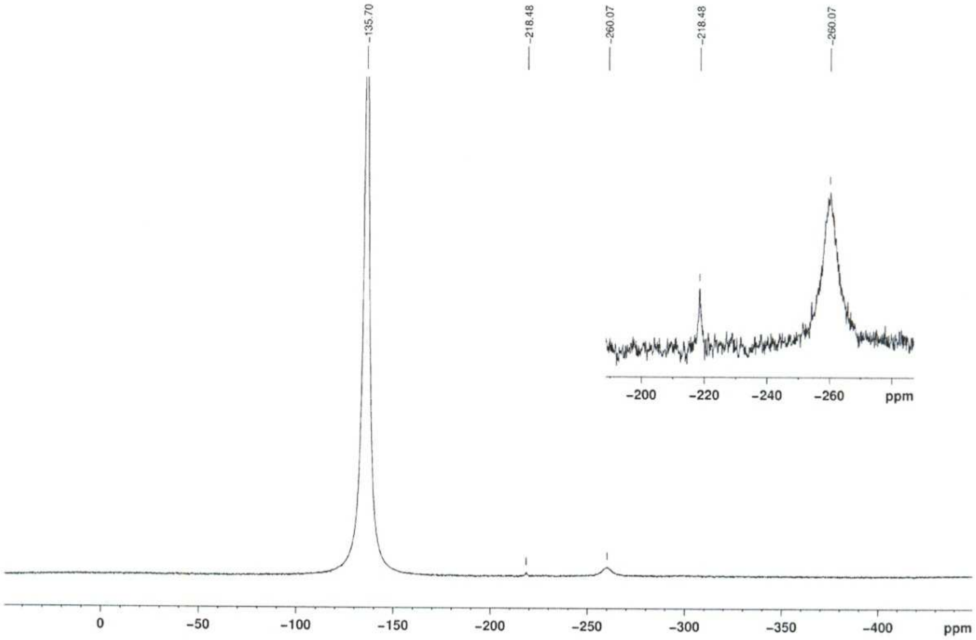


Fig. S10. ^{119}Sn NMR spectrum of compound 4b

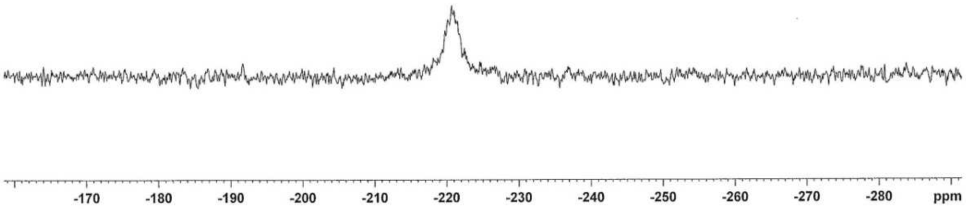


Fig. S11. Differential thermogram (DSC) of compound 3b

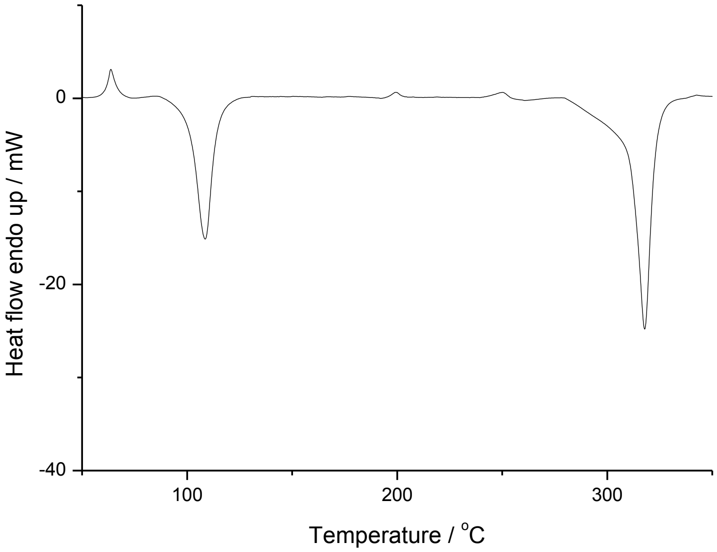


Fig. S12. Differential thermogram (DSC) of compound 4b

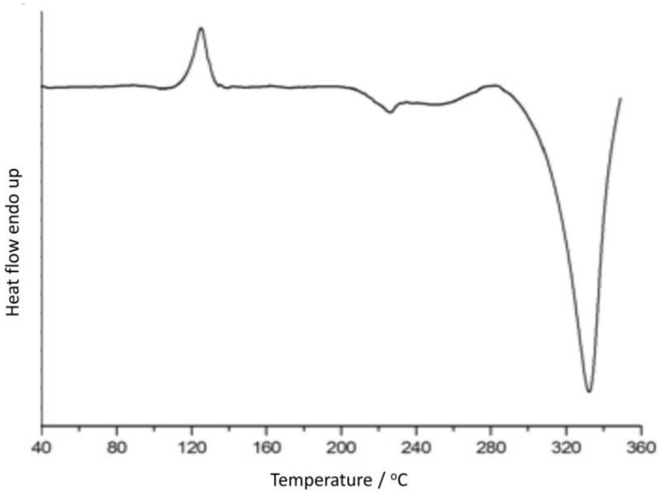
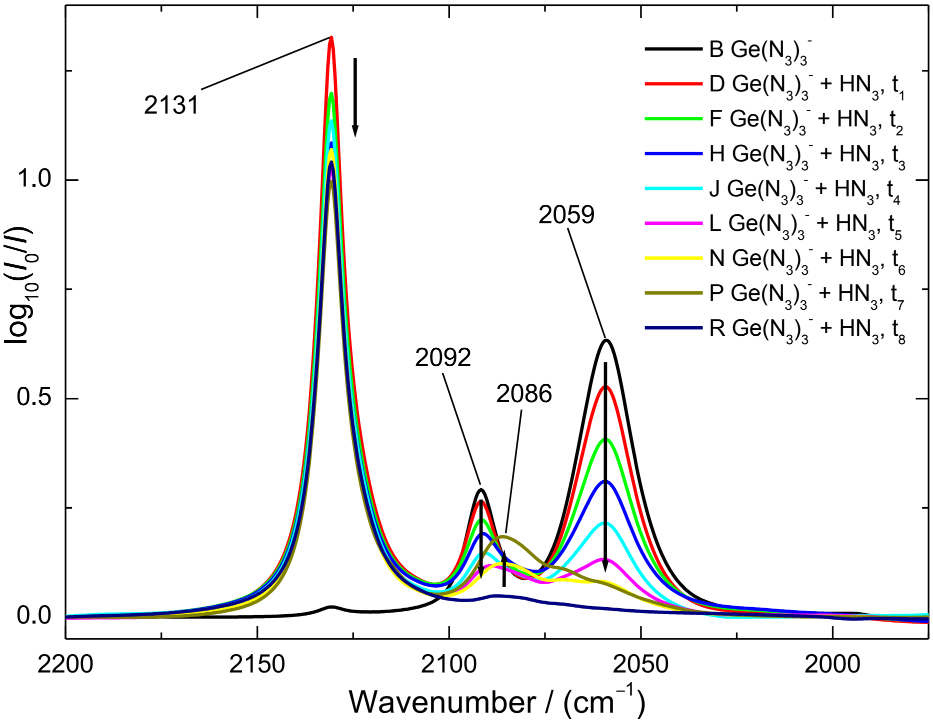
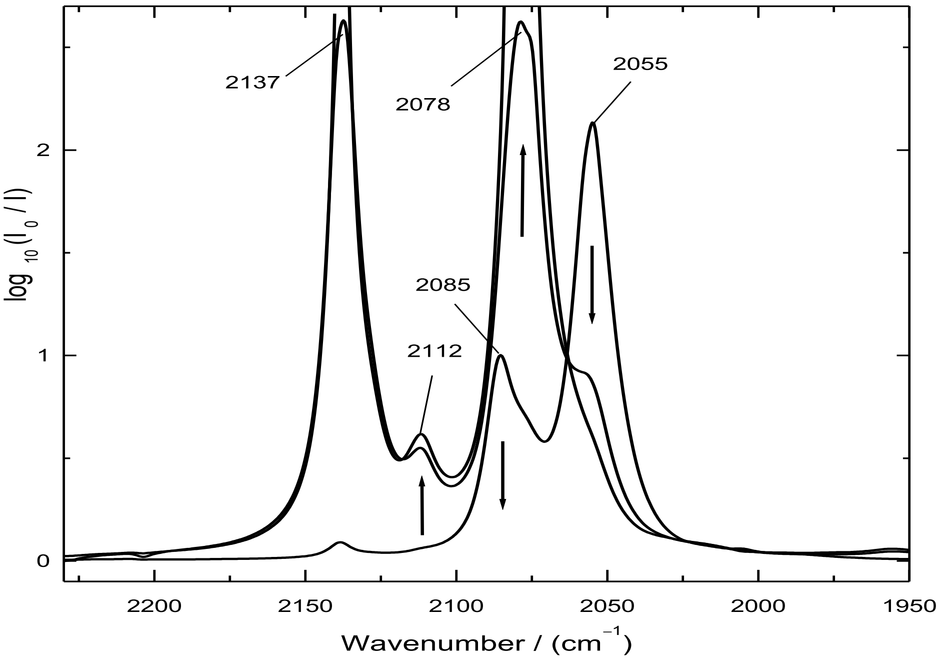


Fig. S13. In situ IR spectra of HN_3 reacting with $Ge(N_3)_3^-$ (3b) in THF solution



Note: The IR spectrum of the precipitate of the reaction contains a $\nu_{as}(N_3)$ stretch characteristic for the symmetric $Ge(N_3)_6^{2-}$ ion and the PPh_4 finger print. The precipitate is therefore ascribed to the formation of $(PPh_4)_2Ge(N_3)_6$, which is expected to be as sparingly soluble in THF as the related $(PPN)_2Ge(N_3)_6$.

Fig. S14. In situ IR spectra of HN_3 reacting with $Sn(N_3)_3^-$ (4b) in MeCN solution



Crystallographic Details

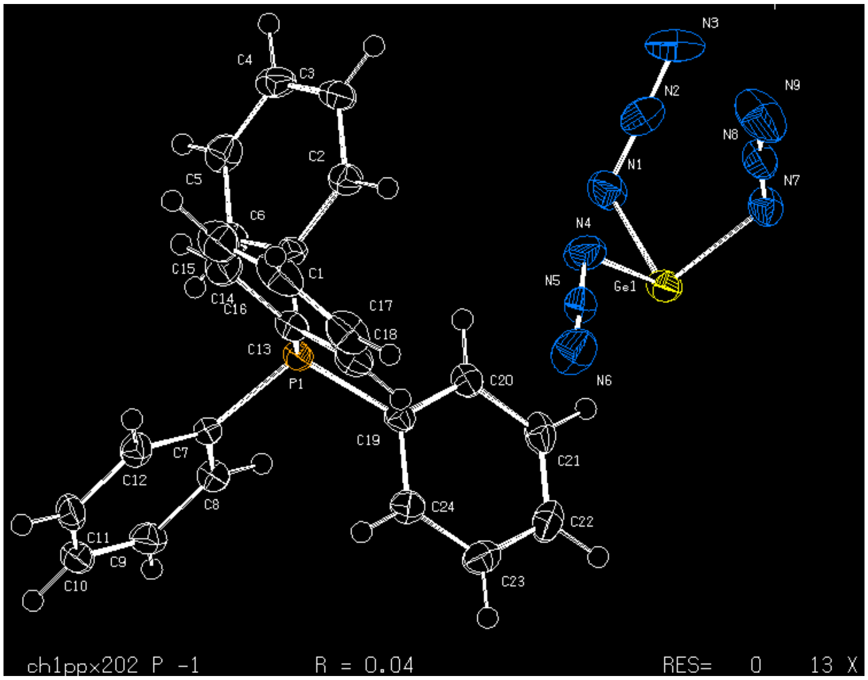


Fig. S15. Asymmetric unit in the single crystal of compound 3b. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for compound 3b

Identification code	ch1ppx202_0m	
Empirical formula	$C_{24}H_{20}GeN_9P$	
Formula weight	538.07	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 7.7712(2) Å	α = 93.278(2)°.
	b = 11.4711(4) Å	β = 99.357(2)°.
	c = 14.2003(4) Å	γ = 100.865(2)°.
Volume	1221.59(6) Å^3	
Z	2	
Density (calculated)	1.463 Mg m^{-3}	
Absorption coefficient	1.351 mm^{-1}	
F(000)	548	
Crystal size	0.27 x 0.27 x 0.06 mm^3	
Theta range for data collection	1.46 to 27.57°.	
Index ranges	$-10 <= h <= 10, -14 <= k <= 14, -18 <= l <= 18$	
Reflections collected	24417	
Independent reflections	5614 [*R*(int) = 0.0598]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9233 and 0.7117	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5613 / 0 / 316	
Goodness-of-fit on F^2	1.090	
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0376$, w$R_2 = 0.0731$	
R indices (all data)	$R_1 = 0.0645$, w$R_2 = 0.0807$	
Largest diff. peak and hole	0.338 and -0.467 e.Å^{-3}	

Table S3. Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for: ch1ppx202_P -1 R = 0.04

Atom	*x*	*y*	*z*	*U*(eq) [Ang^2]
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P1	0.54012(8)	0.77428(5)	0.76571(4)	0.0201(2)
C1	0.6533(3)	0.7889(2)	0.66530(15)	0.0209(7)
C2	0.7692(3)	0.7114(2)	0.65349(16)	0.0252(8)
C3	0.8704(3)	0.7260(2)	0.58192(16)	0.0280(8)
C4	0.8581(3)	0.8171(2)	0.52305(16)	0.0297(8)
C5	0.7419(3)	0.8923(2)	0.53330(16)	0.0297(8)
C6	0.6387(3)	0.8789(2)	0.60476(16)	0.0249(8)
C7	0.4397(3)	0.8996(2)	0.78618(16)	0.0207(7)
C8	0.2832(3)	0.9071(2)	0.72465(16)	0.0246(8)
C9	0.1956(3)	0.9979(2)	0.74118(17)	0.0282(8)
C10	0.2617(3)	1.0819(2)	0.81890(17)	0.0301(8)
C11	0.4173(3)	1.0758(2)	0.87998(17)	0.0285(8)
C12	0.5064(3)	0.9845(2)	0.86427(16)	0.0250(8)
C13	0.7064(3)	0.7630(2)	0.86687(16)	0.0235(8)
C14	0.8666(3)	0.8460(2)	0.88210(17)	0.0311(8)
C15	0.9981(3)	0.8377(3)	0.95825(19)	0.0389(9)
C16	0.9710(4)	0.7485(3)	1.01846(18)	0.0394(10)
C17	0.8130(4)	0.6663(3)	1.00308(18)	0.0377(10)
C18	0.6795(3)	0.6732(2)	0.92706(16)	0.0294(8)
C19	0.3607(3)	0.6476(2)	0.74614(15)	0.0211(7)
C20	0.3290(3)	0.5673(2)	0.66522(16)	0.0248(8)
C21	0.1796(3)	0.4771(2)	0.64957(18)	0.0309(8)
C22	0.0627(3)	0.4652(2)	0.71323(18)	0.0327(8)
C23	0.0950(3)	0.5439(2)	0.79452(18)	0.0304(8)

C24	0.2412(3)	0.6354(2)	0.81121(16)	0.0257(8)
Ge1	0.47171(3)	0.29007(2)	0.68416(2)	0.0277(1)
N1	0.5845(3)	0.37359(19)	0.58397(15)	0.0365(8)
N2	0.6861(3)	0.3245(2)	0.54775(14)	0.0337(7)
N3	0.7808(3)	0.2800(2)	0.51064(16)	0.0489(9)
N4	0.6713(3)	0.3758(2)	0.78702(16)	0.0387(8)
N5	0.6515(3)	0.37344(18)	0.86967(16)	0.0299(7)
N6	0.6393(3)	0.3735(2)	0.94887(16)	0.0456(9)
N7	0.5808(3)	0.14890(18)	0.66729(14)	0.0302(7)
N8	0.7244(3)	0.14444(18)	0.71238(15)	0.0327(8)
N9	0.8565(3)	0.1319(2)	0.75448(19)	0.0589(10)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S4. Hydrogen Atom Positions and Isotropic Displacement Parameters for: ch1ppx202_P -1 R = 0.04

Atom	*x*	*y*	*z*	*U*(iso) [Ang^2]
H2	0.77820	0.64930	0.69440	0.0300
H3	0.94860	0.67340	0.57310	0.0340
H4	0.93040	0.82810	0.47510	0.0360
H5	0.73240	0.95340	0.49140	0.0360
H6	0.55900	0.93080	0.61210	0.0300
H8	0.23720	0.84950	0.67140	0.0290
H9	0.08940	1.00290	0.69910	0.0340
H10	0.20020	1.14390	0.83030	0.0360
H11	0.46300	1.13420	0.93270	0.0340
H12	0.61240	0.97980	0.90660	0.0300
H14	0.88510	0.90750	0.84060	0.0370
H15	1.10770	0.89370	0.96910	0.0470
H16	1.06170	0.74370	1.07080	0.0470
H17	0.79550	0.60480	1.04460	0.0450
H18	0.57030	0.61670	0.91640	0.0350
H20	0.40940	0.57440	0.62110	0.0300
H21	0.15710	0.42240	0.59410	0.0370
H22	-0.04000	0.40300	0.70130	0.0390
H23	0.01550	0.53450	0.83910	0.0360
H24	0.26160	0.69030	0.86640	0.0310

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S5. (An)isotropic Displacement Parameters for: ch1ppx202_P -1 R = 0.04

Atom	*U*(1,1) or *U*	*U*(2,2)	*U*(3,3)	*U*(2,3)	*U*(1,3)	*U*(1,2)
P1	0.0195(3)	0.0203(3)	0.0209(3)	0.0002(3)	0.0037(2)	0.0053(2)
C1	0.0183(12)	0.0228(13)	0.0208(12)	-0.0008(10)	0.0037(9)	0.0030(10)
C2	0.0232(13)	0.0272(14)	0.0255(13)	0.0015(11)	0.0041(10)	0.0065(10)
C3	0.0218(13)	0.0346(16)	0.0278(13)	-0.0053(12)	0.0059(10)	0.0073(11)
C4	0.0239(13)	0.0396(17)	0.0242(13)	-0.0039(12)	0.0077(11)	0.0020(12)
C5	0.0344(14)	0.0318(15)	0.0217(12)	0.0051(11)	0.0055(11)	0.0027(12)
C6	0.0239(13)	0.0269(14)	0.0244(12)	-0.0002(11)	0.0037(10)	0.0074(11)
C7	0.0209(12)	0.0186(13)	0.0237(12)	0.0023(10)	0.0083(10)	0.0031(10)
C8	0.0249(13)	0.0236(14)	0.0261(13)	0.0019(10)	0.0065(10)	0.0056(10)
C9	0.0244(13)	0.0318(15)	0.0313(14)	0.0054(11)	0.0080(11)	0.0093(11)
C10	0.0348(15)	0.0244(14)	0.0373(14)	0.0070(12)	0.0178(12)	0.0107(11)
C11	0.0408(15)	0.0195(13)	0.0267(13)	-0.0005(11)	0.0125(12)	0.0052(11)
C12	0.0289(13)	0.0232(14)	0.0225(12)	0.0026(10)	0.0053(10)	0.0032(10)
C13	0.0229(13)	0.0263(14)	0.0226(12)	-0.0007(10)	0.0045(10)	0.0085(10)
C14	0.0288(14)	0.0315(15)	0.0316(14)	0.0011(11)	0.0025(11)	0.0054(11)
C15	0.0273(15)	0.0417(18)	0.0420(16)	-0.0127(14)	-0.0049(12)	0.0068(13)
C16	0.0377(16)	0.0514(19)	0.0286(14)	-0.0082(14)	-0.0089(12)	0.0241(15)
C17	0.0475(18)	0.0414(18)	0.0286(14)	0.0059(12)	0.0033(13)	0.0221(14)

C18	0.0294(14)	0.0328(15)	0.0279(13)	0.0028(11)	0.0039(11)	0.0118(12)
C19	0.0201(12)	0.0217(13)	0.0220(12)	0.0018(10)	0.0020(9)	0.0068(10)
C20	0.0255(13)	0.0235(14)	0.0253(13)	0.0004(10)	0.0035(10)	0.0062(11)
C21	0.0345(15)	0.0230(14)	0.0312(14)	-0.0057(11)	-0.0014(12)	0.0041(11)
C22	0.0271(14)	0.0224(14)	0.0443(16)	0.0053(12)	-0.0009(12)	-0.0005(11)
C23	0.0257(14)	0.0329(16)	0.0342(14)	0.0093(12)	0.0089(11)	0.0053(11)
C24	0.0266(13)	0.0271(14)	0.0236(12)	0.0028(10)	0.0050(10)	0.0056(11)
Ge1	0.0267(2)	0.0280(2)	0.0311(2)	0.0037(1)	0.0091(1)	0.0087(1)
N1	0.0469(14)	0.0323(13)	0.0369(13)	0.0097(10)	0.0163(11)	0.0150(11)
N2	0.0293(12)	0.0438(15)	0.0263(11)	0.0119(10)	0.0029(10)	0.0022(11)
N3	0.0370(14)	0.080(2)	0.0390(14)	0.0128(13)	0.0190(12)	0.0225(14)
N4	0.0358(13)	0.0440(15)	0.0343(13)	-0.0056(11)	0.0153(10)	-0.0021(11)
N5	0.0278(12)	0.0245(12)	0.0363(13)	-0.0009(10)	0.0064(10)	0.0030(9)
N6	0.0528(16)	0.0497(16)	0.0300(13)	0.0020(12)	0.0105(12)	-0.0024(12)
N7	0.0288(12)	0.0262(12)	0.0349(12)	0.0034(9)	-0.0007(10)	0.0090(9)
N8	0.0341(14)	0.0283(13)	0.0353(12)	-0.0029(10)	0.0036(11)	0.0095(10)
N9	0.0418(16)	0.0620(19)	0.0681(18)	-0.0172(14)	-0.0178(14)	0.0288(14)

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S6. Bond Distances (Angstrom) for: ch1ppx202_P -1 R = 0.04

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)
P1 C19 1.787(3)
P1 C1 1.791(3)
P1 C7 1.791(3)
P1 C13 1.799(3)
C1 C6 1.390(4)
C1 C2 1.402(3)
C2 C3 1.383(4)
C2 H2 0.9500
C3 C4 1.384(4)
C3 H3 0.9500
C4 C5 1.379(4)
C4 H4 0.9500
C5 C6 1.392(4)
C5 H5 0.9500
C6 H6 0.9500
C7 C12 1.395(4)
C7 C8 1.397(4)
C8 C9 1.377(4)
C8 H8 0.9500
C9 C10 1.384(4)
C9 H9 0.9500
C10 C11 1.382(4)
C10 H10 0.9500
C11 C12 1.385(4)
C11 H11 0.9500
C12 H12 0.9500
C13 C18 1.383(4)
C13 C14 1.395(4)
C14 C15 1.381(4)
C14 H14 0.9500
C15 C16 1.376(5)
C15 H15 0.9500
C16 C17 1.377(5)
C16 H16 0.9500
C17 C18 1.385(4)
C17 H17 0.9500
C18 H18 0.9500
C19 C20 1.390(4)
C19 C24 1.408(4)
C20 C21 1.381(4)
C20 H20 0.9500
C21 C22 1.378(4)
C21 H21 0.9500
C22 C23 1.382(4)
C22 H22 0.9500
C23 C24 1.372(4)
C23 H23 0.9500
C24 H24 0.9500

Table S7. Bond Angles (Degrees) for: ch1ppx202_P -1 R = 0.04

N7 Ge1 N1 93.59(10)
N7 Ge1 N4 94.29(10)
N1 Ge1 N4 91.05(11)
N2 N1 Ge1 116.4(2)
N3 N2 N1 177.6(3)
N5 N4 Ge1 118.7(2)
N6 N5 N4 177.4(3)
N8 N7 Ge1 121.3(2)
N9 N8 N7 175.2(3)
C19 P1 C1 111.90(12)
C19 P1 C7 105.21(12)
C1 P1 C7 111.68(12)
C19 P1 C13 111.67(13)
C1 P1 C13 105.89(12)
C7 P1 C13 110.61(12)
C6 C1 C2 120.3(2)
C6 C1 P1 121.98(19)
C2 C1 P1 117.6(2)
C3 C2 C1 119.4(3)
C3 C2 H2 120.3
C1 C2 H2 120.3
C2 C3 C4 120.2(3)
C2 C3 H3 119.9
C4 C3 H3 119.9
C5 C4 C3 120.6(3)
C5 C4 H4 119.7
C3 C4 H4 119.7
C4 C5 C6 120.1(3)
C4 C5 H5 119.9
C6 C5 H5 119.9
C1 C6 C5 119.4(3)
C1 C6 H6 120.3
C5 C6 H6 120.3
C12 C7 C8 119.6(2)
C12 C7 P1 122.3(2)
C8 C7 P1 118.0(2)
C9 C8 C7 120.0(3)
C9 C8 H8 120.0
C7 C8 H8 120.0
C8 C9 C10 120.2(3)
C8 C9 H9 119.9
C10 C9 H9 119.9
C11 C10 C9 120.2(3)
C11 C10 H10 119.9
C9 C10 H10 119.9
C10 C11 C12 120.1(3)
C10 C11 H11 119.9
C12 C11 H11 119.9
C11 C12 C7 119.8(3)
C11 C12 H12 120.1
C7 C12 H12 120.1
C18 C13 C14 120.4(3)
C18 C13 P1 121.4(2)
C14 C13 P1 118.2(2)

C15 C14 C13	119.3(3)
C15 C14 H14	120.3
C13 C14 H14	120.3
C16 C15 C14	120.2(3)
C16 C15 H15	119.9
C14 C15 H15	119.9
C15 C16 C17	120.4(3)
C15 C16 H16	119.8
C17 C16 H16	119.8
C16 C17 C18	120.2(3)
C16 C17 H17	119.9
C18 C17 H17	119.9
C13 C18 C17	119.4(3)
C13 C18 H18	120.3
C17 C18 H18	120.3
C20 C19 C24	119.7(3)
C20 C19 P1	121.7(2)
C24 C19 P1	118.4(2)
C21 C20 C19	119.3(3)
C21 C20 H20	120.4
C19 C20 H20	120.4
C22 C21 C20	120.9(3)
C22 C21 H21	119.5
C20 C21 H21	119.5
C21 C22 C23	120.0(3)
C21 C22 H22	120.0
C23 C22 H22	120.0
C24 C23 C22	120.3(3)
C24 C23 H23	119.8
C22 C23 H23	119.8
C23 C24 C19	119.8(3)
C23 C24 H24	120.1
C19 C24 H24	120.1

Table S8. Torsion Angles (Degrees) for: ch1ppx202_P -1 R = 0.04

N4 -Ge1-N7 -N8	-2.1(2)
N7 -Ge1-N1 -N2	-3.8(2)
N1 -Ge1-N4 -N5	165.9(2)
N4 -Ge1-N1 -N2	90.7(2)
N1 -Ge1-N7 -N8	89.2(2)
N7 -Ge1-N4 -N5	-100.5(2)
C13-P1 -C1 -C2	46.0(2)
C7 -P1 -C1 -C6	-8.7(2)
C13-P1 -C7 -C8	-166.57(18)
C13-P1 -C7 -C12	9.4(2)
C13-P1 -C1 -C6	-129.3(2)
C19-P1 -C1 -C2	-76.0(2)
C19-P1 -C1 -C6	108.8(2)
C1 -P1 -C7 -C8	75.7(2)
C1 -P1 -C7 -C12	-108.4(2)
C7 -P1 -C1 -C2	166.55(18)
C19-P1 -C13-C14	170.42(18)
C19-P1 -C13-C18	-8.0(2)
C1 -P1 -C19-C20	5.3(2)
C1 -P1 -C19-C24	-169.60(18)
C7 -P1 -C19-C20	126.5(2)
C7 -P1 -C19-C24	-48.3(2)
C13-P1 -C19-C20	-113.2(2)
C13-P1 -C19-C24	71.9(2)
C1 -P1 -C13-C14	48.5(2)
C19-P1 -C7 -C8	-45.7(2)
C19-P1 -C7 -C12	130.3(2)
C7 -P1 -C13-C18	108.9(2)
C1 -P1 -C13-C18	-130.0(2)
C7 -P1 -C13-C14	-72.6(2)
P1 -C1 -C2 -C3	-174.60(18)
C6 -C1 -C2 -C3	0.8(3)
P1 -C1 -C6 -C5	174.26(18)
C2 -C1 -C6 -C5	-0.9(3)
C1 -C2 -C3 -C4	0.5(3)
C2 -C3 -C4 -C5	-1.7(3)
C3 -C4 -C5 -C6	1.6(3)
C4 -C5 -C6 -C1	-0.3(3)
C12-C7 -C8 -C9	0.0(3)
P1 -C7 -C8 -C9	176.04(18)
P1 -C7 -C12-C11	-176.10(18)
C8 -C7 -C12-C11	-0.2(3)
C7 -C8 -C9 -C10	-0.2(3)
C8 -C9 -C10-C11	0.6(4)
C9 -C10-C11-C12	-0.9(4)
C10-C11-C12-C7	0.7(3)
P1 -C13-C14-C15	-178.7(2)
P1 -C13-C18-C17	178.6(2)
C14-C13-C18-C17	0.2(4)
C18-C13-C14-C15	-0.2(4)
C13-C14-C15-C16	-0.1(4)
C14-C15-C16-C17	0.4(4)
C15-C16-C17-C18	-0.4(4)
C16-C17-C18-C13	0.1(4)
P1 -C19-C20-C21	-174.32(18)
C20-C19-C24-C23	0.4(3)
C24-C19-C20-C21	0.5(3)
P1 -C19-C24-C23	175.39(18)
C19-C20-C21-C22	-0.5(4)
C20-C21-C22-C23	-0.4(4)
C21-C22-C23-C24	1.3(4)
C22-C23-C24-C19	-1.3(4)

Table S9. Hydrogen Bonds (Angstrom, Deg) for: ch1ppx202_P -1 R = 0.04

C3 -- H3 .. N3	0.9500	2.5700	3.209(3)	125.00	2_766
C6 -- H6 .. N7	0.9500	2.5400	3.305(3)	137.00	1_565

Translation of Symmetry Code to Equiv. Pos

a =[1655.00] = 1+x,y,z
b =[2766.00] = 2-x,1-y,1-z
c =[2666.00] = 1-x,1-y,1-z
d =[2666.00] = 1-x,1-y,1-z
e =[1565.00] = x,1+y,z
f =[1465.00] = -1+x,1+y,z
g =[1455.00] = -1+x,y,z
h =[2767.00] = 2-x,1-y,2-z
i =[2677.00] = 1-x,2-y,2-z
j =[2667.00] = 1-x,1-y,2-z
k =[1455.00] = -1+x,y,z
l =[2667.00] = 1-x,1-y,2-z
m =[1545.00] = x,-1+y,z
o =[2767.00] = 2-x,1-y,2-z
p =[1645.00] = 1+x,-1+y,z

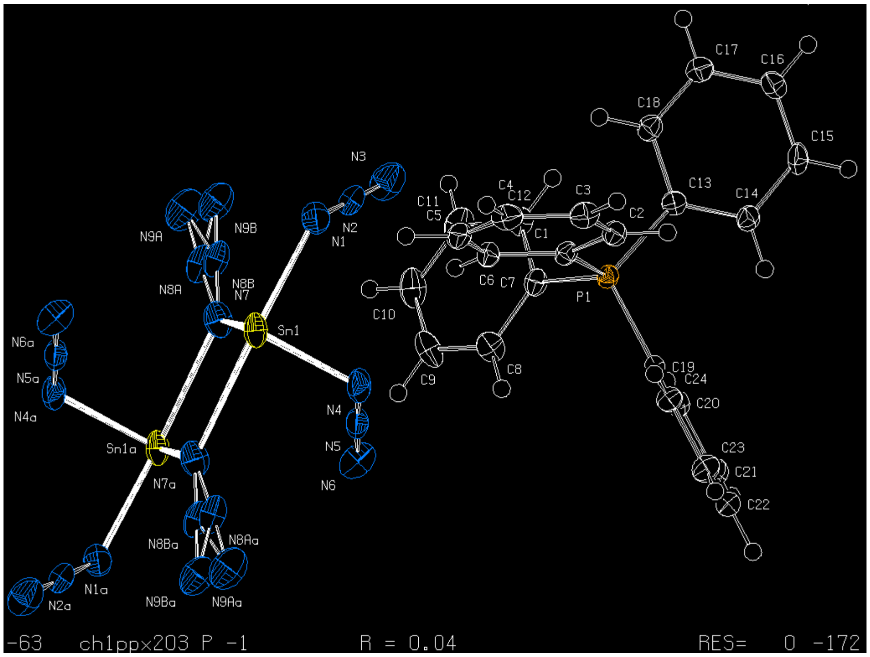

Figure S16. Asymmetric unit in the single crystal of compound 4b. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity.

Table S10. Crystal data and structure refinement for 4b.

Identification code	ch1ppx203_0m	
Empirical formula	$C_{24}H_{20}N_9PSn$	
Formula weight	584.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7560(6) Å	α = 91.668(4)°.
	b = 11.0605(6) Å	β = 108.414(4)°.
	c = 12.3540(7) Å	γ = 116.545(3)°.
Volume	1222.11(12) Å^3	
Z	2	
Density (calculated)	1.587(2) Mg m^{-3}	
Absorption coefficient	1.143 mm^{-1}	
F(000)	584	
Crystal size	0.27 x 0.17 x 0.14 mm^3	
Theta range for data collection	2.1 to 27.2°.	
Index ranges	$-13<=h<=13$, $-14<=k<=15$, $-15<=l<=15$	
Reflections collected	22380	
Unique reflections	5407 [R(int) = 0.055]	
Completeness to theta = 25.00°	99.3 %	
Max. and min. transmission	0.856 and 0.748	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5407 / 38 / 334	
Goodness-of-fit on F^2	1.038	
Final R indices [$I > 2\text{sigma}(I)$]	R_1 = 0.0397, wR_2 = 0.0954	
R indices (all data)	R_1 = 0.0521, wR_2 = 0.1020	
Largest diff. peak and hole	2.30 and –0.91 e Å^{-3}	
Weighting scheme	$w = 1/[s^2(F_o^2) + (0.0500P)^2 + 1.3033P]$; $P = (F_o^2 + 2F_c^2)/3$	
exptl. absorpt. corr. Type	multi-scan	
exptl. absorpt. corr. T_{min} / T_{max}	0.822 / 1.000	
exptl. absorpt. process	sadabs	

Table S11 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for: ch1ppx203_P -1, R = 0.04

Atom	*x*	*y*	*z*	*U*(eq) [Å^2]
P1	0.18907(9)	0.60134(8)	0.76326(7)	0.0163(2)
C1	0.2484(4)	0.5099(3)	0.6861(3)	0.0170(9)
C2	0.3996(4)	0.5720(3)	0.7014(3)	0.0205(10)
C3	0.4500(4)	0.5049(4)	0.6433(3)	0.0234(11)
C4	0.3500(4)	0.3773(4)	0.5705(3)	0.0258(11)
C5	0.2003(4)	0.3148(4)	0.5563(3)	0.0254(10)
C6	0.1477(4)	0.3808(3)	0.6137(3)	0.0207(10)
C7	0.0020(4)	0.4895(3)	0.7529(3)	0.0194(9)
C8	-0.1155(4)	0.4635(4)	0.6497(3)	0.0261(11)
C9	-0.2603(4)	0.3660(4)	0.6346(3)	0.0300(11)
C10	-0.2878(4)	0.2948(4)	0.7218(4)	0.0319(11)
C11	-0.1725(4)	0.3237(4)	0.8258(4)	0.0297(11)
C12	-0.0273(4)	0.4208(3)	0.8427(3)	0.0214(10)
C13	0.3169(4)	0.6563(3)	0.9115(3)	0.0181(9)
C14	0.3868(4)	0.7918(3)	0.9714(3)	0.0199(10)
C15	0.4879(4)	0.8297(3)	1.0859(3)	0.0236(10)
C16	0.5200(4)	0.7332(3)	1.1388(3)	0.0226(10)
C17	0.4489(4)	0.5978(4)	1.0798(3)	0.0229(10)
C18	0.3486(4)	0.5587(3)	0.9667(3)	0.0212(10)
C19	0.1950(4)	0.7475(3)	0.7000(3)	0.0184(9)
C20	0.1236(4)	0.8150(4)	0.7300(3)	0.0244(10)
C21	0.1308(5)	0.9291(4)	0.6828(3)	0.0312(11)
C22	0.2038(5)	0.9730(4)	0.6051(3)	0.0329(11)
C23	0.2723(4)	0.9056(4)	0.5758(3)	0.0301(11)
C24	0.2692(4)	0.7927(3)	0.6237(3)	0.0232(10)
Sn1	0.21121(3)	0.03245(2)	0.03802(2)	0.0262(1)
N1	0.3698(4)	0.0473(3)	0.2157(3)	0.0308(10)
N2	0.3733(4)	0.0964(3)	0.3055(3)	0.0299(10)
N3	0.3818(5)	0.1440(4)	0.3931(3)	0.0433(14)
N4	0.2722(4)	0.2483(3)	0.0923(3)	0.0351(10)
N5	0.1770(4)	0.2765(3)	0.0935(3)	0.0273(9)
N6	0.0894(4)	0.3080(4)	0.0938(3)	0.0396(11)
N7	0.0324(4)	-0.0317(3)	0.1096(3)	0.0317(10)
*N8A	0.0122(16)	-0.1023(12)	0.1793(8)	0.0299(19)
*N8B	0.0431(15)	-0.0791(12)	0.1955(8)	0.0273(19)
*N9A	-0.0055(11)	-0.1674(9)	0.2500(7)	0.0470(19)
*N9B	0.0480(10)	-0.1214(9)	0.2814(6)	0.0400(17)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor; starred Atom sites have a S.O.F less than 1.0.

Table S12 - Hydrogen Atom Positions and Isotropic Displacement Parameters for: ch1ppx203_P -1, R = 0.04

Atom	*x*	*y*	*z*	*U*(eq) [Å^2]
H2	0.46780	0.65970	0.75140	0.0250
H3	0.55280	0.54650	0.65360	0.0280
H4	0.38430	0.33210	0.53000	0.0310
H5	0.13310	0.22660	0.50700	0.0300
H6	0.04500	0.33830	0.60370	0.0250
H8	-0.09650	0.51240	0.58980	0.0310
H9	-0.34060	0.34810	0.56430	0.0360
H10	-0.38650	0.22570	0.71010	0.0380
H11	-0.19290	0.27660	0.88640	0.0360
H12	0.05170	0.44060	0.91440	0.0260
H14	0.36570	0.85820	0.93450	0.0240
H15	0.53460	0.92180	1.12750	0.0280

H16	0.59130	0.75990	1.21590	0.0270
H17	0.46930	0.53150	1.11750	0.0280
H18	0.30110	0.46600	0.92620	0.0250
H20	0.07160	0.78340	0.78140	0.0290
H21	0.08540	0.97780	0.70380	0.0370
H22	0.20610	1.05010	0.57210	0.0400
H23	0.32200	0.93600	0.52270	0.0360
H24	0.31790	0.74660	0.60430	0.0280

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S13 - (An)isotropic Displacement Parameters for: ch1ppx203_P -1, R = 0.04

Atom	*U*(1,1) or *U*	*U*(2,2)	*U*(3,3)	*U*(2,3)	*U*(1,3)	*U*(1,2)
P1	0.0168(4)	0.0145(4)	0.0161(4)	0.0037(3)	0.0073(4)	0.0054(3)
C1	0.0208(17)	0.0148(15)	0.0169(16)	0.0039(12)	0.0092(14)	0.0082(13)
C2	0.0184(17)	0.0201(16)	0.0205(17)	0.0052(13)	0.0074(15)	0.0070(14)
C3	0.0231(19)	0.0265(17)	0.0257(19)	0.0099(15)	0.0132(16)	0.0129(15)
C4	0.036(2)	0.0297(18)	0.0203(18)	0.0070(15)	0.0128(17)	0.0211(17)
C5	0.033(2)	0.0182(16)	0.0221(18)	0.0007(14)	0.0051(16)	0.0134(16)
C6	0.0199(18)	0.0171(15)	0.0209(17)	0.0038(13)	0.0063(15)	0.0063(14)
C7	0.0184(17)	0.0167(15)	0.0232(17)	0.0025(13)	0.0099(15)	0.0071(13)
C8	0.0231(19)	0.0303(18)	0.0228(18)	0.0054(15)	0.0106(16)	0.0097(16)
C9	0.0182(19)	0.039(2)	0.0240(19)	-0.0052(16)	0.0054(16)	0.0088(17)
C10	0.0184(19)	0.0298(19)	0.039(2)	-0.0019(17)	0.0160(18)	0.0015(16)
C11	0.029(2)	0.0274(18)	0.036(2)	0.0084(16)	0.0222(19)	0.0092(16)
C12	0.0214(18)	0.0197(16)	0.0226(18)	0.0026(14)	0.0105(15)	0.0081(14)
C13	0.0194(17)	0.0197(15)	0.0163(16)	0.0060(13)	0.0100(14)	0.0080(14)
C14	0.0186(18)	0.0173(15)	0.0202(17)	0.0055(13)	0.0088(15)	0.0045(14)
C15	0.0216(19)	0.0168(16)	0.0223(18)	-0.0005(13)	0.0089(15)	0.0006(14)
C16	0.0181(18)	0.0255(17)	0.0184(17)	0.0034(14)	0.0058(15)	0.0064(15)
C17	0.0258(19)	0.0227(16)	0.0228(18)	0.0070(14)	0.0099(16)	0.0129(15)
C18	0.0247(19)	0.0184(16)	0.0225(18)	0.0029(14)	0.0099(15)	0.0112(14)
C19	0.0175(17)	0.0150(15)	0.0156(16)	0.0012(12)	0.0013(14)	0.0054(13)
C20	0.0257(19)	0.0238(17)	0.0197(18)	-0.0002(14)	0.0041(15)	0.0117(15)
C21	0.036(2)	0.0246(18)	0.029(2)	-0.0016(16)	0.0009(18)	0.0191(17)
C22	0.033(2)	0.0187(17)	0.029(2)	0.0059(15)	-0.0031(18)	0.0074(16)
C23	0.032(2)	0.0230(18)	0.027(2)	0.0108(15)	0.0091(17)	0.0073(16)
C24	0.0231(19)	0.0206(16)	0.0224(18)	0.0076(14)	0.0077(15)	0.0080(15)
Sn1	0.0186(2)	0.0231(1)	0.0301(2)	-0.0015(1)	0.0119(1)	0.0030(1)
N1	0.0281(18)	0.0281(16)	0.0318(18)	0.0017(14)	0.0085(15)	0.0118(14)
N2	0.0314(19)	0.0181(14)	0.0351(19)	0.0076(14)	0.0116(16)	0.0081(14)
N3	0.061(3)	0.0345(19)	0.039(2)	0.0109(17)	0.028(2)	0.0201(19)
N4	0.0180(17)	0.0218(16)	0.048(2)	0.0014(15)	0.0030(16)	0.0017(13)
N5	0.0264(18)	0.0188(14)	0.0254(17)	0.0009(12)	0.0076(14)	0.0032(13)
N6	0.048(2)	0.0330(18)	0.049(2)	0.0139(17)	0.027(2)	0.0222(18)
N7	0.0212(17)	0.0341(17)	0.0335(18)	0.0015(15)	0.0119(15)	0.0073(14)
N8A	0.030(4)	0.022(3)	0.040(3)	0.002(2)	0.023(2)	0.008(3)
N8B	0.026(4)	0.019(3)	0.038(3)	0.004(2)	0.022(2)	0.005(3)
N9A	0.048(4)	0.039(3)	0.061(3)	0.017(3)	0.034(3)	0.017(3)
N9B	0.039(3)	0.032(3)	0.056(3)	0.015(3)	0.030(3)	0.014(3)

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S4 - Bond Distances (Angstrom) for: ch1ppx203_P -1, R = 0.04

Sn1 N4 2.193(3)
Sn1 N7 2.207(3)
Sn1 N1 2.262(3)
N1 N2 1.203(4)
N2 N3 1.148(5)
N4 N5 1.200(5)
N5 N6 1.143(5)
N7 N8A 1.185(5)
N7 N8B 1.193(5)
N8A N9A 1.157(6)
N8B N9B 1.168(6)
P1 C7 1.788(3)
P1 C13 1.792(3)
P1 C1 1.800(3)
P1 C19 1.800(3)
C1 C6 1.394(5)
C1 C2 1.398(5)
C2 C3 1.391(5)

C2 H2 0.9500
C3 C4 1.384(5)
C3 H3 0.9500
C4 C5 1.385(5)
C4 H4 0.9500
C5 C6 1.396(5)
C5 H5 0.9500
C6 H6 0.9500
C7 C8 1.393(5)
C7 C12 1.400(4)
C8 C9 1.389(5)
C8 H8 0.9500
C9 C10 1.383(5)
C9 H9 0.9500
C10 C11 1.381(6)
C10 H10 0.9500
C11 C12 1.385(5)
C11 H11 0.9500
C12 H12 0.9500
C13 C14 1.391(5)
C13 C18 1.404(4)
C14 C15 1.395(5)
C14 H14 0.9500
C15 C16 1.383(5)
C15 H15 0.9500
C16 C17 1.385(5)
C16 H16 0.9500
C17 C18 1.378(5)
C17 H17 0.9500
C18 H18 0.9500
C19 C24 1.387(5)
C19 C20 1.400(5)
C20 C21 1.386(5)
C20 H20 0.9500
C21 C22 1.392(6)
C21 H21 0.9500
C22 C23 1.369(6)
C22 H22 0.9500
C23 C24 1.388(5)
C23 H23 0.9500
C24 H24 0.9500

Table S15 - Bond Angles (Degrees) for: ch1ppx203_P -1, R = 0.04

N4 Sn1 N7 89.14(13)
N4 Sn1 N1 88.35(12)
N7 Sn1 N1 88.59(12)
N2 N1 Sn1 123.6(3)
N3 N2 N1 177.5(4)
N5 N4 Sn1 119.4(2)
N6 N5 N4 177.5(4)
N8A N7 Sn1 128.2(9)
N8B N7 Sn1 120.2(8)
N9A N8A N7 177.8(15)
N9B N8B N7 175.3(18)
C7 P1 C13 111.20(15)
C7 P1 C1 109.68(15)
C13 P1 C1 106.55(15)
C7 P1 C19 109.14(15)
C13 P1 C19 110.73(15)
C1 P1 C19 109.50(15)
C6 C1 C2 120.5(3)
C6 C1 P1 121.5(3)
C2 C1 P1 117.9(2)
C3 C2 C1 119.7(3)
C3 C2 H2 120.1
C1 C2 H2 120.1
C4 C3 C2 119.8(3)
C4 C3 H3 120.1
C2 C3 H3 120.1
C5 C4 C3 120.6(3)
C5 C4 H4 119.7
C3 C4 H4 119.7
C4 C5 C6 120.4(3)
C4 C5 H5 119.8
C6 C5 H5 119.8
C1 C6 C5 118.9(3)
C1 C6 H6 120.5
C5 C6 H6 120.5
C8 C7 C12 119.8(3)
C8 C7 P1 118.7(3)
C12 C7 P1 121.4(3)
C9 C8 C7 119.9(3)
C9 C8 H8 120.1
C7 C8 H8 120.1
C10 C9 C8 120.0(4)
C10 C9 H9 120.0
C8 C9 H9 120.0
C11 C10 C9 120.2(3)
C11 C10 H10 119.9
C9 C10 H10 119.9
C10 C11 C12 120.5(3)
C10 C11 H11 119.7
C12 C11 H11 119.7
C11 C12 C7 119.4(3)
C11 C12 H12 120.3
C7 C12 H12 120.3
C14 C13 C18 119.8(3)
C14 C13 P1 122.1(2)
C18 C13 P1 118.1(2)
C13 C14 C15 119.8(3)
C13 C14 H14 120.1
C15 C14 H14 120.1
C16 C15 C14 119.9(3)
C16 C15 H15 120.0
C14 C15 H15 120.0
C15 C16 C17 120.3(3)
C15 C16 H16 119.8
C17 C16 H16 119.9
C18 C17 C16 120.4(3)
C18 C17 H17 119.8
C16 C17 H17 119.8
C17 C18 C13 119.8(3)
C17 C18 H18 120.1
C13 C18 H18 120.1
C24 C19 C20 120.7(3)
C24 C19 P1 120.8(3)
C20 C19 P1 118.6(2)
C21 C20 C19 118.4(3)
C21 C20 H20 120.8
C19 C20 H20 120.8
C20 C21 C22 120.7(3)
C20 C21 H21 119.7
C22 C21 H21 119.7
C23 C22 C21 120.4(3)
C23 C22 H22 119.8
C21 C22 H22 119.8
C22 C23 C24 120.0(3)
C22 C23 H23 120.0
C24 C23 H23 120.0
C19 C24 C23 119.8(3)
C19 C24 H24 120.1
C23 C24 H24 120.1

Table S16 - Torsion Angles (Degrees) for: ch1ppx203_P -1, R = 0.04

N1 -Sn1 -N7 -N8B -21.3(7)
N1 -Sn1 -N7 -Sn1_a 169.26(14)
N4 -Sn1 -N7 -N8A -124.9(7)
N4 -Sn1 -N7 -N8B -109.7(7)
N4 -Sn1 -N7 -Sn1_a 80.89(14)
N7_a -Sn1 -N7 -N8A 154.2(7)
N7_a -Sn1 -N7 -N8B 169.4(7)
N7_a -Sn1 -N7 -Sn1_a 0.00(11)
N1 -Sn1 -N7_a -Sn1_a -25.8(3)
N1 -Sn1 -N7_a -N8A_a 131.9(7)
N1 -Sn1 -N7_a -N8B_a 142.8(8)
N4 -Sn1 -N7_a -Sn1_a -92.57(16)
N4 -Sn1 -N7_a -N8A_a 65.1(7)
N4 -Sn1 -N7_a -N8B_a 76.0(8)
N7 -Sn1 -N7_a -Sn1_a 0.00(13)
N7 -Sn1 -N7_a -N8A_a 157.7(7)
N7 -Sn1 -N7_a -N8B_a 168.5(8)
N1 -Sn1 -N7 -N8A -36.6(7)
N4 -Sn1 -N1 -N2 47.0(3)
N7 -Sn1 -N1 -N2 -42.2(3)
N7_a -Sn1 -N1 -N2 -18.4(5)
N1 -Sn1 -N4 -N5 -120.0(3)
N7 -Sn1 -N4 -N5 -31.4(3)
N7_a -Sn1 -N4 -N5 36.8(3)

C19	-P1	-C13	-C18	-167.6(3)
C1	-P1	-C19	-C20	166.5(3)
C1	-P1	-C19	-C24	-13.8(4)
C7	-P1	-C19	-C20	46.4(3)
C7	-P1	-C19	-C24	-133.9(3)
C13	-P1	-C19	-C20	-76.3(4)
C13	-P1	-C19	-C24	103.4(3)
C1	-P1	-C7	-C12	97.9(3)
C7	-P1	-C1	-C2	-168.9(3)
C7	-P1	-C1	-C6	10.7(3)
C13	-P1	-C1	-C2	-48.4(3)
C13	-P1	-C1	-C6	131.2(3)
C19	-P1	-C1	-C2	71.4(3)
C19	-P1	-C1	-C6	-109.0(3)
C1	-P1	-C7	-C8	-77.5(3)
C7	-P1	-C13	-C14	-110.5(4)
C13	-P1	-C7	-C8	164.9(3)
C13	-P1	-C7	-C12	-19.7(4)
C19	-P1	-C7	-C8	42.5(4)
C19	-P1	-C7	-C12	-142.1(3)
C1	-P1	-C13	-C14	130.0(4)
C1	-P1	-C13	-C18	-48.6(4)
C7	-P1	-C13	-C18	70.9(4)
C19	-P1	-C13	-C14	11.0(5)
N8A	-N7	-N8B	-N9A	-3(4)
Sn1	-N7	-N8A	-N8B	62(4)
Sn1	-N7	-N8A	-N9B	71(4)
N8B	-N7	-N8A	-N9B	9(3)
Sn1_a	-N7	-N8A	-N8B	-144(4)
Sn1_a	-N7	-N8A	-N9B	-135(3)
Sn1	-N7	-N8B	-N8A	-126(4)
Sn1	-N7	-N8B	-N9A	-129(3)
Sn1_a	-N7	-N8B	-N8A	41(5)
Sn1_a	-N7	-N8B	-N9A	38(4)
N7	-N8A	-N8B	-N9A	178.6(17)
N7	-N8A	-N8B	-N9B	175.2(16)
N9A	-N8A	-N8B	-N7	-178.6(17)
N9A	-N8A	-N8B	-N9B	-3(2)
N9B	-N8A	-N8B	-N7	-175.2(16)
N9B	-N8A	-N8B	-N9A	3(2)
N8B	-N8A	-N9A	-N9B	7(5)
N9B	-N8A	-N9A	-N8B	-7(5)
N7	-N8A	-N9B	-N8B	-10(3)
N7	-N8A	-N9B	-N9A	178(4)
N8B	-N8A	-N9B	-N9A	-173(5)
N9A	-N8A	-N9B	-N8B	173(5)
N7	-N8B	-N9A	-N8A	3(4)
N7	-N8B	-N9A	-N9B	-170(3)
N8A	-N8B	-N9A	-N9B	-173(5)
N9B	-N8B	-N9A	-N8A	173(5)
N8A	-N8B	-N9B	-N9A	7(5)
N9A	-N8B	-N9B	-N8A	-7(5)
N8A	-N9A	-N9B	-N8B	-1.8(13)
N8B	-N9A	-N9B	-N8A	1.8(13)
C6	-C1	-C2	-C3	0.4(5)
P1	-C1	-C6	-C5	-179.9(3)
P1	-C1	-C2	-C3	-179.9(3)
C2	-C1	-C6	-C5	-0.3(5)
C1	-C2	-C3	-C4	0.2(5)
C2	-C3	-C4	-C5	-1.0(6)
C3	-C4	-C5	-C6	1.1(6)
C4	-C5	-C6	-C1	-0.5(5)
P1	-C7	-C12	-C11	-172.9(3)
P1	-C7	-C8	-C9	173.2(3)
C12	-C7	-C8	-C9	-2.4(6)
C8	-C7	-C12	-C11	2.5(6)
C7	-C8	-C9	-C10	0.0(6)
C8	-C9	-C10	-C11	2.3(7)
C9	-C10	-C11	-C12	-2.2(7)
C10	-C11	-C12	-C7	-0.2(6)
P1	-C13	-C14	-C15	-178.6(3)
C18	-C13	-C14	-C15	0.0(7)
C14	-C13	-C18	-C17	-0.1(7)
P1	-C13	-C18	-C17	178.5(4)
C13	-C14	-C15	-C16	1.0(7)
C14	-C15	-C16	-C17	-1.9(7)
C15	-C16	-C17	-C18	1.8(7)
C16	-C17	-C18	-C13	-0.8(7)
C24	-C19	-C20	-C21	-0.9(6)
P1	-C19	-C24	-C23	179.9(3)
C20	-C19	-C24	-C23	-0.4(6)
P1	-C19	-C20	-C21	178.8(3)
C19	-C20	-C21	-C22	1.7(6)
C20	-C21	-C22	-C23	-1.3(6)
C21	-C22	-C23	-C24	0.0(6)
C22	-C23	-C24	-C19	0.8(6)

Table S17 - Hydrogen Bonds (Angstrom, Deg) for: ch1ppx203_P -1, R = 0.04

C2	-- H2	.. N4	0.9500	2.5500	3.265(5)	132.00	2_666
C20	-- H20	.. N6	0.9500	2.5700	3.518(6)	175.00	2_566
C21	-- H21	.. N9B	0.9500	2.6100	3.544(12)	168.00	2_566

Translation of Symmetry Code to Equiv. Pos

a =[2555.00] = -x,-y,-z
b =[2666.00] = 1-x,1-y,1-z
c =[2667.00] = 1-x,1-y,2-z
d =[1545.00] = x,-1+y,z
e =[2566.00] = -x,1-y,1-z
f =[2556.00] = -x,-y,1-z
g =[2567.00] = -x,1-y,2-z
h =[1566.00] = x,1+y,1+z
i =[2677.00] = 1-x,2-y,2-z
j =[1455.00] = -1+x,y,z
k =[1556.00] = x,y,1+z
l =[2566.00] = -x,1-y,1-z
m =[1565.00] = x,1+y,z
n =[1565.00] = x,1+y,z
o =[1544.00] = x,-1+y,-1+z
q =[2556.00] = -x,-y,1-z
r =[1655.00] = 1+x,y,z
s =[1554.00] = x,y,-1+z

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Supporting Information (Computational Section)
Homoleptic Low-Valent Polyazides of Group 14 Elements

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Contents

I. Description of method used to generate conformers

To investigate the conformational freedom of the compounds, a number of starting points for geometry optimization were generated in the following manner. Each azide was assigned one of three possible directionalities: pointing towards the lone pair of the central atom, pointing away from the lone pair of the central atom, or pointing flat, in the plane of the α-nitrogens. For the triazides, this lead to the identification of 14 unique relative atomic configurations, some of which can be represented by more than one absolute configuration of atom. Only the resultant optimized geometries which would be significantly thermally populated at room temperature ($E_{rel} \leq 5.8$ kJ mol^{-1} higher in energy than the minimum energy conformation) are discussed. Additionally, geometries were optimized using the crystal structures reported in this work as starting points.

Table S7: Summary of energetic differences between conformers of $Ge(N_3)_3$ and $Sn(N_3)_3$

Species	Conformer	E_{rel} / kJ mol^{-1}	G_{rel} / kJ mol^{-1}	Relative pop. at r.t.	No. absolute configurations	Mole fraction
$Ge(N_3)Cl_2$	(*a*)	0.00	0.00	1.00	3	0.84
	(*b*)	4.81	4.13	0.19	3	0.16
$Ge(N_3)_2Cl$	(*a*)	0.00	0.00	1.00	6	0.83
	(*b*)	0.55	2.28	0.40	3	0.17
$Ge(N_3)_3$	(*a*)	0.00	0.00	0.70	3	0.16
	(*b*)	0.35	−0.89	1.00	6	0.47
	(*c*)	1.27	−0.85	0.98	3	0.23
	(*d*)	4.10	2.02	0.31	6	0.14
$Sn(N_3)Cl_2$	(*a*)	0.00	0.00	1.00	3	0.58
	(*b*)	2.57	0.80	0.73	3	0.42
$Sn(N_3)_2Cl$	(*a*)	0.00	0.00	0.83	6	0.62
	(*b*)	0.31	−0.46	1.00	3	0.38
$Sn(N_3)_3$	(*a*)	0.00	0.00	0.84	3	0.32
	(*b*)	0.59	2.55	0.30	6	0.22
	(*c*)	0.72	−0.44	1.00	3	0.38
	(*d*)	3.06	5.03	0.11	6	0.08
	dimer	10.80				
	dimer+BSSE*	21.48				

*BSSE taken from gas phase calculation

Table S8: Summary of ^{14}N NMR calculation results

Species	Conformer	N_α shift / ppm	N_β shift / ppm	N_γ shift / ppm
$Ge(N_3)_3$	(*a*)	−310.0	−152.2	−235.1
	(*b*)	−312.5	−152.8	−235.3
	(*c*)	−309.1	−150.8	−232.2
	(*d*)	−315.5	−155.4	−238.6
	weighted avg.	−311.1	−152.3	−234.6
	exptl.	−263	−136	−207
$Sn(N_3)_3$	(*a*)	−310.4	−151.7	−243.3
	(*b*)	−313.4	−152.6	−244.5
	(*c*)	−308.4	−150.6	−240.7
	(*d*)	−316.1	−154.5	−247.2
	weighted avg.	−310.2	−151.4	−242.5
	exptl.	−260	−136	−218

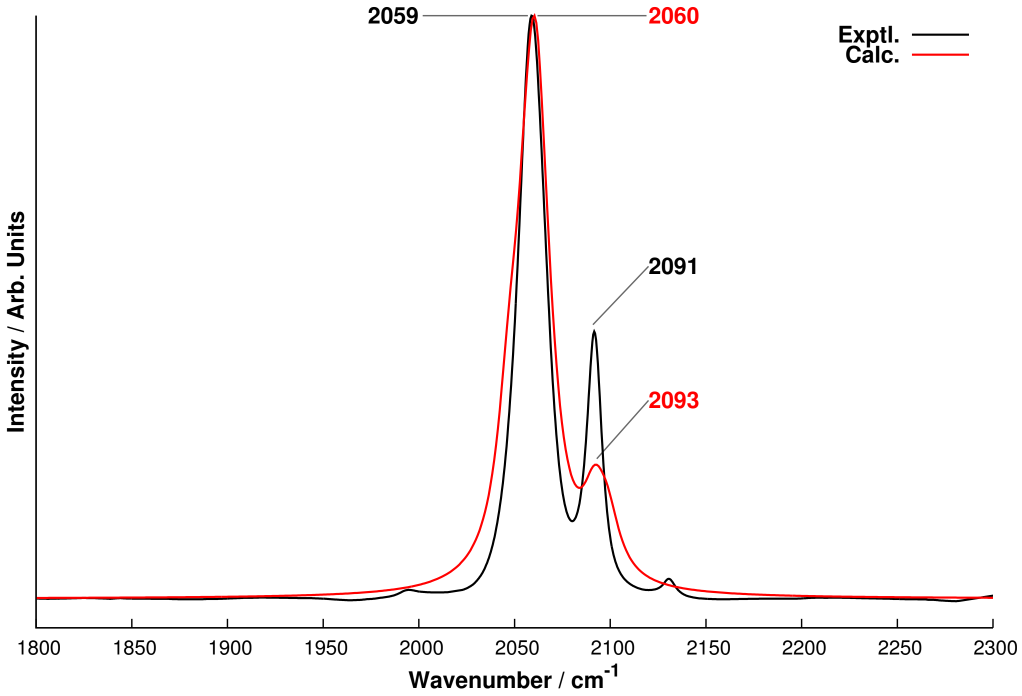


Figure S17: Comparison of simulated and experimental IR spectra (in THF) for Ge(N_3)$_3$. Calculated spectrum fitted with Lorentzian line shapes, fwhm $= 8\mathrm{cm}^{-1}$**, intensities normalised, scaling factor for calculated results** $f = 0.957$

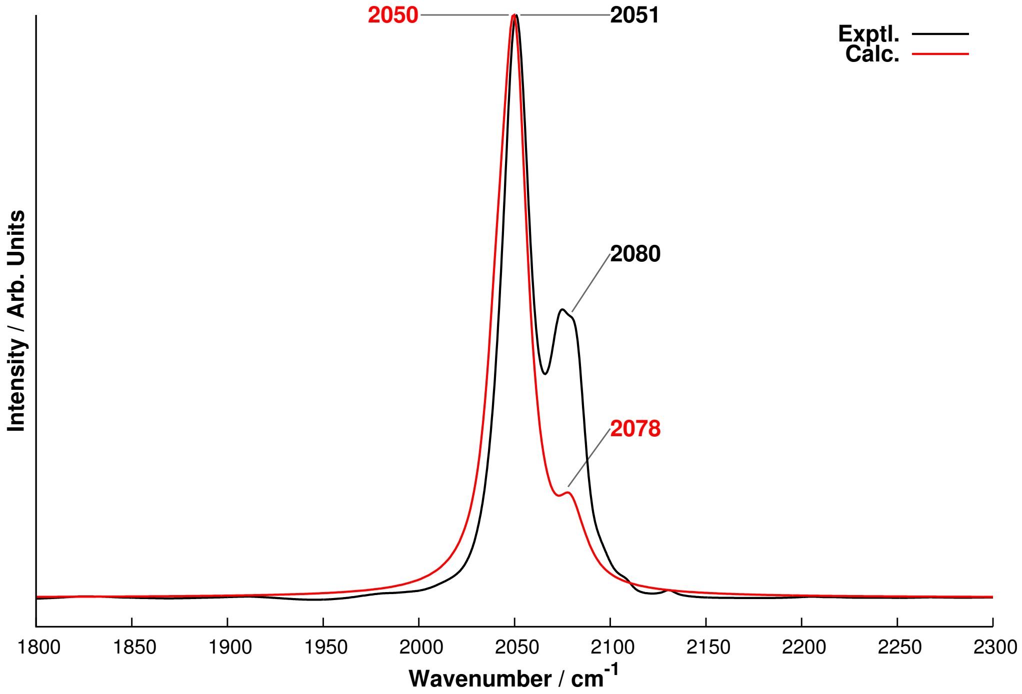
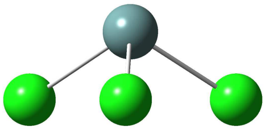


Figure S18: Comparison of simulated and experimental IR spectra (in THF) for Sn(N_3)$_3$. Calculated spectrum fitted with Lorentzian line shapes, fwhm $= 8\mathrm{cm}^{-1}$**, intensities normalised, scaling factor for calculated results** $f = 0.957$

VI. RESULTS OF CALCULATIONS

A. $GeCl_3$



General Information

Formula	:	Cl_3Ge^{1-}	
Charge	:	-1	
Multiplicity	:	1	
Energy	:	-1675.67498424	a.u.
Gibbs Energy	:	-1675.705157	a.u.

Cartesian Co-ordinates (XYZ format)

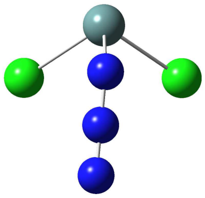
```
4

Ge   0.00065094   0.00062812   0.71731383
Cl   1.95152807   0.61911988  -0.45245218
Cl  -1.51390398   1.37871850  -0.45035630
Cl  -0.43982610  -2.00025153  -0.44795933
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
111.77	0.58
115.10	0.54
142.96	3.24
248.55	184.45
249.52	184.14
300.66	78.68

B. $\mathbf{GeN_3Cl_2}$ (*a*)



General Information

Formula : $Cl_2GeN_3^{1-}$
Charge : -1
Multiplicity : 1
Energy : -1379.66365479 a.u.
Gibbs Energy : -1379.685457 a.u.

Cartesian Co-ordinates (XYZ format)

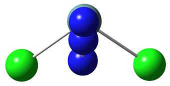
```
6

Ge   0.61459988   0.10697438   0.76287740
Cl   1.08075416  -1.58967674  -0.82864809
Cl   0.26956022   1.86867750  -0.78020644
N   -1.31954908  -0.34432572   1.01396501
N   -2.08813143  -0.40038499   0.08478963
N   -2.84776759  -0.46105239  -0.76348561
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
15.63	0.16
82.38	1.27
116.85	1.67
165.94	1.29
205.63	28.46
244.13	178.78
270.67	102.56
369.85	161.61
634.28	14.63
679.28	19.43
1349.57	261.55
2173.46	1546.64

C. GeN_3Cl_2 (*b*)



General Information

Formula	:	$Cl_2GeN_3^{1-}$	
Charge	:	-1	
Multiplicity	:	1	
Energy	:	-1379.66182128	a.u.
Gibbs Energy	:	-1379.683883	a.u.

Cartesian Co-ordinates (XYZ format)

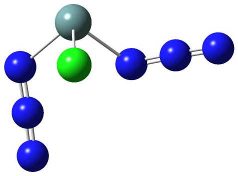
```
6

Cl  -1.36955750   1.35118949  -0.79332709
Cl   0.05752247  -1.86888671  -0.70151442
N    1.27148175   0.63275856   0.90885168
N    1.72884548   0.91914076   1.98627543
N    2.20737982   1.20771563   2.98475790
Ge  -0.57509857  -0.18032663   0.80819345
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
13.61	2.28
101.46	9.60
127.67	2.62
140.82	0.09
173.83	1.22
252.95	176.81
281.49	202.84
367.18	120.28
629.20	9.87
678.44	14.57
1356.37	229.28
2157.63	2151.01

D. $\mathbf{Ge(N_3)_2Cl}$ (a)



General Information

Formula : $\mathrm{ClGeN_6^{1-}}$
Charge : -1
Multiplicity : 1
Energy : -1083.65145424 a.u.
Gibbs Energy : -1083.664417 a.u.

Cartesian Co-ordinates (XYZ format)

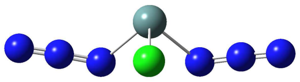
```
8

Ge -0.00865617 -0.43288058 -0.86779916
Cl -0.02321608 -1.79910934  1.09485281
N   1.80837607  0.34692481 -0.62629646
N   2.07508731  1.03848100  0.32723707
N   2.37689042  1.69736099  1.20718551
N  -0.87604499  1.16997659 -0.00324105
N  -2.06122351  1.17772710  0.21285230
N  -3.18143129  1.23435533  0.43555906
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
15.89	0.21
28.39	1.45
67.75	1.81
123.11	3.26
158.98	4.69
176.09	7.73
225.61	41.84
244.90	144.28
349.59	188.84
389.71	129.38
633.31	14.73
634.25	11.43
679.94	20.25
685.74	21.20
1346.88	299.13
1359.66	202.91
2160.32	2132.01
2178.63	1408.51

E. Ge(N$_3$)$_2$Cl (*b*)



General Information

Formula : ClGeN$_6^{1-}$
Charge : -1
Multiplicity : 1
Energy : -1083.65124309 a.u.
Gibbs Energy : -1083.663549 a.u.

Cartesian Co-ordinates (XYZ format)

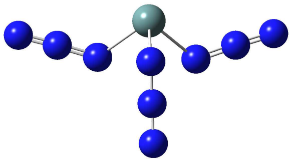
8

Ge	0.01904941	-0.16836825	0.63439000
Cl	-0.09749602	2.04682446	-0.26556686
N	1.41643989	-0.87623292	-0.60739112
N	2.58372474	-0.67150509	-0.38568902
N	3.70339465	-0.50930452	-0.22276916
N	-1.35983515	-0.98797077	-0.55653685
N	-2.53040409	-0.76821864	-0.36901361
N	-3.65230942	-0.59499013	-0.23637135

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
26.38	1.12
36.03	1.36
68.52	4.04
125.78	1.28
168.47	5.54
177.51	8.09
195.97	0.69
242.53	154.37
358.33	298.24
392.69	74.77
633.00	3.27
633.98	18.92
679.72	1.52
685.52	32.04
1353.66	499.49
1362.11	7.37
2153.21	4311.11
2174.63	5.43

F. $\mathbf{Ge(N_3)_3}$ (*a*)



General Information

Formula : GeN_9^{1-}
Charge : -1
Multiplicity : 1
Energy : -787.63869798 a.u.
Gibbs Energy : -787.642050 a.u.

Cartesian Co-ordinates (XYZ format)

10

N	-0.07519415	1.51632261	-0.88694483
N	-0.03265589	2.33588123	-0.00213528
N	0.00600172	3.14457178	0.80304325
N	-1.37786889	-0.39070782	1.00506234
N	-2.53143024	-0.62893927	0.75395465
N	-3.63896871	-0.85028321	0.57092214
N	1.42066777	-0.27423415	0.96209550
N	2.55724573	-0.59581435	0.72728366
N	3.64995193	-0.89003032	0.55939871
Ge	0.00658461	-0.45734254	-0.45596716

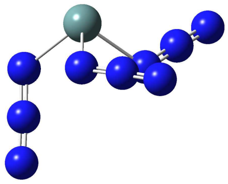
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
18.90	1.59
26.95	0.24
56.57	1.15
71.93	5.18
100.80	0.62
138.62	6.08
186.64	2.34
195.69	10.37
231.60	36.16
330.59	174.75
351.92	278.90
396.48	76.98
633.57	5.34
635.09	15.61
637.39	18.01
679.79	1.02
682.91	13.77
684.35	29.97
1343.54	277.82
1357.63	436.81
1366.74	17.97
2148.16	2000.88
2151.88	3816.02
2186.66	292.79

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-151.8
N_β	-152.2
N_β	-152.6
N_γ	-231.3
N_γ	-236.9
N_γ	-237.0
N_α	-308.3
N_α	-310.5
N_α	-311.2

G. $Ge(N_3)_3$ (*b*)



General Information

Formula : GeN_9^{1-}
Charge : -1
Multiplicity : 1
Energy : -787.63856431 a.u.
Gibbs Energy : -787.642388 a.u.

Cartesian Co-ordinates (XYZ format)

10

Ge	0.06320547	-0.12600827	-0.98242313
N	-1.32782459	-1.48107064	-0.49261984
N	-1.90517426	-1.39921904	0.56480545
N	-2.47674537	-1.36123598	1.55123067
N	1.16668534	-0.33268991	0.71648151
N	2.30615568	-0.71532845	0.64646310
N	3.39285564	-1.07466185	0.62818629
N	-1.01320648	1.37235475	-0.17417537
N	-0.45478186	2.32655954	0.30337688
N	0.03037537	3.25346279	0.76481247

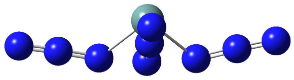
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
15.48	0.68
27.11	1.19
39.91	0.82
73.38	1.30
105.29	5.06
128.00	4.34
180.24	2.24
204.66	18.46
238.14	35.91
333.97	212.34
347.07	186.15
395.86	105.85
630.42	13.87
636.02	6.59
637.99	16.61
679.45	16.88
683.63	20.87
686.94	21.31
1343.49	315.18
1356.74	236.11
1363.15	152.83
2147.56	2621.31
2160.32	1771.32
2186.01	1202.20

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-150.4
N_β	-153.6
N_β	-154.3
N_γ	-231.9
N_γ	-235.3
N_γ	-238.8
N_α	-310.6
N_α	-311.8
N_α	-315.0

H. Ge(N_3)$_3$ (*c*)



General Information

Formula : GeN$_9^{1-}$
Charge : -1
Multiplicity : 1
Energy : -787.63821315 a.u.
Gibbs Energy : -787.642372 a.u.

Cartesian Co-ordinates (XYZ format)

Cartesian Co-ordinates (XYZ format)

10

N	-0.12063761	1.48663902	-0.74094045
N	-0.08289125	1.93992484	-1.85625851
N	-0.05102810	2.41374755	-2.89809680
N	-1.38381684	-0.56326795	0.96471304
N	-2.55541801	-0.57052666	0.68303978
N	-3.67930317	-0.58080053	0.47264567
N	1.39101529	-0.44436622	0.93127692
N	2.55559278	-0.50830281	0.62903649
N	3.67426896	-0.56708884	0.39894921
Ge	-0.01401677	-0.53316593	-0.48965618

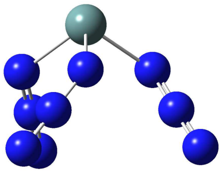
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
17.28	1.44
20.24	1.42
39.62	0.13
70.44	4.52
111.00	6.86
132.26	3.33
184.94	3.09
193.12	9.66
213.34	3.23
330.82	231.14
362.28	275.17
401.64	68.99
633.37	4.22
634.51	16.45
634.88	10.53
679.90	11.11
682.35	2.39
687.81	37.20
1352.95	217.83
1356.15	465.67
1366.75	6.46
2139.22	1787.28
2153.89	4214.83
2185.58	318.86

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-149.2
N_β	-151.3
N_β	-152.0
N_γ	-230.2
N_γ	-232.6
N_γ	-233.7
N_α	-306.8
N_α	-310.0
N_α	-310.6

I. $Ge(N_3)_3$ (*d*)



General Information

Formula : GeN_9^{1-}
Charge : -1
Multiplicity : 1
Energy : -787.63713600 a.u.
Gibbs Energy : -787.641279 a.u.

Cartesian Co-ordinates (XYZ format)

10

N	-0.45199686	-1.67574656	-0.27083799
N	0.20848885	-2.06133533	0.66063797
N	0.81207955	-2.46945143	1.54070008
N	1.68584275	0.43324387	-0.25701377
N	1.67603445	1.20881057	0.66545320
N	1.71324039	1.94603169	1.53746355
N	-1.20796049	1.23276711	-0.28914034
N	-1.88927901	0.85445672	0.63024127
N	-2.56034946	0.53686833	1.49869251
Ge	0.01847167	-0.00733015	-1.31795239

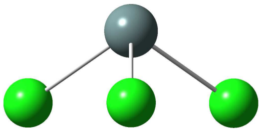
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
11.43	0.13
22.34	0.14
33.97	0.38
103.76	0.86
105.42	0.68
123.28	0.17
192.90	10.75
193.08	10.23
250.67	53.12
324.34	174.03
326.35	173.06
384.10	106.10
630.23	9.36
630.74	9.64
632.63	14.86
675.37	18.30
676.60	23.25
677.62	7.31
1352.68	177.62
1352.90	178.34
1360.57	269.03
2155.01	1286.18
2155.38	1272.35
2193.18	2253.45

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-155.3
N_β	-155.4
N_β	-155.4
N_γ	-238.5
N_γ	-238.6
N_γ	-238.7
N_α	-315.5
N_α	-315.5
N_α	-315.6

J. $SnCl_3$



General Information

Formula	:	Cl_3Sn^{1-}
Charge	:	-1
Multiplicity	:	1
Energy	:	-1595.41895608 a.u.
Gibbs Energy	:	-1595.450569 a.u.

Cartesian Co-ordinates (XYZ format)

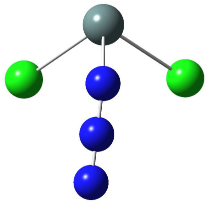
```
4

Cl  -0.00164646   2.16847277  -0.66572833
Cl  -1.87670529  -1.08317018  -0.66614985
Cl   1.87782204  -1.08570933  -0.66576809
Sn   0.00052976   0.00040753   0.64719921
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
89.51	2.10
97.48	2.65
113.61	8.67
230.75	156.22
231.13	155.98
267.82	87.47

K. $\mathbf{SnN_3Cl_2}$ (*a*)



General Information

Formula	:	$Cl_2N_3Sn^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-1299.40311650 a.u.
Gibbs Energy	:	-1299.425946 a.u.

Cartesian Co-ordinates (XYZ format)

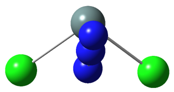
```
6

Cl  -0.95035714  -1.70302856   1.11944604
Cl   0.00401476   1.90492809   1.06838143
N    1.46794653  -0.42739666  -1.05138969
N    2.31839871  -0.46585184  -0.20027427
N    3.15876865  -0.51267689   0.57451630
Sn  -0.62873363   0.12266881  -0.61678874
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
30.25	0.15
73.08	1.95
93.34	3.88
128.07	3.26
165.70	28.71
230.60	149.97
250.56	98.98
327.33	140.43
638.69	13.79
673.50	12.40
1358.20	226.94
2158.12	1729.33

L. $\mathbf{SnN_3Cl_2}$ (*b*)



General Information

Formula	:	$Cl_2N_3Sn^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-1299.40213817 a.u.
Gibbs Energy	:	-1299.425643 a.u.

Cartesian Co-ordinates (XYZ format)

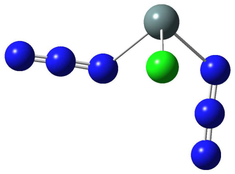
```
6

Cl   1.33471227  1.86944187  0.60705113
Cl   1.40391886 -1.86110640  0.60958695
N   -1.50903940 -0.04306019  0.87011814
N   -2.65238476  0.00416130  0.50240201
N   -3.75792289  0.04751655  0.19929324
Sn   0.16362895 -0.01840312 -0.59714246
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
21.95	2.17
73.15	11.07
93.66	3.44
114.24	1.58
141.17	3.60
235.30	151.60
252.55	166.92
322.82	124.77
636.59	10.07
673.24	10.73
1361.79	203.42
2144.79	2290.77

M. $Sn(N_3)_2Cl$ (*a*)



General Information

Formula : ClN_6Sn^{1-}
Charge : -1
Multiplicity : 1
Energy : -1003.38676624 a.u.
Gibbs Energy : -1003.401083 a.u.

Cartesian Co-ordinates (XYZ format)

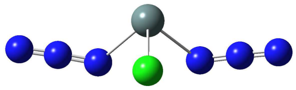
8

Cl	-0.30861107	-1.54018641	1.58950126
N	1.14749002	1.21407020	0.05349260
N	2.32652593	1.15351689	0.27799711
N	3.45051384	1.14637327	0.50457615
N	-1.82360733	0.72068983	-0.61395788
N	-2.01091599	1.48217487	0.30036590
N	-2.23559451	2.21800995	1.14634144
Sn	-0.00712591	-0.51478249	-0.72051954

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
19.07	0.77
38.75	1.70
55.05	3.03
105.85	7.33
132.85	3.36
142.21	6.84
179.46	31.17
235.05	133.03
316.08	157.88
345.74	119.42
639.25	4.08
639.46	21.26
673.72	14.90
677.66	12.13
1355.48	251.55
1365.20	188.11
2146.26	2293.69
2163.84	1583.71

N. $Sn(N_3)_2Cl$ (*b*)



General Information

Formula	:	ClN_6Sn^{1-}	
Charge	:	-1	
Multiplicity	:	1	
Energy	:	-1003.38664916	a.u.
Gibbs Energy	:	-1003.401259	a.u.

Cartesian Co-ordinates (XYZ format)

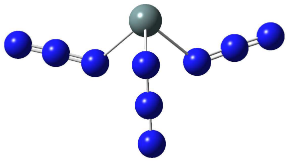
```
8

Cl  0.10516121  2.22633433  0.47285506
N  -1.52099562 -0.85785425  0.80279577
N  -2.70018601 -0.78543258  0.57898486
N  -3.83355212 -0.74423718  0.41303530
N   1.47339654 -0.99046308  0.73477334
N   2.65620899 -0.86968428  0.55558860
N   3.79233789 -0.78733075  0.42931986
Sn -0.01674395 -0.07751111 -0.60818785
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
19.87	2.08
29.46	2.29
58.29	6.75
112.17	3.84
130.19	5.83
140.62	8.66
159.12	0.60
231.89	142.01
318.96	240.51
347.73	85.76
638.15	6.51
639.24	15.65
674.51	0.94
677.26	22.34
1361.71	433.27
1366.57	15.03
2141.36	4624.34
2159.61	46.92

O. $Sn(N_3)_3$ (*a*)



General Information

Formula : N_9Sn^{1-}
Charge : -1
Multiplicity : 1
Energy : -707.37048804 a.u.
Gibbs Energy : -707.376545 a.u.

Cartesian Co-ordinates (XYZ format)

10

N	-0.05694585	1.72549498	-0.88018095
N	0.01756047	2.46108246	0.06999011
N	0.08585451	3.20028806	0.94105345
N	-1.48485708	-0.43180183	1.00372458
N	-2.64080000	-0.70785052	0.82478350
N	-3.75224996	-0.96458071	0.70753855
N	1.53284109	-0.34571251	0.93817836
N	2.65106797	-0.75542593	0.77782321
N	3.72910500	-1.13289094	0.67785144
Sn	-0.00544509	-0.47518414	-0.64115417

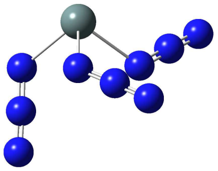
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
14.67	2.19
22.00	0.72
46.90	1.48
59.47	7.78
86.77	0.82
115.32	9.76
149.58	4.91
153.10	5.76
182.98	32.84
308.46	143.95
315.54	228.34
353.37	85.54
638.03	1.92
638.83	18.14
640.53	16.78
672.86	0.96
675.12	15.91
677.30	17.98
1354.47	246.50
1363.87	374.59
1369.77	40.24
2139.59	3091.27
2142.27	2973.23
2172.25	478.23

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-151.0
N_β	-151.2
N_β	-152.9
N_γ	-241.0
N_γ	-244.4
N_γ	-244.6
N_α	-310.1
N_α	-310.2
N_α	-310.9

P. Sn(N$_3$)$_3$ (*b*)



General Information

Formula : N$_9$Sn^{1-}
Charge : -1
Multiplicity : 1
Energy : -707.37026482 a.u.
Gibbs Energy : -707.375570 a.u.

Cartesian Co-ordinates (XYZ format)

```
10

N   -1.62992835 -1.32171059  0.14760077
N   -2.19470215 -0.69577807  1.00753844
N   -2.76374030 -0.13912326  1.82926035
N    1.22721398 -0.00274958  0.90920430
N    2.30106521 -0.49441367  1.13131833
N    3.32757282 -0.93814576  1.38570035
N   -0.83494925  1.53648555 -0.83779126
N   -0.22165418  2.50720882 -0.48190939
N    0.31963950  3.46189094 -0.15381983
Sn   0.08864546 -0.46797472 -0.94606930
```

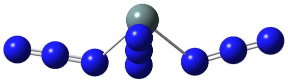
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
21.92	1.44
27.95	1.56
39.54	1.51
67.78	2.60
96.77	4.35
117.46	5.13
138.11	3.24
165.95	17.76
187.10	37.03
309.67	183.04
314.00	143.47
351.98	101.66
636.36	13.86
639.12	7.13
640.46	14.26
673.36	12.20
676.09	15.15
677.89	13.03
1353.71	259.53
1363.04	200.77
1367.40	171.33
2140.17	2906.23
2148.79	1278.78
2173.29	1741.19

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N$_\beta$	-150.2
N$_\beta$	-153.3
N$_\beta$	-154.2
N$_\gamma$	-241.5
N$_\gamma$	-243.0
N$_\gamma$	-249.0
N$_\alpha$	-310.4
N$_\alpha$	-312.2
N$_\alpha$	-317.7

Q. $Sn(N_3)_3$ (*c*)



General Information

Formula	:	N_9Sn^{1-}
Charge	:	-1
Multiplicity	:	1
Energy	:	-707.37021279 a.u.
Gibbs Energy	:	-707.376711 a.u.

Cartesian Co-ordinates (XYZ format)

10

N	1.57325995	-1.08260417	0.70606458
N	2.73471880	-1.07480156	0.39632177
N	3.85355997	-1.09727323	0.14781834
N	-0.17310514	1.56904900	0.79566365
N	-0.18366046	2.69345975	0.37126350
N	-0.19898003	3.78307676	0.01254884
N	-1.41331840	-1.32839453	0.63694870
N	-2.58740187	-1.35365605	0.38016108
N	-3.71420121	-1.41415310	0.17896128
Sn	0.02239348	-0.17902008	-0.57055879

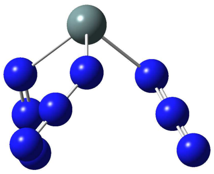
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
14.11	2.45
15.01	2.29
50.36	0.40
59.02	7.86
91.64	9.32
119.14	8.62
143.88	2.79
151.45	7.49
167.90	0.88
307.99	207.50
323.35	227.29
355.51	78.49
637.60	2.71
638.47	18.53
638.54	9.52
674.67	1.08
675.73	8.76
677.48	26.68
1360.51	230.50
1363.78	410.81
1369.88	1.87
2132.66	2286.33
2142.86	4481.36
2170.64	183.29

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-149.8
N_β	-150.6
N_β	-151.3
N_γ	-238.5
N_γ	-241.1
N_γ	-242.6
N_α	-305.7
N_α	-309.3
N_α	-310.3

R. $\mathbf{Sn(N_3)_3}$ (*d*)



General Information

Formula : N_9Sn^{1-}
Charge : -1
Multiplicity : 1
Energy : -707.36932204 a.u.
Gibbs Energy : -707.374631 a.u.

Cartesian Co-ordinates (XYZ format)

10

N	0.40455464	1.13093257	1.42470026
N	1.25980532	0.46017316	1.94069779
N	2.08598995	-0.13878877	2.46022201
N	-0.42262191	-1.78983390	0.33194104
N	0.36459336	-2.30518889	-0.41716874
N	1.10427082	-2.83936071	-1.10842586
N	0.07820622	0.61768800	-1.74233484
N	1.16170299	1.13959968	-1.72183132
N	2.19197655	1.63856649	-1.75253832
Sn	-1.14905393	0.29254848	0.07919108

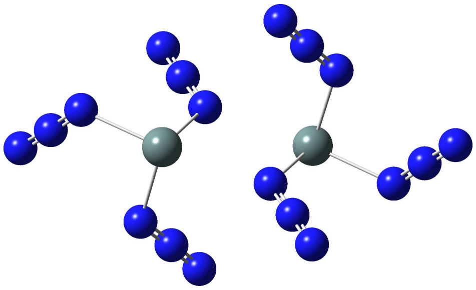
Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
22.76	0.29
24.18	0.38
36.54	1.09
83.29	0.46
95.87	0.57
109.76	0.15
154.03	12.20
156.09	12.37
194.11	57.80
301.43	142.27
301.94	140.08
344.98	98.93
635.86	11.11
636.31	10.31
637.52	12.67
670.46	10.79
671.06	12.39
671.79	10.99
1358.62	153.00
1360.09	155.90
1365.51	271.09
2144.34	1242.47
2146.99	1277.27
2179.64	2650.37

Calculated Chemical Shifts

Atom	Chemical Shift / ppm
N_β	-154.4
N_β	-154.5
N_β	-154.6
N_γ	-246.8
N_γ	-247.3
N_γ	-247.6
N_α	-315.9
N_α	-316.1
N_α	-316.3

S. $Sn(N_3)_3$ dimer



General Information

Formula	:	$N_{18}Sn_2^{2-}$	
Charge	:	-2	
Multiplicity	:	1	
Energy	:	-1414.73686389	a.u.
BSSE energy	:	0.00406934	a.u.
Gibbs Energy	:	-1414.727247	a.u.

Cartesian Co-ordinates (XYZ format)

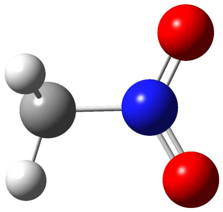
20

Sn	1.78057718	-0.25641242	1.05474651
N	1.67251420	-2.27096105	-1.26113594
N	4.57899952	0.38138852	-0.17238717
N	2.37569022	-1.84971297	-0.38609740
N	0.83928901	1.03514862	-0.54582703
N	1.04133844	-2.70729923	-2.11429191
N	5.35643196	0.07371093	-0.96082819
N	1.93835950	2.76432180	-1.69056857
N	1.42232049	1.91681337	-1.12113822
N	3.80050898	0.73108101	0.66902375
Sn	-1.81431043	0.27676851	-1.06813431
N	-1.62096202	2.23807859	1.28092468
N	-4.59975052	-0.35488862	0.19608045
N	-2.35718584	1.84451699	0.42017007
N	-0.85174239	-1.05391419	0.48631153
N	-0.95671141	2.64738154	2.12223196
N	-5.36399317	-0.05274893	0.99939269
N	-1.96295524	-2.74846530	1.67044652
N	-1.44137800	-1.91708899	1.08274961
N	-3.83586264	-0.69833624	-0.66118306

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
14.05	8.62
18.41	4.71
24.16	0.80
27.17	2.52
32.98	0.27
38.15	1.39
40.27	3.18
49.36	29.42
52.19	2.99
54.58	4.46
57.00	5.07
80.91	0.32
87.71	6.79
93.27	0.30
107.53	0.44
110.30	0.37
116.75	30.41
126.67	0.02
155.29	20.03
158.36	0.33
163.50	2.42
167.14	130.04
185.87	133.35
199.02	0.03
254.34	407.75
272.55	0.34
288.80	0.22
294.18	242.21
315.54	0.17
339.88	149.36
635.73	0.12
636.95	22.77
638.19	18.15
638.45	3.82
644.97	12.54
645.16	11.70
670.13	14.15
670.68	11.14
673.74	10.28
673.77	17.80
676.25	1.53
677.22	23.45
1357.60	448.18
1361.53	0.41
1366.01	375.71
1366.91	0.02
1373.82	122.12
1374.44	192.77
2134.73	0.32
2137.42	3454.48
2142.19	2.10
2144.00	4536.17
2164.45	3954.13
2178.94	0.39

T. Nitromethane



General Information

Formula	:	CH_3NO_2
Charge	:	0
Multiplicity	:	1
Energy	:	-245.11606161 a.u.
Gibbs Energy	:	-245.093639 a.u.
Isotropic shielding constant (N)	:	-158.3070 ppm

Cartesian Co-ordinates (XYZ format)

```
7

C -0.33069599 -1.02452636 -0.00660024
H  0.03638626 -2.04270792 -0.01830546
H  0.03445038 -0.46801373  0.85183263
H -1.41564965 -0.98058385 -0.03636433
N  0.17041318 -0.32407433 -1.22890067
O  0.86919552 -0.95177406 -2.00785780
O -0.15550672  0.84349304 -1.37195802
```

Calculated Harmonic Vibrational Frequencies

Frequency / cm^{-1}	Intensity / km mol^{-1}
50.15	0.18
481.42	1.57
628.34	5.30
657.22	30.74
926.54	16.74
1113.72	20.78
1141.61	1.87
1400.51	77.02
1434.33	66.13
1456.09	80.24
1469.04	17.30
1595.63	461.38
3079.62	0.08
3164.52	0.08
3202.59	2.19