Electronic Supplementary Information for the paper entitled:

Germanium/Phosphorus Cage Compounds with Germanium in Three Different Oxidation States

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Contents:

1. Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard glovebox and Schlenck techniques. All solvents were freshly distilled from appropriate drying agents immediately prior to use. NMR spectra in solution were obtained on either a Bruker AMX 300 or Bruker Avance 400 spectrometer with δ referenced to external $SiMe_4$ (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). The solid-state ^{31}P MAS NMR spectrum of compound **1** was recorded on a Bruker AVANCE300 solid-state spectrometer in a 2.5 mm probe. FD MS spectra were acquired on a Finnigan MAT 95 mass spectrometer. $SnCl_2$ was obtained from Aldrich and used without further purification. The substances $GeCl_2$(diox) [1] and *t*$BuPH_2$ [2] were prepared

according to literature methods.

Synthesis of [$Ge_7(PtBu)_4Cl_6$] 1: To a stirred solution of 0.3 ml *t*$BuPH_2$ (222 mg, 2.5 mmol) in THF (20 ml) at –20°C a *n*-butyllithium solution (1.54 mL, 1.6 M, 2.5 mmol) was added. The reaction mixture was warmed up to ambient temperature and stirred for another hour. After cooling to –70°C to this solution 1 g of solid $GeCl_2$(diox) (4.3 mmol) was added. The solution was stirred for 16 hours at ambient temperature in which the color turned orange. The solvent was changed to toluene and the solution was filtered to remove LiCl. Storage at –25°C for three days results in yellow rods of **1**. Yield: 165 mg (25%)

1: Element. Analysis: $C_{16}H_{36}P_4Ge_7Cl_6$ (1079.4 g/mol): C 18.05 (calc. 17.90); H 3.68 (3.38) %. **MS** (EI, 70 eV): *m/z* (%) = 1074.9 (2.2) [M^+]. **^{1}H NMR** (400.13 MHz, C_6D_6, 25°C, TMS): δ = 1.1 (d, ^3J(P,H) = 16 Hz, 9 H), 1.5 ppm (d, ^3J(P,H) = 16 Hz, 27 H); **^{31}P{^{1}H} NMR** (161.98 MHz, C_6D_6, 25°C, H_3PO_4 85%): δ = 4 (q, ^2J(P,P) = 22 Hz, 1 P), 85 ppm (d, ^2J(P,P) = 22 Hz, 3 P); **^{31}P NMR** (121.49 MHz, C_6D_6, 25°C, H_3PO_4 85%): δ = 4 (m), 85 ppm (m); **^{13}C{^{1}H} NMR** (100.62 MHz, C_6D_6, TMS): δ = 33.3 (s, C-quart.), 33.6 (s, C-quart.), 34.8 (s, CH_3), 41.5 ppm (s, CH_3).

Synthesis of [$Ge_8(PtBu)_4Br_6$] 2: *n*BuLi (1.4 mL, 1.6 M, 2.2 mmol) was added to a solution of 0.26 ml *t*$BuPH_2$ (194 mg, 2.2 mmol) in THF at –20°C. After stirring for one hour at ambient temperature and cooling to –70°C 1 g of solid $GeBr_2$ (4.3 mmol) was added. The red reaction mixture was stirred for additional 16 hours at room temperature. After changing the solvent to toluene, filtration from LiCl and storage at –25°C for three weeks pale yellow crystals of **2** are obtained. Yield: 115 mg (15%).

2: Element. Analysis: $C_{16}H_{36}P_4Ge_8Br_6$ (1412.8 g/mol): C 13.33 (calc. 13.60); H 2.59 (2.57) %. **MS** (EI, 70 eV): *m/z* (%) = 1412.8 (1) [M^+]; **^{31}P MAS NMR** (121.50 MHz, 25°C, 30 kHz, NaH_2PO_4): δ = –92 ppm (s, 2 P2), 58 (s, 2 P1).

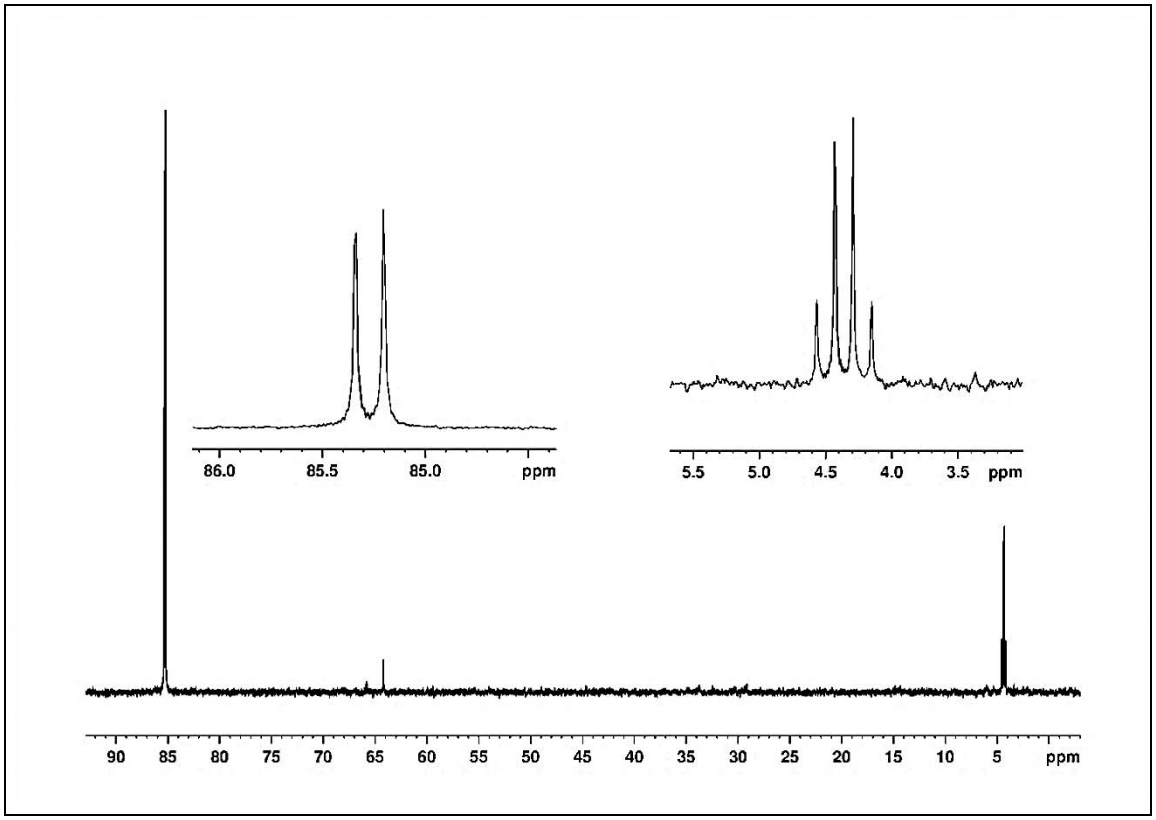

Figure S1: $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K) of the reaction solution of **1**.

2. Crystallographic Details

The crystal structure analyses were performed on an OXFORD Diffraction Gemini R Ultra CCD diffractometer with $Cu_{K\alpha}$ radiation (λ = 1.54184 Å). The structures were solved by direct methods with the program SHELXS-97,[3a] and full matrix least square refinement on F^2 in SHELXL-97[3b] was performed with anisotropic displacements for non H-atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **1**: $C_{22}H_{50}P_4Ge_7Cl_6$, M = 939.73, crystal size: 0.31 × 0.05 × 0.04 mm^3, trigonal, space group $P\bar{3}$, a = 14.2614(4) , b = 14.2614(4), c = 11.0241(2) Å, α = 90°, β = 90°, γ = 120°, V = 1941.77(8) Å^3, T = 123(1) K, Z = 2, $\rho_{calc.}$ = 1.983 g cm^{-3}, μ = 11.567 mm^{-1}, 3245 measured reflections, 1745 independent reflections (R_{int} = 0.0209), R_1 = 0.0343, wR_2 = 0.0758. **2**: $C_{16}H_{36}P_4Br_6Ge_8$, M_r = 1412.61, crystal size: 0.25 × 0.04 × 0.02 mm^3, orthorhombic, space group *Pbcn*, a = 16.9638(2), b = 13.8428(1), c = 16.3948(2) Å, V = 3849.93(7) Å^3, T = 123(1) K, Z = 4, $\rho_{calc.}$ = 1.130 g cm^{-3}, μ = 2.437 mm^{-1}, 10878 measured reflections, 3000 independent reflections (R_{int} = 0.0453), R_1 = 0.0416, wR_2 = 0.1059.

3. Computational Details

The geometry optimisation was performed with the TURBOMOLE program package[4] at the (RI-)[5] BP86[6]/TZVP[6a,7] level of theory including the Multipole Accelerated Resolution of Identity (MARI-J) approximation[8]. The NBO[9] analysis was performed on using Gaussian[10] with the BP86[6] functional and 6-31+G*[11] basis set. The shared electron numbers (SEN) were calculated using TURBOMOLE and correlate with the strength of the covalent bond.[12] The isosurfaces of the frontier molecular orbitals in **2** are depicted in Figure S2. The cartesian coordinates of the optimized geometries of **1** and **2** are given in table S1 and S2, respectively.

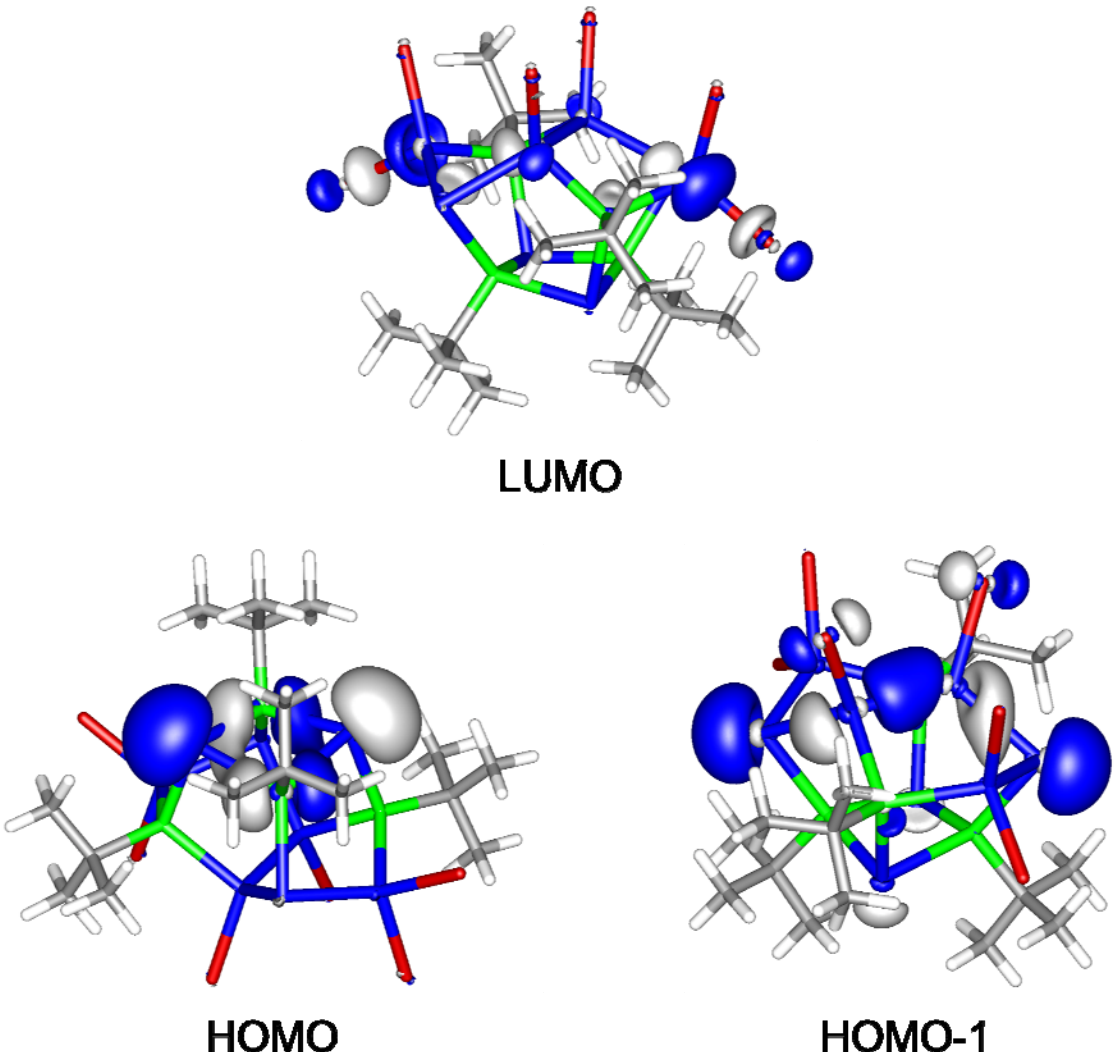

Figure S2. Isosurfaces of the frontier molecular orbitals in **2**.

Table S1. Cartesian coordinates for the optimised geometry of **1** at the BP86/TZVP level of theory.

Atom	x	y	z
C	0.0000000	0.0000000	4.2664373
C	1.1014136	0.9501298	4.7586787
C	-1.3735433	0.4787872	4.7586787
C	0.2721298	-1.4289170	4.7586787
P	0.0000000	0.0000000	2.3300944
H	1.1129214	0.9476224	5.8611467
H	0.9289015	1.9870676	4.4329379
H	2.0985820	0.6467721	4.4100002
H	-1.3771258	0.4900070	5.8611467
H	-2.1853017	-0.1890815	4.4329379
H	-1.6094121	1.4940393	4.4100002
H	0.2642044	-1.4376294	5.8611467
H	1.2564003	-1.7979861	4.4329379
H	-0.4891700	-2.1408114	4.4100002
Ge	-1.9878539	-1.4778133	1.7529231
Ge	2.2737508	-0.9826253	1.7529231
Ge	-0.2858969	2.4604387	1.7529231
P	-0.8822297	-1.9135374	-0.4091572
Ge	-3.0332976	0.5818308	0.6985925
P	2.0982868	0.1927354	-0.4091572
Ge	1.0127686	-2.9178282	0.6985925
P	-1.2160571	1.7208020	-0.4091572
Ge	2.0205291	2.3359974	0.6985925
C	-1.8163347	-3.1515865	-1.5625536
Ge	0.0000000	0.0000000	-1.7651884
Cl	-4.7967397	0.4275332	-0.6655700
Cl	-3.8090307	2.0443279	2.2078155
C	3.6375214	0.0028013	-1.5625536
Cl	2.0281152	-4.3678651	-0.6655700
Cl	0.1340755	-4.3208813	2.2078155
C	-1.8211866	3.1487853	-1.5625536
Cl	2.7686245	3.9403318	-0.6655700
Cl	3.6749553	2.2765534	2.2078155
C	-3.1348366	-2.5008036	-2.0026422
C	-2.0947113	-4.4471773	-0.7860777
C	-0.9321109	-3.4331224	-2.7883148
C	3.7331778	-1.4644463	-2.0026422
C	4.8987241	0.4095154	-0.7860777
C	3.4392266	0.9093295	-2.7883148
C	-0.5983412	3.9652500	-2.0026422
C	-2.8040128	4.0376618	-0.7860777
C	-2.5071157	2.5237929	-2.7883148
H	-2.9729277	-1.5532999	-2.5359819
H	-3.8060186	-2.3038671	-1.1563376
H	-3.6564921	-3.1858664	-2.6916005
H	-2.6763943	-5.1261567	-1.4312702
H	-2.6841111	-4.2643296	0.1237425
H	-1.1715547	-4.9668407	-0.4983144
H	0.0259615	-3.8913200	-2.5104686
H	-0.7316224	-2.5181559	-3.3654291
H	-1.4635269	-4.1345383	-3.4525672
H	2.8316610	-1.7979810	-2.5359819
H	3.8982167	-2.1441753	-1.1563376
H	4.5872873	-1.5736818	-2.6916005
H	5.7775791	0.2452529	-1.4312702
H	5.0350733	-0.1923436	0.1237425
H	4.8871876	1.4688242	-0.4983144

H	3.3570012	1.9681434	-2.5104686
H	2.5465982	0.6254743	-3.3654291
H	4.3123786	0.7998177	-3.4525672
H	0.1412667	3.3512808	-2.5359819
H	-0.0921981	4.4480423	-1.1563376
H	-0.9307952	4.7595482	-2.6916005
H	-3.1011848	4.8809038	-1.4312702
H	-2.3509622	4.4566732	0.1237425
H	-3.7156328	3.4980165	-0.4983144
H	-3.3829628	1.9231767	-2.5104686
H	-1.8149758	1.8926816	-3.3654291
H	-2.8488517	3.3347206	-3.4525672

Table S2. Cartesian coordinates for the optimised geometry of **2** at the BP86/TZVP level of theory.

Atom	x	y	z
Ge	1.5452844	-0.9919296	-1.0760771
Ge	-1.5452844	0.9919296	-1.0760771
Ge	-1.5326862	-2.6913855	1.2540883
Ge	1.5326862	2.6913855	1.2540883
Ge	-0.1561525	1.2704091	2.5328646
Ge	3.1932649	0.8552790	1.8333667
Ge	0.1561525	-1.2704091	2.5328646
Ge	-3.1932649	-0.8552790	1.8333667
P	0.8868889	1.3854819	-0.7168336
P	2.1986820	-1.2954238	1.2604518
P	-2.1986820	1.2954238	1.2604518
P	-0.8868889	-1.3854819	-0.7168336
Br	0.5640391	-2.0658658	4.7338589
Br	-3.8461788	-0.8125372	4.1174945
Br	-5.2601798	-0.9076517	0.6216584
Br	3.8461788	0.8125372	4.1174945
Br	5.2601798	0.9076517	0.6216584
Br	-0.5640391	2.0658658	4.7338589
C	-1.4724682	-2.4217283	-2.2398449
C	-1.0972287	-1.6786691	-3.5301874
C	-2.9943401	-2.6028908	-2.1588273
C	-0.7612398	-3.7830310	-2.1921725
C	1.4724682	2.4217283	-2.2398449
C	3.2843399	-2.8774453	1.4959986
C	-3.2843399	2.8774453	1.4959986
C	1.0972287	1.6786691	-3.5301874
C	2.9943401	2.6028908	-2.1588273
C	0.7612398	3.7830310	-2.1921725
C	4.3173136	-2.9240654	0.3590755
C	2.3481441	-4.0945960	1.4227114
C	3.9860464	-2.8146789	2.8601754
C	-4.3173136	2.9240654	0.3590755
C	-2.3481441	4.0945960	1.4227114
C	-3.9860464	2.8146789	2.8601754
H	-1.4217698	-2.2719938	-4.4008928
H	-0.0104804	-1.5299125	-3.6172492
H	-1.5912550	-0.6977769	-3.5942284
H	-3.3432178	-3.1769230	-3.0334047
H	-3.5231095	-1.6390817	-2.1564538

H	-3.2951520	-3.1545364	-1.2563985
H	-1.0145188	-4.3446967	-1.2808745
H	0.3330556	-3.6729120	-2.2409976
H	-1.0734621	-4.3909684	-3.0573168
H	1.4217698	2.2719938	-4.4008928
H	0.0104804	1.5299125	-3.6172492
H	1.5912550	0.6977769	-3.5942284
H	3.3432178	3.1769230	-3.0334047
H	3.5231095	1.6390817	-2.1564538
H	3.2951520	3.1545364	-1.2563985
H	1.0145188	4.3446967	-1.2808745
H	-0.3330556	3.6729120	-2.2409976
H	1.0734621	4.3909684	-3.0573168
H	4.9465419	-3.8189391	0.4960266
H	4.9739104	-2.0437847	0.3645270
H	3.8404748	-2.9947158	-0.6292217
H	1.8041544	-4.1406991	0.4677997
H	1.6186753	-4.1031332	2.2448507
H	2.9545980	-5.0117126	1.5052044
H	4.5587474	-3.7463124	3.0009423
H	3.2714709	-2.7266814	3.6890951
H	4.6905299	-1.9747954	2.9207909
H	-4.9465419	3.8189391	0.4960266
H	-4.9739104	2.0437847	0.3645270
H	-3.8404748	2.9947158	-0.6292217
H	-1.8041544	4.1406991	0.4677997
H	-1.6186753	4.1031332	2.2448507
H	-2.9545980	5.0117126	1.5052044
H	-4.5587474	3.7463124	3.0009423
H	-3.2714709	2.7266814	3.6890951
H	-4.6905299	1.9747954	2.9207909

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