Supporting Information

for

Zinc as a Versatile Connecting Atom for Zintl Cluster Oligomers

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1. Experimental Details

General. All reactions and manipulations were performed under a purified argon atmosphere using standard Schlenk and glove box techniques. The Zintl compound of nominal composition K_4Ge_9 was synthesized by heating (2 K/min) of a stoichiometric mixture of the elements K (Merck, ≥ 98%) and Ge (99.999% Chempur) at 650 °C in a stainless-steel autoclave for 46 h and slow cooling (1 K/min) to room temperature. Toluene was dried over molecular sieve (4 Å) and thf over a special drying material in a solvent purificator (MBraun MB-SPS). Liquid ammonia was stored over sodium metal and freshly distilled before use. 2.2.2-Crypt (Merck) was dried for 8 h *in vacuo*. The bis-silylated Ge_9 cluster $K_2[Ge_9\{Si(SiMe_3)_3\}_2]$ and the zinc complexes $ZnCp^*_2$ and $Zn_2[HC(Ph_2P{=}NPh)_2]$ were prepared according to the literature.[1-3]

Energy Dispersive X-Ray (EDX) Analysis. Single crystals of compounds **1** and **2** were analyzed with a scanning electron microscope equipped with an energy dispersive X-ray analyzer (Hitachi TM-1000 Tabletop microscope).

NMR Spectroscopy. ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AVIII 400 FT system (*Bruker Corp.*) at 300 K. The chemical shifts are given in δ values (ppm). The signals of the ^{1}H and ^{13}C spectra were calibrated on the rest proton signal of the used deuterated solvents thf-d_8 and benzene-d_6. Signal multiplicities are abbreviated as follows: s - singlet. The spectra were evaluated with MestReNova.[4]

Single-Crystal Structure Determination. Single crystals were fixed on a glass fiber with perfluorinated ether and positioned in a 150 K cold N_2 stream. For single crystal X-ray diffraction data collection, a STOE StadiVari diffractometer (Mo-K_α radiation) was used. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations against F^2 using SHELX-2014.[5] Non-hydrogen atoms were treated with anisotropic displacement parameters. For compound **1** the total amount of solvent molecules was determined by using the Squeeze function.[6] For compounds **1** and **2** several C and N atoms had to be treated with the ISOR command. Table 1 contains selected crystallographic data and refinement details of the crystal structures. Pictures of the crystal structures were created with the program Diamond.[7]

Table 1: Selected crystallographic data of the crystal structures of **1** and **2**.

Compound	**1**	**2**
formula	$C_{114}H_{264}Ge_{36}K_6Si_{32}Zn$	$Ge_9H_{51}N_{17}Zn_2$
fw ($g \cdot mol^{-1}$)	5447.33	1073.62
space group (No.)	$P\bar{1}$ (2)	$P2_1/m$ (11)
a (Å)	16.0588(5)	10.355(2)
b (Å)	22.0076(6)	17.830(4)
c (Å)	37.9459(12)	10.478(2)
α (deg)	85.691(2)	90
β (deg)	88.100(2)	113.42(3)
γ (deg)	70.120(2)	90
V (Å^3)	12575.1(7)	1775.2(7)
Z	2	2
T (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
ρ_{calcd} ($g \cdot cm^{-3}$)	1.439	2.009
μ (mm^{-1})	4.600	8.845
collected reflections	251052	15020
independent reflections	49399	3595
R_{int}	0.0924	0.0566
parameters / restraints	1801 / 126	144 / 18
R_1 [$I > 2\,\sigma(I)$ / all data]	0.0573 / 0.0945	0.0612 / 0.0733
wR_2 [all data / $I > 2\,\sigma(I)$]	0.1363 / 0.1524	0.1624 / 0.1751
goodness of fit	1.083	1.076
max./min. diff. el. Density ($e \cdot Å^{-3}$)	1.02 / –1.19	0.76 / –0.75
CCDC No.	1946668	1946669

Electron Spray Mass Spectrometry (ESI-MS). The preparation of the samples for ESI-MS measurements was performed in a glove box. The solutions were diluted with thf to a concentration of approx. $2.0 \cdot 10^{-4}$ mmol/mL. The measurements were performed on an HCT instrument (*Bruker Corp.*). Analysis of the data was performed using the program Bruker Compass Data Analysis 4.0 SP 5 (*Bruker Corp.*). The dry gas temperature was adjusted at 125 °C and the injection speed at 240 µL/h. Visualization of the spectra was carried out with the programs OriginPro 2015G (*Origin Lab Corp.*) and

Excel 2015 (*Microsoft Corp.*). All observed compounds must bear a single negative charge, due to measurements circumstances, despite of their reasonable charge.

Synthesis of $K_6[Zn\{\eta^1\text{-}Ge_9(Hyp)_2\}_4] \cdot 10.5$ tol (1). 120 mg (96 µmol, 1 equiv.) of $[Ge_9(Hyp)_2]^{2-}$ and 32 mg (96 µmol, 1 equiv.) $ZnCp^*_2$ were dissolved in 3 mL of thf. The brownish suspension was stirred overnight. After removal of the solvent, the residue was dissolved in 3 mL of toluene and filtrated. The volume of the brownish-red solution was reduced to approx. 1 mL, and the solution was stored at -32 °C. After 5 weeks red columns (approx. 5% yield) suitable for single crystal diffractometry were obtained. EDX results: Zn:K:Si:Ge = 1:9.8:28.5:32.8 (calc. 1:6:32:36).
NMR Spectra of K[ZnCp[Ge$_9$(Hyp)$_2$]:* ^{1}H-NMR (400 MHz, thf-d$_8$, 300 K): δ (ppm) = 1.95 (s, 15 H, ZnCp*), 0.20 (s, 54 H, CH_3); ^{13}C-NMR (101 MHz, thf-d$_8$, 300 K): δ (ppm) = 110.4 (ZnCp*), 11.5 (ZnCp*), 3.2 ppm (CH_3); ^{29}Si-NMR (79 MHz, thf-d$_8$, 300 K): d = –9.8 ($Si(SiMe_3)_3$), –106.6 ppm ($Si(SiMe_3)_3$); ESI-MS (negative mode, 4000 V): $\{ZnCp^*[Ge_9(Hyp)_2]\}^-$ (m/z = 1349.8), $\{Zn[Ge_9(Hyp)_3]\}^-$ (m/z = 1462.6), $\{Zn_2[Ge_9(Hyp)_3]\}^-$ (m/z= 1462.6).

Synthesis of $(NH_3)_3Zn\text{–}Ge_9\text{–}Zn(NH_3)_3 \cdot 11\ NH_3$ (2). 30 mg (37 µmol, 1 equiv.) K_4Ge_9, 95 mg (75 µmol, 3.9 equiv.) $Zn_2[HC(Ph_2P{=}NPh)_2]_2$ and 51 mg (135 µmol, 3.6 equiv.) 2.2.2-crypt were weighed out in a Schlenk tube. Approximately 2 mL of liquid ammonia were added, and a brownish-red suspension was formed. After 19 months at –77 °C grey block-shaped crystals (approx. 20% yield) suitable for single crystal diffractometry were obtained. EDX results: Zn:Ge = 1:4.3 (calc. 1:4.5).

2. Determination of Cluster Geometry

The nine atomic clusters E_9 adopt several different geometric shapes with two border cases: a tricapped trigonal prism with D_{3h} symmetry and a monocapped square antiprism with C_{4v} symmetry (Figure S1). An ideal D_{3h} is distinguished by three identical heights *h* and three identical dihedral angles α. A distortion of the trigonal prism by elongation of the heights affects its symmetry. With two identical prism heights, two conformers with C_{2v} symmetry are obtained. Three different heights result in C_s symmetry. With a dihedral angle of 0° and one height identical with the diagonal *d* of the square antiprism the cluster possesses C_{4v} symmetry.[8]

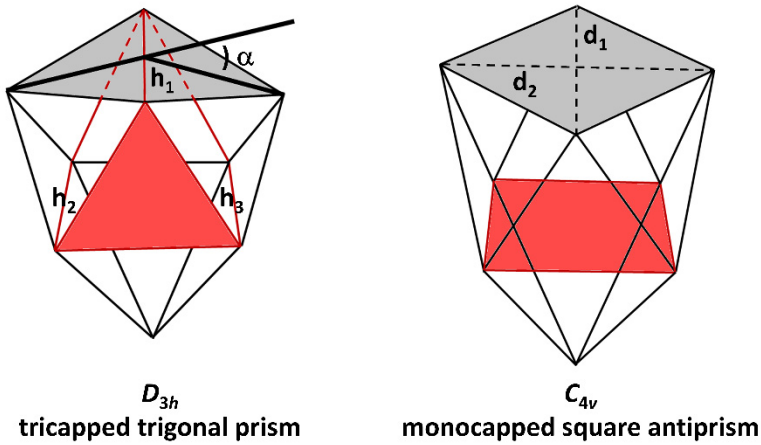

Figure S1: Schematic illustration of the tricapped trigonal prism (left) and the monocapped square antiprism (right) with highlighted geometric parameters.

3. NMR Spectra

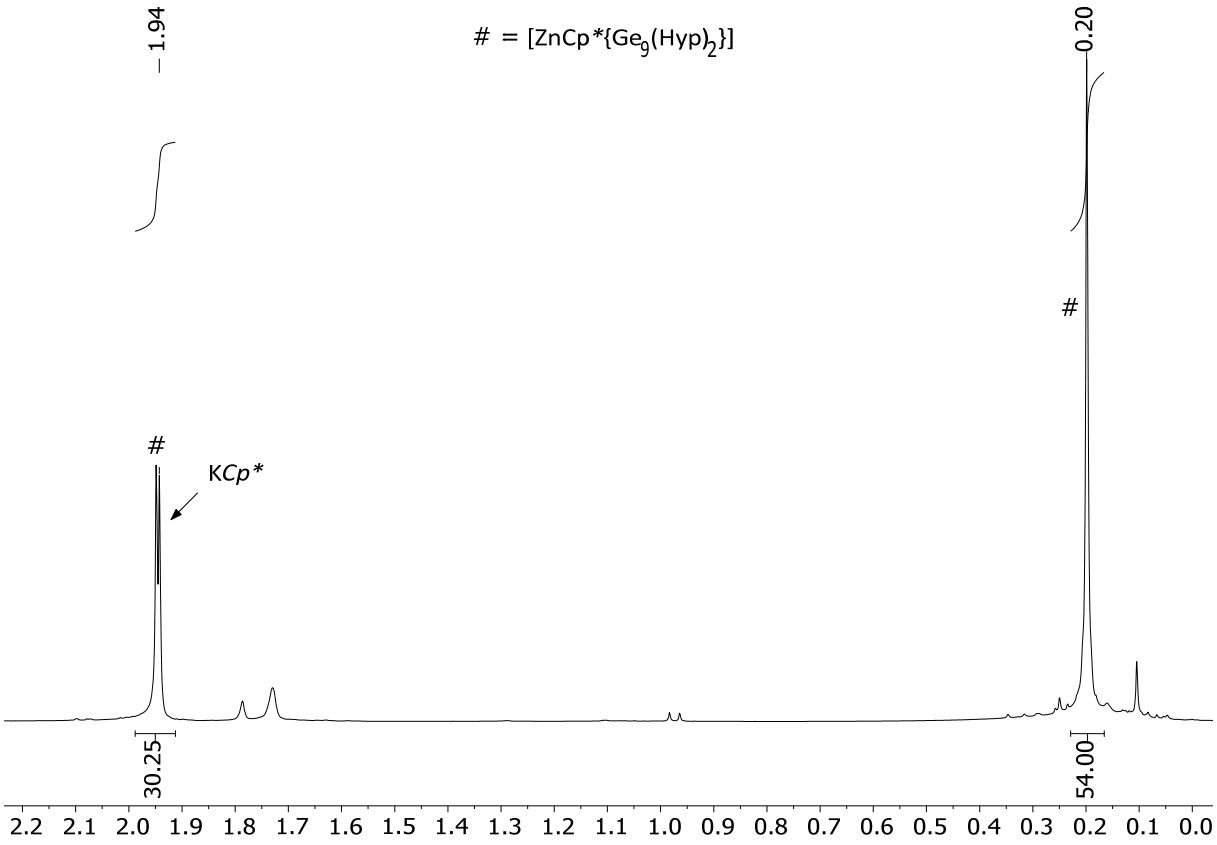

Figure S2: ^{1}H NMR spectrum of ZnCp*$_2$ and $K_2[Ge_9(Hyp)_2]$ with the postulated product $K[ZnCp^*\{Ge_9(Hyp)_2\}]$ in thf-d_8.

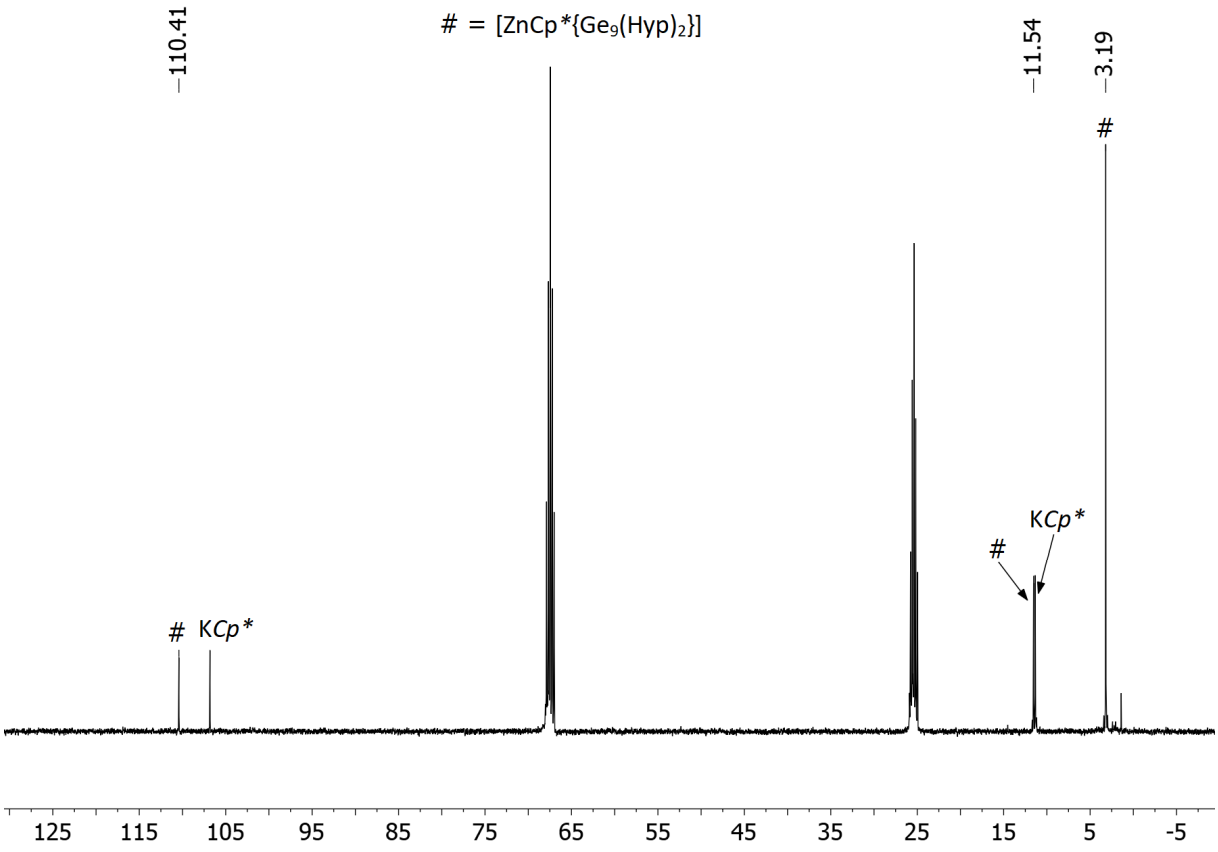

Figure S3: ^{13}C NMR spectrum of $ZnCp^*_2$ and $K_2[Ge_9(Hyp)_2]$ with the postulated product $K[ZnCp^*\{Ge_9(Hyp)_2\}]$ in thf-d_8.

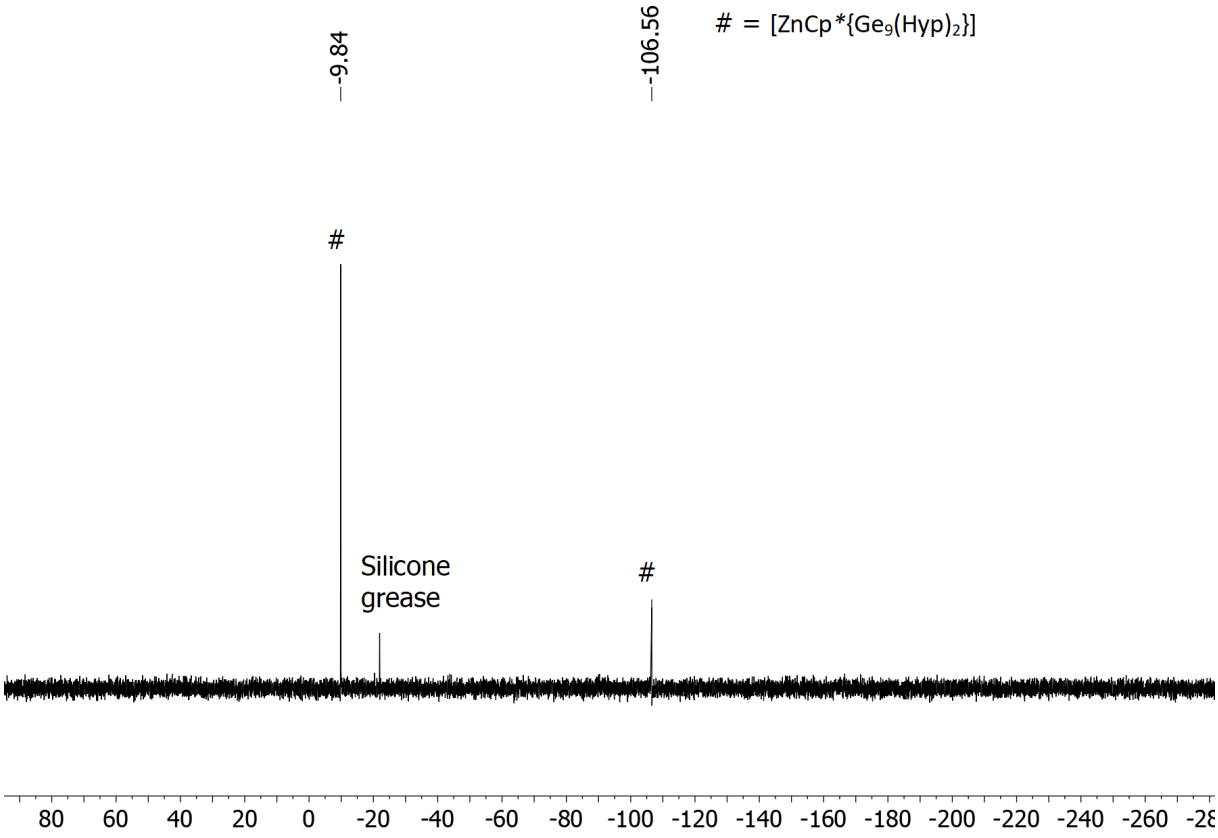

Figure S4: ^{29}Si NMR spectrum of $ZnCp^*_2$ and $K_2[Ge_9(Hyp)_2]$ with the postulated product $K[ZnCp^*\{Ge_9(Hyp)_2\}]$ in thf-d_8.

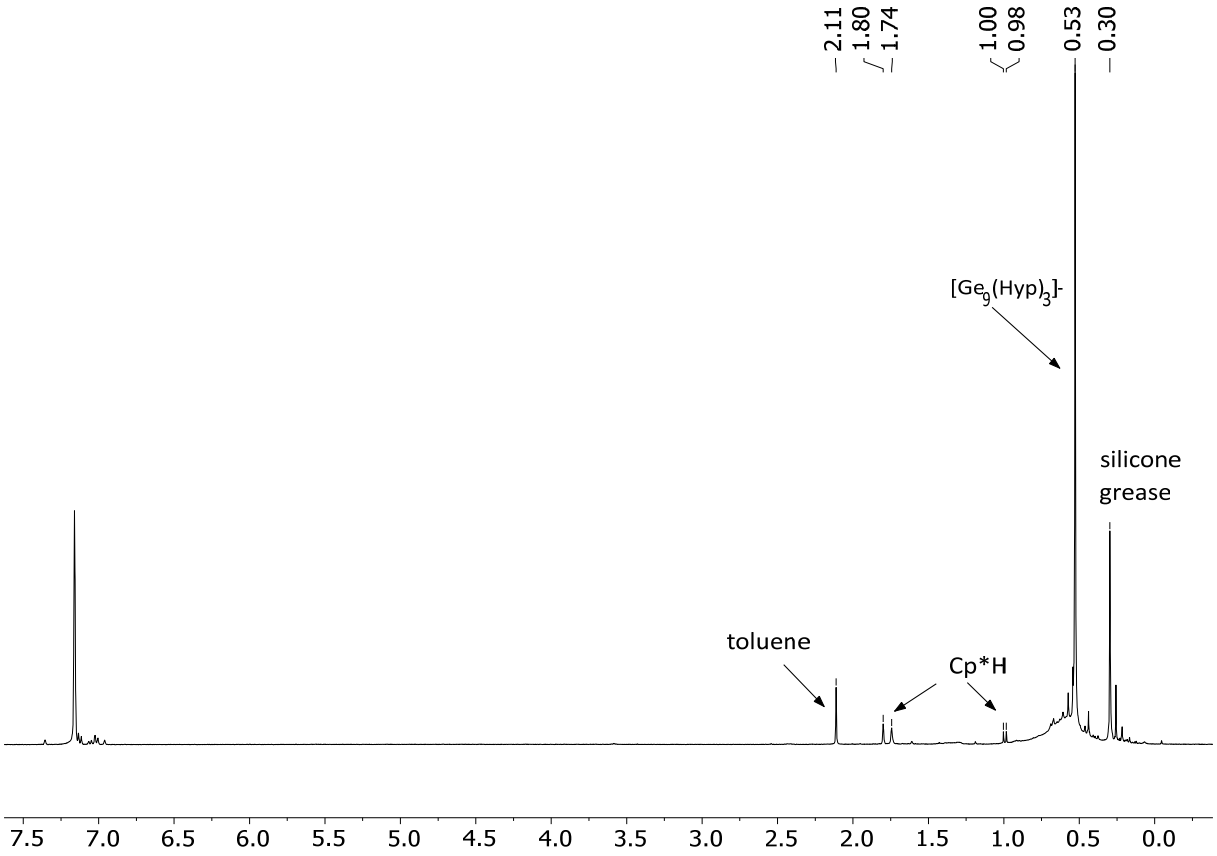

Figure S5: ^{1}H NMR spectrum of the brownish solution from the attempt to dissolve the crystal residue of compound **1** in C_6D_6.

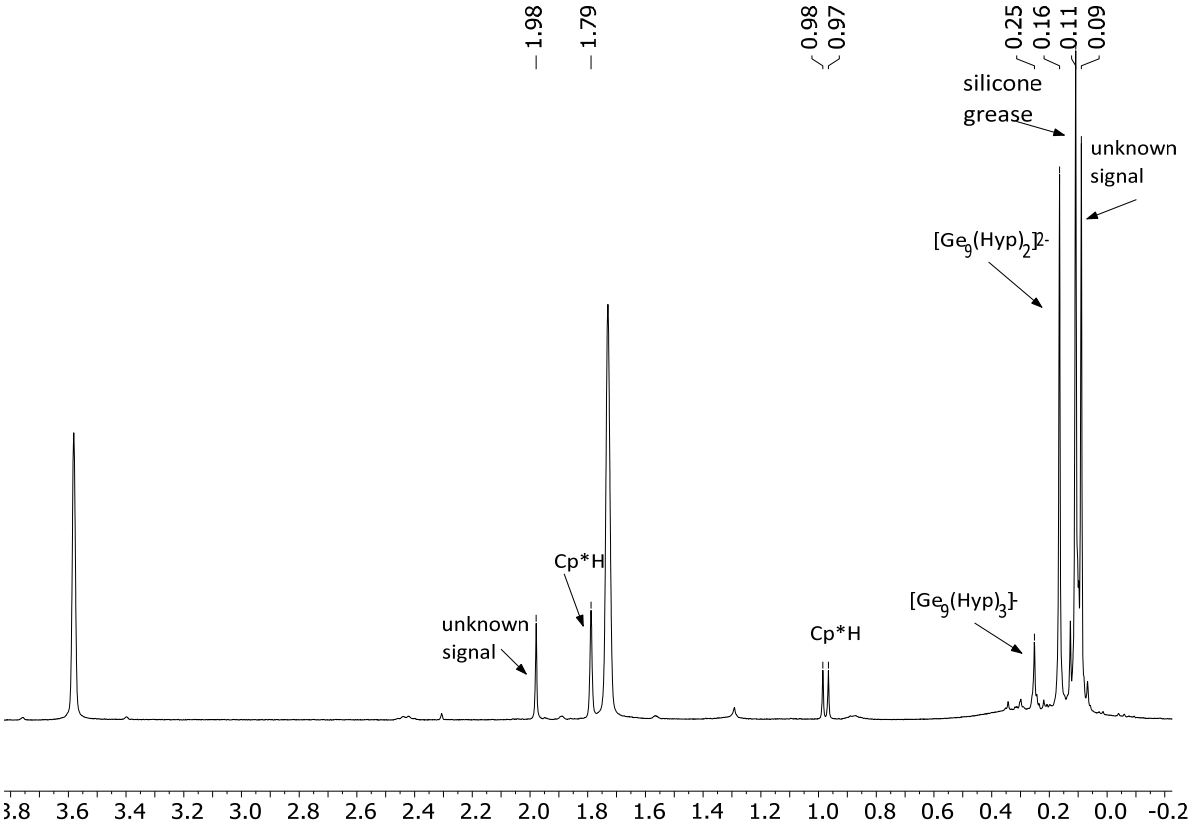

Figure S6: ^{1}H NMR spectrum of the brownish solution from the attempt to dissolve the crystal residue of compound **1** in thf-d_8.

4. ESI-MS Spectra

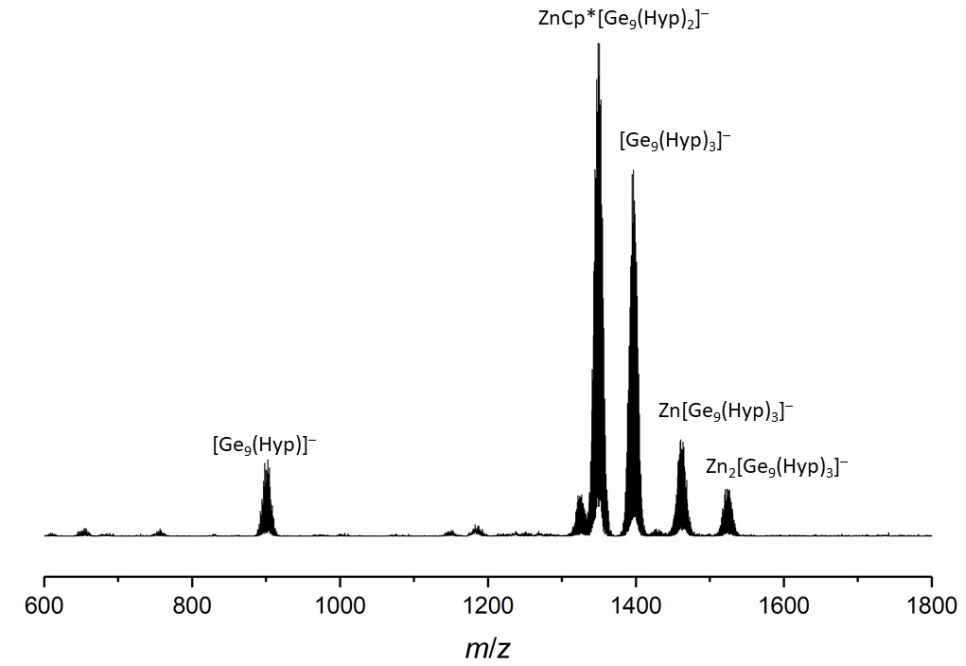

Figure S7: Overview mass spectrum of a thf solution of $ZnCp^*_2$ and $K_2[Ge_9(Hyp)_2]$.

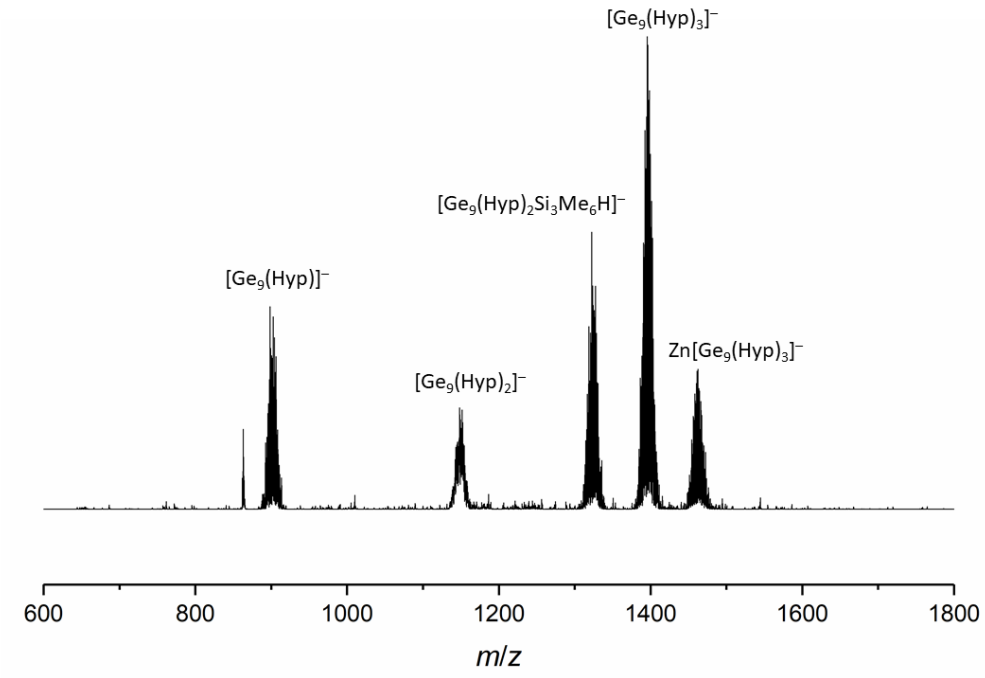

Figure S8: Overview mass spectrum of a toluene solution of $ZnCp^*_2$ and $K_2[Ge_9(Hyp)_2]$.

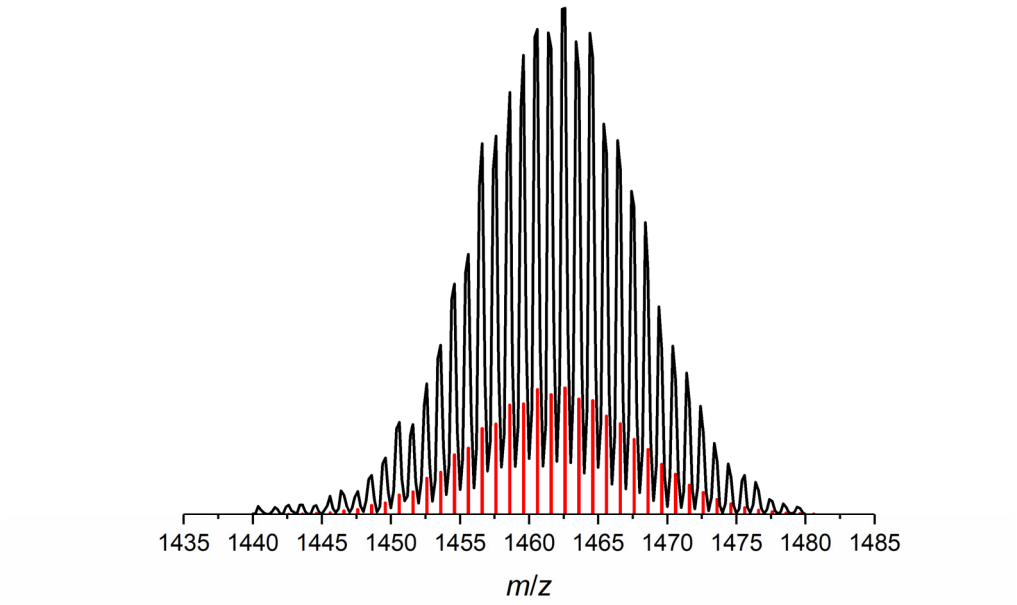

Figure S9: Details of the mass spectrum of $Zn[Ge_9(Hyp)_3]^-$.

5. Selected Bond lengths

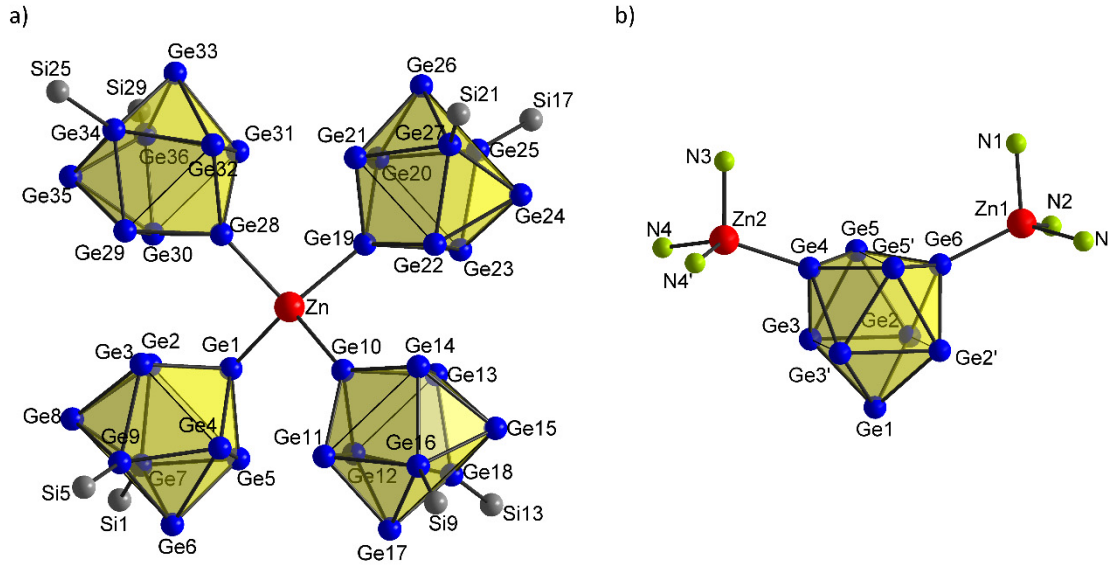

Figure S10: Atom labelling for selected bond lengths in compound **1** (a) and **2** (b), with Ge atoms in blue, Zn atoms in red, Si atoms in grey and N atoms in green. Ge clusters are shown as yellow polyhedra.

Table S2: Selected bond lengths of $K_6[Zn\{\eta^1\text{-}Ge_9(Hyp)_2\}_4] \cdot 10.5$ Tol (**1**).

Cluster 1		Cluster 3	
Ge1 Zn	2.5019(9)	Ge19 Zn	2.5538(10)
Ge1 Ge2	2.5440(10)	Ge19 Ge20	2.5578(10)
Ge1 Ge3	2.5771(11)	Ge19 Ge21	2.5753(9)
Ge1 Ge4	2.5741(10)	Ge19 Ge22	2.5900(10)
Ge1 Ge5	2.5390(9)	Ge19 Ge23	2.5446(11)
Ge2 Ge3	2.7344(10)	Ge20 Ge21	2.7105(10)
Ge2 Ge7	2.5662(9)	Ge20 Ge26	2.6817(9)
Ge2 Ge8	2.6602(11)	Ge20 Ge25	2.5663(11)
Ge3 Ge4	2.9334(10)	Ge21 Ge26	2.6799(10)
Ge3 Ge8	2. 7455(9)	Ge21 Ge27	2.5645(10)
Ge3 Ge9	2.5661(9)	Ge22 Ge23	2.7207(10)
Ge4 Ge5	2.7363(10)	Ge22 Ge24	2.6719(10)
Ge4 Ge6	2.7359(9)	Ge22 Ge27	2.5777(9)
Ge4 Ge9	2.5631(10)	Ge23 Ge24	2.5757(14)
Ge5 Ge6	2.6402(10)	Ge23 Ge25	2.5759(9)
Ge5 Ge7	2.5776(11)	Ge24 Ge25	2.5264(10)
Ge6 Ge7	2.5276(10)	Ge24 Ge27	2.5292(11)
Ge6 Ge9	2.5242(10)	Ge25 Ge26	2.5290(10)
Ge7 Ge8	2.5250(11)	Ge26 Ge27	2.5311(10)
Ge8 Ge9	2.5189(10)		
Ge7 Si1	2.3826(19)	Ge25 Si17	2.377(2)
Ge9 Si5	2.389(2)	Ge27 Si21	2.3889(19)
Cluster 2		Cluster 4	
Ge10 Zn	2.4922(10)	Ge28 Zn	2.5705(10)
Ge10 Ge11	2.5308(10)	Ge28 Ge29	2.5489(11)
Ge10 Ge12	2.5670(9)	Ge28 Ge30	2.5851(10)
Ge10 Ge13	2.5799(10)	Ge28 Ge31	2.5896(10)
Ge10 Ge14	2.5417(9)	Ge28 Ge32	2.5608(9)
Ge11 Ge12	2.7464(10)	Ge29 Ge30	2.7191(10)
Ge11 Ge16	2.5734(10)	Ge29 Ge34	2.5780(10)
Ge11 Ge17	2.6332(10)	Ge29 Ge35	2.6912(11)
Ge12 Ge13	2.9242(9)	Ge30 Ge35	2.6591(11)
Ge12 Ge17	2.7466(10)	Ge30 Ge36	2.5770(10)
Ge12 Ge18	2.5600(10)	Ge31 Ge32	2.7185(10)
Ge13 Ge14	2.7322(10)	Ge31 Ge33	2.6915(10)
Ge13 Ge15	2.7455(10)	Ge31 Ge36	2.5702(10)
Ge13 Ge18	2.5708(10)	Ge32 Ge33	2.7033(10)
Ge14 Ge15	2.6435(11)	Ge32 Ge34	2.5632(11)
Ge14 Ge16	2.5644(10)	Ge33 Ge34	2.5262(11)
Ge15 Ge16	2.5426(11)	Ge33 Ge36	2.5256(9)
Ge15 Ge18	2.5305(9)	Ge34 Ge35	2.5265(9)
Ge16 Ge17	2.5329(9)	Ge35 Ge36	2.5252(11)
Ge17 Ge18	2.5235(10)		
Ge16 Si9	2.378(2)	Ge34 Si25	2.373(2)
Ge18 Si13	2.392(2)	Ge36 Si29	2.389(2)

Table S3: Selected bond lengths of $(NH_3)_3Zn–Ge_9–Zn(NH_3)_3 \cdot 11\ NH_3$ (**2**).

Ge1 Ge2	2.5979(17)	Ge4 Zn2	2.441(2)
Ge1 Ge3	2.5973(17)	Ge6 Zn1	2.423(2)
Ge2 Ge3	2.6794(16)	Zn1 N1	2.104(11)
Ge2 Ge5	2.6387(17)	Zn1 N2	2.058(8)
Ge2 Ge6	2.5793(17)	Zn2 N3	2.061(12)
Ge3 Ge4	2.5783(18)		
Ge3 Ge5	2.6305(17)		
Ge4 Ge3	2.5782(18)		
Ge4 Ge5	2.5497(15)		
Ge5 Ge6	2.5481(15)		

6. Mixed Supporting Information of Compound **2**

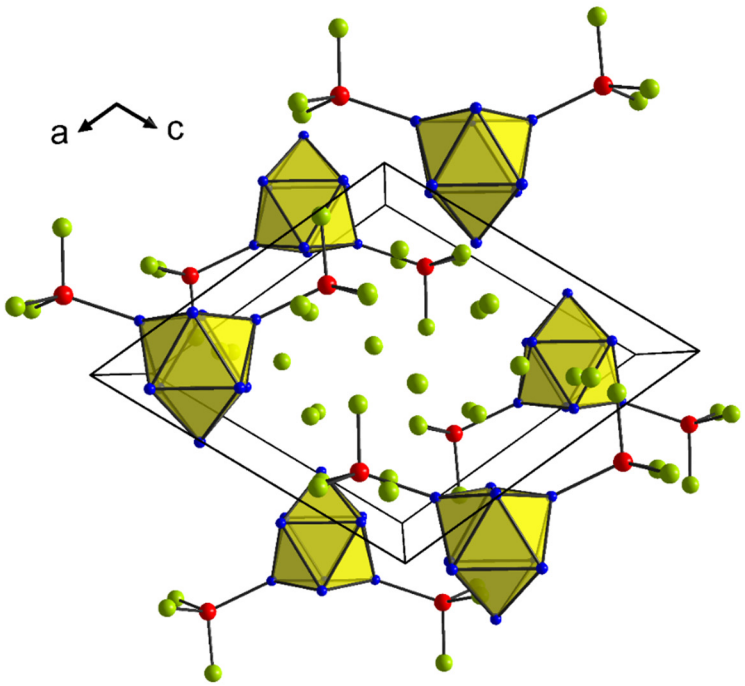

Figure S11: Extended unit cell of compound **2**. Ge atoms in blue, Zn atoms in red, N atoms in green. Ge clusters are shown as yellow polyhedra.

Table S4: Products from reactions of K_4Ge_9 with $Zn_2[HC(Ph_2P{=}NPh)_2]_2$ in liquid ammonia, with different applied reactant ratios. m = main product, b = by-product.[9, 10]

K_4Ge_9:$Zn_2[HC(Ph_2P{=}NPh)_2]_2$			
1:4	1:2	1:1	2:1
$(NH_3)_3Zn–Ge_9–Zn(NH_3)_3$ (m) $[Ge_9–Zn–Ge_9]^{6-}$ (b) $[Ge_9Zn–ZnGe_9]^{6-}$ (b)	$[Ge_9–Zn–Zn–Ge_9]^{6-}$ (m) $[Ge_9Zn–Ge_9–ZnGe_9]^{8-}$ (b)	$[Ge_9Zn–ZnGe_9]^{6-}$ (m) $[Ge_9Zn–Ge_9–ZnGe_9]^{8-}$ (m)	$[Ge_9–Zn–Ge_9]^{6-}$ (m) $[Ge_9]^{4-/3-}$ (b)
Ge_9 Clusters in products Zn atoms in products			

References

1. O. Kysliak and A. Schnepf, *Dalton Trans.*, 2016, **45**, 2404-2408.
2. R. Blom, J. Boersma, P. H. M. Budzelaar, B. Fischer, A. Haaland, H. V. Volden and J. Weidlein, *Acta. Chem. Scand.*, 1986, **40**, 113 - 120.
3. S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese and S. Harder, *Chem. Commun.*, 2010, **46**, 7757-7759.
4. MestreNova, Mestrelab Research, Version 12.0.2-20910, 2018.
5. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
6. A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.
7. K. Brandenburg, Crystal Impact GbR, Bonn, Diamond Version 3.2k.
8. T. F. Fässler, *Coord. Chem. Rev.*, 2001, **215**, 347-377.
9. K. Mayer, L. A. Jantke, S. Schulz and T. F. Fässler, *Angew. Chem. Int. Ed.*, 2017, **56**, 2350-2355.
10. M. M. Bentlohner, L. A. Jantke, T. Henneberger, C. Fischer, K. Mayer, W. Klein and T. F. Fässler, *Chem. Eur. J.*, 2016, **22**, 13946-13952.