Supporting Information

Germanium and Tin Monoxides Trapped by Oxophilic Germylene and Stannylene Ligands

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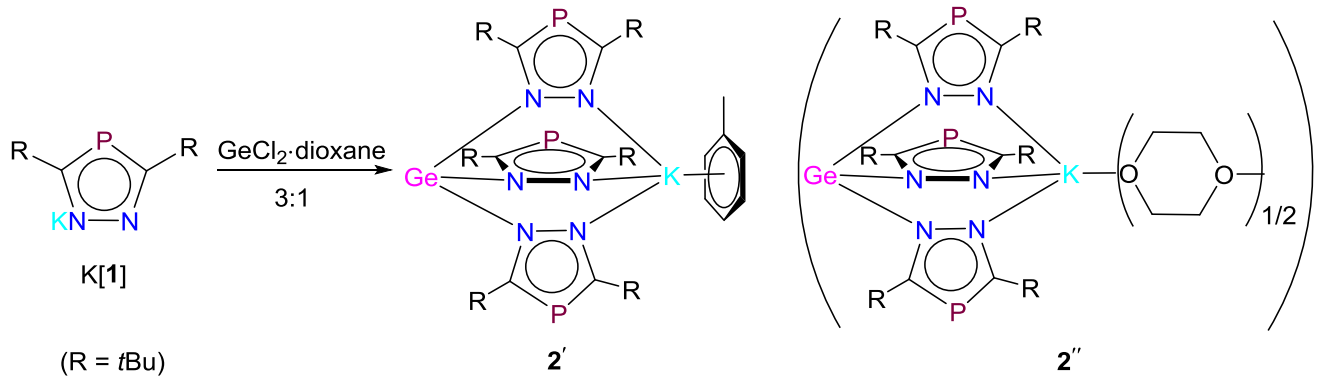
S1. Experimental section



Scheme S1. Synthesis of compounds **2'** and **2''**

2': To a mixture of K[**1**] (0.71 g, 3.0 mmol) and $GeCl_2$·dioxane (0.23 g, 1.0 mmol) was added toluene (20 mL) and dioxane (0.1 mL) under stirring for 1 d at ambient temperature. After workup, the mixture was filtered to afford **2'** as colorless crystals after several days at –10°C. (0.41 g, 51%). Mp >165°C dec.. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): δ = 1.32 (s, 54 H, C*H*$_3$), 2.20 (s, C*H*$_3$ of toluene), 7.30 (br., H on phenyl ring) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 23°C): δ = 129.04, 128.22 (2s, Ph), 35.83, 35.71 (d, $^{2}J_{C–P}$ = 18.0 Hz), 32.79, 32.72 (d, $^{3}J_{C–P}$ = 10.5 Hz, *C*H$_3$) ppm; the expected resonances at about 190 ppm for P*C* doublets was not observed. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 23°C): δ = 74.4(s) ppm. IR(KBr, Nujol, cm^{-1}): 1591(m), 1461(s), 1377(m), 1260(s), 1091(m), 1020(s), 875(w), 799(s); Anal. calcd for $C_{37}H_{62}GeKN_6P_3$ (M_r = 795.53): C, 55.86; H, 7.85; N, 10.56. Found: C, 55.89; H, 7.88; N, 10.63. Single crystals suitable for X-ray diffraction analysis were obtained from toluene at –10°C.

2'': The synthesis of **2''** was similar to the procedure for **2'**, and the single crystals suitable for X-ray diffraction analysis of **2''** were obtained from dioxane at –10°C.

S3. Figures

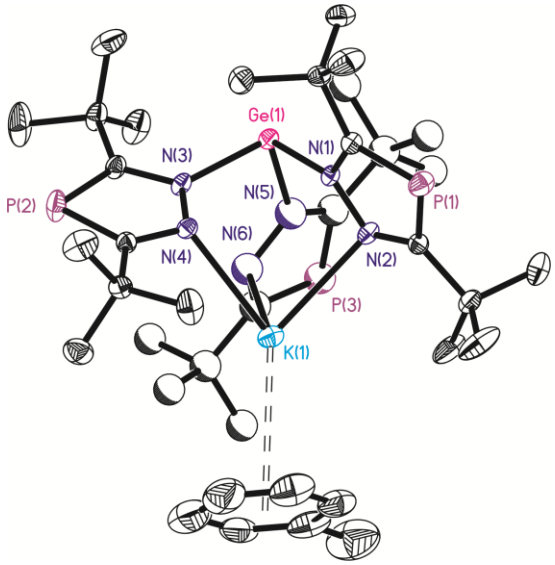


Figure S1.

Molecular structure of **2'** with thermal ellipsoids at the 30% probability level for foreground atoms. Hydrogen atoms and terminal methyl group disorder are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.729(4), P(1)−C(2) 1.742(4), N(1)−C(1) 1.352(4), N(1)−N(2) 1.377(4), Ge(1)···K(1) 3.9605(10), Ge(1)−N(1) 2.020(3), Ge(1)−N(5) 2.023(3), Ge(1)−N(3) 2.010(3), K(1)−N(1) 3.355(3), K(1)−N(2) 2.758(3), K(1)−N(3) 3.445(3), K(1)−N(4) 2.740(3), K(1)−N(5) 3.391(3), K(1)−N(6) 2.764(3); C(1)−P(1)−C(2) 87.64(18), N(3)−Ge(1)−N(1) 96.64(12), N(3)−Ge(1)−N(5) 94.78(12), N(1)−Ge(1)−N(5) 96.34(12).

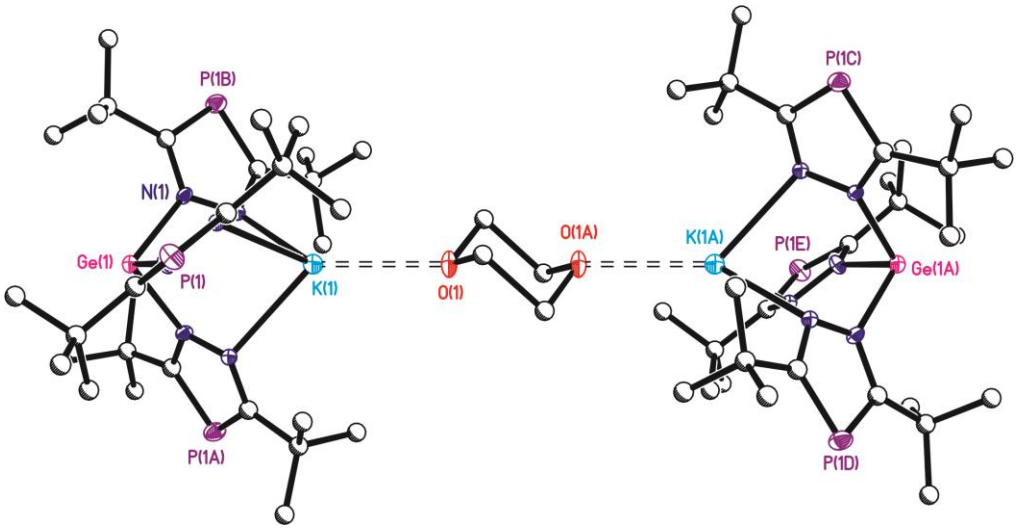


Figure S2.

Molecular structure of **2''**. The solvated complex [Ge(3,5-*t*Bu$_2$dp)$_3$(μ(*O*)-K)]$_2$(μ-1,4-dioxane) (**2''**), which had a symmetrical trigonal geometry (determined in preliminary single-crystal structural analyses), with two [Ge(3,5-*t*Bu$_2$dp)$_3$K)] moieties joined via the two K–O bridges. Crystal data: Trigonal space group *R*-3. a = 16.6430(11), b = 16.6430(11), c = 27.025(4) Å; $\alpha = \beta = 90°$, $\gamma = 120°$; V = 6482.75 Å^3.

The large separation between Sn(1) and Sn(1A) (4.231 Å) and the slightly staggered orientation of the two molecules (Figure S3) suggest that intermolecular Sn···N interactions between the vacant p-orbital of the tin(II) atom and the lone-pair electrons on the nearby nitrogen atoms (Sn(1)···N(1A) 3.543 Å, Sn(1)···N(2(A) 3.445 Å) were less pronounced than that in *N*,*N*′-dimethylbenzimidazolin-2-stannylene (Sn···N 3.052 Å).[1] The dimeric structure with slipped η^2(*N*,*N*)-1,2,4-diazaphospholides is probably as the result of both van der Waals forces and steric interactions. Weak intermolecular Sn···P interactions (Sn···P 3.874 Å) were found between the lone-pair electrons on the phosphorus ($\sigma^2\lambda^3$) atom and the vacant p-orbital of the stannylene atom, causing an architectural component to be constructed and giving an assembly that generates an infinite 2-D grid along the *ab* plane (Figure S4), with P(2)/P(2A) sites acting as pins and Sn sites as holes.

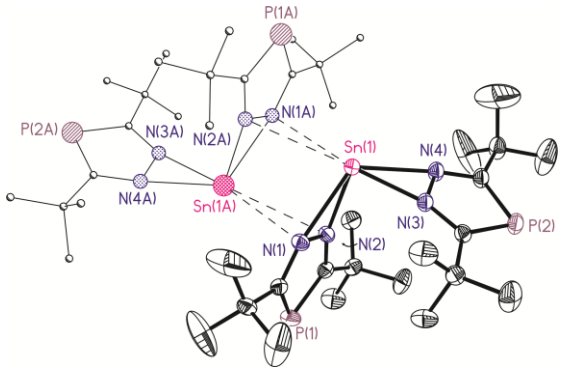


Figure S3.

Dimeric structure of **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)–N(2) 1.375(4), N(1)–C(1) 1.339(5), P(1)–C(1) 1.734(4), Sn(1)···N(1A) 3.543, Sn(1)···N(2A) 3.445; N(3)–Sn(1)–N(2) 89.52(12), N(2)–Sn(1)–N(4) 98.40(12), N(3)–Sn(1)–N(1) 97.71(11), N(4)–Sn(1)–N(1) 121.84(11), C(1)–P(1)–C(2) 87.22(19). Symmetry code: A≡ 1−x, 1−y, 1−z.

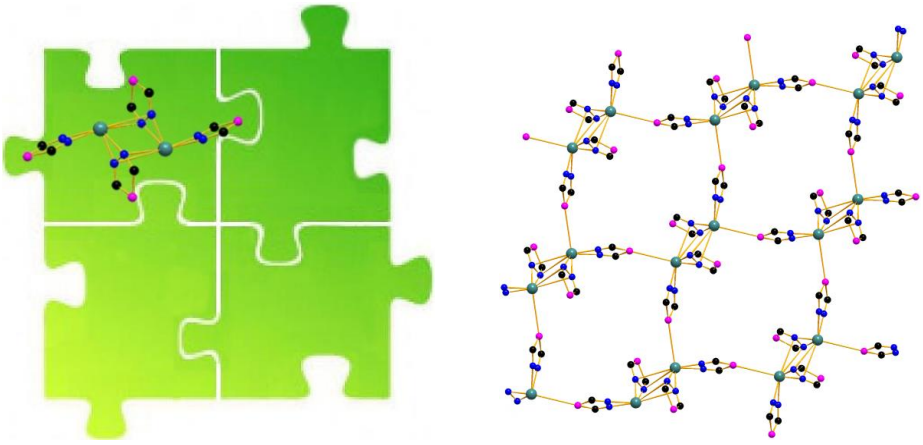


Figure S4.

Packing diagram of **3** with an infinite 2-D grid along the *ab* plane.

In previous studies of 1,2,4-diazaphospholide and pyrazolato titanium complexes, the empty d-orbitals of metal ions favor η^2-bonding over η^1-bonding,[2,3] which may support the conclusion that the tin(II) in **3** could be sp^3d hybridized.[4,5]

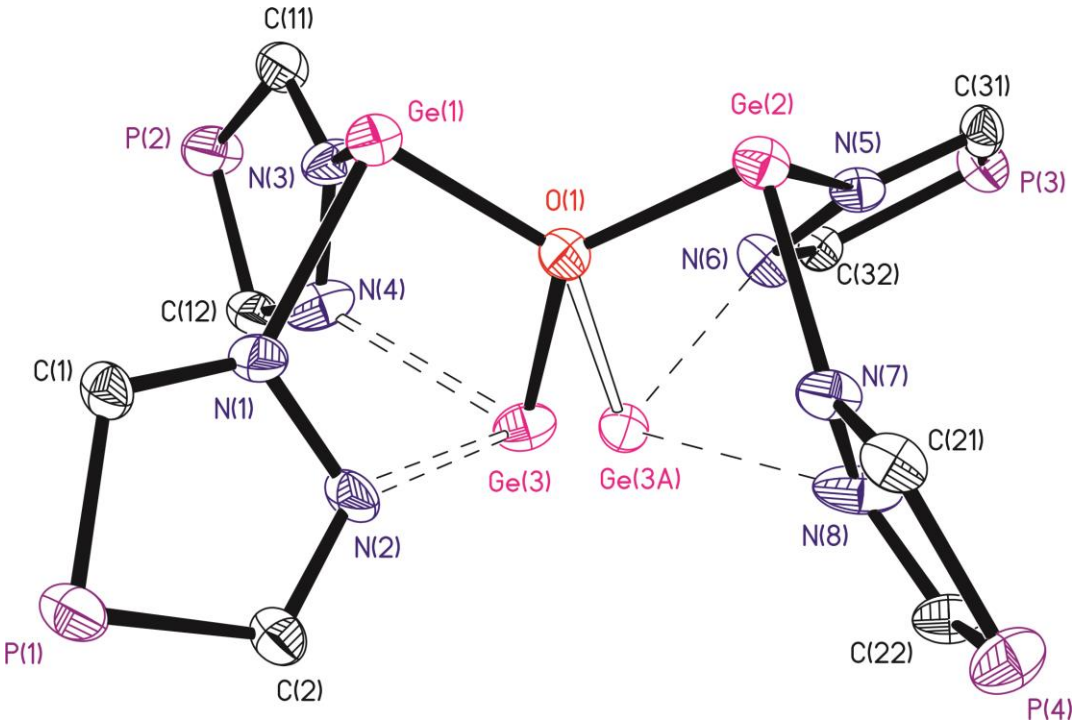


Figure S5.

Core structure of **4** showing the 0.6:0.4 occupation disorder at positions of Ge(3) and Ge(3A). Hydrogen atoms and *t*Bu groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(3)–O(1) 1.852(5), Ge(3A)–O(1) 1.907(5), Ge(3)···N(2) 2.213(7), Ge(3)···N(4) 2.309(8), Ge(3A)···N(6) 2.181(7), Ge(3A)···N(8) 2.400(9), Ge(1)–O(1) 1.869(4), Ge(2)–O(1) 1.911(4), Ge(1)–N(3) 2.008(5), Ge(1)–N(1) 2.046(5), Ge(2)–N(5) 2.022(5), Ge(2)–N(7) 2.009(5); N(3)–Ge(1)–N(1) 94.3(2), O(1)–Ge(1)–N(3) 87.1(2), O(1)–Ge(1)–N(1) 89.4(2), N(2)···Ge(3)–O(1) 82.5(2), N(4)···Ge(3)–O(1) 89.4(2), Ge(1)–O(1)–Ge(3A) 139.1(3), Ge(2)–O(1)–Ge(3A) 107.5(3).

S2. DFT calculation details

By the B3LYP method combined with 6-311G(d,p) basis set for C, N, O, and H atoms and LANL2dz basis set and pseudo potential for Ge and Sn atoms, we optimized the geometries of Ge_3O (**4**) and Sn_3O (**5**). Two structures of each complex with C_2 and C_1 symmetry, respectively, were found (Figure S6). Wherein, C_1-***4***, C_2-***5*** and C_1-***5*** were located as local minima, while C_2-***4*** was identified to be a transition state which links two equivalent C_1 structures. The relative energy is 2.7 kcal/mol from C_2-***4*** to C_1-***4*** and 1.3 kcal/mol from C_2-***5*** to C_1-***5***, respectively. Clearly, C_1-***4*** and C_1-***5*** are the more stable configurations and their optimized geometries are in good agreement with the experimental ones.

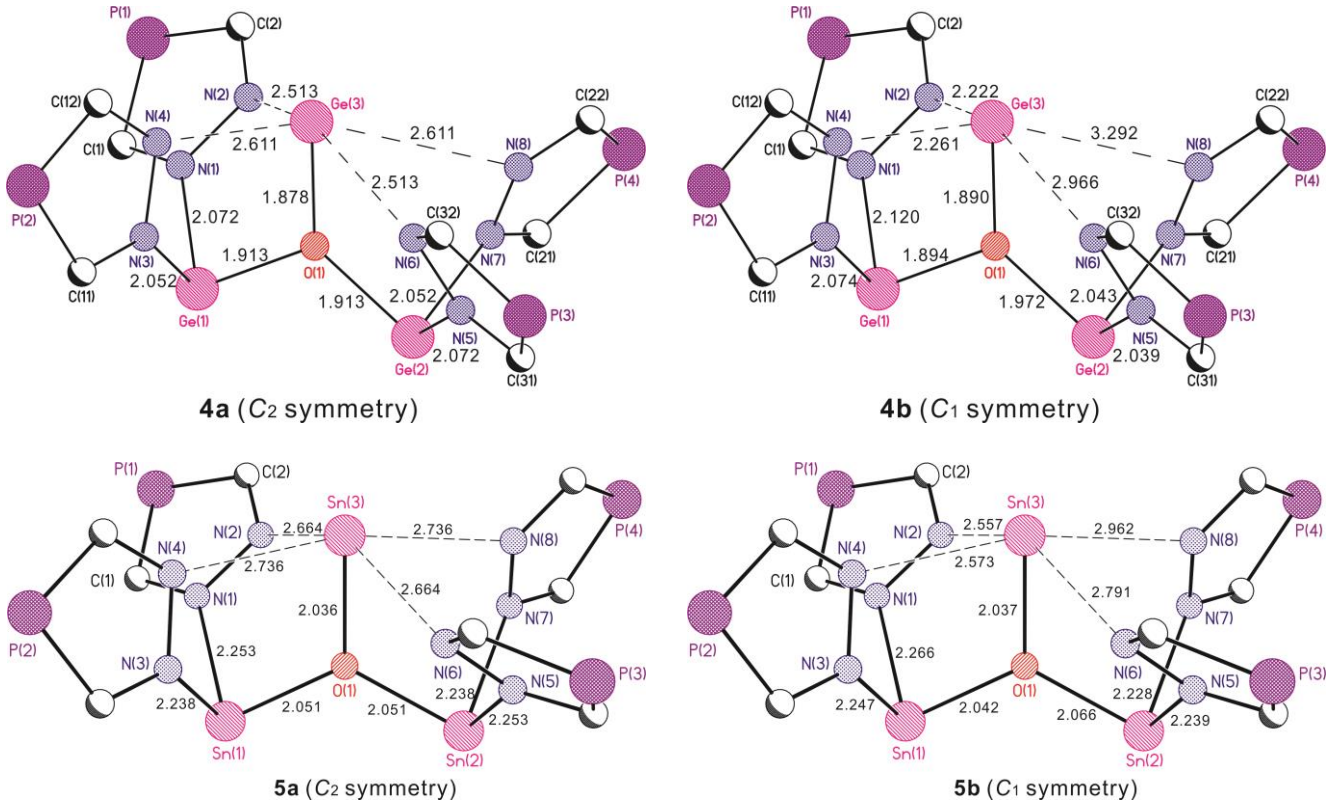


Figure S6.

Optimized structures and main geometric parameters of **a** in C_2 symmetry and **b** in C_1 symmetry for **4** and **5**. For clarity, *t*Bu groups are omitted. Bond lengths are in ångströms. Selected bond angles (deg) for **4a**: Ge(1)–O(1)–Ge(3) 121.57, Ge(1)–O(1)–Ge(2) 116.86, Ge(2)–O(1)–Ge(3) 121.57 and **4b**: Ge(1)–O(1)–Ge(3) 116.48, Ge(1)–O(1)–Ge(2) 115.44, Ge(2)–O(1)–Ge(3) 128.08; **5a**: Sn(1)–O(1)–Sn(3) 119.89, Sn(1)–O(1)–Sn(2) 120.23, Sn(2)–O(1)–Sn(3) 119.89 and **5b**: Sn(1)–O(1)–Sn(3) 118.13, Sn(1)–O(1)–Sn(2) 120.21, Sn(2)–O(1)–Sn(3) 121.65.

To gain a better understanding of the bonding nature in **4** and **5**, the calculated Mayer Bond Indexes of some key bonds of **4** and **5** as well as APT/NBO charges of M atoms and O atom were

listed in Table S1 to illustrate the key bonding interactions among Ge–O/Sn–O and Ge–N/Sn–N bonds. Since the bonding nature of C_2-***4*** and C_2-***5*** is comparable, we thus mainly studied C_2-***4*** in this work.

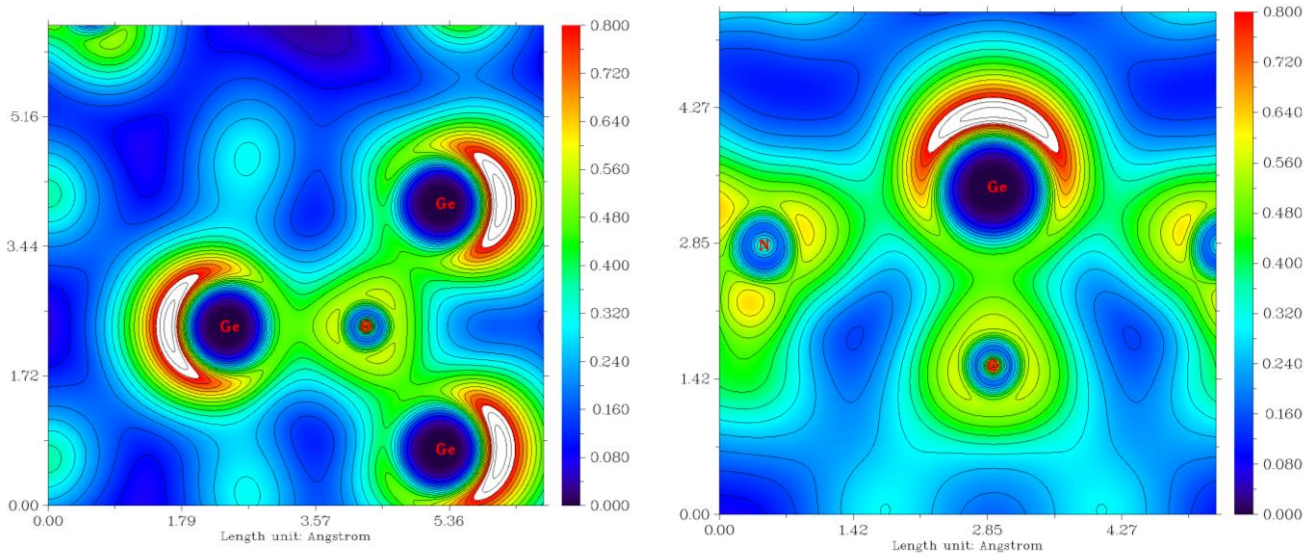
In C_2-***4***, each Ge atom loses two *p*-electrons, four of which filled into the four lone-pair orbitals of N atoms and two others were obtained by the oxygen atom. The three Ge–O bonds can be well described by the coordination effect (σ-coordination in Ge(1)–O/Ge(2)–O and Ge3–O) between the unoccupied lone-pair orbitals of Ge atoms (LP*, nearly pure p orbitals) and the occupied lone pair orbitals of O atoms (LP, mainly sp^n, $n \approx 2$). It is also noteworthy that 2-electron filled p_z orbital of O atom has little π-interaction with the almost unoccupied pure p_z orbital of Sn(3) or with the LP* orbitals of Ge(1) and Ge(2).

From the coefficients of these bonding orbitals (Table S1) we can see that, in each bonding orbital, the contribution of the LP orbital of O atom is predominant (over 90%), which clearly indicates that Ge1–O/Ge2–O and Ge3–O bonds, are highly polarized ones, and can be roughly thought as formed by ionic interaction. This conclusion is supported by the calculated APT and NBO charges on O atom, 1.355 and 1.417, respectively. The bonds of Ge1–N1, Ge1–N3, Ge2–N5 and Ge2–N7 are all coordination bonds formed between lone-pair orbital of N atoms and nearly pure p-orbital of Ge atoms. These results can well explain the structural characters of C_2-***4***: 1) Ge1–O, Ge–O and Ge3–O are all single σ-coordination bonds, so they have the similar bond order and bond length (1.913, 1.913, and 1.878 Å, 2.051, 2.051, and 2.036 Å, respectively); 2) the nearly planar structure of Ge1–OGe3–Ge2 is the result of sp^2 (s, p_x, p_y orbitals) hybrid of O atoms.

One can notice that, in C_2-***4***, Ge3 atom only accepts one pair of lone-pair electrons of O atom, while the other two p-orbitals have little interaction with the lone-pair orbitals of N2, N4, N6, and N8 atoms, due to the long distances (2.513, 2.611, 2.513, and 2.611 Å, respectively). The Ge3 atom deviation from C_2 axis toward two of the four N atoms (N2, N4, N6, and N8) will gain the coordination effect from their lone-pairs, thus resulting in more stable configuration C_1-***4***.

The bonding natures in C_1-***5*** and C_2-***5*** are respectively similar to those in C_1-***4*** and C_2-***4***. The main difference is, in C_1-***5*** and C_2-***5***, all the coordination bonds are greater polarized than those in C_1-***4*** and C_2-***4***., which can be inferred from orbital coefficients, and APT and NBO charges.

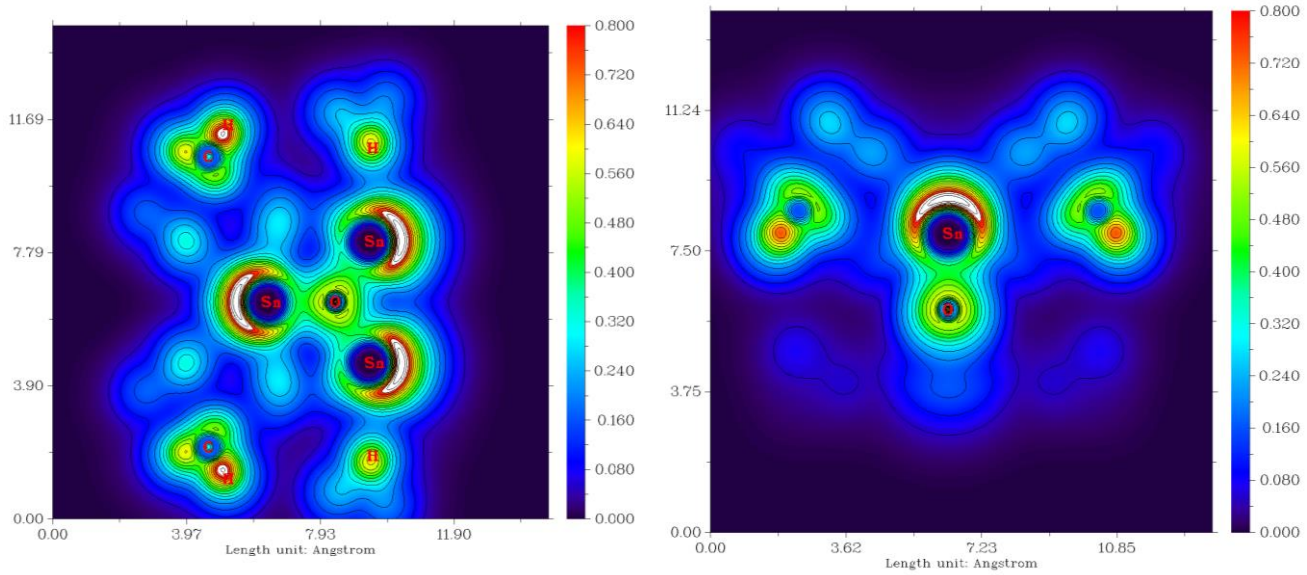
In addition, we analyzed the bonding nature in **4** and **5** (near C_{2v} symmetry) using Localized Orbital Locator (LOL)[6] implemented in Multiwfn 3.3.9,[7,8] and provided the color-filled graphs of LOL each in two planes: i) Plane contains all of the M (M = Ge, Sn) atoms and O atom (Figures S7a and S8a); ii) Plane contains only M(3) and O atoms, which is perpendicular to the plane including three M atoms and O atom (Figures S7b and S8b).



(a) (b)

Figure S7.

(a) Plane contains all of the Ge atoms and O atom; (b) Plane only contains Ge(3) and O atoms, which is perpendicular to the plane including three Ge atoms and O atom.



(a) (b)

Figure S8.

(a) Plane contains all of the Sn atoms and O atom; (b) Plane only contains Sn(3) and O atoms, which is perpendicular to the plane including three Sn atoms and O atom.

From Figure S7a, it can be drawn that, three Ge-O bonds are respectively formed by the coordination of the three lone-pairs of O-atom to the unoccupied orbitals of Ge atoms (nearly pure p-orbitals, revealed by NBO analysis, and deduced from X-Ge-X' angles which are very close to 90°). From Figure S7b, the lone-pair orbital of O-atom perpendicular to the Ge_3O plane is filled with electrons and there is no significant bonding between O and Ge(3) atoms.

The Figure S8 shares the similar situation to that in Figure S7. All these results hence supported that the bonding situation among O atom and three M atoms can be well described as three highly-polarized coordination bonds plus a nearly pure two electron filled O-lone-pair orbital.

S4. Tables

Table S1.

The Mayer Bond Indexes of some key bonds of **4** and **5**, and APT/NBO charges of M atoms and O atom, determined by Gaussian09 program.[9]

	C_1-**4**		*C_2*-**4**	
	APT	**NBO**	**APT**	**NBO**
Ge1	1.511271	1.26724	1.423921	1.27652
Ge2	1.432566	1.27975	1.423921	1.27652
Ge3	1.695754	1.30150	1.979995	1.24595
O	-1.366533	-1.40170	-1.355073	-1.41675
	Mayer Bond index		**Mayer Bond index**	
Ge1–O	0.36105178		0.45241020	
Ge2–O	0.47360015		0.45241020	
Ge3–O	0.41045416		0.42823612	
Ge1–N1	0.47962307		0.49037027	
Ge1–N3	0.49449382		0.49376934	
Ge2–N5	0.40345215		0.49037027	
Ge2–N7	0.42298646		0.49376934	
	Bond components		**Bond components**	
Ge1	BD (0.3499 **Ge1** $sp^{11.25}$+0.9368 **N2** $sp^{2.29}$)		BD (0.2837 **Ge1** $sp^{16.28}$+0.9589 **O** $sp^{2.14}$)	
	BD (0.3435 **Ge1** $sp^{11.80}$+0.9392 **N4** $sp^{2.23}$)		BD (0.3377 **Ge1** $sp^{15.64}$+0.9412 **N1** $sp^{2.22}$)	
	LP $sp^{0.23}$		BD (0.3321 **Ge1** $sp^{16.69}$+0.9432 **N3** $sp^{2.19}$)	
	LP* $sp^{36.58}$		LP $sp^{0.21}$	
Ge2	BD (0.2605 **Ge2** $sp^{20.08}$+0.9655 **O** $sp^{0.15}$)		BD (0.2837 **Ge2** $sp^{16.28}$+0.9589 **O**$sp^{2.14}$)	
	BD (0.3255 **Ge2** $sp^{19.74}$+0.9456 **N1** $sp^{2.21}$)		BD (0.3377 **Ge2** $sp^{15.64}$+0.9412 **N5**$sp^{2.22}$)	
	BD (0.3213 **Ge2** $sp^{19.16}$+0.9470 **N3** $sp^{2.18}$)		BD (0.3321 **Ge2** $sp^{16.69}$+0.9432 **N7**$sp^{2.19}$)	
	LP $sp^{0.17}$		LP $sp^{0.21}$	
O	3LP s^0p^1, $sp^{48.05}$, $sp^{8.34}$,		LP s^0p^1	
Ge3	BD (0.2969 **Ge3** $sp^{26.75}$+0.9549 **N5** $sp^{2.19}$)		BD (0.9707 **O** $sp^{1.75}$ + 0.2405 **Ge3** $sp^{9.23}$)	
	LP $sp^{0.11}$		BD (0.9792 **N2** $sp^{2.28}$+ 0.2028 **Ge3** $sp^{19.09}$)	
	2LP* $sp^{56.10}$ $sp^{19.99}$		BD (0.9794 **N4** $sp^{2.28}$ + 0.2020 **Ge3** $sp^{19.19}$)	
			BD (0.9669 **N6** $sp^{2.61}$ +0.2552 **Ge3** $sp^{99.99}$)	
			LP $sp^{0.08}$	

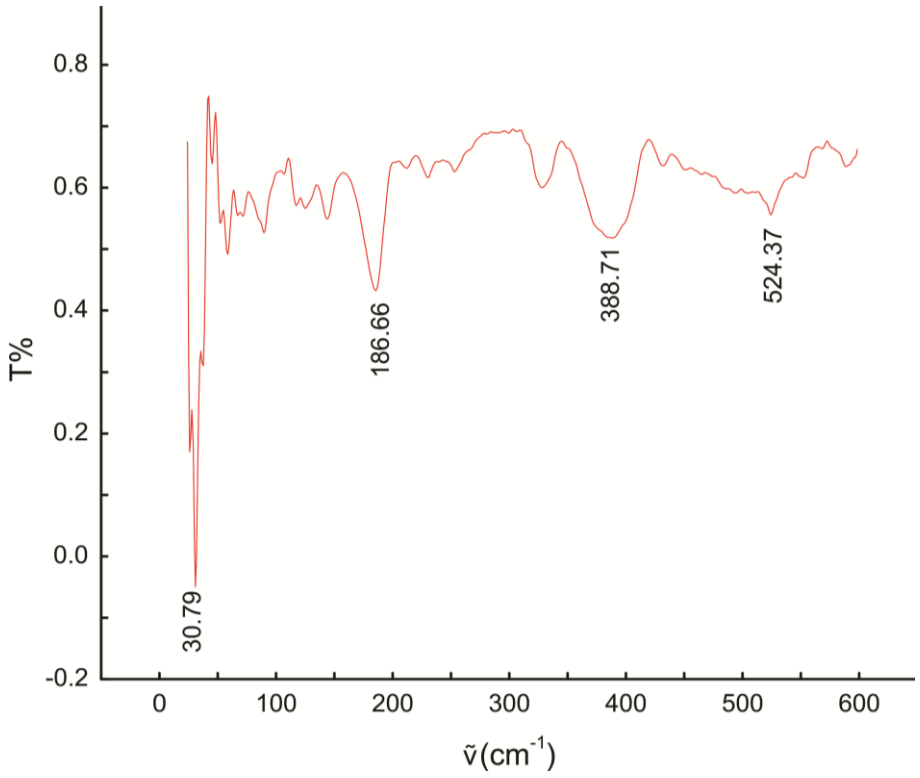
	C_1-5		*C_2-5*	
	APT	**NBO**	**APT**	**NBO**
Sn1	1.523049	1.41332	1.505159	1.41675
Sn2	1.498912	1.41970	1.505159	1.41675
Sn3	1.946965	1.38900	1.990910	1.37965
O	-1.370266	-1.52376	-1.366043	-1.52466
	Mayer BI		**Mayer BI**	
Sn1–O	0.40651274		0.43316834	
Sn2–O	0.45606742		0.43316834	
Sn3–O	0.36182173		0.35500624	
Sn1–N1	0.42135069		0.41043345	
Sn1–N3	0.42911357		0.41529071	
Sn2–N5	0.39800840		0.41043345	
Sn2–N7	0.40361592		0.41529071	
	Bond components		**Bond components**	
Sn1	LP $sp^{0.16}$,		BD (0.2497 **Sn1** $sp^{19.75}$+0.9683 **O** $sp^{2.13}$)	
	3LP* $sp^{6.55}$, $2sp^{99.99}$		BD (0.2928 **Sn1** $sp^{11.25}$+0.9562 **N1** $sp^{2.31}$)	
			BD (0.2869 **Sn1** $sp^{22.12}$ +0.9579 **N3** $sp^{2.30}$)	
			LP $sp^{0.16}$	
Sn2	LP $sp^{0.15}$,		BD (0.2497 **Sn2** $sp^{19.75}$+0.9683 **O** $sp^{2.13}$)	
	3LP* $sp^{7.04}$, $2sp^{99.99}$		BD (0.2928 **Sn2** $sp^{19.76}$+0.9562 **N5** $sp^{2.31}$)	
			BD (0.2869 **Sn2** $sp^{19.76}$+0.9579 **N7** $sp^{2.31}$)	
			LP $sp^{0.16}$	
O	4LP $s^0p^{1.00}$, $sp^{12.83}$, $sp^{98.53}$, $sp^{0.09}$		LP $s^0p^{1.00}$	
Sn3	LP $s^1p^{0.07}$		BD (0.9808 **O** $sp^{1.78}$ + 0.1951 **Sn3** $sp^{10.22}$)	
	3LP* $sp^{16.58}$, $2sp^{99.99}$		BD (0.9835 **N2** $sp^{2.25}$+ 0.2256 **Sn3** $sp^{25.65}$)	
			BD (0.9742 **N4** $sp^{2.63}$ + 0.2256 **Sn3** $sp^{99.99}$)	
			BD (0.9833 **N6** $sp^{2.25}$ + 0.1818 **Sn3** $sp^{25.44}$)	
			LP $sp^{0.07}$	

Table S2

Crystal data and structure refinements for **2'** and **3**–**5**.

Compounds	**2'**	**3**	**4**	**5**
CCDC	1057384	1057381	1057383	1057382
Empirical formula	$C_{37}H_{62}GeKN_6P_3$	$C_{20}H_{36}N_4P_2Sn$	$C_{40}H_{72}Ge_3N_8OP_4$	$C_{40}H_{72}N_8OP_4Sn_3$
Formula weight	795.53	513.16	1022.71	1161.01
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	*P*-1	*Pbca*	$P2_1/c$	*P*-1
a, Å	10.9220(5)	19.896(7)	25.4769(13)	10.2359(3)
b, Å	11.0976(4)	12.361(4)	10.6040(4)	13.8982(4)
c, Å	19.0375(8)	21.124(7)	21.0839(12)	23.2996(7)
α, º	93.162(3)	90	90	72.756(3)
β, º	96.926(3)	90	113.822(7)	89.844(2)
γ, º	98.574(3)	90	90	69.706(3)
Volume, $Å^3$	2258.76(16)	5195(3)	5210.7(4)	2950.53(15)
Z	2	8	4	2
ρ, Mg/m^3	1.170	1.312	1.304	1.307
Absorption coefficient, mm^{-1}	0.907	1.118	1.879	1.401
F(000)	844	2112	2128	1172
Crystal size, mm^3	0.15 × 0.10 × 0.10	0.12 × 0.08 × 0.06	0.15 ×0.15 × 0.10	0.20 × 0.20 × 0.10
θ range, º	2.92 to 25.00	1.93 to 26.01	2.87 to 25.00	2.97 to 26.37.
Limiting indices	-12 ≤ h ≤ 12	-24 ≤ h ≤ 22	-30 ≤ h ≤ 30	-12 ≤ h ≤ 12
	-13 ≤ k ≤ 12	-6 ≤ k ≤ 15	-12 ≤ k ≤ 12	-17 ≤ k ≤ 17
	-22 ≤ l ≤ 22	-25 ≤ l ≤ 24	-24 ≤ l ≤ 25	-29 ≤ l ≤ 29
Reflections collected / unique	15754 / 7921	22322 / 5102	26585 / 9123	35608 / 12063
Data / restraints / parameters	7921 / 60 / 475	5102 / 6 / 245	9123 / 85 / 570	12063 / 46 / 560
GooF on F^2	1.036	0.849	0.970	0.941
R_1, wR_2 [I>2sigma(I)]	0.0592, 0.1297	0.0371, 0.0841	0.0804, 0.1503	0.0390, 0.0966
R_1, wR_2 (all data)	0.0974, 0.1463	0.0776, 0.0932	0.1602, 0.1780	0.0622, 0.1050
Largest diff. peak and hole, $e·A^{-3}$	0.611 and -0.428	0.552 and -0.352	1.035 and -0.792	0.931 and -0.604

S5. The Near-Infrared spectrum of 5



In the IR spectrum below 500 cm^{-1}, three absorption signals concerning M–O and M–N at 524.4, 388.7, and 186.7 cm^{-1} were observed, which might ascribed to Sn–N, Sn(1/2)–O, and Sn(3)–O stretching vibrations.[10-13]

S6. The calculated ^{119}Sn NMR chemical shifts for 5

Based on the optimized geometries by B3LYP method with combined 6-311G(d) for C, N, P and H and LANL2DZ basis set and pseudopotential for Sn, we calculated the ^{119}Sn NMR chemical shield by B3PW91 method[14,15] with the 6-311G(d) basis set for C, N, P and H and ATZP[16] basis set for Sn, with the direct implementation of the gauge including atomic orbitals (GIAO) method.[17-19] The calculated isotropic chemical shifts δ_{DFT} for Sn(1), Sn(2) and Sn(3) in **5**, and Sn in **3** are 2714.88 ppm, 2720.76 ppm and 2914.33 ppm, and 3235.56 ppm, respectively ($\delta_{DFT}(SnMe_4)$ = 2654.06 ppm, very close to the value (2630.95 ppm) calculated at the B3PW91/TZV level).[20] Relative to the calculated isotropic chemical shift of Sn in **3**, the relative isotropic chemical shifts $\delta_{DFT,re}$ ($\delta_{DFT(5)}$–$\delta_{DFT(3)}$) of Sn(1), Sn(2) and Sn(3) in **5** are 514.8, 520.68 and 321.23 ppm, respectively. Since $\delta_{DFT,exp}$ for complex **3** is –741.60 ppm relative to that of $SnMe_4$, the δ_{calc}(**5**, Sn(1)), δ_{calc}(**5**, Sn(2)) and δ_{calc}(**5**, Sn(3)) predicted by theoretical calculations are –226.8, –220.92 and –420.37 ppm, respectively. (Here, δ_{calc} means the predicted chemical shift relative to that of $SnMe_4$). It can be seen that all these chemical shifts of Sn(1), Sn(2), and Sn(3) in **5** appear at down-field relative to that in **3** (–741.60 ppm), and the chemical shift of Sn(3) is at the up-field relative to those for Sn(1) and Sn(2).

B3PW91	T(II) atom	δ_{DFT} (ppm)	$\delta_{DFT,re}$ (ppm)	δ_{DFT}–δ_{DFT}(**3**) (ppm)	Predicated δ_{DFT} (ppm)	Experimental values (ppm)
$SnMe_4$	Sn	2693.37	0			
Complex **3**†	Sn	3254.47	–561.1	0	–741.6	–741.6
Complex **3** in JACS‡	Sn(1)–O	2337.44	355.93	–917.03	175.43	91.8
	Sn(2)–O	2366.19	327.18	–888.28	146.68	91.8
	Sn(3)=O	2467.59	225.78	–786.88	45.28	–95.1
Complex **5**†	Sn(1)–O	2748.81	–55.44	–505.66	–235.94	–372.26
	Sn(2)–O	2753.63	–60.26	–500.84	–240.76	–372.26
	Sn(3)–O	2955.15	–261.78	–299.32	–442.28	–398.29
B3LYP	T(II) atom	δ_{DFT} (ppm)	$\delta_{DFT,re}$ (ppm)	δ_{DFT}–δ_{DFT}(**3**) (ppm)	Predicated δ_{DFT} (ppm)	Experimental values (ppm)
$SnMe_4$	Sn	2654.06	39.31	–581.5	–160.1	–
Complex **3**†	Sn	3235.56	–542.19	0	–741.6	–741.6
Complex **3** in JACS‡	Sn(1)–O	2295.9	397.47	–939.66	198.06	91.8
	Sn(2)–O	2325.18	368.19	–910.38	168.78	91.8
	Sn(3)=O	2429.39	263.98	–806.17	64.57	–95.1
Complex **5**†	Sn(1)–O	2714.88	–21.51	–520.68	–220.92	–372.26
	Sn(2)–O	2720.76	–27.39	–514.8	–226.8	–372.26
	Sn(3)–O	2914.33	–220.96	–321.23	–420.37	–398.29

† In this case.

‡ Reference [21].

S7. Concise report of ^{119}Sn Mössbauer measurement for complex 5 (collected at room temperature)

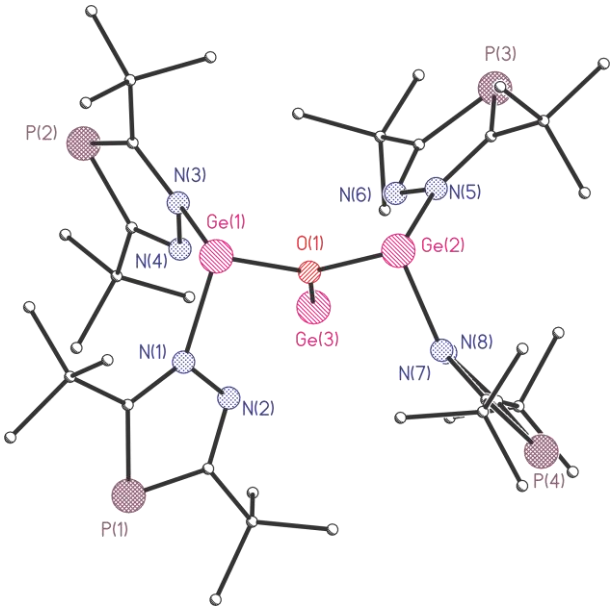
HISTORY: P86.DAT=>FOLD(510.0)=>CAL(VER-FE)
CALIBRATION FACTOR: 3.95317367945880E-0002
ZERO VELOCITY CHANNEL: 2.53718523243745E+0002
SPACE: MEASURED
TITLE OF X AXIS: [mm/s]
TITLE OF Y AXIS: Counts
SETWIN: FFFTTTFFFTFTFFF

MOSSWINN FIT REPORT
2016.12.20.Tuesday.11.15.26
Chisquare => 540.86
Normalized Chisquare => 1.071
Total spectrum area => 27489.83276980
Base Line . Base Line => 928538.09497363 (StD=48.9)
Doublet (1) => 50.8 % ~/S
Doublet (1) . AMPLITUDE => 6985.09896938 (StD=612.1)
Doublet (1) . ISOMER SHIFT => 3.35268000 (StD=FIXED)
Doublet (1) . Q. SPLITTING => 1.87406007 (StD=0.0445)
Doublet (1) . LINE WIDTH => 0.94000000 (StD=FIXED)
Doublet (2) => 49.2 % ~/S
Doublet (2) . AMPLITUDE => 6759.81741551 (StD=594.3)
Doublet (2) . ISOMER SHIFT => 3.10280000 (StD=FIXED)
Doublet (2) . Q. SPLITTING => 2.20543244 (StD=0.0427)
Doublet (2) . LINE WIDTH => 0.87000000 (StD=FIXED)
.END.

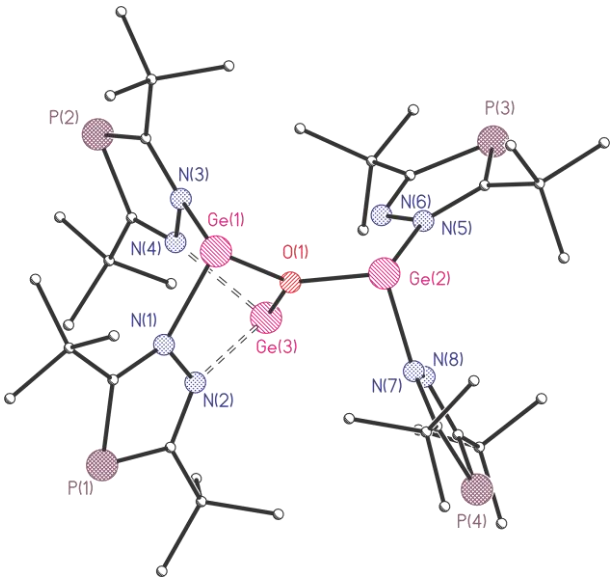
ANCESTOR WINDOW => P86.DAT
DATE OF FIRST LOAD => 2016.12.20.Tuesday.10.24.08
IS REFERENCE => Alpha Iron

S8. XYZ geometries of DFT calculation of 4 and 5

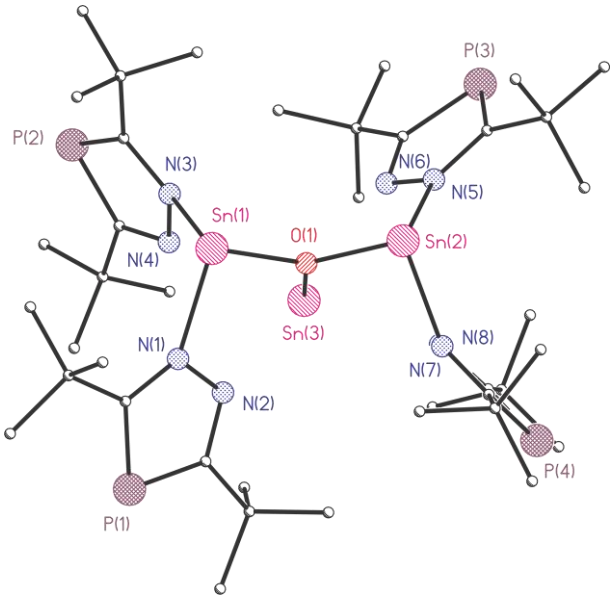
S8-1 The calculated structures of 4 and 5



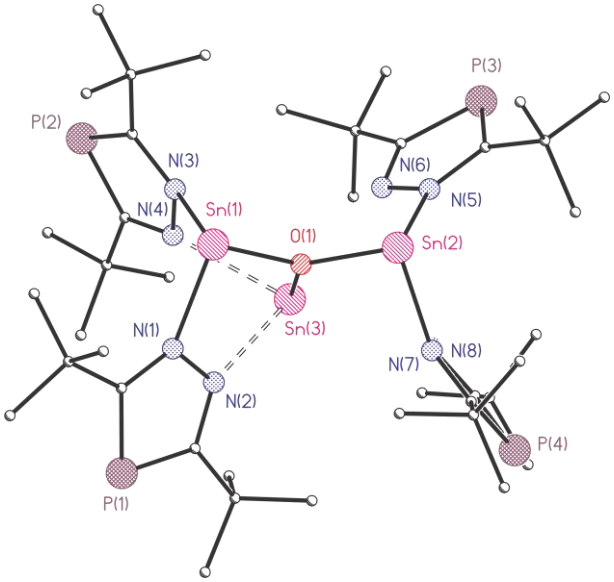
4a (C_2 symmetry). Selected bond lengths (Å) and bond angles (deg): Ge(3)–O(1) 1.878, Ge(1)–O(1) 1.913, Ge(2)–O(1) 1.913, Ge(1)–N(1) 2.072, Ge(1)–N(3) 2.052, Ge(2)–N(5) 2.072, Ge(2)–N(7) 2.052, Ge(3)···N(2) 2.513, Ge(3)···N(4) 2.611, Ge(3)···N(6) 2.513, Ge(3)···N(8) 2.611; Ge(1)–O(1)–Ge(3) 121.57, Ge(1)–O(1)–Ge(2) 116.86, Ge(2)–O(1)–Ge(3) 121.57.



4b (C_1 symmetry). Selected bond lengths (Å) and bond angles (deg): Ge(3)–O(1) 1.890, Ge(1)–O(1) 1.894, Ge(2)–O(1) 1.972, Ge(1)–N(1) 2.120, Ge(1)–N(3) 2.074, Ge(2)–N(5) 2.039, Ge(2)–N(7) 2.043, Ge(3)···N(2) 2.222, Ge(3)···N(4) 2.261, Ge(3)···N(6) 2.966, Ge(3)···N(8) 3.292; Ge(1)–O(1)–Ge(3) 116.48, Ge(1)–O(1)–Ge(2) 115.44, Ge(2)–O(1)–Ge(3) 128.08.



5a (C_2 symmetry). Selected bond lengths (Å) and bond angles (deg): Sn(3)–O(1) 2.306, Sn(1)–O(1) 2.051, Sn(2)–O(1) 2.051, Sn(1)–N(1) 2.253, Sn(1)–N(3) 2.238, Sn(2)–N(5) 2.253, Sn(2)–N(7) 2.238, Sn(3)···N(2) 2.664, Sn(3)···N(4) 2.736, Sn(3)···N(6) 2.664, Sn(3)···N(8) 2.736; Sn(1)–O(1)–Sn(3) 119.89, Sn(1)–O(1)–Sn(2) 120.23, Sn(2)–O(1)–Sn(3) 119.89



5b (C_1 symmetry). Selected bond lengths (Å) and bond angles (deg): Sn(3)–O(1) 2.037, Sn(1)–O(1) 2.042, Sn(2)–O(1) 2.066, Sn(1)–N(1) 2.266, Sn(1)–N(3) 2.247, Sn(2)–N(5) 2.239, Sn(2)–N(7) 2.228, Sn(3)···N(2) 2.557, Sn(3)···N(4) 2.573, Sn(3)···N(6) 2.791, Sn(3)···N(8) 2.962; Sn(1)–O(1)–Sn(3) 118.13, Sn(1)–O(1)–Sn(2) 120.21, Sn(2)–O(1)–Sn(3) 121.65.

S8-2 XYZ geometries of 4a

Ge3_O_C2(one imaginary frequency)
128
symmetry c2

Ge	-1.217187000	1.084320000	-1.818749000
Ge	1.217187000	-1.084320000	-1.818749000
O	0.000000000	0.000000000	-0.817126000
P	0.000000000	5.041003000	0.253646000
P	-5.055073000	0.402137000	0.543908000
P	0.000000000	-5.041003000	0.253646000
P	5.055073000	-0.402137000	0.543908000
N	-0.663250000	2.701751000	-0.648980000
N	0.117695000	2.434037000	0.446538000
N	-2.725208000	0.447770000	-0.581708000
N	-2.470349000	0.775799000	0.722986000
N	0.663250000	-2.701751000	-0.648980000
N	-0.117695000	-2.434037000	0.446538000
N	2.725208000	-0.447770000	-0.581708000
N	2.470349000	-0.775799000	0.722986000
C	-0.836957000	4.022137000	-0.903881000
C	0.555596000	3.548875000	1.033952000
C	1.499470000	3.515002000	2.239590000
C	0.840883000	2.797524000	3.436746000
C	2.809208000	2.805125000	1.834708000
C	1.848933000	4.950148000	2.687883000
C	-1.673784000	4.562391000	-2.069370000
C	-1.012609000	4.225181000	-3.428206000
C	-3.114878000	4.010018000	-2.006619000
C	-1.769947000	6.101812000	-1.975212000
C	-4.023818000	0.173704000	-0.860589000
C	-3.587319000	0.844744000	1.447807000
C	-3.570091000	1.365598000	2.887695000
C	-3.221605000	2.873376000	2.842564000
C	-4.958567000	1.198871000	3.538378000
C	-2.538678000	0.624456000	3.759408000
C	-4.478604000	-0.371180000	-2.221358000
C	-4.525689000	0.730577000	-3.306440000
C	-5.902821000	-0.954708000	-2.086728000
C	-3.538697000	-1.512247000	-2.677607000
C	4.023818000	-0.173704000	-0.860589000
C	3.587319000	-0.844744000	1.447807000
C	3.570091000	-1.365598000	2.887695000
C	4.958567000	-1.198871000	3.538378000
C	3.221605000	-2.873376000	2.842564000
C	2.538678000	-0.624456000	3.759408000

C	4.478604000	0.371180000	-2.221358000
C	3.538697000	1.512247000	-2.677607000
C	5.902821000	0.954708000	-2.086728000
C	4.525689000	-0.730577000	-3.306440000
C	0.836957000	-4.022137000	-0.903881000
C	-0.555596000	-3.548875000	1.033952000
C	-1.499470000	-3.515002000	2.239590000
C	-0.840883000	-2.797524000	3.436746000
C	-1.848933000	-4.950148000	2.687883000
C	-2.809208000	-2.805125000	1.834708000
C	1.673784000	-4.562391000	-2.069370000
C	3.114878000	-4.010018000	-2.006619000
C	1.769947000	-6.101812000	-1.975212000
C	1.012609000	-4.225181000	-3.428206000
H	0.596630000	1.757455000	3.206971000
H	-0.083590000	3.303734000	3.734910000
H	1.520612000	2.797936000	4.297491000
H	3.506052000	2.777760000	2.681540000
H	3.299880000	3.338923000	1.012780000
H	2.631190000	1.778937000	1.507655000
H	0.958270000	5.507163000	2.999374000
H	2.341133000	5.516218000	1.889560000
H	2.535500000	4.909938000	3.541579000
H	-0.000389000	4.641573000	-3.476434000
H	-1.599253000	4.660108000	-4.246423000
H	-0.943507000	3.148091000	-3.605046000
H	-3.156350000	2.923680000	-2.116366000
H	-3.718047000	4.439677000	-2.815326000
H	-3.588152000	4.263689000	-1.052109000
H	-2.246362000	6.420793000	-1.042216000
H	-2.372648000	6.479968000	-2.809077000
H	-0.784185000	6.575186000	-2.033089000
H	-3.202025000	3.287954000	3.858419000
H	-3.968245000	3.429828000	2.264498000
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H	-5.255660000	0.145391000	3.591627000
H	-5.734010000	1.741640000	2.986580000
H	-4.937665000	1.595734000	4.560003000
H	-2.764213000	-0.444960000	3.816449000
H	-2.553167000	1.028230000	4.778949000
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H	-3.532891000	1.132913000	-3.529484000
H	-5.172815000	1.558780000	-2.998436000
H	-4.927001000	0.314167000	-4.238269000
H	-6.626782000	-0.190335000	-1.784130000
H	-5.937310000	-1.764477000	-1.350518000

H	-6.226748000	-1.358293000	-3.052909000
H	-3.927386000	-1.970100000	-3.594961000
H	-3.461611000	-2.290494000	-1.910999000
H	-2.528001000	-1.151056000	-2.896027000
H	4.937665000	-1.595734000	4.560003000
H	5.255660000	-0.145391000	3.591627000
H	5.734010000	-1.741640000	2.986580000
H	2.244595000	-3.039361000	2.380006000
H	3.202025000	-3.287954000	3.858419000
H	3.968245000	-3.429828000	2.264498000
H	1.523646000	-0.740657000	3.371929000
H	2.764213000	0.444960000	3.816449000
H	2.553167000	-1.028230000	4.778949000
H	3.461611000	2.290494000	-1.910999000
H	2.528001000	1.151056000	-2.896027000
H	3.927386000	1.970100000	-3.594961000
H	6.626782000	0.190335000	-1.784130000
H	5.937310000	1.764477000	-1.350518000
H	6.226748000	1.358293000	-3.052909000
H	4.927001000	-0.314167000	-4.238269000
H	3.532891000	-1.132913000	-3.529484000
H	5.172815000	-1.558780000	-2.998436000
H	-0.596630000	-1.757455000	3.206971000
H	0.083590000	-3.303734000	3.734910000
H	-1.520612000	-2.797936000	4.297491000
H	-2.535500000	-4.909938000	3.541579000
H	-0.958270000	-5.507163000	2.999374000
H	-2.341133000	-5.516218000	1.889560000
H	-3.506052000	-2.777760000	2.681540000
H	-3.299880000	-3.338923000	1.012780000
H	-2.631190000	-1.778937000	1.507655000
H	3.718047000	-4.439677000	-2.815326000
H	3.588152000	-4.263689000	-1.052109000
H	3.156350000	-2.923680000	-2.116366000
H	0.784185000	-6.575186000	-2.033089000
H	2.246362000	-6.420793000	-1.042216000
H	2.372648000	-6.479968000	-2.809077000
H	0.943507000	-3.148091000	-3.605046000
H	0.000389000	-4.641573000	-3.476434000
H	1.599253000	-4.660108000	-4.246423000
Ge	0.000000000	0.000000000	1.060529000
Sum of electronic and zero-point Energies=			-3457.161989
Sum of electronic and thermal Energies=			-3457.092548
Sum of electronic and thermal Enthalpies=			-3457.091603
Sum of electronic and thermal Free Energies=			-3457.264178

S8-3 XYZ geometries of 4b

Ge3_O_C1 (near Cs symmetry, no imaginary frequency)
128
symmetry c1

Ge	-1.574970000	0.030906000	-1.747120000
Ge	1.690878000	-0.094184000	-1.815397000
O	0.126402000	-0.021393000	-0.750702000
P	-3.428695000	3.865372000	-0.039652000
P	-4.021809000	-3.173285000	0.435148000
P	3.176070000	-3.862663000	0.508442000
P	4.080808000	2.997307000	0.591146000
N	-2.252571000	1.679480000	-0.756976000
N	-1.505713000	2.122642000	0.293841000
N	-2.458020000	-1.366007000	-0.546588000
N	-2.760253000	-0.898441000	0.697032000
N	2.364234000	-1.616056000	-0.502457000
N	1.600615000	-1.799685000	0.620302000
N	2.413433000	1.416267000	-0.591591000
N	2.321419000	1.083649000	0.732327000
C	-3.308020000	2.468816000	-1.087346000
C	-1.981436000	3.257118000	0.784601000
C	-1.292575000	3.943193000	1.964824000
C	-1.381141000	3.040915000	3.211905000
C	0.179109000	4.226031000	1.607461000
C	-1.976666000	5.283683000	2.291923000
C	-4.271155000	2.176002000	-2.242791000
C	-3.543797000	2.272490000	-3.604386000
C	-4.935839000	0.793541000	-2.074634000
C	-5.403821000	3.224685000	-2.258847000
C	-3.015714000	-2.566515000	-0.865649000
C	-3.580716000	-1.706218000	1.341914000
C	-4.105441000	-1.287564000	2.715716000
C	-5.155800000	-0.172902000	2.508863000
C	-4.767840000	-2.474984000	3.435053000
C	-2.958745000	-0.744721000	3.588899000
C	-2.741664000	-3.302137000	-2.182499000
C	-3.444985000	-2.612642000	-3.374067000
C	-3.285632000	-4.743241000	-2.093958000
C	-1.223521000	-3.395059000	-2.454296000
C	3.253518000	2.433400000	-0.853350000
C	3.169654000	1.781966000	1.498453000
C	3.397514000	1.475507000	2.981050000
C	4.406783000	2.475664000	3.579952000
C	4.002298000	0.057210000	3.084788000
C	2.105229000	1.567848000	3.813559000
C	3.380403000	3.059516000	-2.247212000

C	1.977451000	3.333134000	-2.834019000
C	4.119729000	4.409042000	-2.133539000
C	4.186349000	2.163264000	-3.212468000
C	3.260403000	-2.599510000	-0.711212000
C	1.872681000	-2.940036000	1.262830000
C	1.068605000	-3.425466000	2.473909000
C	1.149938000	-2.446154000	3.662108000
C	1.616513000	-4.784145000	2.955962000
C	-0.402062000	-3.623125000	2.050865000
C	4.249745000	-2.600704000	-1.879994000
C	5.066430000	-1.292689000	-1.881344000
C	5.243332000	-3.770899000	-1.725683000
C	3.516013000	-2.794320000	-3.227099000
H	-0.918057000	2.069723000	3.036504000
H	-2.423519000	2.863752000	3.488655000
H	-0.881549000	3.510492000	4.065854000
H	0.693924000	4.712788000	2.442429000
H	0.246792000	4.890899000	0.741739000
H	0.716537000	3.310927000	1.361607000
H	-3.025541000	5.148121000	2.567905000
H	-1.940819000	5.975113000	1.446049000
H	-1.472207000	5.764034000	3.135773000
H	-3.090613000	3.259446000	-3.728527000
H	-4.255188000	2.121837000	-4.422371000
H	-2.754985000	1.526841000	-3.715681000
H	-4.226006000	-0.033000000	-2.110104000
H	-5.662506000	0.624905000	-2.875209000
H	-5.459131000	0.726030000	-1.118419000
H	-5.982114000	3.212235000	-1.332350000
H	-6.088938000	3.009185000	-3.083624000
H	-5.020036000	4.237326000	-2.401839000
H	-5.558336000	0.160117000	3.471308000
H	-5.991070000	-0.530659000	1.900055000
H	-4.713827000	0.687720000	2.003218000
H	-4.060101000	-3.292272000	3.600074000
H	-5.611429000	-2.875208000	2.866148000
H	-5.148809000	-2.159804000	4.411058000
H	-2.209254000	-1.517706000	3.781562000
H	-3.344731000	-0.405427000	4.555516000
H	-2.462642000	0.095426000	3.103534000
H	-3.060563000	-1.607981000	-3.557925000
H	-4.521472000	-2.539155000	-3.202595000
H	-3.287961000	-3.193495000	-4.288391000
H	-4.364206000	-4.760409000	-1.921983000
H	-2.809654000	-5.306331000	-1.287907000
H	-3.091380000	-5.269336000	-3.033055000

H	-1.037407000	-4.013067000	-3.337959000
H	-0.697234000	-3.844108000	-1.608641000
H	-0.778051000	-2.416839000	-2.648041000
H	4.585858000	2.229755000	4.629882000
H	4.035631000	3.502702000	3.538768000
H	5.370888000	2.443823000	3.066716000
H	3.345299000	-0.695281000	2.649587000
H	4.175964000	-0.203794000	4.133060000
H	4.960179000	0.003375000	2.561218000
H	1.354101000	0.839096000	3.509350000
H	1.656361000	2.559446000	3.740215000
H	2.329729000	1.377018000	4.866742000
H	1.369697000	3.929477000	-2.150216000
H	1.429352000	2.413257000	-3.050720000
H	2.068712000	3.881527000	-3.775713000
H	5.133319000	4.288646000	-1.742852000
H	3.588448000	5.108809000	-1.484646000
H	4.201305000	4.866944000	-3.122543000
H	4.318309000	2.676558000	-4.169159000
H	3.679553000	1.219821000	-3.422119000
H	5.177897000	1.939046000	-2.812111000
H	0.719812000	-1.471539000	3.429114000
H	2.182202000	-2.296900000	3.985943000
H	0.588408000	-2.848593000	4.509777000
H	1.026926000	-5.133542000	3.807354000
H	2.658024000	-4.714552000	3.280680000
H	1.555310000	-5.549122000	2.178262000
H	-0.985964000	-4.012256000	2.889608000
H	-0.482333000	-4.339286000	1.230007000
H	-0.873840000	-2.695696000	1.725788000
H	5.783571000	-1.294250000	-2.707114000
H	5.623084000	-1.179772000	-0.947765000
H	4.441495000	-0.407405000	-1.996313000
H	4.739955000	-4.740303000	-1.745786000
H	5.810943000	-3.704051000	-0.794712000
H	5.957859000	-3.753708000	-2.552804000
H	2.840967000	-1.970938000	-3.463375000
H	2.929881000	-3.716643000	-3.220093000
H	4.243623000	-2.864017000	-4.040931000
Ge	0.381341000	-0.010863000	1.121867000

Sum of electronic and zero-point Energies=	3457.163957
Sum of electronic and thermal Energies=	-3457.093694
Sum of electronic and thermal Enthalpies=	-3457.092750
Sum of electronic and thermal Free Energies=	-3457.268466

S8-4 XYZ geometries of 5a

Sn3_O_C2
128
symmetry c2

Sn	-1.324495000	1.186520000	-1.909905000
Sn	1.324495000	-1.186520000	-1.909905000
O	0.000000000	0.000000000	-0.887985000
P	0.000000000	5.181756000	0.406054000
P	-5.173059000	0.468263000	0.731848000
P	0.000000000	-5.181756000	0.406054000
P	5.173059000	-0.468263000	0.731848000
N	-0.722022000	2.888397000	-0.561557000
N	0.125625000	2.573313000	0.468783000
N	-2.904776000	0.437684000	-0.513691000
N	-2.584214000	0.811418000	0.765385000
N	0.722022000	-2.888397000	-0.561557000
N	-0.125625000	-2.573313000	0.468783000
N	2.904776000	-0.437684000	-0.513691000
N	2.584214000	-0.811418000	0.765385000
C	-0.912760000	4.214426000	-0.736202000
C	0.605114000	3.659937000	1.074182000
C	1.613848000	3.575295000	2.223747000
C	0.982439000	2.906026000	3.461290000
C	2.859817000	2.795556000	1.760145000
C	2.068803000	4.987717000	2.643178000
C	-1.824199000	4.804185000	-1.819251000
C	-1.204025000	4.611342000	-3.222417000
C	-3.235908000	4.185043000	-1.756712000
C	-1.986323000	6.322984000	-1.595647000
C	-4.215812000	0.183870000	-0.711833000
C	-3.660762000	0.922281000	1.541639000
C	-3.566084000	1.484022000	2.963088000
C	-3.067338000	2.943169000	2.872016000
C	-4.951948000	1.478151000	3.636148000
C	-2.607658000	0.663831000	3.845530000
C	-4.753862000	-0.344332000	-2.046310000
C	-4.900664000	0.792345000	-3.083200000
C	-6.150702000	-0.963014000	-1.829219000
C	-3.830722000	-1.447303000	-2.606878000
C	4.215812000	-0.183870000	-0.711833000
C	3.660762000	-0.922281000	1.541639000
C	3.566084000	-1.484022000	2.963088000
C	4.951948000	-1.478151000	3.636148000
C	3.067338000	-2.943169000	2.872016000
C	2.607658000	-0.663831000	3.845530000
C	4.753862000	0.344332000	-2.046310000

C	3.830722000	1.447303000	-2.606878000
C	6.150702000	0.963014000	-1.829219000
C	4.900664000	-0.792345000	-3.083200000
C	0.912760000	-4.214426000	-0.736202000
C	-0.605114000	-3.659937000	1.074182000
C	-1.613848000	-3.575295000	2.223747000
C	-0.982439000	-2.906026000	3.461290000
C	-2.068803000	-4.987717000	2.643178000
C	-2.859817000	-2.795556000	1.760145000
C	1.824199000	-4.804185000	-1.819251000
C	3.235908000	-4.185043000	-1.756712000
C	1.986323000	-6.322984000	-1.595647000
C	1.204025000	-4.611342000	-3.222417000
H	0.663816000	1.882399000	3.261094000
H	0.108889000	3.465053000	3.805040000
H	1.703907000	2.870072000	4.283143000
H	3.601289000	2.744250000	2.563029000
H	3.328447000	3.290645000	0.905552000
H	2.625698000	1.775318000	1.459544000
H	1.235989000	5.595342000	3.006188000
H	2.542224000	5.525024000	1.817879000
H	2.800598000	4.912916000	3.452499000
H	-0.214142000	5.071390000	-3.273121000
H	-1.835267000	5.081051000	-3.982906000
H	-1.095729000	3.560007000	-3.495772000
H	-3.250885000	3.118471000	-1.988810000
H	-3.893516000	4.670710000	-2.483557000
H	-3.675067000	4.306711000	-0.764304000
H	-2.434246000	6.543859000	-0.624151000
H	-2.638043000	6.740661000	-2.368102000
H	-1.030114000	6.847883000	-1.651789000
H	-2.977516000	3.378645000	3.872406000
H	-3.766429000	3.558903000	2.299826000
H	-2.095589000	3.001783000	2.380868000
H	-5.350038000	0.465143000	3.739188000
H	-5.680546000	2.068709000	3.075188000
H	-4.879384000	1.910729000	4.638039000
H	-2.908997000	-0.384876000	3.893298000
H	-2.604444000	1.059701000	4.865548000
H	-1.581531000	0.706410000	3.479481000
H	-3.937676000	1.223443000	-3.366135000
H	-5.532145000	1.596222000	-2.698027000
H	-5.361732000	0.408900000	-3.998436000
H	-6.868369000	-0.226758000	-1.459584000
H	-6.118593000	-1.787902000	-1.113971000
H	-6.535126000	-1.351931000	-2.776321000

H	-4.273052000	-1.886723000	-3.505740000
H	-3.678332000	-2.245386000	-1.876997000
H	-2.847162000	-1.064220000	-2.890257000
H	4.879384000	-1.910729000	4.638039000
H	5.350038000	-0.465143000	3.739188000
H	5.680546000	-2.068709000	3.075188000
H	2.095589000	-3.001783000	2.380868000
H	2.977516000	-3.378645000	3.872406000
H	3.766429000	-3.558903000	2.299826000
H	1.581531000	-0.706410000	3.479481000
H	2.908997000	0.384876000	3.893298000
H	2.604444000	-1.059701000	4.865548000
H	3.678332000	2.245386000	-1.876997000
H	2.847162000	1.064220000	-2.890257000
H	4.273052000	1.886723000	-3.505740000
H	6.868369000	0.226758000	-1.459584000
H	6.118593000	1.787902000	-1.113971000
H	6.535126000	1.351931000	-2.776321000
H	5.361732000	-0.408900000	-3.998436000
H	3.937676000	-1.223443000	-3.366135000
H	5.532145000	-1.596222000	-2.698027000
H	-0.663816000	-1.882399000	3.261094000
H	-0.108889000	-3.465053000	3.805040000
H	-1.703907000	-2.870072000	4.283143000
H	-2.800598000	-4.912916000	3.452499000
H	-1.235989000	-5.595342000	3.006188000
H	-2.542224000	-5.525024000	1.817879000
H	-3.601289000	-2.744250000	2.563029000
H	-3.328447000	-3.290645000	0.905552000
H	-2.625698000	-1.775318000	1.459544000
H	3.893516000	-4.670710000	-2.483557000
H	3.675067000	-4.306711000	-0.764304000
H	3.250885000	-3.118471000	-1.988810000
H	1.030114000	-6.847883000	-1.651789000
H	2.434246000	-6.543859000	-0.624151000
H	2.638043000	-6.740661000	-2.368102000
H	1.095729000	-3.560007000	-3.495772000
H	0.214142000	-5.071390000	-3.273121000
H	1.835267000	-5.081051000	-3.982906000
Sn	0.000000000	0.000000000	1.148265000
Sum of electronic and zero-point Energies=			-3456.058030
Sum of electronic and thermal Energies=			-3455.986608
Sum of electronic and thermal Enthalpies=			-3455.985664
Sum of electronic and thermal Free Energies=			-3456.165460

S8-5 XYZ geometries of 5b

Sn3_O_C1
128
symmetry c1

Sn	-1.756757000	0.042814000	-1.890832000
Sn	1.801710000	-0.095520000	-1.919408000
O	0.044606000	-0.019888000	-0.881656000
P	-3.385388000	3.971202000	0.317042000
P	-4.269347000	-3.022293000	0.700140000
P	3.291394000	-3.964961000	0.527080000
P	4.256332000	2.950227000	0.731106000
N	-2.396454000	1.764350000	-0.609849000
N	-1.533863000	2.126040000	0.390816000
N	-2.549243000	-1.511368000	-0.504228000
N	-2.624381000	-0.991927000	0.760400000
N	2.439680000	-1.738219000	-0.494575000
N	1.575053000	-1.999527000	0.538221000
N	2.499129000	1.527395000	-0.530166000
N	2.447342000	1.070609000	0.762208000
C	-3.433291000	2.613263000	-0.789786000
C	-1.898403000	3.267451000	0.970431000
C	-1.075636000	3.902413000	2.094415000
C	-1.136793000	3.027546000	3.362696000
C	0.382312000	4.088517000	1.633865000
C	-1.639649000	5.291300000	2.455404000
C	-4.521706000	2.413323000	-1.851698000
C	-3.950968000	2.644483000	-3.270035000
C	-5.160796000	1.013279000	-1.743899000
C	-5.652137000	3.442955000	-1.639458000
C	-3.324769000	-2.599349000	-0.716842000
C	-3.506575000	-1.637937000	1.512664000
C	-3.861251000	-1.127976000	2.910923000
C	-4.711482000	0.153209000	2.748937000
C	-4.683418000	-2.178766000	3.679577000
C	-2.603162000	-0.794829000	3.730434000
C	-3.308050000	-3.373340000	-2.039098000
C	-4.112021000	-2.632835000	-3.131713000
C	-3.958798000	-4.757875000	-1.837555000
C	-1.858599000	-3.601179000	-2.520121000
C	3.368210000	2.538114000	-0.727254000
C	3.339621000	1.675581000	1.551081000
C	3.587336000	1.226854000	2.994744000
C	4.709015000	2.071729000	3.630677000
C	4.041101000	-0.248795000	2.973868000
C	2.332976000	1.378439000	3.875560000
C	3.501530000	3.252533000	-2.077014000

C	2.115336000	3.487793000	-2.714691000
C	4.160095000	4.631759000	-1.862263000
C	4.396340000	2.450638000	-3.049043000
C	3.413329000	-2.660912000	-0.640583000
C	1.864886000	-3.140623000	1.167288000
C	1.004653000	-3.688912000	2.310916000
C	1.071504000	-2.772253000	3.549549000
C	1.512445000	-5.081364000	2.737425000
C	-0.452345000	-3.842311000	1.833019000
C	4.502183000	-2.576224000	-1.716311000
C	5.204495000	-1.203335000	-1.685006000
C	5.583403000	-3.645756000	-1.451520000
C	3.911406000	-2.857515000	-3.117111000
H	-0.717228000	2.035033000	3.194602000
H	-2.168833000	2.898978000	3.698376000
H	-0.572373000	3.492260000	4.177217000
H	0.977347000	4.560235000	2.421838000
H	0.429564000	4.731232000	0.750648000
H	0.859066000	3.143829000	1.377117000
H	-2.670097000	5.233852000	2.815126000
H	-1.621213000	5.971727000	1.600446000
H	-1.036889000	5.739915000	3.250360000
H	-3.514044000	3.642791000	-3.352003000
H	-4.746345000	2.560328000	-4.017014000
H	-3.178028000	1.920933000	-3.537073000
H	-4.468468000	0.201931000	-1.976092000
H	-5.991869000	0.923018000	-2.449654000
H	-5.545517000	0.831384000	-0.738390000
H	-6.120401000	3.332985000	-0.658767000
H	-6.426315000	3.300304000	-2.398620000
H	-5.289684000	4.469673000	-1.725948000
H	-4.991186000	0.553862000	3.728940000
H	-5.631812000	-0.054266000	2.196128000
H	-4.159848000	0.924063000	2.207459000
H	-4.123368000	-3.107350000	3.819082000
H	-5.614345000	-2.426136000	3.162980000
H	-4.948954000	-1.795670000	4.669181000
H	-1.957999000	-1.669390000	3.845277000
H	-2.884323000	-0.452026000	4.731004000
H	-2.025126000	0.000358000	3.260936000
H	-3.661252000	-1.675057000	-3.400930000
H	-5.137006000	-2.444473000	-2.803938000
H	-4.153425000	-3.235920000	-4.043973000
H	-5.001530000	-4.674637000	-1.522197000
H	-3.427967000	-5.346039000	-1.085600000
H	-3.941213000	-5.316256000	-2.777824000

H	-1.852611000	-4.237126000	-3.410289000
H	-1.257694000	-4.088706000	-1.749112000
H	-1.357405000	-2.668613000	-2.791813000
H	4.899473000	1.723755000	4.649657000
H	4.441361000	3.130074000	3.686861000
H	5.646185000	1.991093000	3.074637000
H	3.292467000	-0.893938000	2.514949000
H	4.224931000	-0.604751000	3.992420000
H	4.967838000	-0.363084000	2.405672000
H	1.515764000	0.736154000	3.545088000
H	1.971404000	2.408696000	3.879881000
H	2.564680000	1.098327000	4.907345000
H	1.444220000	4.006471000	-2.026830000
H	1.628842000	2.557064000	-3.017127000
H	2.218310000	4.098180000	-3.616369000
H	5.162466000	4.543295000	-1.436595000
H	3.566217000	5.261286000	-1.195833000
H	4.254246000	5.149867000	-2.820490000
H	4.535359000	3.009675000	-3.979177000
H	3.958708000	1.486378000	-3.317406000
H	5.382063000	2.265676000	-2.615780000
H	0.687911000	-1.771389000	3.345370000
H	2.097698000	-2.670743000	3.910021000
H	0.469703000	-3.191428000	4.361450000
H	0.885377000	-5.469341000	3.544808000
H	2.541235000	-5.048316000	3.105132000
H	1.472645000	-5.798561000	1.913988000
H	-1.071409000	-4.269123000	2.627218000
H	-0.509689000	-4.511202000	0.970620000
H	-0.901422000	-2.893647000	1.541481000
H	6.019210000	-1.178302000	-2.414459000
H	5.624441000	-0.999178000	-0.697580000
H	4.539258000	-0.374000000	-1.931295000
H	5.173538000	-4.657617000	-1.485513000
H	6.059482000	-3.507987000	-0.478090000
H	6.360766000	-3.578576000	-2.217512000
H	3.173134000	-2.113215000	-3.421913000
H	3.426248000	-3.836317000	-3.142487000
H	4.705328000	-2.853458000	-3.870064000
Sn	0.131725000	0.019938000	1.152611000
Sum of electronic and zero-point Energies=			-3456.058278
Sum of electronic and thermal Energies=			-3455.986548
Sum of electronic and thermal Enthalpies=			-3455.985604
Sum of electronic and thermal Free Energies=			-3456.167481

S9. References

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