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Electronic Supplementary Information

Cluster expansion and vertex substitution pathways in nickel germanide Zintl clusters

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Contents

1. Experimental Details

1.1. Materials and General Procedures

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). *n*-pentane (pent; Sigma-Aldrich, HPLC grade, ≥99%), *n*-hexane (hex; Sigma-Aldrich, HPLC grade, ≥97%), benzene (Rathburn, HPLC grade, 99.8%) and toluene (Sigma-Aldrich, HPLC grade, 99.8%), were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; Sigma-Aldrich, HPLC grade, ≥99.9%,) was distilled over sodium metal/benzophenone. C_6D_6 (Sigma-Aldrich, 99.5%) and d_8-THF (Sigma-Aldrich, 99.5%) were distilled over sodium metal/benzophenone. All dry solvents were stored under argon in gas-tight ampoules over activated 3 Å molecular sieves. K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements (potassium, 99.95%, Alfa Aesar; germanium powder -100 mesh, 99.999%, Alfa Aesar) at 900 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampules according to previously reported synthetic procedures. $K\{Ge_9[Si(SiMe_3)_3]_3\}$ ($K[Ge_9(Hyp_3)]$) was prepared according to literature procedures.[1] Chlorotris(trimethylsilyl)silane (HypCl; Insight Biotechnology Ltd, 97%), $Ni(COD)_2$ (Alfa Aesar), $NiCp_2$ (Alfa Aesar), $CpNi(PPh_3)Cl$ (Santa Cruz Biotechnology) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Merck) were used as received without further purification.

1.2. NMR spectroscopy

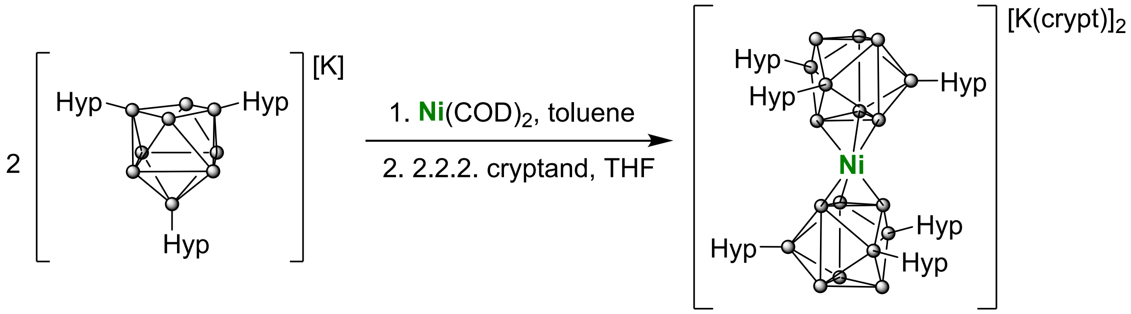
NMR samples were prepared inside an inert atmosphere glovebox in NMR tubes fitted with a gas-tight valve. ^1H NMR spectra were recorded at either 499.9 MHz or 400.1 MHz on a Bruker AVIII 500 or a Bruker AVIII 400 NMR spectrometer, respectively. $^{13}C\{^1H\}$NMR spectra were recorded at either 125.8 MHz or 100.6 MHz on a Bruker AVII 500 fitted with a cryoprobe or a Bruker AVIII 400 NMR spectrometer, respectively. ^{1}H and ^{13}C{^{1}H} NMR spectra are reported relative to TMS and referenced to the most downfield residual solvent resonance.

1.3. Elemental analyses

Elemental analyses were either carried out by Elemental Microanalyses Ltd. (Devon, U. K.). Samples (approx. 10 mg) were submitted in sealed Pyrex ampoules.

2. Synthetic Procedures

2.1. [K(2,2,2-crypt)]$_2$[Ni{Ge$_9$(Hyp)$_3$}$_2$] ([K(2,2,2-crypt)]$_2$[**1**])



K[Ge$_9$Hyp$_3$] (100 mg, 0.07 mmol) and toluene (~3 ml) were added to an ampoule and stirred until an orange solution formed. Ni(COD)$_2$ (10 mg, 0.07 mmol) was then added and the orange solution turned green within 30 minutes. The mixture was stirred for 14 hours with a glass coated stir bar to yield a dark green suspension. A light green-brown solution was filtered off and the black-green precipitate was washed with toluene (2 ml). NOTE: Washing with more toluene results in further dissolution of the product.

The solid was then dissolved in THF (5 ml) to form a dark blue-green solution and dried *in vacuo* at 0.1 mbar over the course of 20 minutes to produce a dark green pyrophoric powder [K(THF)$_n$]$_2$[**1**]. NOTE: if dried at a lower pressure, for longer, or with heating, the formation of an orange powder (K[Ge$_9$(Hyp)$_3$]) occurs. As can be seen in the NMR data, even after careful drying, there is ~3% $[K(THF)_n][Ge_9(Hyp)_3]$ present. Standing in THF also results in partial decomposition to $[K(THF)_n][Ge_9(Hyp)_3]$, for example, standing for 3 days results in a greener solution and black precipitate, analysed as a 70 : 30 ratio of $[K(THF)_n]_2$[**1**] : $[K(THF)_n][Ge_9(Hyp)_3]$ by ^{1}H-NMR spectroscopy. ^{1}H NMR (d_8-THF, 298 K, 400.17 MHz): δ (ppm): 0.37 (s, 162H; CH_3). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 125.81 MHz): δ (ppm): 4.25 (CH_3). ^{29}Si NMR (d_8-THF, 298 K, 79.5 MHz): δ (ppm): –107.10, –10.48.

To obtain crystals suitable for single crystal X-ray crystallography, the powder was mixed with 2,2,2-cryptand (30 mg, 0.08 mmol), dissolved in a minimum amount of THF and left to stand at –40 °C for 1 week, producing green-blue crystals of $[K(2,2,2\text{-crypt})]_2$[**1**]. Elemental analysis calcd. For $C_{90}H_{234}Ge_{18}K_2N_4Ni_1O_{12}Si_{24}$ ($M = 3683.29\ g{\cdot}mol^{-1}$): C 29.35, H 6.40, N 1.52 Found: C 28.61, H 5.96, N 1.78. ^{1}H NMR (d_8-THF, 298 K, 400.17 MHz): δ (ppm): 0.38 (s, 162H; CH_3), 2.58 (t, 24H; CH_2), 3.57 (t, 24H; CH_2), 3.61 (s, 24H; CH_2). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 125.81 MHz): δ (ppm): 4.30 (CH_3), 54.96 (CH_2), 68.64 (CH_2), 71.47 (CH_2). ^{29}Si NMR (d_8-THF, 298 K, 79.5 MHz): δ (ppm): –107.10, –10.48.

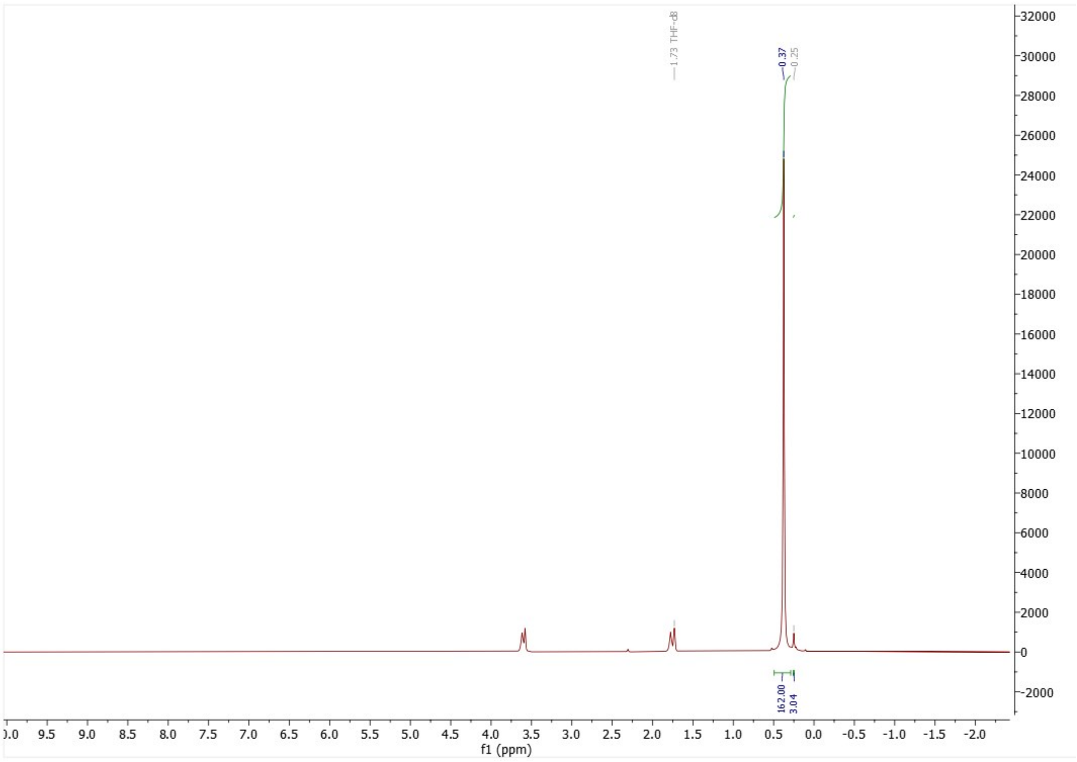


Figure S1. ^{1}H NMR (d$_8$-THF, 298 K, 400 MHz) spectrum of [K(THF)$_n$]$_2$[**1**].

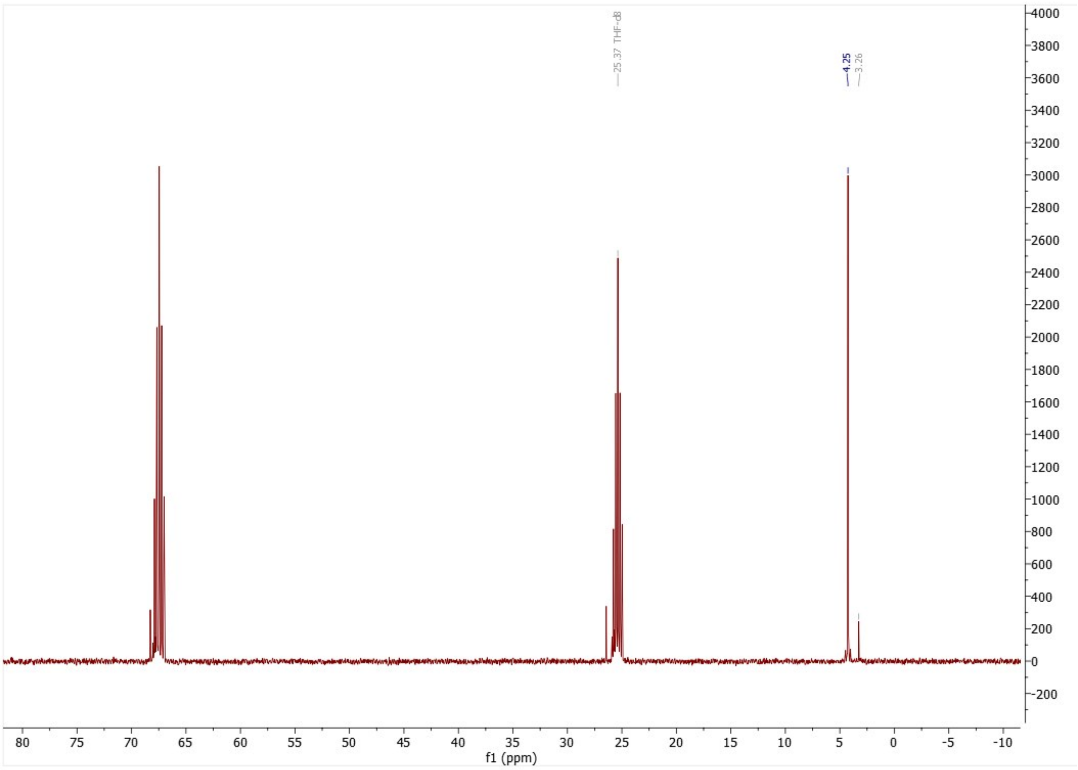


Figure S2. ^{13}C{^{1}H} NMR (d$_8$-THF, 298 K, 125.81 MHz) spectrum of [K(THF)$_n$]$_2$[**1**].

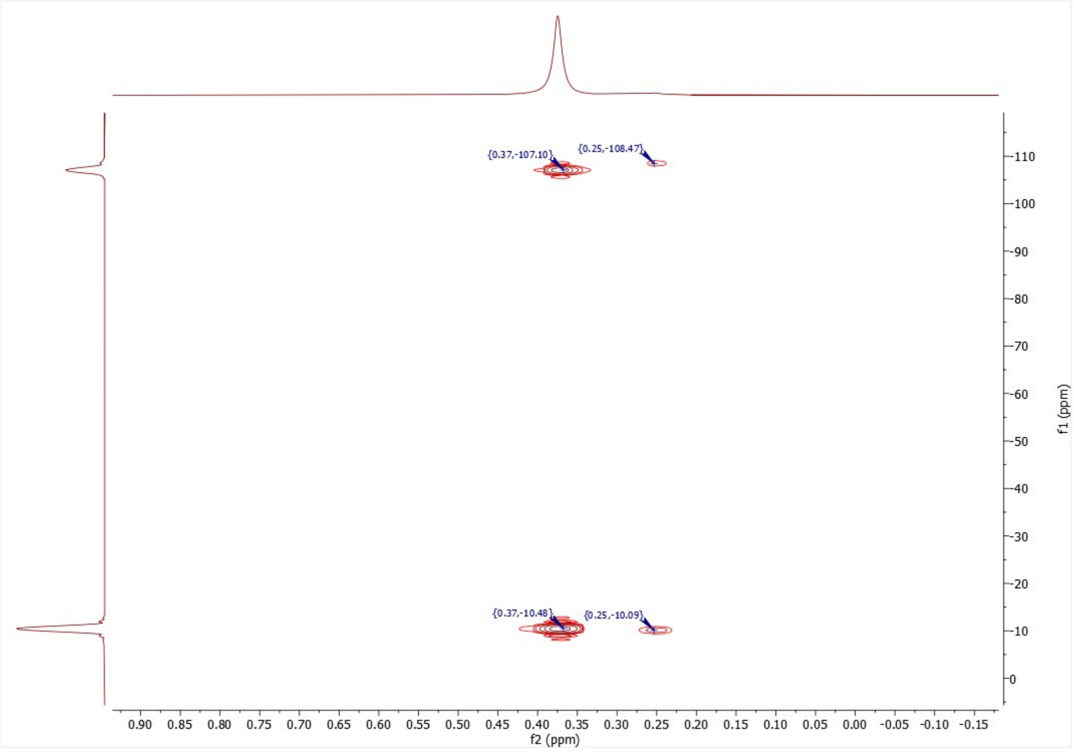


Figure S3. $^{1}H/^{29}Si$ HMBC NMR (d_8-THF, 298 K, 79.5 MHz) spectrum of $[K(THF)_n]_2[\mathbf{1}]$.

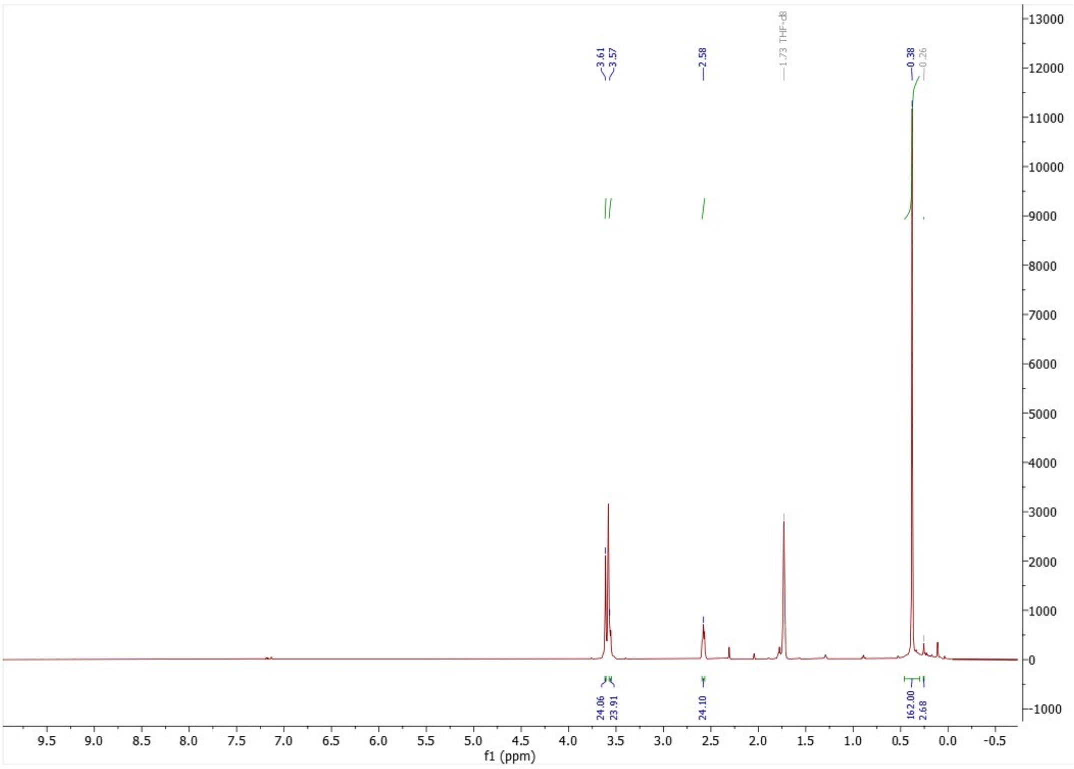


Figure S4. ^{1}H NMR (d_8-THF, 298 K, 400 MHz) spectrum of $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]$.

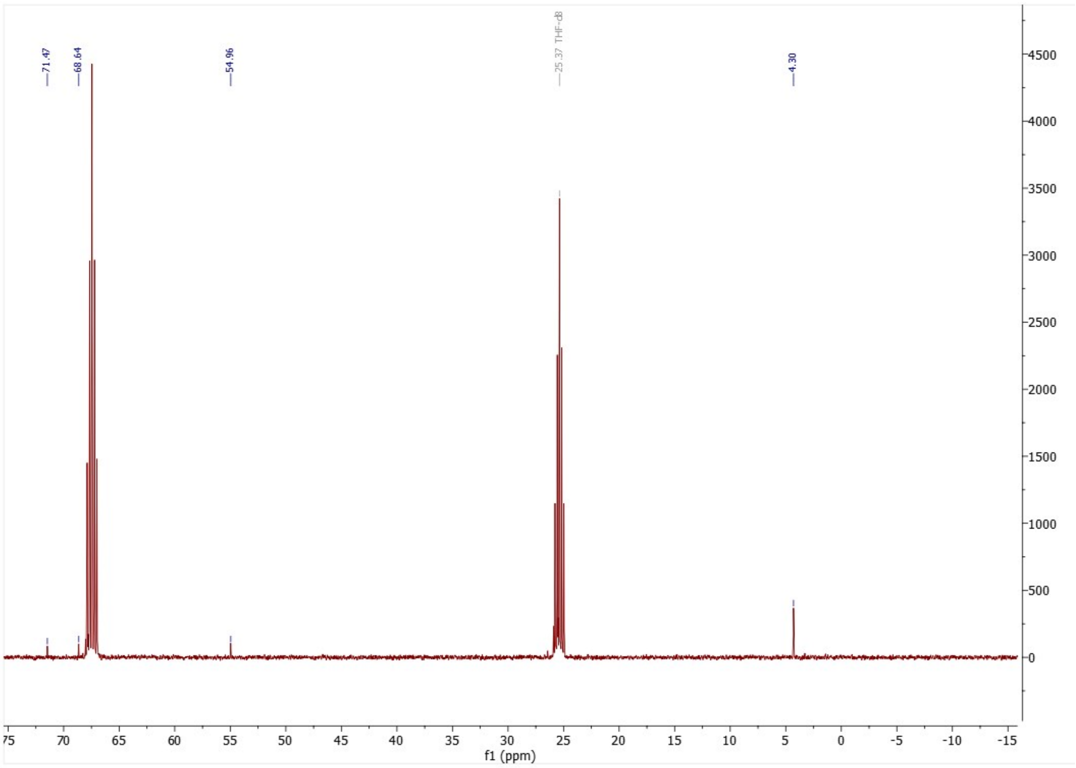


Figure S5. $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 125.81 MHz) spectrum of [K(2,2,2-crypt)]$_2$[**1**].

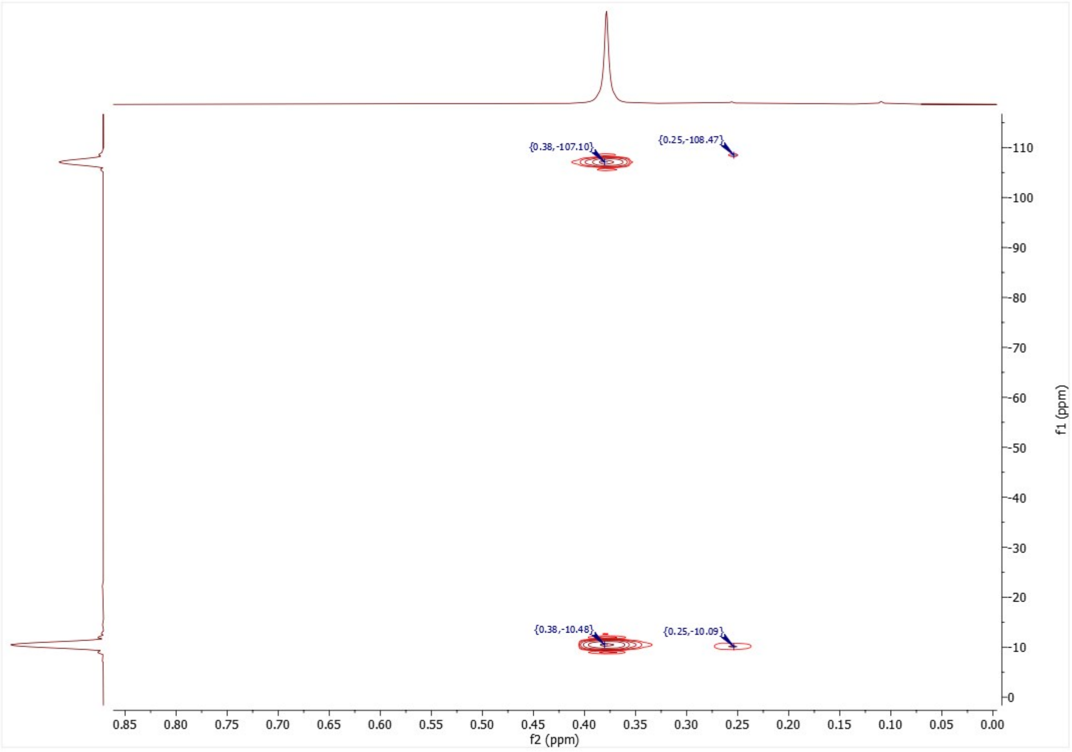


Figure S6. $^1H/^{29}Si$ HMBC NMR (d_8-THF, 298 K, 79.5 MHz) spectrum of [K(2,2,2-crypt)]$_2$[**1**].

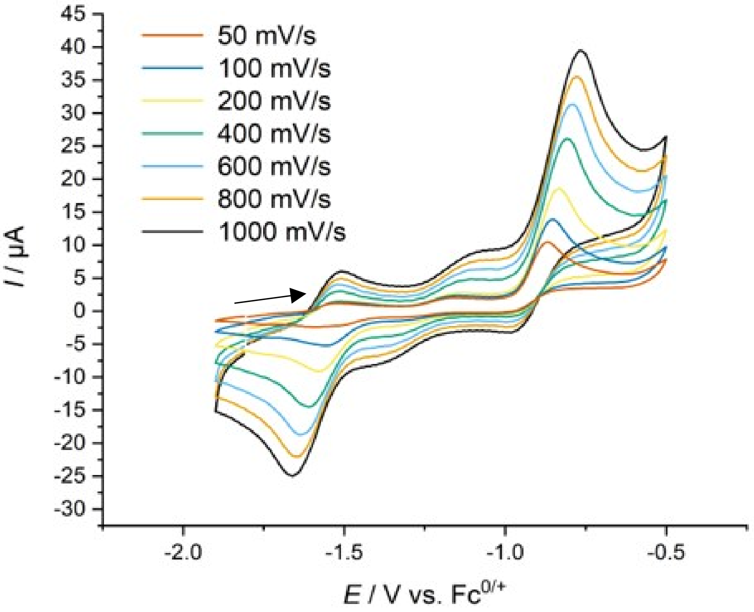


Figure S7. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] (1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature).

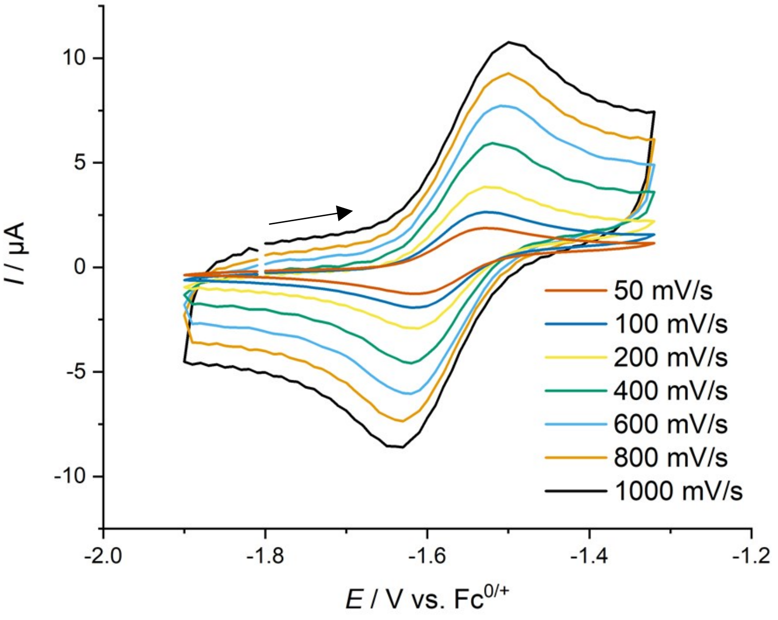


Figure S8. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] (first oxidative event; 1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature).

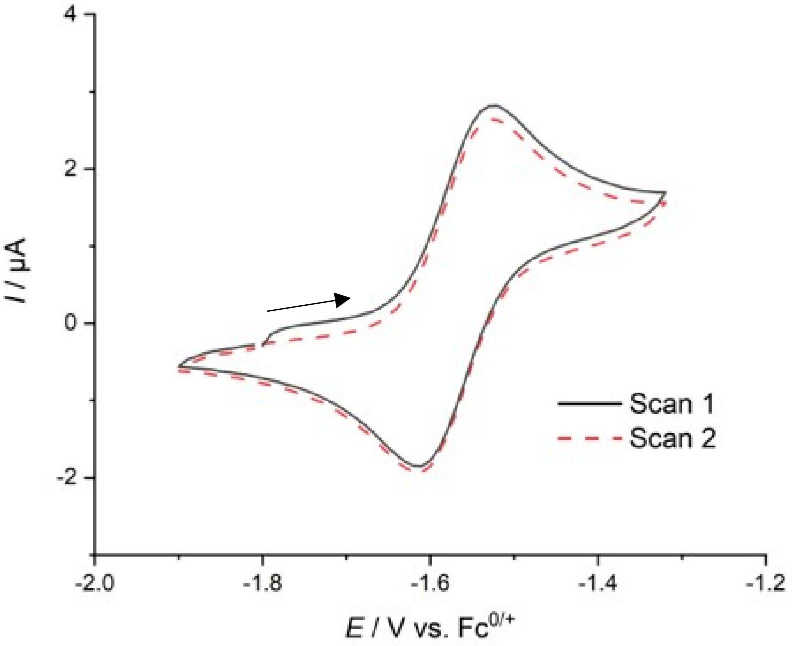


Figure S9. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] (100 mV/s; first oxidative event; 1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature).

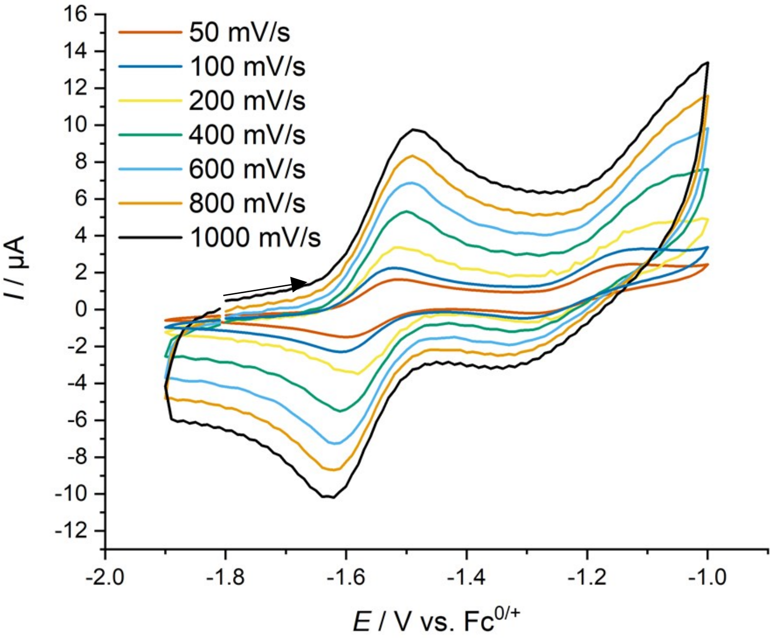


Figure S10. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] (first and second oxidative events; 1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature).

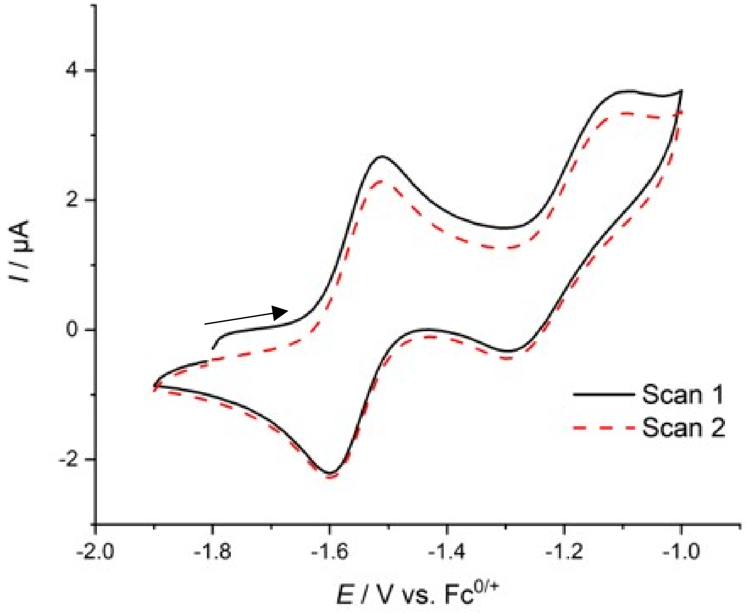


Figure S11. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] (50 mV/s; first and second oxidative events; 1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature)

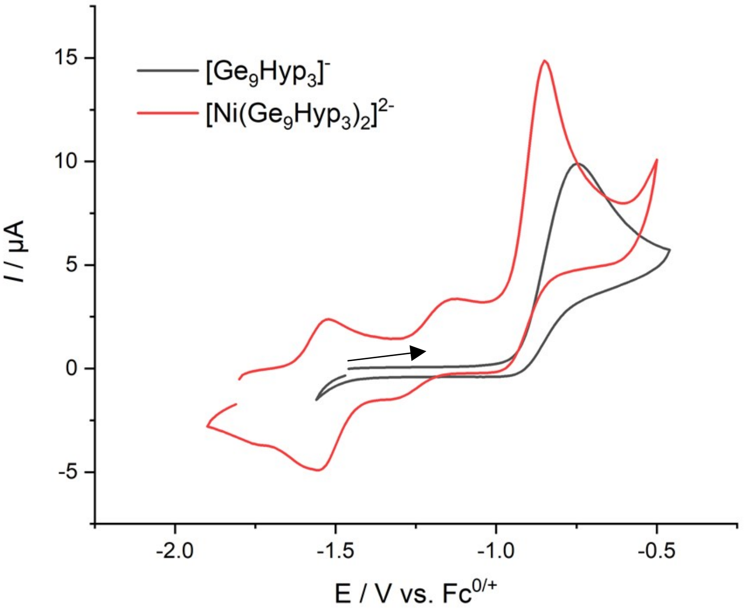


Figure S12. Cyclic voltammogram of complex [K(2,2,2-crypt)]$_2$[**1**] and [K(crypt)][Ge$_9$(Hyp)$_3$] (100 mV/s; 1.0 mM, 0.2 M [NBu$_4$][PF$_6$], THF, room temperature)

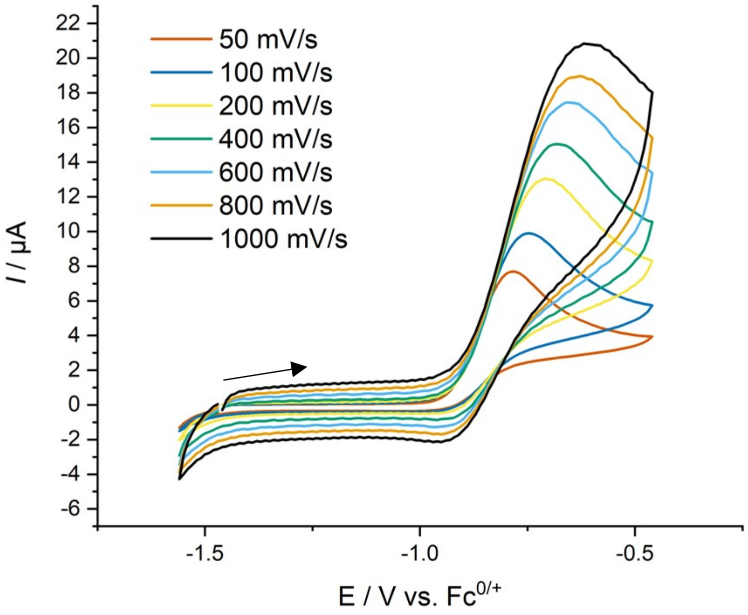


Figure S13. Cyclic voltammogram of complex [K(crypt)][Ge_9($Hyp)_3$] (1.0 mM, 0.2 M [NBu_4][PF_6], THF, room temperature)

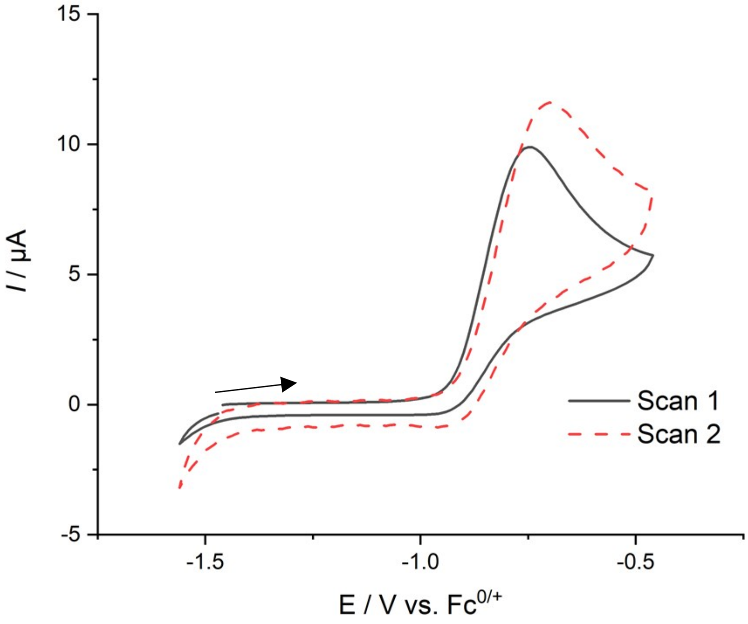
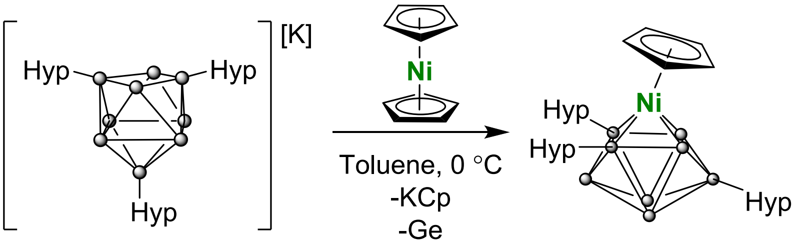


Figure S14. Cyclic voltammogram of complex [K(crypt)][Ge_9($Hyp)_3$] (100 mV/s; 1.0 mM, 0.2 M [NBu_4][PF_6], THF, room temperature)

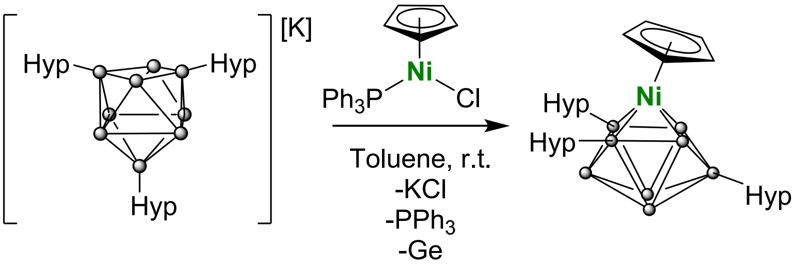
2.2. (Cp)Ni[$Ge_8(Hyp)_3$] (**2**)

Synthesis A:



A toluene (20 ml) solution of $NiCp_2$ (26 mg, 0.14 mmol) was added dropwise to a solution K[$Ge_9(Hyp)_3$] (200 mg, 0.14 mmol) in toluene (20 ml) over the course of 25 minutes at 0 °C. The orange solution was stirred overnight to yield a dark brown mixture. This was filtered, washing the pyrophoric grey solid with toluene (3 × 5 ml). The toluene was then removed *in vacuo* and the product was extracted in *n*-hexane (3 × 10 ml) as a dark green-brown solution. This was reduced in volume to 2−3 ml and left to stand in a –80 °C freezer for 14 hours, producing needle-like emerald green crystals of **1** (60 mg, 30%). Emerald green crystals of **1** suitable for single crystal X-ray crystallography were grown from a concentrated solution of toluene, rather than *n*-hexane.

Synthesis B:



To a solid mixture of (Cp)Ni(PPh_3)Cl (30 mg, 0.07 mmol) and K[$Ge_9(Hyp)_3$] (100 mg, 0.07 mmol), toluene (10 ml) was added at room temperature. The dark brown solution was stirred to a dark brown mixture overnight. The toluene was then removed *in vacuo* and the product was extracted in *n*-hexane (3 × 10 ml) as a dark green-brown solution. The *n*-hexane was then removed *in vacuo* and excess PPh_3 was removed by sublimation at 80 °C. The green-brown product was then re-dissolved in *n*-hexane (3 ml) and left to stand in a –80 °C freezer for 14 hours, producing emerald green crystals of **1** (35 mg, 35%). Elemental analysis calcd. For $C_{32}H_{86}Ge_8Ni_1Si_{12}$ (M = 1447.86 g·mol^{-1}): C 26.55, H 5.99, Found: C 26.52, H 5.82. ^{1}H NMR (C_6D_6, 298 K, 400.17 MHz): δ (ppm): 0.49 (s, 54H; CH_3), 0.60 (s, 27H; CH_3), 5.18 (s, 5H; CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125.81 MHz): δ (ppm): 3.31 (CH_3), 4.24 (CH_3), 87.73 (CH). ^{29}Si NMR (C_6D_6, 298 K, 79.5 MHz): δ (ppm): –101.1, –76.1, –8.4.

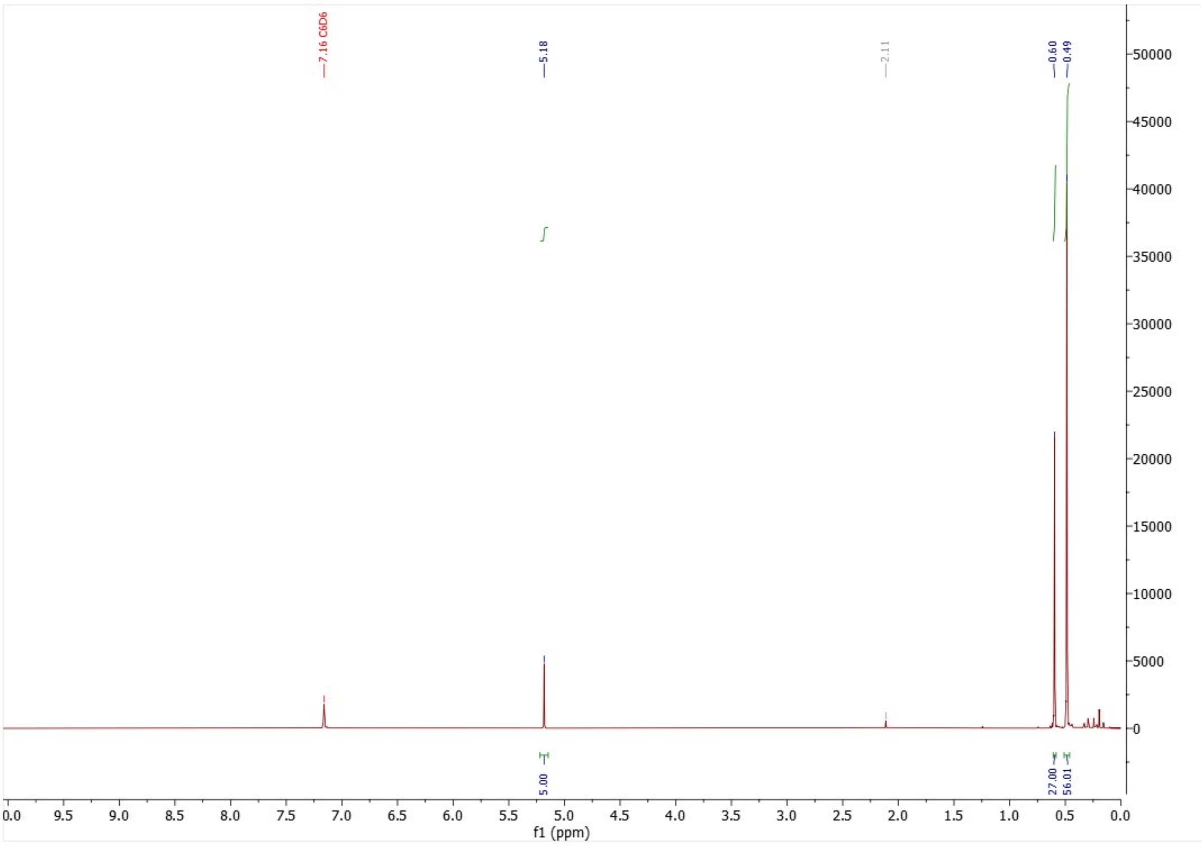


Figure S15. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) spectrum of **2**.

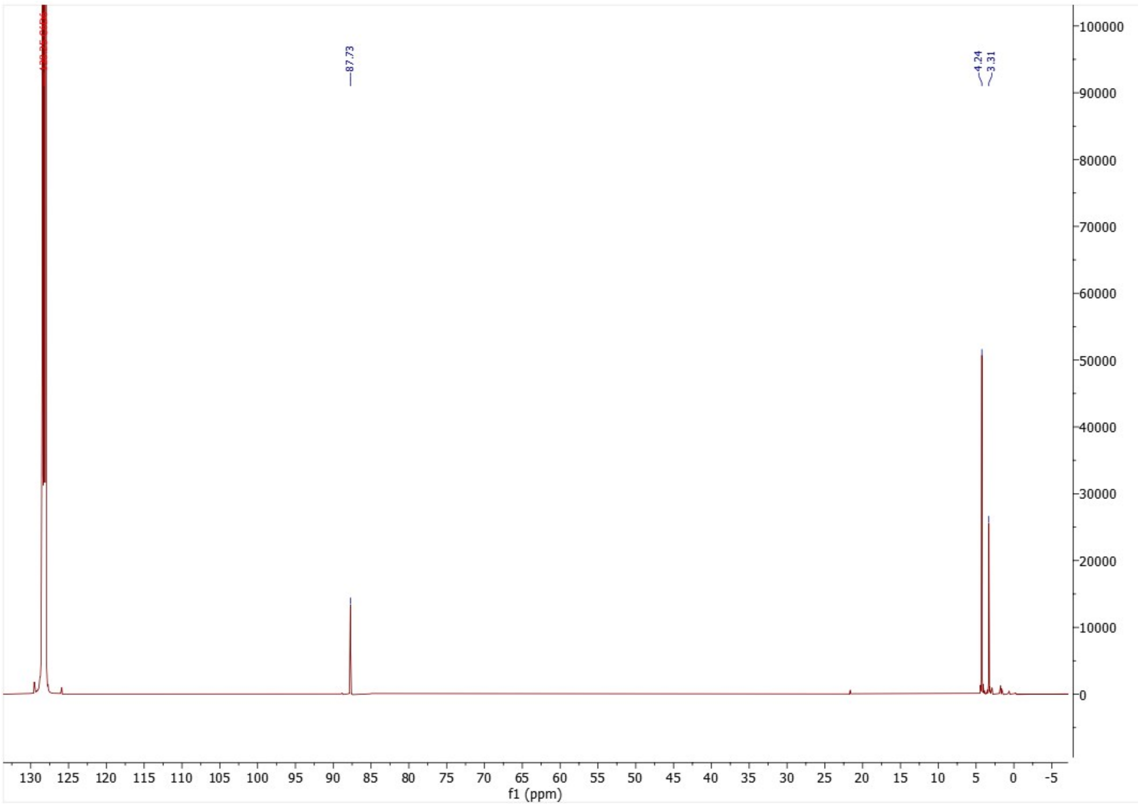


Figure S16. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.81 MHz) spectrum of **2**.

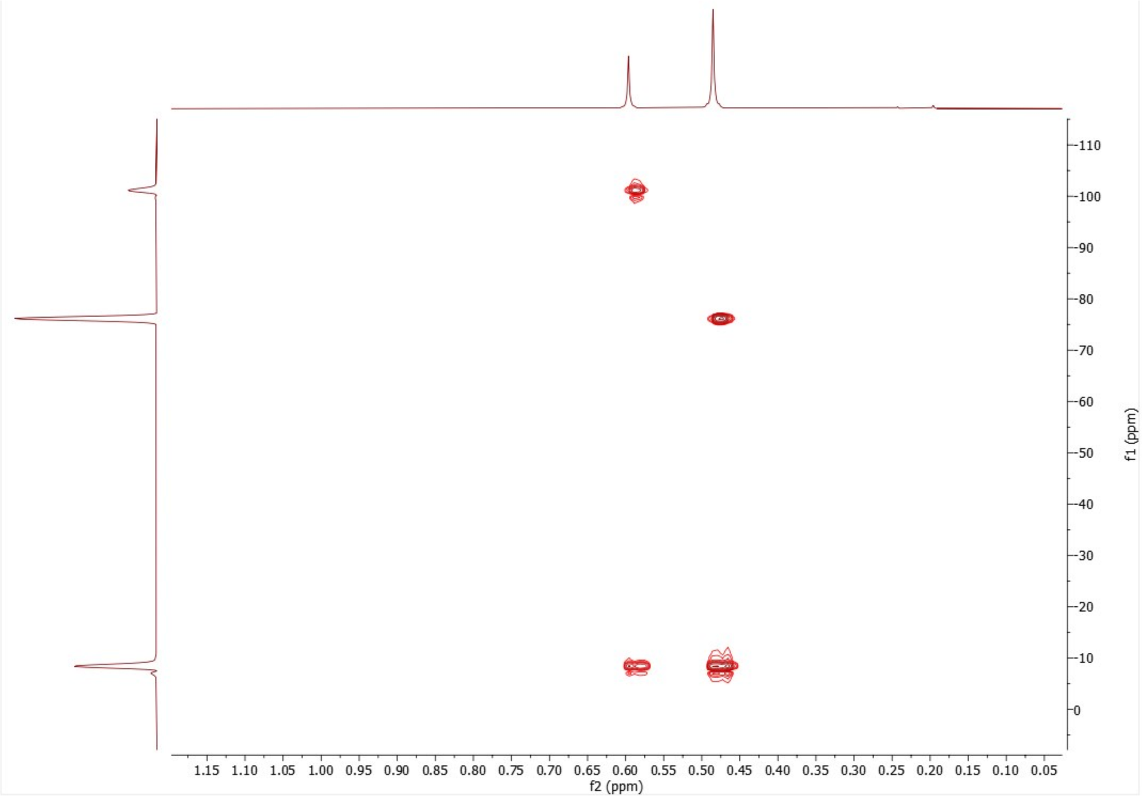


Figure S17. $^{1}H/^{29}Si$ HMBC NMR (C_6D_6, 298 K, 79.5 MHz) spectrum of **2**.

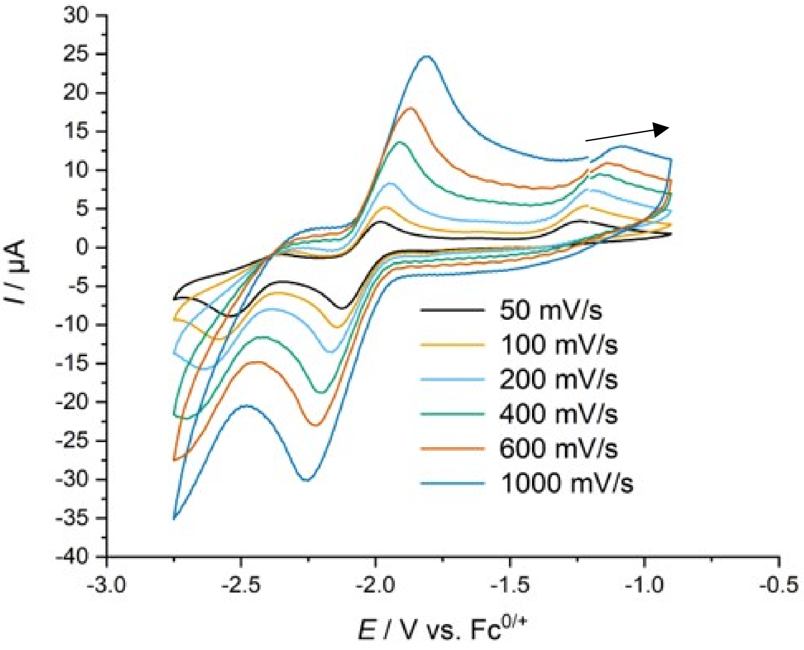


Figure S18. Cyclic voltammogram of complex **2** (1.0 mM, 0.1 M $[NBu_4][PF_6]$, THF, room temperature).

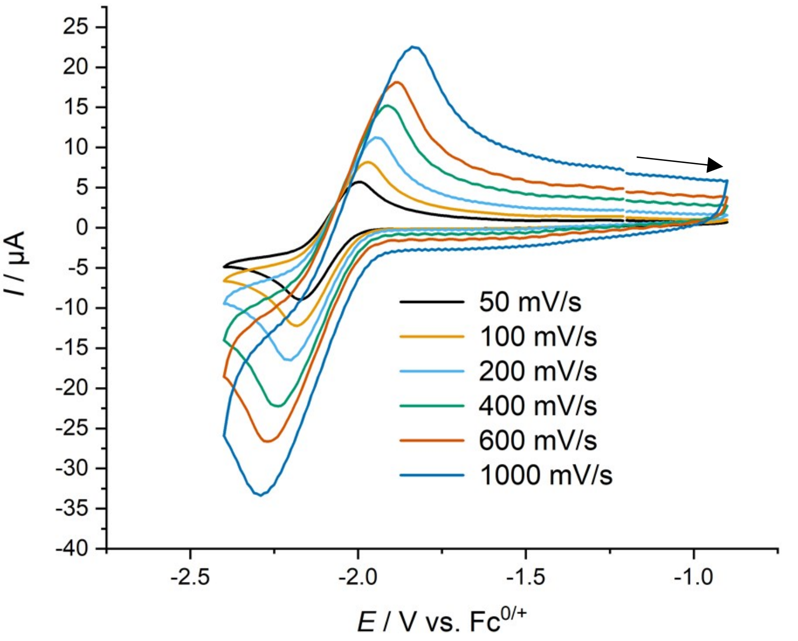


Figure S19. Cyclic voltammogram of complex **2** (first reductive event; 1.0 mM, 0.1 M $[NBu_4][PF_6]$, THF, room temperature).

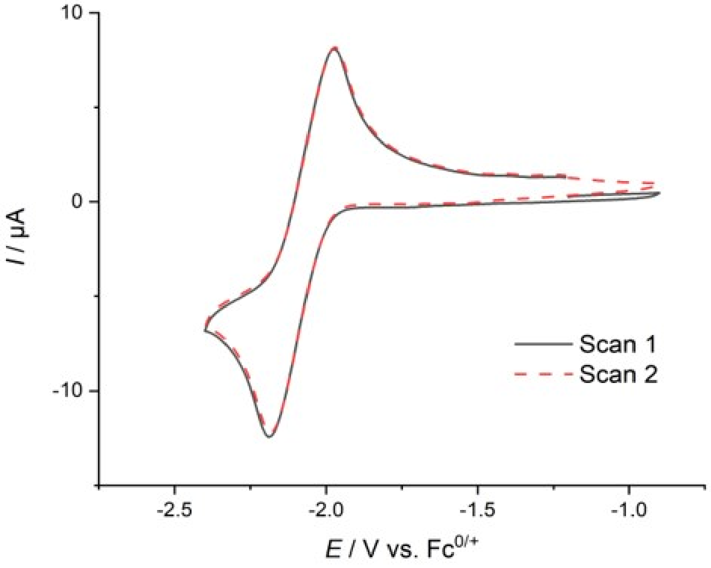


Figure S20. Cyclic voltammogram of complex **2** (100 mV/s; first oxidative event; 1.0 mM, 0.1 M [NBu_4][PF_6], THF, room temperature).

3. Single crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected at 150 K using mirror monochromated Cu K_α (λ = 1.54184 Å) radiation and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[2] Structures were subsequently solved using direct methods.[3]

Table S1. Selected X-ray data collection and refinement parameters for $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]\cdot 2THF$ and $\mathbf{2}\cdot 1.5tol$.

	$[K(2,2,2\text{-crypt})]_2[\mathbf{1}]\cdot 2THF$	$\mathbf{2}\cdot 1.5tol$
Formula	$C_{98}H_{250}Ge_{18}K_2N_4NiO_{14}Si_{24}$	$C_{42.5}H_{98}Ge_8NiSi_{12}$
CCDC	2087498	2087499
Fw [g mol^{-1}]	3826.69	1585.71
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	15.6461(3)	9.5585(4)
b (Å)	16.2709(4)	14.6574(6)
c (Å)	18.7924(3)	27.0969(12)
α (°)	85.101(2)	97.455(4)
β (°)	69.035(2)	97.365(4)
γ (°)	82.861(2)	102.627(3)
V (Å^3)	4428.43(17)	3624.8(3)
Z	1	2
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184
Temp (K)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.435	1.453
μ (mm^{-1})	5.785	6.059
Reflections collected	55057	27423
Independent reflections	18293	12793
Parameters	754	604
R(int)	0.0366	0.0770
R1/wR2,[a] $I \geq 2\sigma I$ (%)	3.17/7.53	5.32/11.11
R1/wR2,[a] all data (%)	4.35/8.37	9.24/13.28
GOF	1.055	0.931

$R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0345 and 1.61 for $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]\cdot 2THF$ and 0.370 and 0.00 for $\mathbf{2}\cdot 1.5tol$.

X-ray refinement of **2**·1.5tol: The structure crystallises with 1.5 molecules of toluene in the asymmetric unit, one of which (that defined by C1T−C7T) is disordered about centre of symmetry. All non-hydrogen atoms in the structure were refined anisotropically. The anisotropic displacement parameters for the toluene solvent were restrained using the SIMU and DELU commands as follows:

```
SIMU C1S C2S C2S C3S C3S C4S C4S C5S C5S C6S C6S C7S C7S C2S

DELU C1S C2S C2S C3S C3S C4S C4S C5S C5S C6S C6S C7S C7S C2S

SIMU C1T C2T C2T C3T C3T C4T C4T C5T C5T C6T C6T C7T C7T C2T

DELU C1T C2T C2T C3T C3T C4T C4T C5T C5T C6T C6T C7T C7T C2T
```

4. References

[1] (a) F. Li, S. C. Sevov, *Inorg. Chem.* 2012, **51**, 2706–2708; (b) O. Kysliak, A. Schnepf, *Dalton Trans.* 2016, **45**, 2404–2408.

[2] *CrysAlisPro*, Agilent Technologies, Version 1.171.35.8.

[3] (a) G. M. Sheldrick in SHELXL97, *Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467−473; (c) G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, 71, 3–8.