Supporting Information for:

"Water Compatibility and Organic Transformations of Organo-Zintl Deltahedral Clusters"

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Experimental

General Methods. All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen. 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Acros, 99%) was dried over sodium in ether, recrystallized, and further purified by pumping under vacuum. K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements (K: 99+%, Strem; Ge: 99.999%, Alfa Aesar) at 950 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampoules according to previously reported synthetic procedures.[1] 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane, Acros, 98%), $H\text{-}C{\equiv}C\text{-}CH_2NH_2$ (propargylamine, Acros, 99%), and FcCHO (ferrocene carboxaldehyde, Aldrich, 98%) were used as received. $[K\text{-crown}]_2[Ge_9\text{-}(CH{=}CH_2)_2]$, $[K\text{-crypt}]_2[Ge_9\text{-}(CH_2\text{-}CH(CH_2)_2)_2]$, and $[K\text{-crypt}]_2[Ge_9\text{-}(Sn(Me)_3)_2]$ were synthesized according to previously reported procedures.[2-4]

CAUTION!!!: Propargylamine is highly toxic! Inhalation, ingestion, and contact with the skin must be strictly avoided. All personal protection steps recommended in the MSDS should be followed.

Mass Spectrometry. Electrospray mass spectra were recorded from ethylenediamine, DMF, or pyridine solutions (0.03-0.4 M) on a Micromass Quattro-LC triple quadropole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 2.8 kV capillary voltage, and a 35 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 20 μL/min. Spectra were taken in the negative-ion mode.

NMR Spectroscopy. Deuterated pyridine (Cambridge Isotope Labs, 99.9%) was stored over molecular sieves. ^{1}H NMR spectra were recorded on a Varian Unity*Plus* 300 MHz spectrometer, locked on the deuterium signal of the deuterated pyridine, and referenced against the farthest downfield peak of the solvent residuals.

Synthesis of [K-crypt]$_2$[Ge$_9$-(CH=CH-CH$_2$NH$_2$)$_2$]. K_4Ge_9 (0.090 g, 0.11 mmol) was dissolved in 1.5 mL of ethylenediamine (red solution) in a test tube inside the glovebox. Propargylamine (0.034 g, 0.62 mmol) was added dropwise slowly and the reaction mixture was stirred for four hours. The solution was centrifuged, filtered, and 2,2,2-krypt added (0.149 g, 0.36 mmol). The solution was layered with toluene and left undisturbed for a week. After diffusion large red-orange crystals formed on the side of the test tube: triclinic, P-1, a = 10.8104(2), b = 12.8700(2), and c = 22.1394(4) Å, α = 83.502(1), β = 88.186(1), and γ = 86.678(1)°, V = 3054.34(4) Å^3, Z = 1. The identical cluster anion can be synthesized with 18-crown-6-sequested potassium cations by substitution 0.126 g 18-crown-6 in place of 2,2,2-crypt. The latter complex did not yield crystals suitable for X-ray diffraction. ^{1}H NMR (d_5-pyridine): δ 1.45 (t, 6.7 Hz $[Ge_9\text{-}(CH{=}CH\text{-}CH_2N\mathit{H}_2)_2]^{2-}$), 3.50 (s, 18-crown-6), 4.07 (dt, 6.7 Hz, 6.7 Hz $[Ge_9\text{-}(CH{=}CH\text{-}C\mathit{H}_2NH_2)_2]^{2-}$), 6.54 (dt, 11.5 Hz, 6.7 Hz $[Ge_9\text{-}(CH{=}C\mathit{H}\text{-}CH_2NH_2)_2]^{2-}$), 7.05 (d, 11.5 Hz, $[Ge_9\text{-}(C\mathit{H}{=}CH\text{-}CH_2NH_2)_2]^{2-}$); ^{13}C NMR ($d_5$-pyridine): δ 41.7 ($[Ge_9\text{-}(CH{=}CH\text{-}\mathit{C}H_2NH_2)_2]^{2-}$), 138.2 ($[Ge_9\text{-}(CH{=}\mathit{C}H\text{-}CH_2NH_2)_2]^{2-}$), 144.1 ($[Ge_9\text{-}(\mathit{C}H{=}CH\text{-}CH_2NH_2)_2]^{2-}$). ES-MS (pyridine, negative-ion mode): m/z = 765 $[Ge_9\text{-}(CH{=}CH\text{-}CH_2NH_2)_2]^-$, 804 $\{(K^+)[Ge_9\text{-}(CH{=}CH\text{-}CH_2NH_2)_2]^{2-}\}^-$.

Synthesis of [K-(18-crown-6)]$_2$[Ge$_9$-(CH=CH-CH$_2$-N=CH-Fc)$_2$]. [K-*(18-crown-6)*]$_2$[Ge$_9$-(CH=CH-CH$_2$NH$_2$)$_2$] (0.104 g, 0.074 mmol) was dissolved in 3 mL of pyridine (orange solution) in a test tube inside the glovebox. Fc-C(=O)H (0.063 g, 0.29 mmol) was added and the reaction mixture was stirred for one hour before taking the sample for mass spectrometry. ES-MS (pyridine, negative-ion mode): m/z = 1002 $\{[K^+][Ge_9\text{-}(CH{=}CH\text{-}CH_2\text{-}N{=}CH\text{-}Fc)]^{2-}\}^-$, 1157 $[Ge_9\text{-}(CH{=}CH\text{-}CH_2\text{-}N{=}CH\text{-}Fc)_2]^-$, 1264 $\{[K^+\text{-crown}][Ge_9\text{-}(CH{=}CH\text{-}CH_2\text{-}N{=}CH\text{-}Fc)]^{2-}\}^-$.

Substrate Compatibility Studies. [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$] was synthesized according to previously reported procedures. Approximately 0.1 mmol of was dissolved in 0.75 mL of d_5-pyridine and placed in a NMR tube for each sample. An equimolar amount of ^{t}BuCl and FcCHO were added to each sample of cluster. A ^{1}H NMR spectrum was taken. No precipitation or color change was observed in any case. No changes in the NMR spectra were observed either, except the presence of the new peaks corresponding to the organic substrate.

Water Stability Studies. [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$], [K-crypt]$_2$[Ge$_9$-(CH$_2$-CH(CH$_2$)$_2$)$_2$], and [K-crypt]$_2$[Ge$_9$-(Sn(Me)$_3$)$_2$] were synthesized according to previously reported procedures. Approximately 0.1 mmol of each was dissolved in 0.75 mL of d_5-pyridine and sealed in a septum-equipped, screw-capped NMR tube. A ^{1}H NMR spectrum was taken of each sample prior to water addition to confirm purity and spectral properties of each specific sample. Deionized water (20 μL) was then injected into the NMR tube and the sample shook. No precipitation or color change was observed in any case. No changes in the NMR spectra were observed either, except the presence of the new, large, broad water peak. The pyridine solution was then used to run an electrospray mass spectrometry experiment to confirm that the clusters were intact and unchanged.

Crystallographic Structure Determination. Single-crystal X-ray diffraction data of [K-crypt]$_2$[Ge$_9$-(CH=CH-CH$_2$NH$_2$)$_2$] was collected on a Bruker X8 APEX-II diffractometer equipped with a CCD area detector at 100 K using graphite-monochromated Mo Kα radiation. The crystal was selected under Paratone-N oil, mounted on the fiber, and positioned in the cold stream of the diffractometer. The structure was solved by direct methods and refined on $F2$ using the SHELXTL V6.21 package.[5] Crystal data: [K-crypt]$_2$[Ge$_9$-(CH=CH-CH$_2$NH$_2$)$_2$] - triclinic, P-1, a = 10.8104, b = 12.87, and c = 22.1394 Å, α = 83.5, β = 88.19, and γ = 86.68, V = 3054.34 Å^3, Z = 1, R1/wR2 = 3.4/7.5 % for the observed data ($I \geq 2\sigma_I$), R1/wR2 = 4.7/10.4 % for all data. CCDC 873396 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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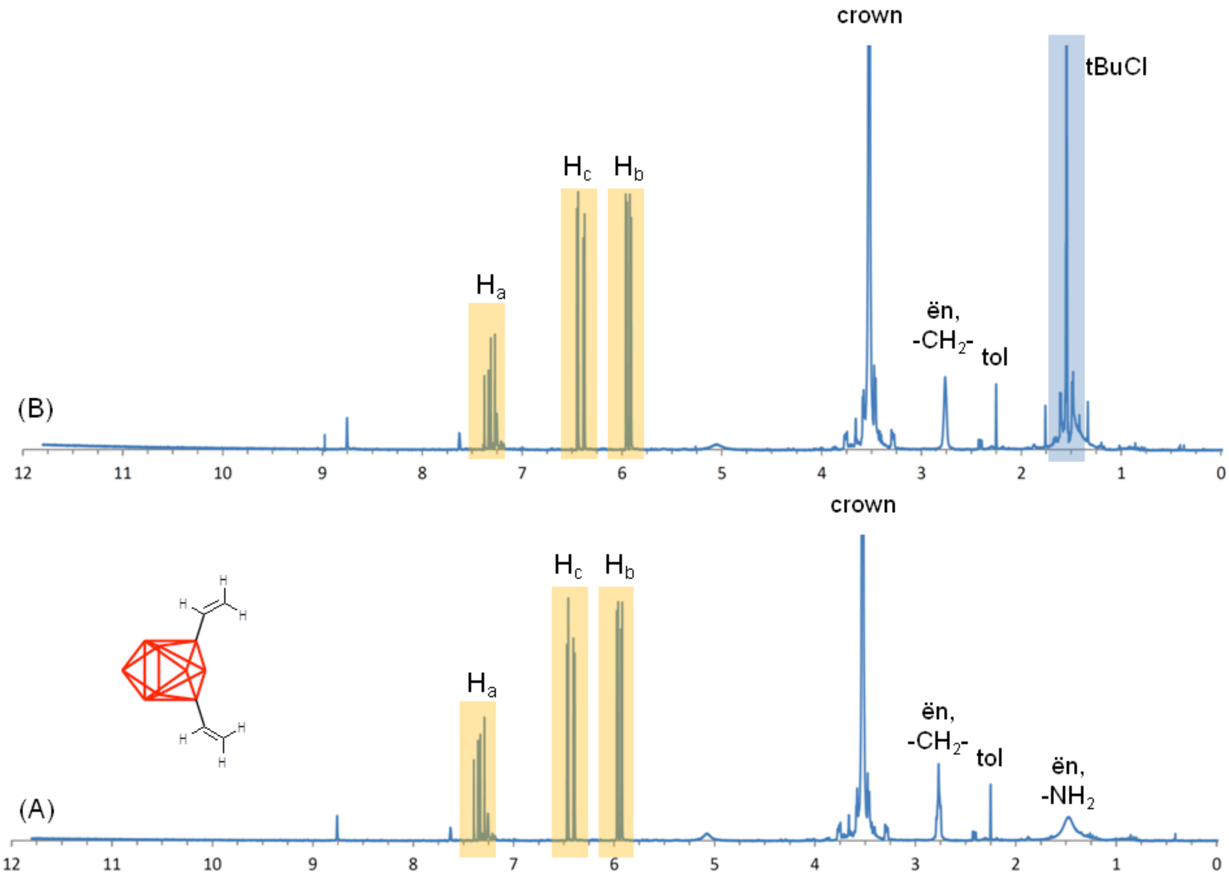

Figure S1: ^{1}H NMR of (**A**) [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$] and (**B**) [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$] + ^{t}BuCl in d_5-pyridine. The three different vinyl protons H_a, H_b, and H_c are clearly visible in both spectra.

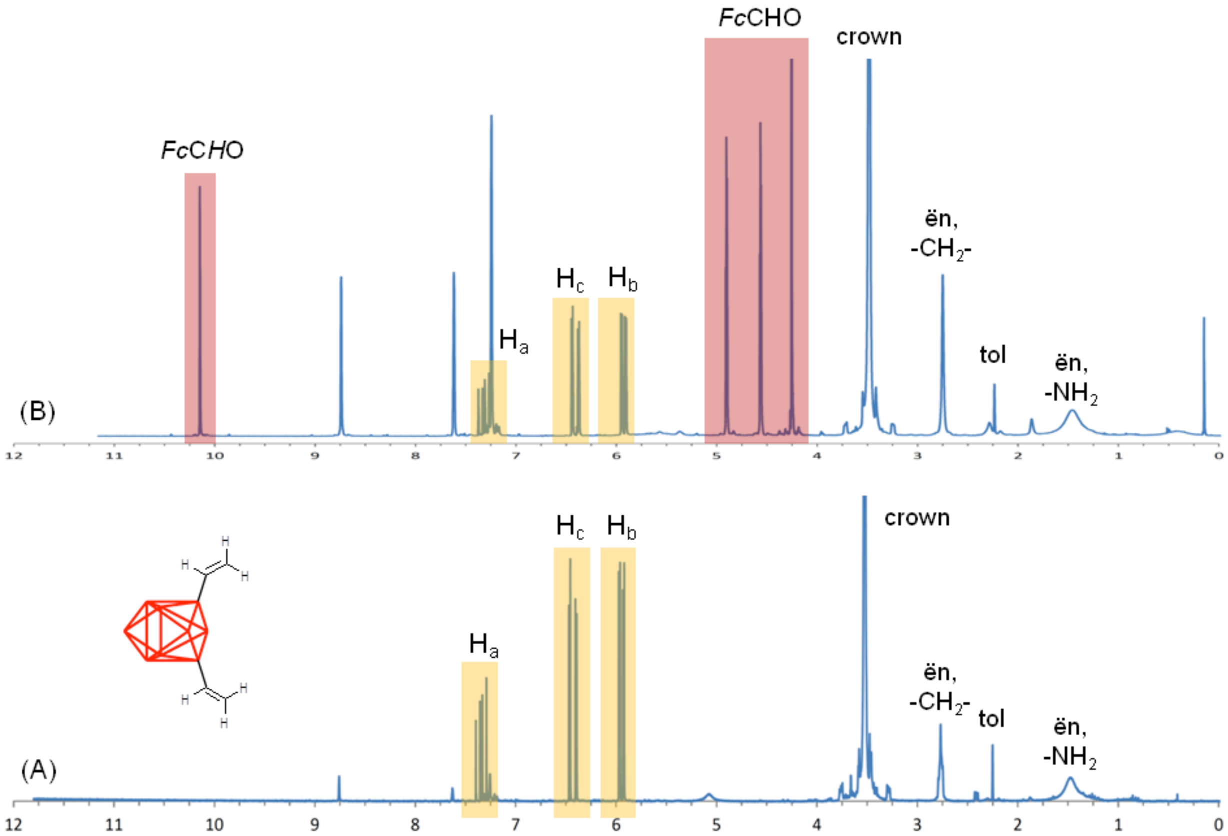

Figure S2: ^{1}H NMR of (**A**) [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$] and (**B**) [K-crown]$_2$[Ge$_9$-(CH=CH$_2$)$_2$] + FcCHO in d_5-pyridine. The three different vinyl protons H_a, H_b, and H_c are clearly visible in both spectra.

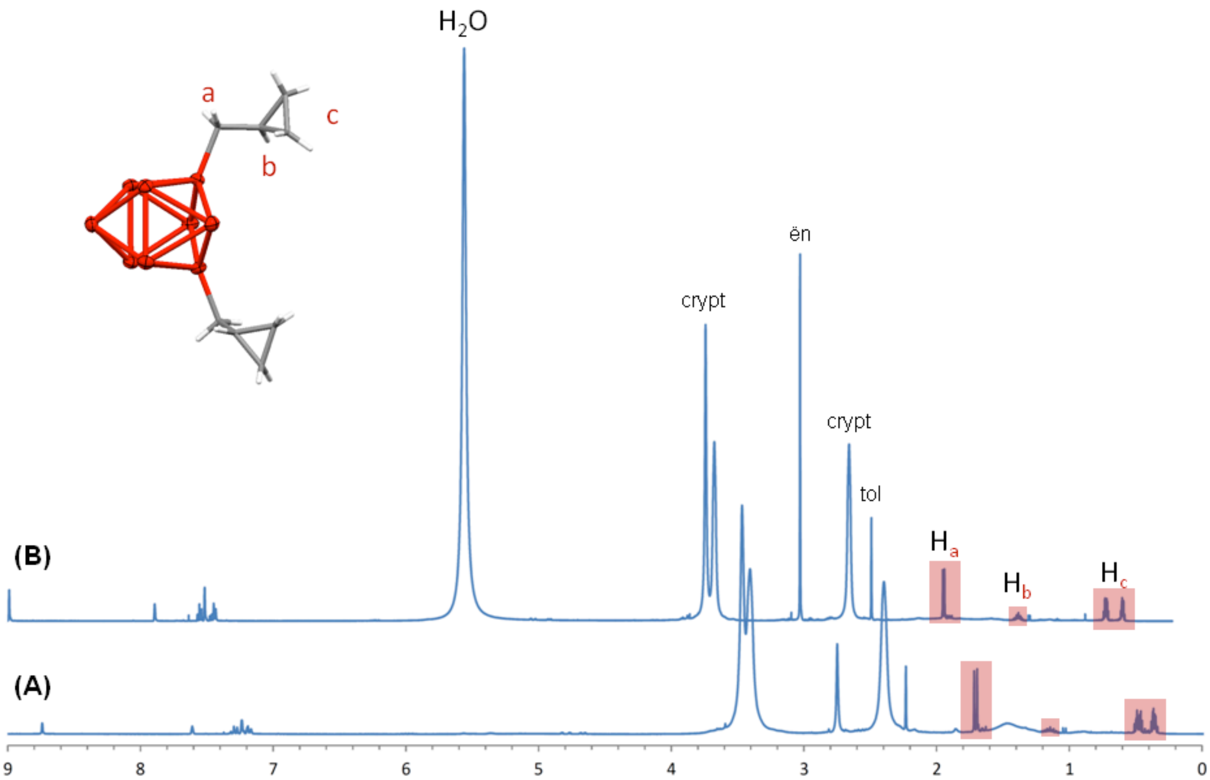

Figure S3: ^{1}H NMR of [K-crypt]$_2$[Ge$_9$-(CH$_2$CH(CH$_2$)$_2$)$_2$] in *d*$_5$-pyridine before (A) and after (B) the addition of H_2O. The three different protons of the organic substituent are clearly visible in both spectra.

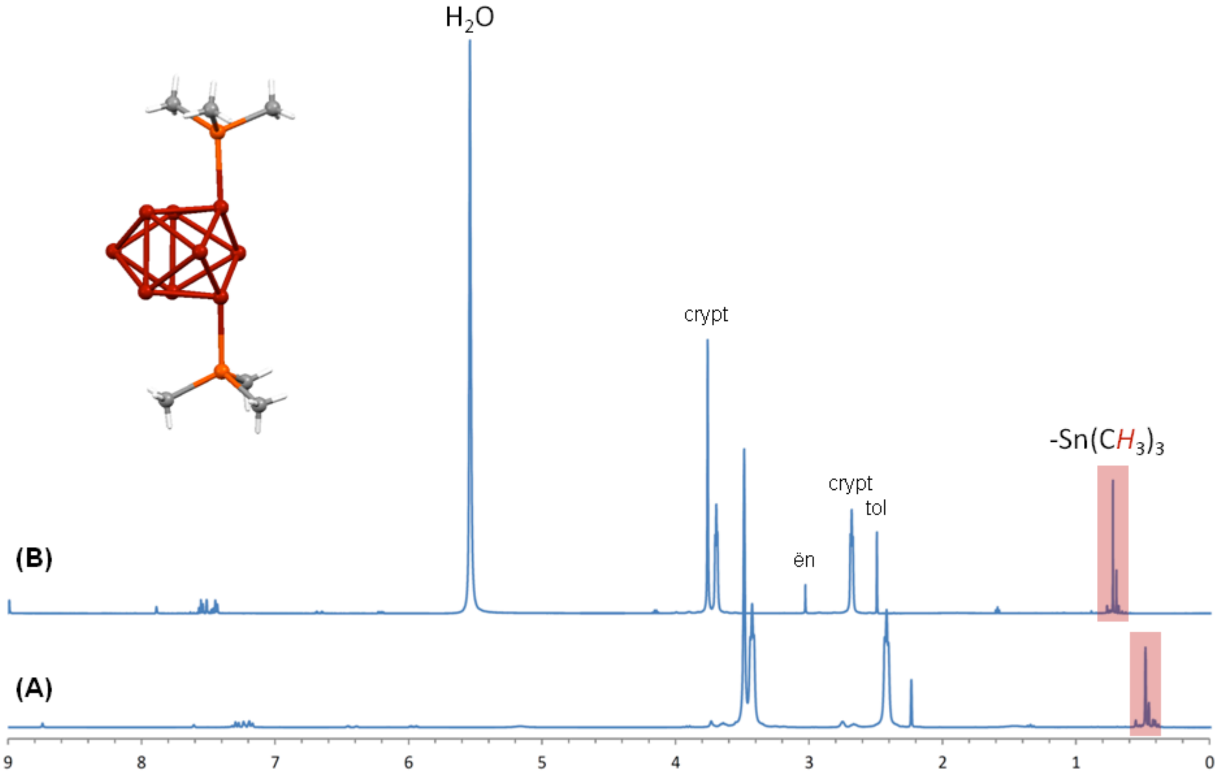

Figure S4: ^{1}H NMR of $[K\text{-crypt}]_2[Ge_9\text{-}(Sn(CH_3)_3)_2]$ in *d*$_5$-pyridine before (A) and after (B) the addition of H_2O. The methyl protons are clearly visible in both spectra.

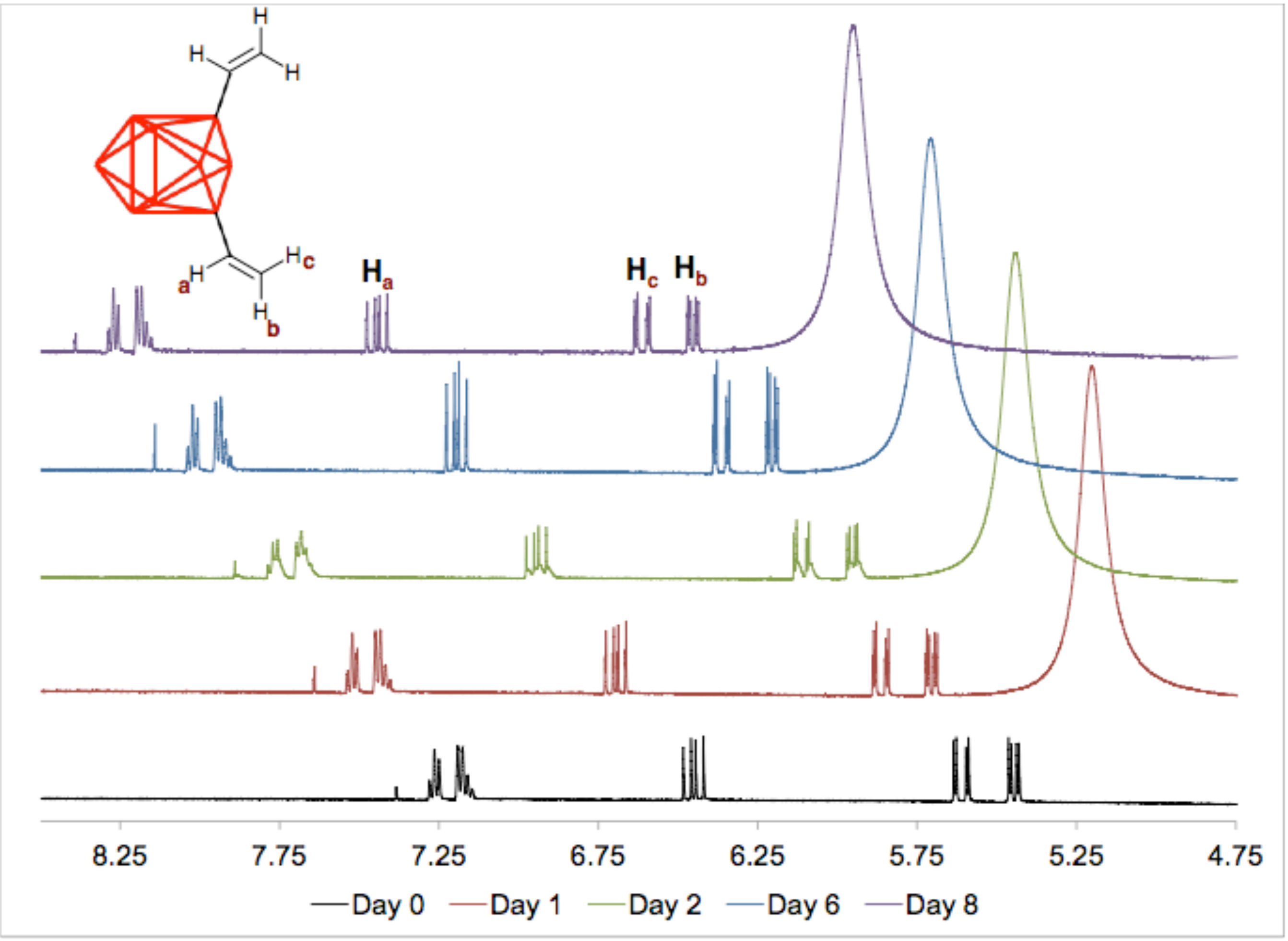

Figure S5: A sequence of ^{1}H NMR spectra of $[Ge_9\text{-}(CH{=}CH_2)_2]^{2-}$ with water over 8 days showing the same unchanged signals from the protons of the vinyl groups attached to the Ge_9-cluster.

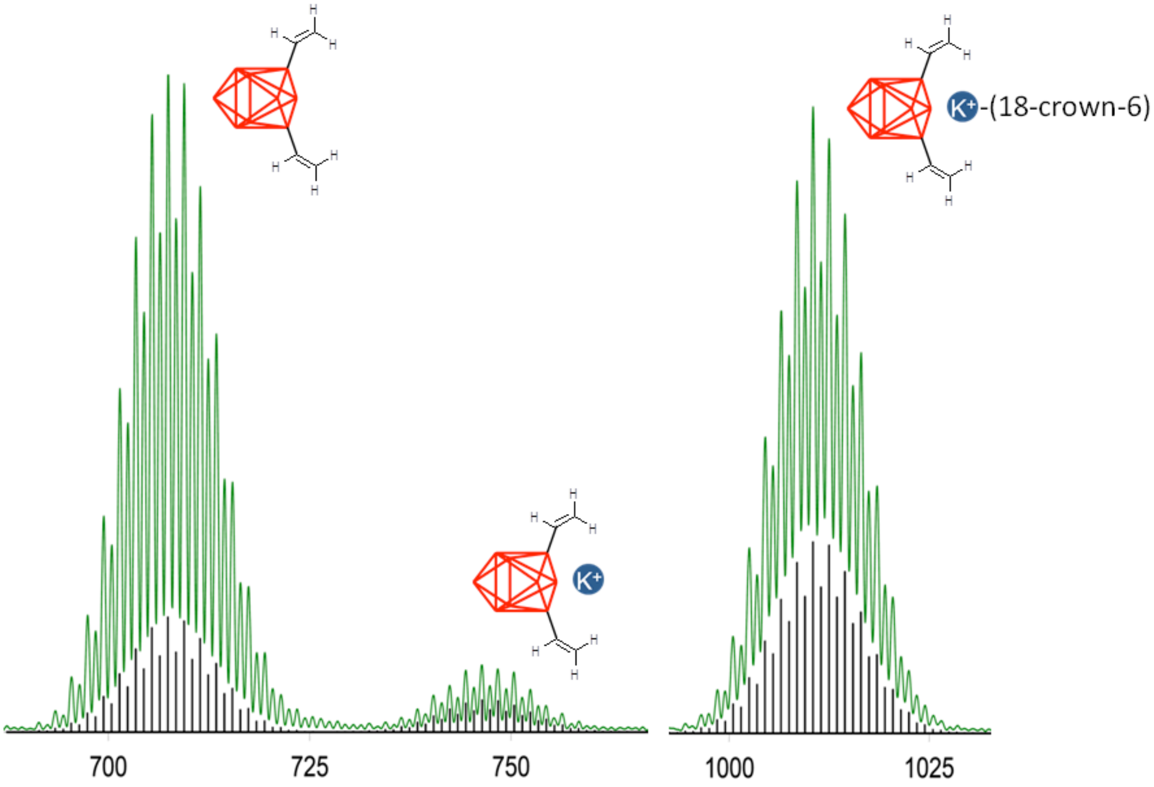

Figure S6: Representative electrospray mass spectra of $[K\text{-}(18\text{-crown-}6)]_2[Ge_9\text{-}(CH{=}CH_2)_2]$ in DMF after addition of water (green = experimental data; black bars = theoretical) showing the di-substituted clusters unchanged.

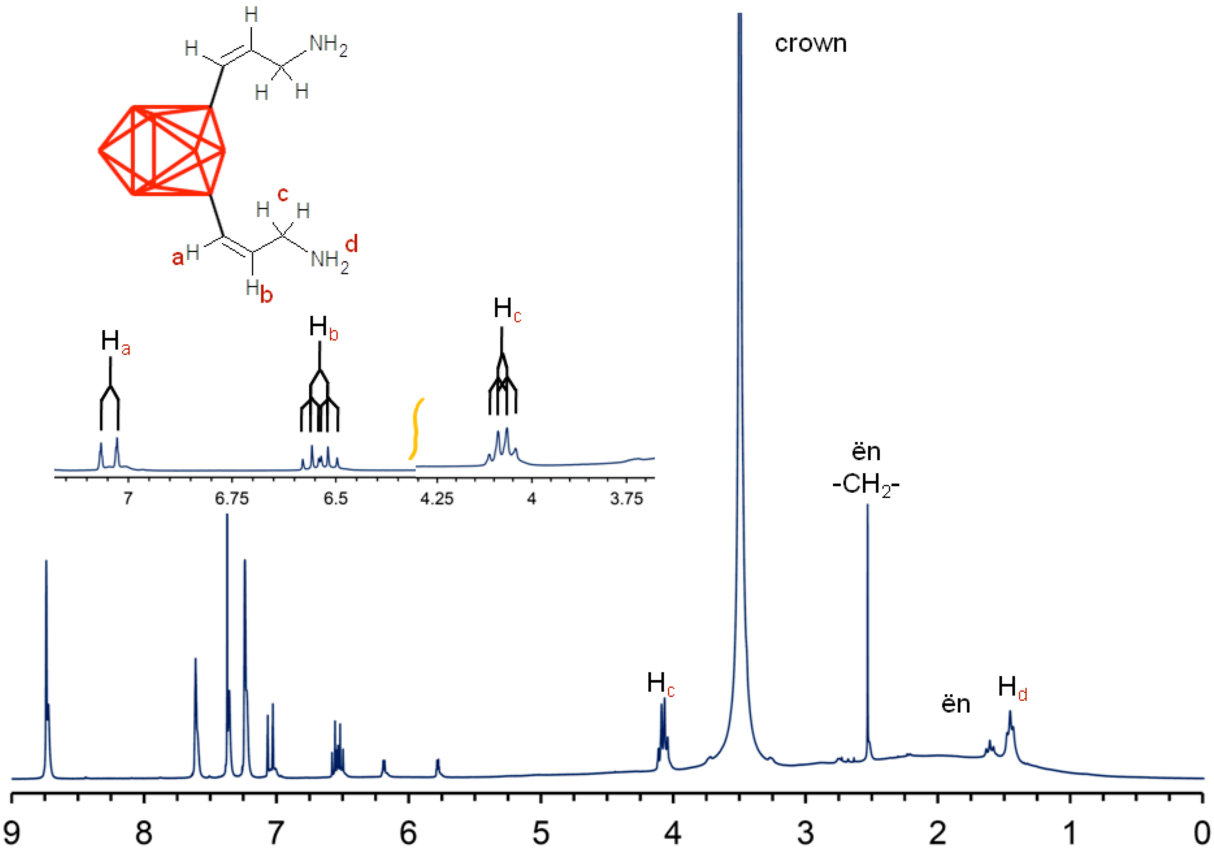

Figure S7: ^{1}H NMR of $[K\text{-}(18\text{-crown-}6)]_2[Ge_9\text{-}(CH{=}CH\text{-}CH_2NH_2)_2]$ in d_5-pyridine.

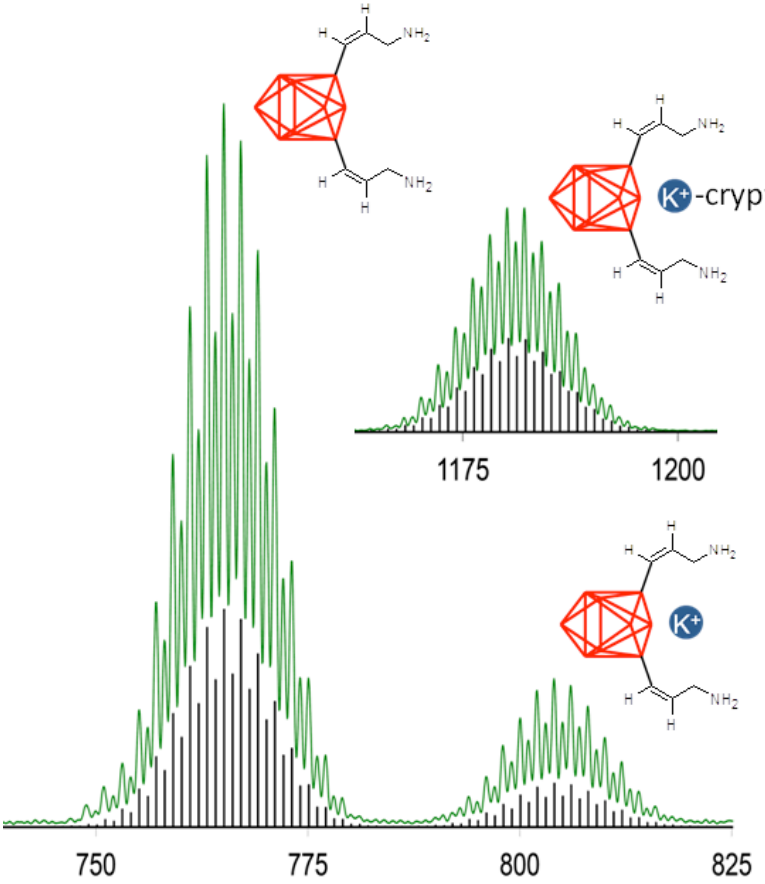

Figure S8: Electrospray mass spectra of $[\text{K-crypt}]_2[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2)_2]$ (green = experimental data; black bars = theoretical).